

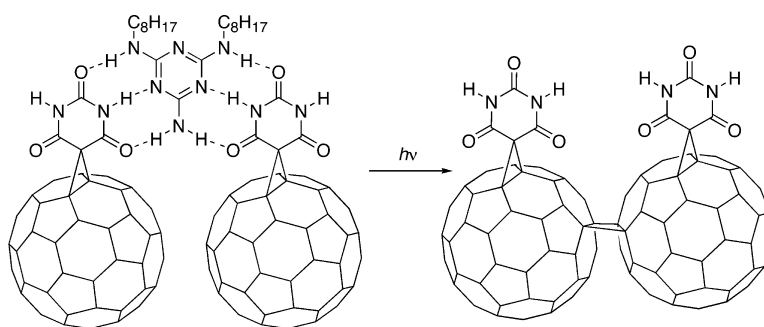
Communication

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Facile Synthesis of a Fullerene-Barbituric Acid Derivative and Supramolecular Catalysis of Its Photoinduced Dimerization

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A major feature of self-assembly processes is that individual components will spontaneously combine in a predetermined fashion due to the presence of complementary molecular recognition sites.¹ Recently, this approach has been applied to the preparation of fullerene-containing materials through the incorporation of complementary hydrogen-bonding (H-B) sites used to assemble individual C₆₀ molecules in an ordered fashion.² Examples of appended recognition elements include the ureidopyrimidinone unit developed by Meijer et al.³ and the 2,6-diacylamidopyridine moiety.^{2d} An important characteristic of these systems is their high self-association constant, which can be used to direct the formation of dimers and homopolymeric species.^{2a-d} However, self-complementarity is a generally undesirable property in self-assembly processes as self-association competes with the formation of multicomponent architectures.⁴ In this regard, the use of non-self-complementary binding sites allows for a wider diversity of architectures to be programmed into the molecular constituents. One such system, based on melamine and barbituric acid, has proven to be a highly versatile approach to assemble 1:1 architectures into closed, rosettelike assemblies, or open tape and crinkled tape structures.⁵

The propensity of C₆₀ to undergo highly efficient photodimerization in the solid but not in solution is reminiscent of other [2+2] photoaddition reactions that are under topochemical control. Juxtaposition of the reactive double bonds within a supramolecular assembly can accelerate the formation of photoproduct upon excitation. We⁶ and others⁷ have shown that the ensuing excited-state reaction proceeds with retention of topology. This strategy should be applicable to the construction of fullerene photodimers and linear polymers, subject to the availability of suitably substituted fullerene derivatives incorporating a melamine or barbiturate H-B element. Although previous reports of such compounds are scarce,⁸ the similarity of barbituric acid to diethylmalonate prompted us to attempt the direct synthesis of **1** via a modified Bingel reaction.⁹

The reaction of C₆₀ with 1 equiv of barbituric acid under modified Bingel conditions (CBr₄, DBU) resulted in the formation of a complex mixture of products. Analysis by APCI-MS revealed the presence of products whose mass and isotopic distribution pattern are consistent with those of dibromo-methanofullerene adducts. We reasoned that these may be formed by the attack of C₆₀ by a dibromocarbene intermediate, formed by the action of DBU on bromoform (a byproduct of the initial bromination of the active methylene group in barbituric acid), or from CBr₄. This suggested that use of the 5-bromobarbituric acid intermediate may circumvent the formation of fulleroid side products. Under the reaction conditions described in Figure 1, HPLC analysis of the reaction mixture revealed the formation of only one product, whose characterization is consistent with the proposed structure.

The preparation of compound **1** is remarkable in that it introduces, in one step, the six hydrogen-bonding sites present in barbituric acid. These sites are non-self-complementary, and their

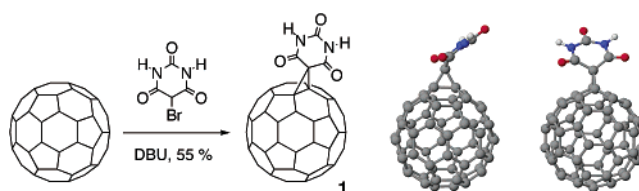


Figure 1. A one-step synthesis allows the efficient preparation of a fullerene derivative bearing a non-self-complementary hydrogen-bonding motif. Molecular modeling of **1** (PM3) shows the barbiturate moiety to be bent from the normal of the C₆₀ surface by ca. 45°.

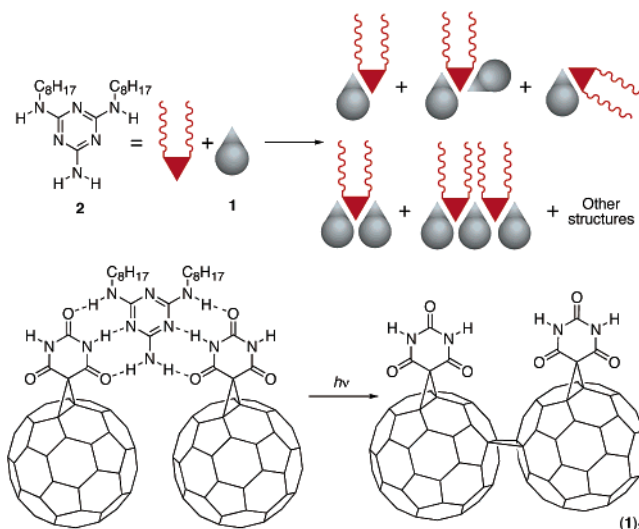


Figure 2. In the presence of the complementary melamine derivative **2**, a variety of supramolecular species incorporating **1** can be formed in solution. Efficient cyclodimerization is expected upon irradiation of assemblies in which two fullerene moieties are adjacent (bottom).

spatial arrangement makes **1** well-suited for the construction of fullerene-containing architectures. As compared to previous multistep syntheses of C₆₀ appended with molecular recognition units, the preparation of **1** is straightforward and paves the way for the construction of diverse supramolecular fullerene assemblies. Because a great deal of work has been done on the study of both biological and synthetic barbiturate receptors, the design of new architectures using **1** is greatly facilitated.

Molecular modeling of **1** (PM3 calculations, Figure 1) reveals that the plane of the barbiturate moiety is offset from the normal of the C₆₀ sphere by ca. 45° due to nonbonded interactions between the carbonyl groups in the 4 and 6 positions and the fullerene. The symmetry of **1** is thus lowered to C_v, a fact reflected in the ¹³C NMR spectrum. The same observation has been reported by Lamparth et al.^{8b} for an analogous N-alkylated fullerene-barbituric acid derivative. The structural rigidity of **1** is a result of the cyclopropane ring linking C₆₀ and barbiturate moieties. Unlike the

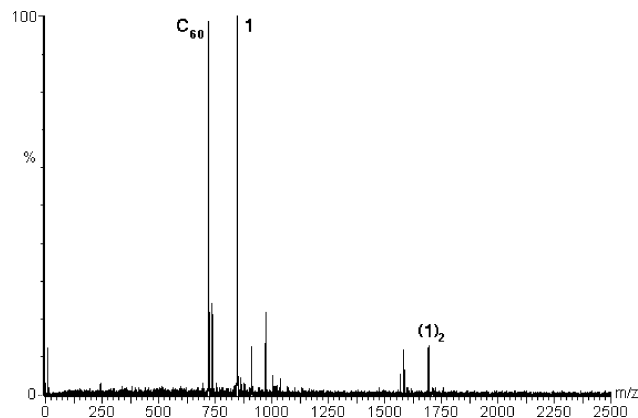


Figure 3. MALDI-TOF spectrum of 1:1 solutions of **1** and **2** after short irradiation times. Peaks at 720 (C_{60}) and 1566 correspond to the loss of a barbiturate moiety from **1** and $(1)_2$, respectively.

use of flexible tethers, this presents the advantage of precisely positioning the two components within a supramolecular architecture. This is of considerable importance for the interpretation of photophysical measurements in photoactive assemblies, such as electron and energy transfer processes, which are orientation- and distance-dependent phenomena.

Our previous work on the supramolecular catalysis of photoinduced [2+2] cycloadditions led us to believe that the photodimerization of **1** might be similarly enhanced. In the presence of the complementary melamine derivative, several 1:1 and 2:1 complexes may be formed, one of which places two fullerene units in close proximity. Irradiation of such an assembly is expected to lead to efficient photodimerization, as illustrated in Figure 2. Although the magnitude of the binding constants in these systems is generally insufficient for the formation of larger tape-like structures, stepwise dimerization may provide a supramolecular route to the formation of the elusive linear fulleropolymer structures.

Irradiation of dilute (5×10^{-4} M) solutions of **1** and a 1:1 mixture of **1** and **2** in degassed *o*-dichlorobenzene (*o*-DCB) resulted in the gradual disappearance of **1** as judged by HPLC analysis. The irradiated solutions were then analyzed by MALDI-TOF MS using elemental sulfur as the matrix.¹⁰ Typical results are shown in Figure 3, where it can be seen that in the case of samples containing the melamine template, a clear signal for the $(1)_2$ dimer is observed. The formation of H-B structures between **1** and **2** is supported by the fact that in the absence of **2**, a small amount of DMSO is required to completely dissolve **1** in hydrocarbon solvents such as *o*-DCB. In the absence of **2**, no signals corresponding to the formation of either C_{60} dimer or $(1)_2$ could be detected by MALDI-TOF MS under identical irradiation conditions. However, it is interesting to note that a small dimer signal is observed in the MS spectrum of the **1** + **2** mixtures even in the absence of prior irradiation (control experiments). We believe that this results from photoinduced dimerization upon desorption/ionization using the N_2 laser ($\lambda_{\text{irr}} = 337$ nm) and points to the formation of H-B tape structures in the solid. No such signal is observed in the absence of **2**.

To date, the photoinduced dimerization (or polymerization) of fullerene has been limited to the irradiation of solid samples¹¹ and microheterogeneous suspensions.¹² The first homogeneous example reported involves the intramolecular dimerization of a linked bisfullerene derivative,¹³ whose structure is similar to that achieved supramolecularly in the 1:2 complex formed between the melamine template and two molecules of **1**. To the best of our knowledge, this represents the first example of intermolecular photodimerization of a fullerene derivative in solution.

Prolonged irradiation of **1** in the presence of **2** is expected to lead to the formation of fullerene polymer structures. Unfortunately, although this leads to complete consumption of **1**, no signals corresponding to the formation of extended polyfullerene structures are identifiable by MS. However, heating (refluxing *o*-DCB, 5 min) the irradiated solutions does result in the formation of **1** and C_{60} , a behavior that is often associated with thermal scission of poly(fullerene) structures of this type. Further work on the unambiguous identification of the adducts formed upon irradiation is in progress.

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Supporting Information Available: Synthesis of **1**, its characterization (1H and ^{13}C NMR, HRMS, HPLC), and details of irradiation experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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