Fullerenes

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Filling Helical Nanotubes with C_{60}**

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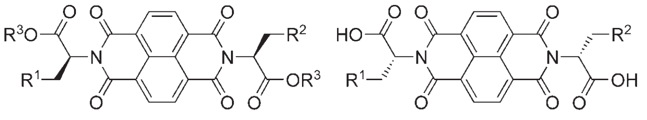
We report herein the complexation of a string of buckminsterfullerenes in chloroform by our recently discovered self-assembled, helical nanotubes.[1] The poorly soluble C_{60} molecules are solubilized by the nanotubes and they also experience the helicity of the environment, as demonstrated by induced circular dichroism (ICD). Previously reported C_{60} receptors—mostly aza-crown ethers, calixarenes, and porphyrins[2]—require lengthy syntheses and only bind isolated fullerenes. Our polymeric, dynamic receptor is prepared in one step and represents an entirely new class of C_{60}-complexing structures; it also allows the hitherto unknown formation of a one-dimensional C_{60} array.

We recently reported the synthesis[3] of α-amino acid functionalized naphthalenediimides (Scheme 1) and their self-assembly into hydrogen-bonded nanotubes.[1] The crystal structure of these helical superstructures shows the presence of tubular cavities with a mean diameter of 12.4 Å, which is well-suited to accommodate C_{60} molecules with a van der Waals (vdW) radius of about 10.3 Å.[4]



L-**1**: $R^1 = R^2 =$ STrt, $R^3 =$ H
L-**2**: $R^1 = R^2 =$ OBzl, $R^3 =$ H
L-**3**: $R^1 = R^2 = (CH_2)_3NHBoc$, $R^3 =$ H
4: $R^1 = R^2 =$ STrt, $R^3 =$ Me
5: $R^1 =$ S*t*Bu, $R^2 =$ OBzl, $R^3 =$ H

D-**1**: $R^1 = R^2 =$ STrt
D-**2**: $R^1 = R^2 =$ OBzl
D-**3**: $R^1 = R^2 = (CH_2)_3NHBoc$

Scheme 1. Amino acid derivatives of NDI.[5] Boc = *tert*-butyloxycarbonyl, Bzl = benzyl, Trt = trityl.

Colorimetric studies were carried out to test the C_{60} complexation ability of the helical nanotubes. Solutions of L- and D-**1**–**3** as well as **5** in chloroform were left to stand over solid C_{60}. A drastic color change from pale yellow to dark orange or brown was seen within a few minutes. This color change is quite different from that observed upon mere addition of a saturated solution of C_{60} in chloroform (pale purple) to the initial solution (Figure 1, inset). The visible region of the absorption spectrum (Figure 1, inset) is marked by the appearance of the absorbance bands characteristic of C_{60}, as well as an additional, broad band centered around 452 nm (identified with *). This band, best visualized by subtracting the naphthalenediimide (NDI) spectrum from the spectrum of the complex (Figure 1, blue trace), is very similar to an absorbance normally only seen in C_{60} films[6] and aggregates;[7] it has been attributed to interactions between fullerenes.[8] This proximity effect, which has not previously been reported[4] for C_{60} constrained within channels, indicates that the fullerenes are tightly packed within our system, although we cannot rule out a contribution from NDI–C_{60} interactions.

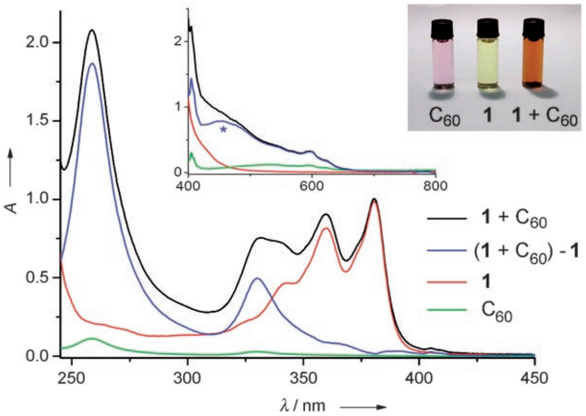


Figure 1. UV/Vis spectra of **1**, C_{60}, **1** + C_{60}, and the C_{60} contribution to the **1** + C_{60} solution (blue trace) in $CHCl_3$. The inset contains the visible region of the spectrum and a photographic comparison of the solutions. The concentration of **1** for the measurement of the visible spectrum was 40× higher than for the UV region.

The uptake of C_{60} corresponds to the appearance of the bands at 258 and 328 nm in the UV region of the absorption spectrum of **1** + C_{60}. Comparison of a solution of **1** + C_{60} in chloroform with known NDI concentration and a saturated solution of C_{60} in chloroform allows calculation of the C_{60} uptake. We found that depending on NDI concentration, and, to a lesser degree, on the amino acid side chain, the C_{60} concentration increased up to 16-fold in the presence of NDI nanotubes relative to the solubility of C_{60} in chloroform.

The amount of C_{60} taken up into the nanotubes is in good agreement with C_{60} being contained inside the nanotubular core rather than interacting with the outside of the tubes. To quantify the ratio of NDI to C_{60} molecules, we recorded the absorbance of a C_{60} solution of known concentration and found the extinction coefficient of C_{60} at 258 nm to be

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approximately 198 000 L mol^{-1} cm^{-1}. The ratios [NDI]/[C_{60}] calculated from the increase in the band at 258 nm, and the concentrations used for this measurement are summarized in Table 1. The crystal structure of the nanotube[1] reveals a helix pitch of 9 Å and three NDI units per turn. The vdW radius of 10.3 Å for C_{60} suggests that more than three units of NDI are necessary to take up one C_{60} molecule. With **1** and **2**, this is in good agreement with almost complete filling of the nanotubes with guest molecules, which in turn confirms the proximity of C_{60} molecules that the visible absorption spectrum suggests. In the case of **3** and the asymmetrical derivative **5**, somewhat lower filling ratios were observed. However, the visible part of the spectra retained the absorption band at 452 nm, assigned to C_{60}–C_{60} interactions.

Table 1: Quantitative C_{60} uptake data.[a]

NDI derivative	[NDI][b] [M]	C_{60} solubility enhancement[c]	[NDI]/[C_{60}][d]
1	1.32×10^{-2}	16.0	3.7
2	1.16×10^{-2}	12.1	4.1
5	1.59×10^{-2}	13.8	5.4

[a] For derivative **3**, the C_{60} uptake data were dependent on concentration (see the Supporting Information). [b] At lower NDI concentrations (10^{-3} M) the [NDI]/[C_{60}] ratio remained constant. [c] Reported as multiples of C_{60} solubility in absence of nanotube. [d] Calculated from the extinction coefficient of C_{60}.

In contrast with these results, the methyl ester **4**, which is unable to form supramolecular nanotubes, did not enhance the solubility of C_{60} in chloroform, which supports the thesis that the C_{60} molecule is complexed in the inner nanotubular cavity (see the Supporting Information).

Chiroptical studies of solutions of L- and D-**1**–**3** as well as **5** revealed that the nanotubes remain intact upon uptake of C_{60}, as the characteristic features of their circular dichroism (CD) spectra in the UV range remain essentially unchanged.[9] However, there is a small, but significant, decrease in the intensity of most CD bands, which we attribute to subtle changes in geometry[10] and/or electronic properties.

The visible region of the CD spectra indicates that the chirality of the nanotubes is sensed by the fullerenes. A weak but significant Cotton effect at 595 and 663 nm (Figure 2) is observed in the CD spectrum of L-**1** + C_{60},[11] with molar ellipticities of −13 and −26 deg cm^2 mol^{-1}, respectively. As these effects are observed in a region in which NDI absorbance is negligible, they can be attributed to electronic transitions of C_{60}. In addition, chiral exciton coupling can be seen on the broad C_{60}–C_{60} interaction band at 452 nm, an effect similar to that observed by Diederich and co-workers for a chiral covalent fullerene dimer.[12] Similar results were obtained for all the derivatives studied with the exception of the control compound **4** (see the Supporting Information).

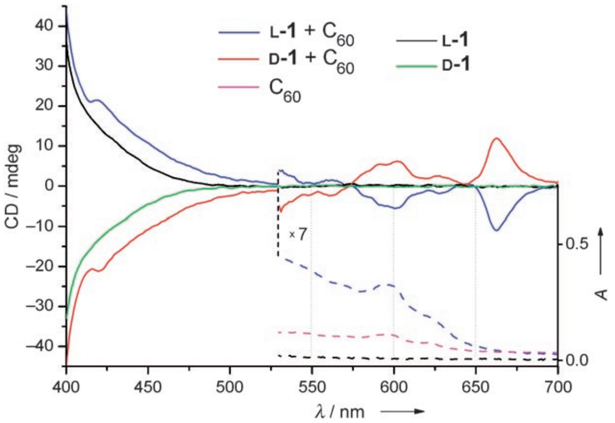

Figure 2. CD spectra (full traces) of $CHCl_3$ solutions of L-**1** and D-**1** in the presence (blue and red) and in the absence (black and green) of C_{60}. The corresponding visible spectra are shown with dashed lines.

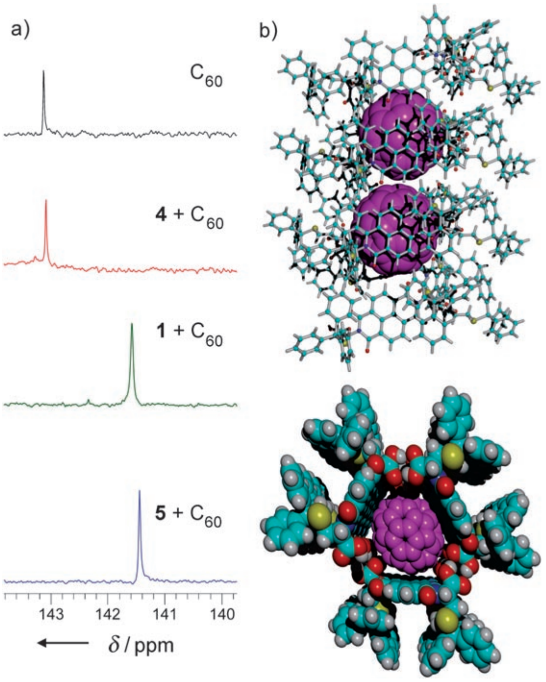

Figure 3. a) The ^{13}C NMR spectrum in $CDCl_3$ of C_{60} with and without NDI derivatives. b) Side and top views of the inclusion complex as found in molecular modeling studies.[9]

^{13}C NMR studies indicate that C_{60} experiences a different environment in presence of NDI nanotubes than in a saturated solution in chloroform. An upfield shift of more than 1.4 ppm was observed in the ^{13}C NMR signal of C_{60} upon complexation by NDI nanotubes (Figure 3), indicative of a shielding effect due to the proximity of the naphthyl units. Retention of the high symmetry of the fullerene upon binding within the nanotube indicates fast spinning of the fullerenes on the ^{13}C NMR timescale.

Complexation of C_{60} also strikingly demonstrated the self-sorting of nanotubes of opposite helicity. When L-**1** and D-**1** were mixed, the CD signal characteristic of the nanotubes disappeared as expected. However, the racemic mixture was still capable of taking up C_{60} as observed by UV/Vis spectroscopy: the [NDI]/[C_{60}] ratio of 3.9 matches (within experimental error) the one obtained for optically pure samples of either L-**1** or D-**1**. This result indicates that there is essentially quantitative self-sorting of the two helical nanotube enantiomers formed by the supramolecular assembly of

L-**1** and D-**1**. This self-sorting in turn is indicative of the strong cooperativity in the self-assembly of NDIs into helices, a process that is not merely the result of carboxylic acid dimerization.

We have discovered a new class of receptors for C_{60} which has several advantages over most previously published systems. The synthesis of our NDI derivatives is straightforward and allows room for variations, given the wide range of available and easily accessible amino acid derivatives. By varying the side chain of the amino acid used, solubility and optoelectronic properties can be tuned and additional recognition units or reactive centers can be appended to our helical nanotubes. Studies on the solid-state properties of the NDI nanotubes and the response to other fullerenes are currently underway, as well as work towards derivatization of the amino acid side chain.

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[9] Given that upon addition of C_{60} the changes in the UV and CD spectra of an NDI solution are irregular (unlike in a dilution experiment in which we observe changes in the mean length of the nanotubes), we assume that the length of the helices is unaffected by the uptake of C_{60}. We are currently investigating the length of the nanotubes in solution and the solid state. These results will be published elsewhere.

[10] Molecular modeling studies (Hessian matrix and geometry optimization) were performed at AM1 semiempirical level by using the GAMESS package. The starting geometries for the 8-mer nanotube and two fullerene molecules were obtained from X-ray data for the free nanotube and the free fullerene. The convergence criterion was $0.01\ \text{kcal}\,\text{Å}^{-1}\,\text{mol}^{-1}$. During the calculations a slight increase in the nanotubular diameter was observed upon C_{60} complexation. This may explain the slight decrease in the ICD intensity in the UV region upon C_{60} complexation (see the Supporting Information).

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