Cooperativity between π–π and H-bonding interactions–a supramolecular complex formed by C_{60} and exTTF†

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A highly stable supramolecular complex from C_{60} and exTTF ($K_a \approx 10^6$ M^{-1}) has been achieved by means of π–π and H-bonding interactions; experimental evidence reveals the formation of a radical–ion pair (τ = 9.3 ps) upon photoexcitation.

The strong electron donating character of 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF) has drawn interdisciplinary interest in the fields of non-linear optics,[1] self-assembled monolayers,[2] and photovoltaics.[3] Its peculiar shape, that is, a highly distorted geometry, in which exTTF adopts a butterfly-shape configuration, has resulted in the formation of electrically conducting charge transfer complexes.[4]

It is only recently that the geometrical properties of this ditopic molecule have been employed to form supramolecular complexes with geometrically and electronically complementary convex surfaces such as fullerenes.[5] Still, attempts to form supramolecular complexes (C_{60}–exTTF) have been unsuccessful.[6] Molecular tweezers, on the other hand, where two exTTF units are linked through isophthalic ester moieties emerged as powerful complexing agents that give rise to binding constants (K_a) in the range of 3–8 × 10^3 M^{-1}.[7]

In an attempt to form 1 : 1 complexes[8] (exTTF:C_{60}) we implemented a strategy of pre-organizing the interacting exTTF and C_{60} components. In particular, ammonium–crown ether recognition motifs have been chosen. Threading ammonium salts through crown ethers is governed by binding constants (K_a) that are typically on the order of $\sim 10^3$ M^{-1} ($CDCl_3$).[9]

We wish to report on the preparation and characterization of very stable supramolecular complexes utilizing the cooperativity between H-bonds and π–π interactions as two disparate recognition motifs.

The key building blocks, namely **1** and **2**, prepared for the synthesis of supramolecular complex **3** are shown in Chart 1. Compound **1**, which is derived from exTTF, was prepared from hydroxymethyl-exTTF by following the procedures previously reported in the literature.[10] Incorporation of the benzo-18-crown-6 macrocycle (B18C6) to give exTTF derivative **1** was carried out by an esterification reaction with a B18C6 carboxylic acid derivative.[11] Using *N*,*N*′-dicyclohexylcarbodiimide (DCC) in dichloromethane, in the presence of 4-dimethylaminopyridine (DMAP), afforded compound **1** in moderate yields. On the other hand, fullerene derivative **2** bearing a benzylammonium group has been previously used for complexing fullerenes by a porphyrin derivative endowed with a crown ether—forming a supramolecular porphyrin:C_{60} dyad.[12]

Threading the fullerene-containing benzylammonium unit (**2**) through the B18C6 macrocycle bearing the exTTF unit afforded the donor–acceptor pseudorotaxane-like supramolecular complex **3**.

Evidence in favor of complexing **1** and **2** to form **3** was obtained from absorption assays in different solvents. In the absorption spectra we see, for example, when titrating **1** (1.41 × 10^{-5} M) with variable amounts of **2** (0, 0.41, 0.78, 1.27, 1.71, 2.22, 2.65, 3.21, 3.67 and 4.05 × 10^{-5} M) the formation of a new absorption band that is broad and that ranges from 470 nm to 600 nm. Fig. 1 documents the spectral changes in chlorobenzene at ambient temperature. Concomitant with this newly formed absorption, we see the exTTF absorptions that maximize around 440 nm fading. Implicit is a charge transfer absorption band, whose formation has been

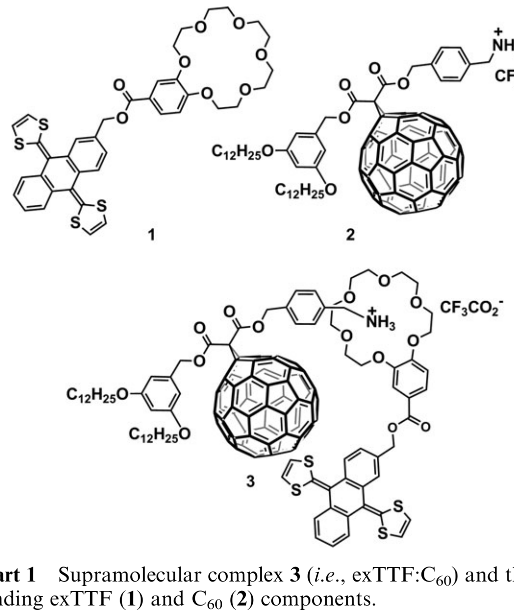

Chart 1 Supramolecular complex **3** (*i.e.*, exTTF:C_{60}) and the corresponding exTTF (**1**) and C_{60} (**2**) components.

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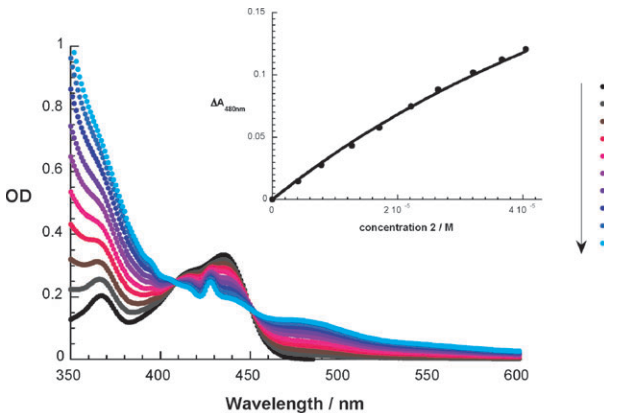

Fig. 1 Absorption spectral changes of **1** (1.41×10^{-5} M, chlorobenzene, 298 K) upon addition of fullerene **2** (0, 0.41, 0.78, 1.27, 1.71, 2.22, 2.65, 3.21, 3.67 and 4.05×10^{-5} M—see arrow/color code). Inset displays the absorption changes at 480 nm as a function of fullerene concentration.

facilitated through the initial hydrogen bonding interactions. A similar behavior is seen when to a fixed concentration of **2** (4.47×10^{-6} M) several concentrations of **1** (0, 0.17, 0.34, 0.50, 0.65, 0.79, 0.93, 1.19, 1.43, 1.65, 1.85, 2.22×10^{-5} M) were added. Again, the same charge transfer bands develop.

The appearance of an isosbestic point at 449 nm suggests a 1 : 1 stoichiometry, which was confirmed by Job plot analysis (see ESI†). The variation in absorption at 431 nm fits best to a 1 : 1 binding isotherm (Fig. 1, inset) affording a binding constant of $(1.58 \pm 0.82) \times 10^6$ M^{-1} in chlorobenzene. Interestingly, the formation of supramolecular complex **3** in chloroform as solvent was quite similar with a binding constant of $K_a = (2.01 \pm 0.79) \times 10^6$ M^{-1} (see ESI†).

Cyclic voltammetric studies, carried out in dichloromethane at room temperature, also support the formation of **3**. The oxidation potential values, as determined for exTTF (**1**), are, for example, anodically shifted by nearly 100 mV (*i.e.*, **1**: $E^{1,\mathrm{ox}} = 0.19$ V; **3**: $E^{1,\mathrm{ox}} = 0.29$ V) upon complexing the fullerene containing ammonium salt (**2**)—see Fig. 2. While this shift is significant, weaker changes are noted when inspecting the fullerene reduction: **2**: −0.84, −1.23, −1.68, −1.86 V; **3**: −0.83, −1.23, −1.67, −1.84 V. Please note that in this respect the delocalization of charges is a key factor in suppressing the potential shift.

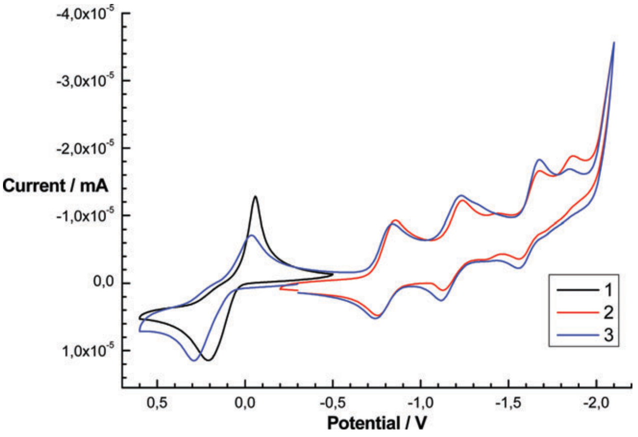

Fig. 2 Cyclic voltammograms of **1**, **2** and **3** in CH_2Cl_2 using $n\mathrm{Bu_4NClO_4}$ as supporting electrolyte, $Ag/AgNO_3$ as reference electrode, and glassy carbon as working electrode. Scan rate: 100 mV s^{-1}.

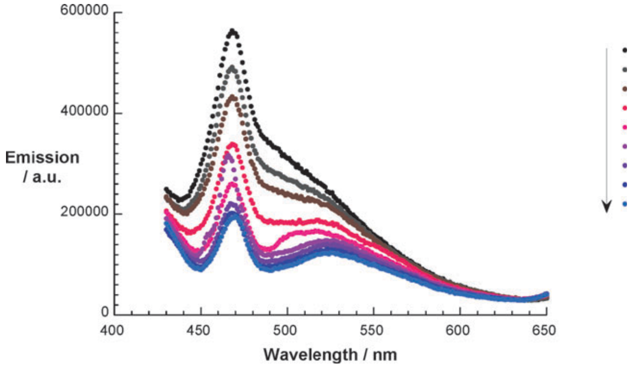

Fig. 3 Fluorescence spectral changes ($\lambda_{\mathrm{exc}} = 410$ nm) of **1** (298 K, chlorobenzene, 1.41×10^{-5} M) upon addition of different amounts of **2** (0.4, 0.5, 0.6, 0.7, 0.9, 1.0, 1.2, 1.3 and 1.4×10^{-4} M—see arrow/color code).

As a complement to the absorption experiments, we turned to fluorescence experiments. In this context, two different objectives were pursued. Firstly, to confirm the charge transfer features and, secondly, to follow the intrinsic emission features of C_{60}. Indeed, mirror image to the charge transfer absorptions, charge transfer emissions—Fig. 3—evolve at around 526 nm when photoexciting at 410 nm. Considering the energetic positions of both features we derive an energy of about 2.46 eV. These are, like in previous instances, solvent dependent, since these charge transfer features are susceptible to solvent assisted stabilization and destabilization in more polar and less polar solvents, respectively.

For example, switching to more polar solvents exerts a notable red shift. Interactions with the electron donating exTTF of **2** lead also to a concentration dependent quenching of the C_{60} centered fluorescence—see Fig. S4.† Implicit is a deactivation that involves either electron transfer and/or energy transfer quenching. The exponential quenching was further used to determine the association constant of 8.23×10^5 M^{-1} by assuming a charge transfer stoichiometry of 1 : 1.

Interestingly, when looking at the binding constants that were derived for the newly formed electron donor–acceptor hybrid we postulate the following conclusions: π–π and charge transfer interactions are by far the dominating contribution, while hydrogen bonding interactions with a maximum strength of 10^3 M^{-1} play a secondary role in the overall interactions between exTTF and C_{60}. In other words, K_a is increased by three orders of magnitude relative to the values found for the complexation of the same ammonium cation with other crown ether derivatives lacking the exTTF unit. This is also reflected in the tied charge transfer interactions, which lead to a rapid charge recombination, once the radical–ion pair state is formed—*vide infra*. Threading the benzylammonium salt (**2**) through the crown ether in **1** facilitates the close proximity of the exTTF unit to the C_{60} moiety by π–π interaction between the benzene rings of the exTTF unit and the fullerene sphere,[13] similarly to that previously observed in the related tweezers and other related analogues.[14]

Finally, we turned to time resolved transient absorption spectroscopy with the newly formed electron donor–acceptor hybrid and the individual components. Again, we pursued two

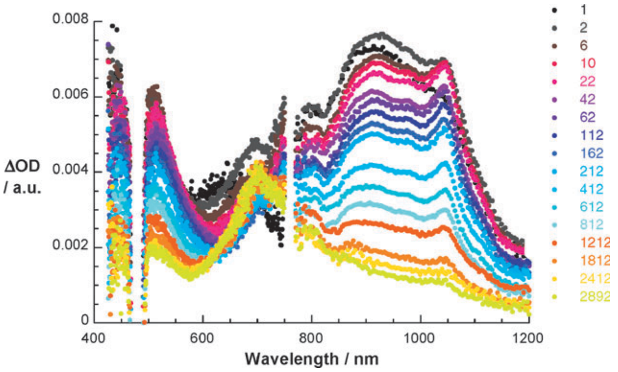

Fig. 4 Transient absorption spectra of **1** (9.6×10^{-5} M) and **2** (4.8×10^{-4} M) in Ar-saturated chlorobenzene upon femtosecond flash photolysis (λ_{exc} = 480 nm) at different time delays between 1 ps and 2532 ps—see legend for details.

complementary sets of experiments. The first set focused on the direct excitation of the charge transfer features. Here we used 480 nm as the excitation wavelength. Due to the lack of exTTF and C_{60} absorptions—at least within the chosen concentration range—no appreciable transient was seen for the individual components, that is, **1** and **2**. Excitation at 387 nm, on the other hand, reaches mainly the C_{60} absorptions (*i.e.*, 387 nm). Importantly, 480 nm excitation leads to the instantaneous formation of features in the visible and near-infrared range with maxima at 698 nm and 1043 nm, respectively. Their close resemblance with photolytically, radiolytically and spectroelectrochemically generated one electron reduced C_{60} radical anion and one electron oxidized exTTF radical cation helped in the spectroscopic identification of the photoproduct.[15] Taking this into consideration, we conclude the successful formation of the radical–ion pair state. The time-absorption profiles also corroborate that the radical–ion pair state is meta-stable, namely, decaying with a lifetime of 9.3 ps in chlorobenzene.

Quite different is the picture when exciting at 387 nm. Initially, the transient spectra are dominated by the C_{60} centered singlet excited state features. Although they decay rather rapidly, it is, however, only that fraction that is associated with exTTF that gives rise to these marked changes. Concomitant with the fast decay, characteristic changes evolve in the differential absorption spectrum. Similar to what is illustrated in Fig. 4, the singlet excited state features (*i.e.*, maxima at 550 and 870 nm) transform over the course of 400 ps into a new set of maxima, which evolve in the visible region (*i.e.*, 645 nm) as well as in the near-infrared region (*i.e.*, 1043 nm). On the contrary, the fraction of C_{60} that is not associated or complexed with the electron donating exTTF intersystem crosses (*i.e.*, 1.4 ns)—like in reference experiments—to the corresponding triplet manifold. The latter process is nearly quantitative and accompanied by strong changes in the absorption spectrum—a new transient maximum at 720 nm that is stable even on the microsecond time scale.

In summary, formation of a highly stable supramolecular complex ($K_a \approx 10^6$ M^{-1} in chlorobenzene or chloroform) between C_{60} and the strong electron donor exTTF has been achieved by pre-organizing the two electroactive species through an ammonium–crown ether recognition motif. Spectroscopic and electrochemical evidences reveal the electronic communication between the exTTF and C_{60} units in the ground state, due to π–π interactions between both units. Photophysical measurements show the photoinduced generation of a charge separated state with a short lifetime (9.3 ps in chlorobenzene), thus mimicking the photosynthetic process.

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