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Spectroscopic and Optical Imaging Studies of Fullerene Complexes and Single-Walled Carbon Nanotubes

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ABSTRACT

Spectroscopic and Optical Imaging Studies of Fullerene Complexes and Single-Walled Carbon Nanotubes

by

Dmitri Anatolyevich Tsyboulski

Photophysical and optical imaging studies were performed on fullerene molecular complexes and individual single-walled carbon nanotubes (SWNTs).

First, we investigated the reversible dimerization reaction of the newly discovered isomer of C$_{60}$ oxide, [5,6]-open C$_{60}$O. This oxide was found to undergo spontaneous dimerization in solution to form a new isomer of C$_{120}$O$_2$, which was structurally and photophysically characterized. This C$_{120}$O$_2$ compound can be easily converted back to its [5,6]-C$_{60}$O precursor under optical irradiation. These compounds represent a unique fullerene system in which composition can be easily controlled through adjustment of concentration, temperature, and light exposure.

Further, we describe a new aspect of fullerene-porphyrin interactions. The effect manifests itself in a vast increase of the fullerene triplet-singlet radiative rate. Strong emission, that is C$_{70}$ phosphorescence, appears in the near-infrared (NIR) wavelength region. We carefully characterized C$_{70}$-palladium octaethylporphyrin (PdOEP) supramolecular interactions and also found a similar effect with other fullerenes. The complex formation mechanism and its photophysical characterization are described.

Third, we present NIR-fluorescence microscopy as a versatile method to visualize and study individual SWNTs. We demonstrate observation of individual nanotubes in a
variety of environments including solid polymeric films and liquid media. SWNT identities are confirmed with spectroscopic and optical anisotropy measurements. Also, we demonstrate optical length measurements of individual nanotubes that were at least several micrometers long. Emission spectra of different parts of a single nanotube have been examined for the first time.

Finally, we discuss future uses of SWNTs as novel nanoscale fluorescence markers. They supersede conventional fluorophores, which are fluorescent dyes or quantum dots (QD), in terms of both optical anisotropy and photostability. The relative ease of their detection allows one to perform a number of studies at the single nanoparticle level. Unrestricted translational and rotational motions of SWNTs are recorded and analyzed. The observed variation of translational diffusion coefficients reflects the length distribution of SWNTs in the sample. Rotational diffusion constants were found to correlate well with SWNTs translational coefficients. Promising directions for future research are outlined.
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polarized light for excitation and 60X 1.4 NA oil-immersion objective for light collection.
CHAPTER I INTRODUCTION

Fullerenes and carbon nanotubes display a large variety of physical phenomena and attract many researchers who hope to utilize those phenomena for novel applications. Fullerenes, discovered in 1985 in Rice University by Kroto, Curl and Smalley\(^1\) are another allotropic form of carbon along with previously known graphite, diamond and amorphous carbon. \(C_{60}\) and \(C_{70}\) are the two most abundant fullerenes generated by the standard production process\(^2\). Fullerenes and their derivatives are viewed today as potential elements of solar-energy conversion systems owing to their electron-acceptor ability and hold promise in medical applications as drug delivery agents, antioxidants and magnetic resonance imaging (MRI) contrast agents. Their photophysical characterization is essential since optical methods can play important roles in applications development.

Carbon nanotubes are yet another form of carbon structurally related to fullerenes but with quite different characteristics. Discovered in 1991 by Iijima\(^3\), nanotubes' exceptional physical properties became known to the scientific community and sparked immense interest. Nanotubes were predicted to be exceptionally strong, lightweight, and electrically conducting or semiconducting depending on their structure\(^4,5\). Their potential future uses include nanoscale electric circuitry for molecular electronics, super strong composite materials, lightweight electrical cables, sensors, others that emerge as new discoveries are made. The following paragraphs will serve as a general introduction to relevant photophysical phenomena that occur in these molecular systems. More detailed and specific descriptions will be given in the beginning of each chapter.
A. Fullerenes

1. Photophysical processes. Figure 1.1. illustrates a typical molecular energy level diagram and energy transfer pathways. The excitation from a singlet ground state $S_0$ to an excited singlet state is followed by rapid relaxation to the ground state via nonradiative decay or radiative decay, also called "fluorescence". The excited molecule may also undergo an "intersystem crossing" that is a change of its spin state from singlet to triplet. In fullerenes this is often the most efficient singlet state deactivation process with probability approaching 1. For the lower fullerenes, typical singlet state decay rates are ca. $10^{-9}$ s. Fullerenes are known as weak fluorophores with fluorescence quantum yields no larger than $10^{-3}$. Excited triplet state decay pathways include nonradiative and radiative "intersystem crossing". Fullerene triplet-state lifetimes are governed by nonradiative processes and range from tens of ms to a few $\mu$s or less. Radiative $T_1 \rightarrow S_0$
transition is called "phosphorescence". Fullerene phosphorescence is very inefficient and therefore rarely observed at normal conditions. While an excited molecule occupies its lowest triplet state, observation of transient $T_2 \leftrightarrow T_1$ absorption is possible. This process is referred to as "triplet-triplet absorption" and can be used to measure fullerene triplet state lifetimes through standard pump-probe techniques. A molecule in its $T_1$ state may also be thermally excited back into the $S_1$, leading to additional $S_1 \rightarrow S_0$ emission. This is called "thermally activated delayed fluorescence". The intensity of such emission has a Boltzmann factor dependence on temperature and therefore can be used to measure $T_1$-$S_1$ energy gaps.

2. Energy transfer reactions with fullerenes. Energy transfer is a radiationless process that results in exchange of energy between two colliding species. The efficiency of this process depends on many factors including distance between colliding species, their spin state and energy level difference. Fullerene excited triplet states are efficiently quenched by molecular oxygen. This quenching is a basic example of intermolecular energy transfer. The lowest electronic state of molecular oxygen is a triplet. Two molecules in triplet states may combine to form either spin singlet, triplet or quintet. The singlet state is formed with probability 1/9 in such encounters. The low-lying energy level of singlet oxygen, only 22 kcal/mol above its triplet ground state, makes oxygen a powerful quencher of excited states.

3. Charge transfer reactions with fullerenes. Charger transfer (CT) or electron transfer (ET) processes involve formation of an intermediate "charge separated" state between electron donor and electron acceptor moieties. Charge transfer is evidenced as an appearance of new red-shifted bands in the absorption spectra and is responsible for
the color of many minerals and solutions. Of ultimate importance is the photoinduced electron transfer (PET) that lies in the core of all photosynthetic reactions and light harvesting devices. In PET, excitation leads to a formation of metastable charge separated state that later undergoes relaxation to the ground state. The formation of a charge transfer state must be energetically favorable to occur. Environment strongly influences the formation of CT states. For example, polar media stabilize CT states, thus increasing the likelihood of their formation. Fullerenes are good electron acceptors due to the presence of low lying and degenerate LUMO’s (lowest unoccupied molecular orbital). For example, C$_{60}$’s LUMO is triply degenerate and therefore able to contain up to 6 extra electrons$^{7,8}$. Any molecule that has substantially higher energy and long-lived excited state may serve as an efficient electron donor. Due to the electron-donating abilities of porphyrins and chlorophylls, a large variety of their conjugates with fullerenes have been synthesized for studies of PET.
B. Single-Walled Carbon Nanotubes.

1. Nomenclature. Single-walled carbon nanotubes can be envisioned as nanometer thick rolled up graphene sheets that vary in their length, diameter and wrapping angles. Classification of these structures is illustrated in Figure 1.2. SWNT type is defined by two indices \((n,m)\) that characterize a nanotube roll-up vector on a graphene lattice in the \(k_1, k_2\) basis set. The length of this vector equals \(\pi\) times the nanotube’s diameter. Chiral angle is the other parameter that characterizes a nanotube. Chiral angle is defined as the angle between roll-up and \(k_1\) vectors. It varies only between 0° and 30°.
since further increase produces same structures. In two limiting cases SWNT are called zigzag (chiral angle 0°) and armchair (chiral angle 30°).

2. SWNT electronic structure. SWNTs can be either metallic or semiconducting depending on their structure. Semiconducting nanotubes have non-zero bandgaps between their conducting and valence electronic bands while metallic have a continuum

![Figure 1.3. Energy level diagram of semiconducting and metallic SWNT.](image)

of electronic states and no bandgap. Quantum chemical calculations predict that 1/3 of all SWNTs are metallic. There is a simple rule to differentiate metallic and semiconducting nanotubes: if the difference n-m is divisible by 3, the nanotube is metallic. In Figure 1.2 (n,m) indices of metallic nanotubes are shown in red color. For instance, all armchair structures are metals since n = m. As shown at Figure 1.3, SWNT density of states (DOS) diagrams reveal a number of sub-bands, each with a sharp peak called a van Hove singularity. These are sequentially numbered in the conduction and valence zones. According to tight-binding calculations, the gaps between corresponding singularities (E11, E22, etc.) depend almost inversely on SWNT diameter.
Figure 1.4. "Kataura plot"\textsuperscript{10}: subband energies of semiconducting (hollow circles) and metallic (filled circles) nanotubes.

representation of these band-gap energies versus SWNT diameter (Fig. 1.4) is often referred to in the literature as a Kataura plot\textsuperscript{10}. It is interesting to note that band-gap energies of metallic and semiconducting nanotubes are well separated.

3. Synthesis. Carbon nanotubes were found 25 years ago in soot from an arc discharge chamber\textsuperscript{5,11}. These nanotubes represented several concentric cylinders of various diameters, i.e. multi-walled carbon nanotubes. Soon thereafter single-walled carbon nanotubes were observed\textsuperscript{12}. A variety of synthetic methods to produce carbon nanotubes have been developed over the years. Widespread techniques include arc-
discharge, chemical vapor deposition (CVD), laser ablation and high pressure CO (HiPco). An arc-discharge apparatus utilizes carbon electrodes doped with metal catalyst particles, such as Fe, Ni and Co. Nanotubes are produced in the arc discharge under an inert atmosphere\textsuperscript{3}. In the laser ablation technique nanotubes are produced by pulsed laser evaporation of a graphite target in a furnace at 1200\textdegree C\textsuperscript{13,14}. The CVD method utilizes catalytic decomposition of carbon based vapors (acetylene, methanol, etc.) at 600-900\textdegree C\textsuperscript{15,16}. In HiPco method, CO gas at high pressure and temperature decomposes in the presence of catalyst metallic nanoparticles into carbon and CO\textsubscript{2}. Reaction of carbon atoms on the surface of metal catalyst nanoparticles then yields single-walled carbon nanotubes\textsuperscript{17}. Nanotubes can also be produced by other more exotic methods, for instance "ball milling"\textsuperscript{18}, "fullerene decomposition"\textsuperscript{19}, etc. Synthesis methods are being constantly refined and modified to provide better control over output nanotube material in terms of quality, structural homogeneity and purity. Characterizing bulk nanotube material is becoming increasingly important.

4. Characterization methods. High resolution techniques are required to observe carbon nanotubes. Scanning tunneling microscopy (STM) provides highest resolution but is the most complicated and demanding technique\textsuperscript{20}. Under optimal conditions, positions of individual atoms can be resolved to identify SWNT (n,m)-type, observe defects and determine DOS structure. Transmission electron microscopy (TEM) is widely used to examine carbon nanotubes. Its subnanometer resolution allows observation of SWNT and measurement of their diameters\textsuperscript{3}. This method is also considered expensive and complicated. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have poorer resolution and therefore allow only nanotube observation and length
measurements. Even using these sophisticated tools, it is a formidable challenge to characterize complex nanotube samples.

5. SWNT optical transitions. Due to the simplicity and versatility of optical methods their application to study carbon nanotubes was inevitable. Knowledge of SWNTs optically allowed transitions is required to understand and interpret spectroscopic data. To determine those, one must evaluate the transition dipole moment matrix \( D \) defined as:

\[
D = \langle \Psi_f | \nabla | \Psi_i \rangle
\]  

(1.1)

where \( \Psi_f, \Psi_i \) are wavefunctions of initial and final electronic states. The wavefunctions definition and evaluation of \( D \) in (1.1) for carbon nanotubes was extensively described by Gruneis, et al.\textsuperscript{21} and Samsonidze, et al.\textsuperscript{22} Simple selection rules were formulated for SWNTs interband transitions. It was found that for light linearly polarized along the SWNT axis, optically allowed transitions are those that occur between Van Hove singularities with the same indices \( \mu \). Optical transitions between van Hove peaks with \( \Delta \mu = \pm 1 \) are also possible, but only for light polarized perpendicular with respect to SWNT axis. These selection rules predominantly determine the high optical anisotropy of SWNTs, since parallel or perpendicular excitation polarization will have different resonance energies. It is clear, however, that SWNT optical anisotropy is expected to be wavelength dependent. Jorio, et al. demonstrated the presence of these effects with resonance Raman spectroscopy\textsuperscript{23}. 
6. SWNT Raman spectroscopy. Raman spectroscopy was one of the first optical methods applied to study carbon nanotubes. Raman scattering is an example of inelastic scattering that arises due to interaction of light and molecular vibrations. The resulting

![Graph showing Raman-active normal vibrational modes and frequencies (cm⁻¹) of a (10,10) nanotube. Unit cell is shown in the upper right corner.](image)

**Figure 1.5.** Raman-active normal vibrational modes and frequencies (cm⁻¹) of a (10,10) nanotube. Unit cell is shown in the upper right corner.

emission is offset from the excitation frequency by a constant value of a molecular vibration frequency. Only vibrational modes that change polarizability of the molecule are Raman active. For nanotubes, these vibrational modes are shown at Fig. 1.5. Certain features in a Raman spectrum provide information about nanotube structure. For instance the nanotube radial breathing mode (RBM) frequency is inversely proportional to its diameter. High-energy vibrations around 1600 cm⁻¹ form a so-called G-band. Rao, et al. demonstrated the use of G-band to differentiate metallic and semiconducting nanotubes.
Finally, defects in a nanotube produce a D-band that has slightly lower energy than G-band. Although Raman spectroscopy is a powerful method it cannot precisely determine SWNT structure.

7. **SWNT fluorescence spectroscopy.** Fluorescence of SWNTs remained unknown for a long period of time. Nanotubes were produced in large bundles and ropes bound by van-der-Waals attraction forces of their extended π-electron systems. Their separation was difficult since disruption of the strong van-der-Waals interaction was required. In 2002, O’Connell et al. first developed a procedure to produce isolated SWNTs\textsuperscript{26} in bulk. Ultrasonication processing of HiPCO nanotube material in aqueous sodium dodecyl sulfate (SDS) 1\% was used. Ultrasonication broke SWNT bundles and the surfactant molecules prevented individual nanotubes from re-aggregating. Subsequent

![Graph](image)

**Figure 1.6.** Overlapped absorption and emission spectra of micelle-encapsulated individual SWNT in aqueous SDS 1\%\textsuperscript{26}.
centrifugation separated remaining undispersed SWNT bundles from individual tubes. These samples showed near-infrared emission that contained a number of overlapping peaks (Fig. 1.6). Each peak in the emission spectrum matched its parent in the absorption spectrum. These experimental facts suggested that the nanotube band gap fluorescence was observed and that different peaks corresponded to particular nanotube structures.

![2D excitation-emission matrix of micelle-encapsulated SWNT in aqueous SDS (1%); emission peaks positions and visible patterns](image.png)

**Figure 1.7.** (a) – 2D excitation-emission matrix of micelle-encapsulated SWNT in aqueous SDS (1%); (b) – emission peaks positions and visible patterns\(^{27}\).

Subsequent spectrofluorimetric measurements revealed a number of peaks in the excitation-emission 2D spectrum of these samples (Fig. 1.7a). Guided by the idea that each emission peak corresponds to particular (n,m)-type nanotube structure, Bachilo and colleagues analyzed peak positions (Fig. 1.7b). Certain patterns can be easily seen.
The mechanism of SWNT fluorescence, as shown at Figure 1.8, is similar to fluorescence of semiconductors. A semiconductor absorbs photons if their energy is greater than the semiconductor band-gap. Due to specific SWNT sub-band structure, excitations into $E_{11}$, $E_{22}$, $E_{33}$, etc. van Hove transitions are most efficient. Upon excitation

![Energy vs Density of Electronic States](image)

**Figure 1.8.** Mechanism of SWNT fluorescence.

electron and hole are formed in a conduction and valence band. They both undergo rapid relaxation to the lowest excited and highest occupied electronic states. Finally, radiative or nonradiative recombination of electron and hole occurs. In fact, 2D excitation-emission spectrofluorimetry measures the $E_{11}$ and $E_{22}$ optical transitions energies of isolated nanotubes. Nanotube family consists of a number species with gradual variations in their chemical structure. Correspondingly, monotonic variations of their physical
properties can be expected. In their Science publication, Bachilo et al. demonstrated that obvious patterns in the positions of spectrofluorimetric peaks in Fig. 1.7 reflect these variations. Tight-binding quantum chemical calculations of E_{11}/E_{22} energies revealed qualitative similarity with experimental patterns. Raman spectroscopy was used to determine relative diameters of SWNTs in the sample. Combining these data resulted in a final assignment of SWNT structures to their excitation/emission spectra. The assignment

Figure 1.9. SWNT (n,m)-assignment of spectrofluorimetric data.

is shown at Fig. 1.9.

The discovery\textsuperscript{26} and (n,m)-structural assignment\textsuperscript{27} of SWNT fluorescence spectra created a large and novel research area of SWNT studies. The simplicity and power of
spectrofluorimetric technique to characterize mass-produced SWNT samples has been demonstrated later in many reports\textsuperscript{28,29}. SWNT fluorescence was reported to be sensitive to pH\textsuperscript{30} and glucose\textsuperscript{31} under specific conditions, thus creating the basis for their use as biological and chemical sensors. Discovery of the new also effect sparked fundamental investigations into SWNTs optical properties. Ma, et al. found SWNT excited state lifetimes in the picosecond range\textsuperscript{32}. Hartschuh, et al. first measured individual SWNT spectra\textsuperscript{33} in dry SDS. Individual SWNT absorption anisotropy and photostability were reported. Lefebvre, et al. measured absorption and fluorescence optical anisotropy of individual SWNT\textsuperscript{34}. Htoon, et al. investigated individual SWNT spectra at cryogenic temperatures\textsuperscript{35}. Despite considerable effort, many photophysical parameters that are essential for precise characterization of bulk samples remain unknown at this time. These include excited state lifetimes, extinction coefficients, fluorescence quantum yields and optical anisotropies of different (n,m)-type nanotubes.
CHAPTER II  REVERSIBLE DIMERIZATION OF [5,6]-C_{60}O

A. Introduction

Fullerenes have been found to participate in many chemical reactions that provide routes for their derivatization with different functional groups. The simplest example is the reaction of oxidation yielding well-known [6,6]-C_{60}O (an epoxide) \(^{36}\). Intense interest in fullerene oxides had led to the finding that [6,6]-C_{60}O reacts with C_{60} near 200°C to form C_{120}O, an oxygen-bridged dimer containing a furan linkage between the fullerene cages.\(^{37,38}\) The most basic fullerene dimer may be considered the dumbbell-shaped C_{120} molecule, which was first synthesized through a KCN-catalyzed mechanochemical [2+2] cycloaddition reaction of C_{60} \(^{39,40}\) and characterized in subsequent studies \(^{41-46}\). A dimeric fullerene oxide with the formula C_{120}O_{2} was first prepared by Gromov et al. through the 400°C thermolysis of solid C_{120}O \(^{47}\). These species were found to have C_{2v} symmetry and two furanoid bridges linking the fullerene cages; it has since been the subject of various experimental and theoretical investigations \(^{43,48-56}\). Two additional C_{120}O_{2} isomers of C_{1} symmetry are reportedly formed as byproducts in the 200°C solid state reaction between C_{60} and C_{60}O \(^{57}\).

It is interesting to note that two plausible and thermodynamically stable C_{60} oxide structures were predicted more than twenty years ago: [6,6]- and [5,6]-C_{60}O \(^{58}\) (see Fig. 2.1). It was only recently that Weisman and colleagues found a simple way to synthesize the [5,6]-open oxidoannulene (oxa-homo[60]fullerene) through photolysis of the ozonide C_{60}O_{3} \(^{59}\).
**Figure 2.1.** Chemical structures of [5,6]- and [6,6]-C\textsubscript{60}O.

Further research showed that the new [5,6]-C\textsubscript{60}O species spontaneously dimerizes at room temperature in solution to form a new isomer of C\textsubscript{120}O\textsubscript{2}. This was apparently the most facile reaction yet found for producing a fullerene dimer. We have performed structural characterization and investigated photophysical properties of the newly discovered C\textsubscript{120}O\textsubscript{2} isomer. Most intriguingly, our C\textsubscript{120}O\textsubscript{2} has been found to photodissociate with relatively high efficiency to regenerate the [5,6]-C\textsubscript{60}O monomer. The [5,6]-C\textsubscript{60}O / C\textsubscript{120}O\textsubscript{2} system thus provides the first example of reversible fullerene dimerization.

**B. Materials and experimental methods**

1. **Synthesis.** C\textsubscript{120}O\textsubscript{2} was synthesized using thermal dimerization of [5,6]-open C\textsubscript{60}O (oxa-homo[60]fullerene). The C\textsubscript{60}O reactant was prepared according to the procedure in a recent report\textsuperscript{59} by treating a ~2.5 mM solution of C\textsubscript{60} in o-xylene with a stream of O\textsubscript{3} in O\textsubscript{2} from a discharge ozone generator (Ozone Services GE60).\textsuperscript{59} The resulting C\textsubscript{60}O\textsubscript{3} adduct was isolated on a Shimadzu HPLC equipped with a SPD-M10A photodiode array detector and a semi-preparative Cosmosil 5PYE column that was
cooled to 0°C. The mobile phase was toluene. Immediate irradiation of this fraction with an incandescent light source photolyzed the C_{60}O_3 to produce O_2 and [5,6]-open C_{60}O^{59}. The dimerization reaction was induced simply by evaporating the toluene solution of [5,6]-open C_{60}O to higher concentration or dryness using rotary evaporation at 40°C under partial vacuum. After redissolving the resulting solid in toluene, C_{120}O_2 product was isolated and purified by HPLC using the Cosmosil 5PYE column.

2. \textbf{\textsuperscript{13}C NMR spectroscopy}. The solubility of C_{120}O_2 in ODCB-d_4 was sufficiently high (≈1.4 mg/mL) to allow obtaining a \textsuperscript{13}C NMR spectrum on a Bruker Avance500 spectrometer (\textsuperscript{1}H = 500.13 MHz, \textsuperscript{13}C = 125.77 MHz). The solution contained 1.1 mg of 4\% \textsuperscript{13}C-enriched sample, along with 10 mg of Cr(acac)_3 as a paramagnetic relaxation agent and 10 \textmu L of tetramethylsilane (TMS) as a chemical shift reference. A vortex plug just contacting the solution was used to prevent solvent evaporation during the experiment, as a change in concentration would broaden each signal by slightly changing the chemical shift. The sample was kept at 303°C throughout the experiment to prevent precipitation. A total of 48,856 scans were taken over a 96 hr period.

3. \textbf{Mass spectrometry}. Two different mass spectrometry methods were applied in this project. Matrix assisted laser desorption ionization – time of flight (MALDI-TOF) mass-spectrometric analysis was performed with a Bruker Biflex III instrument using 9-nitroanthracene as a matrix. Atmospheric pressure chemical ionization (APCI) mass-spectrometry measurements were made on a Finnigan MAT 95 instrument.
4. **Photophysical measurements.** Ground state UV-VIS absorption spectra were measured with a Cary 400 spectrophotometer. Fluorimetry studies were performed on a Spex Fluorolog 3-211 instrument equipped with a Hamamatsu R636-10 photomultiplier. We made transient absorption measurements using a home-made pump-probe apparatus (Fig. 2.2) that employed 532 nm pulses from a small Q-switched Nd:YAG laser for excitation, and monochromated light from a stabilized tungsten-halogen lamp for probing. An amplified silicon or germanium photodiode served as the detector. A

![Diagram](image)

**Figure 2.2.** Experimental setup for transient spectroscopy.

Tektronix TDS-430A digitizing oscilloscope recorded output signals from the detector and averaged them over multiple excitation shots.

5. **Quantum chemical computations.** All computations were performed using Gaussian® 98W Revision A.11.2. Molecular geometries and relative energies were
obtained using the AM1 and PM3 semi-empirical methods and the B3LYP density functional method with various basis sets. To compute $^{13}$C NMR chemical shifts, we used the Gaussian Independent Atomic Orbitals (GIAO) method incorporated in Gaussian code with optimized molecular geometries at different levels of theory. Many of these computations required one to two weeks of execution time per species on an Athlon MP 1.2 GHz workstation.

C. Experimental results and discussion

1. Dimerization reaction of [5,6]-C$_{60}$O. Figure 2.3 shows a chromatogram of the mixture formed by evaporating a solution of [5,6]-C$_{60}$O to dryness near room temperature and then redissolving in toluene. In addition to the peak near 5 min retention time from unreacted [5,6]-C$_{60}$O, there is a major peak at 8.4 min attributed to a C$_{120}$O$_2$.

![Chromatogram](image)

**Figure 2.3.** Chromatogram of the evaporated and redissolved [5,6]-C$_{60}$O on Cosmosil 5PYE semi-prep column (flow rate – 8 ml/min).
dimeric product. Up to 60% conversion of monomer was seen. Minor peaks at longer retention times, such as the one near 16.3 min, probably represent higher oligomers.

To study the reaction kinetics, a ca. 130 μM solution of [5,6]-C_{60}O was thermostated in a constant-temperature water bath and sampled at various intervals for HPLC analysis of reactant and product concentrations. Figure 2.4a shows the inverse reactant concentration as a function of time as measured at four different sample temperatures. The linearity of each plot indicates pure second-order kinetics for the consumption of [5,6]-C_{60}O. The bimolecular rate constants found from these data are 1.2, 2.4, 3.4, and 6.0 × 10^{-2} M^{-1} s^{-1} at 40, 50, 60, and 70°C, respectively. Figure 2.4b shows an Arrhenius plot of these rate constants along with a linear best-fit that indicates an overall activation energy of 48 kJ·mol^{-1} for the bimolecular reaction of [5,6]-C_{60}O. (After correcting for the temperature-dependent viscosity of the toluene solvent, we estimate an intrinsic activation energy of 39 kJ·mol^{-1}.)

2. **Structural characterization.** In an attempt to confirm the reaction product’s suggested identity as C_{120}O_2, we performed MALDI-TOF and APCI mass spectrometry measurements. However, neither of these methods showed a signal near the expected parent mass of C_{120}O_2 (1472 amu). Instead, mass spectral signals were observed at masses 720, 736 and 752, corresponding to C_{60}, C_{60}O and C_{60}O_2. At relatively weak MALDI-TOF excitation powers, only the C_{60}O peak at 736 amu was visible. This behavior presumably reflects fragmentation of the sample compound under the influence of optical or thermal excitation. For comparison, we note that mass spectrometry of similar fullerene dimer C_{120} under analogous conditions also failed to show a parent peak. As illustrated in Figure 2.5 and table in Appendix A the^{13}C NMR spectrum shows
Figure 2.4. (a) – dimerization kinetics of [5,6]-C_{60}O at various temperatures. (b) – Arrhenius plot for the [5,6]-C_{60}O dimerization kinetics.
Figure 2.5. $^{13}$C NMR spectrum of C_{120}O_2 in ODCB-d_4 at 303 K showing sp$^3$ (a) and sp$^2$ (b) regions.

two sp$^3$ signals with nearly equal intensities at $\delta$82.25 and $\delta$91.45 and 56 sp$^2$ signals from $\delta$151.67 to $\delta$135.50. This pattern immediately excludes several isomers from consideration. It is clear that this compound cannot be the isomer of $C_{2v}$ symmetry reported previously,$^{47,61}$ which ideally would give 26 double-intensity sp$^2$ signals, 4 single-intensity sp$^2$ signals, and 2 double-intensity sp$^3$ signals.$^{62}$ It is equally obvious that
this sample is not the isomer of $D_{2h}$ symmetry with a central cyclobutane ring and an epoxide group on the opposite side of each $C_{60}$ moiety, as too many signals are present in our spectrum and there is no reasonable expectation that such a dimer would form from the [5,6]-open oxidoannelene $C_{60}O$. It is also apparent that our sample has far too few signals to be a $C_1$-symmetry isomer of $C_{120}O_2$, including either described in a prior report.\textsuperscript{57} The measured $^{13}$C NMR signals are noticeably narrower than those shown previously for $C_{2v}$-$C_{120}O_2$.\textsuperscript{47,61} in which only 27 of the 30 different $sp^2$ signals were resolved at the same field strength used here. Still, only 56 of the 58 expected $sp^2$ signals are clearly visible for our sample. A highly expanded plot with no line broadening and 4-fold zero-filling to even better define lineshape clearly shows that the δ143.51 signal is both taller and broader than the adjacent signals, with an area two to three times that of the others.

The number of observed signals with similar heights indicates a single isomeric species with one symmetry element, and thus a point group symmetry of $C_2$, $C_s$ or $C_i$. A compound of such symmetry would ideally give two $sp^3$ signals and 58 $sp^2$ signals of equal intensity. From the observation of two $sp^3$ signals with nearly equal intensity, we deduce that the $C_{60}O$ moieties are linked by two bonds involving four $sp^3$-hybridized carbon atoms. (A structure with one linking bond would be unstable because of radical centers; one with three bonds would not show $sp^3$ signals of equal intensity; and one with four bonds would show a higher ratio of $sp^3$ to $sp^2$ signals.) Although one could imagine a $C_{120}O_2$ peroxide of $C_2$ or $C_s$ symmetry, we consider such a structure unlikely because it could be formed only by substantial rearrangement of the parent $C_{60}O$, giving a dimerization activation energy higher than the observed value.
Thus, we conclude that the dimer contains four sp³ carbon atoms and retains the [5,6]-open oxidoannulene character of the monomer. Bonding between the C₆₀O moieties in such structures would resemble that in C₁₂₀, the dumbbell-shaped dimer of C₆₀ that is linked by two single bonds formed in a 2+2 cycloaddition process. The sp³ chemical shift values observed for our C₁₂₀O₂ isomer suggest that those atoms are deshielded by proximity to an oxygen atom. The most plausible structures satisfying these constraints are those with oxygen atoms directly bound to the sp³ carbons and an overall symmetry of C₅, C₂, or C₁. Figure 2.6 shows these candidate structures. Note, however, that one cannot immediately exclude other structures of these symmetries in which the oxygen atom is located one bond further away from the bridging sites.

Figure 2.6. Possible structures of C₁₂₀O₂ having C₂, C₅ or C₁ symmetries suggested by NMR results.
For any of the structures, the \( \text{sp}^2 \) carbon bound to oxygen would, of course, be much further downfield than the two \( \text{sp}^3 \) signals,\(^{36,63}\) so 58 relatively deshielded \( ^{13}\text{C} \) signals would be expected for a dimeric oxidoannulene that has either a rotation, reflection, or inversion symmetry element. Of the two \( \text{sp}^3 \) carbons, one could reasonably expect the one bound to oxygen to be more deshielded.

Other \( \text{C}_{120} \) dimer structures with a central cyclobutane ring do not exhibit two such deshielded cyclobutane carbon signals, i.e., having both cyclobutane signals downfield of 82 ppm rather than at least one signal at 76 ppm or further upfield.\(^{39,47,64-69}\) The difference between the more upfield \( \text{sp}^3 \) chemical shift in \( \text{C}_{2v}-\text{C}_{120}\text{O}_2 \) and in our isomer of \( \text{C}_{120}\text{O}_2 \) is striking (\( \delta 72.19 \) vs. \( \delta 82.25 \)), whereas the difference between the more downfield \( \text{sp}^3 \) chemical shifts is much smaller (\( \delta 92.11 \) vs. \( \delta 91.45 \)) and in the reverse order. Clearly, the electronic environment around the \( \text{sp}^3 \) carbon not bonded to oxygen in our isomer is significantly different than in the other cyclobutanes and reflects a correspondingly different chemical shift tensor.

The observed (isotropic) chemical shift \( \delta_{\text{iso}} \) is the average of the three principal values of the chemical shift tensor, which lie along three mutually perpendicular directions. Thus, if one or more of the principal values are unusually deshielded, this will be reflected in the observed chemical shift. The chemical shift tensor is well known to be sensitive to local structure; modest changes in bond distances and bond angles can lead to variations in the calculated principal values of the chemical shift tensor and, therefore, in the isotropic chemical shift.\(^{70}\) The relative similarity of the isotropic chemical shifts for the more downfield (and presumably oxygen-bound) \( \text{sp}^3 \) carbons in \( \text{C}_{2v}-\text{C}_{120}\text{O}_2 \) (\( \delta 92.11 \))
and our isomer (891.45) suggests that opposing changes in the principal values of the chemical shift tensor are occurring that nearly offset each other.

The structures in Figure 2.6 are also consistent with known examples of dimerization reactions among analogous anti-Bredt compounds – those with highly reactive, torsionally strained double bonds. The classic example in this class is the dimerization reaction of adamantene.\textsuperscript{71}

3. Quantum chemical findings. To obtain a more detailed structural interpretation of experimental NMR data, we have performed extensive quantum chemical computations on each of the isomers shown in Figure 2.6. Approximate equilibrium geometries were found using the PM3 semi-empirical method. Those structures were then refined through \textit{ab initio} calculations that used DFT-B3LYP gradient-based geometry optimizations with basis sets of increasing size. Computational expense was minimized by the appropriate use of symmetry. Because of the large size of these molecules, we performed a full vibrational analysis at the DFT level only for the reference TMS molecule. The B3LYP/3-21G* equilibrium geometries were then used for computations of $^{13}$C NMR chemical shifts with the GIAO (B3LYP/3-21G* or B3LYP/6-31G*) \textit{ab initio} method in Gaussian 98W. A study on taxol reported that GIAO computations can predict $^{13}$C chemical shifts within an accuracy of several ppm even with HF/6-31G* wavefunctions, and DFT-B3LYP wavefunctions can provide still better results\textsuperscript{72}. Several investigators have also reported successful computations of $^{13}$C NMR chemical shifts for some fullerene derivatives\textsuperscript{73,74}. We ran calibration calculations on previously characterized fullerene oxides and dimeric fullerenes to assess the method's reliability for such compounds. We paid special attention to sp\textsuperscript{3} chemical shift values, with the goal of
using the two widely spaced experimental signals in this region to distinguish among the possible $C_{120}O_2$ isomeric structures. As shown in Table 2.1, we found that the chemical shifts of $sp^3$ carbons in these model fullerene compounds were predicted quite accurately using the smaller basis set. We note that the experimental dependence of chemical shifts on solvent is weak enough (only 0.3 ppm difference between $C_{120}O$ in ODCB-$d_4$ and CS$_2$-CD$_3$COCD$_3$) to neglect when comparing experimental and calculated values.

Table 2.2 compares the measured $sp^3$ chemical shifts of our new $C_{120}O_2$ isomer with values computed for various possible structures. The results point to the class of structures shown in Figure 2.6 because the computed chemical shifts for these structures differ from experiment by less than 10 ppm. By contrast, the $sp^3$ chemical shifts computed for the "$C_1 (+1)$" isomer (representing the class of structures with oxygen atoms one bond further from the bridging site) differ substantially from the measured values. Such large discrepancies let us exclude that class of structures and indicate that the new $C_{120}O_2$ isomer has one of the structures shown in Figure 2.6. Moreover, the most likely candidates are the ones labeled $C_2(a)$ and $C_2(b)$ because their predicted chemical shifts lie closest to the measured values.

Another guide to the identity of the observed isomer comes from computed energies of formation. The results of our computations using several methods are listed in Table 2.3. The most stable isomer is predicted to be $C_2(a)$, with an energy lower than that of two monomers by 126 kJ mol$^{-1}$ (from B3LYP/3-21G*). We find that the energies of $C_1$ and $C_s$ isomers are considerably higher than those of the two $C_2$-symmetry structures. This result plus the NMR chemical shift predictions of Table 2.2 let us rule out the $C_s$ and
$C_1$ isomers, leaving the $C_2(a)$ and $C_2(b)$ structures as the remaining candidates, with $C_2(a)$ very slightly preferred on energetic grounds.

**Table 2.1.** Comparison of calculated and experimental $^{13}$C chemical shifts of sp$^3$ atoms in previously studied fullerene compounds.

<table>
<thead>
<tr>
<th>compound</th>
<th>calculated chemical shifts (ppm)</th>
<th>measured chemical shifts (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP/3-21G*</td>
<td>B3LYP/6-31G* (3-21G* geom.)</td>
</tr>
<tr>
<td>C$_{60}$O epoxide</td>
<td>90.5</td>
<td>96.3</td>
</tr>
<tr>
<td>C$_{120}$</td>
<td>76.2</td>
<td>80.2</td>
</tr>
<tr>
<td>C$_{120}$O</td>
<td>78.7</td>
<td>82.4</td>
</tr>
<tr>
<td></td>
<td>97.9</td>
<td>102.7</td>
</tr>
<tr>
<td>C$_{120}$O$<em>2$ (C$</em>{2v}$)</td>
<td>73.2</td>
<td>76.2</td>
</tr>
<tr>
<td></td>
<td>91.4</td>
<td>96.1</td>
</tr>
</tbody>
</table>

$^a$ measured in benzene-$d_6$ solution; $^b$ measured in ODCB-$d_4$ solution; $^c$ measured in 98:2 CS$_2$:CDCl$_3$ solution

**Table 2.2.** Pairs of $^{13}$C sp$^3$ chemical shift values (in ppm) computed for five possible C$_{120}$O$_2$ isomers at two levels of theory, and the values measured experimentally.

<table>
<thead>
<tr>
<th>C$_{120}$O$_2$ isomer</th>
<th>B3LYP / 3-21G* (3-21G* geom.)</th>
<th>B3LYP / 6-31G* (3-21G* geom.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$ (a)</td>
<td>81.2</td>
<td>88.2</td>
</tr>
<tr>
<td>C$_2$ (b)</td>
<td>83.2</td>
<td>92.9</td>
</tr>
<tr>
<td>C$_1$</td>
<td>86.3</td>
<td>96.1</td>
</tr>
<tr>
<td>C$_5$</td>
<td>81.8</td>
<td>100.1</td>
</tr>
<tr>
<td>C$_1$ (+1)</td>
<td>72.2</td>
<td>74.1</td>
</tr>
<tr>
<td>observed values</td>
<td>82.25</td>
<td>91.45</td>
</tr>
</tbody>
</table>
Experimental observations of HPLC retention times provide further structural information about our C_{120}O_{2} isomer. We used previously reported methods to synthesize small amounts of several dimeric fullerenes and fullerene oxides (C_{120}, C_{120}O and C_{120}O_{2} (C_{2v})) \textsuperscript{38,40,47}. Examination of the retention times of these species on Cosmosil 5PBB and Buckyprep columns reveals certain elution patterns. We find that compounds in this group elute in order of increasing molecular mass on the Buckyprep column. However, on the 5PBB column their retention times (for similar mass) depend mainly on molecular dipole moment, with higher dipole moments giving shorter retention times. Table 2.4 shows the increasing order of retention times for C_{120}, C_{120}O and C_{120}O_{2} (C_{2v}) on the Buckyprep column and the reversed order on the PBB column. The lower rows of this table show retention times measured under the same conditions for our new C_{120}O_{2} isomer, along with the dipole moment values computed for the C_{2}(a) and C_{2}(b) candidate structures. Although the dipole moment of the C_{2}(a) isomer does not vanish by symmetry, our computations predict it to be very small. The long PBB retention time of the new isomer strongly suggests that it is essentially nonpolar, thereby favoring assignment to the C_{2}(a) structure shown in Figure 2.6. Note that we have also observed HPLC and UV-VIS evidence for the presence of a second isomer of the dimer with a shorter PBB retention time and a yield near 7% of the main one. This minor isomer may be the C_{2}(b) species.
Table 2.3. Relative energies (in kJ mol$^{-1}$) of C$_{120}$O$_2$ isomers as computed by various methods.

<table>
<thead>
<tr>
<th>isomer</th>
<th>AM1</th>
<th>PM3</th>
<th>B3LYP/3-21G*</th>
<th>B3LYP/6-31G* (3-21G* geom.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$ (a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C$_2$ (b)</td>
<td>+37</td>
<td>-2</td>
<td>+12</td>
<td>+2</td>
</tr>
<tr>
<td>C$_i$</td>
<td>+109</td>
<td>+67</td>
<td>+72</td>
<td>+75</td>
</tr>
<tr>
<td>C$_s$</td>
<td>+102</td>
<td>+50</td>
<td>+108</td>
<td>+99</td>
</tr>
</tbody>
</table>

Table 2.4. Computed dipole moments and experimental HPLC retention times measured under the same conditions for several dimeric fullerenes and fullerene oxides.

<table>
<thead>
<tr>
<th>compound</th>
<th>computed dipole moment, B3LYP/3-21G* (Debye)</th>
<th>retention time on Buckyprep column (min)</th>
<th>retention time on PBB column (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{120}$</td>
<td>0</td>
<td>7.3</td>
<td>17.4</td>
</tr>
<tr>
<td>C$_{120}$O</td>
<td>0.65</td>
<td>7.7</td>
<td>17.0</td>
</tr>
<tr>
<td>C$_{120}$O$<em>2$ (C$</em>{2v}$)</td>
<td>1.02</td>
<td>8.3</td>
<td>15.1</td>
</tr>
<tr>
<td>C$_{120}$O$_2$ observed</td>
<td>--</td>
<td>8.1</td>
<td>19.0</td>
</tr>
<tr>
<td>C$_{120}$O$_2$ (C$_2$ (a))</td>
<td>0.01</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C$_{120}$O$_2$ (C$_2$ (b))</td>
<td>0.80</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

4. Basic photoproperties. Figure 2.7a shows ground state absorption spectra of C$_{120}$O$_2$ and [5,6]-C$_{60}$O, its monomeric precursor, in room temperature toluene solutions prepared with equal mass concentrations. The near-UV peak of the dimer lies at 329 nm, blue-shifted by approximately 6 nm relative to the monomer, and it lacks the monomer’s absorbance minimum near 450 nm. Both of these differences reflect the presence of sp$^3$ derivatization sites only in the dimer. C$_{120}$O$_2$ also shows a S$_1 \leftarrow$ S$_0$ absorption onset near 710 nm that is intensified and red-shifted by ca. 20 nm compared to the monomer.
Photophysical experiments on the new C$_{120}$O$_2$ isomer quickly revealed that the compound is chemically unstable when optically illuminated. In Figure 2.7b we show the changing absorption spectrum of a C$_{120}$O$_2$ sample during exposure to a photolyzing light source. The spectrum evolves into that of [5,6]-C$_{60}$O during irradiation, and HPLC data confirm this photochemical conversion from dimer into monomers. The observed process resembles the photodissociation of C$_{120}$ into C$_{60}$ studied earlier by Bachilo, et al. in this laboratory. We also found that the rate of C$_{120}$O$_2$ photodissociation is several orders of magnitude higher in degassed toluene solution than in aerated solution. This difference strongly suggests that dissociation occurs from the lowest triplet state, which is efficiently quenched by dissolved oxygen. The presence of isosbestic points (the points where absorption does not change as the reaction proceeds) near 572 nm and 624 nm indicates that the photo-transformation of C$_{120}$O$_2$ involves no long-lived intermediate species. Because the absorbance change is also very minor near 360 nm, this spectral region can be considered nearly isosbestic. We therefore determined the molar absorptivity of the dimer using absorbance data at 360 nm and previous absorptivity results found for the monomer. The molar absorptivity deduced for C$_{120}$O$_2$ is 115,000 ± 2000 M$^{-1}$ cm$^{-1}$ at the 329 nm peak.
Figure 2.7. (a) – Absorption spectra of \( \text{C}_{120}\text{O}_2 \) (1 x \( 10^{-5} \) M) and [5,6]-\( \text{C}_{60}\text{O} \) (2 x \( 10^{-5} \) M) in toluene. (b) – Spectral changes during photolysis of \( \text{C}_{120}\text{O}_2 \). The inset shows spectrophotometrically deduced concentrations of monomer and dimer species as a function of irradiation time.
To locate the $S_1$ origin energy of $C_{120}O_2$, we measured its fluorescence excitation and emission spectra. The measured excitation spectrum shown in Figure 2.8 closely matches the compound's absorption spectrum, as expected. The emission spectrum has distinct maxima at 718 nm and 793 nm. In Figure 2.9 we show overlaid plots of $C_{120}O_2$ fluorescence and absorption spectra near 700 nm. To allow proper comparison, we have divided the absorbance values by frequency ($\nu$), divided the emission intensities (in photons per second per unit frequency) by $\nu^3$, and scaled the results to match amplitudes of the first peaks. The resulting mirror relation shown in Figure 2.9 implies a value of $14,090 \pm 70$ cm$^{-1}$ for the $S_1$-$S_0$ energy spacing of $C_{120}O_2$ in toluene.

5. Triplet state photophysics. Studies of $C_{120}O_2$ triplet state properties were hampered by the tendency of samples to photochemically change composition during experimental runs. To suppress this problem, we measured triplet-triplet absorption kinetics using fewer than ten low-power excitation pulses. Figure 2.10 shows such induced absorbance data acquired with a freshly prepared $-2.5 \cdot 10^{-6}$ M sample, a probe wavelength of 715 nm, and averaging over only five excitation pulses. Kinetic analysis of this trace as a mixture of concurrent first- and second-order decays gave a first-order triplet state lifetime of $34 \pm 2$ $\mu$s for $C_{120}O_2$ in toluene at 298 K. As expected, second-order decay was found to be negligible. The 34 $\mu$s intrinsic triplet state lifetime is somewhat shorter than the value of 44 $\mu$s found earlier for $C_{120}$ under comparable conditions$^{46}$, but it is quite similar to the 31 $\mu$s triplet lifetime of [5,6]-$C_{60}O$ $^{59}$.

Because our measurements of transient absorption spectra are made by combining separate kinetic scans at many probe wavelengths, additional precautions were needed to ensure sample stability during such data acquisition. We used a stirred sample cell
Figure 2.8. Fluorescence excitation and emission spectra of $C_{120}O_2$ in toluene.

Figure 2.9. Absorption and fluorescence spectra of $C_{120}O_2$, transformed and overlaid to estimate the $S_1$ origin energy.
of relatively large volume (8 mL), reduced the excitation energy to ca. 0.04 mJ per pulse, and added enough oxygen to the sample to reduce the triplet state lifetime to approximately 6 μs, thereby lowering the photodissociative quantum yield. To scan the entire spectrum, we prepared two identical sample portions having concentrations near 4 x 10⁻⁶ M. The first portion was used for a scan from 600 to 800 nm by 5 nm steps, with a filter shielding the sample from shorter probe wavelengths. Then the second, fresh sample was scanned from 740 to 1100 nm with a different shielding filter. Only five excitation pulses were used at each probe wavelength, and HPLC sample analysis following the measurements confirmed that less than 10% of the dimer had been photolyzed. Figure 2.11 shows the resulting composite transient spectrum, in which the second data segment has been scaled by a factor of 0.98 to provide amplitude matching with the first. The spectrum shows a strong Tₙ→T₁ maximum at 715 nm and a shoulder near 830 nm. Both of these features are typical of C₆₀ adducts containing two adjacent sp³ sites ⁷⁵. We measured the quantum yield of triplet state formation by comparing the intensities of ¹O₂ luminescence from absorbance-matched samples of C₁₂₀O₂ and C₇₀ that were photoexcited in the presence of dissolved oxygen. The samples were saturated with O₂ at 1 atm in order to minimize photodissociation of C₁₂₀O₂ and to maximize the oxygen luminescence signals, which arose from energy transfer to oxygen during fullerene triplet quenching. HPLC analysis of the C₁₂₀O₂ samples after measurement showed less than 1% photodissociation. It was necessary to correct the observed oxygen luminescence signals for differences in ¹O₂ lifetimes between the sample solutions (25 and 29 μs for the C₁₂₀O₂ and C₇₀ samples, respectively). Taking the triplet quantum yield, Φₜ, of the C₇₀ reference to be 1.0 ⁷⁶, we found that Φₜ of C₁₂₀O₂ equals 1.0 ± 0.1.
Figure 2.10. Triplet-triplet absorption kinetics of $\text{C}_{120}\text{O}_2$ in toluene at 297 K, measured at 715 nm following 532 nm pulsed excitation.

Figure 2.11. Induced (triplet-triplet) absorption spectrum of $\text{C}_{120}\text{O}_2$ in toluene following 532 nm excitation.
Our attempts to directly determine the energy of the $\text{C}_{120}\text{O}_2$ $T_1$ state by phosphorescence spectroscopy were unsuccessful, so we instead used the indirect method of finding the $S_1$-$T_1$ energy gap through thermally activated delayed fluorescence (TADF) measurements and then combining this gap value with the spectroscopically determined $S_1$ energy to obtain the $T_1$ energy. The TADF measurements on $\text{C}_{120}\text{O}_2$ were unusually challenging because this compound seems to be photochemically unstable in polymer films, the preferred medium for such experiments. We prepared samples in fluid solution but had to suppress complications from triplet-triplet annihilation by using low concentrations, reduced excitation energies, and a paraffin/toluene solvent mixture with higher viscosity. To limit sample photolysis we also restricted the number of excitation pulses and used a large volume cuvette with magnetic stirring. Measured intensities of delayed fluorescence were scaled to the prompt fluorescence amplitudes in order to compensate for any changes in sample concentration or temperature dependence in the fluorescence quantum yield. Figure 2.12 shows an Arrhenius-type plot of the measured delayed fluorescence intensity. From the linear least-squares fit we find an activation energy of 27 kJ/mol ($\approx 2300 \pm 200 \text{ cm}^{-1}$), which represents the $S_1$-$T_1$ energy gap. This value is consistent with an independent determination based on the ratio of delayed and prompt fluorescence intensities in our sample, as described in $^{77}$. We therefore deduce that the $T_1$ origin lies 11,800 ± 200 cm$^{-1}$ above the ground state.

6. Dissociative photochemistry. Initial data on photodissociation kinetics were obtained from HPLC analyses of irradiated $\text{C}_{120}\text{O}_2$ solutions. A set of replicate samples was prepared, carefully degassed, and then photolyzed for various times with 532 nm pulses from a Nd:YAG laser. To ensure homogeneous irradiation, we used a defocused
**Figure 2.12.** Arrhenius-type plot showing the temperature dependence of the intensity of initial delayed fluorescence. Symbols mark experimental data and the solid line is a linear best fit.

Laser beam, a low pulse repetition rate (~1 Hz), and magnetic sample stirring. HPLC analysis then provided reactant and product concentrations as a function of irradiation time. The resulting $C_{120}O_2$ concentrations showed first-order decay with a constant, $k_{\text{transform}}$, of 0.00167 s$^{-1}$. To convert this value into a photochemical quantum yield, we applied the following relation (valid for optically thin samples):

$$\Phi_{\text{dist}} = \frac{k_{\text{transform}} N}{2.303 \ A \ P_0},$$

(2.1)

where $N$ is the total number of sample molecules in the cell, $A$ is the initial absorbance at the photolysis wavelength, and $P_0$ is the incident laser power in photons per second. Evaluating equation 2.1 with our experimental parameters, we found that $C_{120}O_2$ in
degassed toluene at 297 K has a quantum yield for photodissociation of 0.025. Although quite accurate, this method for measuring the photochemical quantum yield is tedious. For further measurements we applied a simpler method based on the difference in molar absorptivities between the monomer and dimer. At 329 nm, the absorbance of a C$_{120}$O$_2$ solution decreases by approximately 30% when it dissociates into two monomers. The concentration change of the dimer can therefore be found from $\Delta A$, the absorbance change, using the following expression:

$$\Delta [C_{120}O_2] = \frac{\Delta A^{329}}{(e_{C_{120}O_2}^{329} - 2e_{C_6O}^{329}) l}$$

We measured 329 nm absorbance changes as a function of irradiation time to find $k_{\text{trans}}$ at various sample temperatures. Analysis using equation 1 then confirmed the quantum yield value deduced from HPLC data and also showed that $\Phi_{\text{diss}}$ increases sharply, from 0.025 to 0.425, between 297 and 343 K.

To investigate this variation in photodissociative quantum yield, we made temperature-dependent measurements of induced absorption kinetics over the same range, using the procedure described earlier. These results showed that the triplet state decay constant, $k_T$, also varies strongly with temperature. Measured $k_T$ values are plotted in the Figure 2.13a. Also plotted in this figure are the rate constants for dissociation of triplet state C$_{120}$O$_2$, $k_{\text{diss}}$, which were obtained by dividing the temperature-dependent $\Phi_{\text{diss}}$ values by the corresponding triplet state lifetimes. Over the studied temperature range, this dissociation rate constant varies from 730 to 19,600 s$^{-1}$. The final trace in the Figure 2.12a shows the difference between $k_T$ and $k_{\text{diss}}$, which we identify as $k_{\text{ISC}}$, the
rate constant for $T_1 \rightarrow S_0$ radiationless decay. We can see that the photophysical relaxation represented by $k_{ISC}$ has very little temperature dependence over the studied range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) – $C_{120}O_2$ temperature-dependent rate constants for overall triplet state decay ($k_T$), $T_1 \rightarrow S_0$ intersystem crossing ($k_{ISC}$), and triplet state dissociation ($k_{diss}$); (b) – Arrhenius plot of $k_{diss}$. Inset: Temperature variation of $\Phi_{diss}$, the photodissociation quantum yield.}
\end{figure}
Figure 2.13b shows an Arrhenius plot of the deduced dissociation rate constants along with a linear best fit. The slope implies an activation energy for triplet state dissociation of 60 kJ mol\(^{-1}\) (5000 cm\(^{-1}\)). The Arrhenius prefactor is approximately \(2.3 \times 10^{13} \text{ s}^{-1}\), corresponding to an attempt frequency near 800 cm\(^{-1}\). These values indicate that once \(C_{120}O_2\) reaches the \(T_1\) state, it can undergo vibrationally activated dissociation over a modest potential barrier to regenerate \([5,6]-C_{60}O\).

**D. Conclusions**

We have found that the recently discovered oxidoannulene isomer of \(C_{60}O\) readily dimerizes in room temperature solution to form a new isomer of \(C_{120}O_2\). The \(C_{120}O_2\) product contains a four-membered bridging ring, as in \(C_{120}\), and has \(C_2\) symmetry. When optically excited, this dimer undergoes intersystem crossing to populate its triplet state with near-unit efficiency. The \(C_{120}O_2\) triplet state lies 11,800 cm\(^{-1}\) above its ground state, shows an intrinsic lifetime of 34 μs (at 297 K), and has an absorption peak at 715 nm. All of these values are typical for \(C_{60}\) derivatives. However, the triplet state also undergoes unusual thermally activated dissociation to regenerate the \([5,6]-C_{60}O\) precursor with quantum yields that reach 43% at 70°C. These compounds therefore form the first fullerene system containing monomers and dimers in a dynamic balance that can be easily controlled through adjustment of concentration, temperature, and light exposure.

This new isomer of \(C_{120}O_2\) should prove useful as a stable reactant for the convenient photolytic generation of \([5,6]-C_{60}O\). The high reactivity found for \([5,6]-C_{60}O\) in this initial study of its chemical behavior apparently arises from the strained \(sp^2\) bonds adjacent to the oxygen atom. The ability of \([5,6]-C_{60}O\) to undergo chemical reactions under mild conditions may provide novel routes to fullerene derivatization.
CHAPTER III NEAR-INFRARED EMISSION OF C\textsubscript{70} – PALLADIUM

OCTAETHYLPOPHYRIN SUPRAMOLECULAR COMPLEX

A. Introduction

Photoinduced electron-transfer (PET) is an important process that lies at the core of photosynthesis and solar energy conversion. Covalently linked porphyrin-fullerene molecular complexes have been widely used as models to study PET due to porphyrin electron donor and fullerene electron acceptor\textsuperscript{78} abilities. Recently, formation of non-covalently linked porphyrin – fullerene complexes in solution was discovered \textsuperscript{79–80}. It has been shown that fullerene and porphyrin are able to form solid state and liquid-phase supramolecular structures due to van-der-Waals and possibly charge transfer interactions\textsuperscript{81;82}. Recent works demonstrated that the binding constants of specifically designed porphyrin derivatives with fullerene in solution could range from $10^2$ to $10^5$ M\textsuperscript{-1} \textsuperscript{79;83}. Significantly higher binding constants of porphyrin-based host and fullerene guest (~ $10^8$ M\textsuperscript{-1}) were also reported\textsuperscript{84}. Variable temperature NMR spectroscopy served as a method to quantitatively characterize porphyrin-fullerene interaction. Complexation can be qualitatively evidenced as an appearance of red-shifted absorption bands in UV-VIS spectra of porphyrin-fullerene mixtures \textsuperscript{79;83–85}. Only one report included detailed photophysical studies of the non-covalently linked supramolecular porphyrin-fullerene systems were not performed in most of the cited reports except for \textsuperscript{80}. Investigation of photophysical processes was otherwise limited to covalently linked porphyrin-fullerene systems.
In degassed non-polar solution mixtures of C\textsubscript{70} and palladium octaethylporphyrin (PdOEP) we observed an intense and unusual emission that was an order of magnitude stronger and red-shifted compared to fullerene fluorescence. The new emission was completely quenched in the presence of oxygen. This phenomenon appears unique and previously unknown. It also seems rather general, since similar emissions were observed in C\textsubscript{60}-PdOEP mixtures. This intriguing finding stimulated us to further investigate the origin and properties of the unusual emission.

Qualitatively similar effects were recently reported for several covalently linked porphyrin-fullerene dyads. These dyads displayed weak and red-shifted emissions with respect to their luminescence\textsuperscript{86-91}. The emissions also featured strong sensitivity to solvent polarity. An intermediate CT state was suggested to be the origin.

B. Materials and experimental methods

1. Materials. The chemicals PdOEP from Aldrich Chem. Co. (90% dye content) and C\textsubscript{70} (99%) from SES Research were purchased and used without further purification. Major impurities in PdOEP stock (residual solvent) were spectroscopically inactive and therefore not likely to interfere with photophysical measurements. We found traces of free-base octaethylporphyrin present in amounts below 1\%. The HPLC grade hexane and toluene solvents were obtained from Fisher Optima.

2. Experimental Methods. Experimental setups and instrumentation described in Chapter II were used to measure UV-VIS absorption, fluorescence, triplet-triplet absorption kinetics and spectra. A Spex Fluorolog 3-12 spectrofluorometer equipped with a liquid nitrogen-cooled InGaAs photodiode was used to measure emissions in the near-infrared range.
We have employed an Oxford Instruments Optistat cryostat to control sample temperatures during cryogenic transient absorption measurements. Either a Q-switched Nd:YAG laser at 532 nm or pulses from a tunable dye laser were used for sample excitation. Amplified silicon photodiodes with time constants of 0.70 μs and 0.12 μs served as the detectors.

C. Experimental results and discussion

1. Photophysical properties of C_{70} and PdOEP. Chemical structures of C_{70} and PdOEP are shown in Figure 3.1. It is worthwhile to summarize known photophysical properties and parameters of C_{70} and PdOEP that are essential for this work. C_{70} is known as a weak fluorophore: the C_{70} fluorescence lifetime and quantum yield in toluene are 0.66 ns and 5.7·10^{-4}, respectively (Φ_F = 5.9·10^{-4} in hexane)\textsuperscript{92,93}. Excited \textsuperscript{1}C_{70}^* undergoes quick and efficient intersystem crossing to the triplet state, with a triplet quantum yield ~ 1.0\textsuperscript{77,92}. Intrinsic triplet state lifetime of C_{70} is very long: 24.5 ms at ambient temperature in a PMMA film\textsuperscript{77}. However, in liquid solution it is hardly possible to observe such a
long-lived triplet state of pure C_{70} due to various quenching mechanisms, such as triplet-triplet annihilation, quenching by impurities and self-quenching by ground state C_{70}. As a result, we find an apparent C_{70} triplet lifetime in solution of approximately 2 ms, in agreement with a previous report^{94}.

Although PdOEP is a well-studied molecule, its photophysical properties have not been thoroughly documented yet. The reported extinction coefficients of PdOEP in benzene at the maxima of its Soret and α-bands were $\varepsilon^\text{PdOEP}_{395} = 191,000$ and $\varepsilon^\text{PdOEP}_{548} = 58,900 \text{ M}^{-1}\text{cm}^{-1}$ respectively^{95,96}. To determine the extinction coefficient of PdOEP in toluene and hexane a reference solution of PdOEP in benzene was repeatedly evaporated and redissolved in toluene, hexane and benzene again. Absorption spectra were taken after each cycle and compared with the reference. In toluene the extinction spectrum was found to be essentially the same as in benzene, while in hexane $\varepsilon^\text{PdOEP}_{392} = 187,600 \text{ M}^{-1}\text{cm}^{-1}$ (Soret band) and $\varepsilon^\text{PdOEP}_{546} = 75,500 \text{ M}^{-1}\text{cm}^{-1}$ (α-band). In degassed solutions PdOEP exhibit strong phosphorescence emission and comparatively weak fluorescence. The previously reported value of PdOEP’s triplet state lifetime in polystyrene is 0.99 ms at room temperature^{97}. During the course of our studies we estimated its triplet state lifetime ($\tau_{\text{PdOEP}}$) as 1.53 ms in PMMA film at room temperature. This value does not differ much from the previously measured value of 1.9 ms in an n-octane matrix at 77 K^{98}, suggesting a weak temperature dependence of major triplet state deactivation pathways. Indeed, one of the main factors here is the spin-orbit interaction with heavy atom Pd, providing for the relatively high value of the phosphorescence quantum yield ($\Phi_{\text{Ph}} \sim 0.2$ at 298 K)^{97}. By contrast, spin-orbit coupling of another widely used metal porphyrin, ZnOEP, is considerably weaker and its triplet state lifetime changes noticeably with temperature.
from 5 ms at 298 K to 57 ms at 77 K \(^{99}\). The phosphorescence quantum yield of ZnOEP also is rather small even at 77 K \((\Phi_{\text{ph}} = 0.065)\) \(^{99}\). We were unable to detect any phosphorescence signal of ZnOEP under normal conditions.

General trends of porphyrin-fullerene interactions are well known \(^{100-104}\). A porphyrin-fullerene dyad shows charge transfer (CT) behaviour, where the porphyrin usually serves as an electron donor and the fullerene as an acceptor. In a mixed solution, quenching of the fullerene triplet states by porphyrin is usually observed. The reported rate constants for this process approach the theoretical diffusion limit in polar solvents, suggesting a very high probability of quenching due to charge transfer \(^{100;103;104}\).

Another ongoing process in the system is the triplet-triplet energy transfer between solute molecules. Energy transfer commonly occurs in the direction from porphyrin to fullerene given that the energy of the porphyrin triplet state is usually higher than the \(C_{70}\) triplet \(^{101;102}\). Due to the large difference between \(C_{70}\) and PdOEP extinction coefficients above 600 nm it is possible to selectively excite only the \(C_{70}\) component in a binary mixture. Our transient absorption measurements in degassed solutions did not show any noticeable indication of energy transfer from \(3C_{70}^*\) to \(1\text{PdOEP}\) at room temperature after selectively exciting the fullerene at 610 nm. \(3\text{PdOEP} \rightarrow 1C_{70}\) Energy transfer was clearly evidenced as a rise in the triplet-triplet absorption signal of \(3C_{70}^*\) after simultaneous excitation of fullerene and PdOEP with 532 nm Nd:YAG laser pulses.

2. Steady-state absorption and fluorescence spectroscopy of fullerene-PdOEP solutions. The new emission was observed only in non-polar solvents. Fig. 3.2 shows luminescence spectra of binary hexane solutions of the two most abundant fullerenes and PdOEP. The difference between degassed and air-saturated sample spectra clearly
exhibits the unknown near-infrared (NIR) emission. Quite remarkable is the emission intensity that can exceed the $C_{70}$ fluorescence intensity almost by a factor of 20 under certain conditions, as shown in Fig. 3.2a. The new emission for the $C_{70}$ and PdOEP mixture has two distinct maxima at $782 \pm 2$ nm and $863 \pm 4$ nm. For a mixture of $C_{60}$ with PdOEP, the maxima appear at $772 \pm 4$ nm and $863 \pm 6$ nm (Fig. 3.1b). We note that the peak at $647$ nm in Fig. 3.2b is a fluorescence signal of a free-base octaethylporphyrin impurity that becomes excited by $595$ nm radiation. We recorded the excitation spectrum of the $C_{70}$-PdOEP mixture by monitoring the NIR emission signal at $850$ nm while scanning the excitation monochromator between $350$ and $650$ nm. The resulting spectrum represents superimposed absorption spectra of $C_{70}$ and PdOEP. This finding indicates that NIR emission precursors can be both excited $C_{70}$ and PdOEP.

Since the discovered NIR emission was present only in binary solutions of $C_{70}$ and PdOEP, it is, obviously, a result of their interaction. The tendency of porphyrins and fullerenes to form supramolecular structures suggested a $C_{70}$-PdOEP complex as a plausible source of the novel emission. Searching for additional evidence of such complex formation, we closely examined absorption spectra of $C_{70}$ and PdOEP solutions. It is known, for instance, that the absorption spectra of the porphyrins and particularly their Soret bands are strongly influenced by a nearby electron acceptor $^{86}$. Ground state interactions inside porphyrin-fullerene dyads are usually evidenced as the appearance of red-shifted absorption bands $^{86-91}$. However, the measured absorption spectra of $C_{70}$ with PdOEP in toluene and hexane at various concentrations (up to $100 \mu M$) did not show any noticeable deviations from superimposed spectra of the two isolated components. In fact,
Figure 3.2. Emission spectra of degassed and air saturated solution of a) $C_{70}$ (2 μM) and PdOEP (8 μM) ($\lambda_{\text{exc}} = 600$ nm); b) $C_{60}$ and PdOEP (10 μM) ($\lambda_{\text{exc}} = 595$ nm) in hexane.

the failure to detect ground state interaction of non-covalently bound porphyrin with fullerene even in polar solvents was reported earlier\textsuperscript{103}.
3. Time-resolved spectroscopy of NIR emission in solutions. In order to further investigate the nature of the complex formation we compared time resolved transient absorption and emission kinetics. A degassed $5.0 \cdot 10^{-6}$ M solution of C$_{70}$ and PdOEP in hexane was prepared. The transient absorption and emission kinetics were recorded using our apparatus for transient absorption measurements equipped with Si-photodiode detector (time constant 0.70 μs) while exciting the sample with dye laser pulses at 610 nm. Excitation at this wavelength allowed us to selectively excite only the C$_{70}$ component in a binary mixture. Fig. 3.3 shows the triplet-triplet absorption signal of C$_{70}$ measured at its maximum around 960 nm and NIR emission kinetics at 850 nm. We note that C$_{70}$ delayed fluorescence signal at this wavelength is negligible (see Fig. 3.2a). The emission kinetic trace was found to almost exactly match the triplet-triplet absorption kinetics of C$_{70}$. The same result was obtained when the sample was excited at 532 nm.

![Graph](image)

**Figure 3.3.** Triplet-triplet absorption kinetics of C$_{70}$ and near IR emission kinetics of degassed bimolecular mixture of C$_{70}$ and PdOEP (5 μM) in hexane ($\lambda_{exc} = 610$ nm).
4. Time-resolved spectroscopy of NIR emission in polymeric film. The C$_{70}$-PdOEP complex emission was also observed in a rigid polymeric film. In the film the diffusional motion of large molecules is essentially stopped. However, the emitting complex can be formed when C$_{70}$ and PdOEP randomly appear near each other. A PMMA film with large concentrations of porphyrin and fullerene (~ 0.5 mM) was prepared. The sample film was degassed and the time-resolved emission spectra were recorded after it was excited by Nd:YAG laser pulses at 532 nm. Dye laser excitation at 610 nm was found to be insufficient to obtain reliable signals over the whole spectral range due to both lower excitation pulse intensity and a smaller extinction coefficient of C$_{70}$ at this wavelength. Fig. 3.4a shows time-resolved emission spectra of C$_{70}$ and PdOEP in a degassed PMMA film. We found that the emission was represented by three overlaid spectral components with different lifetimes. Two long-lived components with lifetimes above 10 μs corresponded to the phosphorescence signal of isolated PdOEP and the delayed fluorescence of C$_{70}$. The third, fast-decaying component had a spectrum similar to the NIR emission spectra observed in C$_{70}$-PdOEP binary solutions. Our detector with a 0.70 μs time constant failed to resolve the emission kinetics, thus suggesting that the NIR emission lifetime in polymer is considerably shorter than the detector response time. We were able to partially resolve that short-lived component with our faster although less sensitive Si-photodetector that had a response time near 0.12 μs. The partially resolved emission kinetic trace is shown in Fig. 3.4b. We fit the data using a custom FORTRAN program called “RBWfit”. In this procedure the instrument response function is convoluted with a specified kinetic model, for instance, single exponential decay. The
model parameters are automatically varied until best possible agreement with experimental trace is found.

The sample emission kinetics at 980 nm was fit reasonably well with the sum of three exponential decays. The shortest component (lifetime \( \sim 2 \) ns) and the longest component (lifetime \( > 10 \) \( \mu \)s) obviously match signals from fast luminescence and/or scattered light, and long-lived phosphorescence/delayed fluorescence of the sample, respectively. The intermediate kinetics corresponds to the emission of interest, with estimated lifetime \( \sim 150 \) ns. It is likely that the porphyrin-fullerene complexes formed either in PMMA films or in solution do not have a uniform, well-defined geometry and cannot be expected to have identical photophysical characteristics. However, our 150 ns estimate can be considered as the average lifetime of the emitting C\(_{70}\)-PdOEP species.

We performed cryogenic emission measurements on C\(_{70}\) and C\(_{70}\)-PdOEP polymeric samples to investigate the NIR emission dependence on temperature and compare it to C\(_{70}\) phosphorescence. We note that low temperature measurements of C\(_{70}\) have been reported earlier \(^{105,106}\). Measurement of the C\(_{70}\) phosphorescence emission at 298 K was hampered by the presence of the intense delayed fluorescence signal. Nonetheless phosphorescence peaks were clearly visible above the infrared part of the fluorescence spectrum. At 90 K this thermally activated delayed fluorescence is completely absent \(^{77}\). At low temperatures the C\(_{70}\) phosphorescence emission is intensified and the spectral line broadening due to phonon coupling is significantly reduced. As shown in Fig. 3.5a, the C\(_{70}\) emission signal at 90 K consists of overlaid prompt fluorescence and phosphorescence signals. Low temperature time-resolved NIR
Figure 3.4. (a) – Time-resolved emission spectra of C\textsubscript{70}-PdOEP complex isolated in degassed PMMA matrix (\(\lambda\text{_{exc}} = 532\) nm, photodetector response 0.70 \(\mu\)s); (b) – Partially resolved emission kinetics of C\textsubscript{70}-PdOEP complex at 980 nm. Photodetector with 0.12 \(\mu\)s response time was used.
emission spectra of the C\textsubscript{70}-PdOEP complex in rigid polymer were recorded in a similar manner as described earlier. Fig. 3.5b shows the short-lived C\textsubscript{70}-PdOEP complex emission at 290 and 90 K. Obviously, the complex emission appears in the same spectral region as the phosphorescence of isolated C\textsubscript{70}. However, lower temperature seems to have little effect on the spectral shape and intensity of the NIR emission. The complex

![Graph showing emission spectra](image)

**Figure 3.5.** (a) – C\textsubscript{70} fluorescence and phosphorescence spectra in PMMA film at 90 K; (b) – Time-resolved emission of C\textsubscript{70}-PdOEP complex in PMMA film (emission signals are normalized per maxima, long-lived background component
emission spectrum remained structureless even at 90 K, which may be an indication of the inhomogeneous local environment due to close proximity of porphyrin or of variations in structure among the complexes. Small spectral shifts to shorter wavelengths at low temperatures were observed in both cases (C$_{70}$ and C$_{70}$-PdOEP in PMMA) and are likely related to thermally induced changes in the PMMA host. The C$_{70}$-PdOEP complex emission intensity also did not change significantly with temperature. It appeared to be slightly reduced (~ 10 %) at low temperatures, but these variations could be induced by macroscopic changes of experimental conditions (film cracking, thermal shrinking, etc.).

5. Dynamics of C$_{70}$-PdOEP complex formation. The experiments described above gave important insights into the nature and specifics of the complex formation. It is possible to identify the emitting complex precursor as $^3$C$_{70}^*$, since NIR emission appears in degassed solutions after exciting the C$_{70}$ component. $^3$C$_{70}^*$ can be formed directly by C$_{70}$ excitation or indirectly by energy transfer from $^3$PdOEP*, which is expected to be less efficient. This explains the presence of both C$_{70}$ and PdOEP absorption components in the excitation spectrum. We observed similar emission spectra in solid matrices and liquid media. The short emission signal in the film and long emission kinetics matching the C$_{70}$ triplet state decay suggest the dynamic nature of the complex formation in a solution. Indeed, we know that $^3$C$_{70}^*$ in solution exists long enough to encounter porphyrin and be quenched. Near-IR emission likely appears as an additional deactivation pathway of C$_{70}$ triplets besides quenching through a charge transfer complex. The emitting C$_{70}$-PdOEP complexes may dynamically form in solution before excitation as well. However, we did not find any noticeable interaction between solute molecules in absorption spectra. NIR emission kinetics shown at Fig. 3.3 consists of two components:
a short unresolved emission peak at the time of excitation followed by a long decay. The short component, which possibly includes the C\textsubscript{70} fluorescence and C\textsubscript{70}-PdOEP complex emission, is much smaller than the total signal. The short excited state lifetime of the complex (\(\sim 150\) ns) explains the nearly perfect match of the triplet-triplet absorption and emission kinetics. The formation of the complex through bimolecular encounters occurs on the order of tens of microseconds at our typical PdOEP concentrations and is a rate determining step.

A reasonable approximation is to consider each collision between C\textsubscript{70} and PdOEP as the dominant step in complex formation and disregard second order processes such as triplet-triplet annihilation of C\textsubscript{70}, etc. Indeed, at low excitation powers and sufficiently high porphyrin concentration the PdOEP quenching of the triplet C\textsubscript{70} is the principal process. The general kinetic scheme of the complex formation when only the C\textsubscript{70} component is excited can then be written as:

\[
C\textsubscript{70} \overset{k_{\text{exc}}}{\rightleftharpoons} 3C^{*}_{\text{70}} \quad k_{r,\text{70}}
\]

\[
3C^{*}_{\text{70}} + \text{PdOEP} \overset{k_{\text{diff}}}{\rightleftharpoons} X^{*} \quad k_{\text{dis}}
\]

\[
X^{*} \rightarrow C\textsubscript{70} + \text{PdOEP}
\]

where \(X^{*}\) and \(3C^{*}_{\text{70}}\) represent the excited complex and triplet state C\textsubscript{70} respectively; \(k_{r,\text{70}}\) is the first order decay constant of \(3C^{*}_{\text{70}}\) in solution; \(k_{\text{diff}}\) is the diffusion-limited bimolecular rate constant; \(k_{\text{dis}}\) is the constant for excited complex dissociation into \(3C^{*}_{\text{70}}\) and PdOEP; \(k_{r} + k_{\text{nr}}\) gives the sum of radiative \((k_{r})\) and non-radiative \((k_{\text{nr}})\) excited complex first-order decay constants. Rate constant \(k_{r}\) describes the observed NIR
emission process, while $k_{nr}$ is a sum of all non-radiative quenching mechanisms. Using
the near IR emission signal as a measure of the complex concentration, we can construct
a Job's plot to determine complex stoichiometry. Although a 1:1 ratio of C$_{70}$ to PdOEP
might be expected, the Job's plot may provide further support to the dynamic complex
formation model. To construct such a plot, we measured the NIR emission intensity while
varying the relative fraction of the two components of the complex and keeping their total
concentration constant at 10$^{-5}$ M. The mixtures containing different component ratios
were degassed and their steady state emission spectra were recorded with our Spex
instrument. The complex dependence of emission intensity on the concentration of the
components is shown at Fig. 3.6a. Using the kinetic scheme above and steady-state
equilibrium condition we can show that the emitting complex concentration $X^*$ is
proportional to:

$$X^* \sim \frac{[C_{70}] \cdot [PdOEP]}{k_C^{C_{70}} + k_{diff} \cdot P \cdot [PdOEP]}; \quad P = \frac{k_r + k_{nr}}{k_r + k_{nr} + k_{dis}}$$ (3.2),

where $P$ is the probability of excited complex deactivation and $(k_C^{C_{70}} + k_{diff} \cdot P \cdot [PdOEP])^{-1}$
is the triplet state lifetime of C$_{70}$, measured independently. Thus we must normalize the
emission intensity signal by the $^3$C$_{70}^*$ lifetime to get the Job's plot representation in a
standard form that properly reveals complex composition. Figs. 3.6b and 3.6c show the
measured C$_{70}$ triplet state decay constant and concentration dependence of emission from
the complex. The symmetric form found for the Job's plot, with a maximum at 5·10$^{-6}$ M,
confirms that the complex of C$_{70}$ and PdOEP is formed in the ratio 1:1. Because the
shape of the Job's plot is smoothly parabolic instead of triangular, we conclude that the
equilibrium constant for complex formation is not very high. However, since the absolute
complex concentration is unknown, it is not possible to estimate the equilibrium constant with reasonable accuracy using these data.

![Graph](image)

**Figure 3.6.** (a) - Measured NIR emission intensity dependence on the concentration of bimolecular mixture components. (b) - $^3C_{70}^*$ decay rate dependence on the concentration of PdOEP in hexane; (c) - Job's plot of $C_{70}$-PdOEP complex formation (NIR emission signal corrected by $^3C_{70}^*$ lifetime and normalized per maximum).
An alternative way to estimate the binding constant is to measure the lifetime of the excited complex; however, the dynamic nature of the complex formation in solution makes these measurements impossible. One can assume that the excited complex lifetimes \((k_r + k_{nr})^{-1}\) in non-polar media with similar dielectric constants are roughly the same. This value was approximately estimated for the C\textsubscript{70}-PdOEP complex in solid PMMA (~ 150 ns). In our kinetic model in solution, the excited \(^3\)C\textsubscript{70}*-PdOEP pair has two decay pathways: dissociate either without changing the electronic states of its components, or with quenching. The dissociation rate constant is related to probability of quenching in (3.2). Hence, the equilibrium constant of the complex formation \(K_{EQ}\) can be determined as follows:

\[
K_{EQ} = \frac{k_{diff}}{k_{dis}} = \frac{k_{diff}}{k_r + k_{nr}} \cdot \frac{P}{1-P}
\]  

(3).

Using input data from Table 3.1, we find the binding constants ~ 2\(\cdot\)10\(^2\) and 6\(\cdot\)10\(^2\) M\(^{-1}\) for hexane and toluene solutions respectively. These values seem realistic when comparing with similar experimental data from the previous reports. The estimated equilibrium constants are several times smaller than those reported in the case of specifically designed porphyrin conjugates\(^{79}\). It should be noted that estimated equilibrium constants describe the complex formation in the electronically excited state.

6. Photophysical characteristics of \(^3\)C\textsubscript{70}*-PdOEP complex. Similarly to previous studies of ZnOEP and C\textsubscript{70}/C\textsubscript{60} interactions in solutions\(^{103,104}\), we observed efficient quenching of \(^3\)C\textsubscript{70}* by PdOEP. By measuring the \(^3\)C\textsubscript{70}* lifetime at different PdOEP concentrations we found the quenching rate constants values of (1.4\(\pm\)0.1)\(\cdot\)10\(^9\) M\(^{-1}\)s\(^{-1}\) in hexane and (2.8\(\pm\)0.3)\(\cdot\)10\(^9\) M\(^{-1}\)s\(^{-1}\) in toluene (see Fig. 3.6b).
Using previously established values of the $C_{70}$ fluorescence quantum yield we can estimate the quantum yield of emission for the complex. Steady-state fluorescence spectra of air-saturated and degassed bimolecular solutions of $C_{70}$ (2 $\mu$M) and PdOEP (8 $\mu$M) in hexane and toluene were recorded while selectively exciting the $C_{70}$ component in the sample with light near 600 nm. To minimize the error of measurements, background emission for an 8 $\mu$M PdOEP air-saturated solution was measured separately and then subtracted. NIR emission quantum yields were computed as $\Phi_{\text{Fl}} (S_{\text{NIR}}/S_{\text{Fl}})$. These and other parameters are summarized in Table 3.1.

Table 3.1. Photophysical parameters of $C_{70}$-PdOEP emitting complex in toluene and hexane.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solvent</th>
<th>toluene</th>
<th>hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion constant at 25 ºC, M$^{-1}$s$^{-1}$</td>
<td>$k_{\text{dif}}$</td>
<td>$1.1\cdot10^{10}$,$^{99}$</td>
<td>$2.1\cdot10^{10}$,$^{99}$</td>
</tr>
<tr>
<td>$^{3}C_{70}$* quenching rate constant by PdOEP, M$^{-1}$s$^{-1}$</td>
<td>$k_{Q}$</td>
<td>$(2.8 \pm 0.3)\cdot10^{9}$</td>
<td>$(1.4 \pm 0.1)\cdot10^{9}$</td>
</tr>
<tr>
<td>Probability to quench $^{3}C_{70}$* per collision</td>
<td>$k_{Q}/k_{\text{dif}}$</td>
<td>0.26</td>
<td>0.07</td>
</tr>
<tr>
<td>NIR emission quantum yield</td>
<td>$\Phi_{\text{NIR}}$</td>
<td>$(9\pm3)\cdot10^{-4}$</td>
<td>$(1.0\pm0.1)\cdot10^{-2}$</td>
</tr>
<tr>
<td>Complex excited state lifetime, ns</td>
<td>$\tau$</td>
<td>$\sim 150$*</td>
<td>$\sim 150$*</td>
</tr>
<tr>
<td>Complex radiative rate constant, s$^{-1}$</td>
<td>$\Phi_{\text{NIR}}/\tau$</td>
<td>$\sim 6\cdot10^{3}$*</td>
<td>$\sim 7\cdot10^{4}$*</td>
</tr>
</tbody>
</table>

* - assuming decay rate of the complex in PMMA is the same as in solution.
7. Origin of NIR emission. The NIR emission of C_{70}-PdOEP complex has certain similarities with the previously reported cases of emitting porphyrin-fullerene dyads^{86,88-90}: it is red shifted with respect to C_{70} fluorescence and is very sensitive to solvent polarity. In these reports the origin of the NIR porphyrin-fullerene dyad emission was suggested to be not the fullerene moiety but the intermediate CT state of the porphyrin-fullerene system. Nevertheless, we believe that the new NIR emission corresponds to a spin-forbidden T_1 \rightarrow S_0 transition of C_{70} induced by close proximity of Pd atom, i.e. an external heavy atom effect.

First of all, we know that the precursor of the emissive state is the C_{70} triplet state. The emission lies in exactly the same spectral region as C_{70} phosphorescence in hexane (see Fig. 3.4) and toluene, implying the same transition energy from the emitting state as from the C_{70} triplet. If the emission observed occurs from a CT state, then there must be a corresponding ground CT state of a porphyrin-fullerene pair, which should be detectable with absorption spectroscopy^{86-91}. However, as was noted earlier^{103} and as we found in these studies, the ground-state CT interaction of non-covalently linked porphyrin and fullerene could not be detected. We note, however, that our failure to detect this state does not entirely exclude the possibility of its existence.

Non-polar media cannot stabilize a charge-separated state as efficiently as polar media, thus making CT interaction in the ground state energetically unfavorable. The excited CT state of the C_{70}-PdOEP complex must appear above \( \text{3} \text{C}_{70}^* \) to match the energy of C_{70}'s T_1 \rightarrow S_0 transition, which means its formation is energetically unfavorable.

Sensitivity of the NIR emission to solvent polarity can be understood if one considers properties of the solvents, their polarity and polarizability in particular. Charge
transfer, one of the major deactivation pathways of $^3\text{C}_{70}^*$, depends strongly on the solvent polarity $^{103,104}$. In non-polar solvents, such as toluene and hexane, polarizability is the important factor. More polarizable media stabilize the charge-separated state, thus increasing the $^3\text{C}_{70}^*$ quenching rate and decreasing radiative probability. This trend was clearly observed experimentally: the complex emission was the strongest in the least polarizable solvent, n-hexane (dielectric constant 1.89, refractive index 1.375), weaker in toluene (dielectric constant 2.44, refractive index 1.496) and undetectable in polar solvents in which CT processes are dominant.

A parallel set of experiments with ZnTPP and ZnOEP was performed in an attempt to detect similar NIR emission from mixed solutions. These porphyrins have similar electronic structure to PdOEP and show similar interactions with fullerenes $^{100,104}$. ZnTPP and ZnOEP do not contain heavy atoms and they do not exhibit any noticeable phosphorescence in degassed solutions at normal conditions. We were also unable to detect C$_{70}$'s NIR emission signal in the mixed solutions.

These observations suggest that the discovered emission is likely to be phosphorescence of fullerenes induced by the heavy atom Pd. Earlier reports showed qualitatively similar behavior resulting in a changed and intensified C$_{70}$ phosphorescence in halogenated solvents $^{106,107}$. In our case Pd greatly increases the radiative rate constant of C$_{70}$ up to $\sim 10^5$ s$^{-1}$.

D. Conclusions

A new and unusual NIR emission of a noncovalent porphyrin-fullerene complex was discovered. We extensively investigated C$_{70}$-PdOEP throughout this work, but this effect appears to be more general. The emission was clearly observed for the two most
abundant fullerenes, $C_{60}$ and $C_{70}$, in different non-polar media. Similar but weak emission was also observed for [5,6]-$C_{60}O^{59}$. We suggest that the emission observed is phosphorescence of $C_{70}$ induced by the heavy atom Pd inside the porphyrin cage. As a result of their interaction, the radiative rate constant of $^3C_{70}^*$ is greatly increased up to $10^5$ s$^{-1}$ in hexane. The radiative pathway for $^3C_{70}^*$ deactivation competes against non-radiative quenching processes involving the charge transfer. In non-polar media the NIR emission intensity strongly depends on solvent polarizability. NIR emission is undetectable in a polar environment where CT processes are dominant.

We would like to note that the fundamental nature of the discovered effect may serve as an aid to better understanding of photophysical processes of porphyrin-fullerene systems.
CHAPTER IV. VISUALIZATION OF INDIVIDUAL SINGLE-WALLED CARBON NANOTUBES WITH NEAR-INFRARED FLUORESCENCE SPECTROSCOPY

A. Introduction

Single-walled carbon nanotubes (SWNT) continue to attract intense research attention because of their unique electronic, mechanical, thermal, and optical properties. The synthesis, processing, and study of nanotubes are guided by a number of powerful visualization and characterization methods that include scanning electron microscopy (SEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). These microscopic methods can provide very high spatial resolutions that allow determinations of nanotube lengths and even diameters, but at the cost of experimental complexity, instrumentation expense, limited imaging speed, and restricted sample environments. Recently, optical methods with coarser spatial resolution have also been applied to image nanotubes through scanning resonant Raman microscopy, using both confocal and near-field approaches.

Fluorescence microscopy offers yet another tool for nanotube observation and characterization. Several groups have reported the successful sidewall derivatization of nanotubes with fluorescent markers that make observation of single nanotubes possible using conventional fluorescent microscopes. It is often preferable, however, to microscopically image the intrinsic near-infrared fluorescence of pristine semiconducting SWNT. The first benefit of this approach is that a nanotube's precise diameter and chirality can be deduced from its near-infrared spectral emission signature because SWNT fluorescence wavelengths have been successfully assigned to specific \((n,m)\)
species \(^{27}\). In addition, the unusual near-infrared wavelengths of SWNT fluorescence provide high discrimination against background emission by other sample components. The absorption and emission transitions of SWNT are strongly polarized along the tube axis, allowing determination of a nanotube's orientation through polarization measurements. Finally, the use of pristine nanotubes avoids the need for derivatization reactions and allows observation of intrinsic nanotube behavior unperturbed by chemical alterations. Although SWNT exhibit low fluorescence quantum yields (~10\(^{-3}\)), several groups have reported microscopic spectral measurements on individual nanotubes \(^{29,33-35,115}\). Hartschuh et al. have also used a confocal scanning approach to construct near-infrared fluorescence images of smaller-diameter nanotubes that emit at wavelengths short enough to be observed with a silicon detector \(^{33}\). We describe here the use of a conventional far-field microscope coupled to a two-dimensional InGaAs photodiode array to conveniently visualize a wide range of individual pristine SWNT in a variety of environments, including polymeric matrices and liquid media. The parallel, non-scanning detection advantage afforded by our method allows images with more than 80,000 pixels to be captured in as little as 50 ms, permitting the tracking of individual nanotube motions. In addition, the instrument is readily coupled to a spectrograph to provide spatially resolved emission spectra and \((n,m)\) identification of individual nanotubes.

**B. Materials and experimental methods**

1. **Experimental setup.** Fluorescence microscopy was performed using a Nikon TE-2000 inverted microscope coupled via one of its output ports to an Indigo Alpha NIR InGaAs camera (320 x 256 pixels) that had been modified for reduced dark current backgrounds. Some images were obtained using a prototype OMA-V:2D liquid-nitrogen
cooled InGaAs camera from Roper Scientific. Samples were excited with an external 660 nm diode laser whose beam was focused by an aspheric lens (f=18.4 mm) mounted on an XYZ translation stage. The excitation power at the sample was approximately 20 mW, and the excitation intensity could be varied from ca. 1 to 30 kW/cm². The polarization plane of the excitation laser was adjusted by rotation of a half-wave retardation plate. Nanotube emission was collected with a Nikon PlanApo 60x/1.4 oil-immersion objective. To selectively transmit the near-IR nanotube emission and block excitation light, we used a dichroic beamsplitter in series with a dielectric long-pass filter having a cut wavelength of either 946 or 1125 nm. Single-frame acquisition times of 2 s were used with the Indigo camera. To measure spatially resolved emission spectra of objects in the microscope’s observation field, a second output port of the Nikon TE-2000 was coupled to the input slit of a J-Y C140 spectrograph with a cryogenically cooled 512-element InGaAs array (Roper OMA-V) at its focal plane. The entrance slit gave a spectral bandpass of 3 nm. Its physical dimensions of 0.5 x 0.1 mm encompassed a 10 x 2 pixel region of the camera at 60X magnification. The spectrum of a nanotube could be easily measured by moving it to a specific position in the imaged field and then switching the microscope from its imaging port to the spectrograph port. Spectra were typically acquired by averaging 10 exposures of 20 s each.
2. Materials and Sample Preparation. HiPCO SWNT with diameters between 0.6 and 1.4 nm were obtained from the Rice Carbon Nanotechnology Laboratory. Aqueous suspensions of SWNT in SDBS (sodium dodecylbenzenesulfonate) were prepared by ultrasonic dispersion and ultracentrifugation, as previously reported.\textsuperscript{26,27} We prepared solid films of nanotubes by dissolving PVP (poly(vinylpyrrolidone), 40,000 average molecular weight) in DI water in amounts up to ca. 0.1 g/mL to yield moderately viscous solutions, and then adding aqueous SDBS suspensions of nanotubes in desired amounts. The resulting suspensions of nanotubes in SDBS and PVP (or in SDBS only) were spin-coated onto fused silica microscope slides and dried to obtain solid films containing separated nanotubes. To prepare liquid samples for microscopy, several
microliters of aqueous SWNT suspensions were spread and sealed between a microscope slide and a cover slip.

Although as-grown HiPco samples generally contain a fraction of SWNT with lengths of several micrometers, normal dispersion through vigorous ultrasonication appears to cut these longer nanotubes and leave only sub-micrometer species. To achieve dispersion while preserving the long nanotubes, we added several micrograms of raw HiPco product into 10 mL of 1% SDBS/H₂O solution and applied 5 to 10 W of power to a small ultrasonic immersion probe for just 5 to 10 seconds. After this processing, the samples contain mainly sub-micrometer nanotubes with a small number of longer ones. Other workers have also reported the use of brief sonication to obtain dispersions containing long SWNT. Following the dispersion process, our samples were coarse-filtered to remove large residual nanotube aggregates, added to aqueous PVP solution, deposited onto a fused silica substrate, and dried.

C. Experimental results and discussion

1. Visualization of individual SWNT. Fluorescence from SWNT in solid films was readily imaged using the near-infrared microscope described above. Figure 4.2a shows many emission centers in the fluorescence image of a sample with relatively high SWNT concentration. Figure 4.2b is a similar image of a film that is much more dilute in nanotubes. Here the emitters appear sparse and isolated. The apparent diameter of individual emission features is approximately 1 μm, near the estimated optical resolution of our system. Although scanned confocal images have been reported previously in a study that used a Si CCD to capture fluorescence from the smallest diameter SWNT at wavelengths below ca. 1030 nm, the InGaAs camera used here is sensitive from 900 to
1600 nm, allowing detection of a wide range of semiconducting nanotube species. The image in Figure 4.2c shows a different intensity pattern in the sample of Figure 4.2b when the excitation beam’s polarization axis is rotated by 80°. Note that the detection system has no polarization selection. Variations in emission intensity with excitation polarization are plotted in Figure 4.2d for the three labeled points. All show a strong \( \cos^2 \) dependence, as is consistent with individual SWNT undergoing excitation of \( E_{22} \) van Hove transitions polarized along the tube axis. The differing angles of maximum intensity reveal the random azimuthal orientations of nanotubes in the sample.

2. Individual SWNT spectroscopy. To confirm the observation of individual nanotubes with near-IR microscopy, we recorded emission spectra of the isolated emission centers in PVP and PMMA films. As shown in Figure 4.3, each center gives a distinct, relatively narrow spectrum representing the \( E_{11} \) transition of a specific \( (n,m) \) SWNT. The observation of well-defined emission peaks and strong polarization effects indicates that each of these emitting centers is a single SWNT. Peak #3 arises from a (7,5) nanotube; peak #2 is assigned as an (8,6); and peak #1 is tentatively identified as (13,3). For larger diameter nanotubes that have \( E_{11} \) values below 1 eV (emission wavelengths greater than 1200 nm), the high spectral density can make \( (n,m) \) identification based on emission spectra ambiguous unless additional excitation wavelengths are available.
Figure 4.2. Near-IR fluorescence images of SWNT in PVP films at high (a) and low (b, c) concentrations. The excitation beam polarization angle was 80° in b) and 160° in c). The dependence of fluorescence intensity on polarization angle is plotted in frame d) for the three labeled objects in images b) and c).
Many of the emission spectra observed for single nanotubes in dried SDBS show full-widths at half-maximum of approximately 24 meV (185 cm⁻¹). This value is consistent with the widths found in bulk samples in aqueous SDBS suspension. However, some individual nanotubes in dried SDBS show narrower emission widths of only ca. 12 meV (e.g., peak #1 in Fig. 2a), which is similar to the 10 to 15 meV widths reported by Lefebvre et al. for individual air-suspended nanotubes at room temperature. In addition, our spectra of individual tubes in PVP films reveal broader emission linewidths of 30 to 35 meV, as shown in Figure 4.2b. It appears then that much of the spectral width for typical nanotubes in condensed environments arises from inhomogeneous broadening within a single tube. This suggests the presence of multiple emission centers along the tube axis with locally differing environments. It seems that energy migration processes between fluorophore regions may be related to the complex temperature-dependent spectra reported in a study of individual SWNT at cryogenic temperatures ³⁵.
Figure 4.3. Emission spectra of selected individual nanotubes in dried aqueous SDBS (a) and PVP (b).
3. Visualization of "long" individual SWNT. Further insights have been obtained by examining SWNT that are long enough to be optically resolved in our fluorescence microscope. Using samples prepared with the mild sonication procedure described earlier in Experimental Methods, we were able to observe clearly elongated fluorescence images, as shown in Figure 4.4. The objects imaged in frames a), b), and c) are approximately 8, 3, and 4 μm long, respectively. To verify that these emitters are single nanotubes, we have measured spatially resolved polarization dependences (averaging data over 25 adjacent pixels) and emission spectra. Emitters that show linear images, such as in Figure 4.4a and 4.4b, display a strong polarization dependence with no phase variation from one end to the other. By contrast, however, measurements of excitation polarization dependence for the curved object in Figure 4.4c reveal a phase shift of 25 ± 3° between the two ends, as plotted in Figure 4.4d. This shift matches the geometric angle of 25 ± 4° determined from the image of Fig. 4.4c, confirming that the object is a bent nanotube with $E_{22}$ optical absorption polarized strongly along the local tube axis. We have also measured emission spectra of selected regions within single nanotubes. The traces labeled #1 and #2 in Figure 4.4c show such spectra for opposite ends of the object in Fig. 4.4b. The near-coincidence of these emission peaks clearly indicates that the entire nanotube has a consistent, well-defined $(n,m)$ identity. However, there is a small spectral shift of ca. 2 meV between the two ends, which apparently reflects differences in local environment within the polymer host. For the bent nanotube of Fig. 4.4c, we find a larger intra-tube spectral shift of approximately 4 meV (traces #3 and #4). The distinct spectra and polarization maxima observed for different segments
within individual SWNT indicates an upper limit of a few micrometers on the distance that excitons can migrate within a nanotube during their lifetime.

It should be noted that the weakly ultrasonicated samples also contained large nanotube bundles visible in bright field microscopy. Emission from these objects was observable in our near-IR microscope, but with properties dramatically different from the individual nanotubes described above. First, emission from the bundles was completely insensitive to polarization of the excitation beam. Second, the bundles' emission spectra were broad and diffuse. We suggest that this emission arises from efficient light absorption followed by rapid nonradiative relaxation and consequent transient heating of the bundle and its surroundings to give nearly featureless thermal emission.
Figure 4.4. Near-infrared fluorescence images of single nanotubes recorded with magnifications of 60X (a), 90X (b,c). Each image area is 15 x 15 μm. (d) – Dependence of emission intensity on excitation polarization for the two ends of the nanotube in (c). (e) – Spatially resolved emission spectra of the ends of the nanotubes in frames (b) and (c).
4. Visualization of SWNT motion. Near-infrared fluorescence microscopy also permits real-time tracking of nanotube motions in fluid media. Thin films of aqueous SWNT suspensions between fused silica slides were excited with laser powers near 400 W/cm² (~80 μm spot diameter) and the emission was imaged using our microscope and the prototype Roper OMA-V:2D near-IR camera. Nanotubes in fluids can be clearly imaged only if they remain relatively stationary during the exposure time needed to capture the image. With exposures of only 50 ms, our apparatus achieved signal-to-noise ratios near 5 for the most strongly fluorescing nanotubes. Figure 4.5 shows sequential 50 ms images of an individual nanotube as it is driven by Brownian motion and possibly convection caused by laser heating. Crosshairs drawn in each frame mark the nanotube's position in the preceding image. Analysis of these images reveals a mean square displacement (MSD) of 0.82 μm² per frame, which, using the relation $D = \frac{MSD}{4\Delta t}$, gives a diffusion coefficient of approximately 4 μm² s⁻¹. We note that this estimated diffusion coefficient is a factor of ~10 greater than the value reported for arc-grown SWNT coated with biopolymers ¹¹⁷. We interpret the changes in emission intensity as reorientation of the nanotube's axis relative to the polarization plane of the excitation laser. To our knowledge, fluorescence microscopy currently provides the only method capable of monitoring motions of pristine nanotubes on the sub-second time scale. We expect that higher excitation intensities will allow the time resolution of this method to be brought into the low millisecond range.
Figure 4.5. Sequential images revealing the motion of one nanotube in aqueous SDBS suspension. Each frame shows a 10 x 10 μm area and was acquired with a 50 ms exposure. Frames are sequenced from left to right starting at the top row. Dotted crossed lines show the nanotube's position in the previous frame.
D. Conclusions

Near-infrared fluorescence microscopy is a useful new method for detecting and characterizing pristine semiconducting single-walled carbon nanotubes in a variety of media. When compared to established techniques such as AFM, STM, and SEM, fluorescence microscopy offers the advantages of relative experimental simplicity, rapid image acquisition through parallel detection, and versatility of sample environments. Although the method is limited to ca. 1 \( \mu \text{m} \) in spatial resolution and is inapplicable to metallic, semi-metallic, or heavily derivatized SWNT, it can be combined with emission spectroscopy to provide \((n,m)\)-level identification of individual nanotubes. Alternatively, narrow-band optical filters can be added to generate \((n,m)\)-selected images. The spectral properties of different segments within longer nanotubes can be studied to reveal inhomogeneous interactions of the nanotube with its environment and to check for spatial consistency of \((n,m)\) structure. With time resolutions in the millisecond range, near-IR imaging will also permit kinetic studies of nanotube physical and chemical processes. Finally, SWNT fluorescence microscopy should find increasing use as a tool for noninvasively studying the interactions between nanotubes and biological systems.\(^{118}\).
CHAPTER V VISUALIZATION OF UNRESTRICTED TRANSLATIONAL AND ROTATIONAL MOTION OF INDIVIDUAL SINGLE-WALLED NANOTUBES WITH NEAR-INFRARED FLUORESCENCE MICROSCOPY.

A. Introduction

The ability to visualize SWNT motion opens new possibilities for their applications. SWNT, being highly photostable and optically anisotropic, may serve as a unique fluorescent markers which currently have no analogs. Fluorescent tags in the form of organic dye molecules or quantum dots (QD) are widely used today in many applications including bio-imaging and materials science. However, each has certain disadvantages and limitations. Individual fluorescent dyes that are commonly used for visualization and tracking have poor photostability and are photobleached within seconds. Recently developed QD are superior emitters. Although considered to be relatively photostable, they experience photobleaching as well. Furthermore, QD emission intermittency and weak optical anisotropy prevent them from being used as efficient fluorescent tags to probe orientation or visualize rotational motion. Nevertheless, recent developments of new QD materials suggest that this may eventually be possible.

A rotational motion analysis requires either observing object orientation or measuring its optically anisotropic signal. Numerous reports have demonstrated visualization of rotational motion using fluorescently labeled particles with spatially resolved dimensions. However, diffraction-limited optical resolution does not allow imaging the rotations of nano-scale objects. Individual fluorophore molecules usually are optically anisotropic but not photostable, so their rotational motion can be observed only
for a few seconds\textsuperscript{121,122,133-136}. Extending lifetime of a dye requires special conditions. Deschenes and Vanden Bout demonstrated continuous monitoring of rhodamine 6G rotational motions in degassed PMMA samples under a nitrogen atmosphere\textsuperscript{120}. Individual molecules are small. Observing the rotational dynamics of individual molecules requires restriction of their mobility by attachment to larger objects or placement in highly viscous media\textsuperscript{120,134}. Molecular fluorescence intermittency, absorption saturation due to finite excitation lifetime, and small absorption cross-section make these observations quite challenging.

Individual SWNTs represent a new class of fluorophores with unique optical properties. They also present their own specific requirements and experimental challenges. SWNT emissions are widely spread over the near-infrared spectral range between ca. 900 and 1600 nm, depending on SWNT (n,m)-type\textsuperscript{27}. Absorption and emission transitions of individual SWNT are quite narrow, that is a single SWNT efficiently absorbs and emits light at specific wavelengths, helping to distinguish its fluorescence signal from broad and structureless background emissions. SWNT photostability is remarkable and its limits have not been found yet, as SWNT fluorescence has been observed for several minutes without noticeable change of the emission signal\textsuperscript{33,137}. Fluorescence from an individual SWNT represents emissions from excitons that may be temporarily localized in its different sections. The short excited state lifetime of SWNT excitons (ca. 100 ps)\textsuperscript{32} provides for rapid relaxation to the ground state, thus setting a high absorption saturation limit\textsuperscript{137}. SWNT absorption and emission are highly anisotropic. Experimentally reported absorption and fluorescence anisotropies of individual SWNT reached 75-85\% \textsuperscript{33,34,138,139}. The low fluorescence efficiency
(estimated quantum yield $\sim 10^{-3}$)\textsuperscript{26,140} is compensated by a large absorption cross-section. As demonstrated in our previous report\textsuperscript{138}, SWNT can be easily observed with appropriate near-infrared multichannel detectors. In this chapter, visualization of unrestricted translational and rotational diffusion of individual nanotubes in aqueous SDBS suspensions will be described.

**B. Materials and Experimental Methods**

Near-infrared fluorescence microscopy measurements were performed using inverted Nikon TE-2000U microscope coupled via one of its output ports to a liquid nitrogen cooled InGaAs 2D-OMA V camera made by Roper Scientific. The combination of a dichroic beamsplitter to deflect excitation light and transmit near-infrared emission and a dielectric long-pass filter with a 946 nm cut wavelength was used to select emission in the desired near-infrared wavelength range. Images were obtained with either Nikon PlanApo 60x/ 1.4 NA oil-immersion or 60X/1.0 NA water-immersion objectives. Samples were excited with an externally mounted 785 nm diode laser (power at the target $\sim 50$ mW). An aspheric lens ($f = 18.4$ mm) mounted on an XYZ translation stage focused laser radiation to a spot diameter of ca. 30 μm. The excitation energy density at the sample was $\sim 7$ kW/cm$^2$. Laser polarization was controlled with a crystalline polarizer and $\lambda/4$ and $\lambda/2$ quartz retardation plates. Linear polarization purity was greater than 97%; circular polarization ellipticity was $\sim 10\%$. To reduce the camera readout time to 5 ms, only a small region of interest, 30x30 μm containing 3600 pixels, was used to record SWNT motion. SWNT trajectory measurements were performed using 50 ms signal acquisition times. At least 350 consecutive frames were acquired during each measurement.
Aqueous suspensions of SWNT in SDBS (sodium dodecyl benzyl sulfonate) were prepared in the same way as previously reported\textsuperscript{26} and were used in further sample preparations. 1.5 μL of dilute (1-10 nanograms/mL) SWNT suspension were spread between a quartz microscope slide and cover slip yielding aqueous films \( \sim 2 \mu m \) thick. Such a film thickness is approximately equal to the optical depth of field of the 60X/1.0 water-immersion objective. The sides of the sample plate were sealed to prevent evaporation of the liquid and convection flows.

C. Experimental results and discussion.

1. Translational diffusion of individual SWNT. Each aqueous SWNT suspension in SDBS is a heterogeneous sample that contains nanotubes ranging from below 100 nm to several micrometers in length. All SWNT micelle diameters are approximately the same, on the order of several nanometers. SWNT in micelles have large aspect ratios and can be considered as rigid cylinders, whose diffusion behavior is well-known. The relations describing diffusion coefficients of rigid cylinders are written as follows:

\[
D_{tr}^{\parallel} = \frac{k_B T}{2 \pi \eta_s} \frac{\ln (L/d) + \gamma_{\parallel}}{L}; \quad D_{tr}^{\perp} = \frac{k_B T}{4 \pi \eta_s} \frac{\ln (L/d) + \gamma_{\perp}}{L}
\]  

(5.1),

where \( D_{tr}^{\parallel} \) and \( D_{tr}^{\perp} \) are diffusion coefficients of cylinder motion parallel and perpendicular to its axis, \( k_B \) is the Boltzmann constant, solution temperature \( T = 296 \text{ K} \), water viscosity \( \eta_s = 0.89 \text{ mPa}\cdot\text{s} \), end correction coefficients \( \gamma_{\perp} = -0.0114 \) and \( \gamma_{\parallel} = 0.886^{131;141} \), effective rod diameter \( d = 5 \text{ nm} \), and \( L \) is the rod length.
By focusing inside the liquid layer we were able to observe Brownian motion of individual SWNTs. Because of sufficiently small film thickness, SWNTs stayed in focus for extended periods of time. We chose to monitor only the motions of the brightest nanotubes whose absorptions appeared to be nearly resonant with the excitation laser.\(^{27}\) Moreover, only SWNT with unresolved spatial dimensions were selected, thus ensuring that SWNT lengths were less than 1.5 \(\mu m\). Motions of approximately twenty SWNTs whose spatial dimensions were not resolved were recorded and then analyzed using custom Matlab programs. We have applied standard mean-squared displacement (MSD) analysis to measure the translational diffusion coefficient. The MSD\((n \cdot \delta t)\) for discrete intervals of time \(n \cdot \delta t\) is computed as follows:\(^{141}\):

\[
MSD(n \cdot \delta t) = \frac{1}{N - n} \sum_{i=n}^{N} \left[ x_i, y_i(i \cdot \delta t + n \cdot \delta t) - x_i, y_i(i \cdot \delta t) \right]^2
\] (5.2),

where \(x, y\) are the nanotube's position coordinates and \(N\) is the total number of observations. In a two dimensional case, its relation to the translational diffusion coefficient is defined as:

\[
MSD(n \cdot \delta t) = 4D_{tr}^{meas} \cdot n \cdot \delta t + \text{const}
\] (5.3)

Figures 5.1 and 5.2 show MSD graphs and their linear fits for different SWNT trajectories. Experimental data of the same color at Fig. 5.1 represent two successive measurements of the same nanotube using linearly and circularly polarized excitation. Good reproducibility of the MSD graphs for different trajectories of the same SWNT was observed. Different slopes in Fig. 5.1 demonstrate the variety of SWNT lengths in the sample. Linear MSD dependences were observed in approximately 50% of the cases. The rest of the nanotubes showed either super-linear or sub-linear MSD dependence(Fig. 5.2).
We have applied second order polynomial fits to those to extract the first order slope coefficients. Estimated diffusion coefficients according to (5.3) ranged from 1 to 6 $\mu$m$^2$/s.

![Graph of MSD vs. n \(\delta t\) (a)](image)

![Graph of MSD vs. n \(\delta t\) (b)](image)

**Figure 5.1.** (a) – Mean squared displacement graphs of individual SWNTs translational diffusion trajectories. Hollow and filled symbols of the same color correspond to two successive trajectory measurements of the same nanotube. Solid lines represent linear fits of these data-points. (b) – Linear, sub-linear and super-linear MSD graphs observed.
Since SWNT motions occurs in three dimensions while we resolve only two, the measured average translational diffusion coefficient can be written as follows\textsuperscript{131}:

$$D_{tr}^{meas} = \frac{k_B T}{6 \pi \eta_s} \cdot \frac{2 \ln(L/d) + \gamma_{||} + \gamma_{\perp}}{L}$$  (5.4)

The SWNT lengths computed by solving equation (5.4) for L vary between 300 and 3000 nm. These values are obviously overestimated since we can expect to resolve spatial dimensions of SWNT with lengths above 1500 nm. Possible errors arising from incorrect hydrodynamic cylinder radius d, viscosity $\eta_s$, and end-correction coefficients $\gamma_{||}$ and $\gamma_{\perp}$ are not significant enough to explain such a large discrepancy. Instead, the systematic deviation arises due to well known wall-drag effect\textsuperscript{131,142} that manifests itself in an increased viscous drag coefficient near the solid/liquid interface. Using the procedure described by Li and Tang\textsuperscript{131} to account for these effects, we have estimated corrected SWNT lengths between 200 and 1400 nm. These values appear reasonable as the nanotube lengths are expected to be near or below our optical resolution limit. These values, however, are approximate. Correct estimation of SWNT lengths will require more precise knowledge of hydrodynamic diameter d for SWNTs in micelles, careful evaluation of the length dependent near-wall apparent viscosity, accounting for electrostatic interactions\textsuperscript{142} and better control of the liquid film thickness.

2. Photostability of individual SWNT in aqueous suspension. SWNT have been dubbed as photostable fluorophores in the sense that they are not photobleached over long periods of time and in most cases do not exhibit fluorescence intermittency. Earlier reports\textsuperscript{33,137,143} investigated the stability of nanotube emission intensity in solid media, mostly dried SDS/SDBS. However, high experimental noise in those studies has
prevented rigorous measurements of stability of SWNT emission. In this project we have also investigated time-resolved nanotube fluorescence. In our liquid samples majority of individual SWNTs are mobile. However, we observed a small fraction of immobilized SWNTs that appeared to be stuck at a liquid/glass interface in a surfactant layer. Their identity as individual nanotubes was confirmed with polarization and spectroscopic measurements\textsuperscript{138}. These nanotubes represent excellent subjects to investigate the stability of their emission signals under similar experimental conditions. SWNT images and corresponding emission traces with different time resolutions are shown in Fig. 5.2. Remarkable is the fact that even at acquisition times of 50 ms or lower, SWNT emission intensities can be measured by our detector with high signal-to-noise ratios (~30) as for SWNT in Fig. 5.2a. The nanotube shown in Fig. 5.2b is $2.5 \pm 0.5$ \textmu m long. Its emission signal recorded with 10 ms integration time shows small fluctuations. We attribute those to bending motions of the SWNT that are visible in a measurement movie. Its average emission signal acquired during only 1 ms has $12 \cdot 10^3$ counts and a signal-to-noise ratio of 12. This sets a new record on the timescale of individual SWNT detection. The unsurpassed emission signal stability and optical anisotropy of SWNTs allows one to study rotational motion of individual nanotubes without having to resolve their spatial dimensions.
Figure 5.2. Near-IR fluorescence signal stability in time of individual SWNTs recorded with different time resolutions of 50, 10 and 1 ms. SWNTs are excited with linearly polarized light (excitation power \( \sim 7 \text{ kW/cm}^2 \)). Pixel size in the image is 0.5 \( \mu \text{m} \).
3. Rotational diffusion of individual SWNT. SWNT exhibit intense blinking as they diffuse in a thin liquid film. Considering the emission signal stability of immobilized nanotubes, this intermittency is entirely due to the SWNTs rotational diffusion. Moreover, the frequency of blinking correlates with the translational diffusion coefficient that, in turn, depends on SWNT length. Time-resolved emission traces of freely moving SWNTs were analyzed. SWNT emission intensities were calculated as a sum over the 7x7 pixel matrix centered on a pixel of maximal emission intensity. Background signals were obtained with a similar procedure except that the central pixel being was offset from a maximum by 12 pixels in either X or Y direction. Emission and background intensities and backgrounds were offset to give average background values of 0 and normalized by (I)/0.2715 (the meaning of the 0.2715 constant will be clarified later). Fig. 5.3 shows emission traces of different nanotubes recorded with linearly and circularly polarized excitation. The intensity fluctuations for the slowest SWNT are large as opposed to those for SWNTs moving at higher speeds. Indeed, recorded signals represent integrations over all SWNT orientations during the measurement interval, and faster rotation will result in a greater averaging. Excitation with circularly or linearly polarized light yields qualitatively different emission traces, these differences are apparent for slower moving nanotubes.

Due to the high optical anisotropy of SWNTs, they can be modeled as dipole absorbers and emitters. In the case of linearly polarized light, SWNT absorption and emission intensities can be written as:

\[ I_{abs} \sim \left( \overrightarrow{\mu_{abs}} \cdot \overrightarrow{E} \right)^2 \sim \sin^2 \theta \cdot \cos^2 \varphi \]

\[ I_{fluor} \sim I_{abs} \left( \overrightarrow{\mu_{fluor}} \cdot \cos \theta \right)^2 \sim \sin^4 \theta \cdot \cos^2 \varphi \] (5.5)
Figure 5.3. Fluctuating emission signals of SWNTs with different translational diffusion coefficients. Graphs on the left and the right represent two subsequent measurements with linear and circular excitation polarization respectively.

Acquisition time – 50 ms, images obtained with a 60X 1.0 NA water immersion objective.
where $\mu_{\text{abs}}$ and $\mu_{\text{flour}}$ are the nanotube's absorption and emission transition dipole moments that are directed along its axis, $E$ is the electric field vector of the excitation laser light, and $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$ are angular polar coordinates that define the SWNT orientation in space (see Fig. 5.4). An instantaneous emission signal is approximately proportional to $\sin^4 \theta$ for circularly polarized light. As the nanotube reorients, its emission signal will eventually reach a certain average value that can be calculated. It is easy to show that $\langle \sin^4 \theta \cos^2 \phi \rangle = 0.2667$, while $\langle \sin^4 \theta \rangle = 0.5333$. These numbers, in fact, represent the ratio of average signal of a freely rotating SWNT to the maximum theoretically possible signal of this nanotube acquired over same period of time $\langle I \rangle / I_{\text{max}}$. However, in case of high numerical aperture collection optics, these values are somewhat different. $\langle I \rangle / I_{\text{max}}$ equals 0.2715 and 0.3091 for light collection with 1.0 and
1.4 numerical apertures for linearly polarized excitation, and twice that for circularly polarized light. For a complete analysis refer to Appendix B.

Evidently, rotational motion of SWNT in aqueous SDBS suspensions is not completely resolved, as the emission traces shown at Fig. 5.3 never reach one or zero. We can approximately estimate the SWNT rotational diffusion constant $D_{\text{rot}}$ using the following equation:

\[
D_{\text{rot}} = \frac{3k_B T}{\pi \eta_s} \cdot \frac{\ln(L/d) + \gamma_r}{L^3}
\]

(5.6),

where $\gamma_r = -0.447$ is the rotational correction coefficient\textsuperscript{131,141}. $D_{\text{rot}}$ of a 1 μm nanotube in aqueous suspension then equals 25 rad\textsuperscript{2}/s. Rotational diffusion is similar to the previously described two-dimensional diffusion in a plane (equation 5.3). During a 50 ms measurement interval the nanotube will rotate on average by 130° (calculated as $\sqrt{4D_{\text{rot}} \delta t}$ ) and produce a random unresolved signal. Given the inverse proportionality of $D_{\text{rot}}$ to $L^3$, resolving rotational motion of submicrometer nanotubes does not seem feasible even at ms time resolution. The nanotube rotation speed can be decreased by increasing the viscosity of the medium. We increased the solution viscosity 10 times by adding 60% of glycerin by mass to SWNT suspensions\textsuperscript{144}. SWNT emission intensity strongly depends on environment and is reduced several times in a glycerin/water mixture. However, it is still possible to observe individual SWNT and record their motion. Nearly resolved SWNTs emission traces are shown in Fig.5.5 These emission traces apparently have asymmetric distributions of the signal around its average value. This is consistent with the predicted $\sin^4 \theta \cos^2 \varphi$ SWNT emission signal dependence.
**Figure 5.5.** Nearly resolved emission traces of SWNT in glycerin/water mixture ($\eta_s = 10^{-3}$ Pa·s). The traces have asymmetric intensity distributions around the average value as predicted by $I(\theta, \varphi)$ dependence. Acquisition time – 50 ms, images obtained with 60X 1.0 NA water immersion objective.
The difficulty of time-resolving nanotube rotational motion demands new experimental approaches.

Given the remarkable stability of SWNT emission signals we suggest using the standard deviation of $\langle I \rangle/I_{\text{max}}$ as a quantitative measure of SWNT rotation. Reference values are required for comparison with experimental data. To obtain those we performed "random walk on a unit sphere" numerical simulations to mimic rotational Brownian motion and find the corresponding emission signal for a given experimental geometry. Input rotational diffusion coefficients were computed using equation (5.6). 50000 sequential measurements, each consisting of 10000 steps, were used to generate time resolved emission traces of freely rotating nanotubes. These simulated traces are shown at Fig. 5.6. Excellent qualitative agreement is observed between these and our experimental data (see Fig. 5.4, 5.5, 5.6). To quantitatively compare those, standard deviations $\sigma_{\text{int}}$ of SWNT emissions were computed. Since SWNT emission intensity is measured against a noisy background, we corrected the standard deviations of experimental intensity signal as follows: $\sigma_{\text{corr}} = \sqrt{\sigma_{\text{int}}^2 - \sigma_{\text{backgr}}^2}$. We plot $\sigma_{\text{corr}}$ values against experimental translational diffusion coefficients. For the simulated traces, $\sigma_{\text{int}}$ are plotted against theoretically predicted translational diffusion coefficients.
Figure 5.6. Simulated emission traces of freely rotating SWNTs of various lengths. These traces were generated for specific experimental geometry: numerical aperture - 1.0, signal acquisition time - 50 ms, photodetector readout time - 5.6 ms.
Figure 5.7. Standard deviation of SWNT emission signal dependence on experimental translational diffusion coefficients. Solid lines represent theoretical calibration graphs. Their difference is explained in the text.

Figure 5.7 compares experimental and simulation data. Evident correlation is observed, as higher standard deviation values correspond to SWNTs moving at slower rates. Solid blue line in Fig. 5.7 represents calibration graph obtained from simulated emission traces. Corresponding standard deviation values are plotted against the theoretical translational diffusion constants calculated according to (5.4) for different nanotube lengths.
The greatest discrepancy arises from wall-drag effects that result in a reduction of experimental translational diffusion coefficient\textsuperscript{131,142}. Using the procedure described by Li and Tang\textsuperscript{131}, we calculated expected translational diffusion coefficients in a confined geometry using our experimental setup parameters. The corrected graph is shown at Fig. 5.7 as a solid black line. Better agreement with experimental data is apparent. Evidently, wall-drag effects influence rotational motion\textsuperscript{131} as well, and therefore the fluorescence signal of a rotating SWNT. These corrections have not yet been accounted for.

There are obvious systematic deviations from an ideal calibration graph that can be explained qualitatively. There are different sources of noise that are small and hard to account for, arising from many factors including instability of laser excitation, SWNT motion along the observation axis, possible inhomogeneity of the laser field due to interference with scattered/reflected light, statistical noise in the emission signal and inherent instability of the SWNT fluorescence. Therefore, we can expect experimental standard deviation values to be overestimated. Moreover, their relative contributions are larger for the shortest SWNTs moving at higher speeds, since their emission signals are generally lower.

Another systematic error possibly arises from either non-ideal optical anisotropy or bending of individual SWNT, or both. We have investigated bending effects by observing SWNT with spatially resolved dimensions. Long SWNT were obtained from HiPCO material using short ultrasonication times as described in the previous chapter\textsuperscript{138}, except that the resulting suspensions were not dried but imaged directly as fluids.
Fig. 5.7a,b shows two examples of such long nanotubes. Although these are not immobilized, their diffusional motion is sufficiently slow to allow measuring their spectra. This requires focusing laser radiation to increase excitation power up to 60 kW/cm² and positioning the nanotube onto a predetermined location in the camera's

![Graph and Images]

Figure 5.8. Bending of long individual nanotubes. (a), (b) – selected frames from a recorded motion of (8,7) and (11,3) nanotubes that display evident bending. Images of SWNT (8,7) in a) and (11,3) in b) were recorded with 30 ms and 1 ms signal integration respectively. SWNTs identities were determined from the emission spectra maxima shown in (c). Images were obtained with using circularly polarized light for excitation and a 60X 1.4 NA oil-immersion objective for light collection.
field. The spectrum is then acquired by switching from camera to the spectrograph output port. Although we cannot image the SWNT during measurement, its emission spectrum is detected while it stays in the designated area. Individual SWNT spectra can be acquired within a second. Recorded spectra, as shown at Fig. 5.8c, contain a single main peak that is characteristic for individual nanotubes of a particular (n,m)-species. We have identified these two nanotubes as (8,7) and (11,3) from their emission maxima at 1267 and 1197 nm\textsuperscript{27}. We note that 2\textsuperscript{nd} Van Hove absorptions of these nanotubes are in resonance or nearly in resonance with the excitation laser. Images in Figure 5.8 reveal noticeable bending of individual SWNT. Analyzing the SWNT shapes shows that the curvature radius can be as small as \textasciitilde 5-10 \(\mu\)m. Therefore, SWNT bending for nanotubes with lengths of \textasciitilde 1 \(\mu\)m and below is negligible. We note, however, that SWNT bending stiffness depends strongly on diameter, and further research is necessary to give a reliable assessment of these bending effects.

Optical anisotropy \(r\) is defined as

\[
    r = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}
\]

(5.7),

where \(I\) represents the intensity of absorbed or emitted light polarized parallel or perpendicular to the SWNT axis. In our numerical simulation 100\% optical anisotropy was assumed. However, experimentally reported absorption and emission anisotropies of individual SWNT have reached only 75-85\% \textsuperscript{33,34,138,139}. The cause of SWNT anisotropy was briefly discussed in Chapter I. Different selection rules for parallel and perpendicular polarization relative to the SWNT axis (\(\Delta \mu = 0\) for parallel, \(\Delta \mu = \pm 1\) for perpendicular, where \(\mu\) is the index of van Hove electronic sub-band) result in a different resonance
energies for these polarizations. Certainly, partial overlap between these two types of transitions is possible. Moreover, optical anisotropy values of SWNT may be wavelength dependent. Unfortunately, in the current experimental setup it is not possible to control either SWNT (n,m)-type or excitation wavelength to match E₂₂ resonance absorption. Further research is required to fully understand and characterize SWNTs anisotropic optical properties.

D. Conclusions.

Visualization of translational and rotational motion of individual semiconducting SWNTs using their intrinsic fluorescence has been demonstrated for the first time. Analysis showed various translational diffusion coefficients ranging between 1 and 6 μm²/s. These variations are expected since SWNTs of various lengths were present in the sample suspension. After introducing corrections for wall-drag effects, SWNT lengths between 300 and 1200 nm were deduced. These values are consistent with a priori known SWNT lengths near or below our optical resolution limit of ca. 1 μm. However, accurate determination of SWNT lengths based on translational diffusion data requires better control of experimental system parameters, such as the thickness and homogeneity of the liquid layer. Also, knowledge of the effective hydrodynamic diameter d (equation 5.4) and electrostatic screening effects (Debye length) is required.

SWNTs have unique optical properties, namely high optical anisotropy and fluorescence signal stability in time, which allows studying rotational motion of these individual fluorophores. We studied SWNT rotational diffusion using the anisotropic emission signal as a probe. Measurements were performed with 55 ms time resolution, which proved insufficient to resolve SWNT rotation. However, the rotation was nearly
resolved in solutions with 10 times higher viscosity. The observed emission signals were consistent with the expected functional dependence given in equation (5.5).

During our measurement interval, SWNT emission is averaged due to fast rotation. A clear correlation was established between SWNT translational diffusion coefficients and SWNT intensity fluctuations. Given the stability of SWNT fluorescence, we attempted to analyze these averaged signals to determine rotational diffusion constants. The analysis is based on the following ideas. Over a sufficient period of time the integrated emission signal of any nanotube will reach its average value. When normalized to the theoretical maximum fluorescence signal, this average value is constant for all nanotubes. Moreover, this value can be calculated for a given experimental geometry and SWNT optical anisotropy. These calculations are discussed in detail in Appendix B. Emission traces of different nanotubes normalized to their average signal can be quantitatively compared. We used standard deviation (SD) as a measure of the rotationally-induced fluctuations in SWNT fluorescence emissions. A monotonic dependence of measured SD values on the corresponding translational diffusion coefficients was observed.

To compare theory and experiment, we performed “random walk on a unit sphere” numerical simulations to mimic the fluorescence signal of a freely rotating nanotube. Computer-generated traces displayed similar patterns as the experimental fluorescence signals. Good qualitative agreement was observed, as demonstrated at Figure 5.7. However, excessive scatter in the experimental data suggests that further improvements are necessary. Alternatively, development of new optical techniques to analyze SWNT rotation would be valuable.
This research represents a first step towards utilization of SWNT optical properties for practical applications. As rigid rods of a well-defined shape, SWNTs may serve as individual rheological nanoprobe s to study liquid properties in small volumes. Various fluid phenomena including phase transitions, viscosity variations, and near-wall effects can be explored using rotational diffusion data. Simultaneous analysis of translational and rotational motion will provide valuable consistency checks. Earlier studies of molecular rotational motion represented either measurements in bulk or restricted rotations of individual molecules prone to blinking, absorption saturation and photobleaching. The high photostability, high saturation limit, and strongly anisotropic absorption and emission make individual nanotubes exceptional fluorescence tags that should find their application in many disciplines.
CHAPTER VI. SUMMARY AND FUTURE STUDIES

Optical studies of several carbon nanostructures have been performed. The diversity of structural forms that carbon may take is reflected in a variety of chemical and physical phenomena that have to be explored.

In Chapter II, we focused on the dimerization reaction of a recently discovered isomer of C\textsubscript{60} oxide, [5,6]-C\textsubscript{60}O. This C\textsubscript{60} oxide isomer has highly reactive sites, which are torsionally strained double bonds induced by insertion of the oxygen into the fullerene cage. A dimerization reaction occurs spontaneously under ambient conditions yielding a previously unknown isomer of C\textsubscript{120}O\textsubscript{2}. We found that the activation energy for this reaction equals 48 kJ/mol. The chemical structure of the new C\textsubscript{120}O\textsubscript{2} discovered isomer, as well as its photochemical and photophysical properties, were investigated. On the basis of its \textsuperscript{13}C NMR spectrum and \textit{ab initio} computations, the structure of C\textsubscript{120}O\textsubscript{2} product is deduced to have C\textsubscript{2} symmetry and a form similar to "dumb-bell shaped C\textsubscript{120}"\textsuperscript{40}. It has a four-member bridging ring with oxygen atoms directly connected to the bridging carbons. Its S\textsubscript{1}-S\textsubscript{0} electronic transition has an origin at 14100 cm\textsuperscript{-1}. When optically excited, this dimer undergoes intersystem crossing to populate its triplet state with near-unit efficiency. The C\textsubscript{120}O\textsubscript{2} triplet state lies 11,800 cm\textsuperscript{-1} above its ground state and shows an intrinsic lifetime of 34 \mu s (at 297 K), which is typical for C\textsubscript{60} derivatives. The triplet state also undergoes unusual thermally-activated dissociation to regenerate the [5,6]-C\textsubscript{60}O precursor with quantum yields that reach 43% at 70\textdegree C. Further developments may include exploitations of the [5,6]-C\textsubscript{60}O reactivity to create new classes of fullerene
conjugates with other molecular systems. The C_{120}O_{2} isomer may serve as a storage form of highly reactive [5,6]-C_{60}O.

Chapter III describes the discovery and characterization of an unusual and previously unknown intense near-infrared luminescence from degassed non-polar solutions of fullerenes and PdOEP. A thorough investigation was performed on C_{70}-PdOEP solutions, in which this effect was most pronounced. The new luminescence arises when C_{70} is optically excited in mixed solutions. Sensitivity to the presence of oxygen (a triplet state quencher), as well as high probability for formation of triplet state of C_{70} suggested the origin of the NIR emission to be 3C_{70}^\ast. When PdOEP and C_{70} molecules encounter each other, an emitting C_{70}-PdOEP complex may form. The dynamic nature of the complex formation in solution made its excited state lifetime measurements impossible. However, we found similar emission in polymeric films doped with C_{70} and PdOEP, where static emitting complexes may be formed. Time-resolved measurements estimated the complex excited state lifetime to be ca. 150 ns. We suggested the external heavy atom effect as a plausible mechanism to account for the appearance of the NIR emission. The emission photon energy is the same as the C_{70} T_{1}-S_{0} energy gap. Similar fullerene-porphyrin systems without a heavy atom in the porphyrin cage do not display such effect. The observed dependence of the photophysical behavior on solvent is also consistent with our model. C_{70} phosphorescence is only one of many, and by no means the major 3C_{70}^\ast deactivation pathway. Dominant mechanisms include radiationless decay and well-known charge-transfer quenching by porphyrins. CT depends strongly on the solvent. For instance, in polar solvents NIR emission cannot be detected because of strong CT quenching. Quenching rate constants were found to be
higher (see Table 3.1) in non-polar solvents with higher polarizability. Radiative and nonradiative decays dominate CT quenching in less polarizable media. This is evidenced by a dramatic increase of \( ^3C_{70}^* \) PdOEP-induced phosphorescence quantum yield in hexane as compared to toluene. It would be interesting to further explore this effect. Fundamental understanding of the effect may be obtained by examining interactions of \( C_{70} \) with different heavy atoms inside porphyrins to allow maximizing the phosphorescence quantum yield. Emission intensity can also be maximized by suppressing CT quenching. The least polarizable media fluorocarbon solvents could be used. Such studies may lead to development of a new class of near-infrared emitters.

Fluorescence spectroscopy of individual SWNT is a new and quickly developing research area. We have pioneered microscopic observation of isolated SWNTs using their intrinsic near-infrared fluorescence. Chapter IV describes experimental visualization techniques and spectroscopic studies of individual SWNTs. Fluorescence images of SWNT under the microscope can be acquired in less than 50 ms, thus permitting visualization of their motion and the targeting of selected nanotubes for spectroscopy. Due to diffraction-limited optical resolution of ca. 1 \( \mu m \), SWNT lengths below that limit cannot be resolved. However, we have developed a simple procedure to prepare several micron long SWNT and have demonstrated their microscopic observation. Visualization of SWNT diffusion with near-infrared fluorescence microscopy was also demonstrated. Studying SWNT diffusion is particularly interesting due to unique photostability and high optical anisotropy of single SWNTs. Therefore, individual SWNTs have the potential to be used as unique fluorescent markers whose translational and rotational behavior can be explored in detail. In Chapter V translational and rotational diffusion of individual
micelle-encapsulated nanotubes is presented. Analysis of the translational diffusion of individual SWNTs revealed a distribution of diffusion constants falling between 1 and 6 μm²/s. These variations were expected due to differences in SWNT lengths. We estimated approximate SWNT lengths ranging between 200 and 1400 nm, values consistent with our instrumental resolution limit of 1 μm. Precise SWNT length determination through diffusion measurement requires better control of experimental parameters, such as hydrodynamic rod diameter, thickness of the liquid layer, and better understanding of wall-drag effects and electrostatic interactions. We have attempted to analyze SWNT rotational motion as well using imaging measurements performed with 55 ms time resolution. We found that the SWNT emission signal fluctuates as the nanotube rotates while being excited with either linearly or circularly polarized radiation. The frequency and amplitude of these fluctuations correlate to the SWNT’s translational diffusion constant, and therefore, its length. SWNT rotation in water is fast and cannot be resolved with currently available instrumentation. Increasing solution viscosity 10-fold allows rotations of some SWNTs to be resolved. However, determination of their rotational diffusion constants is rather complicated and requires further research. The standard method to determine rotational constant of rigid rods is autocorrelation function analysis. However, autocorrelation function for our particular task is not known and must be evaluated. Given the stability of SWNT emission, we have developed a simple method to estimate nanotube rotational diffusion constants. The degree of spatial signal averaging during the frame interval may serve as a quantitative measure of SWNT average rotation rate. Numerical simulations were performed to provide reference values for comparison. Qualitative similarity of the experimental and theoretical results was demonstrated.
However, excessive scatter in the experimental data prevented a reliable determination of rotational diffusion constants. To eliminate this problem, better control of the experimental parameters, as well as thorough characterization of SWNTs optical anisotropic properties will be required. It would be particularly interesting to experimentally calibrate this approach by analyzing length-separated SWNT suspensions\textsuperscript{145}.

Near-infrared fluorescence microscopy as a method to visualize individual SWNT may have many fundamental and practical applications. For example, analysis of the bending motions of individual SWNTs with spatially resolved dimensions will allow estimation of their bending modulus. Moreover, this mechanical parameter can be found as a function of tube diameter by using emission spectra to identify (n,m) species. As nearly rigid rods of well-defined shape, SWNT may also serve as individual rheological nanoprobes to study liquid properties in small volumes. Various nano-scale liquid phase phenomena including phase transitions, viscosity variations and near-wall effects can be explored using SWNT rotational diffusion data.
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APPENDIX A

Table A1. $^{13}$C NMR shifts (in ppm) observed for C$_{120}$O$_2$ in o-dichlorobenzene-$d_4$

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APPENDIX B

The high optical anisotropy of SWNTs has been experimentally confirmed. Therefore, SWNTs can be represented as single emitting dipoles for simulation purposes. The angular dependence of a dipole emission profile is usually considered to be

![Diagram of 3D dipole emission profile and observation cone]

Figure B.1. Experimental setup: 3D dipole emission profile and observation cone.

proportional to \( \cos^2(\alpha) \), where \( \alpha \) is the angle between dipole’s axis and the direction of observation (equation 5.5). This approximation is valid only in the case of observation in small numerical apertures. In reality, the dipole emission profile is a 3D figure, as shown at Figure B.1, formed by rotation of \( \cos^2(\alpha) \) 2D profile around the dipole axis. Axis Z is the direction of observation. The emission is collected from a cone with known angular aperture A. Let vector \( \mathbf{R}(\theta, \phi) \) define this 3D dipole emission surface. In the general case, this vector is defined in spherical coordinates \((\theta, \phi)\) as follows:
\[ R(\theta, \varphi) = 1 - \left( -\sin(\alpha) \cdot \sin(\theta) \cdot \cos(\varphi) + \cos(\alpha) \cdot \cos(\theta) \right)^2 \]  

(B.1)

Recorded emission signal \( I(\alpha) \) is proportional to the volume overlap of the observation cone and the dipole emission torus. \( I(\alpha) \) can be calculated as follows (elementary volume of a square pyramid is \( 1/3 \cdot R(\theta, \varphi)^3 \sin \theta \, d\varphi \, d\theta \)):

\[ I(\alpha) = \frac{1}{3} \int_0^{2\pi} \int_0^\pi \left[ 1 - \left( -\sin(\alpha) \cdot \sin(\theta) \cdot \cos(\varphi) + \cos(\alpha) \cdot \cos(\theta) \right)^2 \right]^3 \sin(\theta) \, d\varphi \, d\theta, \]  

(B.2)

This function \( I(\alpha) \) can be analytically evaluated. It is also convenient to normalize it per maximum to allow for easy comparison with a still dipole. For the 60X 1.0 NA water immersion objective (\( A = 48.75^\circ \)) it equals:

\[ I_{\text{fluor}}^{\text{norm}}(\alpha) = 1 + 0.1860 \cdot \cos^6(\alpha) - 0.8694 \cdot \cos^4(\alpha) - 0.2395 \cdot \cos^2(\alpha), \]  

(B.3)

Now, we can evaluate the normalized average emission signal of a randomly rotating dipole that is excited with linearly polarized light. Let the excitation light be polarized along the X axis.

\[ \langle I_{\text{obs}}^{\text{NA}=1.0} \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi I_{\text{abs}}^{\text{norm}}(\theta, \varphi) \cdot I_{\text{fluor}}^{\text{norm}}(\theta) \cdot \sin(\theta) \, d\varphi \, d\theta = 0.2715 \]  

(B.4)

where \( I_{\text{abs}}^{\text{norm}}(\theta, \varphi) = \sin^2 \theta \cdot \cos^2 \varphi \) for small angular apertures. Note that we have changed angular definitions (\( \alpha = \theta \)) to preserve the standard representation of polar coordinate angles as in equation (5.5).

Similarly, one can evaluate the average signal for the case of oil immersion objectives with \( \text{NA} = 1.4 \) (\( A \approx 68^\circ \), \( \langle I_{\text{obs}}^{\text{NA}=1.4} \rangle = 0.3091 \)). However, care must be taken when using this value. Angular aperture is calculated as \( \arcsin(1.4/n) \), where \( n=1.5 \) is the refractive index of the media (oil). Refractive index of the sample (water, \( n=1.33 \)) is...
considerably smaller. This results in a different effective aperture that depends on the position of an emitting dipole along the observation axis, as well as Fresnel reflections at an interface.

In case of circularly polarized excitation light the expression for excitation will change to $I_{\text{abs}}^{\text{norm}}(\theta, \varphi) = \sin^2 \theta$. The resulting average emission signals equal 0.5430 for NA = 1.0 and 0.6182 for NA = 1.4, which are twice the signals calculated in case of linearly polarized excitation.