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COMMUNICATION

Balancing binding strength and charge transfer lifetime in supramolecular associates of fullerenes†‡§

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A macrocyclic exTTF host for fullerenes offers control over the electronic coupling between an electron donor and an acceptor, and stabilizes the charge separated state lifetimes into the range of 500 ps.

Investigation on the association of fullerenes by synthetic hosts started immediately after the former became available in gram quantities.[1] Among the various fullerene hosts described to date, macrocyclic structures have proven particularly effective in terms of both affinity and selectivity.[2] Following this strategy, some of us have recently reported macrocyclic bis-exTTF hosts (Fig. 1) capable of associating C_{60} and/or C_{70} with affinities as high as micromolar.[3] These macrocyclic hosts have been designed as an evolution of our exTTF-tweezers.[4] Importantly, the alkyl linker provides the necessary means for preorganization and serves as a source of positive van der Waals interactions. To this end, among the macrocyclic hosts we have investigated,[3] **1** reveals by far the best performance in terms of hosting C_{60}.[3a]

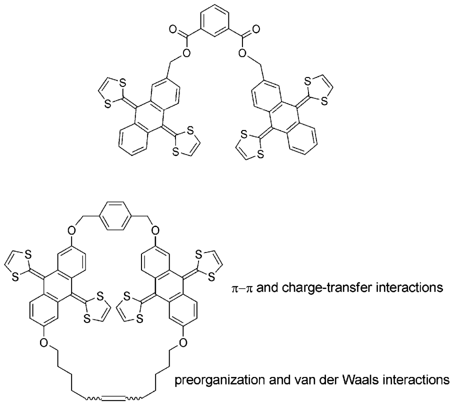

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Fig. 1 Structures of exTTF-tweezers and exTTF-macrocycle **1**.

We have previously demonstrated that upon light irradiation of our tweezers-like host–guest systems, fully charge-separated $C_{60}^{\bullet-}$/exTTF$^{\bullet+}$ states are formed. These charge-separated states are short-lived, with lifetimes in the range of around 10 picoseconds.[4a] Such photoinduced electron transfer processes within exTTF/fullerene supramolecular species are poised for numerous applications, especially in the context of constructing more efficient optoelectronic devices[5] through self-assembly.[6] Here, we wish to report on the detailed investigations regarding the electron transfer chemistry in $\mathbf{1}\cdot C_{60}$ and $\mathbf{1}\cdot C_{70}$.

Initially, we have employed absorption assays, in which approximately 2.0×10^{-5} M of **1** was titrated against variable concentrations of C_{60} or C_{70} (*i.e.* from 0 to 5.0×10^{-5} M). As a general feature, facilely formed charge transfer complexes—$\mathbf{1}\cdot C_{60}$ or $\mathbf{1}\cdot C_{70}$—were seen to develop in a variety of solvents (*i.e.* toluene, chlorobenzene, and benzonitrile, Fig. S1–S3, ESI§). For C_{60} in benzonitrile, the growth of a new broad transition at 475 nm goes hand in hand with the decrease of the exTTF absorption at 430 nm. Concomitantly, a low energy isosbestic point evolves around 460 nm. Relative to benzonitrile, hypsochromic shifts were noted in chlorobenzene and in toluene, where the maxima for the charge-transfer band are discernible at 470 and at 465 nm, respectively. The fact that the corresponding maxima tend to blue-shift with decreasing solvent polarity leads us to postulate a redistribution of charge density in the ground state from the electron donating exTTF to the electron accepting C_{60} or C_{70}, to afford the corresponding $C_{60}^{\delta-}/\mathbf{1}^{\delta+}$ or $C_{70}^{\delta-}/\mathbf{1}^{\delta+}$. Throughout the solvent change the absorption maximum of exTTF is, however, not affected. For C_{70}, the maxima for the charge-transfer band were at 467 nm in chlorobenzene and 473 nm in benzonitrile. In the next step, we subjected the absorption changes at 470 nm during the titration experiments to non-linear fitting functions assuming formation of the 1 : 1 complex.[3] K_a values of 4.2×10^4, 9.7×10^5, and 1.1×10^6 M^{-1} were calculated for the formation of $\mathbf{1}\cdot C_{60}$ in toluene, chlorobenzene, and benzonitrile, respectively (see ESI§). The corresponding $\mathbf{1}\cdot C_{70}$ values were 5.6×10^5 M^{-1} in chlorobenzene and 5.8×10^5 M^{-1} in benzonitrile. These values are in good agreement with those obtained by global multivariable analysis.[3]

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‡ Dedicated to Professor Jochen Mattay, on the occasion of his 65th birthday.

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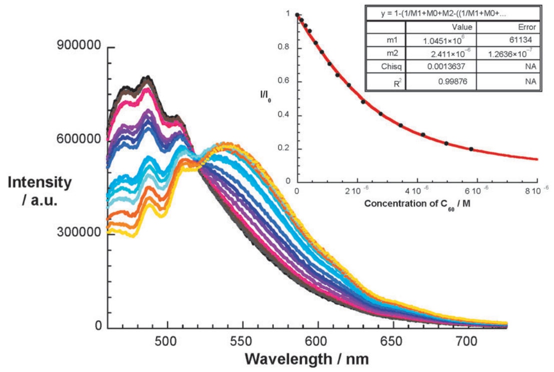

Fig. 2 Emission spectra upon 450 nm excitation of a solution of **1** (1.56×10^{-5} M) in benzonitrile with variable concentrations of C_{60} (0; 3.36×10^{-7} M; 6.67×10^{-7} M; 9.96×10^{-7} M; 1.48×10^{-6} M; 1.96×10^{-6} M; 2.59×10^{-6} M; 3.22×10^{-6} M; 4.13×10^{-6} M; 5.28×10^{-6} M; 6.67×10^{-6} M; 8.28×10^{-6} M; 1.00×10^{-5} M; 1.2×10^{-5} M; 1.39×10^{-5} M and 1.60×10^{-5} M). Inset: plot of the normalized intensity I/I_0 at 462 nm *versus* concentration of C_{60} used to determine the association constant.

Fig. 2, in which a complementary fluorescence assay is displayed, documents that even in the excited state mutual interactions prevail between the electron donating exTTF and the electron accepting C_{60}/C_{70}. As in the absorption assays, a new feature appears around 538 and 541 nm in the presence of variable C_{60} or C_{70} concentrations at the expense of the exTTF centered excited state features of **1**, which were seen to diminish around 470 nm. Again, we postulate that a charge transfer is responsible for the newly developing features. Notable is the mirror image between the charge transfer absorption and the charge transfer emission. For **1**·C_{60} and **1**·C_{70}, the $C_{60}{}^{\delta-}/\mathbf{1}^{\delta+}$ and $C_{70}{}^{\delta-}/\mathbf{1}^{\delta+}$ features are discernible in non-polar as well as polar solvents with emission quantum yields of about 10^{-3}. A substantial red shift of 30 nm accompanies the solvent change, which infers a significant solvent stabilization of the charge transfer state. For **1**·C_{70} the most prominent $C_{70}{}^{\delta-}/\mathbf{1}^{\delta+}$ features are maxima at 515 nm in chlorobenzene, and 541 nm in benzonitrile.

The exponential quenching of the steady-state fluorescence of **1** was further used to quantify the association between **1** and C_{60} or **1** and C_{70}.[7] In particular, we have plotted the emission intensity gathered at 462 nm *versus* the concentration of C_{60}/C_{70} (Fig. 2, inset). A nonlinear curve fitting allowed the association constants for the formation of **1**·C_{60} to be estimated as 5.1×10^4 (toluene)/1.04×10^6 M^{-1} (benzonitrile) and 3.4×10^5 (chlorobenzene) and 3.8×10^6 M^{-1} for **1**·C_{70} (benzonitrile).

In the next step, with the help of femtosecond laser pulses at 387 nm the fate of localized exTTF and C_{60}/C_{70} singlet excited states was probed. In addition, 480 nm photoexcitation experiments were conducted to direct the excitation into the charge transfer state. Please note in this context the lack of ground state absorption of exTTF and C_{60} at the 480 nm excitation wavelength. Following the time evolution has emerged in our earlier work as a convenient approach to identify spectral features of the initial excited state and the resulting charge transfer products, and to determine absolute rate constants for their formation as well as their decay.[4a]

In transient absorption measurements with **1** only one transient intermediate evolved. This excited state intermediate is centered on exTTF and appears simultaneously with the conclusion of the 387 nm laser pulse. Spectral characteristics of this very short-lived excited state (1.2 ps) are 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, with a strong second-order vibronic spin–orbit coupling.[8]

The differential absorption changes, taken right after the excitation of C_{60}/C_{70} at 387 nm, show the instantaneous transformation of high lying singlet excited states into the lowest vibrational state of the associated singlet excited states. In particular, marked transitions develop in the near-infrared region with maxima at 960 nm for C_{60} and 860/1140 nm for C_{70}. These singlet excited states with energies of about 1.80 eV deactivate slowly *via* intersystem crossing to the energetically lower lying triplet excited state. The intersystem crossing lifetimes were determined from multi-wavelength analyses as 1.6 ns. The newly appearing band at 750 nm reflects the diagnostic signature of the triplet excited state of C_{60}, for which a lifetime of 45 μs has been determined. For C_{70}, the corresponding triplet excited state spectrum is dominated by a maximum at 950 nm.[9]

The differential absorption changes obtained upon photo exciting **1**·C_{60} in benzonitrile into the charge transfer features at 480 nm are gathered in Fig. 3. The spectral features clearly reveal the instantaneous (*i.e.* <1 ps) formation of photoexcited $C_{60}{}^{\delta-}/\mathbf{1}^{\delta+}$ with features that include maxima at 540, 655, 950, and 1080 nm. The instantaneous appearance of the $C_{60}{}^{\delta-}/\mathbf{1}^{\delta+}$

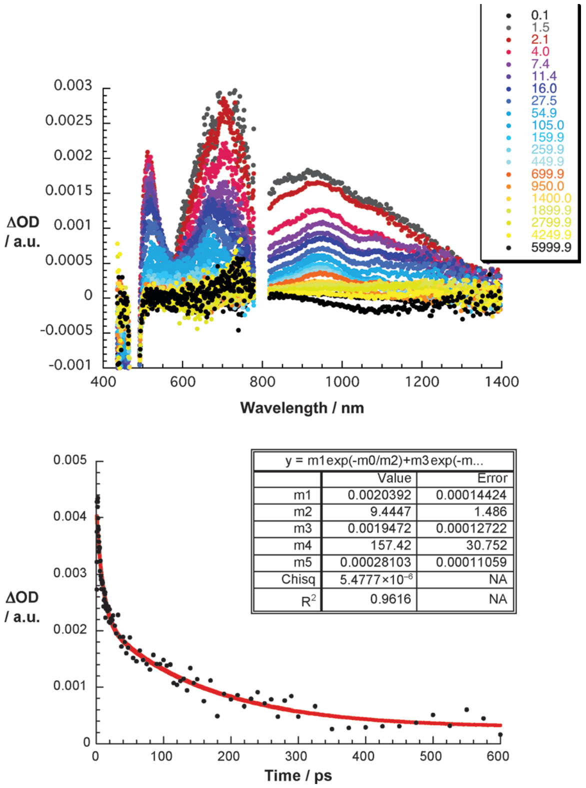

Fig. 3 Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (480 nm) of **1**·C_{60} in Ar-saturated benzonitrile with time delays between 0.1 and 6000 ps at room temperature. Lower part: time-absorption profile at 655 nm, reflecting the transformation of $C_{60}{}^{\delta-}/\text{exTTF}^{\delta+}$ into the fully $C_{60}{}^{\bullet-}/\mathbf{1}^{\bullet+}$ charge separated state and charge recombination kinetics.

excited state further confirms the intimate interactions between C_{60} and exTTF in $\mathbf{1}\cdot C_{60}$. The $C_{60}^{\delta-}/\mathbf{1}^{\delta+}$ excited state is, however, short-lived and transforms within 6.7 ± 0.5 ps into a fully $C_{60}^{\bullet-}/\mathbf{1}^{\bullet+}$ charge separated state. In this regard, the transient centred at around 665 nm is assigned to the one-electron oxidized radical cation of exTTF. This assignment is in accordance with previous studies conducted with photolytic and radiolytic techniques.[10] The one-electron reduced radical anion of C_{60}, on the other hand, shows up in the near-infrared (*i.e.* 1080 nm).[11] The charge separated state lifetimes, as determined from a multiwavelength analysis (*i.e.* decay at 665, 950, and 1080 nm), were 157 ± 31 ps. Products of the charge recombination are the energetically lower lying C_{60} singlet excited state (1.8 eV) and C_{60} triplet excited state (1.55 eV) as identified by maxima at 960 and 750 nm, respectively. In complementary experiments, chlorobenzene was probed as solvent. Essentially, the same spectral features of the $C_{60}^{\delta-}/\mathbf{1}^{\delta+}$ excited state were seen as it transforms into the fully $C_{60}^{\bullet-}/\mathbf{1}^{\bullet+}$ charge separated state with kinetics of 9.0 ± 0.5 ps before charge recombination populates the C_{60} triplet excited state with 137 ± 11 ps. Longer lifetimes in benzonitrile compared to chlorobenzene are in line with dynamics that are placed in the normal region of the Marcus parabola. In other words, the large reorganization energy that exTTF reveals in electron transfer reactions is insufficiently compensated by the exceptionally small reorganization energy of C_{60}.[10,11] In addition, the low driving forces for the charge recombination (*i.e.* <1.0 eV) prevent the processes to be beyond the thermodynamic maximum.[12]

Turning to the photoexcitation of $\mathbf{1}\cdot C_{70}$, the $C_{70}^{\delta-}/\mathbf{1}^{\delta+}$ features were seen to evolve in chlorobenzene with maxima at 540, 665, 860, and 1140 nm. Following its instantaneous formation, transformation to the corresponding $C_{70}^{\bullet-}/\mathbf{1}^{\bullet+}$ charge-separated state takes over with 5.1 ± 1.5 ps. Evidence for the formation of the latter is based on the signatures of the one-electron-reduced radical anion of C_{70} at 880 and 1220 nm, in line with pulse radiolytic investigations,[13] and of one-electron oxidized radical cation of exTTF at 665 nm. A multi-wavelength analysis of the $C_{70}^{\bullet-}/\mathbf{1}^{\bullet+}$ features at 503, 665, 950, and 1200 nm helped to establish a lifetime of 371 ± 27 ps. In line with what has been seen for $C_{60}^{\bullet-}/\mathbf{1}^{\bullet+}$, studies in benzonitrile revealed an even longer lifetime of 482 ± 36 ps (Fig. S5, ESI§). Notable is that charge recombination in both solvents affords the C_{70} triplet excited state.

In a nutshell, a macrocyclic exTTF host efficiently incorporates C_{60} or C_{70} with binding constants that range from 4.2×10^4 to 3.8×10^6 M^{-1}. The binding is driven in large by charge transfer interactions and, in turn, dominates the electronic ground state with the unambiguous formation of $C_{60}^{\delta-}/\mathbf{1}^{\delta+}$ or $C_{70}^{\delta-}/\mathbf{1}^{\delta+}$ charge transfer states. These charge transfer states reveal distinct absorption and emission features and transform in the excited state into fully $C_{60}^{\bullet-}/\mathbf{1}^{\bullet+}$ or $C_{70}^{\bullet-}/\mathbf{1}^{\bullet+}$ charge separated states. Remarkable are the charge separated state lifetimes reaching into the 500 ps domain, which correlate with a weak electronic coupling between an electron acceptor (*i.e.* C_{60}/C_{70}) and an electron donor (*i.e.* exTTF). Support for this hypothesis comes from extinction coefficients of $C_{60}^{\delta-}/\mathbf{1}^{\delta+}$ in $1\cdot C_{60}$ relative to that seen in exTTF bis-crown ether$\cdot C_{60}$ with values of 4000 and 5500 L mol^{-1} cm^{-1}, respectively (see Fig. S4, ESI§). In comparison to exTTF bis-crown ether and exTTF-tweezers,[4a,6c] which feature lifetimes on the 10 to 50 ps time scale, the alkyl chain in **1** is key: it provides an alternative source for positive non-covalent interactions and assures that C_{60} or C_{70} remains encapsulated by the macrocycle despite weaker electronic coupling with the exTTF units.

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