DOI: 10.1002/anie.200704983

Fullerenes

Templated Amplification of an Unexpected Receptor for C_{70}**

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We recently reported that a self-assembled helical nanotube[1] formed of naphthalene diimide (NDI) molecules functionalized with amino acids[2] (Figure 1a) can complex a string of C_{60} fullerene molecules.[3] We now show that C_{70} templates the formation of a new discrete receptor at the expense of preformed nanotubes.[4] This behavior, which resembles that of a dynamic combinatorial system,[5] was unexpected. As C_{60} and C_{70} share the same small diameter (Figure 1b), we had anticipated that the same complexation mode would be possible (Figure 1c).

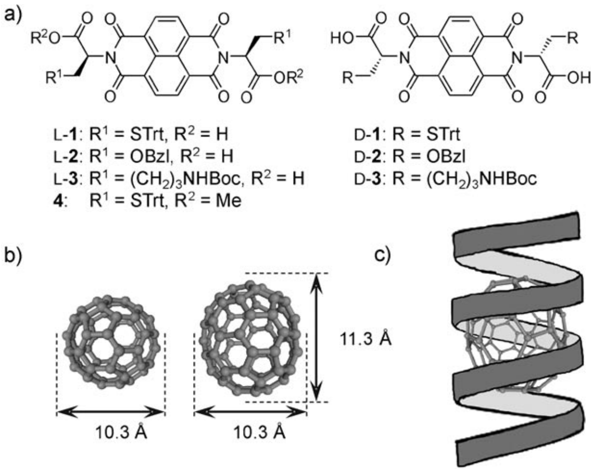

Figure 1. a) NDI derivatives. Boc = *tert*-butoxycarbonyl, Bzl = benzyl, Trt = CPh_3. b) Comparative view of the sizes of C_{60} and C_{70}. c) Expected complexation mode of C_{70} by NDI derivatives.

When a solution of **1** nanotubes (denoted $\mathbf{1}_N$) in dry chloroform was allowed to stand over excess solid C_{70}, it significantly darkened over time (Figure 2a, inset). Figure 2 shows the UV absorption spectra of different solutions of **1** and C_{70}. Precise calculation of solubility enhancement and NDI/C_{70} ratios was difficult and unreliable, as the extinction coefficient for the complex is not the sum of the individual contributions of NDI and C_{70}, as can be seen for the 384-nm band of NDI (Figure 2a). The NDI/C_{70} ratio was calculated to be around five using measurements at 258 nm. Other wavelengths, both in the UV and visible regions of the spectra, did not yield reliable values for the NDI/C_{70} stoichiometry.

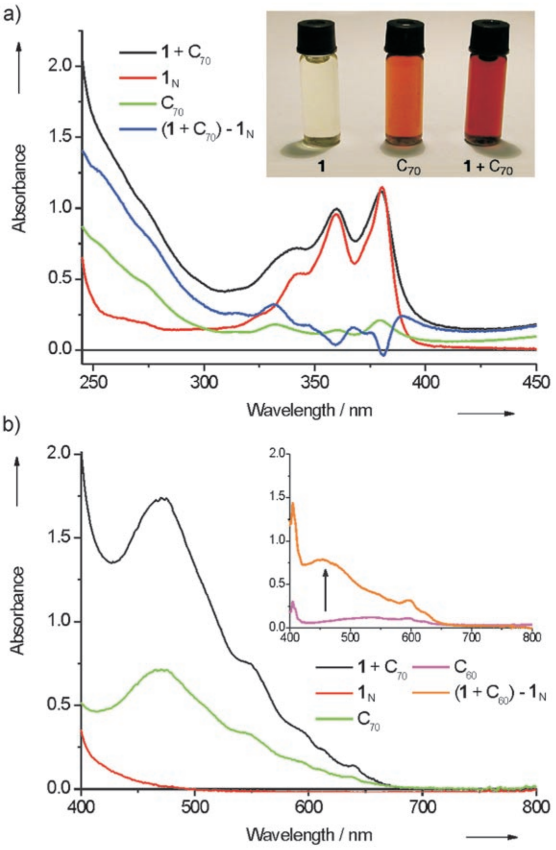

Figure 2. Photographical comparison of solutions of NDI and C_{70} in chloroform (inset in (a)). a) UV absorption spectra. b) Vis absorption spectra. The inset in (b) shows the effect of close contacts in the case of C_{60}.

Unlike the C_{60}-solubilizing NDI nanotube,[3] the NDI/C_{70} complex gives no indication of interactions between C_{70} molecules in the visible absorption spectrum (Figure 2b). Close contacts between C_{70} molecules have been reported to shift the 470-nm maximum to 490 nm in solid films[6] and aggregates.[7] The absence of a peak corresponding to interactions between C_{70} molecules is a strong indication that the C_{70} receptor is radically different in nature from the C_{60} one.

This supposition is confirmed by the difference of circular dichroism (CD) spectra between $\mathbf{3}_N$ alone and **3**/C_{70} solutions, both shown in Figure 3 for the same enantiomer of **3**. Although the signal at 384 nm changes to the opposite sign with increasing concentration, this is not the case for all parts of the spectrum. This evolution to a radically different CD spectrum and the fact that derivatives **1** and **2** give similar CD

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[**] We thank EPSRC and Pembroke College (J.R.F. for G.D.P.) for funding.

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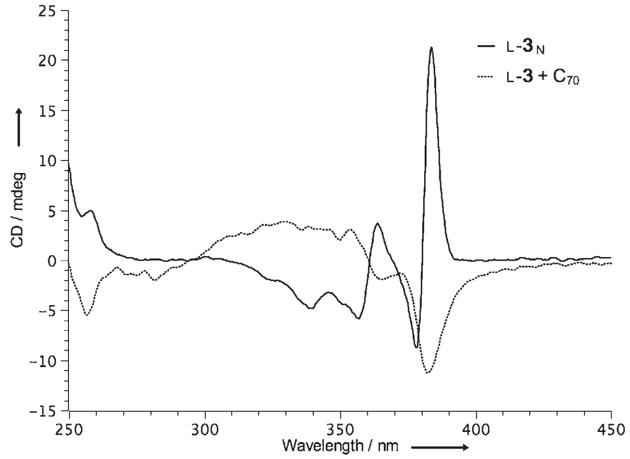

Figure 3. CD spectra of L-**3** in the absence and in the presence of C_{70} at $[\mathbf{3}] = 3.86\times10^{-4}$ M.

signatures in the presence of C_{70} is indicative of the formation of a new supramolecular structure. Most likely, it is governed by H-bonds, as ester **4** neither solubilizes C_{70} nor gives any notable CD signal, and increasing the temperature at which the experiments were conducted decreases the CD intensity for **1**–**3**/C_{70} (see the Supporting Information).

The nanotube and the C_{70} receptor give distinct ^{1}H NMR spectral signatures, so the area of the nanotube aromatic peak should give some information on the stoichiometry of the C_{70} receptor. Starting from a solution of two NDI molecules per C_{70} and titrating with NDI, the nanotube peak starts appearing when all C_{70} molecules are saturated with NDI ligands. CD experiments conducted at similar concentrations (10^{-4} M and above) confirm that in these conditions the C_{70} receptor is very strongly favored over the empty nanotube.

Figure 4a shows the evolution of the area of the nanotube α-proton peak with respect to the relative C_{70} receptor peaks as a function of equivalents of NDI **2** per equivalent C_{70}. A linear regression on the region where nanotubes start to appear gives a stoichiometry of 5.74 NDI molecules per C_{70} molecule. If we assume an integer ratio of NDI/C_{70}, this result indicates a stoichiometry of 6:1, or possibly 5:1.

The ^{1}H NMR spectrum (Figure 4b) of $\mathbf{2}_N$ shows a high degree of symmetry experienced by the NDI unit, as opposed to the signature of the C_{70} receptor, which shows four doublets for the aromatic protons, three of which have a similar chemical shift, one being shifted downfield by 0.78 ppm. Similarly, there are two signals for α-protons of the C_{70} receptor rather than one in the nanotube. A NOESY experiment demonstrates the dynamic character of this new structure (see the Supporting Information). ^{13}C NMR spectra of C_{70} in the absence and in the presence of NDI indicate clear shift differences with roughly equal effects (2.0–2.4 ppm) on all five inequivalent carbon atoms.

The four aromatic signals observed in the ^{1}H NMR spectrum of the C_{70} receptor can arise, at first sight, from four different situations (Figure 5b–e): four inequivalent protons on a single NDI molecule (b), four equivalent protons on each of four inequivalent NDI molecules (c), or

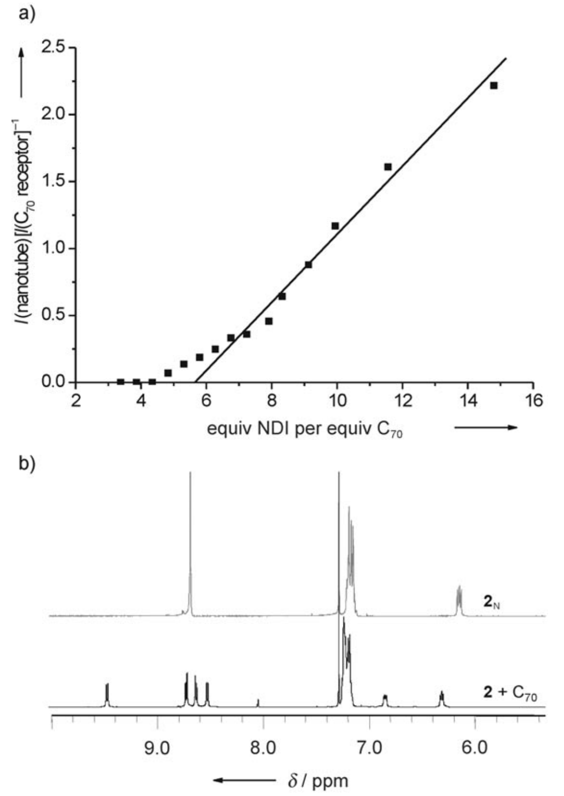

Figure 4. a) Evolution of the ratio of peak areas (^{1}H NMR spectroscopy, α-proton signals of the nanotube vs. the C_{70} receptor) of **2** with NDI/C_{70} ratio. b) ^{1}H NMR spectra of empty nanotube and C_{70} receptor in dry chloroform.

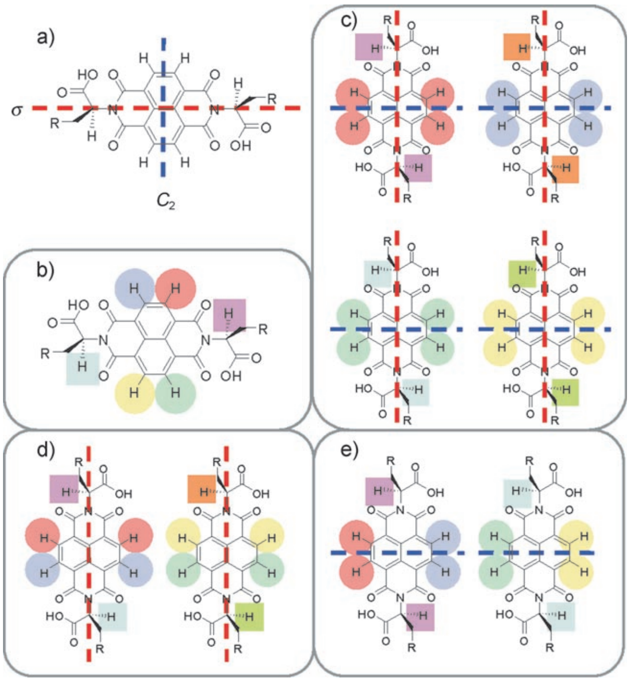

Figure 5. a) Symmetry elements of an NDI derivative: symmetry plane σ (red) and two-fold axis (blue); b–e) different combinations of symmetry elements and number of inequivalent NDI molecules that give rise to four aromatic signals.

two pairs of protons on two inequivalent NDI molecules (d,e). Situations (c) and (d) can be ruled out, as they would give rise to four different signals of the α-protons rather than two. Situation (e) can also be ruled out, as it would result in four singlets for the aromatic protons. The number and multiplicity of the signals in the ^{1}H NMR spectrum of **2**/C_{70} clearly point to situation in Figure 5b. Therefore, all NDI molecules are equivalent, yet none of them lie on a symmetry element of the assembly.

The presence of several homochiral molecules leaves only finite chiral point groups (Figure 6, groups shown on a grey background), that is, groups C_1, C_n, D_n, T, O, and I. C_1 can be ruled out as it has no symmetry elements; T, O, and I would require at least 12, 24, and 60 NDI molecules, respectively.

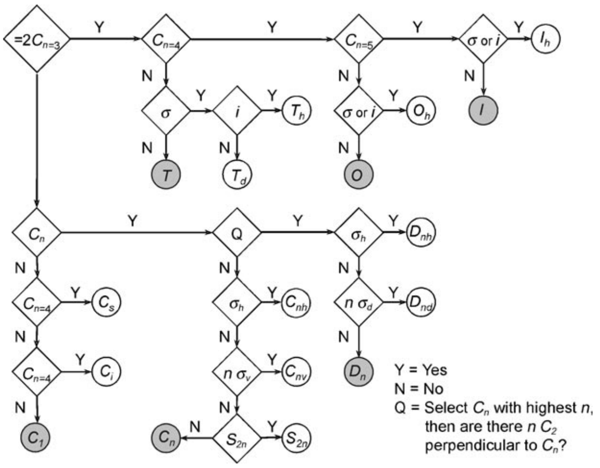

Figure 6. Chart showing the finite point symmetry groups (in circles). Starting in the top left-hand corner, the point group of an object can be found by answering the questions (in diamonds) and following the arrows. A gray background marks chiral groups.

Thus, a 5:1 stoichiometry would imply C_5 as the point group, and a 6:1 stoichiometry would lead to either C_6 or D_3. Two of these groups can be excluded by a simple argument based on the ^{1}H and ^{13}C NMR spectra of the host and guest, respectively. Comparing the ^{1}H NMR spectra of the C_{70} receptor with those of the NDI nanotube ($\mathbf{2}_N$), we observe that the most strongly downfield-shifted signal is shifted by $\Delta\delta = 0.78$ ppm from 8.66 to 9.44 ppm, which corresponds to a frequency difference of about 400 Hz on our spectrometer. The largest ^{13}C NMR shift difference between free and complexed C_{70} is 2.4 ppm (see the Supporting Information), corresponding to 300 Hz. These very similar timescales indicate that chemical exchange is slow on both ^{13}C and ^{1}H chemical-shift timescales. Therefore the two "poles" of the C_{70} molecule must be equivalent in its complexed state, eliminating the C_n symmetry groups. This leaves a 6:1 stoichiometry with a D_3 point-group symmetry as the only plausible structural class of the C_{70} receptor.

On the basis of this symmetry analysis, we conclude that at the "poles" of the C_{70} receptor, three NDI molecules have to bind to each other in a C_3-symmetrical manner, requiring angles of 120° (Figure 7b). Carboxylic acids are not known to trimerize, and a trimer cannot be easily envisaged given the electronic distribution in a carboxylic acid. Weak CH···O hydrogen bonding to an imide or carboxylic acid carbonyl group could explain the chemical shift change of more than 0.7 ppm for one aromatic proton in the C_{70} receptor (Figure 3b). Indeed, such an arrangement can give rise to a favorable trimeric interaction mode (Figure 7b), accounting for formation of one trimeric "half" of the receptor. Similar interaction modes have been observed in several crystal structures, and the formation of tapes by alanine phthalimide[8] (Figure 7d) is closely related to the proposed binding mode in the C_{70} receptor.

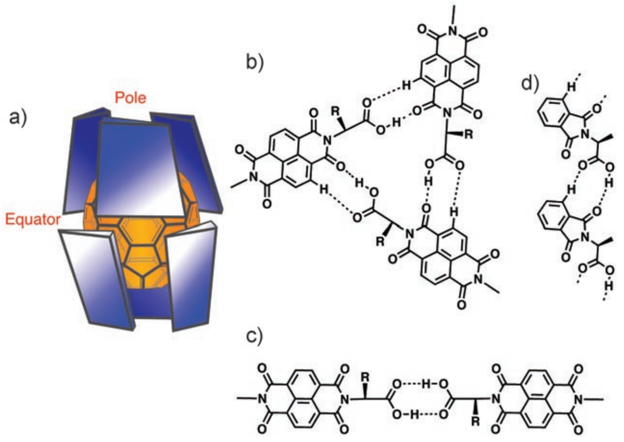

Figure 7. a) Cartoon representation of the C_{70} receptor. b, c) Proposed interaction motifs between NDI molecules at the poles (b) and the equator (c) of the C_{70} receptor. d) Alanine phthalimide tapes.[8]

In the proposed arrangement, consistent with D_3 point symmetry for the complex, one carboxylic residue per NDI unit would remain free for carboxylic acid dimerization with the NDI counterpart of the other hemisphere, at the equator of the C_{70} receptor. Figure 7a shows a cartoon representation of the proposed geometry of the C_{70} receptor.

Owing to the dynamic nature of the C_{70} receptor and the failure to crystallize it, its precise molecular structure and geometry have hitherto remained elusive. Nevertheless, rigorous analysis of the NMR spectra allows unambiguous assignment of stoichiometry, symmetry group, and hence geometry.

In both this new receptor and the NDI nanotube, two groups of H-bond donors (acidic and aromatic protons) and two groups of H-bond acceptors (carboxylic and imide carbonyl oxygen atoms) are involved, but their pairing relationship is inverted. The relative stabilities of these two hydrogen-bonding arrangements must be delicately poised, as the equilibrium can be shifted from one to the other by C_{70}, thus demonstrating eloquently the power of dynamic systems to respond to subtle new stimuli by generating unexpected outcomes. The spontaneous formation of the C_{70} receptor, presumably arising from the more effective van der Waals interaction between NDI and C_{70} versus C_{60}, may lead to the discovery of complexes with higher fullerenes. This NDI series is therefore a dynamic combinatorial system in which hydrogen bonding is the reversible exchange reaction. We are currently exploring its response to other possible templates.

Received: October 28, 2007

Keywords: fullerenes · host–guest systems · hydrogen bonds · self-assembly

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