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Engineering Single Walled Carbon Nanotube Assemblies: From Ruthenium Complexes Assisted Dispersions to Networks on Different Platforms

by

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ABSTRACT

Engineering Single Walled Carbon Nanotube Assemblies:
From Ruthenium Complexes Assisted Dispersions to Networks on Different Platforms

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Manufacturing large area networks have potential applications in electronic devices such as thin film transitors, transparent conductive electrodes, and organic photovoltaics among others. The design of two-dimensional SWCNT networks necessitates addressing the challenges of nanotube individualization and organization of networks on different scaffolds. Chapter 1 describes a comprehensive overview of ongoing research in the field of nanotube networks on different platforms.

Efficient individualization of SWCNTs in chlorosulfonic acid (CSA) has been reported earlier but preparation of networks on suitable scaffolds still requires attentions. To address that, we have demonstrated a simple solution based technique to produce SWCNTs networks. Chapter 2 describes the deposition of protonated SWCNTs (p-SWCNTs) on the external surface of porous materials. SWCNTs are
dispersed in CSA *via* protonation before the deposition and placed in contact with mesoporous and microporous silicates. Furthermore, the nanotubes are deprotonated using vinyl pyrrolidone, while immobilized resulting in a network of mostly individual pristine SWCNTs on the surface of microporous and mesoporous materials.

In chapter 3, we applied a solution based approach to design thin films on the surface of non-porous silica. SWCNTs networks were formed on fused silica using a simple, efficient dip coating technique. We found the properties of these networks could be tuned by changing the density of SWCNTs in the network. For example, when we prepared low-density films, NIR photoluminescence from individual SWCNTs was observed on the surface of fused silica after deprotonation with diethyl ether. Our findings also support the arguments of reversible protonation of sidewall of SWCNTs during dispersion by CSA. Finally, for high-density films, we achieved sheet resistance of 471 Ω/Sq with 86% transparency. The opto-electronic performance of our films was compared with other recent works reported in literature.

Chapter 4 presents the aqueous dispersion of SWCNTs using non-photoluminescent ruthenium polypyridyl complexes with extended π-
systems by non-covalent dispersion. We further used photoluminescent complexes, which cannot only disperse SWCNTs but can also be monitored in photo-excited state to achieve photo-excited electron transfer processes with potential applications to light harvesting.

In the final chapter, a study was reported on the vapoluminescence of encapsulated rhenium metal complexes in zeolite supercages. Upon exposure to solvent vapors, the hybrid materials show characteristic emission maxima, intensity and lifetime decay. This work shows detection of solvent vapors in a simple unambiguous way, which may find applications in the area of sensing.
Acknowledgments

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<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>bpy</td>
<td>bipyridine</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter(s)</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>wavenumbers</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CSA</td>
<td>Chlorosulfonic Acid</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyl Trimenthylammonium Bromide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>2-D</td>
<td>2-Dimensional</td>
</tr>
<tr>
<td>3-D</td>
<td>3-Dimensional</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift in parts per million</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>dppn</td>
<td>benzo[i]dipyrdo-[3,2-a:2'.3'-c]phenazine</td>
</tr>
<tr>
<td>dppz</td>
<td>dipyrdo[3,2-a:2'.3'-c]-phenazine</td>
</tr>
<tr>
<td>DTAB</td>
<td>Dodecyl Trimethylammonium Bromide</td>
</tr>
<tr>
<td>ESI</td>
<td>Electron Spray Ionization</td>
</tr>
<tr>
<td>eV</td>
<td>electron Volt</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FOM</td>
<td>Figure of Merit</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>g</td>
<td>Gravitational acceleration</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HA</td>
<td>Hydroxyapatite</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>HiPco</td>
<td>High-Pressure Carbon Monoxide</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant (in NMR spectroscopy)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$\lambda_{exc}$</td>
<td>Excitation wavelength</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-by-Layer</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid Crystal Display</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LSZ</td>
<td>Lysozyme</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>µ</td>
<td>Micron</td>
</tr>
<tr>
<td>MCM</td>
<td>Mobil Composition of Matter</td>
</tr>
<tr>
<td>mg</td>
<td>milligram(s)</td>
</tr>
<tr>
<td>µg</td>
<td>microgram</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-Ligand Charge Transfer</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>MO-PPV</td>
<td>Poly[(2-Methoxy,5-Octoxy) 1,4-Phenylenevinyle]</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>µs</td>
<td>Microsecond</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi walled Carbon Nanotubes</td>
</tr>
<tr>
<td>NaY</td>
<td>Sodium exchanged zeolite Y</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infrared</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-Pyrrolidone</td>
</tr>
</tbody>
</table>
NMR  Nuclear Magnetic Resonance
ns  Nanosecond
Ω  Ohm
OPV  Oligo(p-phenylenevinylene)
PDMS  Polydimethylsiloxane
PEDOT:PSS  Poly(ethylenedioxy thiphene): poly(styrene) sulfonate
PEN  Polyethylene Napthalate
PET  Polyethylene Terephthalate
P3HT-PCBM  Poly(hexyl)thiophene-[6-6]phenyl-C_{61}-Butyric acid Methyl Ester
ppm  parts per million
pSWCNTs  protonated Single Walled Carbon Nanotubes
PTFE  Polytetrafluoroethylene
PVP  Polyvinylpyrrolidone
Py  Pyrene
Ru(bpy)_{3}^{2+}  Tris(bipyridine)ruthenium(II)
SBA  Santa Barbara Amorphous-16
S cm\(^{-1}\)  Siemens per centimeter
SDS                      Sodium Dodecyl Sulfate  
SEM                      Scanning Electron Microscope  
sq                       square  
SWCNTs                   Single Walled Carbon Nanotubes  
t                       triplet  
TBACl                    Tetra-n-butylammonium chloride  
TEM                      Transmission Electron Microscopy  
THF                      Tetrahydrofuran  
tppz                     tetrapyrido[3,2-a:2'.3'-c:3'',2''-h:2'',3''-j]phenazine  
USY                      Ultrastabilized zeolite Y  
UV                       Ultra Violet  
VOC                      Volatile Organic Compound  
Vis                      visible  
VP                       Vinylpyrrolidone  
wt%                      Weight Percent  
w/v                      mass/volume  
XPRD                     X-ray Powder Diffraction  
XPS                      X-ray Photoelectron Spectroscopy
Chapter 1

Carbon Nanotubes on the Surface of Different Platforms

Note: This chapter was copied from a paper that I submitted for review.

1.1. Introduction

Carbon nanotubes (CNT) are one of the most studied materials in the past two decades. These carbon nanoarchitectures are 1D cylindrical structures consisting of wrapped single or multi-layer graphene sheets. Extensive research has been done to explore this promising nanoscale material, due to their potential technological and biomedical applications. Although individual CNTs possess excellent electronic and mechanical properties such as extremely high electron
mobility (100 000 cm² V⁻¹ s⁻¹),² high electrical conductivity (10⁴ S cm⁻¹),³ high thermal conductivity (3500 W m⁻¹ K)⁴ and exceptionally good mechanical strength (tensile strength of 100 GPa for individual multi-wall tube),⁵ the properties of the bulk material depend on how the CNT are organized. At the same time, the fabrication of large-scale materials with specific control over the position of the CNTs building blocks is difficult due to intrinsic difficulties in manipulating individual nanotubes. On the other hand, large area networks of CNTs can be assembled with a reasonable compromise in properties in comparison with individual tubes. For example, field effect mobility of 1236 cm² V⁻¹ s⁻¹,⁶ and electrical conductivity is about 12825 S cm⁻¹ has been reported for CNT networks.⁷ Due to their potential applications, two dimensional (2D) nanotube networks have been investigated by numerous research groups. Recently, 3D nanotube networks are also gaining interest among scientists.⁸ CNT thin films (a special case of 2D carbon nanotube networks) have been reviewed previously with most emphasis on the electrical properties of the network and their application in electronics,⁹-¹³ however not on the variety of substrates and interactions between substrates and networks. Controlling the nature of substrates diversifies the applications of carbon nanotube networks. Therefore,
here I described a comprehensive compilation of different classes of substrates in terms of shapes (e.g. spherical, flat, and porous), and discussed fabrication techniques and applications of the formed nanotube networks.

1.2. Preparation of Carbon Nanotube Networks

The fabrication of CNT networks can be broadly classified in two types. First is direct growth, where networks are synthesized using a dry metal catalyst in the presence of gaseous precursors. Another procedure is the use of solution-based techniques, which involves deposition from carbon nanotube suspensions. In this section I will briefly discuss the fundamental for these methods.

Chemical vapor deposition (CVD) techniques are primarily used for the direct growth of single-walled carbon nanotubes (SWCNTs) networks. Carbon nanotube networks grown directly on the substrate can be randomly oriented or aligned. Usually Fe/Co/Mo catalyst is deposited on a SiO$_2$/Si substrate and a carbon source is feed into the system at high temperature. During this process the carbon source decomposes and precipitates over the catalyst to grow CNTs. The CVD
method can produce long CNT with tunable nanotube density, alignment, and semiconducting/metallic characteristics.\textsuperscript{14-16} The directionality of the networks can be controlled by the nature of substrate,\textsuperscript{17} and growth parameters such as heating process, and electric field induction. Apart from the conventional Si substrate, mesoporous silica, nanoporous silica,\textsuperscript{18,19} and alumina\textsuperscript{20} has been used to fabricate SWCNTs assemblies. A SEM image of a CNT network grown from SBA-16 (Santa Barbara amorphous type 16) thin films is shown in Figure 1.1a.\textsuperscript{18} Recently, Han et al. reported CVD grown networks on a nanoporous silica surface.\textsuperscript{19} Interestingly, they observed denser networks on porous silica-coated forming a SiO\textsubscript{2}/Si substrate than on uncoated smooth silica, due to efficient precursor delivery and higher population of the catalyst on the porous layer (Figure 1.1b).

The other kind of fabrication technique for producing CNT networks is based on deposition from solution. Solution-based techniques involve the production of the carbon nanotube network from a suspension containing the pre-individualized CNTs. Due to the simplicity of this approach, many variations have been studied. For example, nanotube networks in planar substrates can be fabricated by
using spray coating, spin coating, and even ink-jet impression, while network on particles are usually generated by direct contact. This popular method of network fabrication will be discussed more extensively throughout the text.

1.2.1. Nanotube Networks on Flat Surfaces

In this section, I cover the fabrication of CNT networks on rigid and flexible flat surfaces. CNT networks can be fabricated in variety of
flat substrates such as SiO$_2$,$^{21-23}$ PET,$^{24-28}$ polyethylene napthalate (PEN),$^{29}$ glass,$^{30-37}$ metal coated Si wafer$^{38}$ and SiO$_2$.$^{39}$

**Figure 1.2** Schematic diagram of different techniques for making carbon nanotube networks on planar surfaces: (a) electrophoretic deposition, (b) spin coating, (c) spray coating, (d) dip coating, and (e) vacuum filtration.

Solution-based techniques are widely used to produce CNT networks on flat surfaces. Figure 1.2 illustrates different CNT network preparation techniques. Electrophoretic deposition is a scalable technique where CNTs in colloidal dispersion coat the surface of an electrode upon applying direct current.$^{40}$ Spin coating involves the preparation of a CNT dispersion followed by dropwise addition of the
solution in a spinning surface of interest. Dip coating is another scalable method where planar substrates such as PET, glass, and fused silica can be covered with a nanotube network when submerged into a CNTs suspension. Spray coating is an efficient method to form nanotube networks on glass, PET, and silica substrates where nanotubes are commonly dispersed in surfactants or organic solvents and sprayed onto a heated substrate. Vacuum filtration is another extensively used method where a dispersion of CNTs is forced through a membrane forming a homogenous network on its planar surface. Other techniques also available for fabrication of CNT networks on flat substrates include bar or rod coating, ink-jet printing, layer-by-layer assembly (LBL method), and drop casting. In all these procedures, the nature of the substrate and the quality of the CNT dispersion play important roles in the homogeneity of the carbon nanotube network.

Although CNT networks are commonly fabricated on substrates by direct methods, an alternative method is network transfer. For example, the high temperature required for CVD methods may make this technique incompatible for the fabrication of CNT networks on
flexible flat substrates. Grüner and coworkers demonstrated that directly grown nanotube networks can be transferred from SiO₂/Si to a polyimide substrate in a three step process involving metal patterning, polyimide coating, and etching of the SiO₂ layer. Rogers et al. further produced CNT films on flexible polyethylene terephthalate (PET) substrate using Cr/Au patterning and polydimethylsiloxane (PDMS) as intermediate transferring substrate. Transferring CVD grown networks to flexible substrates was further explored and has motivated the use transferring techniques in CNT networks produced by solution-based techniques. However the drawbacks of the CNT network transfer process are that (a) it is a multistep process, and (b) commonly requires a chemical etchant such as hydrofluoric acid (HF), which may cause damage to the nanotube network. Recently, direct transferring has been reported by Liu et al. where CNT networks grown on a SiO₂ surface were transferred to other substrates by a simple contact printing method. Indeed, the efficiency of CNT network transfer can be increased by reducing intermediate steps and avoiding harsh chemical conditions.
One important point in making these networks is the compatibility between the substrates and the fabrication techniques. For example, Park et al. reported growing random carbon nanotube networks on thermal silicon oxide, while Bao research group noticed that SWCNTs cannot be adsorbed on the same substrate by spin coating unless they functionalized the SiO$_2$ surface.$^{21,42}$ Recently there has been a crescent interest in fabricating thin nanotube networks on flexible and stretchable plastic substrates for making thin film devices. Flexible plastic substrates can make the electronic devices more portable. However, the challenge of using plastic substrates lies in the fact that they have a reduced thermal conductivity. Unlike SiO$_2$, plastic substrates could not assist in heat dissipation of the nanotube network, which might lead to electrical breakdown. Alternatives such as surface functionalization of the substrate might improve the thermal conductivity reducing this problem.

Very recently, Hata research group reported an interesting morphological study on nanotube networks. They have dispersed the carbon nanotubes (>3 wt%) by jet milling and spin coated them on flat glass surface.$^{35}$ Intriguingly, ultralong nanotubes form dendritic
structure whereas shorter tubes such as HiPco SWCNTs assembled in a random mesh structure. This study suggests that CNT length is an important parameter to consider, in addition to the substrate and the techniques used to fabricate the CNT network.

1.2.2. Nanotube Networks on Solid Concave Substrates

Silica nanospheres are the most extensively studied spherical substrate for the formation of carbon nanotube networks. To cover silica spheres or other spherical object with SWCNTs one need to take into account different factors such as curvature of the substrate, length of the nanotubes, and surface interactions between nanotubes and substrates. Usually smaller spherical particles have a high degree of curvature hence less retention properties, also shorter tubes tend to have more affinity toward the external surface of spherical substrates. Larger nanotubes are observed to protrude out from the sphere and might act as bridges between two spheres, leading to aggregation between particles.

Huang reported the grow of aligned CNTs on patterned sub-micron sized SiO₂ spheres, where the tubes are isolated due to the curvature of the sphere. Controlling the density of nanotubes by
introducing the curvature on substrate can be beneficial since optimum density is desirable in application such as field emission.\textsuperscript{69} Li et al. also observed the effect of the curvature of silica spheres on the synthesis of SWCNTs.\textsuperscript{70} They noted that nanotubes tend to grow along the surface of large spheres but away from the surface of smaller spheres. Apart from direct growth of nanotubes on silica spheres, several research groups have used solution-based techniques to disperse nanotubes on the outer surface of silica particles. In some of these approaches CNTs were chemically modified and shortened by oxidation or dissolved in water or common organic solvents.\textsuperscript{71,72} Functionalized nanotubes have more adhesion to the surface of silica spheres due to Columbic interactions. Villani research group deposited functionalized SWCNTs and MWCNTs on mesoporous silica particles.\textsuperscript{71} Recently Nakshima \textit{et al.} reported uniform coating of amino-functionalized silica spheres from pristine SWCNT dispersions in NMP.\textsuperscript{72-74} Figure 1.3 shows the images of SWCNT/NH$_2$ silica spheres ranging in size from 3.5 \( \mu \text{M} \) - 200 nm.\textsuperscript{72} Denser SWCNT networks on larger silica spheres indicates stronger adhesion between nanotubes and the sphere surface, which can be rationalized considering less curvature and larger external areas for larger silica spheres. Moreover, Nakahima group have used SWCNTs-
silica composite to investigate the interaction between nanotubes and phthalocyanine dyes.\textsuperscript{73} Apart from silica spheres, researchers have deposited carbon nanotube networks on the surface of other spherical substrates such as carbonyl iron spheres, polystyrene spheres,\textsuperscript{75,76} carbon microparticles.\textsuperscript{77}

\textbf{Figure 1.3} SEM images of pristine SWCNT/NH$_2$-silica nanoparticles. Diameters of the NH$_2$-silica spheres are: (a) 3.5 μm, (b) 1.0 μm, (c) 500 nm and (d) 200 nm. Larger silica spheres promote more effective SWCNT-coatings. Reprinted from ref. 72, Copyright (2011), with permission from Elsevier.
1.2.3. Nanotube Networks on Porous Substrates

Although considerable research efforts have been made for making carbon nanotube coating on smooth/non-porous surfaces, fewer works have been reported to produce nanotube networks on porous materials. Fabrication of nanotube network on porous substrates has potential application in nanoelectronics, sensing,\textsuperscript{19,78} and separation,\textsuperscript{77} among others. Specifically, the porosity of the substrate enhances the diffusion of molecules for transport and sensing applications. For example, Han et al. have demonstrated sensing of ammonia with directly grown SWCNTs on porous silica, where the silica support also is implicated in contributing to a better gas diffusion during the sensing experiments. In a different approach, Elimelech et al. prepared thin film composite membranes by forming the CNT network on a microporous polyvinylidene fluoride (PVDF) membrane through vacuum filtration.\textsuperscript{77} These membranes show remarkable antibacterial properties and separates bacterial contaminants from water. Figure 1.4a and b show the SEM images of \textit{E. coli} cells after separation through these CNT membranes filters.

Recently, three dimensional (3D) porous LiFePO\textsubscript{4} has been obtained containing interconnected CNTs to improve electronic and
lithium ion transport. Zhou and coworkers deposited CNT by sol-gel methods on the external and internal pore surface of LiFePO₄, enhancing the electrochemical performance of the composite by increasing the discharge capacity ~66.6% with respect to pristine LiFePO₄. Furthermore, Yang et al. modified the surface of LiFePO₄ with nitrogen doped CNTs to make more uniform networks (Figure 1.4c and d).

Porous silica materials have large surface areas, which enable them to have potential applications in fields including chromatography, adsorption, and sensing. Indeed, composite materials between carbon nanotube and porous silica are a promising area that requires more attention. Although extensive research have been done on coating mesoporous silica with carbon by Nishihara research group, there are few reports on CNT porous silica composite materials. Our work shows the deposition of individual SWCNTs on the external surface of micron-size microporous and mesoporous silica (see Chapter 2). Furthermore, we encapsulated a photoactive tris(2,2'-bipyridine)ruthenium(II) metal complex in the internal cavities of the silicate material to study the interaction between nanotubes and the
metal complex. Upon exciting the metal complex, we observed considerable quenching of the excited state lifetime due to the presence of SWCNTs on the surface of the particles.

![SEM images](image1.png)

**Figure 1.4** (a) SEM image of *E. coli* cells on microporous PVDF membrane, (b) SEM image of *E. coli* cells on SWCNT network filter. Reprinted from ref. 81, Copyright 2008, John Wiley and Sons Inc. Schematic illustrations of (c) porous LiFePO$_4$ (d) 3D CNT-LiFePO$_4$ composites. Reproduced from ref. 83, permission of The Royal Society of Chemistry.

### 1.2.4. Self-standing Nanotube Networks

Self-standing CNT networks (Figure 1.5) provide a great opportunity to study CNTs in a network not supported by any substrate and the effect of external stimulation such as IR photo-excitation,$^{83,84}$ compression,$^{85}$ and audio current.$^{86}$ In addition, self-standing films have been reported to have potential applications in making air filters,$^{87}$ absorber for
ultrafast laser excitation, polarized incandescent radiation sources, and thermoacoustic devices, among others. An interesting work by Haddon research group shows that the electrical conductivity of freely suspended CNT networks in vacuum can be increased upon excitation with light. Fabrication of free-standing CNT networks commonly involve similar approaches as non-free standing or substrate supported networks except for the fact that the substrate here is used as a sacrificial support. General procedures including drop-casting, spin coating, spray coating, vacuum filtration, and direct deposition are employed for the preparation of free-standing network, with the subsequent removal of the substrate. It is noteworthy that self-supported nanotube networks require long, high purity CNTs. For example, Nakashima et al. used ultra-long CNTs (ca. 100 μM) to make free-standing films. Recently, Jin group used ca. 15-25 μM long SWCNTs to prepare free-standing films with high tensile strength (850 MPa for 20 nm thick film). Since the yield stress of nanotube networks increases with tube length, it is preferable to use longer nanotubes to obtain better inter-tube interaction.
Several research studies have been reported on hollow carbon nanotube cages or capsules of self-assembled nanotube networks without any additional support. Sano et al. reported the fabrication of CNT cages depositing oxidized CNTs on a sacrificial template (amine-functionalized silica gel).\textsuperscript{92} Nanotubes get adsorbed on the surface of silica gel by layer-by-layer assembly due to favorable nanotube-amine
interaction. Then, the silica gel template is etched chemically resulting in self-standing nanotube cages. In a similar approach, hollow spheres of CNTs were fabricated using removable polystyrene templates.\textsuperscript{93-95}

Another interesting class of free-standing nanotube network is made by ionic liquid-nanotube composites. Aida group shows that as synthesized highly bundled CNTs form gelatinous soft materials or ‘bucky gels’ in presence of ionic liquids.\textsuperscript{96-98} Typically, a dispersion of HiPco nanotubes in imidazolium-based ionic liquids is grinded with a mortar. A viscous gel is formed in the residue after centrifugation, possibly due to weak cation-π interactions between ionic liquids and CNTs. Recently, they improved the mechanical strength of this bucky gel by introducing millimeter long ‘supergrowth” nanotubes in their preparations.\textsuperscript{99} Simply by casting the gel followed by drying, they were able to obtain self-supporting fibrous nanotube networks.

\textbf{1.3. Cross-linked Nanotube Networks}

To improve the mechanical and electronic properties of CNT networks, a variety of methods to cross-link CNT, within the networks have been developed with the purpose of enhancing the interaction among nanotubes. The two most common strategies for achieving
efficient cross-linking are high-energy electron beam and chemical modification.\textsuperscript{100} The electron beam technique yields highly cross-linked and strong networks, however, the disadvantage of this method is that cross-linking can only be done in a small scale and cannot get a real usable network of CNTs.\textsuperscript{101-104}

A different methodology is chemical cross-linking of CNT networks. One of the first examples of chemical cross-linking of SWCNTs was achieved by [2+1] cycloaddition of a series of diazidocarbonate polyglycolesters.\textsuperscript{105} Also, acyl chloride modified SWCNTs were found to be readily cross-linked with a series of poly[(2-methoxy,5-octoxy)1,4-phenylenevinylene] (MO-PPV), with potential applications for solar cells.\textsuperscript{106} Carboxylic acid functionalized SWCNTs can also react with poly(allylamine) hydrochloride to produce mechanically robust composites when compared with the non-crosslinked composites.\textsuperscript{107} In a recent manuscript, highly conductive buckypaper have been processed by stretching CNT buckypapers to produce partial CNT alignment and followed by irradiation, which initiates a polymerization of pre-covalently functionalized CNTs with triple bonds. The resulting buckypapers possess high conductivity and high tensile strength up to 6200 S cm\textsuperscript{-1} and 220 MPa respectively.\textsuperscript{108}
Apart from SWCNTs, multi-walled carbon nanotubes (MWCNTs) have also been studied. For example, thiolated MWCNTs (MWCNT-SH) have been cross-linked with benzoquinone to form mats by taking advantage of the Michael addition pathway. By increasing the ratio of benzoquinone to MWCNT-SH from 5:1 to 10:1, the tensile strength increased from 1.98 MPa to 3.63 MPa.109 An \textit{ab initio} study on the crosslinking of thiocarboxylic functionalized nanotubes with dithiocarboxylic esters claimed that surface defects play an important role in stabilizing the bonds among nanotubes.110 Oxidized MWCNTs with carboxylic acid and hydroxyl functional groups were found to be efficiently cross-linked by spark plasma sintering, which gives rise to an order of magnitude increase in conductivity from 2 S cm\(^{-1}\) to 24 S cm\(^{-1}\) and a strength of 100 MPa.111 Another way to crosslink MWCNTs is to de-fluorinate previously fluorinated MWCNTs under thermal heating. During the process, the resulting sp\(^3\)-hybridized carbons combine with each other to crosslink the MWCNTs.112

**1.4. Applications of Nanotube Networks**

Networks of CNTs have large range of applications. In this section I will discuss some of the novel applications of these networks to fields
such as biology, sensing, transparent conductive electrodes, and thin film transistors. Furthermore, I will discuss the application of these networks for making hydrophobic surfaces and materials.

1.4.1 Biological Applications

CNT networks have been reported to have a broad variety of applications in fields such as sensing,\textsuperscript{113,114} and tissue engineering.\textsuperscript{115-119} Thin film transistors made of CNTs have been widely used for bioelectronic sensing. There are already some excellent reviews on the biosensing by CNTs.\textsuperscript{120,121} An interesting work reported by Davis \textit{et al.} shows that carbon nanotube networks in combination with antibacterial lysozyme (LSZ) proteins can have effective \textit{in vitro} antimicrobial properties.\textsuperscript{122} Based on Columbic interactions between cationic LSZ-SWCNT and anionic DNA-SWCNT dispersions, they prepared LBL-films on a variety of flat substrates including silicon, gold, glass, and mica. Interestingly, surface layers containing LSZ-SWCNTs show significant enzymatic dissociation of cell walls of Gram-positive bacteria, while no activity was observed for films terminated with DNA-SWCNTs.
Carbon nanotube coatings on 3D porous bioglass scaffolds have shown interesting functionalities with applications to bone tissue engineering.\textsuperscript{115,118} In these works, MWCNTs were dispersed in the non-ionic surfactant Triton X-100, with a subsequent addition of iodine. Then, negatively charged nanotubes were deposited uniformly on a bioglass scaffold by electrophoresis. Carbon nanotube coated scaffolds showed to have more controlled nucleation and subsequent nanostructured layer formation of hydroxyapatite (HA) than uncoated scaffolds. Hirata \textit{et al.} recently showed that 3D collagen coated with carboxylated MWCNTs present better \textit{ex vivo} bone formation.\textsuperscript{117,123} Enhanced bone formation was accounted for a better adsorption of osteoblast cell to the MWCNTs surface in comparison with the uncoated scaffold. SWCNTs coatings have also been investigated in the area of biomineralization.\textsuperscript{124} A recent review on the aspect of biological applications of carbon nanotube coatings describes the details of ongoing work in this area.\textsuperscript{125}

\textbf{1.4.2. Hydrophobic Surface Formation}

In the past few years, the formation of hydrophobic surfaces has captured the attention of several research groups due to their industrial
applications and scarcity of natural superhydrophobic surfaces. Superhydrophobic surfaces are extremely water repellant with very low surface energy (contact angle for water droplet ≥ 150°) and usually associated with surface roughness. Carbon nanomaterials such as graphite, amorphous carbon, graphene, CNTs, and hybrids between them are considered as promising candidates in designing hydrophobic surfaces. Furthermore, the unique physicochemical properties of CNTs can add other desirable functionalities to hydrophobic surfaces such as optical transparency, electrical conductivity, and flexibility. Gleason et al. reported superhydrophobic properties of polytetrafluoroethylene PTFE-coated directly-grown aligned CNTs on oxidized silicon substrate. Aligned CNT films have been the focus for making anisotropic superhydrophobic surfaces. However, as mentioned earlier, the disadvantages for direct growth of nanotube films is that there are limited choices of substrates and the size of the preparations are limited. An alternative approach is to prepare superhydrophobic films from CNT dispersions in common solvents. However, it has been observed that coatings with bare pristine nanotubes are not stable for long time in ambient conditions. In a recent report, Srinivasan et al. coated mica, glass, and metal substrates using
self-assembly of CNTs and oligo(p-phenylenevinylene)s (OPV). OPV acts as stabilizer and increase the hydrophobicity of composite layers.

### 1.4.3. Thin Film Transistors

To replace commercial polycrystalline-Si based field effect transistors (FET), researchers are looking for emerging materials, which can provide high electron mobility, high $I_{on}/I_{off}$ ratio, and high flexibility. Nanotubes networks have all these characteristics, thanks to the unique 1D structure of CNT and presence of band gap in the energy levels of individual semiconducting SWCNTs. However, one challenge in this area is that as synthesized SWCNTs is a mixture of semiconducting and metallic CNT. Large concentrations of metallic tubes increase the percolation threshold, and therefore $I_{off}$ will increase resulting in enhanced operation voltages. To address this challenge one needs to optimize the density of tubes in the CNT network. Several other strategies such as preferential functionalization of metallic tubes, electrical breakdown, self-sorted deposition via surface treatment, and e-beam/UV irradiation have been developed to fabricate networks enriched in semiconducting CNTs. Li et al. demonstrated that $I_{on}/I_{off}$ of nanotube arrays on a nickel oxide film (NiO)
can be increased from 5 to $\sim 10^3$ when metallic tubes are preferentially etched by a carbothermic reaction. However they also noted slight reduction in electron mobility due a decreased population of metallic SWCNTs and degradation of the network after the reaction. In selective functionalization, residual functionalized metallic tubes still may affect the transport properties of FETs. An alternative way to solve this is to transform metallic tubes into vapor or amorphous carbon through current induced electrical breakdown. Although this breakdown process can eliminate metallic tubes selectively, it also damaged semiconducting tubes to some extent. Bao research group reported a single step, non-destructive approach to functionalize a SiO$_2$ substrate surface with aminosilane, followed by selective deposition of semiconducting nanotubes via spin coating. This networks present average $I_{on}/I_{off}$ of ca. 200,000.

FETs of thin CNTs networks have been immensely explored in the past two decades. Several recent reviews have described the progress of this fast evolving research area in great detail. Nevertheless, the objective to substitute commercial technologies has not been met yet. There are still opportunities to improve electron mobility and
I$_{on}$/I$_{off}$ possibly via fabrication techniques, which should avoid multi-steps and high temperature/high vacuum processing to be cost-effective.

1.4.4. Opto-electronic Devices

CNT films have been extensively studied to exploit their superior opto-electronic properties. Higher transparency and electrical conductivity are desirable for maximum photon and electrons flux in electronic devices such as photovoltaic cell, resistive touch screens, and liquid crystal displays (LCD). Theoretically, the two intrinsic parameters that determine optical transparency and electrical conductivity are band gap and carrier mobility. If the band gap of the top layer matches the wavelength for visible light, transparency will be reduced. Also reduced carrier mobility will decrease the collection of generated electrons upon excitation. Currently, indium tin oxide (ITO) is the industrial standard to make transparent-conductive films. However, factors such as flexibility and cost are indulging scientists to invest considerable efforts in making devices using CNT networks. Figure 1.6 shows the sheet resistance vs transmittance (related to transparency) plot of the best performed CNT network films reported in literature to date.$^{7,24,33,48,54}$ One of the key issues about conductive CNT networks is
that researchers mostly report the performance of p-doped nanotube films, which may not be stable for long term applications. For example, Hecht *et al.* reported a conductivity of 12825 S cm\(^{-1}\) from a CNT film prepared by vacuum filtration of a nanotube-superacid solution.\(^7\) However, the conductivity is reduced by 15\% within the first two days. One possible explanation is that p-doped nanotubes tend to aggregate with long term storage in presence of humidity. Recently, Pasquali research group reported stable nanotube films with 90\% transparency and 100 Ohm/sq sheet resistance.\(^33\) Increasing stability is mandatory for commercialization. Another challenge is to increase the conductivity beyond ITO. Coleman research group hypothesized that hybrid 2D graphene/1D nanotubes films may achieve superior conductivity since graphene can provide a percolation network between two separated CNTs.\(^148\) The question still remains about the efficiency of flux of electrons between CNTs and graphene. Hersam *et al.* took an ingenious approach to separate metallic tubes from as synthesized mixtures and fabricate conductive films from intrinsically conductive metallic tubes.\(^52\) Nonetheless, their separation technique involves ultra-sonication, which shortens the nanotubes and therefore the conductivity of CNT networks.
Figure 1.6 Film resistance vs transmittance plot of best performed transparent and conductive CNTs thin films (reported in literature).

Carbon nanotube networks have also been used as transparent electrodes in photovoltaic devices.\textsuperscript{149} In the mentioned work, a SWCNT film was transferred on top of a poly-(ethylene terephtalate) (PET) substrate. CNT composite films showed to be efficient anodes for solar cells. For example, Chhowalla research group designed photovoltaic cells using SWCNTs thin films (anode) on glass and poly(hexyl)thiophene-[6-6]phenyl-C\textsubscript{61}-butyric acid methyl ester (P3HT-PCBM) showing higher conversion efficiency (0.99\%) in comparison with glass-ITO/ poly(ethylenedioxy thiphene): poly (styrene) sulfonate
PEDOT:PSS reference cell (0.69%). Very recently, Jung et al. fabricated CNT/silicon (p-n) junction solar cells by depositing p-type SWCNT films on n-type Si wafer. They prepared SWCNT film on glass slide depositing from nanotube-chlorosulfonic acid dispersion. Upon transferring the SWCNTs layer on n-doped Si wafer, they constructed p-n junction solar cell, which shows very high conversion efficiency (>11%).

1.5. Conclusions

The study of CNT networks is an emerging research field, which has a wide range of applications ranging from bio-medics to electronics. The use of CNT networks in industrial applications and everyday devices require addressing keys challenges including large-scale and cost-effective fabrication. Lowering the production cost of nanotubes with precise length and chirality is an ongoing enterprise. However, the production of economically viable CNTs assemblies/network with specific control of their properties is yet to be achieved. In this introductory chapter of my dissertation, I have presented a brief overview on different substrates that have been reported to manufacture carbon nanotube networks. My survey shows that
substrates underneath the network can be varied from planar to concave to porous, playing a crucial role for synthesis and applications of nanotube networks. Overall, the study of substrates is of great interest and present opportunities in further advancing the field of CNT networks. In addition, a thrust for novel hybrid materials containing CNTs networks has been evident in recent years. Impressive mechanical and chemical properties of CNTs have motivated researchers to synthesize composite materials involving silica, aluminosilicates, proteins, and DNA, among others. Although more research is needed to fully exploit the outstanding properties of CNT networks, this is an important area of research that promises to have a lasting impact in future commercial applications and technologies.

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Chapter 2

Single-Walled Carbon Nanotubes on the Surface of Porous Silica

Note: This chapter was copied from a paper that I coauthored.¹

2.1. Introduction

Single-walled carbon nanotubes (SWCNTs) on the surfaces of microparticles have important applications as stationary phases for chromatography,²⁻⁴ sensors,⁵ and the formation of carbon microstructures such as carbon microspheres.⁴,⁶ We have chosen the porous silicates zeolite-Y and MCM-41 as substrates for the immobilization of SWCNTs. Zeolites are crystalline microporous materials with defined pore structures.⁷ The zeolite framework is
composed by silicon atoms tetrahedrally coordinated by oxygen and linked together forming a porous silicate structure. Commonly, some of the silicon atoms are substituted by aluminum, imparting an intrinsic negative charge to the site. This charge is stabilized by a cation, generally sodium, although any cationic species specially, alkali or alkaline metals, can act as the counterion of these negative sites. Due to their channel structure, ion-exchange properties, and molecular and size recognition, many ions and molecules have been immobilized within zeolites channels. MCM-41 silicates are also silicate materials such as zeolites, but with larger pores and channels, and less crystalline structures. In this work we report how to efficiently cover the surface of porous silicates (Zeolite-Y and MCM-41) with different pore sizes, framework structures and aluminum content, with SWCNTs (Figure 2.1). The SWCNTs dispersed on the surface of these silicates are immobilized and individualized without the assistance of any wrapping molecules such as surfactants. Furthermore, we present experimental evidence that protonated SWCNTs can be converted back to pristine nanotubes with the full recovery of their photophysical properties, including van-Hove transitions and photoluminescence.
Figure 2.1  Pictorial representation of the deposition of SWCNTs. SWCNTs are immobilized on the surface of a porous silicate material followed by the subsequent loading of the photoactive molecule Ru(bpy)$_3^{2+}$ within the pores of the silicate particle.

2.2. Results and Discussion

2.2.1. Synthesis and Characterizations of MCM-41

We have used two types of MCM-41 samples. MCM-41 bought from Aldrich was denoted as MCM-41-A. Also, we synthesized MCM-41 in lab, which is denoted as MCM-41-B. This synthesis was performed following the work by Ryu et al.$^{15}$ Typically aqueous solution of dodecyl trimethyammonium bromide (DTAB) surfactants are used as template. Sodium silicate solution was added dropwise as silica precursor. The silica precursor condensed over the lyotropic liquid crystalline template of surfactants through aging for around 7 days. The
resulting mesostructured solid/surfactant composites were filtered and washed with copious amounts of ethanol to remove surfactants. Thereafter, it was calcined at 600 °C in ambient atmosphere to remove residual surfactants.

**Figure 2.2** Mechanism of mesoporous MCM-41 formation from surfactant templates (a) Spherical micelle of surfactant, (b) Rod shaped micelle, (c) Lyotropic liquid crystalline phase, (d) Mesostructured/surfactant hybrid after the condensation of silica precursor, (e) final product of MCM-41 after removal of surfactant by calcination. This diagram represents the hexagonal arrangement formed by seven cylindrical channels in a pseudo closed packed arrangement. The bulk material extends in 2-dimensions in structures similar to those in Figure 2.5a.
Figure 2.2 shows the mechanism of MCM-41 formation templated by cylindrical surfactant micelle. Once the synthesis of MCM-41 was accomplished, I characterized this material using different techniques. X-ray powder diffraction, and BET are common characterization techniques for mesoporous silica. Although MCM-41 is amorphous silica, it has sharp diffraction peaks due to the regular arrangement of channels (Figure 2.2). Table 2.1 shows d values of diffraction peaks and corresponding (h, k, l) planes.

![X-ray powder diffraction (XPRD) patterns of MCM-41 samples.](image)

**Figure 2.3** X-ray powder diffraction (XPRD) patterns of MCM-41 samples.
Table 2.1 Miller indices and corresponding diffraction peaks of MCM-41 samples.

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Nitrogen adsorption isotherms were performed to determine the surface area and pore size of MCM-41 (Figure 2.4). Before analysis, all the samples were degassed at 473 K for 18 h. Characteristic features of sharp capillary condensations are visible. However, the position of condensations steps is shifted to higher relative pressure in case of MCM-41-A due to slight differences in mesopore size in comparison with MCM-41-B. Figure 2.4 shows Barrett-Joyner-Halenda (BJH) pore
size distribution where the estimated pore size of MCM-41-A and MCM-41-B are 2.9 nm and 2.2 nm respectively.

![Figure 2.4](image)

**Figure 2.4** (a) Nitrogen adsorption isotherm and (b) pore size distributions of MCM-41 samples. Nitrogen adsorption isotherms were performed at 77K on Autosorb AS-3B adsorption analyzer.

The MCM-41 samples were further characterized by transmission electron microscopy (TEM). Imaging of mesoporous silica was done
using a high-resolution field emission gun transmission electron microscope. Micron sized mesoporous particles were dispersed in ethanol by bath sonication and drop casted on lacey carbon grid. Figure 2.5 shows the images of MCM-41 samples from different perspectives. TEM images also confirm the pore size of 2.9 nm for MCM-41-A samples.

![TEM images of MCM-41 sample](image)

**Figure 2.5** TEM images of MCM-41 sample from (a) transverse section showing regular hexagonal pores, and (b) longitudinal section showing straight channel structures.

### 2.2.2. Dispersion of SWCNTs in Surfactants

The immobilization of individualized CNTs in silicate materials was performed by a solution-based approach, where SWCNTs were
dispersed in a solvent followed by deposition. As-synthesized SWCNTs form bundled structures, which are difficult to individualize and bring into solution due to their large cohesive energy (> 0.5 eV/nm).\textsuperscript{16} A more efficient approach to disperse bundled SWCNTs is ultrasonication with an aqueous surfactant solution. Surfactant-stabilized aqueous solutions of SWCNTs (SWCNTs with sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), and pluronic-F 68 micelles) were placed into contact with MCM-41 and zeolites, showing precipitation of the SWCNTs but no incorporation on the silicate after 24h (Figure 2.6). It is envisioned that when carbon nanotubes in a surfactant solution come into contact with porous silicate materials, many of the surfactant may diffuse into the pores of silicates. This will cause a decrease in the effective concentration of surfactant, reducing their ability to induce Coulombic repulsion among nanotubes. Alternatively, the silicate materials could act as nucleation centers, providing a surface where carbon nanotubes can bind and aggregate. We indeed saw that carbon nanotubes are precipitated out of solution after stirring 24h in the presence of these materials. Since we observe inhomogeneous precipitation of SWCNTs on silicate materials by naked eye, we didn't perform additional characterizations. However, it is important to point
out that monolayers of HiPco SWCNTs have been deposited on amino functionalized silica spheres by Nakashima group where they have exploited strong interaction between amino group and nanotube surfaces.\textsuperscript{17}

\textbf{Figure 2.6} Photographs showing initial attempts to deposit HiPco SWCNTs with (a) 1\% DTAB solution with MCM-41, (b) 1\% Pluronic-F 68 solution with MCM-41, (c) 1\% DTAB solution with NaY, and (d) 1\% Pluronic F-68 solution with NaY. Images were taken after stirring the surfactant-dispersed solution with respective scaffolds for 24 hours. Nanotubes are crashing out of solution forming a heterogeneous layer on MCM-41 or NaY. The images show a white powder (zeolite or MCM-41) on the bottom of the flask, generally covered with a layer of black powder. Two layers can be distinguished more easily on (c) and (d).
2.2.3. Dispersion of SWCNTs in Chlorosulfonic Acid

A less common, but more effective method of dissolving SWCNTs as individuals is by using superacids such as fuming sulfuric and chlorosulfonic acids (CSA).\textsuperscript{18-21} The solubilization is driven by the protonation of the SWCNTs walls (pSWCNTs), which results in a strong electrostatic inter-SWCNT repulsion. Figure 2.7 shows a typical UV-absorption spectrum of HiPco SWCNTs dissolved in CSA showing the absence of van-Hove singularities due to protonation. Superacids are a convenient dissolution medium because silicates are stable in them. We dissolved SWCNTs in CSA and placed the solutions in contact with MCM-41-A (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 80), MCM-41-B (100% SiO\textsubscript{2}), and the zeolite-Y materials NaY (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 5.1) and USY (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 80). The retention of SWCNTs was followed by UV-Vis spectroscopy of the supernatant after filtration, and absorption isotherms were generated as shown in Figure 2.7 (the adsorption isotherms were not followed until saturation because solutions of SWCNTs in CSA above 16 ppm form a gel when in contact with silicates). The resultant residue was washed with chlorosulfonic acid. Subsequent washes with pure CSA didn’t extract any nanotubes from the residue. We noted that vacuum assisted filtration could not completely remove all the residual acid. The reason
to remove the entire acid was to characterize the materials more easily. After filtration, the composite materials look wet and were also fuming initially when placed in air. The excess of chlorosulfonic acid not extracted by vacuum filtration was removed by heating at 300 °C, in a furnace under nitrogen atmosphere.

**Figure 2.7** (a) Dissolution of HiPco SWCNTs in chlorosulfonic acid (CSA). The absence of van-Hove transitions is noticeable. (b) Adsorption isotherms of SWCNTs with the silicate materials MCM-41-A (—), MCM-41-B (—), NaY (—), and USY (—).

Figure 2.7 indicates that the composition of the materials plays an important role in their affinity to SWCNTs. MCM-41-B has the lowest affinity towards SWCNTs of all the materials studied. Interestingly, MCM-41-A and -B have a similar pore size (2.9 and 2.2 nm respectively) and framework structure, differing more substantially in the amount of aluminum present. The zeolite-Y samples, NaY and USY, with SiO₂/Al₂O₃
equal or smaller than MCM-41-A, also show good SWCNTs uptake, which tends to indicate that aluminum content might have a role in the binding of SWCNTs to silicates. In fact, NaY retains slightly more SWCNTs that USY, which is consistent with the higher aluminum content of the first. It is likely that protonated positively charged SWCNTs are attracted to the negatively charged aluminum sites on the surface of aluminosilicates; these aluminum sites can act as counterions for pSWCNTs or participate in proton transfer reactions between pSWCNTs and the aluminosilicate material. Although aluminum sites seem to have a role in modulating the affinity of silicate materials towards SWCNTs, it appears that it is not the only factor. For example, MCM-41-A has a larger SiO₂/Al₂O₃ ratio than NaY, however presented nearly quantitative adsorption at all the concentrations studied. Therefore, other factors such as the surface structure and the size of the external pores might have considerable effect on the binding of SWCNTs.

2.2.4. Characterizations of SWCNT-silicate Materials

In order to characterize thoroughly the produced materials, a set of spectroscopic techniques were used to study the electronic structure of SWCNTs on these silicates. The diffuse reflectance spectrum of SWCNTs
immobilized on the surface of MCM-41 (SWCNTs@MCM-41) presented in Figure 2.8 lacks the common van Hove transitions that are expected from pristine individual SWCNTs, which is consistent with the UV-Vis spectrum of pSWCNTs in CSA (Figure 2.7). Diffuse reflectance is a technique, which is analogous to UV-Vis absorption spectra of solutions but used for non-transparent materials. The optical interband transitions in the UV-Vis are sensitive to the aggregation state of the SWCNTs or to chemical modification. To assess whether the absence of van Hove transitions was due to SWCNT bundling or to protonation, we used Raman spectroscopy. The Raman spectrum of pSWCNTs in CSA ($\lambda_{\text{exc.}} = 784$ nm) shows only a broad featureless band, which is characteristic of the protonation of SWCNTs (Figure 2.8). Electromagnetic excitation at 784 nm shows little contribution to the Raman scattering cross section since the electrons responsible for the in-resonance transitions are largely depleted due to the protonation process.\textsuperscript{18} The Raman spectrum of SWCNTs@MCM-41 is similar to the spectrum of pSWCNTs and different from non-protonated pristine SWCNTs. This indicates that the removal of CSA from the material leaves protonated SWCNTs on their surface (hereafter, we call these materials pSWCNTs@MCM-41). Furthermore, photoluminescence cannot
be observed from pSWCNTs@MCM-41 or pSWCNTs@NaY. The lack of SWCNTs photoluminescence, together with the absence of transitions in Raman and diffuse reflectance indicates that the SWCNTs are still protonated after washing and drying off the CSA.

**Figure 2.8** (a) Diffuse reflectance spectrum of pSWCNTs@MCM-41 0.67% (w/w) (---). (b) Raman spectra ($\lambda_{\text{exc.}} = 784$ nm) of a pSWCNTs@MCM-41 0.67% (w/w) (---), SWCNTs solution in chlorosulfonic acid.

Similar spectra are obtained for materials with other SWCNTs@NaY, SWCNTs@USY, and SWCNTs@MCM-41-A and -B with different concentrations of SWCNTs with only variations in their intensities.

An alternative way to characterize the coverage of porous silicate by CNTs is by surface area determinations. Since mesoporous silica has
large surface area, we expected to obtain less surface area once the carbon nanotubes cover the external surface. Coating the openings of channel with nanotube network will reduce the nitrogen adsorption (pore blockage), which in turn will reduce the measured surface area. We observe the surface area of MCM-41 reduced from 1332 m²/g to 868 m²/g when nanotubes coated the external surface.

![Diagram](image)

**Figure 2.9** Nitrogen adsorption isotherm of MCM-41 and SWCNT@MCM-41.

We also imaged our resulting SWCNT-silicate composites by microscopy techniques. Although it would be reasonable to think that pSWCNTs in the surface of silicate materials are mostly individualized due to the electrostatic repulsion among their protonated walls, we tried to assess
the degree of individualization using imaging techniques such as SEM and TEM. Figure 2.10 shows the SEM of pSWCNTs@NaY; individual SWCNTs are difficult to distinguish on the surface of the silicate materials, and can be mostly distinguished when they protrude out of their surface. In this image intertwined SWCNTs departing from the surface of NaY can be seen. Figure 2.10b shows a lower magnification image of pSWCNTs-MCM-41 in which complete coverage of the particle by SWCNTs is observed. All of the structures seen in Figure 2.10a and 2.10b are less than 15 nm in diameter, indicating that small bundles can be found. This contrast with bundles of hundreds of nanometers found for pristine purified SWCNTs materials. Nevertheless, this doesn’t rule out that a large population of pSWCNTs are individual. It is more likely that individual SWCNTs are below the resolution of the SEM instrument used to monitor our samples (HiPco SWCNTs have diameters from 0.8 to 1.2 nm). Therefore, bundled structures, which have larger diameters, stick out on the microscopy images since their larger sizes are within the microscope resolution.
Figure 2.10 Microscopic images of pSWCNT-silicates. (a) SEM images of pSWCNTs@NaY zeolite, and (b) pSWCNTs@MCM-41. (c) and (d) HR-TEM images of SWCNTs on the surface of MCM-41.
2.2.5. Deprotonation of p-SWCNT-silicate Materials

Once immobilized on the surface of the porous silicate materials, it would be desirable to deprotonate the pSWCNTs to recover a material with individual pristine SWCNTs; (pristine SWCNTs have more interesting photophysical and electronic properties than functionalized SWCNTs). pSWCNTs can be easily deprotonated using ethyl ether and water. Figure 2.11 shows the Raman spectrum of a sample of pSWCNTs@MCM-41 treated with ethyl ether. Although the common features expected for pristine SWCNTs are recovered, which confirms that SWCNTs are deprotonated, a very intense band at 261 cm\(^{-1}\) of comparable intensity to pristine purified SWCNTs is observed. This band is due to the in-resonance Raman transition of (10,2) SWCNTs and is sometimes called the “roping peak” because its intensity has been associated to the degree of aggregation of SWCNTs.\(^{22-24}\) Therefore, the appearance of this band, of comparable intensity to that of pristine roped SWCNTs, indicates that deprotonation by ethyl ether causes aggregation. Similar results have been obtained with acetone, water and ammonia gas. This strong aggregation is not observed in chlorinated solvents such as dichloromethane and chloroform, which however do not cause
deprotonation. It is worth to mention that the mobility of p-SWCNTs on the surface of porous silica upon addition of ether is remarkable. Indeed the strong van der Waals attraction among tube plays a crucial role. In our subsequent project, when we deposited p-SWCNTs on non-porous fused silica, p-SWCNTs appear to be less mobile upon quenching with ethyl ether. The higher mobility of p-SWCNTs on porous silica can be conceptualized considering the porous and non-planar morphology of MCM-41. Nanotubes covering the empty pores and having less interaction with the surface tends to aggregate more once deprotonated in presence of ethyl ether. On the other hand, SWCNT networks covering planar fused silica have stronger interaction and less mobility even after deprotonation (see Chapter 3).
Figure 2.1  Raman spectrum of SWCNTs crashed out of MCM-41-A by addition of ethyl ether. The Raman spectrum of SWCNTs extracted in this way shows recovery of the roping peak. Moreover, the Raman spectrum is practically indistinguishable from the Raman spectrum of the pristine bundled SWCNTs powder.

In order to deprotonate pSWCNTs immobilized on the surface of silicate materials without inducing aggregation, vinyl pyrrolidone (VP) was used. VP has a similar structure as methylpyrrolidone (NMP), that is a solvent commonly used for the dispersion of SWCNTs. VP however has a vinyl group that will polymerize in acidic environments to form polyvinylpyrrolidone (PVP). We hypothesized that VP would deprotonate pSWCNTs and at the same time, polymerize on their surface preventing their aggregation. Figure 2.12 shows the diffuse reflectance spectrum of
VP-treated SWCNTs@MCM-41 (vpSWCNTs@MCM-41) where the van Hove transitions are completely recovered. The recovery of the van Hove transitions not only indicates that the SWCNTs are deprotonated but also indicates that they are individualized. For comparison, we determined the diffuse reflectance of the mechanical mixture of MCM-41-A and bundled pristine SWCNT powders. In this mixture no sharp van Hove transitions can be observed due to the highly bundled state of the nanotubes (Figure 2.12). Furthermore, in the case of mechanical mixture, most of the light is reflected out of the sample and little absorption can be seen, probably due to the fact that the silicate particles, not covered by SWCNTs anymore, reflect most of the light out without absorption.
Figure 2.12  (a) Diffuse reflectance spectra of vpSWCNTs@MCM-41 0.67% (w/w) (—), and mechanically mixed SWCNTs and MCM-41 0.67% (w/w) (—). (b) Raman spectra \((\lambda_{\text{exc.}} = 784 \text{ nm})\) of pristine SWCNTs powder (—), and vpSWCNTs@MCM-41 0.67% (w/w) (—).

The Raman spectrum of vpSWCNTs@MCM-41 is presented in Figure 2.12 and Figure 2.13 showing recovery of the common features of pristine SWCNTs. Commonly, the ratio between the G band (tangential mode band at ca. 1590 cm\(^{-1}\)) and the D band (disordered mode at ca. 1300 cm\(^{-1}\)) is used to assess the integrity of the CNTs sidewalls. A D/G ratio of less than 1/20 is common for HiPco SWCNTs with pristine sidewalls.\(^{25}\) The D/G ratio of vpSWCNTs@MCM-41 is ca. 1/28 (same as pristine SWCNTs not treated with CSA) confirming that pristine SWCNTs are immobilized on the surface of MCM-41 (Figure 2.12). Moreover, the roping peak at 261 cm\(^{-1}\) is greatly reduced in intensity in comparison with pristine SWCNTs indicating that most
CNTs are unbundled.\textsuperscript{25} This is also consistent with the decrease in broadening and increase in the intensity of the Raman RBM bands (around 225 cm\textsuperscript{-1}, for expanded spectra Figure 2.13). Furthermore, the roping peak doesn't increase in size with increasing the concentration of SWCNTs on the silicate materials indicating that the aggregation state is not dependent on SWCNT concentration, in contrast with other works. SWCNTs@MCM-41 materials of up to 1.3\% (w/w) have been prepared presenting just marginal SWCNTs aggregation.
Figure 2.13 Expanded Raman spectra of the RBM region for pristine SWCNTs (black) and vpSWCNTs@MCM-41 (blue).

To further characterize the deprotonation process, we used photoluminescence spectroscopy. The diffuse reflectance and Raman spectra show that SWCNTs on vpSWCNTs@MCM-41 materials are individual and pristine, indicating that their photophysical properties are intact. Therefore, the solid material vpSWCNTs@MCM-41 should present photoluminescence in the near-infrared. Reports of photoluminescence from SWCNTs in solid materials are not common.
in the literature and are restricted to sparse SWCNTs deposited on planar glass surfaces or trapped into thin polymeric films.\textsuperscript{26,27} Although some preliminary studies have suggested that the photoluminescence of SWCNTs can be regenerated after chemical modification (including protonation)\textsuperscript{28} we present here conclusive evidence that pSWCNTs can recover their photoluminescence when deprotonated as long as they remain unbundled. Figure 2.14 shows the photoluminescence spectra of vpSWCNTs@MCM-41. This photoluminescence is a definite proof of individualization (quenching of photoluminescence is highly efficient in SWCNTs bundles) and is in line with the conclusions from Raman and diffuse reflectance.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_14.png}
\caption{Recovered photoluminescence spectra of vpSWCNTs@MCM-41 0.67\% (w/w) (---) and SWCNTs dispersed in NMP (---).}
\end{figure}
2.2.6. Quenching of Ru(bpy)$_3^{2+}$ by pSWCNTs on MCM-41

Although porous materials with individual SWCNTs on their surface possess potential applications in different fields (as was mentioned in the introduction) it would be important to demonstrate how these materials can be used for studying the interaction between photoactive molecules and SWCNTs. In the past few years a lot of interest have been generated in studying the interaction of SWCNTs with photoactive molecules such as porphyrins, however this has always required the chemical functionalization of the photoactive species with anchoring groups that will allow their binding to SWCNTs,$^{29,30}$ or their direct covalent attachment.$^{31,32}$ In this approach, we have decided to take advantage of the supramolecular framework of pSWCNTs@MCM-41 to encapsulate a photoactive metal complex such as tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)$_3^{2+}$) in close proximity to p-SWCNTs. This ruthenium(II) metal complex has been extensively studied, especially for its application in light harvesting materials, and it is a potential candidate for the fabrication of hybrid materials with SWCNTs, Ru(bpy)$_3^{2+}$ was loaded into MCM-41 following the procedure from Bottinelli et al.$^{33}$ Typically Ru(bpy)$_3$(PF$_6$)$_2$ was dissolved in dichloromethane and stirred with dry p-SWCNTs@MCM-41.
Encapsulation of ruthenium complexes in the mesopore is driven by entropy and stabilized by non-specific interactions. The resulting material was filtered and washed with excess dichloromethane. It is worth to mention that residual CSA is washed away during the loading of the photoactive molecules (CSA is highly soluble in dichloromethane). Although the interaction of Ru(bpy)$_3^{2+}$ with electron acceptors is generally studied by steady-state photoluminescence quenching, in this case, SWCNTs on the surface of the MCM-41 particle absorb some of the light, preventing it from reaching Ru(bpy)$_3^{2+}$, and therefore making steady-state quenching analysis unreliable. In order to overcome this, we used time-resolved photoluminescence spectroscopy, since photoluminescence lifetime is not sensitive to the intensity of the excitation light, but it is sensitive to quenching by photoinduced electron transfer reactions. Figure 2.15 shows the time-resolved decays for Ru(bpy)$_3^{2+}$ loaded into MCM-41 (Ru-MCM-41) or into pSWCNTs@MCM-41 (Ru-pSWCNTs@MCM-41). The red curve represents the slowly decaying photoluminescence of Ru-MCM-41 showing a bi-exponential decay with a lifetime of 186 and 681 ns, while Ru-pSWCNTs@MCM-41 shows a biexponential decay with a lifetime of 8.2 and 600 ns. This short lifetime of 8.2 ns can be assigned to
quenching of Ru(bpy)$_3^{2+}$ inside the MCM-41 channels but that are near the surface, in close proximity to SWCNTs. The long lifetime observed is probably due to Ru(bpy)$_3^{2+}$ that are buried inside the channels of the MCM-41 particle and therefore far from the SWCNTs. Binding of Ru(bpy)$_3^{2+}$ to SWCNTs on the surface is less likely, first because positive charge of pSWCNTs would repel Ru(bpy)$_3^{2+}$ dications, and secondly because previous studies have shown that Ru(bpy)$_3^{2+}$ has little affinity for SWCNTs.$^{34}$ A question may arise that quenching of metal complex is due to presence of residual superacid even after drying but not due to the excited state electron transfer. We would like to point out that if superacid is involved in quenching of Ru(bpy)$_3^{2+}$, it would quench both short and long decay components due to the expected homogeneous distribution of acid molecules within MCM-41 channels. Nonetheless, we observed the quenching of the short component only, which nullified the argument of acid quenching of Ru(bpy)$_3^{2+}$. Furthermore, acid is not expected to be co-encapsulated with Ru(bpy)$_3^{2+}$ since we washed the resulting material with dicholomethane to remove unbound Ru(bpy)$_3^{2+}$ and any residual acid (as mentioned above).
Figure 2.15 Time-resolved fluorescence spectrum for Ru(bpy)$_3^{2+}$ in MCM-41 (red) and pSWCNTs@MCM-41 (blue).

To the best of our knowledge, this is the first time that photoinduced electron transfer to protonated SWCNTs has been reported. Our results present a proof-of-concept of these materials, especially, considering the large amount of different molecules that can be immobilized in the internal cavities of these silicates. Porous supramolecular framework materials can be used as an alternative strategy to study the interaction of SWCNTs with photoactive species immobilized in their internal framework. Furthermore, different
photoactive molecules can therefore be studied using these scaffolds, without time consuming chemical modifications with anchoring agents.

### 2.3. Conclusions

In conclusion, we report the immobilization of individual SWCNTs on the surface of microporous and mesoporous silicate materials using chlorosulfonic acid. Spectroscopic studies demonstrate that these materials are covered with mostly individual protonated SWCNTs. Treatment with VP deprotonates the SWCNTs and prevents their aggregation, as shown by Raman, diffuse reflectance, and near-infrared photoluminescence emission from these materials. Notably, the recovery of photoluminescence from protonated SWCNTs deposited on MCM-41 is novel, and combined with high surface area and porosity of these zeolite materials, presents unique advantages that can be exploited in the construction of new hybrid materials with interesting physical and electronic properties. Furthermore, the possibility of encapsulating photoactive species such as Ru(bpy)$_3^{2+}$ within the channels and cavities of these
materials, provides an easy way to study their interaction with SWCNTs on the surface without the need of anchoring molecules. This is an example of how supramolecular systems can be combined with nanomaterials to produce novel hybrid materials with interesting properties.

2.4. Experimental Section

Synthesis of MCM-41-B

MCM-41-B has been synthesized following the procedure of Ryoo et al.\textsuperscript{15,35} A clear solution of silica precursor was prepared by combining 14.2 g of 1.00 M aqueous NaOH solution with 4.3 g of Ludox HS40 colloidal silica, 40 wt% suspension in water (Aldrich). The resulting mixture was heated with stirring for 2 h at 353 K. The silica source was added dropwise to a polypropylene bottle containing 2.2 g of ~4.3% aqueous solution of dodecyltrimethylammonium bromide (DTAB, 99% Sigma). The overall molar composition of the resultant mixture is (4 Si: 1DTAB: 100 H\textsubscript{2}O). During addition of the silica source, the surfactant solution was stirred vigorously and the temperature was kept at 65 °C. After stirring for one more hour, the resultant mixture was heated for 24
hrs at 100 °C (without stirring). Then, the mixture was cooled to room temperature, and the pH was adjusted to 10 with 30 wt% acetic acid in water. The mixture after pH adjustment was heated again for 48 hrs at 100 °C. The procedure of pH adjustment and subsequent heating for 1 day was repeated once more. The precipitated MCM-41-B with surfactant template was finally filtered and washed with ~300 mL of Ethanol:HCl:Water solution (84.1: 1.0: 14.9 mol/mol) and calcined in air in a furnace. The temperature was increased slowly to 500 °C over 10 hr and maintained at 500 °C for 4 hr. It is important to ramp slowly since ethanol is flammable at high temperatures.

**Purification of HiPco SWCNTs**

HiPco SWCNTs were purified as described elsewhere.\(^{36}\) ~1 g of raw HiPco tubes was weighed in a large petri dish. Care must be taken not to inhale the tubes. Distilled water was added to it. After that, the dish covered with aluminium foil was put into the oven (at 80 °C) with constant supply of air bubble through water. The water level was monitored every 5-6 hrs. After 10-12 hrs of annealing, the temperature was increased to 200 °C and kept for another 12 hrs. At this point, water level was monitored in every 3-4 hrs. Following this,
the resulting nanotubes were stirred with 500 mL 6M HCl for ~1-2 hrs. Then, nanotubes were soxhlet extracted until the extract becomes colorless (to remove all the FeCl$_3$). It takes usually 4-5 days for extraction. Then the tubes were vacuum filtered and washed with water until the pH remained neutral (tested with litmus). Subsequently, it was washed with a saturated solution of sodium bicarbonate in water and pure water. The wet material was vacuum dried and subsequently dried at 110 °C in vacuum. The purified nanotubes were characterized by Raman and TGA.

**Dissolution and Deposition of SWCNTs**

In a typical SWCNT deposition experiment, 1-4 mg SWCNT are placed in a vacuum oven at 110 °C for 12h. Following this, SWCNTs were dissolved in 6 mL CSA (inside glove box) and stirred for 24h. Subsequently, the calcined silicate (either MCM-41, NaY or USY) was added to SWCNTs CSA solution. Important: The silicate material was allowed to cool down for ~10 min inside glovebox before adding the solution. After 24 h constant stirring the mixture was filtered (2.0 µM PTFE supported Zefluor™) and the supernatant collected and analyzed by UV-Vis spectroscopy (Shimatzu UV-2450) using 1 cm
pathlength quartz cuvettes. The supernatants were diluted by a factor of 20 before absorption measurements. The concentration of SWCNTs absorbed was determined from UV-Vis absorption spectroscopy using an extinction coefficient calculated by Rai et al. The concentration of SWCNTs absorbed was calculated by subtracting the concentration of SWCNTs before deposition experiments (calculated by UV-Vis). These concentrations were used for the construction of the adsorption isotherms. The collected black solid was washed three times with pure CSA and dried at 300 °C for 4h. We noted that the black solid is hygroscopic if we didn’t dry them and keep it in ambient atmosphere. The dry samples were kept in a dry inert atmosphere. For vinyl pyrrolidone (VP) treatment, ~50 mg of samples were added to 2 ml of VP and stirred for 30 min followed by bath sonication for 10 s.

Characterization of the Materials

Samples were analyzed using a Raman microscope (Renishaw in Via MicroRaman Spectrometer). pSWCNTs-silicate materials were characterized as soon as possible after removing from glovebox and all the samples are carried in vacuum container with drierite. SEM images were obtained on a FEI Quanta 400 ESEM FEG. To prepare
samples for SEM, dry powder materials were added to carbon tape. TEM were obtained using a JEOL 2100 Field Gun Transmission Electron Microscope. Diffuse reflectance was obtained using a UV-Vis spectrometer (Shimadzu UV-2450) equipped with an integrating sphere. For the physical mixture of SWCNT and MCM-41, the dry powders were grounded and mixed together with a mortar and pestle. Photoluminescence characterizations of SWCNTs were performed in a Model NS1 NanoSpectralyzer (Applied NanoFluorescence) from 1050 to 1530 nm relative to matched references (with fixed excitation lasers 638, 687, and 783 nm). One short-pass dielectric filter (FES 1000, Thorlabs) was inserted before the sample compartment to block unwanted excitation lines present in the laser. Another neutral density filter ~42% transmittance was utilized to decrease the laser intensity.

**Quenching Experimental Procedures**

Commercially available Ru(bpy)$_3$Cl$_2$ was ion exchanged to corresponding hexafluorophosphate salt by excess addition of ammonium hexafluorophosphate and further precipitation. Loading of Ru(bpy)$_3^{2+}$ into MCM-41 was performed by dissolving 1.32 mg of
Ru(bpy)_3(PF_6)_2 in 5 ml of dichloromethane and placing this solution in contact with 200 mg of MCM-41 or pSWCNTs@MCM-41. After two hours of stirring, no Ru(bpy)_3^{2+} could be detected in the supernatant solution. Then, the material was filtered and washed thoroughly with dichloromethane, after which the solvent was evaporated. The dry material was used to make a dilute suspension in dichloromethane (0.05% w/v) and purged with ultrapure nitrogen. Time-resolved decays of these suspensions were obtained using an Edinburgh Instruments OD470 single photon counting spectrometer with a 443.6 nm picosecond pulse diode laser, and monitoring at 620 nm.

2.5. Experimental Contributions

My contribution to the experimental work described in this chapter are the following, synthesis and characterization of MCM-41, dissolution and deposition of SWCNTs on the surface of MCM-41 and zeolite silicates, and microscopic and spectroscopic characterizations of SWCNTs-silicate materials. Dr. Saunab Ghosh provided assistance for NIR-photoluminescence characterization of vpSWCNTs@MCM-41 materials. Dr. Natnael Behabtu provided initial training for working with CSA and glovebox.
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Chapter 3

Fabrication of Thin Films with Tunable Properties by Dip Coating

Note: This chapter was taken in most part from a manuscript I coauthored.1

3.1. Introduction

In the past few years, much research interest has been focused on the fabrication of random or oriented single-walled carbon nanotube (SWCNT) networks on various substrates. The motivation for forming such SWCNT films is their potential applications in electronic devices such as organic light emitting displays,2-4 thin film transistors,5,6 and organic photovoltaics.7,8 Conventional transparent conducting films of
indium tin oxide (ITO) lack flexibility and are relatively expensive, whereas films based on SWCNTs could potentially display high flexibility and lower cost. Various film fabrication techniques have been reported, including spin coating, spray coating, bar coating, dip coating, drop casting, and vacuum filtration. All of these methods are classified as solution-based deposition techniques as they require dispersing the SWCNTs in a suitable solvent, followed by deposition onto the substrate of interest. Spin coating is a simple and effective method for depositing SWCNT on substrates, but it is not easily scaled up for large-scale fabrication. Spray coating is also a simple method but it is not well suited to making uniform thin films because SWCNT droplets form an inhomogeneous distribution in the mist. Although vacuum filtration leads to uniform reproducible films, the transfer process to suitable substrates may enhance the cost in industrial applications. Compared to all other aforementioned methods, dip coating is elegantly simple and has the advantage of scalability to large and non-planar substrates.

In our previous work, we have showed that SWCNTs protonated by chlorosulfonic acid (CSA) adhere efficiently to silicon oxide
microporous and mesoporous particle surfaces.\textsuperscript{24} We hypothesized that a similar behavior could be obtained for such protonated nanotubes (p-SWCNTs) on flat silicon oxide surfaces. Here we have described the photophysical and electronic properties of films made by SWCNT deposition from CSA onto flat fused silica windows (Figure 3.1). Oddly, although fused silica is widely used in many applications including photovoltaics, monitors, LCD displays, and UV transparent windows, there seem to be no reports of two-dimensional SWCNT networks on fused silica. A detailed study of how to make such fused silica-SWCNT composites, together with a thorough characterization of their properties, is pivotal for potential applications that range from display technologies to sensors to solar cells. In this chapter we describe a general methodology to allow the straightforward fabrication of SWCNT films on fused silica substrates, with properties that can be tailored from highly photoluminescent to highly conductive by adjusting the nanotube concentration.
3.2. Results and discussion

3.2.1. Photoluminescence of Low-density Thin-films

Photoluminescence of SWCNTs occurs due to the band structure of semiconducting carbon nanotube. The theory states that mobile excitons (bound excited electron and hole) are generated upon light excitation on individual tubes followed by photoemission due to charge recombination. The photoluminescence intensity depends on intrinsic features like dopants, surface defects and extrinsic factors such as external chemical reaction or dielectric constant of the environment. For example, surface defects on the carbon atom based SWCNTs sidewall reduces mobility of exciton, therefore decreases the possibility
of NIR-photoemission. Therefore, NIR-photoluminescence of individual nanotubes usually indicates the degree of defects and chemical modification on the surface of SWCNTs.

Our previous work demonstrated that the bulk NIR-photoluminescence of SWCNTs can be regenerated by deprotonating the SWCNT surface.\textsuperscript{24} One of our objectives in this project is to recover the NIR-photoluminescence of individual SWCNTs after their deposition on flat fuse silica windows. Individualization of SWCNTs was achieved by using CSA (similar to the technique employed in our previous project\textsuperscript{24}), which dissolves SWCNTs by reversibly protonating their walls resulting in coulombic repulsion between CNTs and facilitates disaggregation by counteracting the strong intertube van der Waals attractions.\textsuperscript{25,26} Recovering individual tube photoluminescence after deprotonation supports the concept of reversible sidewall functionalization in presence of CSA. To regenerate photoemission of individual tubes on the fused silica substrate, a film was made from a dilute SWCNT CSA solution with concentrations ranging from 0.005 mg/mL to 1 mg/mL and then treated the films with diethyl ether. Figure 3.2 shows the photoluminescence image of such a film. NIR
photoluminescence from isolated centers is observed, as is consistent with the presence of emissive individual SWCNTs. Further evidence that these spots correspond to SWCNTs comes from the variations in emission intensity of individual centers with excitation polarization (Figure 3.2b). The dominant absorption and emission transitions of SWCNTs are known to be strongly polarized parallel to the nanotube axis,\textsuperscript{27,28} so the intensity modulation shown in Figure 3.2b is a signature of an individual SWCNT rather than an aggregate with randomly oriented nanotubes.
Figure 3.2 (a) NIR photoluminescence image of SWCNTs on a fused silica slide prepared by deposition from a 5 μg/ml CSA solution followed by deprotonation with diethyl ether. (b) Normalized intensity of an individual emission spot vs excitation beam polarization angle. The solid curve is a fit of the form sin²θ.

We have also recorded spectra of the emissive centers that confirm their identities as individual SWCNTs. Figure 3.3 shows such spectra for 7 different spots whose distinct peak positions indicate different \((n,m)\) species. The peak wavelengths appear to be red-shifted from those reported for individual CVD-grown SWCNTs suspended in air, but they are similar to those observed for individual SWCNTs coated with surfactants. The emission full-widths at half-maximum, between ca. 15 and 23 meV, are also similar to those of surfactant-coated nanotubes\(^{29,30}\) and broader than spectral widths reported for bare
SWCNTs suspended in air.$^{28,31,32}$ As these samples had not been exposed to surfactants, we suggest that the spectral differences compared to air-suspended SWCNTs arise from interactions with the fused silica substrate.

![Normalized emission spectra of individual tubes dried on a fused silica substrate upon (a) 740 nm and (b) 840 nm laser excitation.](image)

**Figure 3.3** Normalized emission spectra of individual tubes dried on a fused silica substrate upon (a) 740 nm and (b) 840 nm laser excitation.

We also noted significant loss of SWCNT photoluminescence after the films on fused silica had been exposed to air for several days. This exciton quenching effect seems consistent with the reversible surface oxidation of SWCNTs reported by Dukovic *et al.*$^{33}$ Following this slow reduction of emission, the photoluminescence efficiency of our films could be restored by an additional immersion in diethyl ether. We suggest that p-doping caused by atmospheric oxygen in the presence of
residual acid is reversed by proton transfer to diethyl ether, through a reaction analogous to the acid-catalyzed ether fission that is well known in organic chemistry.\textsuperscript{34}

Decreased photoluminescence efficiency was observed for films prepared from more concentrated SWCNT solutions. We attribute this effect to electronic coupling between contacted nanotubes. Such coupling allows optical excitations to flow from semiconducting to metallic SWCNTs, where rapid nonradiative decay prevents luminescence. We note that photoluminescence was still observable from individual SWCNTs in films prepared from nanotube concentrations as high as 0.03 mg/mL in CSA (Figure 3.4).

\textbf{Figure 3.4} NIR photoluminescence image of SWCNTs on a fused silica slide prepared by deposition from a 0.03 mg/ml solution in CSA followed by deprotonation with diethyl ether.
3.2.2. Fabrication of Transparent and Conductive Networks

In my introductory chapter (Chapter 1), I have described in details the importance and applications of transparent conductive nanotube networks. Maximum flux of photon and electron is desirable for better performance of transparent conductive networks in electronic devices such as photovoltaic cells. Keeping in mind the significance of transparent conductive films, we have implemented a dip-coating approach similar to the one we used to fabricate low-density photoluminescent films. Our studies indicate that denser nanotube networks are accompanied by an increase in conductivity of the film. To prepare conductive films it is desirable to have a closely packed interconnected network of SWCNTs to increase the number of electrical pathways. We hypothesized that p-doped nanotubes (p-SWCNTs) would have high affinities toward non-porous flat fused silica substrates, similar to those of mesoporous aluminosilicates in spite of the morphological differences. By varying the dipping time and concentration of the SWCNT solutions, we obtained CNT networks with different densities, allowing the study of their optical and conductive properties. A common way to show the performance of conductive thin
films is by plotting sheet resistance vs. transmittance of visible light (usually at 550 nm, near the peak of the eye's response curve). As the film transparency decreases in denser networks of SWCNTs, the number of electrical pathways increases, reducing the sheet resistance. Resistive touch-screen applications require films with high visible transparency and low sheet resistance (85-90% transmittance and 300-500 ohm/sq sheet resistance). Figure 3.5 shows our results for sheet resistance vs. transmittance (along with visible transmission spectra) for different SWCNT depositions. We achieved sheet resistance as low as 212 and 471 ohm/sq with transmittance of ~76% and ~86% respectively, which slightly outperforms films made of metallic sorted HiPco SWCNTs (ca. 231 ohm/sq with 75% transmittance). It is notable that our films made of p-SWCNTs and ether-treated SWCNTs (which are deprotonated) show similar performance (Figure 3.5a), despite previous reports that acid-doped SWCNTs should give higher film conductivities. The reasons for this lack of doping enhancement are not yet clear, but it seems possible that the identity of the conjugate base and the degree of protonation play roles in modulating the conductivity of the films. Evidence of doping in p-SWCNT film is evident from X-ray photoelectron spectra (see below).
Figure 3.5 (a) Sheet resistance vs transmittance of SWCNTs films with different transparencies. Resistances of both protonated p-SWCNTs films and depronated films are shown in the figure with respect to % transmittance. (b) % Transmittance of p-SWCNTs films with different sheet resistances were measured at 550 nm wavelength.

The performance of transparent conductive films can also be expressed with a figure of merit (FOM), which can be described in different but essentially equivalent ways.\textsuperscript{13,37,38} Recently Dan \textit{et al.} formulated the following relation between sheet resistance ($R_s$) and transmittance ($T$):\textsuperscript{13}

$$R_s = -\frac{\alpha \rho}{\ln T} \quad (1)$$

Here the product of Beer-Lambert absorption coefficient ($\alpha$) and resistivity ($\rho$) was defined as the FOM. The advantage of using ($\alpha \rho$) as a
FOM is that it is independent of the film thickness, allowing better comparison among films produced by different groups. It is known that the properties of conductive SWCNT films depend strongly on the type of nanotubes they contain and on the fabrication method\textsuperscript{17,22,39}. We therefore chose to compare the performance of our films with others that were made from HiPco SWCNTs, or were prepared using dip-coating. Figures 3.6a and 3.6b show previously reported sheet resistance vs. transmittance data for these two classes of conductive SWCNT films, along with our current findings. It can be seen that our p-SWCNT and ether-treated films show performances comparable with some of the best prior reports. We note that almost all of the other films included in this comparison had been further doped with either HNO\textsubscript{3} or SOCl\textsubscript{2} before sheet resistance measurements.
Figures 3.6c and 3.6d show FOM plots, based on equation 1, for HiPco and dip-coated films. In these figures, sheet resistance varies linearly with $-1/\ln T$, with a slope equal to FOM ($\alpha \rho$). Thus, films with favorable properties (higher transparency and lower sheet resistance) will show lower slopes (lower FOM) in 3.6c and 3.6d. Roth and coworkers have reported HiPco dip-coated conductive films with

![Figure 3.6](image)

**Figure 3.6** Performance comparison of our p-SWCNTs and ether-treated films with previously reported (a) HiPco films and (b) dip-coated films. Figure (c) and (d) illustrate comparative FOM plots for HiPco and dip coating, respectively.
slightly better FOM than the ones prepared in this study.\textsuperscript{17} Interestingly, they suspended the CNTs in surfactants using strong sonication, which would lead to SWCNTs significantly shorter than the ones we used.\textsuperscript{40} The fact that such networks of shorter SWCNTs showed better performance than the networks of relatively long, bare SWCNTs used here challenges the current understanding of SWCNT film conductivity, such as the finding of Hecht \textit{et al.} that electrical conductivity increases as average bundle length raised to the power 1.46.\textsuperscript{41} There is clearly a need for further fundamental studies to clarify the factors that control electrical properties in CNT two-dimensional networks.

When we measured sheet resistance at various positions to study the spatial uniformity of our SWCNT films on fused silica, we observed that resistance variations decreased with increasing initial concentration of SWCNTs in CSA. This observation may reflect the formation of more homogeneous SWCNT networks at higher concentrations, giving a more uniform sheet resistance (See error bars in Figure 3.5a).
3.2.3. Structural Characterizations of Films

In order to characterize the morphology and composition of the SWCNTs films, we have used microscopic techniques such as atomic force microscopy (AFM), and spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Figure 3.7 shows atomic force microscopy (AFM) images of SWCNT thin films on fused silica using different concentrations of SWCNTs in CSA. As can be seen from the figure, CNTs form a continuous web over the substrate, where larger bundles of SWCNTs become more prevalent as the concentration is increased, and preferential orientation of these bundles becomes noticeable.

![AFM images of SWCNT films prepared from SWCNT solutions of (a) 0.05 mg/mL, (b) 1 mg/mL (~90% transparency), and (c) 2 mg/mL (~ 70% transparency) concentrations.](image)

**Figure 3.7** AFM images of SWCNT films prepared from SWCNT solutions of (a) 0.05 mg/mL, (b) 1 mg/mL (~90% transparency), and (c) 2 mg/mL (~ 70% transparency) concentrations.
X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical modification of the dry nanotube films before and after quenching with diethyl ether (see Figure 3.8). The large C1s peak due to sp\(^2\)-hybridized carbon appears at 284.0 and 284.3 eV for p-SWCNT and ether-quenched films respectively. The downshift of p-SWCNTs is consistent with p-type doping.\(^{42}\) For the p-SWCNTs films, we observe small shoulder peaks in the higher energy range of 290-293 eV. These unexpected shoulder peaks are likely due to the presence of -CF\(_2\) moieties.\(^{43}\) Arguably, mild oxidation of nanotube sidewalls might also be responsible for the presence of the small peaks. However, the presence of fluorine in the survey spectra (Figure 3.9) supports the assignment to -CF\(_2\) groups, which could represent contamination from the PTFE septa used for our preparations. These shoulder peaks essentially disappeared on treatment with diethyl ether. The weak signal near 168 eV in the S2p region probably comes from residual SO\(_3\)Cl. Sreekumar \textit{et al.} also observed the S2p XPS spectra in their SWCNT films prepared from oleum dispersions.\(^{44}\) However, we did not observe any additional S2p peak at 164.1 eV, which indicates the absence of any S in the (II) oxidation state (-C-S-C- bond).\(^{22,42}\) Our XPS results show that carbon
atoms are not significantly oxidized or chemically bonded to sulfur during film preparation.

**Figure 3.8** High-resolution XPS spectra of thin SWCNT films on fused silica substrate in the (a) C1 region and (b) S2p region.
The Raman spectra of diethyl ether treated nanotube films excited at 785 nm are presented in Figure 3.10. The peak intensity ratio between the D band (disorder mode near 1300 cm\(^{-1}\)) and G band (tangential mode at \textit{ca.} 1590 cm\(^{-1}\)) is \(\sim 1/7, \sim 1/8, \) and \(\sim 1/16\) for the films with 92.4\%, 80.3\%, and 69.1\% transparencies, respectively. These ratio are larger than for pristine HiPco samples (less than 1/20). The increased D/G ratio suggests defect formation on SWCNT sidewalls, which may have been catalyzed by the fused silica surface during the heating step used to remove excess solvent. The lower D/G ratio in higher density films could then be attributed to thicker films that have a significant population of CNTs shielded from direct contact with the

\textbf{Figure 3.9} Survey XPS spectra of (a) p-SWCNTs and (b) ether treated films on fused silica substrate. Amount of fluorine is reduced in ether treated films which is associated with reduced shoulder peak of C1s peak.

The Raman spectra of diethyl ether treated nanotube films excited at 785 nm are presented in Figure 3.10. The peak intensity ratio between the D band (disorder mode near 1300 cm\(^{-1}\)) and G band (tangential mode at \textit{ca.} 1590 cm\(^{-1}\)) is \(\sim 1/7, \sim 1/8, \) and \(\sim 1/16\) for the films with 92.4\%, 80.3\%, and 69.1\% transparencies, respectively. These ratio are larger than for pristine HiPco samples (less than 1/20). The increased D/G ratio suggests defect formation on SWCNT sidewalls, which may have been catalyzed by the fused silica surface during the heating step used to remove excess solvent. The lower D/G ratio in higher density films could then be attributed to thicker films that have a significant population of CNTs shielded from direct contact with the
fused silica surface (see Figure 3.10). For Raman spectra of HiPco samples obtained with 785 nm excitation, the radial breathing mode (RBM) feature at 267 cm\(^{-1}\) is associated with bundled SWCNTs.\(^{45,46}\) Figure 3.10b shows an increase in the relative intensity of this peak as the film transparency decreases from 92.4% to 69.1%, indicating an increased proportion of bundled nanotubes in the thicker films. Still, judging from the RBM intensities, the degree of aggregation is nonetheless lower than in as-produced undispersed pristine SWCNTs.

**Figure 3.10** (a) Raman spectra of the SWCNT films of three different transparencies after quenching with diethyl ether; peaks are normalized with respect to G-band intensity. (b) Radial breathing mode region of SWCNT films of three different transparencies; peaks are normalized with respect to 233 cm\(^{-1}\) peak intensity.
3.3. Conclusions

In summary, we have illustrated a simple and easily scalable technique that allows the preparation of SWCNT thin films with tailored properties. Fused silica substrates are dip-coated in solutions of SWCNTs in CSA. Adjusting the concentration of this solution allows the preparation of low density SWCNT networks showing photoluminescence, or higher density networks that form transparent conductive films. A clear advantage of this methodology is that “bare” SWCNTs free of surfactant coatings are quickly deposited on the fused silica surface, and the SWCNTs are not shortened by ultrasonic processing prior to deposition, as is generally the case in surfactant-based methods. The performance of these films as transparent conductors is competitive with state-of-the-art nanotube-based films recently reported by other groups. We expect that our solution-based dip-coating process will enable low cost and large-scale production of thin films with conductive or photoluminescent properties.

As a final note, the performance of the nanotube network can be further improved using long, metallic-enriched SWCNTs. As mentioned earlier, conductivity of nanotube films is dependent on the length of
individual nanotubes and percolated network metallic tubes. In that sense, HiPco SWCNTs may not be an ideal candidate for fabrication since the average length is ~1 μm and they are a mixture of various semiconducting and metallic nanotubes. Recently, Pasquali research group reported scalable dip-coated nanotube films with 90% transparency and 100 Ω/sq sheet resistance using ~10 μm double-walled carbon nanotubes. Both of our research shows that efficient dip coating from SWCNT-CSA dispersion can produce very high quality nanotube films which has potential for industrial applications.

3.4. Experimental Section

Materials

The SWCNTs (HiPco bath 195.1) used in this study were synthesized by the high-pressure carbon monoxide (HiPco) process at Rice University and were purified by low temperature oxidative annealing and acid treatment as reported in Chapter 2. Planar fused silica windows (12.5 x 45 mm) were obtained from Starna Cells. ACS certified chlorosulfonic acid (density = 1753 kg/m³) was used as received from Sigma Aldrich.
**SWCNT Film Preparation**

Concentrated solutions of SWCNTs in CSA (1.0 mg/mL, 1.5 mg/mL and 2.0 mg/mL) were prepared following procedures described in previous chapter. Fused silica slides were thoroughly cleaned (bath sonication in chromic acid and water both for 10 minutes) to remove impurities, dried at 450 °C and immersed vertically (manually) in a beaker containing a SWCNT solution of the desired concentration for 0 to 20 s. Chromic acid was prepared using the following steps: dissolution of 20 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 40 ml water, slow addition of 360 mL of concentrated sulfuric acid through the sidewall of beaker containing the aqueous dichromate solution. Also, a dedicated waste container was used for chromic acid disposal. The dipping procedures were carried out in a glove box with a constant dry air supply to keep the humidity to a minimum. I put the dip-coated fused silica in a 100 ml round bottom flask connected with a glass adapter. Then the round bottom flask containing the fused silica was taken outside the glove box and dried at 150 °C in vacuum (Welch® CHEMSTAR, 1400N vacuum pump) for 20 minutes. A liquid nitrogen trap was used to prevent CSA damage to
the pump. Four-probe measurements (Keithley® 2400 Sourcemeter) were performed after drying the film to determine its resistance. The sheet resistances were obtained at eight different spots on the fused silica to check the uniformity of the film. Since dip-coating covered both sides of the fused silica window, one side was wiped off thoroughly (with methanol and Kimwipe wipes) before making the transmittance measurements. For transmittance measurements, clean fused silica had been used in baseline measurements. To deprotonate the film, the p-SWCNTs film was dipped in diethyl ether for 1 minute. The deprotonated SWCNT films were then dried in vacuum (at room temperature) for about 10 min before measuring the sheet resistance. For NIR photoluminescence experiments, fused silica windows were dipped into SWCNT-CSA solutions with concentrations ranging from 0.005 mg/mL to 1 mg/mL. These films were typically dried at ca. 100 °C for about 10 min or directly dipped in ether for ca. 5 min. For photoluminescence measurement, the films were carried inside a vacuum desiccator to prevent the SWCNTs aggregation by moisture. In fact, we observed loss of photoluminescence on several trials due to humidity of environment.
Films Characterization

Fluorescence microscopy of individual semiconducting SWCNTs (on fused silica substrates) was performed using a customized Nikon TE-2000U inverted microscope equipped with a Nikon Plan 60x (NA = 1) water immersion objective and an InGaAs camera. SWCNTs were excited with light from a cw Ti:sapphire laser at 785 nm or 840 nm. The optical transmission of dense nanotube films at 550 nm were obtained using a UV-Vis spectrophotometer (Shimadzu UV-2450). The sheet resistances of SWCNTs films on fused silica were determined with a Keithley 2400 sourcemeter and a linear four-point probe. Raman spectra were obtained using a Renishaw in Via MicroRaman Spectrometer. X-ray photoelectron spectra were obtained on a PHI Quantera SXM Scanning X-ray Microprobe.

3.5. Experimental Contributions

My contribution to the experimental work described in this chapter are the following: fabrication SWCNTs thin film by dip coating, deprotonating the film by subsequent dipping in ether, measuring the transparency and sheet resistance, characterizing the film using AFM,
Raman, and XPS. Dr. Saunab Ghosh performed NIR-photoluminescence characterization of deprotonated low-density SWCNTs film.

3.6. References


Aqueous Dispersion of Carbon Nanotubes Using Polypyridyl Ruthenium Complexes

4.1. Introduction

The dispersion of Single Walled Carbon Nanotubes (SWCNTs) is still an important field of research, specially to exploit the excellent electrical, optical, and structural properties of individual SWCNTs. Researchers over the past two decades have tried to overcome the formidable Van der Waals attraction of carbon nanotubes (that leads to bundle formation) by a variety of dispersion techniques. For example
chemical functionalization, such as oxidization of SWCNTs at the ends and sidewalls, can produce aqueous dispersions of SWCNTs, however this technique also creates defect sites on the carbon backbones and accordingly leads to the destruction of the extended $\pi$-system. On the other hand, dispersion with surfactants and DNA by non-covalent interactions keeps the carbon backbone intact and preserves the electronic properties of SWCNTs.$^{2,3}$

Recently there has been a considerable interest in bringing metal complexes in close contact with SWCNTs with applications that include catalysis,$^{4}$ photoinduced electron transfer,$^{5,6}$ and information storage.$^{7}$ Many of these composites involve the attachment of the metal complexes (such as porphyrins) to SWCNTs in different organic solvents using an anchoring group (such as pyrenes).$^{5,6,8}$ Recently, a tetradeutate copper complex has been reported that binds SWCNTs in chloroform when in a square planar conformation,$^{9}$ however new alternatives for binding metal complexes to SWCNTs in aqueous solutions are scarce. This area of research can be benefited by research on ligands that can allow the close binding of non-planar metal complexes to SWCNTs.

In this study, we have used octahedrally coordinated, positively charged ruthenium metal complexes containing ligands with extended
planar $\pi$ systems as a prototype to disperse and solubilize SWCNTs in aqueous solutions, while also allowing a metal complex functionality near the CNTs.

4.2. Results and Discussion

4.2.1. Dispersion in Dipyridophenazine Ruthenium Complexes

In this study, three different ruthenium(II) dipyridophenazine complexes possessing ligands with extended $\pi$ systems $[\text{Ru(bpy)}_2(\text{dppz})]^2^+ (1)$ (bpy = 2,2'$\prime$-bipyridine; dppz = dipyrido[3,2-a:2'$\prime$.3'$\prime$-c]-phenazine), $[\text{Ru(bpy)}_2(\text{dppn})]^2^+ (2)$ (dppn = benzo[i]dipyrido[3,2-a:2'$\prime$.3'$\prime$-c]phenazine) and $[(\text{bpy})_2\text{Ru(tpphz)}\text{Ru(bpy)}_2]^4^+$ (3) (tpphz = tetrapyrido[3,2-a:2'$\prime$.3'$\prime$-c:3$''$,2$''$-h:2$''$',3$''$'-j]phenazine) have been studied with respect to their capability of dispersing SWCNTs in aqueous media (Figure 4.1). To the best of our knowledge, no investigations concerning dispersion of nanotubes in aqueous media by ruthenium(II) polypyridyl complexes have been reported previous to this work.$^1$ We choose these complexes because their extended planar $\pi$ systems are hypothesized to interact with the nanotube sidewall to facilitate dispersion.
Figure 4.1 Dipyridophenazine ruthenium complexes used to disperse SWCNTs in this work.

These ruthenium polypyridyl complexes were obtained as their water soluble chloride salts and used as such. The solubilization of SWCNTs by water-soluble ruthenium polypyridyl complexes was carried out according to the following procedure: a total of 10 mL solutions of 1, 2 and 3 were prepared to yield final concentrations of 0.1 g/L (0.01 wt%[Ru(II)]) to 0.5 g/L. These were added to 3 mg each of SWCNTs. The resulting dispersions were tip sonicated (40 minutes), centrifuged (12,470g for 60 minutes) and decanted to yield the corresponding SWCNT-Ru complex composites. These solutions are considerably darker than the solutions without CNTs indicating a significant uptake of SWCNTs into aqueous solution. The resulting
dispersions were stable for weeks without observing any visible flocculation (SWCNT-2 and SWCNT-3 solutions are stable for several months, see Figure 4.2). It is observed that the optimal concentration for the maximum uptake of SWCNTs by Ru(II) complexes was between 0.03 to 0.04 wt% (see Figure 4.2).

**Figure 4.2** Concentration dependent absorption profile of SWCNTs in Ru(II) complexes-SWCNTs composites (absorbance obtained at 642 nm). The bottom panels show the photographs of SWCNT-1, SWCNT-2, and SWCNT-3 after centrifugation.
4.2.1.1. Spectroscopic Characterizations of SWCNTs Dispersions

The dispersions were analyzed for Vis-NIR absorption and emission in a model NS1 Nanospectralyzer with excitation from 642, 659 and 784 nm diode lasers. The absorbance and photoluminescence spectra of dispersed SWCNTs were also compared to the spectra of SWCNTs dispersed in an aqueous solution of the ionic surfactants SDS and CTAB ([SDS], [CTAB] = 1 wt%). Identical process parameters (initial SWCNT concentration, sonication power, sonication time, and centrifugation conditions) were utilized in order to ensure comparability. SDS is a surfactant commonly used for aiding in the dispersion of SWCNTs in water and is known to yield well-resolved SWCNT absorption and emission features at an optimal concentration of 1 wt%. Figure 4.3 shows the Vis-NIR spectra of SWCNT-1, SWCNT-2 and SWCNT-3 solutions compared to SWCNTs dispersed using 1% (w/v) SDS. It is important to note that van-Hove singularities, which are a sign of individualization, are preserved in SWCNT–Ru(II) solutions. The characteristic features arising from the interband transitions in the density of states of the SWCNTs in SWCNT–Ru(II) composites are discernible, clearly indicating that the darkening of the Ru(II) complexes solutions is due to the uptake and dispersion of CNTs. Among the
complexes, Ru(bpy)$_2$(dppn)$_2^{2+}$ (2) showed the highest ability to disperse SWCNTs, probably due to its more elongated π-electron system allowing a better interaction with the SWCNTs, while at the same time minimizing the steric effect and increasing the distance between the SWCNT and the positive charges of the ruthenium complex. We confirmed the pivotal role of ligands with an elongated π-electron system in the solubilization of SWCNTs by treating SWCNTs with tris(2,2'-bipyridyl) ruthenium(II) (Ru(bpy)$_3^{2+}$), which only contains short bipyridine ligands. The obtained solution didn't show any uptake of SWCNTs, indicating that Ru(bpy)$_3^{2+}$ cannot form stable composites with SWCNTs probably due to the lack of an extended π-electron system (Figure 4.3, bottom line).

**Figure 4.3** Vis-NIR absorption spectra of dispersions of SWCNTs-Ru(II) complexes, SWCNT-Ru(bpy)$_3^{2+}$ and SWCNTs dispersed in SDS and CTAB after centrifugation.
NIR emission spectroscopy is a powerful tool in CNT characterization, especially when the aggregation state is investigated, since the photoluminescence of semiconducting SWCNTs is quenched in CNT bundles through interaction with metallic SWCNTs (the terms semiconducting and metallic SWCNTs refer to carbon nanotubes that present an electronic band structure analogously to semiconducting or metallic materials respectively); therefore only individualized semiconducting SWCNTs are detected.\textsuperscript{10,11} The radiative photoluminescence transitions are directly observed across the band gap of semiconducting nanotubes from 800–1600 nm range, a region important in fiber optic communications and bio-imaging. The emission spectra of SWCNT–Ru(II) complexes solutions were recorded at three different excitation wavelengths $\lambda_{\text{exc}} = 642$ and 659 nm, and $\lambda_{\text{exc}} = 784$ nm exciting the first-order transitions (S11) and the second-order band gap transitions (S22) respectively. Figure 4.4 shows the normalized emission spectra of SWCNT-1, SWCNT-2, and SWCNT-3, and SWCNT-2 in comparison to SWCNT–SDS and SWCNT–CTAB solutions. SWCNT-1/2/3 solutions show photoluminescence signals clearly revealing that SWCNTs are not only dispersed but also individualized by the planar dppz, dppn and tpphz ligands. The signals are also red shifted probably due to $\pi$–$\pi$ stacking interactions of the tubes with the planar ligands.
Most importantly, the characteristic NIR photoluminescence of well dispersed and individualized nanotubes persists in the SWCNT–Ru(II) complex composites indicating that individualization of nanotubes has occurred, and that the electronic properties of SWCNTs remain intact. Other researchers have observed that interaction of SWCNTs with organic aromatic molecules (by $\pi$–$\pi$ stacking) or with metal complexes (by heavy atom effect) results in a complete quenching of photoluminescence from SWCNTs.\textsuperscript{5,6,9} We speculate that the preservation of SWCNTs photoluminescence is due to the steric constrains imposed by the ruthenium complexes three dimensional structures. In order to keep the ruthenium complex away from the CNT axis, the SWCNTs–Ru(II) composites depart from the idealized $\pi$–$\pi$ stacking interaction required for efficient quenching. However, some quenching due to partial $\pi$–$\pi$ stacking interaction and heavy atom contribution cannot be completely ruled out.
Figure 4.4 NIR-photoluminescence spectra of (a) SWCNT-1, (b) SWCNT-2, and (c) SWCNT-3 at three different excitations ($\lambda_{\text{exc}} = 642\text{nm}, 659\text{nm}, 784\text{nm}$). Figure (d) shows the spectrum of SWCNT-2 in comparison with the spectra of SWCNT-SDS, and SWCNT-CTAB ($\lambda_{\text{exc}} = 642\text{ nm}$).

4.2.1.2. Microscopic Characterizations of SWCNTs Dispersion

To further confirm the degree of debundling/individualization of the nanotubes dispersed in aqueous solution using dipyridophenazine Ru(II) complexes, microscopic techniques were employed. Atomic force microscopy (AFM) analysis was performed in order to compare the degree of individualized nanotubes in aqueous solutions of Ru(II)
complexes to an aqueous solution of CTAB. Figure 4.5 shows representative AFM images of SWCNT–Ru(II) supernatants after spin coating. To ensure maximum uptake of 3 mg of SWCNTs in the solutions of Ru(II) complexes, the sample with the highest absorption intensity in Vis-NIR spectra was investigated by AFM ([Ru(II)] = 0.03 wt%).

![AFM images](image)

**Figure 4.5** Representative 10 x 10 µm AFM images of (a) SWCNT-CTAB, (b) SWCNT-1, (c) SWCNT-2, and (d) SWCNT-3 after spin coating the supernatant of centrifuged samples.

The AFM images of SWCNT–Ru(II) solutions confirm the conclusion drawn from the photoluminescence spectra, as individual SWCNTs are observed besides small bundles. The lengths of the individual and bundled SWCNTs range from 20 nm to several µm. As shown in the height distribution histogram (Figure 4.6), the observed
diameters are consistent with individual SWCNTs (HiPco SWCNTs = 0.9 -1.2 nm) covered with metal complexes with ca. 1 nm diameter. It has to be mentioned that diameters do not appear completely uniform along the lengths of the carbon nanotubes in SWCNT–CTAB and SWCNT–Ru(II) composites. Presumably, the CNTs are not uniformly coated by the ruthenium(II) complexes (or CTAB) in the dry mica substrate, so that areas of bare SWCNTs are observed along with surfactant or ruthenium(II) complexes-coated areas.\textsuperscript{12} As a general observation, we have often seen structures with larger diameters in the center than in the edges, which might indicate that as the solvent evaporates, the ruthenium complexes tend to aggregate preferentially near the center of the nanotube leaving bare tips (Figure 4.6).
Figure 4.6 AFM histogram analysis of the heights of SWCNT-1, SWCNT-2, and SWCNT-3. Bottom figure shows AFM image of SWCNT-3 with larger thickness in center than tip.
The morphology of the SWCNT-1 and SWCNT-2 solutions was further imaged by TEM ([Ru(II)] = 0.03 wt%). The TEM micrographs in Figure 4.7 show that SWCNT–Ru(II) complexes appear in both bundles with diameters in the range of 3 to 10 nm and individual tubes with a mean diameter in the range of 1 to 2 nm.

![Representative TEM images of SWCNT-1 and SWCNT-2 ([Ru(II)] = 0.03 wt%, [SWCNT] = 3mg/ml).](image)

**Figure 4.7** Representative TEM images of SWCNT-1 and SWCNT-2 ([Ru(II)] = 0.03 wt%, [SWCNT] = 3mg/ml).
4.2.2. Dispersion of SWCNTs by Photoluminescent Ruthenium Polypyridyl complexes

We demonstrated that SWCNTs can be efficiently dispersed in water with the aid of ruthenium dipyridophenazine complexes. However, we didn't observe any photoemission from excited ruthenium complexes in presence of SWCNTs. This might be attributed to the weak photoluminescence of the aforementioned complexes in aqueous solution. Being able to detect the photoluminescence from ruthenium polypyridyl complexes on the surface of SWCNTs would allow us to study the nature of the electronic interactions between photoexcited ruthenium metal centers and SWCNTs. Therefore, we synthesized photoluminescent ruthenium complexes where ethynylpyrene functional groups are attached to phenanthroline ligands (Ru-Py, see Figure 4.8). In this complex, the ethynylpyrene moiety works as a SWCNT anchoring group.
Figure 4.8 Pictorial representation of the attachment of pyrene group to the surface of SWCNTs. Ru-Py is hypothesized to disperse SWCNTs due to pyrene-SWCNTs interaction.

Pyrenyl groups are known to bind SWCNTs due to their long aromatic structure. The ruthenium complex Ru-Py was synthesized by a 5-step reaction followed by ion-exchange of the PF$_6^-$ counter ion with chloride. The HiPco SWCNTs were dispersed in aqueous solution of Ru-Py using the following procedure: preparation of 0.1% (m/v) solution of Ru-Py in water, followed by addition of different amounts of HiPco SWCNTs (1, 2, and 3 mg/ml) to prepare different concentrations of the SWCNTs dispersion. The resulting mixtures were tip sonicated (30 minutes), centrifuged (12000g, 45 minutes) and the top layer was collected to yield the corresponding Ru-Py and HiPco composites. Other sources of SWCNTs such as Arc and Comocat SWCNTs were also studied following the same procedure. In order to investigate the electron
transfer between Ru-Py and SWCNTs, the free Ru-Py molecules were removed by dialysis membrane for 16 hrs.

**4.2.2.1. Spectroscopic Characterizations of SWCNTs Dispersion**

The dispersion results of Ru-Py and HiPco composites in aqueous solution were investigated by both UV-Vis and Near-IR absorption. Figure 4.9 shows the UV-Vis spectra of stable dispersion solutions of Ru-Py and HiPco SWCNT composites, using a Ru-Py 0.1% (w/v) solution with different initial HiPco concentration from 0 to 3 mg/mL. The absorption spectrum of Ru-Py in water has a characteristic band at 420 nm, which is attributed to metal-to-ligand charge transfer (MLCT), while the bands 285 nm and 235 nm correspond to the ligand-to-ligand π-π* transition. There are no observable bands in water above 600 nm for Ru-Py (Figure 4.9). As the amount of SWCNTs was increased, the absorbance band at 420 nm decreased gradually due to the attachment of Ru-Py to the undispersed SWCNTs, which were subsequently removed by centrifugation. For further investigation of the electron transfer between Ru-Py and SWNTs, the extra free Ru-Py was removed by dialysis using Nominal MWCO 2000 membranes in water. After removal of the unbound ruthenium complex, it can be seen that the 2 mg/mL HiPco SWCNT initial concentration gives the maximal
dispersion of carbon nanotubes as can be seen from Figure 4.9b (blue line).

**Figure 4.9** UV-Vis absorption spectra of Ru-Py /HiPco composites (a) before and (b) after dialysis for 16 hours using nominal 2000 MW membrane. Dispersion solutions were prepared in 0.1% (w/v) Ru-Py solutions with 0 (black line), 1mg/mL (red line), 2mg/mL (blue line) and 3mg/mL (cyan line), initial concentration of HiPco SWCNTs respectively. Inset of figure (a) shows van Hove singularities in magnified wavelength region between 500 to 800 nm.

After 16-hour dialysis, the absorbance bands below 550 nm decreased substantially (these bands belong to the ruthenium complex), while those above 600 nm (from SWCNTs) stayed basically the same. The phenomenon provides evidence that free Ru-Py molecules can be removed effectively from the dispersion by dialysis, without major effect on the dispersed SWCNTs. It was observed that if the dialysis goes above 16hrs, while the ratio of absorbances at 420 nm to 660 nm does
not change, the dispersion starts crashing out. This indicates that almost all the free Ru-Py can be removed by dialysis, yielding a Ru-Py/SWCNT composite suspension which is stable in aqueous media.

The observation of van-Hove singularities in the NIR absorbance of HiPco SWCNTs suggests individualization of SWCNTs in solution. Figure 4.10 shows Vis-NIR absorbance of HiPco SWCNTs in Ru-Py 0.1% (w/v) aqueous solution. The absorbance of 2mg/ml SWCNT initial concentration is the highest, in consistency with the UV-Vis spectra in Figure 4.9b. We also obtained the Near-IR absorbance (not shown) of HiPco SWCNTs in Ru-Py aqueous solution after dialysis. The only noticeable change was a reduction in the absorbance bands below 550 nm, which are due to the removal of free Ru-Py after dialysis. On the other hand, the NIR absorbance due to SWCNTs, (i.e. E22 absorption bands) was fundamentally the same. Individualization of SWCNTs could also be analyzed by Near-IR photoluminescence of SWCNTs dispersions. Individual semiconducting nanotubes have narrow emission peaks whereas bundled SWCNTs have quenched emission due to energy transfer to metallic nanotubes. Figure 4.10b shows Near-IR photoluminescence of SWCNTs dispersed in Ru-Py/water and SWCNTs dispersed in SDS surfactants (λ_{exc} = 642 nm, and 659 nm). SDS is a well-
known dispersing agent for the individualization of SWCNTs in water. The presence of narrow peaks in the Near-IR region demonstrates individualization of nanotubes. We note large red-shift (~30 nm) in emission maxima of SWCNTs in Ru-Py in comparison with SDS aqueous solution. This is probably due to π-π stacking between the sidewalls of carbon nanotubes and pyrene.

**Figure 4.10** Visible-NIR absorption spectra of Ru-Py/HiPco composites (diluted 5 times before taking the spectra). Comparison of NIR-photoluminescence spectra of HiPco SWCNTs dispersed with Ru-Py and SDS aqueous solutions.

### 4.2.2.2. Microscopic characterizations

Debundling of SWCNTs was further characterized by microscopic techniques. Figure 4.11 shows representative AFM images of SWCNTs deposited on mica. The average height of tubes were estimated as ~2.1
nm, which corresponds to the diameter of individual or mostly debundled SWCNTs.

![AFM image of SWCNTs](image)

**Figure 4.11** Representative AFM images of spin coated Ru-Py/HiPco composites on mica.

The morphology of SWCNTs dispersed with Ru-Py are further visualized by TEM (Figure 4.12). A HiPco SWCNTs solution (1 mg/ml) was diluted 4 times and placed in a TEM grid. The TEM image shows two to three individual SWCNTs wrapped with amorphous components, which suggests the attachment of Ru-Py complexes on the surface of SWCNTs.
Figure 4.12 Representative TEM images of Ru-Py/HiPco composites. Tubular SWCNTs are visually wrapped with a diffuse layer of Ru-Py complexes. Scale bar is 5 nm.

4.2.2.3 Excited State Quenching of Ruthenium Complex

We monitored excited state decay profile of aqueous solution of Ru-Py and HiPco composites (Figure 4.13). Aqueous HiPco Ru-Py composites were dialyzed before lifetime measurements. Table 4.1 shows lifetime data of Ru-Py and the composites. We observed significant decrease in the photoluminescence lifetime of Ru-Py in presence of HiPco SWCNTs, which can be resulted from excited state electron transfer from photoluminescent metal complex to SWCNTs.
Figure 4.13 Time-resolved photoluminescence decays of Ru-Py and Ru-Py/HiPco composites.

Table 4.1 Lifetime data of Ru-Py and different concentrations of HiPco Ru-Py composites

<table>
<thead>
<tr>
<th></th>
<th>0.02 mg/mL Ru-Py</th>
<th>1 mg/mL HiPco Ru-Py</th>
<th>2 mg/mL HiPco Ru-Py</th>
<th>3 mg/mL HiPco Ru-Py</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-Py</td>
<td>821 µs</td>
<td>614 µs</td>
<td>443 µs</td>
<td>603 µs</td>
</tr>
</tbody>
</table>

Interestingly, we didn't observe the linear relation between quenching and the initial HiPco SWCNTs concentrations. However, we did notice that 2 mg/ml HiPco Ru-Py solutions with the highest
concentration of nanotubes, presents maximum quenching. These results are confirmed by the lower lifetime of Ru-Py in 2 mg/mL HiPco composites (443 µs) in comparison with 0.02 mg/mL Ru-Py solution (821 µs).

4.3. Conclusions

In conclusion we have demonstrated that SWCNTs can be efficiently dispersed with a pronounced degree of individualization by non-covalent interactions, using water soluble Ru(II) polypyridyl complexes containing extended π systems. In our initial work, three dipyridophenazine ligands dppz, dppn, and tpHz ruthenium complexes were studied. We observed that the SWCNTs composites made with [Ru(bpy)₂(dppn)]²⁺ (SWCNT-2) showed maximum dispersion and solubilization, probably due to its larger extended π system. These metal complexes have certain advantages over previous methods used to attach metal complexes to SWCNTs such as easy synthesis, high individualization without chemical modification of the SWCNTs surface, stable solutions, and the retention of the SWCNTs photoluminescence. Other complexes with extended π systems were also studied in this work to further explore the electronic interaction between SWCNTs and dispersant. Pyreneethylene attached to photoluminescent ruthenium
polypyridyl complex also showed to effectively disperse SWCNTs. Preliminary results suggest quenching of the excited state lifetime of Ru-Py complexes, which indicates excited state electron transfer from Ru-Py to SWCNTs. These studies can result in important applications in photovoltaics and also provide proof-of-concept of photo-induced electron transfer in SWCNTs/Ru-Py composite systems.

4.4. Experimental Section

Materials

The SWCNTs used in this study were synthesized by the high-pressure carbon monoxide (HiPco) process at Rice University and were purified by low temperature oxidative annealing and acid treatment as described in Chapter 2. All reagents and chemicals were obtained from commercial sources and used as received without further purification. Cis-Dichlorobis(2,2’-bipyridine)ruthenium (II) hexahydrate was purchased from Strem Chemicals. 1-bromopyrene (1,10) phenanthroline, and (trimethylsilyl)acetylene were purchased from Alfa Aesar, USA. Potassium hexafluorophosphate was purchased from TCI America. All other chemicals were purchased from Sigma-Aldrich. Dialysis membrane with Nominal MWCO 2000 was purchased from Membrane Filtration Products, Inc.
Synthesis of Ru(II) Dipyridophenazine Complexes

The ruthenium complexes 1-3,\textsuperscript{14,15} studied in this work were prepared in a similar way by reaction of [Ru(bpy)\textsubscript{2}Cl\textsubscript{2}].2H\textsubscript{2}O with the bidentate ligands dppz, dppn and tpphz in methanol/water or ethanol/water (1:1 v/v) at reflux for 4-24 hours. They were then precipitated from aqueous solution with saturated ammonium hexafluorophosphate solution. The water-soluble chloride salts were produced by dissolving the complex in acetone followed by the addition of a saturated aqueous solution of tetra-n-butylammonium chloride (TBACl). The chloride salts were further purified by biphasic recrystallization in methanol-ethyl acetate (1:10), (v/v) and used as such. The ligands were prepared by the condensation of phenanthroline-5,6-dione with substituted o-diamino compounds (see scheme 4.1).\textsuperscript{14,15} The analytical characterization data is in accordance with that reported in literature.\textsuperscript{14,15}
Scheme 4.1 Synthetic scheme for the preparation of Ru(II) dipyridophenazine complexes.

**Synthesis of Ru-Py Complex**

Scheme 4.2 Synthetic scheme for the preparation of Ru-Py complex
Synthesis of Compound 5

This compound was synthesized based on literature methods. In a typical synthesis, 2.4 g of 1,10-phenanthroline were placed in a heavy wall glass reaction tube with a Teflon screw top fitted with a Viton-O-ring. The reaction vessel was placed in an ice bath, and 8mL of oleum (18%) and 0.4 mL of bromine were added. The reaction tube was placed in a silicon oil bath, and the temperature was slowly raised to 135 °C. After 24 hrs, the reaction mixture was cooled to room temperature, poured over ice, and neutralized with ammonium hydroxide. The mixture was extracted with chloroform. The red extracts were stirred with charcoal and then dried over sodium sulfate. The crude product was recrystallized from hot diethyl ether with a little amount of dichloromethane. $^1$H NMR (400 MHz, CDCl3) δ (ppm) 9.214 (t, J = 4.8, 2H), 8.675 (d, J = 8.4, 1H), 8.184 (d, J = 8.0, 1H), 8.150 (s, 1H), 7.750 (dd, J = 4.4, 1H), 7.652 (dd, J = 4.4, 1H).

Synthesis of Compound 6

This compound was synthesized based on literature methods. The mixture of cis-dichlorobis(2,2'-bipyridine)ruthenium(II) dehydrate (0.260 g) and compound 5 (0.130 mg) was heated to reflux for 2 hours in ethanol/water. After this, it was cooled down to room temperature...
and 150 mg of potassium hexafluorophosphate were added. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography in 75% yield using acetonitrile/dichloromethane (1:4 vol) eluent. \(^1\)H NMR (400 MHz, CD3CN) \(\delta\) (ppm) 8.742 (d, \(J = 8.4\), 1H), 8.742 (d, \(J = 8.4\), 1H), 8.602 – 8.538 (overlapping m, 6H), 8.202 (dd, \(J = 6.8\), 2H), 8.116 (t, \(J = 8.0\), 2H), 8.024 (t, \(J = 8.4\), 2H), 7.903 (m, 2H), 7.850 (dd, \(J = 5.2\), 1H), 7.781 (dd, \(J = 5.2\), 1H), 7.610 (m, 2H), 7.489 (t, \(J = 6.4\), 2H), 7.280 (m, 2H). ESI-MS: m/e 817.0 (M - PF6 -), 337.0 ([M - 2PF6 -]/2).

**Synthesis of Compound 7**

This compound was synthesized based on Sonogashira coupling reported in literature.\(^1^8\) A mixture of 1-bromopyrene (560 mg), \(\text{Pd(PPh}_3\text{)}_2\text{Cl}_2\) (175 mg), \(\text{CuI}\) (50 mg) in 30 mL THF/TEA (1:1) was bubbled with nitrogen for 20 minutes. Then the trimethylsilylacetylene was added and the resulting solution was heated at 110 °C overnight under nitrogen. The mixture was rotovaped and the residue was subjected to a column chromatography on silica gel, eluting with hexane to yield a yellow crystalline product. \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) (ppm) 8.567 (d, \(J = 9.2\), 1H), 8.228 – 8.002 (overlapping m, 10H), 0.395 (s, 9H).
Synthesis of Compound 8

This compound was synthesized based on literature methods.\textsuperscript{18} A mixture of compound 7 (300 mg) and potassium bicarbonate (690 mg) in methanol/THF mixture was stirred at room temperature for one hour. After removing the solvent, the crude compound was purified by column chromatography on silica gel, eluting with hexane and dichloromethane mixture (10:1).

Synthesis of Final Compound Ru-Py (4)

This compound was synthesized based on literature methods. Compound 6 (100mg), compound 8 (46 mg), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (35 mg), and CuI (9.8 mg) were added to a 50 mL round bottom flask under nitrogen. Then nitrogen purged (2-hours) DMF and HN(i-Pr)\textsubscript{2} mixture (10mL, 3:2) were added to the flask. The resulting mixture was stirred at room temperature for 24 hours. At the end of the reaction, the mixture was filtered and concentrated under reduced pressure. The crude compound was further purified by column chromatography on silica gel with acetonitrile and dichloromethane mixture (1:4) as eluent. $^1$H NMR (400 MHz, CD\textsubscript{3}CN) $\delta$ (ppm) 8.799 (d, $J = 8.0$, 1H), 8.552 (m, 4H), 8.458 (d, $J = 8.8$, 1H), 8.366 (d, $J = 8.4$, 1H), 8.210 – 8.003 (overlapping m, 10H), 7.939 (d, $J = 7.6$, 1H), 7.900 (d, $J = 130
7.2, 2H), 7.840 (s, 2H), 7.799 (t, J = 7.6, 1H), 7.767 (m, 1H), 7.696 (dd, J = 8.0, 2H), 7.625 (m, 2H), 7.500 (t, J = 7.2, 2H), 7.345 (t, J = 6.8, 1H), 7.294 (t, J = 6.8, 1H). ESI-MS: m/e 963.1 (M - PF6-), 409.2 ([M - 2PF6-]/2).

**Dispersion of SWCNTs in Ru-Py Water**

10-40 mg purified HiPco (Batch # 195.1) SWCNTs were weighed in different vials, followed by addition of 0.1% (m/v) Ru-Py aqueous solution to prepare different SWCNT concentrations. The resultant mixture was sonicated by probe sonicator (Sartorius, LABSONIC® M) for 30 minutes and then centrifuged (VWR centrifugator) for 45 minutes at 12,000 g. The supernatant was collected carefully and diluted for further analysis.

**4.5. Experimental Contributions**

Dr. Disha Jain synthesized and characterized all ruthenium dipyridophenazine complexes. My contribution to the experimental work described in this chapter is the following: dispersion of SWCNTs, characterization of individual SWCNTs by AFM and TEM. Dr. Jain and myself collaborated in the characterization by UV-Visible and NIR-photoluminescence spectroscopy. Kewei Huang performed synthesis
and characterization of the Ru-Py complex. TEM and AFM were performed by me. Both Dr. Jain and Kewei Huang contributed to the optimization of the dispersion method in this work.

4.6. References


Sensing of Organic Solvents Vapors Using Metal Complexes Encapsulated within Zeolite NaY

Note: This chapter was copied from a manuscript I coauthored and that is submitted for publication.

5.1. Introduction

The use of supramolecular assemblies have gained a wide popularity in the past few years in areas such as catalysis, gas sequestration, and separation. Interesting approaches for the detection of toxic gases and vapors of volatile organic compounds (VOC) have been proposed by different groups in an effort to produce an
“artificial nose” capable of identifying these species in an unambiguous and simple way.\textsuperscript{7-9} One area that stands out is the detection of vapors by crystalline arrays of transition metal complexes,\textsuperscript{10} whose electronic transitions are sensitive to the presence of a variety of volatile molecules.\textsuperscript{11-20} Although metal complexes of platinum,\textsuperscript{12,14} gold,\textsuperscript{18,20} palladium,\textsuperscript{21} and copper\textsuperscript{22} have been widely employed for vapor detection, rhenium on the other hand has been seldomly used. In this work we present the use of a (1,10 phenanthroline)tricarbonylchlororhenium(I) complex (Re(phen)(CO)\textsubscript{3}Cl) encapsulated within a faujasite NaY zeolitic framework (Re(phen)(CO)\textsubscript{3}Cl@NaY) as a photoluminescent sensor for solvent vapors (Figure 5.1).
Figure 5.1 Schematic representation of encapsulation of Re(phen)(CO)$_3$Cl in supercages of zeolite NaY

Zeolites are aluminosilicates with a repeating microporous structure composed of AlO$_4$ and SiO$_4$ building blocks.$^{23}$ The internal framework is a network of cavities (supercages) interconnected by channels (Figure 5.1). Supercages have diameters of 13 Å that can be accessed by 7.4 Å pores made of 12 atom rings (Si and O) openings on the surface. This structure allows zeolites to behave as molecular sieves with applications ranging from catalysis$^{24,25}$ to light harvesting$^{26}$ systems. Due to their porous structure, ion-exchange properties and molecular and size recognition, many ions and molecules have been
immobilized within zeolites.\textsuperscript{27-30} We used the ship-in-the-bottle method to synthesize Re(phen)(CO)\textsubscript{3}Cl in the cavities of NaY. The ligands and the metal react in the NaY supercages, forming the Re(phen)(CO)\textsubscript{3}Cl complex. The zeolite NaY supercage has diameters of approximately 13 Å, large enough to accommodate the ca. 9 Å complex,\textsuperscript{31} however the 7.4 Å pores are too small to allow the complex to diffuse out becoming entrapped.

We noticed that upon exposure to solvent vapors, the Re(phen)(CO)\textsubscript{3}Cl@NaY material presents vapoluminescence (change in photoluminescence intensity) and luminescence vapochromism (change in photoluminescence maximum). Interestingly, we also observed changes in photoluminescence lifetime of the material upon vapor treatment, and termed this behavior vapokronism. To the best of our knowledge, changes in lifetimes have not been studied before in the context of vapors detection. By determining just three photophysical parameter from this material upon exposure to solvent vapors (photoluminescence intensity, emission wavelength and lifetime) unambiguous identification of the vapors will be demonstrated by correlation with a simple 3-D vapor map.
5.2. Results and Discussion

5.2.1. Synthesis and Characterizations of Re(phen)(CO)$_3$Cl@NaY

One of the most widely explored photoluminescent metal complex synthesized within zeolite supercages is tris(2,2’-bipyridine)ruthenium(II) (Ru(bpy)$_3^{2+}$).\textsuperscript{32} (Ru(bpy)$_3^{2+}$) is synthesized in situ by a ship-in-the-bottle method, which involves sequential loading of a ruthenium salt within NaY followed by the ligand 2,2’-bipyridine.\textsuperscript{33} The Ru(bpy)$_3^{2+}$ complex is formed inside the supercage and therefore it becomes entrapped within the zeolite. The material is fundamentally composed of a zeolite framework, with supercages occupied by individual Ru(bpy)$_3^{2+}$ forming a true solid solution.

Inspired in the aforementioned work, we refluxed neutral rhenium pentacarbonyl chloride (Re(CO)$_5$Cl) toluene solution with calcined zeolite NaY. Since Re(CO)$_5$Cl has a smaller size than the pore opening of NaY, it can be inserted in the supercavities. The resulting Re(CO)$_5$Cl@NaY was stirred with phenanthroline solution in toluene. The chelating ligand 1,10-phenanthroline can react easily with the rhenium precursor to form Re(phen)(CO)$_3$Cl@NaY (Figure 5.2). It is worth to mention that Re(phen)(CO)$_3$Cl can also be synthesized and
immobilized on the external surface NaY. To remove such unwanted products and unreacted phenanthroline, we did soxhlet extraction of as synthesized Re(phen)(CO)$_3$Cl@NaY in chloroform. We choose chloroform because it cannot coordinate with the metal center to replace the labile rhenium-chlorine bond, and because of the high solubility of Re(phen)(CO)$_3$Cl in chloroform. The concentration of extracted impurities was monitored by UV-Vis absorbance.
Figure 5.2 Illustrations of Re(phen)(CO)₃Cl@NaY synthesis. Sphere denotes the supercages of NaY. Blue colored Re(phen)(CO)₃Cl (synthesized on external surface) and phenanthroline represent impurities, which are removed by Soxhlet extraction.

To characterize the reaction product, the material was analysed using IR spectroscopy (Figure 5.3). NaY shows two major bands at 3500 and 1640 cm⁻¹ (Figure 5.3a), which are assigned to the bending vibration of lattice water molecules and surface silanol groups.
respectively.\textsuperscript{34} Re(phen)(CO)\textsubscript{3}Cl presents two closely spaced bands at \textasciitilde1890 cm\textsuperscript{-1} and \textasciitilde1920 cm\textsuperscript{-1} due to two equatorial CO stretching and a sharper band at \textasciitilde2013 cm\textsuperscript{-1} due to axial CO stretching (Figure 5.3b).\textsuperscript{35} From Figure 5.3c it can be appreciated that the IR spectrum of Re(phen)(CO)\textsubscript{3}Cl\@NaY is basically a superposition of the spectra of Re(phen)(CO)\textsubscript{3}Cl and NaY. This provides evidence of the formation of Re(phen)(CO)\textsubscript{3}Cl, and also that neither the NaY framework or the complex have suffered significant changes in their structure due to the encapsulation procedure.
The absorption and photoluminescence spectra of Re(phen)(CO)\(_3\)Cl encapsulated within NaY were also investigated. The diffuse reflectance and UV-Vis spectrum in acetonitrile were obtained for Re(phen)(CO)\(_3\)Cl@NaY and Re(phen)(CO)\(_3\)Cl respectively (see Figure 5.4a). We observed \(~\)5 nm blue shift of the metal-to-ligand charge transfer (MLCT) band of Re(phen)(CO)\(_3\)Cl@NaY with respect to
Re(phen)(CO)$_3$Cl in acetonitrile solution. This blue shift is consistent with studies of Re(phen)(CO)$_3$Cl at 77K in EPA.$^{36}$ In Figure 5.4b, the photoluminescence spectrum of Re(phen)(CO)$_3$Cl-NaY shows a large blue shift when compared with Re(phen)(CO)$_3$Cl in acetonitrile. The corrected emission maxima of Re(phen)(CO)$_3$Cl@NaY film and Re(phen)(CO)$_3$Cl in acetonitrile are 542 nm and 625 nm respectively. The large blue shift upon encapsulation in NaY can be explained by “photoluminescence rigidochromism” as previously described by Wrighton and Morse for these kind of complexes.$^{36}$ Blue shifts of emission maxima have also been observed when Ru(bpy)$_3^{2+}$ is encapsulated in zeolite supercages.$^{37}$
Figure 5.4 Spectroscopic characterizations of Re(phen)(CO)$_3$Cl. (a) Comparison of diffuse reflectance of Re(phen)(CO)$_3$Cl@NaY and 20 µM solution of Re(phen)(CO)$_3$Cl in acetonitrile. (b) Photoluminescence spectra of Re(phen)(CO)$_3$Cl@NaY and 20 µM solution of Re(phen)(CO)$_3$Cl in acetonitrile.

Photoluminescence lifetimes were studied for the encapsulated materials and for Re(phen)(CO)$_3$Cl in solution to further characterized the excited state properties of Re(phen)(CO)$_3$Cl@NaY. The luminescence decay of Re(phen)(CO)$_3$Cl@NaY presents a biexponential lifetime with values of 137 and 737 ns (average lifetime $\langle \tau \rangle = 541$ ns), which is larger than the monoexponential lifetime of Re(phen)(CO)$_3$Cl dissolved in acetonitrile and dichloromethane solution (180 ns and 306 ns respectively). Wrighton and Morse have demonstrated that the emissive excited state of the Re(phen)(CO)$_3$Cl complex has a strong triplet character, which certainly explains the relatively long lifetime of
this complex.\textsuperscript{36} Additionally, the same researchers showed that the emission maximum depends on the polarity and rigidity of the medium. As the environment becomes more rigid, emission becomes more intense, blue-shifted and longer lived.\textsuperscript{36} This is consistent with the observation that Re(phen)(CO)\textsubscript{3}Cl encapsulated within NaY has a longer lifetime and a shorter emission wavelength than the complex in dichloromethane and acetonitrile solution.

To explore whether Re(phen)(CO)\textsubscript{3}Cl is just absorbed onto the surface or truly encapsulated within NaY, Re(phen)(CO)\textsubscript{3}Cl was dissolved in dichloromethane and put in contact with NaY. Given that the effective diameter of Re(phen)(CO)\textsubscript{3}Cl (9 Å) is larger than the pore size of NaY (7.4 Å), immobilization of Re(phen)(CO)\textsubscript{3}Cl in NaY occurs by impregnation on the outer surface. The emission maxima of the impregnated material is 10 nm red-shifted from Re(phen)(CO)\textsubscript{3}Cl@NaY (emission maxima 552 nm and 542 respectively). Furthermore, the photoluminescence lifetime is much shorter (biexponential decay with 4 ns and 58 ns lifetime, $\langle \tau \rangle = 51$ ns) for the impregnated material than for Re(phen)(CO)\textsubscript{3}Cl@NaY (137 and 737 ns, $\langle \tau \rangle = 541$ ns). These results suggest that our experimental procedure produces a material with
Re(phen)(CO)$_3$Cl encapsulated in the interior cavities of NaY, with no detectable Re(phen)(CO)$_3$Cl impregnated on the surface.

### 5.2.2. Sensing Vapor of Solvents by Re(phen)(CO)$_3$Cl@NaY

We observed that the photoluminescence of Re(phen)(CO)$_3$Cl@NaY is sensitive to the presence of solvent vapors. Specifically, a general enhancement of emission intensity (vapoluminescence) and lifetime (vapokronism), as well as shifts in the photoluminescence maxima (luminescence vapochromism) were seen when Re(phen)(CO)$_3$Cl@NaY films were exposed to different solvent vapors. Figure 5.5a shows the changes in intensity of Re(phen)(CO)$_3$Cl@NaY when exposed to a variety of vapors. The change in intensity can go from a 5 fold (water) to 75 fold increase (DMF).
Figure 5.5 (a) Photoluminescence spectra of Re(phen)(CO)$_3$Cl@NaY after treatment with different solvent vapors showing the change in emission intensity. (b) Normalized spectra from (a), emphasizing the different photoluminescence maxima with different vapors.

Figure 5.5b shows the normalized photoluminescence spectra that highlight the shifts in the photoluminescence maxima. These changes in photoluminescence maxima directly affect the color of the emitted light, as seen in Figure 5.6.

Figure 5.6 Digital photographs of the vapor-treated Re(phen)(CO)$_3$Cl@NaY material under UV light.
Furthermore, Figure 5.7 shows how the photoluminescence lifetime of Re(phen)(CO)₃Cl@NaY is influenced by exposure to vapors. For example, significant increases in lifetime were observed when Re(phen)(CO)₃Cl@NaY films were exposed to polar aprotic solvents such as acetonitrile, DMF, and DMSO, which are values comparable with the lifetime of Re(phen)(CO)₃Cl in polyester resin (3,670 ns). Shorter lifetime values were obtained for non-polar solvents, with the lowest value determined for water vapors.

Figure 5.7 Time-resolved photoluminescence decays of Re(phen)(CO)₃Cl@NaY under different solvent vapors.
Interestingly, we observed that each solvent vapor produces a unique combination of photophysical parameters (emission maxima, intensity and lifetime), which can be used as a “fingerprint” for the identification of a specific solvent. Figure 5.8a shows a 3-D plot of the three photophysical parameters studied in this work (a complete collection of the photophysical parameters including error bars are included in Table 5.1). It is important to point out that each of these points represent the average of at least 3 independent experiments, still showing a remarkable reproducibility. More interestingly, it appears that vapors with similar features (e.g. polarity) tend to present comparable properties, and therefore to group in specific region in the 3-D space. This has allowed us to identify regions in the 3-D space where solvents group together, depending on their characteristics. Figure 5.8b shows four different regions forming the solvent map. For example, polar aprotic solvents produce blue shifted emission, large increase in emission intensity and longer lifetimes, which put them in the upper left part of the map. On the other hand, protic solvents such as water and ammonia, present short lifetimes and red shifts, which put them in the lower right part of the map. Interestingly, alcohols have lifetimes and maxima shifts that slightly overlap with aprotic solvents, however their
increase in photoluminescence is rather similar to non-polar, which puts them in a completely deferent region in the 3-D map. The usefulness of the 3-D map is that it would allow us to classify a completely unknown vapor in one of these categories taking into consideration solely its photophysical parameters derived from their interaction with Re(phen)(CO)₃Cl@NaY.

**Figure 5.8** Plots of the photophysical parameters for Re(phen)(CO)₃Cl@NaY. (a) Three-dimensional representation of photoluminescence intensity, average lifetime and photoluminescence maxima for Re(phen)(CO)₃Cl@NaY upon exposure to different solvent vapors. (b) Flatten 3-D map showing the four distinct regions identified in this study: aprotic, alcohols, non-polar and protic. The numbers in parentheses show the range of photoluminescence intensities for that region.
Table 5.1 Complete collection of photophysical parameters of Re(phen)(CO)$_3$Cl@NaY after exposing with twelve solvents vapors.

<table>
<thead>
<tr>
<th>Solvents vapors</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Intensity change</th>
<th>Average lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl formamide</td>
<td>552 (±0)</td>
<td>74.6 (±13.1)</td>
<td>2858 (±51)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>541 (±1)</td>
<td>68.6 (±4.9)</td>
<td>2630 (±80)</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>547 (±1)</td>
<td>52 (±12.8)</td>
<td>3381 (±245)</td>
</tr>
<tr>
<td>Pyridine</td>
<td>532 (±1)</td>
<td>43.3 (±6.8)</td>
<td>4085 (±190)</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>536 (±2)</td>
<td>21 (±1.7)</td>
<td>2814 (±53)</td>
</tr>
<tr>
<td>Methanol</td>
<td>546 (±0)</td>
<td>14 (±1.7)</td>
<td>1855 (±56.6)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>560 (±9)</td>
<td>17 (±1.4)</td>
<td>1029 (±62.6)</td>
</tr>
<tr>
<td>Benzene</td>
<td>551 (±2)</td>
<td>16.3 (±5.9)</td>
<td>1130 (±39.6)</td>
</tr>
<tr>
<td>Toluene</td>
<td>552 (±1.7)</td>
<td>14 (±2.16)</td>
<td>1246 (±95.1)</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>549 (±0)</td>
<td>19.6 (±2.3)</td>
<td>1204 (±60.1)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>567 (±0)</td>
<td>13.3 (±0.57)</td>
<td>1000 (±35.53)</td>
</tr>
<tr>
<td>Water</td>
<td>566 (±1)</td>
<td>4.7 (±0.47)</td>
<td>648 (±35.53)</td>
</tr>
</tbody>
</table>

The question remains as to why there is such large changes in emission intensity, maxima shift and lifetime after treating of Re(phen)(CO)$_3$Cl@NaY with solvents vapors. Changes in photoluminescence maxima can be explained by specific interaction of the solvent vapors with Re(phen)(CO)$_3$Cl causing either stabilization or
destabilization of the emissive excited state energy, and therefore increasing (blue shifts) or decreasing (red shift) the energy gap. In the case of changes in the lifetime and emission intensity, it is reasonable to think that in the dry material the Re(phen)(CO)\textsubscript{3}Cl complexes strongly associate with the NaY framework resulting in quenching of their photoluminescence intensity and lifetime. The diffusion of solvent vapors into the cavities of NaY disturbs this association, by interacting with both, the framework and the metal complex. This will likely diminish non-radiative deactivation processes, producing a concomitant increase in photoluminescence intensity and lifetime. An additional factor is that, when Re(phen)(CO)\textsubscript{3}Cl@NaY is exposed to solvent vapors, these gases will likely block the zeolite pores and cavities inhibiting the diffusion of oxygen. Consequently, quenching effects of the triplet state from molecular oxygen are greatly reduced that results in increasing photoluminescence intensity and emission lifetime.

5.3. Conclusions

In summary, we have designed a novel platform for detecting solvent vapors based on the entrapment of a Re(phen)(CO)\textsubscript{3}Cl within the zeolite NaY framework. This material presents vapoluminescence,
luminescence vapochronism, and vapokronism. Our results show that obtaining three simple photophysical parameters (i.e. emission intensity, emission maximum and lifetime) allow the unambiguous identification of a solvent vapor. These data were used to build a 3-D map that facilitates the categorization of solvents based on photophysical characteristics. Therefore, the collection of these photophysical parameters for Re(phen)(CO)₃Cl@NaY exposed to a given vapor will allow: (1) identifying a given solvent vapor if the spectroscopic parameter are in the database, or (2) if the spectroscopic parameters obtained for Re(phen)(CO)₃Cl@NaY exposed to the solvent vapor are not in the database (i.e. a vapor not previously characterized), it will at least permit identifying to what category it belongs (protic, polar aprotic, alcohols, or non-polar). Our approach has desirable properties such as being based on a single-probe, easy synthesis, and with a simple methodology that doesn’t require complex statistical or computational analyses to identify the solvent vapor. This system can be improved by adding more solvent vapors to the database and by identifying more regions in the 3-D space for other kind of solvents.
As a final note, we can explore the possibility of sensing gases by Re(phen)(CO)$_3$Cl@NaY. Faster adsorption of gases than solvents vapors should reduce the response time of detection. However, to make this material as reusable sensor, desorption of gas/solvent vapor should also be very efficient. Another important feature of practical sensors is humidity-resistant. Our first generation sensors show changes in emission maxima in presence of moisture. To the best of our knowledge, this is the first time the large void fraction of zeolite has been exploited in vapour sensing applications. Considering the commercial availability of zeolite materials, our research can paved the way to encapsulate other vapochromic complexes to fabricate more efficient sensing devices.

5.4. Experimental Section

Preparation of Re(phen)(CO)$_3$Cl@NaY Material

6.0g of NaY zeolite was calcined for 24h at 550 °C to remove intra-zeolitic water. The dried zeolite was added to a round bottom flask containing 400 mL warm toluene and 50 mg of Re(CO)$_5$Cl. Before addition, zeolite was cooled down at least for 10 minutes in dessicator.
The solution was refluxed for 24h at 110-120 °C under N₂ and constant stirring. After reflux, the solution was vacuum filtered (using Whatman® 50 filter paper), washed with warm toluene, and dried overnight. This material is called Re(CO)₅Cl@NaY. Then, 100 mg 1,10-phenanthroline were dissolved in 40 mL warm toluene in a round bottom flask. The Re(CO)₅Cl@NaY was added to the round bottom and stirred overnight under N₂. The solution was rotovapped and the product collected and heated to 150 °C under high vacuum to sublimate excess phenanthroline. This product was named Re(phen)(CO)₃Cl@NaY(first loading).

The Re(phen)(CO)₃Cl@NaY(first loading) was then washed for about two weeks via Soxhlet extraction with chloroform to remove excess phenanthroline and Re(phen)(CO)₃Cl formed on the external surface of the zeolite. UV-Vis spectroscopy was used to monitor phenanthroline and Re(phen)(CO)₃Cl concentrations in the extract. After washing, the purified Re(phen)(CO)₃Cl@NaY(first loading) was dried in desiccator and then at 110 °C under vacuum.

The procedure above was repeated one more time to increase the loading of Re(phen)(CO)₃Cl within NaY. The material resulting after
purification is called \( \text{Re(phen)(CO)}_3\text{Cl@NaY} \). The amount of \( \text{Re(phen)(CO)}_3\text{Cl} \) within \( \text{NaY} \) was determined by X-ray Photoelectron Spectroscopy (XPS). Dry \( \text{Re(phen)(CO)}_3\text{Cl@NaY} \) was added to indium foil to perform a wide-scan survey. The ratio of atomic concentrations for Si:Na:Re in \( \text{Re(phen)(CO)}_3\text{Cl@NaY} \) is 99:31:1.

**Preparation of \( \text{Re(phen)(CO)}_3\text{Cl-NaY Film and Vapor Treatment} \)**

To prepare the \( \text{Re(phen)(CO)}_3\text{Cl-NaY} \) film, 10 mg/ml composite material was bath sonicated in dicholomethane for 20 minutes. The resulting suspension was added on the inside wall of a dry quartz cuvette with screw cap and Teflon stopper (Starna cells) and dried at room temperature to form a white colored film on the cuvette wall. Then the film was dried at 100 °C under vacuum overnight. Photoluminescence measurements were done to determine the emission maxima and intensity at this point, using front-face detection.

For vapor treatment ~ 25 ml solvents were added to a 100 ml bottle (with screw cap) followed by careful insertion of the cuvette and equilibration in a closed environment at room temperature for 8 hrs.
Finally, the cuvette was removed, closed with the screw cap and the photoluminescence of the film determined after exposure to the vapor.

**Spectroscopic Characterization**

Steady-state photoluminescence of Re(phen)(CO)$_3$Cl@NaY films were performed using NanoLog™ Horiba Yvon spectrometer (Model no. FL-1013, front face detection). All the films were excited at 370 nm and the spectra were taken with 1 nm excitation and emission slits. Time-resolved photoluminescence decays were obtained using Edinburgh Instruments OD470 single-photon counting spectrometer. Samples were excited with a 375 nm picosecond pulse diode laser with a 530 nm filter inserted before detection to prevent unwanted scattering. Time decays were collected at the photoluminescence maximum. UV-Vis absorbance of Re(phen)(CO)$_3$Cl solutions were obtained with a UV-Vis spectrometer (Shimadzu UV-2450). In case of diffuse reflectance, an integrating sphere was attached to UV-Vis spectrometer and the experiment performed on the powder in a Starna quartz cuvette for powders. XPS survey spectra were obtained on a PHI Quantera SXM scanning X-ray microprobe.
5.5 Experimental Contributions

My contributions to the experimental work described in this chapter are the following: synthesis and characterization of Re(phen)(CO)$_3$Cl@NaY, design and perform vapor sensing experiments, perform all the spectroscopic experiments. Zack Panos assisted in the synthesis of Re(phen)(CO)$_3$Cl@NaY. Ty Hanna contributed in designing the synthetic procedure of Re(phen)(CO)$_3$Cl@NaY. Kewei Huang provided pure Re(phen)(CO)$_3$Cl. Mayra Hernandez Rivera assisted in initial planning of vapochromic experiments.

5.6 References


    
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