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Self-Assembly and Characterization of Supramolecular [60]Fullerene-Containing 2,6-Diacylamidopyridine with Uracil Derivative by Hydrogen-Bonding Interaction

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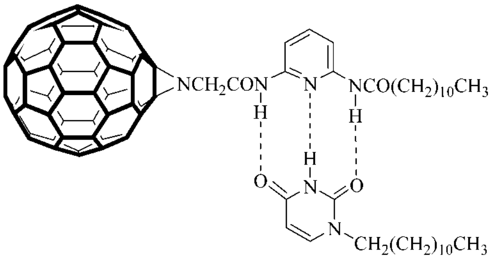
ABSTRACT



Novel self-assembly systems of uracil derivatives with organofullerene by a three-point hydrogen-bonding interaction were designed and established. The formation of hydrogen bonding was established by ^{1}H NMR studies in $CDCl_3$.

There has been an increasing interest in design and self-assembly of fullerene derivatives by hydrogen bonds into one-, two-, and three-dimensional supramolecular architecture as a result of their potential applications as new photoelectric materials. Hydrogen bonds are essential for molecular recognition and self-organization of molecules in supramolecular chemistry and have been used for the design of various molecular aggregates in solid state or in solution.[1−5] Meanwhile, energy and electron-transfer processes have also been investigated in the assembled supramolecular systems through hydrogen bonds.[2,3] Very recently, Guldi[6] and Hummelen[7] reported, respectively, the synthesis and photophysical properties of the first quadruple hydrogen bonded fullerene dimer.

We sought to develop a complementary strategy for the synthesis of a donor system and an acceptor unit containing [60]fullerene that would form a class of supramolecular systems that were structurally different from previously reported ones. Here we report the synthesis of new organofullerenes containing a 2,6-diacylamidopyridine unit and self-assembly with a compound bearing the uracil moiety to form a hydrogen-bonded supramolecular system (Scheme 1). The donor and acceptor are linked by a three-point hydrogen

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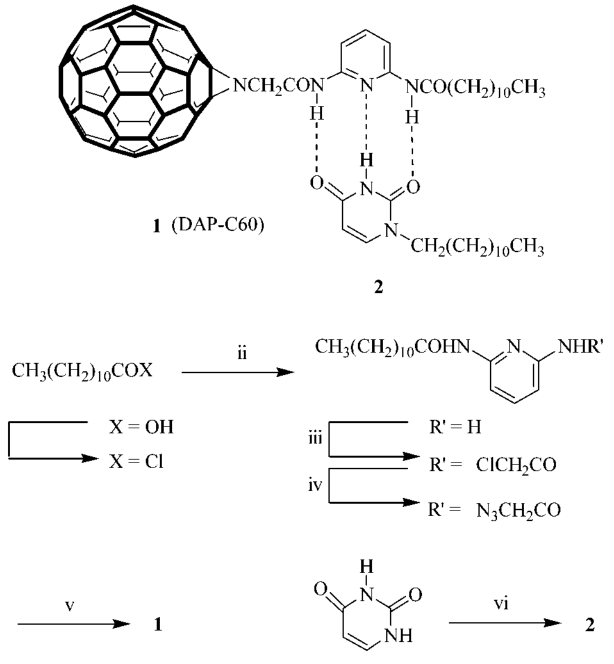
Scheme 1[a]



[a] (i) Thionyl chloride, 90°, 90%; (ii) 2,6-diaminopyridine, THF, rt, 18 h, 94%; (iii) chloroacetanoyl chloride, THF, rt, 24 h, 82%; (iv) sodium azide, 10% water/ethanol, reflux, 24 h, 94%; (v) C_{60}, chlorobenzene, reflux, 72 h, 21%; (vi) 1-bromoundecane, DMSO, 40°, 24 h, 70%.

bond. The formation of hydrogen bonds between the uracil and 2,6-diaminopyridine groups has proved to be an efficient way to construct a supramolecular assembly.[2,6]

The synthesis of the organofullerene DAP-C60 (**1**) is sketched in Scheme 1. The 2,6-diaminopyridine was monoamidated with lauroyl chloride, and then 2-amino-6-lauroylaminopyridine[8] was further amidated with chloroacetanoyl chloride to afford 2-chloroacetanoylamino-6-lauroylaminopyridine.[9] Nucleophilic substitution of chloride with sodium azide yielded 2-azidoacetanoylamino-6-lauroylaminopyridine.[10] The DAP-C60[11] was prepared by reaction of 2-azidoacetanoylamino-6-lauroylaminopyridine with 1 equiv of C_{60} in chlorobenzene under reflux, which relied on the cycloaddition reaction of the azide group with C_{60}, pioneered by the Wudl group.[12] This methodology has proven to be a simple and versatile method for synthesis of C_{60} dyads systems. The condensation product **2**[13] of uracil and 1-bromoundecane was obtained at ambient temperature. It is expected that the introduction of long alkyl chain in **1** and **2** exceedingly enhances the solubility of the compounds in organic solvents.

The addition of azides to C_{60} in this reaction proceeds via intermediate triazolines, which rearrange to closed 1,2-aza-bridged isomers as the major monoaddition product after extrusion of N_2. With high symmetry, the closed 1,2-aza-bridged isomer keeps the framework of C_{60} well also, which can be confirmed by the ^{13}C NMR spectrum. Except for two sp^3-C peaks that appear at δ 83.22 ppm, all other sp^2-C peaks of C_{60} appear at a closed region of δ 149−140 ppm (Figure 1).

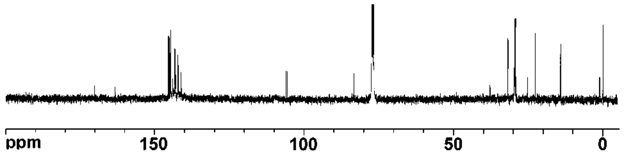


Figure 1. The ^{13}C NMR spectrum of compound **1**.

Our evidence for the formation of hydrogen bonding self-assembly came from ^1H NMR spectroscopic studies. It is well-known that the characteristic of the formation of a three-point hydrogen bonding complex between the uracil and 2,6-diaminopyridine groups is the downfield shifts for their amidic protons.[1,5] Upon complexation of compound **2** by compound **1**, the imide proton signal undergoes a significant downfield shift of several ppm in the NMR titration experiment since the electron densities of the protons involved in H-bonds are decreased and consequently their NMR signals are shifted to lower magnetic fields.[14,15] The association constant of this three-point hydrogen bond is in a range of 300−600 M^{-1}.[5] The interaction of **1** with compound **2** was investigated by ^1H NMR spectroscopic titrations carried out in chloroform-*d*. For the ^1H NMR studies, the concentration of the host was kept constant (3 mM) and the change in the chemical shift was followed as

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(8) Select data for 2-amino-6-lauroylaminopyridine: ^1H NMR ($CDCl_3$, ppm) δ 0.79 (t, $J = 6.6$ Hz, 3H), 1.16 (m, 16H), 1.60 (m, 2H). 2.32 (t, $J = 7.5$ Hz, 2H), 5.42 (bs, 2H, NH_2), 6.30 (d, $J = 7.7$ Hz, 1H), 7.40 (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.7$ Hz, 1H), 8.77 (bs, 1H); ^{13}C NMR ($CDCl_3$, ppm) δ 172.5, 155.1, 147.7, 142.0, 104.6, 102.5, 37.7, 31.9, 29.6, 29.5, 29.3, 29.2, 25.2, 22.7, 14.1; EI-MS 291 (M^+).

(9) Select data for 2-chloroacetanoylamino-6-lauroylaminopyridine: ^1H NMR ($CDCl_3$, ppm) δ 0.90 (t, $J = 6.6$ Hz, 3H), 1.24 (m, 16H), 1.73 (m, 2H). 2.40 (t, $J = 7.5$ Hz, 2H), 4.21 (s, 2H), 7.78 (t, $J = 7.7$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 1H), 7.97 (d, $J = 7.7$ Hz, 1H), 8.83 (bs, 2H); ^{13}C NMR ($CDCl_3$, ppm) δ 171.3, 164.1, 148.3, 146.6, 140.2, 109.2, 108.1, 44.8, 41.7, 36.7, 30.9, 28.6, 28.4, 28.3, 28.1, 24.2, 21.6, 13.1; EI-MS 367 (M^+).

(10) Select data for 2-azidoacetanoylamino-6-lauroylaminopyridine:^1H NMR ($CDCl_3$, ppm) δ 0.91(t, $J = 6.6$ Hz, 3H), 1.25 (m, 16H), 1.72 (m, 2H). 2.38 (t, $J = 7.5$ Hz, 2H), 4.16 (s, 2H), 7.64 (bs, 1H), 7.72 (t, $J = 7.7$ Hz, 1H), 7.95 (d, $J = 7.7$ Hz, 1H), 7.79 (d, $J = 7.7$ Hz, 1H), 8.39 (bs, 1H); ^{13}C NMR ($CDCl_3$, ppm) δ 169.9, 163.1, 147.7, 146.3, 139.2, 108.3, 107.5, 51.0, 35.9, 30.0, 27.7, 27.5, 27.4, 27.3, 27.1, 23.4, 23.2, 20.8, 12.2; EI-MS 346 (M − 28).

(11) Select data for compound **1**: ^1H NMR ($CDCl_3$, ppm) δ 0.87 (t, $J = 6.5$ Hz, 3H), 1.25 (m, 16H), 1.74 (m, 2H). 2.44 (t, $J = 7.4$ Hz, 2H), 4.59 (s, 2H), 7.84 (m, 1H), 8.03 (m, 2H), 9.86 (bs, 2H); ^{13}C NMR ($CDCl_3$, ppm) δ 170.5, 164.3, 145.3, 144.9, 144.8, 144.6, 143.8, 143.2, 142.9, 142.1, 141.6, 106.6, 105.8, 83.3, 37.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 25.3, 22.7, 14.2; MS 1067 (M + 1).

(12) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.

(13) Select data for compound **2**:^1H NMR ($CDCl_3$, ppm) δ 0.88 (t, 6 Hz, 3H), 1.26 (m, 16H), 1.68 (m, 4H), 3.72 (t, 7.4 Hz 2H), 5.70 (d, 8.2 Hz, 1H), 7.14 (d, 8.2 Hz, 1H), 9.11 (bs, 1H); ^{13}C NMR ($CDCl_3$, ppm) δ 163.9, 150.9, 144.5, 102.1, 48.9, 31.9, 29.6 (2C), 29.5, 29.4, 29.3, 29.52, 29.1, 26.4, 22.7, 14.1; FAB-MS 281 (M + 1).

(14) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond: Recent Developments in Theory and Experiments*; North-Holland: Amsterdam, 1976; Vols. 1−3.

(15) Konrat, R.; Tollinger, M.; Kontaxis, G.; Kraufler, B. *Monatsh. Chem.* **1999**, *130*, 961.

a function of increasing guest concentration. The NMR titration experiments reveal a significant downfield shift of the amidic proton signal due to melamine complexation (Figure 2). Therefore, hydrogen-bond-mediated complex formation could be unambiguously demonstrated in chloroform. Specifically, as illustrated in Figure 3, analysis of the downfield shift for the amidic proton as a function of increasing concentration of **1** provided support for a 1:1 binding model and yielded an association constant of K_a = 323 ± 45 M^{-1}.[16] This result showed that hydrogen bonding took place between **1** and **2**, and these assembly motifs exhibit a significantly high stability.

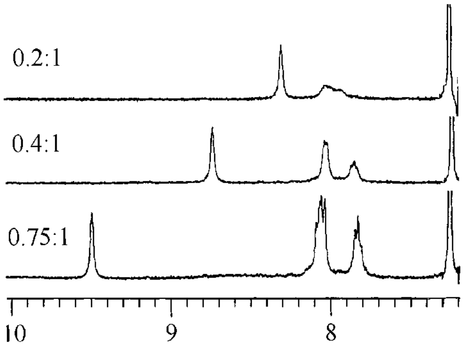

Figure 2. Partial ^{1}H NMR spectra of **1**−**2** supramolecular systems in different concentration ratio in $CDCl_3$ at room temperature.

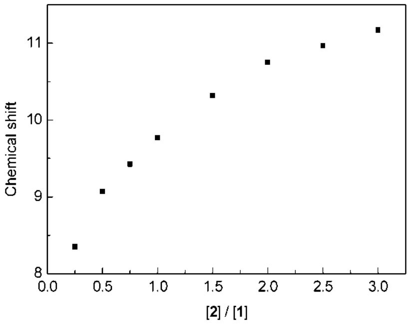

Figure 3. ^{1}H NMR binding isotherm for **1** with **2** in $CDCl_3$ at room temperature. The concentration of **1** was kept constant at 3 mmol/L.

As shown in the UV−vis spectra (Figure 4), the formation of the **1**−**2** supramolecular system lead to an obvious blue shift of compound **2** by 7 nm in chloroform. This change of the small molecule **2** in electronic transition cannot be explained by the formation of hydrogen bonds alone but suggests additional contributions resulting from the influence of the redox-active chromophore of C_{60} through the hydrogen bonds.

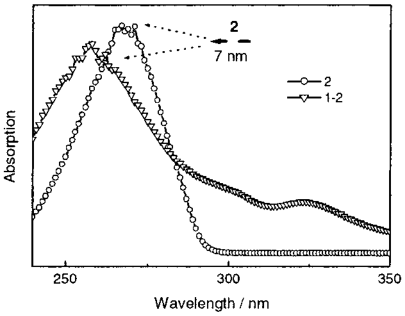

Figure 4. The absorption spectra of the **1**−**2** system in chloroform.

Considering the self-assembling behavior of **1** with **2** in organic solvents, it can be assumed that they will construct three-dimensional superstructures that are stabilized by intermolecular hydrogen bonding through uracil group and 2,6-diaminopyridine moiety and chain interaction. In fact, the self-assembled balls of **1** with **2** could be observed in field emission scanning electron microscopy (FESEM) images. Figure 4 shows the FESEM and the size distribution histograms of the assemblies result from the solutions of the **1**−**2** system in chloroform/hexane (10^{-5} M).

The assemblies formed are in the range of 20−115 nm (the average size is 45 nm) for the **1**−**2** system. The size

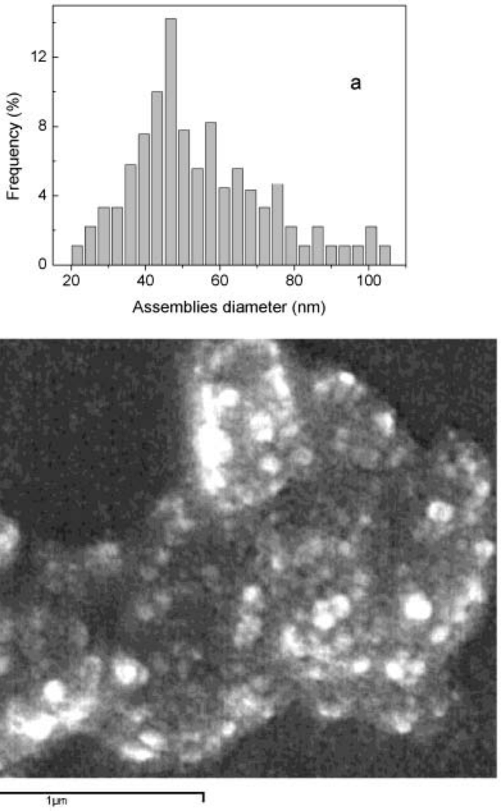

Figure 5. FESEM image and size distribution histogram of assemblies resulting from 10^{-5} M **1**−**2** in chloroform/hexane.

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(16) Král, V.; Furuta, H.; Shreder, K.; Lynch, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 1595.

distribution is broad, showing strong structure factors corresponding to the stacking of forming hydrogen-bond-directed arrangement of **1** with **2**. From the fact that the diameter of the smallest ball in Figure 5 is about 20 nm, we presume that the superstructures of the ballslike assemblies are constructed from the numerous molecules of **1** with **2** by intermolecular hydrogen bonding and $\pi-\pi$ interaction.

In conclusion, the self-assembly of the hydrogen-bonded ball-like structure of a uracil derivative with organofullerene can be used to design new supramolecular systems based on [60]fullerene. The possibility of producing a well-defined supramolecular structure like the ball presented here could be of interest for the construction of three-dimensional nanomaterials for future applications as photoelectric devices.

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