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Supramolecular organization of fullerenes by quadruple hydrogen bonding†

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Quadruple hydrogen bonded fullerene dimer 8 with a very high dimerisation constant ($K_a \geqslant 1.0 \times 10^6$ M^{-1}) was synthesised and fully characterised.‡

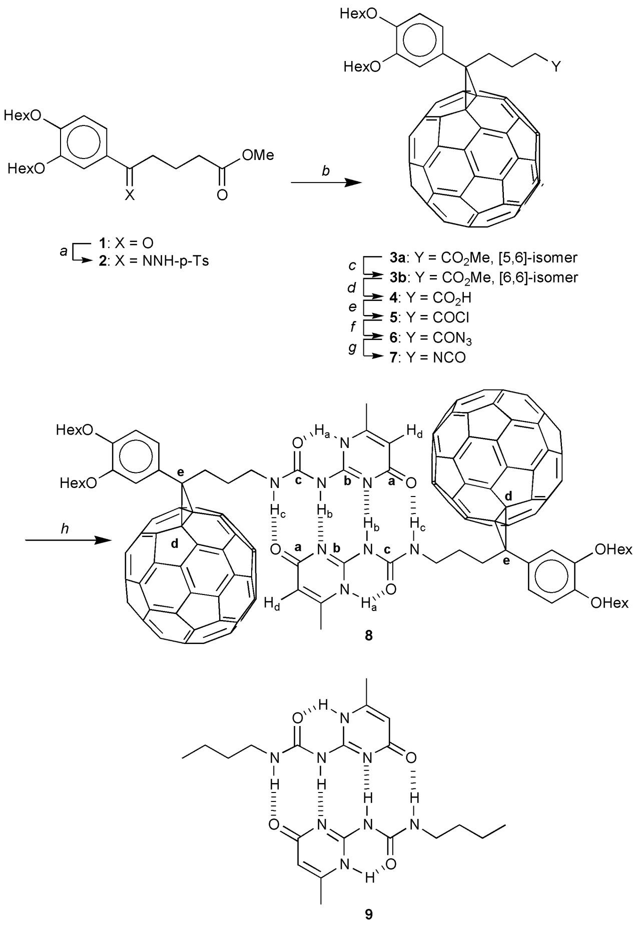
Fullerenes have interesting properties that may be utilised in applications such as organic photovoltaic (PV) devices.[1] The bulk-heterojunction version of such cells especially has received much attention recently. In this type of device, a blend of an electron donor (for example a π-conjugated polymer) and an electron acceptor (for example a fullerene derivative) serves as the active PV layer.[2] Very recently, influencing the morphology of the bulk heterojunction layer by simply changing the spincoating solvent resulted in a substantial increase of the PV power conversion efficiency to a record value of 2.5%.[3] A more intimate mixing of the components most likely resulted in both a larger internal donor–acceptor interface area and increased percolation of at least one of the components. Charge carrier transport in the polymer phase was further improved on the nanoscopic scale due to enhanced polymer inter-chain interactions.

Another potential way to obtain desired bulk-heterojunction architectures is through supramolecular assembly of the constituents. Hydrogen bonding is particularly useful in the construction of supramolecular structures.[4] Strong non-covalent binding can be obtained using multiple hydrogen bond arrays, especially with Meijer's self-complementary 2-ureidopyrimidin-4-ones.[5] With this unit, ultra-strong non-covalent coupling can be achieved, reaching association constants of $> 10^8$ M^{-1}.[5c]

Here we report on the preparation of a [60]fullerene derivative bearing one 2-ureidopyrimidin-4-one moiety as the hydrogen bonding unit. This molecule serves as a model compound for supramolecular fullerene arrays based on multiple hydrogen bonding interactions.

The synthesis of target molecule **8** started from easily accessible 1,2-bis(hexyloxy)benzene.[6] Friedel–Crafts acylation yielded keto ester **1**,[7] which was transformed into the corresponding *p*-tosylhydrazone **2**. Subsequently, carboxylic acid **4** was prepared using the following one pot procedure:[8] first, heating the anion of **2** in the presence of [60]fullerene in *o*-dichlorobenzene (ODCB) at 80–90 °C gave fulleroid **3a**, together with methanofullerene **3b**, higher adducts and [60]fullerene. This crude mixture was photoisomerised quantitatively to a mixture of **3b**, higher adducts and [60]fullerene. Hydrolysis of this mixture yielded crude acid **4**, which was purified by column chromatography. The overall yield for the conversion of **2** into **4** was 36%. Carboxylic acid **4** was converted into the corresponding acid chloride **5**, after which reaction with sodium azide yielded the corresponding acyl azide **6**. Heating **6** in the presence of 6-methylisocytosine at 80 °C for 2 h afforded **8** in good yield.

Dimer **8** showed 29 signals for C_{60}-sp^2 carbons in ^{13}C NMR, in accordance with C_{2h} symmetry. The resonances at δ 172.8 (**a**), 156.5 (**b**) and 154.4 (**c**) are characteristic for the 2-ureidopyrimidin-4-one moiety.[5a] The signals at δ 80.6 and 52.4 are diagnostic for the cyclopropyl moiety.[8] The ^{1}H NMR spectrum recorded in $CDCl_3$ showed the typical resonances[5a] for the four dimer bonding hydrogen atoms of **8** at δ 11.81 (H_b) and δ 10.40 (H_c), a signal at δ 12.98 for the intramolecularly bonded H_a, and one at δ 5.75 for the vinylic proton H_d (Scheme 1). When the concentration of compound **8** was lowered to 1.0×10^{-5} mol l^{-1} no dissociation was observed, thus giving a lowest estimate of the dimerisation constant of 1×10^6 M^{-1}, in good agreement with the values obtained for other ureidopyrimidinone derivatives.[5a] To probe a possible influence of the fullerene core on the hydrogen bonding unit, equimolar amounts of dimer **8** and dimer **9** of *N*-butylaminocarbonyl-6-methylisocytosine (**9**)[5] were dissolved in $CDCl_3$. A statistical mixture of the possible dimers was obtained (Fig. 1) as was concluded from the integration of the absorptions of all protons



Scheme 1 (*a*) *p*-TsNHNH$_2$, MeOH, 6 h., Δ, 61%; (*b*) 1. NaOMe, py, 30 min., rt, C_{60}, ODCB, 80–90 °C, 16 h; (*c*) ODCB, 500 W flood lamp, 100 min; (*d*) ODCB, HOAc, HCl, H_2O, 16 h, 36% (2→4, 3 steps); (*e*) $SOCl_2$, $CHCl_3$, 1 h; (*f*) NaN_3, ODCB, DMAC, rt 75 min; (*g* + *h*) 2-amino-4-hydroxy-6-methylpyrimidine, py, 70–80 °C, 2 h, 71% (4→8, 3 steps).

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† Electronic supplementary information (ESI) available: details of preparation and spectroscopic characterization of all compounds. See http://www.rsc.org/suppdata/cc/b0/b008006n/

‡ See also the following paper in this issue: J. J. González, S. González, E. M. Priego, C. Luo, D. M. Guldi, J. de Mendoza and N. Martín, *Chem. Commun.*, 2001, DOI: 10.1039/b008005p.

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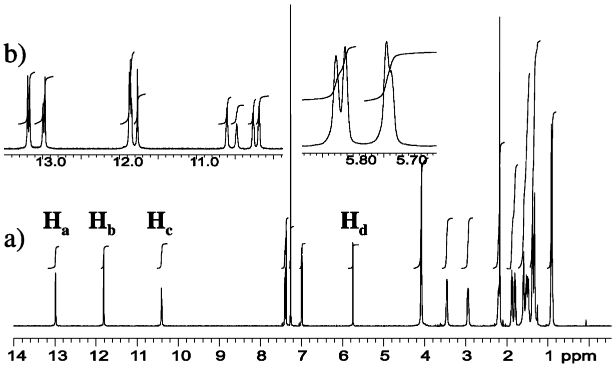

Fig. 1 (a) ^1H NMR of **8** in $CDCl_3$. (b) ^1H NMR of equimolar solution of **8** and **9** in $CDCl_3$.

Table 1 Redox properties

Com.[a]	E^1_{red}[b]	E^2_{red}[b]	E_{1red}[c]	E^3_{red}[b]	E_{2red}[c]	E^4_{red}[b]
3b	−0.66	−1.04	—	−1.55	—	−2.00
4	−0.72	−1.09	—	−1.60	−1.80	−2.02
8	−0.68	−1.01	−1.15	−1.56	−1.84	−2.02
C_{60}	−0.60	−1.09	—	−1.63	—	−2.07
9	—	—	−1.02	—	−1.60	—

[a] Experimental conditions: V: *vs.* Ag wire, GCE as the working electrode, Bu_4NPF_6 (0.1 M) as the supporting electrolyte, ODCB–MeCN (4 : 1) as the solvent, 100 mV s^{-1} scan rate. [b] Waves corresponding to the reduction processes of the C_{60} cage. [c] Waves corresponding to the reduction processes of the ureidopyrimidinone moiety.

H_{a-d} in ^1H NMR. The most pronounced shift is observed for the resonance of H_c.

While **8** shows characteristic absorptions for a methanofullerene in UV-Vis, the FTIR-spectrum showed a peak pattern at 1695, 1658, 1586 and 1513 cm^{-1}, indicative of a pyrimidin-4(1*H*)-one dimer[9] and the typical fullerene absorption at 526 cm^{-1}. The MALDI-TOF spectrum of **8** featured a parent peak at m/z = 1217.8 for the monomer.

The redox behaviour of fullerene derivatives **3b**, **4**, **8**, and that of **9**[5a] was determined by cyclic voltammetry (Table 1). The cyclic voltammogram of **3b** showed four reversible waves corresponding to reduction of the fullerene core, with values typical for methanofullerenes.[8] In the case of carboxylic acid **4** an additional wave was observed at −1.80 V, which was attributed to the reduction of the acid moiety. Finally, the cyclic voltammogram of **8** showed the similar four waves corresponding to reduction of the fullerene core as well as a weak wave at −1.84 V and a shoulder at −1.15 V. The latter two waves are related to the 2-ureidopyrimidin-4-one moiety as was confirmed upon comparison with **9**[5a] (−1.02 and −1.60 V).

In an exploratory experiment towards application in a PV device, the processability of dimer **8** was shown as follows: When filtered solutions of MDMO-PPV[10] and **8** [both 1.0 (m/v) % in chloroform] were mixed in a ratio of 1 : 4 and the mixture was subsequently spincoated on a glass substrate, an optical quality film was obtained.

Other supramolecularly interacting fullerene compounds have been reported recently.[11] The synthesis of **8**, however, represents the first example of a hydrogen bonded fullerene dimer. With both fullerene cages connected through the very strong quadruple hydrogen bonding motif, provided by the ureidopyrimidinone moiety, the application in supramolecular electronics is within reach. Non-covalent multifullerene arrays based on bis(ureidopyrimidinone) substituted fullerenes are currently under investigation.

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