

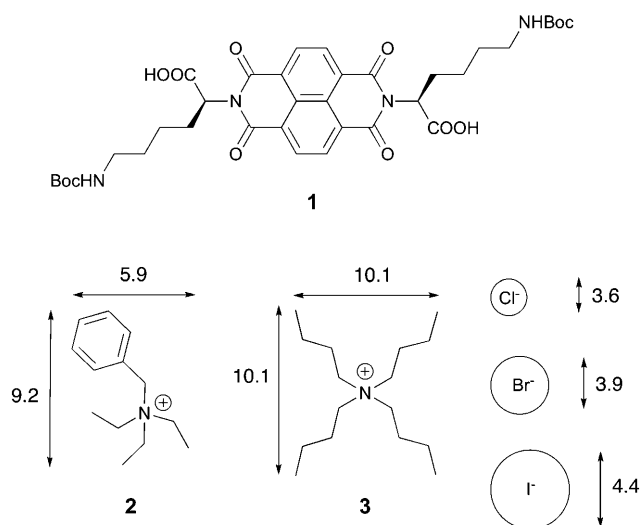
Ion Pairs and C₆₀: Simultaneous Guests in Supramolecular Nanotubes

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We have recently reported that supramolecular nanotubes constituted of amino acid-functionalised naphthalenediimides (NDIs)^[1] act as receptors for fullerenes,^[2] condensed aromatic systems and quaternary ammonium ions.^[3] We showed that C₆₀ forms a closed-packed one-dimensional array inside the nanotube and that the ion pair complexation ability of the nanotubes is size selective. We now report the remarkable ability of the supramolecular nanotubes to form mixed fullerene-ion pair inclusion complexes. The formation of the mixed complexes is directly dependent on the size of the ion pair component. These unusual results highlight the versatile nature of NDI nanotubes as selective receptors in apolar solvents.

We have previously shown that NDI nanotubes can readily take up C₆₀ in chloroform, increasing its solubility up to 16 times.^[2] A sharp colour change from pale yellow to brown is observed upon complexation of C₆₀, as well as an upfield shift of the fullerene ¹³C NMR signal. The chirality of the nanotube is sensed by the guest as shown by a weak but significant Cotton effect at 593 and 660 nm (C₆₀ absorbance). We envisaged that, through these spectroscopic responses, this system could be used as a platform for studying the relative binding affinities of fullerenes and ion pairs for the NDI nanotube. Measurement of conventional binding constants is not practical due to the unknown and probably undefined stoichiometry of the interaction and, in the case of C₆₀, complications arising from low solubility (see the Supporting Information).

Colorimetric studies were carried out to test the ability of different ion pairs to displace C₆₀ from a fullerene-saturated solution of **1** (Scheme 1) in chloroform.^[5] The addition of one equivalent of **2·Cl** to a 10 mM solution of C₆₀·**1** results in a cloudy suspension due to the precipitation of solid C₆₀.



Scheme 1. Lysine-functionalised NDI (**1**) and dimensions of the ammonium ions (**2** and **3**) and anions (in Å).^[4]

Once the solid has settled, a clear colour change from brown to light orange can be observed in the supernatant. Addition of bromide and iodide salts of the same ammonium ion (**2·Br** and **2·I** respectively) did not produce the same colour change and no precipitation of C₆₀ was observed (Figure 1). UV/Vis spectroscopy confirms that the intensity of the bands at 593 and 660 nm decreases dramatically upon addition of one equivalent of **2·Cl** to a solution of C₆₀·**1** in chloroform (see the Supporting Information). On the other hand, the UV/Vis spectrum of the C₆₀·**1** solution remains unchanged upon addition of **2·Br** or **2·I**. The induced CD signals (ICD) observed on the C₆₀ absorbance bands (at 593 and 660 nm) are also affected by the presence of the ion pairs in solution (Figure 2). The intensity of the negative ICD bands is dramatically decreased upon addition of **2·Cl** to a C₆₀·**1** solution, while it remains essentially unchanged in the presence of the larger ion pairs, **2·Br** or **2·I**. These observations, together with the significant precipitation of a black solid observed only when **2·Cl** is added to C₆₀·**1**, are

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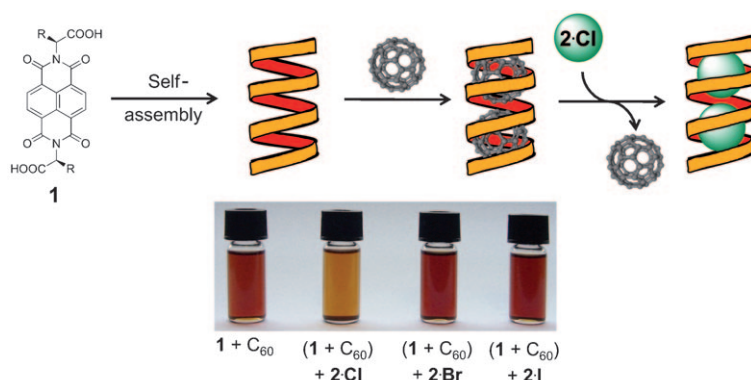


Figure 1. Schematic representation of the self-assembled nanotube and the competition experiment with C_{60} and ion pairs. Picture: photographical comparison of a solution of **1** + C_{60} in the presence of different ion pairs.

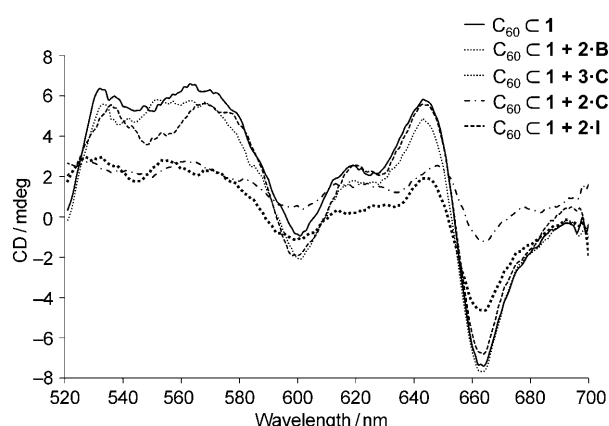


Figure 2. CD spectra of a 10 mM solution of **1** + C_{60} in $CHCl_3$ in the presence of one equivalent of different ion pairs. Spectra recorded at 21 °C.

clear indications that C_{60} is readily displaced from the cavity of the nanotube in the presence of an appropriate competing guest. Consequently this suggests that **2-Br** or **2-I** interact less strongly with the NDI nanotube than **2-Cl** and C_{60} itself, as they are not capable of displacing C_{60} from the cavity of the host.

The size of the cation also affects the binding affinity of the ion pair: a control experiment with tetrabutylammonium chloride (**3-Cl**) shows that in the presence of a bigger cation (Scheme 1) the decrease in intensity of the bands at 593 and 660 nm is smaller than that observed for **2-Cl**. These observations were mirrored in the CD spectra, where the ICD observed on the C_{60} absorbances is reduced in the presence of **3-Cl** to a lower extent than in the presence of **2-Cl** (Figure 2). From this observation it is possible to propose a scale of decreasing binding affinity between the NDI nanotubes and the ion pairs tested: **2-Cl** > **3-Cl** > **2-Br** ≈ **2-I**.

The closed-packed one-dimensional array of C_{60} inside the cavity of the nanotube also generates an intense absorption band at 452 nm. This band has previously been attributed to fullerene-fullerene interactions;^[6] it is therefore a characteristic spectroscopic signature for fullerenes that are in

close contact (Figure 3).^[2] The same band would not be observed in the case of isolated C_{60} molecules complexed by smaller NDI oligomers. As shown in Figure 3 the addition of increasing amounts of **2-Cl** to a C_{60} ⊂**1** solution results in a rapid decrease of the intensity of the band at 452 nm. This indicates that the closed-packed C_{60} array is partially disrupted in the presence of the appropriate competing guest. This observation suggests the forma-

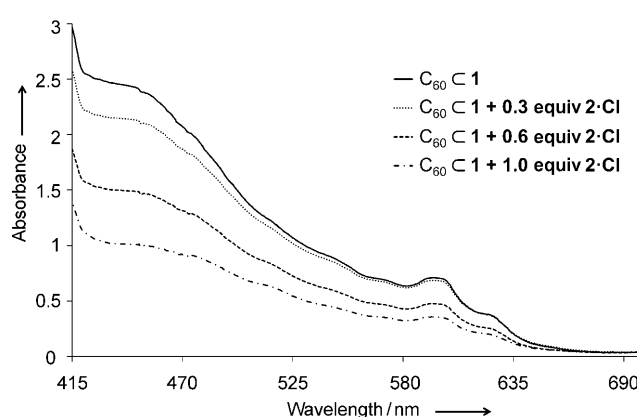


Figure 3. UV/Vis spectra of a 10 mM solution of **1** + C_{60} in $CHCl_3$ in the presence of increasing amounts of **2-Cl**. Spectra recorded at 21 °C.

tion of a mixed complex ion-pair/ C_{60} ⊂**1**, where the ion pair is intercalating between the fullerenes.

Chiroptical studies in the UV region of the spectrum (from 280 to 400 nm) show that the nanotubes remain intact in the presence of one equivalent of the ion pairs tested. The persistence of the nanotube in solution is monitored by the presence of a strong induced Cotton effect band at 383 nm (and other minor bands between 300 and 378 nm),^[1] which are the result of the fixed geometrical relationship between successive NDI units in the helical nanotube.^[7] Computational studies on a model system based on the solid-state structure of the NDI nanotubes showed that the shape of the CD spectrum observed in solution is strictly dependent on the orientation of the NDI units with respect to each other. Small changes of the angle between consecutive NDI units in the nanotubular structure result in significant changes of the predicted CD spectrum.^[7] The addition of ammonium ions to a 0.7 mM solution of **1** in chloroform results in negligible changes on the intensity of the ICD band at 383 nm and it does not alter the overall appearance of the spectrum (see the Supporting Information). This indicates that the overall structure of the nanotubes is un-

changed upon complexation of the ion pairs. This is not surprising since the nanotube structure is conserved upon complexation of C_{60} and extended aromatic systems.^[3] The structure of the nanotubes remains intact (as shown by CD and NMR) in the presence of up to the 7.5 equivalents of MeOH per NDI, indicating its stability in the presence of small amounts of hydrogen-bond competitors.^[3]

The NDI nanotube inclusion complexes have characteristic NMR signatures. The presence or absence of an upfield shift in the 1H NMR spectrum of **1** upon addition of a potential guest molecule is a diagnostic and reliable way to assess the formation of a host-guest complex in solution. In this case, the magnitude of the chemical shift recorded for the NDI α protons in the presence of the four different ion pairs tested in this study follow the same trend as observed for the C_{60} competition experiments followed by UV/Vis spectroscopy. A $\Delta\delta$ of 0.08 ppm for **2-Cl**, 0.03 ppm for **3-Cl** and about 0.02 ppm for **2-Br** and **2-I** is obtained when one equivalent of ion pair is added to a 10 mM solution of C_{60} in $CDCl_3$. 1H NMR titrations using **1** and **2-Cl**, **2-Br** and **2-I** confirm this chemical shift difference over a range of concentrations of ion pairs (see the Supporting Information). This highlights the size-discrimination ability of the NDI nanotubes in complexing ion pairs.

The ^{13}C NMR spectrum of C_{60} is strongly influenced by the presence of the NDI nanotubes. An upfield shift of more than 1.4 ppm was observed for the ^{13}C signal of C_{60} upon inclusion in the nanotube cavity, indicating a shielding effect due to the proximity of other aromatic units (Figure 4).^[2] Upon addition of increasing amounts of **2-Cl** (0.5 and 1 equivalent) to a 10 mM solution of C_{60} in $CDCl_3$, a small but significant downfield shift, towards the uncomplexed position, of the fullerene signal is observed.

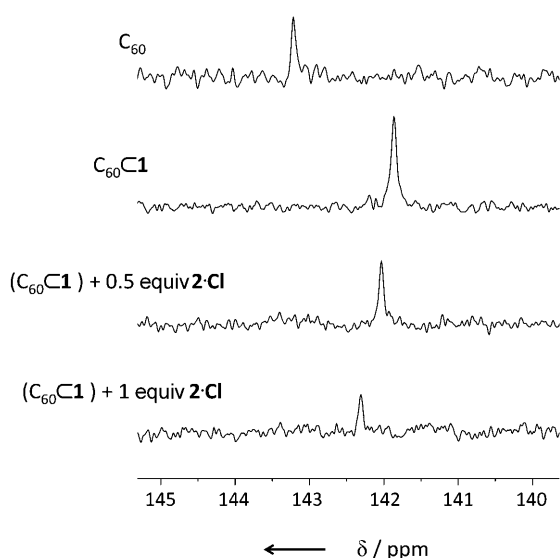


Figure 4. ^{13}C NMR spectra of a saturated solution of C_{60} and of a 10 mM solution of **1** + C_{60} in the presence of different amounts of **2-Cl**. 1024 scans were acquired for each ^{13}C spectrum of the complexes, and 11000 scans were acquired for a saturated solution of C_{60} in $CDCl_3$.

This is also accompanied by a decrease of the intensity of the ^{13}C signal indicating that C_{60} is released in solution in the presence of the competing ion pair. As a result of the poor solubility of C_{60} in chloroform, the released fullerene quickly precipitates out of solution making it difficult to detect the presence of free C_{60} by ^{13}C NMR spectroscopy. The presence of a C_{60} signal even after the addition of one equivalent of ion pair indicates that not all the C_{60} has been displaced from the nanotube's cavity. This is possible only if a new mixed host-and-two-guests complex has formed, in which the fullerene and ion pairs are simultaneously complexed inside the tubular receptor. This is supported by the decrease in intensity observed for the C_{60} signal, which is a direct measure of the amount of C_{60} complexed. The downfield shift, towards the uncomplexed position, observed for the same peak is also indicative of the disruption of the close packed one-dimensional array of C_{60} . This allows us to propose that the initial upfield shift in the C_{60} resonance is due to the shielding produced by a combination of the NDI cores and the neighbouring C_{60} molecules. In the mixed complex the influence of the neighbouring C_{60} molecules is reduced, accounting for the downfield shift observed for the C_{60} resonance. The presence of the ion pair inside the tubular cavity is confirmed by the expected upfield shift observed in the 1H NMR spectrum, for the cation's benzyl protons (see the Supporting Information).

The reverse experiments in which C_{60} was added to solutions of **2-Cl** led to the formation of the same nanotube-fullerene-ion pair mixed complex. UV and NMR experiments confirm that C_{60} partially displaces ion pairs from the nanotube's cavity even when the host is saturated with the ion pair guest (see the Supporting Information). This is indicative of the dynamic nature of the systems and the propensity of these nanotubes to form mixed complexes.

In conclusion we have demonstrated through competition experiments with C_{60} that NDI-based helical nanotubes act as selective receptors for ion pairs. The selectivity is based on the relative size of the ion pairs and is a direct measure for the association strength between the nanotubes and ion pairs. Virtually all the receptors currently available for binding ion pairs display specific ion binding motifs such as crown ethers, amides and ureas, calixarenes and calixpyrroles^[8] or combinations of these to generate heterotopic receptors that are able to bind simultaneously multiple ions.^[9] We believe that the unexpected results reported above show that the NDI nanotubes represent an unprecedented and unique example of a self-assembled non-specific receptor for ion pairs. Furthermore, we have shown that the nanotubes have a tendency to form mixed complexes in which both ion pairs and C_{60} are present simultaneously in the nanotubes' cavity. This leads us to suggest that the nanotubes have the potential to act as nanoscale reactors in which the effective molarity of the reactants is increased dramatically by complexation within the confined nanotube cavity.

Acknowledgements

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Keywords: fullerenes • host–guest chemistry • ion pairs • receptors • self-assembly

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