A new approach to supramolecular C_{60}-dimers based in quadruple hydrogen bonding

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A C_{60}-dimer connected through a highly directional fourfold hydrogen bonding motif has been synthesized; photophysical measurements reveal a strong electronic coupling through the hydrogen bond edge.†

The design and synthesis of [60]fullerene dimers is currently attracting considerable attention.[1] Different strategies have been adapted for the construction of C_{60}-dimers: the net result is, however, that the two monomeric units are, in the resulting dimers, attached through diversified, covalent linkages.

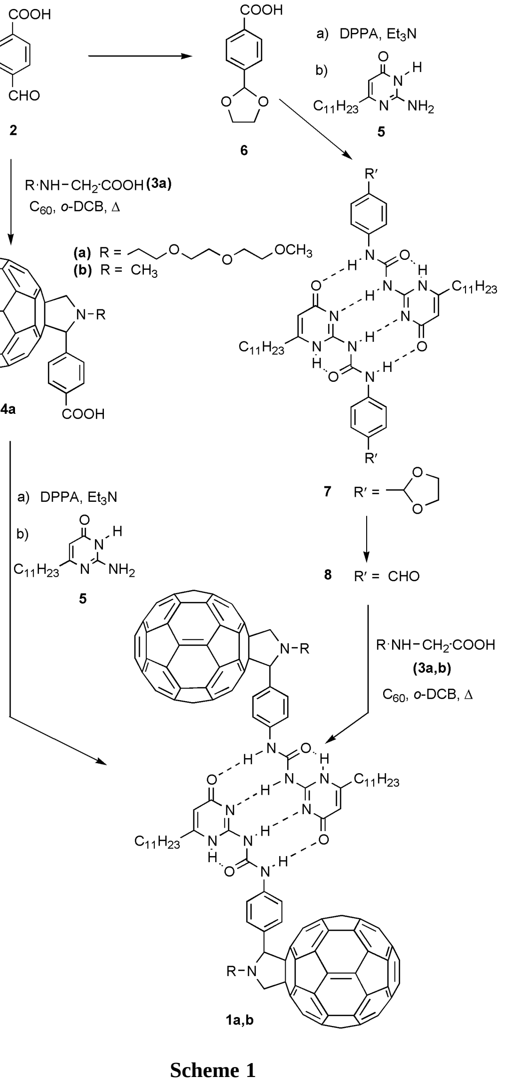
Sijbesma, Meijer *et al*. have reported the preparation of remarkably stable dimers ($K_s > 10^6$ M^{-1}) evolving from derivatives of the 2-ureido-4-pyrimidone moiety, *via* a self-complementary array of four hydrogen bonds.[2] The same strategy was afterwards employed for the synthesis of calix[4]arene dimers.[3]

In this communication, we wish to report on the synthesis of the first, rigid noncovalent C_{60}-dimer system, in which both molecular subunits are linked by a self-complementary DDAA (donor–donor–acceptor–acceptor) array of hydrogen bonding.[4] The selected four-point hydrogen bond motif, based on a 2-ureido-4-pyrimidone moiety, guarantees the molecular recognition in solution and leads to a novel noncovalent constructed model system.

Two different routes, as summarized in Scheme 1, were pursued to synthesize dimers **1a**,**b**. In particular, *N*-substituted 2′,5′-dihydro-1′*H*-pyrrolofullerene **4a** was prepared from *p*-formylbenzoic acid (**2**) and *N*-(3,6,9-trioxadecyl)glycine (**3a**).[5] The polyether chain, located on the pyrrolidine ring, allows the sufficient solubility of compound **4a** in most organic solvents. In **4a**, the carboxy functionality was then transformed into the corresponding isocyanate by a Curtius rearrangement of the intermediate acyl azide generated with diphenylphosphoryl azide (DPPA).[6] Reaction with aminopyrimidone (**5**) afforded dimer **1a** in a 3% overall yield.‡ The poor yield for this three-step, one-pot process can be rationalized in terms of competitive reactions either of the azido group in DPPA or of the amino group in **5** with the C_{60} core of **4a**.

Performing first the C_{60}-based reaction with aldehyde dimer **8**, already containing the ureidopyrimidinone dimerization edge, successfully circumvented these interfering reactions. Accordingly, the reaction of acetal **6** with DPPA, followed by *in situ* reaction of the resulting isocyanate with aminopyrimidone **5**, afforded **7**. Subsequent deprotection of **7** with catalytic $HClO_4$ in 5 : 1 dioxane–$CHCl_3$ led to **8** in a 50% yield from **6**. Reaction of dimer **8** with C_{60} and *N*-substituted glycines **3a**,**b** under the same conditions used for the preparation of pyrrolidinofullerenes, gave the respective dimers (**1a**,**b**) in moderate yields (*ca.* 50%).

From the FTIR spectra characteristic evidence was derived for both subunits, namely, C_{60} and the heterocycle. It is worth mentioning that although a diastereomeric mixture should be formed, the ^1H-NMR spectra (500 MHz) show only the presence of a pure compound. Thus, the ^1H-NMR spectra of **1a**,**b** disclose the signals of the pyrrolidine protons at *ca*. 5.2 and 4.3 ppm (J = 9.6 Hz; geminal hydrogens) and a singlet at 5.1 ppm (CH), in good agreement with similar monoadducts. Large downfield shifts were found for the urea NH protons in compounds **1a**,**b**, at *ca.* 12.0 ppm, ($CDCl_3$). This observation is consistent with four DDAA hydrogen bonds in the noncovalent



Scheme 1

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† See also the preceding paper in this issue: M. T. Rispens, L. Sánchez, J. Knol and J. C. Hummelen, *Chem. Commun.*, 2001, DOI: 10.1039/b008006n.

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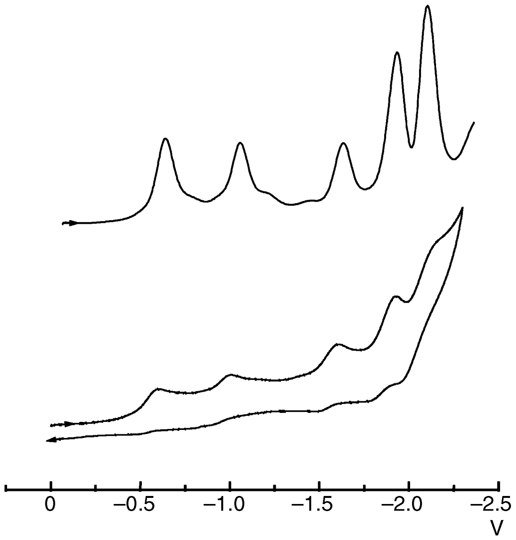

Fig. 1 Cyclic voltammogram and squarewave voltammogran (in V *vs* Ag/ Ag^+) of compound **1a** in toluene : MeCN (4 : 1 *v*/*v*) solution containing 0.1 M *n*-Bu_4NClO_4 with glassy carbon; scan rate at 200 mVs^{-1}.

C_{60}-dimer system. In addition, the chelated NH at position 1 was observed at *ca.* 13.0 ppm.

The CV of dimers **1a**,**b** give rise to four reduction waves in deoxygenated CH_2Cl_2, while six reduction waves were found when a toluene–acetonitrile solvent mixture (4 : 1 v/v) was used (Fig. 1). As can be seen from an inspection of the parent C_{60} and related pyrrolidinofullerenes, the waves at −0.62, −1.01, −1.60, −2.08 V (in toluene–MeCN), and −0.69, −1.05, −1.61 V (in CH_2Cl_2) correlate to the one-electron reduction steps of the C_{60} moiety. These values are, nevertheless, cathodically shifted relative to those of C_{60}.[7]

However, it is important to point out that the voltammograms of dimers **1a**,**b** indicate that both fullerene moieties are reduced simultaneously. This observation, in conjunction with the above-listed spectroscopic characterization, supports the critical argument that there is little, if any, electronic interaction between the two C_{60} subunits in the dimers.

The remaining signals at −1.14 and −1.85 V (in toluene–MeCN) and −1.18 V (in CH_2Cl_2), are associated with redox processes of the heterocyclic ureido(oxo)pyrimidinyl addend.

The excited states properties of **1a** were studied by steady-state emission and time-resolved flash photolysis. Emission experiments, carried out with an excitation wavelength of 400 nm, gave rise to a distinctive solvent dependence. For instance, conditions that leave the hydrogen-bonded C_{60}-dimer intact (*i.e.* chlorobutane or CH_2Cl_2), led to an almost 50% quenching of the fullerene fluorescence around 710 nm relative to a 2′,5′-dihydro-1′H-pyrrolofullerene reference (see Table 1). This implies a markedly accelerated deactivation of the fullerene singlet excited state within the C_{60}-dimers and, hereby, resembling a trend established earlier for the most prominent fullerene dimer, namely, C_{120}.

Table 1 Fluorescence quantum yields[a] of **1a** in various solvents, a fulleropyrrolidine reference and C_{120} at room temperature

Compound solvent	Fluorescence quantum yields **1a**
Dichloromethane	3.05×10^{-4}
Chlorobutane/ethanol	3.3×10^{-4}
Chlorobutane/trifluoroethanol	3.65×10^{-4}
Chlorobutane/hexafluoroisopropanol	4.9×10^{-4}
Fulleropyrrolidine dichloromethane	6.0×10^{-4}
C_{120}[b] toluene	3.95×10^{-4}

[a] Measured at 710 nm. [b] See reference 8.

Upon adding protic solvents, such as ethanol, trifluoroethanol and hexafluoroisopropyl alcohol to a CH_2Cl_2 solution of **1a** a progressive enhancement of the fullerene fluorescence was observed. It should be noted that the solvents employed reveal different protic strengths and, therefore, different affinities to interfere in a disruptive manner with the hydrogen bonding along the following order: ethanol < trifluoroethanol < hexafluoroisopropyl alcohol. Importantly, in the most protic solvent (*i.e.* hexafluoroisopropyl alcohol), the emission quantum yield reached almost the value of a reference 2′,5′-dihydro-1′H- pyrrolofullerene. From this we may propose that under the experimental conditions probed the dissociation into monomer subunits is essentially complete. On the other hand, the quantum yield in the weakest protic solvent (*i.e.* ethanol) is close to the values determined in chlorobutane or CH_2Cl_2, suggesting a nearly dimeric appearance of **1a** under such conditions.

In conclusion, we have synthesized the first C_{60}-dimer linked *via* a highly directional fourfold hydrogen bonding motif. Electrochemical results indicate that there is no mutual interaction in the ground state between both C_{60} subunits. In contrast, the photophysical data, disclosing distinguishable differences between the monomer and the dimer, can be taken as first evidence for the strong electronic coupling mediated through the hydrogen bond edge.

Work is currently in progress directed to interface strong electron donor units with the C_{60} core through a self-complementary array of hydrogen bonds.

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Notes and references

‡ **1a**: Brown solid; 48% yield; FTIR (KBr): br 3431, 1699 (C=O), 1655 (C=O), 527 (C_{60}) cm^{-1}; ^1H-NMR ($CDCl_3$, 500 MHz, 25 °C): δ = 13.02 (s, 2H; NH), 12.26 (s, 4H; NH), 7.78 (br s, 8H; ArH), 5.94 (br s, 2H; pyrim), 5.23 (d, *J*(H,H) = 9.66 Hz, 2H; CH_2N), 5.14 (s, 2H; NCHR), 4.30 (d, *J*(H,H) = 9.66 Hz, 2H; CH_2N), 4.05–3.93 (2m, 4H), 3.80 (br s, 8H), 3.75–3.72 (m, 4H), 3.59–3.50 (m, 4H), 3.38 (m, 8H), 2.80–2.86 (m, 2H), 2.52–2.47 (m, 4H; CH_2), 1.69–1.65 (m, 4H; CH_2), 1.26 (br s, 32H; CH_2), 0.89–0.86 (m, 6H; CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ 173.38, 157.07, 154.99, 154.94, 154.80, 154.10, 154.06, 153.17, 147.68, 147.27, 146.94, 146.81, 146.68, 146.62, 146.59, 146.53, 146.50, 146.46, 146.31, 146.28, 146.16, 145.99, 145.94, 145.91, 145.87, 145.69, 145.63, 145.59, 145.51, 145.11, 145.03, 144.80, 143.52, 143.37, 143.04, 142.92, 142.90, 142.72, 142.70, 142.52, 142.47, 142.41, 142.33, 142.29, 142.05, 141.90, 140.53, 140.49, 140.33, 139.98, 138.91, 137.32, 137.02, 136.21, 136.08, 132.77, 130.52, 128.78, 128.17, 120.68, 106.63, 82.49, 76.80, 72.47, 71.19, 71.11, 71.06, 71.02, 69.69, 68.16, 59.48, 52.44, 33.15, 32.30, 30.09, 29.99, 29.86, 29.72, 29.62, 29.27, 27.38, 23.09, 14.54; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 (159148.9), 274 sh (150209.0), 324 sh (69361.6), 430 (8036.3); MS (MALDI-TOF): 1292 (M^+, 100), 1028 ($M - pyrim^+$, 40).

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