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A Supramolecular Array of Fullerenes by Quadruple Hydrogen Bonding**

Luis Sánchez, Minze T. Rispens, and
Jan C. Hummelen*

Fullerenes have interesting properties that may be utilized in a variety of applications including organic photovoltaic (PV) devices.[1] Especially organic bulk-heterojunction PV cells consisting of a blend of a π-conjugated polymer and a fullerene derivative[2] have received much attention recently. A way to improve the efficiency of these so called "plastic" solar cells is the optimization of the morphology of the photoactive layer. A potential way to attain this goal is through supramolecular assembly of the constituents. Hydrogen bonding is particularly useful in the construction of supramolecular structures.[3] Relatively little work on C_{60}-based polymers[4] and supramolecular C_{60} derivatives has been performed.[5] So far, only dimeric compounds have been obtained by a supramolecular approach.[6] Monofunctionalized C_{60} derivatives bearing one or two hydrogen-bonding moieties on the substituent can serve as building blocks for the preparation of fullerene-containing dimers and arrays, by using the strength, directionality, and specificity, characteristic of hydrogen bonding.[3] Our group[7] and the group of Martín[8] have recently reported on the synthesis of supramolecular C_{60} dimers bearing Meijer's self-complementary 2-ureido-4-pyrimidinones which have a donor donor acceptor acceptor (DDAA) hydrogen bonding motif. This motif gives rise to a very high dimerization constant ($K_d \geq 6 \times 10^7\,\mathrm{M}^{-1}$), as a result of attractive secondary interactions.[9] The presence of two ureidopyrimidinone groups in a molecule results in supramolecular polymers of exceptional properties.[10] After our first exercise on a fullerene with *one* coupling unit,[7] we now report the synthesis and spectroscopic characterization of the first hydrogen-bonded supramolecular array, formed by a (methano)fullerene with *two* coupling units.

The synthesis of target monomer **8** (Scheme 1) started with the conversion of diethyl-4-oxopimelate (**1**) into *para*-tosylhydrazone **2**. Heating the anion of **2** in the presence of C_{60} in 1,2-*ortho*-dichlorobenzene (ODCB) at 100 °C[11] gave fulleroid **3a**, together with methanofullerene **3b**, higher adducts, and C_{60}, through the intermediate diazo compound and diazoline adduct. The isomeric mixture **3a**/**3b** was isolated and photoisomerized quantitatively to the [6,6]-isomer **3b**. Hydrolysis of **3b** yielded acid **4**, which was fully characterized despite its insolubility in all common solvents. Target methanofullerene **8** was prepared using a one-pot procedure:

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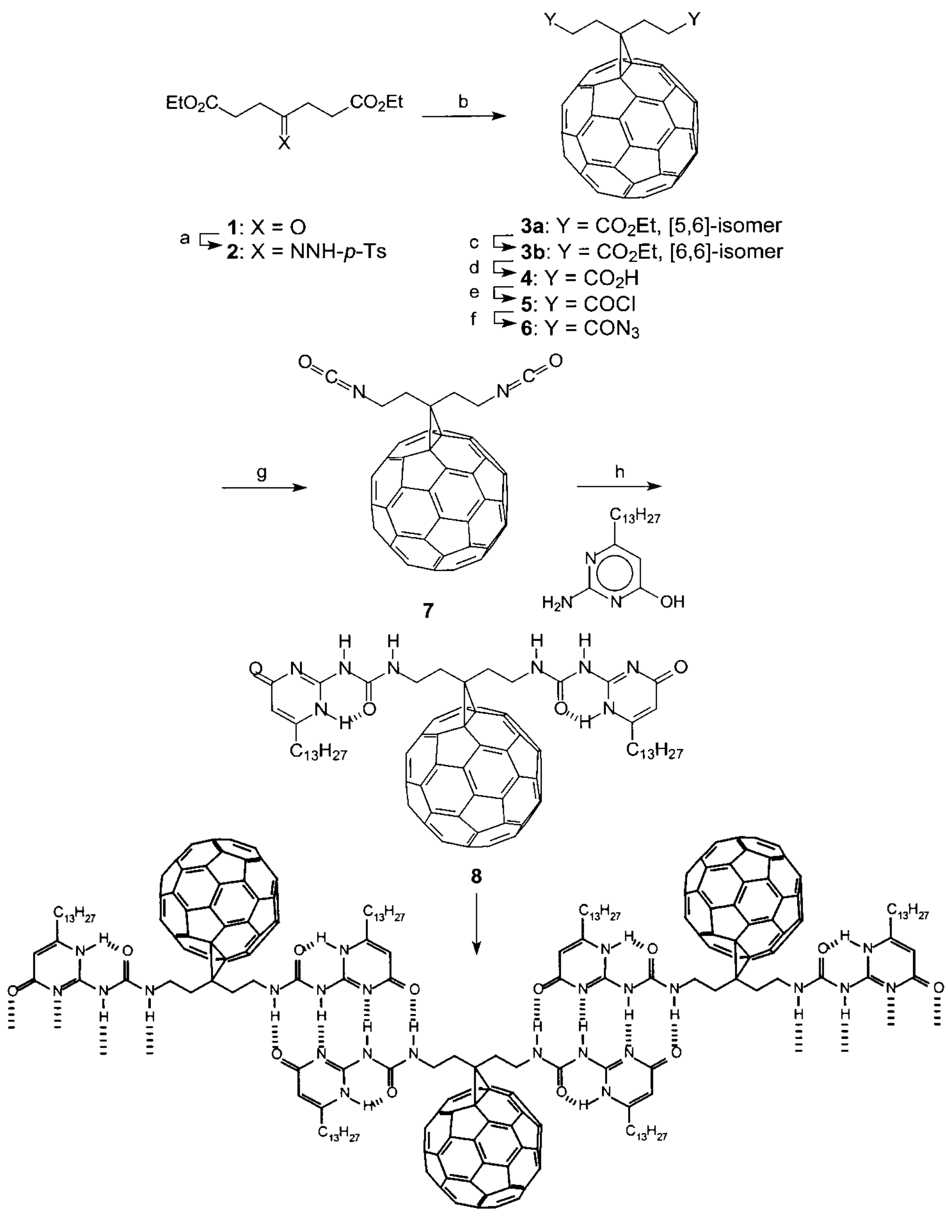

Scheme 1. Synthesis of methanofullerene **8**. a) p-TsNHNH$_2$, EtOH, overnight, Δ, 85%; b) NaOMe, py, 30 min, RT; then C_{60} in ODCB, 80 °C, 16 h; c) ODCB, 500 W flood lamp, RT, overnight, 49% (b,c); d) ODCB, AcOH, HCl, H_2O, Δ, overnight, 83%; e) $SOCl_2$, 1 h; f + g) NaN_3, ODCB, Me_2NCOMe, 75 °C, 30 min; h) 2-amino-4-hydroxy-6-tridecylpyrimidine, py, 100 °C, overnight, 43% (e–h); Ts = tosyl, py = pyridene, Ac = acetyl.

carboxylic acid **4** was converted into acid chloride **5**, after which reaction with sodium azide yielded acyl azide **6**. Heating **6** in the presence of 6-tridecylisocytosine at 100 °C overnight afforded **8** in good yield (43%, four steps, starting from **4**) via bisisocyanate **7**. Full experimental details are in the Supporting Information.

The ^1H NMR spectrum of a relatively concentrated (100 mM) sample of remarkably soluble (oligo and polymeric) target compound **8** in $CDCl_3$ showed the typical resonances for the six (polymeric) hydrogen-bonding protons at $\delta = 12.87$ (intramolecular, 2H) and at $\delta = 11.63$ and $\delta = 10.65$ (intermolecular, 4H) as well as at $\delta = 5.72$ for the vinylic proton (2H) (Figure 1a). Disrupting all **8**-to-**8** hydrogen bonding by the addition of a small amount of [D$_1$]trifluoroacetic acid (TFA) resulted in converging of all the resonances from the hydrogen-bonding protons at $\delta = 11.33$. The hydrogen-bonded array can be fully restored, as witnessed by the recovery of the original NMR spectrum by precipitation of the TFA-disrupted polymer with methanol, drying, and subsequent dissolving in $CDCl_3$.

The dynamic behavior of the supramolecular polymer was investigated by ^1H NMR spectroscopy by lowering the concentration to 10 mM in $CDCl_3$ (Figure 1b). In addition to all the resonances corresponding to the hydrogen-bonded and vinylic protons observed at 100 mM, new sets of multiple signals appeared. This behavior can be explained by the existence of oligo- and polymeric aggregates in the concentrated solution and a mixture of polymeric and low molecular weight cyclic aggregates in the diluted solution, and is in full agreement with earlier results on supramolecular polymers held together by this coupling unit.[9, 10, 12] Theoretically, based on an association constant of $6 \times 10^7\,M^{-1}$ in $CHCl_3$,[9] the population of associates of ultra pure **8** at 100 mM is expected to peak at a M_n of $\approx 3.6 \times 10^6$. In reality, however, the effect of tiny amounts of (monofunctional) impurities substantially lowering the dynamic molecular weight distribution has to be taken into account.

Further support for the polymeric nature of **8** at high concentration was obtained upon investigating the processability and thin-film behavior of **8**: When a filtered solution of **8** (10 mM in $CHCl_3$) was spin-coated on a glass

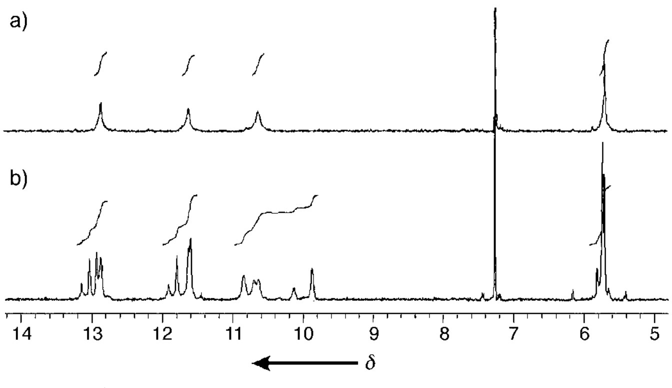

Figure 1. ^1H NMR spectra of compound **8** in $CDCl_3$ at different concentrations, a) 100 mM and b) 10 mM.

substrate, a macroscopically homogeneous film was obtained in contrast to the behavior of many low molecular weight fullerene materials. Upon spin-coating, the concentration of **8** increases dramatically, instantly generating higher molecular weight polymer. The UV/Vis spectrum of the film showed substantial scattering, but subtraction of a weighted $1/\lambda^4$ curve regenerated the solution spectrum, albeit somewhat red shifted in the 500–550 nm region. This behavior resembles that of C_{60} in solution and solid-state spectra.[13]

The ^{13}C NMR spectrum of polymeric **8** (at 100 mM in $CDCl_3$) showed 15 signals for the fullerene core in accordance with a C_{2v} symmetry for the monomer. Additional resonances at $\delta = 172.87$, 156.63, 154.10, and 152.33, which correspond to the 2-ureido-4-pyrimidinone moiety, and at $\delta = 78.21$ and 39.92, diagnostic for the cyclopropyl moiety, were observed. The UV/Vis of **8** revealed the characteristic absorptions for a methanofullerene. There were no significant spectral shifts in the 400–750 nm region upon varying the concentration between 0.01 and 4 mM, which indicates little or no ground-state interfullerene interaction in the "supra polymer". The FT infrared (IR) spectrum of **8** (KBr pellet) showed the typical peak pattern for a 4[1*H*]-ureidopyrimidinone derivative (1697, 1656, 1585, 1524 cm^{-1}) together with a peak at 526 cm^{-1}, diagnostic for a (monomethano)fullerene. Finally, in the matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrum of **8** a parent peak at m/z 1457.79 was detected, which corresponds to the monomer formula. No higher aggregates were observed.

The redox behavior of **8** (at 0.3 mM in ODCB:MeCN 4:1) was studied by cyclic voltammetry (Figure 2). Four quasi-reversible fullerene-core reduction waves were observed, with values typical for this type of methanofullerene.[7] A small wave at −1.79 V, which corresponds to the reduction of the ureidopyrimidinone moiety was also observed. In the dimer, this moiety showed two reduction waves at −1.15 (sh) and −1.84 V.[7] In **8** only the latter can be distinguished, probably because of overlapping of the first with the second reduction wave of the fullerene moiety, as indicated by the increased size of the 2nd reduction wave, compared to the first. The presence of a clean set of waves indicates that there is little or no interaction between the fullerene cages, in agreement with the redox behavior determined for the corresponding supramolecular dimers (Figure 2).[7]

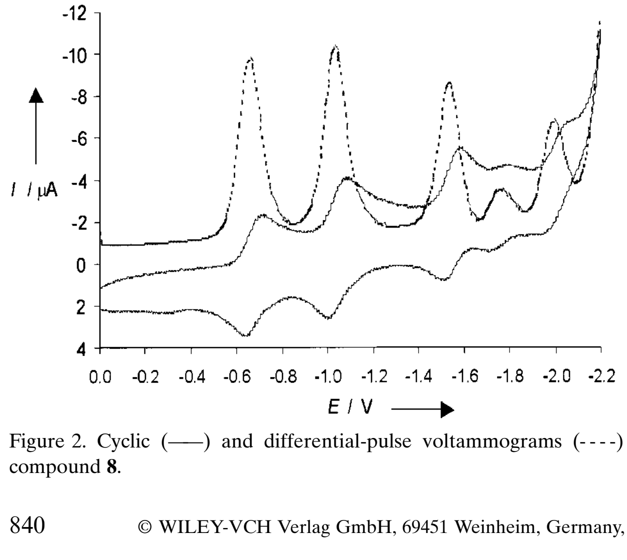

Figure 2. Cyclic (——) and differential-pulse voltammograms (----) of compound **8**.

Polymer **8** is first example of a hydrogen-bonded fullerene array. In the highly dynamic polymeric state, the chemical integrity of the monomeric moiety is fully preserved, also with respect to its redox and UV/Vis behavior. Application in supramolecular electronics, for example, in combination with (supra)molecular donor materials, is now underway.

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