

## A New exTTF-Crown Ether Platform To Associate Fullerenes: Cooperative $n-\pi$ and $\pi-\pi$ Effects

Bruno Grimm,<sup>†</sup> José Santos,<sup>‡</sup> Beatriz M. Illescas,<sup>‡</sup> Antonio Muñoz,<sup>‡</sup> Dirk M. Guldi,<sup>\*,†</sup> and Nazario Martín<sup>\*,‡,§</sup>

*Institute of Physical and Theoretical Chemistry and Interdisciplinary Center for Molecular Materials, University of Erlangen, 91058 Erlangen, Germany, Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain, and Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Campus UAM, Cantoblanco, E-28049 Madrid, Spain*

Received September 28, 2010; E-mail: dirk.guldi@chemie.uni-erlangen.de; nazmar@quim.ucm.es

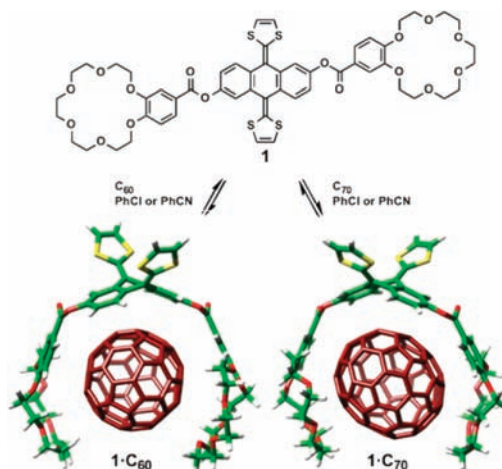
**Abstract:** A new and readily available exTTF-bis(crown ether), **1**, efficiently recognizes  $C_{60}$  as well as  $C_{70}$  by means of cooperative  $\pi-\pi$  and  $n-\pi$  interactions. The geometrical (concave–convex) and electronic (donor–acceptor) complementarity accounts on one hand for remarkable binding strengths, with association constants reaching  $10^7 M^{-1}$  in benzonitrile, and on the other hand for lifetimes of the photogenerated radical ion pair state on the order of 45 ps.

Energy- and electron-transfer processes in supramolecular electron donor–acceptor nanohybrids offer important incentives for designing efficient electron-transfer mimics of the photosynthetic apparatus and for constructing artificial devices, namely, photovoltaic cells.<sup>1</sup> To this end, nanohybrids of fullerenes (as electron acceptors) with porphyrins,<sup>2</sup> tetrathiafulvalenes (TTFs),<sup>3</sup> phthalocyanines,<sup>4</sup> and ferrocenes or oligomers<sup>5</sup> (as electron donors) have been widely studied. On the other hand, we have focused on exploring 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) as a template to realize a variety of supramolecular nanohybrids with  $C_{60}$  and/or  $C_{70}$ . For example, we have exploited both hydrogen bonding in preorganized systems with ammonium crown ether recognition motifs<sup>6</sup> and  $\pi-\pi$  interactions making use of the match between the concave aromatic surface of exTTF and the convex surface of fullerenes.<sup>7</sup> Whereas systems that are based purely on  $\pi-\pi$  interactions require at least two exTTF groups to form stable complexes with fullerenes, 1:1 complexes (exTTF· $C_{60}$ ) could be obtained by introducing single ammonium crown ethers. Recently, we reported the formation of room-temperature-stable supramolecular complexes with a 1:1 stoichiometry, exTTF· $C_{60}$  (association constant  $K_a \approx 1.6 \times 10^6$  in chlorobenzene), employing the cooperativity between hydrogen bonding and  $\pi-\pi$  interactions.<sup>6c</sup>

The first-ever reported molecular receptor for fullerenes consisted of aza-crown ethers carrying suitable alkyl chains on the nitrogens.<sup>8</sup> Ample evidence suggests the involvement of electron-transfer processes with either  $C_{60}$  or  $C_{70}$ .<sup>9</sup>

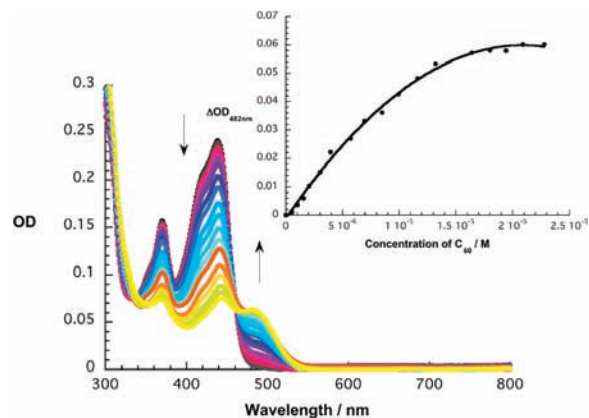
In the current work, we designed exTTF-bis(crown ether) **1**, a new exTTF platform for binding  $C_{60}$  and  $C_{70}$ , by means of introducing two crown ethers as recognition motifs to optimize the complex stability (Scheme 1). **1** was synthesized by esterification of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-2,6-diol<sup>10</sup> with the carboxylic acid of benzo-18-crown-6. Complete charac-

**Scheme 1.** exTTF-bis(crown ether) **1** and Its Complexes with  $C_{60}$  and  $C_{70}$



terization of **1** was performed using standard spectroscopic and analytical techniques (see the Supporting Information).

We started with absorption assays in which  $1.4 \times 10^{-5} M$  solutions of **1** were titrated against variable concentrations of  $C_{60}$  (i.e., 0 to  $2.2 \times 10^{-5} M$ ), giving rise to a rapidly formed charge-transfer complex. An illustration thereof is shown in Figure 1. During the titration, the evolution of a new broad transition at 480



**Figure 1.** Absorption spectra of a dilute benzonitrile solution of **1** ( $1.4 \times 10^{-5} M$ ) with variable concentrations of  $C_{60}$  (0,  $5.3 \times 10^{-7}$ ,  $1.0 \times 10^{-6}$ ,  $1.55 \times 10^{-6}$ ,  $2.0 \times 10^{-6}$ ,  $3.0 \times 10^{-6}$ ,  $4.0 \times 10^{-6}$ ,  $5.7 \times 10^{-6}$ ,  $6.9 \times 10^{-6}$ ,  $8.5 \times 10^{-6}$ ,  $9.9 \times 10^{-6}$ ,  $1.2 \times 10^{-5}$ ,  $1.3 \times 10^{-5}$ ,  $1.5 \times 10^{-5}$ ,  $1.6 \times 10^{-5}$ ,  $1.8 \times 10^{-5}$ ,  $1.9 \times 10^{-5}$ ,  $2.1 \times 10^{-5}$ , and  $2.3 \times 10^{-5} M$ ). Arrows indicate the progression of the titration. The inset shows the binding isotherm.

<sup>†</sup> University of Erlangen.

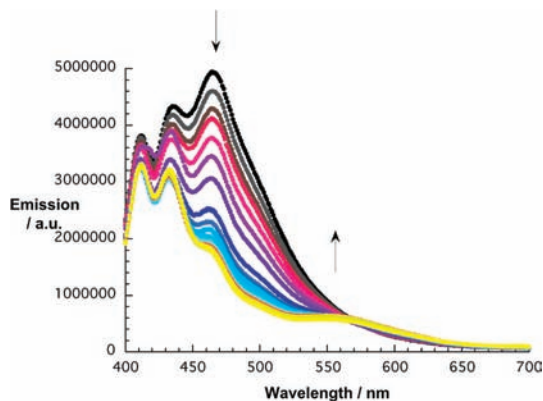
<sup>‡</sup> Universidad Complutense.

<sup>§</sup> Instituto Madrileño de Estudios Avanzados en Nanociencia.

nm in benzonitrile at the expense of the 438 nm absorption maximum of exTTF was observed, along with a low-energy isosbestic point around 460 nm. The latter revealed a considerable hypsochromic shift in going from polar benzonitrile to less polar chlorobenzene, where the isosbestic point was found to be at 453 nm. Hypsochromic shifts were also noted for the maximum, which was found to be at 488 nm in benzonitrile, while in chlorobenzene it appeared at 480 nm. It is notable, however, that the absorption maximum of exTTF was not affected by the solvent change. The fact that the corresponding maxima tend to be blue-shifted with decreasing solvent polarity leads us to postulate a redistribution of charge density from the electron-donating exTTF moiety to the electron-accepting  $C_{60}$ , affording  $C_{60}^{\delta-}/\text{exTTF}^{\delta+}$ .

Treating the absorption changes at 450 nm for  $1 \cdot C_{60}$  in the concentration range from 0 to  $2.3 \times 10^{-5}$  M with an exponential fitting function allowed the association constant,  $K_a$ , to be calculated. Good fits to the data were observed when the formation of a 1:1 complex was assumed. In fact, the Job's plot confirmed the 1:1 stoichiometry. With this assumption, a  $K_a$  value of  $5.00 \times 10^6 \text{ M}^{-1}$  was calculated for the formation of  $1 \cdot C_{60}$  in benzonitrile. In chlorobenzene, where the charge-transfer band evolves at 478 nm, the  $K_a$  value was determined to be  $5.01 \times 10^6 \text{ M}^{-1}$  (see the Supporting Information).

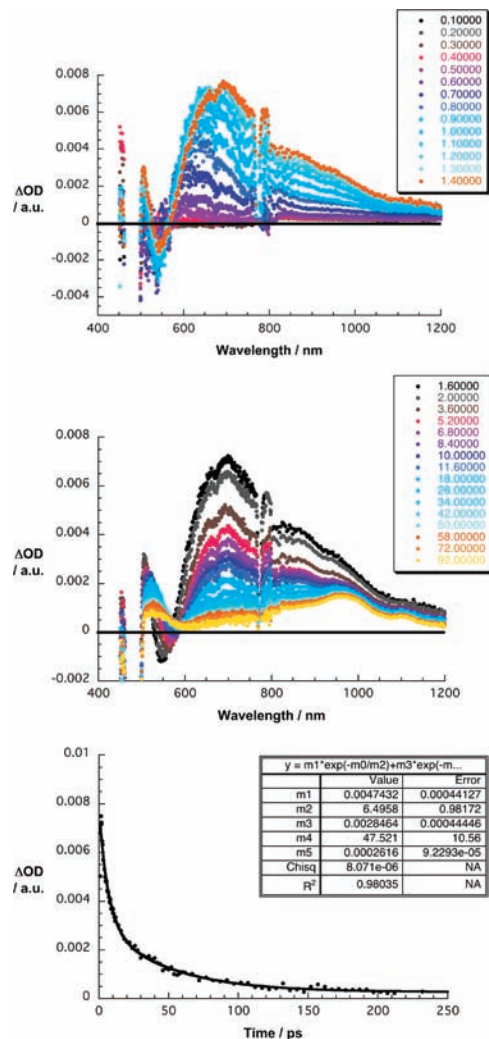
Notably, these  $K_a$  values are among the highest reported for the complexation of  $C_{60}$ .<sup>7,11,12</sup> It is important to note that **1** features only a single exTTF, in sharp contrast to recent work on molecular tweezers with two or more exTTFs. In addition,  $10^6 \text{ M}^{-1}$  is comparable to values realized with highly preorganized exTTF architectures.<sup>7f</sup> In fact, performing analogous absorption assays with  $C_{70}$  instead of  $C_{60}$  (Figure S1 in the Supporting Information) afforded a  $K_a$  value of  $2.57 \times 10^7 \text{ M}^{-1}$  for  $1 \cdot C_{70}$  in benzonitrile.



**Figure 2.** Emission spectra upon 450 nm excitation of a dilute benzonitrile solution of **1** ( $1.4 \times 10^{-5}$  M) with variable concentrations of  $C_{60}$  (0,  $5.3 \times 10^{-7}$ ,  $1.0 \times 10^{-6}$ ,  $1.55 \times 10^{-6}$ ,  $2.0 \times 10^{-6}$ ,  $3.0 \times 10^{-6}$ ,  $4.0 \times 10^{-6}$ ,  $5.7 \times 10^{-6}$ ,  $6.9 \times 10^{-6}$ ,  $8.5 \times 10^{-6}$ ,  $9.9 \times 10^{-6}$ ,  $1.2 \times 10^{-5}$ ,  $1.3 \times 10^{-5}$ ,  $1.5 \times 10^{-5}$ ,  $1.6 \times 10^{-5}$ ,  $1.8 \times 10^{-5}$ ,  $1.9 \times 10^{-5}$ ,  $2.1 \times 10^{-5}$ , and  $2.3 \times 10^{-5}$  M). Arrows indicate the progression of the titration.

Figure 2 and Figure S4 document that fluorescence assays, as a complement to the above absorption assays, confirmed mutual interactions between the electron-donating exTTF and the electron-accepting  $C_{60}$  and  $C_{70}$  in  $1 \cdot C_{60}$  and  $1 \cdot C_{70}$ , respectively. As in the absorption assays, the exTTF-centered excited-state features of **1** at 470 nm decreased in the presence of increasing  $C_{60}$  concentrations concomitantly with the rise of a new feature centered around 550 nm. Again we conclude that charge transfer is responsible for the emissive features. Notable is the mirror image between charge-transfer absorption and charge-transfer emission. For  $1 \cdot C_{60}$ , the  $C_{60}^{\delta-}/\text{exTTF}^{\delta+}$  features were discernible in nonpolar as well as polar

solvents with emission quantum yields of  $\sim 10^{-3}$  and emission lifetimes shorter than our time resolution of 100 ps. Interestingly, a fairly large red shift of  $\sim 35$  nm (515 nm in chlorobenzene to 550 nm in benzonitrile) reflects a significant change in solvent stabilization of the charge-transfer state.



**Figure 3.** (top) Differential absorption spectra (visible and near-IR) obtained upon femtosecond flash photolysis (480 nm) of  $1 \cdot C_{60}$  in benzonitrile with time delays between 0.1 and 1.4 ps at room temperature. (middle) Differential absorption spectra (visible and near-IR) obtained upon femtosecond flash photolysis (480 nm) of  $1 \cdot C_{60}$  in benzonitrile with time delays between 1.6 and 92 ps at room temperature. (bottom) Time-absorption profile at 684 nm, reflecting the transformation of  $C_{60}^{\delta-}/\text{exTTF}^{\delta+}$  into the fully charge-separated  $C_{60}^{\delta-}/\text{exTTF}^{\delta+}$  state and the charge-recombination dynamics.

The gradual quenching of the steady-state fluorescence intensity of **1** was used to quantify the association between **1** and  $C_{60}$  or  $C_{70}$ . Emission intensity data collected at 680 nm were plotted versus the concentration of  $C_{60}$  or  $C_{70}$ , and nonlinear curve fitting allowed the association constant for the formation of  $1 \cdot C_{60}$  in benzonitrile to be estimated as  $2.2 \times 10^5 \text{ M}^{-1}$ . The corresponding  $K_a$  value for  $1 \cdot C_{70}$  is  $9.44 \times 10^6 \text{ M}^{-1}$ .

In transient absorption measurements with **1**, only one transient evolved. This excited state transient was centered on exTTF and appeared simultaneously with the conclusion of the 387 nm laser pulse. Spectral characteristics of this very short lived excited state (1.2 ps) included transient maxima around 465, 605, and 990 nm as well as transient bleaching at <450 nm. The short lifetime is

rationalized by the presence of the sulfur atoms, which give rise to strong second-order vibronic spin-orbit coupling.

The differential absorption changes measured immediately after excitation of C<sub>60</sub> or C<sub>70</sub> at 387 nm showed the instantaneous transformation of high-lying singlet excited states into the lowest vibrational state of the singlet excited state of C<sub>60</sub> or C<sub>70</sub>. In particular, marked transitions developed in the near-IR region with maxima at 960 nm (C<sub>60</sub>) and 890 nm (C<sub>70</sub>). These singlet excited states with energies of ~1.80 eV deactivated slowly via intersystem crossing to the energetically lower-lying triplet excited states. The lifetime of intersystem crossing was determined from a multiwavelength analysis to be 1.6 ns. The newly developing bands at 750 or 970 nm reflect the diagnostic signature of the triplet excited state of C<sub>60</sub> or C<sub>70</sub>, respectively, with lifetimes of ~45 μs.

Figure 3 shows the differential absorption changes obtained upon photoexcitation of 1•C<sub>60</sub> in benzonitrile into the charge-transfer bands at 480 nm. The spectral features clearly reveal the instantaneous (>1 ps) formation of photoexcited C<sub>60</sub><sup>δ-</sup>/exTTF<sup>δ+</sup>, with features that include a sharp minimum at 540 nm followed by maxima at 648, 950, and 1120 nm. In this context, the lack of ground state absorption of 1 at the 480 nm excitation wavelength on one hand and the significant differences relative to those seen upon excitation of C<sub>60</sub> on the other hand should be noted. The instantaneous appearance of the C<sub>60</sub><sup>δ-</sup>/exTTF<sup>δ+</sup> state further confirms the intimate interactions in 1•C<sub>60</sub>. The latter is, however, short-lived and transforms within 6.5 ps into the fully charge-separated C<sub>60</sub><sup>-</sup>/exTTF<sup>+</sup> state. In particular, the transient centering at ~695 nm relates to the one-electron-oxidized radical cation of the tweezer, in accordance with previous photolytic and radiolytic studies.<sup>13</sup> The one-electron-reduced radical anion of C<sub>60</sub>, on the other hand, shows up in the near-IR (i.e., 1100 nm). The lifetime of the charge-separated state, as determined from a multiwavelength analysis (i.e., decay at 695, 950, and 1100 nm), was very short (45 ps). Products of the charge recombination are the energetically lower-lying C<sub>60</sub> singlet excited state and C<sub>60</sub> triplet excited state, as identified by maxima at 960 and 750 nm, respectively.<sup>14,15</sup>

In summary, exTTF-bis(crown ether) 1, a new exTTF platform with a concave geometry, very efficiently recognizes C<sub>60</sub> and C<sub>70</sub>. The resulting association constants, which were determined both by absorption and fluorescence titrations, are as high as 10<sup>7</sup> M<sup>-1</sup> in benzonitrile and thus are among the highest ever reported for fullerenes. These values are particularly remarkable in view of the low degree of preorganization in 1 and the presence of a single exTTF. We attribute the stability of 1•C<sub>60</sub> and 1•C<sub>70</sub> to cooperative effects stemming from π-π and n-π interactions.<sup>16</sup> The latter should be considered as one of the most efficient means for binding these carbon allotropes.

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**Supporting Information Available:** Experimental details and Figures S1–S5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Upon excitation at 387 nm, the locally exTTF excited state transforms into the same C<sub>60</sub><sup>-</sup>/exTTF<sup>+</sup> charge-separated state seen in the aforementioned 480 nm excitation experiments.
- (15) For 1•C<sub>70</sub>, the corresponding C<sub>70</sub><sup>-</sup>/exTTF<sup>+</sup> charge-separated state [with a signature of the one-electron-reduced radical anion of C<sub>70</sub> at 1290 nm (Figure S5)] decays with a lifetime of 77 ps in benzonitrile.
- (16) In a control experiment carried out using the same exTTF without crown ethers, no significant changes were found in the electronic spectra of pristine exTTF (chlorobenzene, 298 K, 4.09 × 10<sup>-5</sup> M) upon addition of C<sub>60</sub> (chlorobenzene, 298 K, 4.05 × 10<sup>-3</sup> M). See ref 7a.

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