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Carbon Nanotubes

Noncovalent Binding of Carbon Nanotubes by Porphyrin Oligomers**

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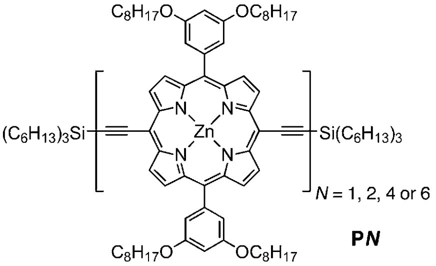
Carbon nanotubes (CNTs) have unique electronic[1,2] and mechanical[3] properties, leading to diverse potential applications.[4] However, their insolubility and tendency to form multistrand aggregates hamper device fabrication. Noncovalent complexation is a powerful strategy for improving the solubility of CNTs and for introducing functionality, while not damaging the electronic structure.[5] Composites based on this concept are being developed for sensors,[6] field-effect transistors,[7] and photovoltaic devices.[8] Porphyrin–CNT complexes are promising materials for photovoltaic application, due to their light-harvesting characteristics, long-lived charge-separated states,[9] and the charge-transport behavior of CNTs.[2] The molecular-scale engineering of these materials requires an understanding of their noncovalent chemistry. Here we analyze the binding of a series of porphyrin oligomers to single-walled CNTs. We show that UV/Vis and fluorescence titrations can be used to probe the thermodynamics, kinetics, and stoichiometry of these binding processes, and to monitor the debundling of multitube aggregates.

Porphyrin monomers and polymers have previously been shown to solubilize CNTs in organic solvents.[10] We chose to study the effect of oligomer length on the binding behavior using the series: monomer **P1** ($N=1$), dimer **P2** ($N=2$), tetramer **P4** ($N=4$), and hexamer **P6** ($N=6$). The optical absorption and fluorescence spectra of these oligomers are sensitive to the molecular geometry, because the π-conjugation is controlled by the torsion angle between neighboring porphyrin units.[11] Sonication of HiPCO[12] CNTs with excess porphyrin oligomers **P2**, **P4**, and **P6** in THF (ca. 0.1 mM porphyrin concentration) results in complete dissolution of the CNTs, whereas the monomer **P1** does not solubilize CNTs under these conditions. The CNT complexes of **P2**, **P4**, and **P6** were filtered off (200 nm, nylon membrane) and washed with THF to remove excess unbound porphyrin. Isolated CNT complexes of **P4** and **P6** prepared in this way can be redissolved in THF and display good stability, whereas the complex of **P2** is unstable; in the absence of excess porphyrin dimer the CNT precipitates.



P*N*

When **P4** and **P6** bind to CNTs, their long-wavelength (Q) absorption bands become sharper and are red-shifted by about 120 nm (220 meV, Figure 1 a), while their Soret bands become broader. These spectral changes (which have also been reported in porphyrin polymer–CNT complexes)[10b] are clear evidence for planarization of the porphyrin oligomer π-system.[11,13,14] The many absorption peaks in the region of the first E_{11} transitions of the CNTs ($\lambda > 1000$ nm) show that numerous nanotube species are present, each defined by different chiral indices (n,m).[1] Photoluminescence excitation (PLE) maps show distinct cross-peaks for each type of semiconducting nanotube, thereby allowing the selectivity in CNT binding to be assessed by comparison with non-selective surfactants.[15] PLE maps of HiPCO CNTs bound to **P4** and **P6** in THF (Figure 1 b and c, respectively) show significantly fewer emitting species than the PLE map of the same CNTs dispersed in D_2O[16] using the surfactant sodium dodecylbenzene sulfonate (SDBS, Figure 1 d). The E_{11} emission wavelengths of CNTs complexed with **P4** and **P6** are shifted to longer wavelengths by about 50 nm compared to those of the SDBS complex, due to the different electronic environment.[15] Comparison of the absorption (Figure 1 a) and emission spectra indicates that (8,6) and (7,5) tubes emit more efficiently than the other CNTs in the presence of **P4** and **P6**. Fluorescence is quenched in CNT bundles due to the presence of metallic tubes,[17] thus the brighter fluorescence from (8,6) and (7,5) tubes indicates stronger binding, and more efficient debundling, by **P4** and **P6**.

The PLE maps also reveal energy transfer from the porphyrin oligomers to the nanotubes. Excitation of the porphyrin Q band (850–900 nm) results in nanotube emission in a region of the PLE map where emission is not observed in the absence of porphyrin (horizontal dashed lines in Figure 1 c,d). The efficiency of energy transfer to (8,6) CNTs is approximately 10–20 % (see the Supporting Information).

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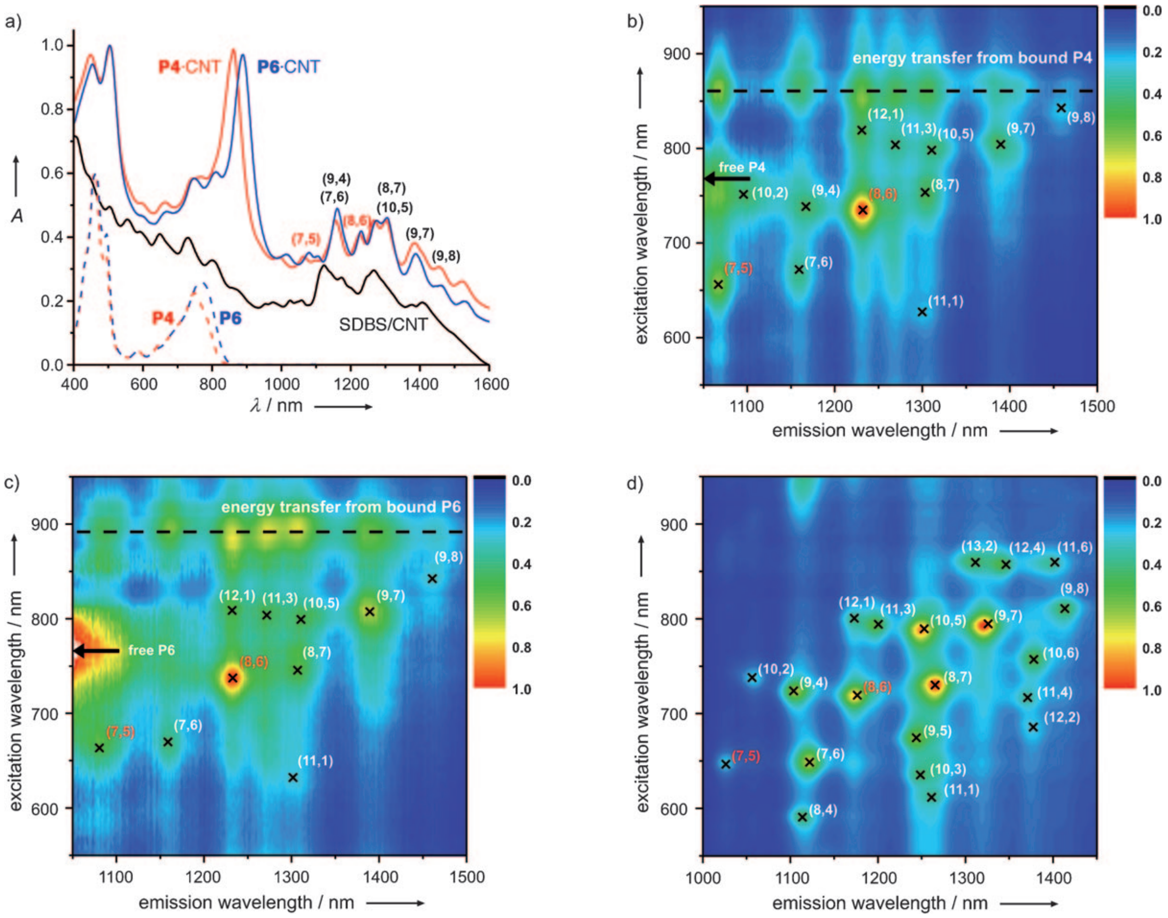

Figure 1. a) Vis/NIR absorption spectra of **P4** (dashed red line), **P6** (dashed blue line), **P4**·CNT (red line), **P6**·CNT (blue line) all in THF and SDBS-solubilized CNT (black line) in D_2O; b) PLE map of **P4**·CNT in THF; c) PLE map of **P6**·CNT in THF; d) PLE map of SDBS/CNT in D_2O. (Emission intensity in all maps is normalized and tube species are labeled with their (*n*,*m*) indices according to Weisman et al.[1,18] Horizontal dashed lines in (b) and (c) indicate energy transfer from porphyrin oligomers.)

Binding to CNTs completely quenches emission from the porphyrin oligomers. The only emission from **P6**·CNT that does not originate from the CNT results from traces of unbound **P6**, as demonstrated by the perfect match of the excitation spectrum of **P6**·CNT, detected at 1020 nm, with the absorption spectrum of free **P6** (Figure 2a). The efficient quenching of porphyrin fluorescence in **P4**·CNT and **P6**·CNT, together with the modest efficiency of energy transfer, implies that excited-state deactivation is dominated by another channel, such as electron transfer.[9] The quenching effect can be exploited to determine the stoichiometry of the CNT complexes. When CNT is added to a solution of **P6** ([**P6**] = 0.3 μM = 2.1 mg L^{-1} in THF), the porphyrin fluorescence intensity decreases linearly with increasing CNT concentration (Figure 2b). When all the **P6** is bound, its fluorescence is totally quenched; the **P6**/CNT mass ratio at this end point is 1.35, corresponding to a number of CNT carbon atoms per porphyrin subunit of $n_{C/P} = 132$. The UV/Vis absorption spectrum of the **P6**·CNT complex isolated on a preparative scale (using [**P6**] = 70 μM = 500 mg L^{-1}) shows a 40% higher porphyrin/CNT ratio than the absorption spectrum at the end point of this fluorescence titration (see Supporting Information, Figure S6), due to the greater debundling at high **P6** concentration. The isolated **P6**·CNT complex has $n_{C/P} = 94$, which means that each **P6** molecule saturates a segment of (8,6) CNT of length 4.9 nm. Molecular mechanics calculations[19] show that three molecules of **P6** can form a tight layer around an (8,6) tube. Based on this result, the measured stoichiometry is visualized in Figure 2c: Three **P6** molecules wrap around 14.7 nm (3 × 4.9 nm) of (8,6) nanotube to give almost monolayer coverage.[20] Incomplete monolayer formation may be due to partial CNT bundling, which reduces the available surface area. High-resolution TEM provides direct evidence for the binding of **P6** to the nanotube surface (Figure 2d); the **P6** coating on the walls of the nanotube can be clearly identified (Figures S14 and S15).

UV/Vis and fluorescence titrations are often used to quantify supramolecular interactions. To the best of our knowledge, these techniques have not previously been applied to measure the stability of CNT complexes, perhaps because pristine CNTs are insoluble in most solvents.[21] 1,2-Dichlorobenzene (DCB) is one of the few solvents that gives stable CNT dispersions.[22] We titrated CNTs with all the porphyrin oligomers in DCB, using both absorption and fluorescence spectroscopy, as exemplified for **P6** in Figure 3a,b.[23] In each case, the binding curves were fitted to a 1:1 binding isotherm, assuming that one porphyrin oligomer binds to one CNT binding site and that these binding sites act

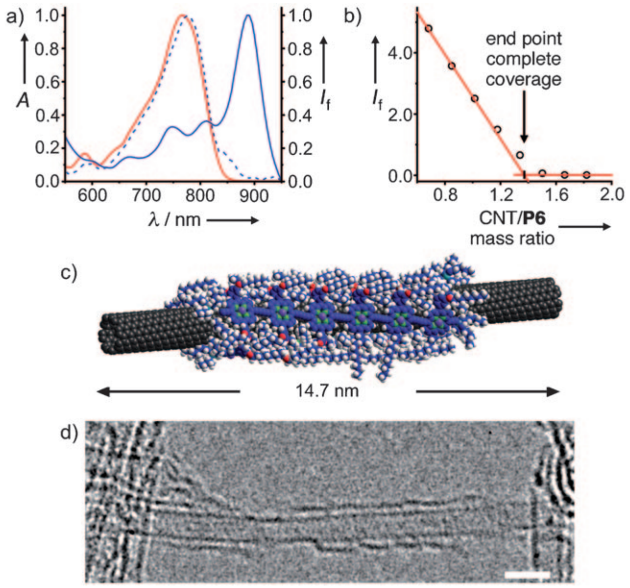

Figure 2. a) Vis/NIR absorption spectra of **P6** (red line), **P6**·CNT (blue line), and excitation spectrum of **P6**·CNT at 1020 nm (blue dashed line) all in THF; b) **P6** emission at 930 nm with increasing concentration of CNT. The arrow marks the point where all porphyrin is bound to CNT. [**P6**] = 2.1 mg L^{-1}; c) molecular mechanics[19] optimized structure of 3 × **P6**·(8,6) CNT based on the calculated mass ratio; d) HRTEM image of **P6**·CNT (scale bar 2 nm).

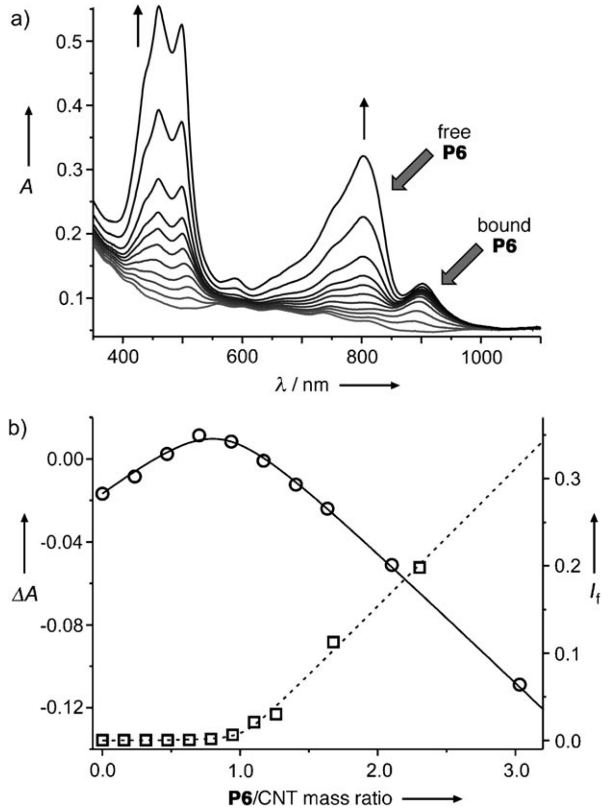

Figure 3. Titration of CNT with **P6** in DCB at 298 K: a) Vis/NIR absorption spectra; b) curves from Vis/NIR absorption (circles, $\Delta A = A_{900\,nm} - A_{800\,nm}$) and fluorescence titrations (squares, emission at 825 nm; excitation at 460 nm), fitted to a 1:1 binding isotherm.

independently. The two parameters obtained from each titration are the binding constant K_{PN} (averaged over all CNT species) and the number of carbon atoms corresponding to a CNT binding site ($Nn_{C/P}$). The affinities of **P4** and **P6** for CNTs are too strong to measure by UV/Vis or fluorescence titrations ($K > 10^9\,\text{M}^{-1}$), as illustrated by the sharp end points for titration with **P6** in Figure 3b. The binding constant of **P2** is $K_{P2} = (4.7 \pm 0.6) \times 10^7\,\text{M}^{-1}$ from absorption titrations; fluorescence titrations gave a similar value (Figure S10). In contrast, titrations of CNTs with monomer **P1** in DCB gave no change in absorption or fluorescence, and no indication of complex formation.

The relative affinities of **P2**–**P6** for CNTs were also investigated by UV/Vis/NIR competition experiments. The Q bands of the porphyrin oligomers occur at progressively longer wavelengths, so that, for example, it is possible to observe the Q band of bound **P6** in the presence of a high concentration of free **P2**. We found that an 800-fold excess of **P2** does not displace CNT-bound **P4**, and even a 2500-fold excess of **P2** does not displace CNT-bound **P6** (Figure S12). If **P4** or **P6** is added to the CNT after binding of **P2**, then the longer oligomer still binds, although this displacement process is slow, taking about 24 h to reach equilibrium. These competition experiments demonstrate that both **P4** and **P6** bind to CNTs extremely strongly ($K > 10^{11}\,\text{M}^{-1}$, see the Supporting Information). Attempted competition experiments between **P4** and **P6** did not reach equilibrium after 24 h; whichever oligomer was added first remained bound to the CNT, even in the presence of an excess of the other oligomer.

The number of CNT carbon atoms per porphyrin in the **P6**·CNT complex formed in DCB ($n_{C/P} = 115$) is intermediate between the value from fluorescence titrations in THF ($n_{C/P} = 132$) and the value for the isolated complex ($n_{C/P} = 94$), indicating an intermediate level of debundling in DCB. When comparing oligomers **P2**–**P6** in DCB, we observe a slight increase in $n_{C/P}$ from 115 for **P6** to 150 for **P4** and a substantial increase for **P2** (420). The weaker porphyrin–nanotube interaction in **P2**·CNT evidently results in a much lower degree of debundling. Kinetic observations support this conclusion: When **P6** or **P4** is added to CNTs in DCB, complexation is biphasic. Rapid initial binding is followed by a slower process (debundling) with a half-life of 6 ± 1 min, for both **P4** and **P6**. In the case of **P2**, only the fast initial process is observed (see the Supporting Information). These results correlate perfectly with the ability of the oligomers to solubilize CNTs in THF.

In conclusion, we have shown that UV/Vis and fluorescence titrations can be used to probe the kinetics and thermodynamics of noncovalent CNT-binding processes, and to monitor nanotube debundling. The affinity for CNTs increases sharply with the length of the porphyrin oligomer, and the binding is strongest with chiral (7,5) and (8,6) tubes. The photophysical properties of these complexes are currently being investigated to explore their scope for photovoltaic applications.

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