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Thermally reversible C_{60}-based donor–acceptor ensembles

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Diels–Alder cycloaddition of anthracene derivatives—bearing fused π-extended TTFs—to C_{60} yielded thermally reversible donor–acceptor materials which function as fluorescence switches.

Donor–acceptor ensembles, built around the electron and energy accepting C_{60} core, have been attracting much attention in the field of molecular materials.[1] The reaction of C_{60} with anthracene, for instance, yields 1 : 1 addition products,[2–5] which, due to their instability, fractionate *via* retro-Diels–Alder reaction into the starting components. The addition of anthracene to C_{60} is not only limited to a single addition step. Elegant advances towards the regiospecific bisfunctionalization of C_{60}, for example, infer intermolecular anthracene transfer in a crystalline 6,6-monoadduct, providing an antipodal bisanthracene addition pattern.[6]

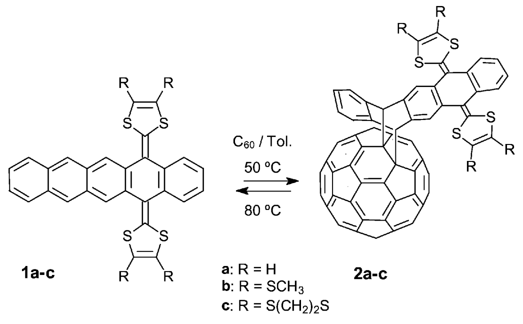
In this communication, we present molecular ON/OFF switches, using non-fluorescing Diels–Alder adducts of C_{60} which, upon heating, revert to the starting materials, which exhibit strong light emission. The anthracene building blocks reported here bear fused electron donor (π-extended)TTFs and form thermally reversible donor–acceptor dyads.

Dyads **2a**–**c** were prepared by reacting equimolecular amounts of 5,14-bis(1,3-dithiol-2-ylidene)-5,14-dihydropentacenes (**1a**–**c**)[7] with C_{60}, in toluene at 50 °C (Scheme 1). The initially brown–yellow colour of the solution, due to unreacted C_{60} and (π-extended)TTF, turned green as the reaction proceeded. After 30 hours the reaction was stopped and the solvent was subsequently evaporated under reduced pressure below 60 °C. The [4 + 2] cycloadducts **2a**–**c** were separated by column chromatography with cyclohexane–toluene (1 : 2 *v*/*v*) on silica gel to give dark green solids (10–12% yield), whose structures were resolved on the basis of spectroscopic data.†

The ^1H NMR spectra of **2a**–**c** showed the resonance of the hydrogen atoms—located on the bridgehead sp^3 carbon atoms—as a single signal at δ 5.85–5.92. This is significantly upfield, relative to resonances (δ 8.31) seen typically in anthracene and related derivatives.[2–6] Between 27 and 43 resonance signals are found in the ^{13}C-NMR spectra of **2a**–**c**. The signals at δ_C 72.4–72.8 are ascribable to the quaternary bridgehead carbons of the C_{60} moiety, while those at δ_C 58.3 are due to methine carbons of the pendant bridgehead. In addition, the data let us to conclude that dyads **2a**–**c** present C_s symmetry and that the cycloaddition occurs exclusively at the [6,6] rings junction. In the MALDI-TOF mass spectrometry, only a weak molecular ion peak (M^+) was observed. More intense are the peaks of C_{60} (*m*/*z* 720) and (π-extended)TTFs (*m*/*z* 480–664). In principle, this observation is similar to what has already been seen for C_{60}-anthracene derivatives and confirm that these molecules undergo a facile fragmentation into C_{60} and anthracene (*i.e.*, **1a**–**c**) constituents.

We followed the course of the retro-cycloaddition in dyads **2a**–**c** by temperature variable ^1H-NMR experiments in toluene. Fig. 1 illustrates the changes associated with the temperature variation for the bridgehead protons and the SCH_3 groups in compound **2b**. At low temperature, the signals that correspond to the bridgehead protons are found as singlets, while those of the methylthio groups appear as sets of two singlets, integrated as six protons. Upon increasing the temperature, the bridgehead protons become broader and decrease in intensity. The SCH_3 protons, on the other hand, split into four singlets due to the simultaneous presence of educt (**1b**) and cycloadduct (**2b**). The retro-cycloaddition process starts around 50 °C and continues during the 50–80 °C range. At 80 °C the observed ^1H-NMR spectrum relates mainly to **1b**, besides small, residual traces of the bridgehead protons of cycloadduct **2b**.[8]

Another retro-cycloaddition assay implies cyclic voltammetry (CV) measurements. Dyads **2a**–**c** gave rise to the presence of four one-electron reduction steps, all relating to the fullerene core. The underlying reduction potentials are shifted to negative values relative to those of pristine C_{60}, as a consequence of the partial loss of conjugation in C_{60}, which raises the LUMO energy of the resulting adducts. In the anodic region, a quasireversible oxidation wave, involving two electrons, to the dication of (π-extended)TTF unit were observed.[9]



Scheme 1

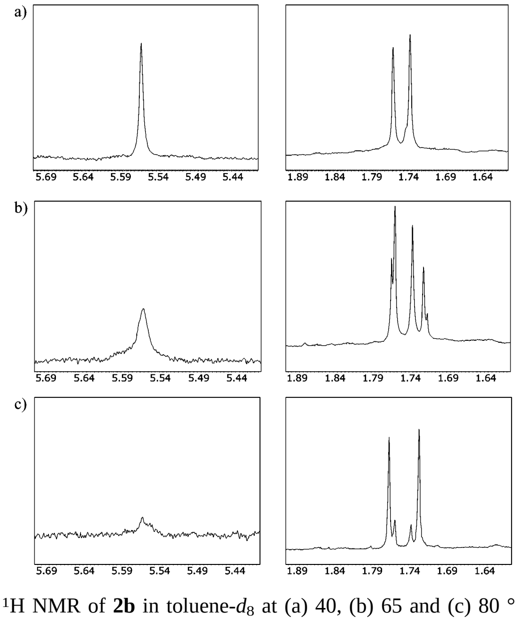


Fig. 1 ^1H NMR of **2b** in toluene-d_8 at (a) 40, (b) 65 and (c) 80 °C (δ in ppm).

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The same samples—heated to 80 °C and subsequently brought to room temperature—show reduction and oxidation waves corresponding to the precursor materials, that is, parent C_{60} and **1a**–**c**.

The fullerene fluorescence, although weak ($\Phi = \sim 6.0 \times 10^{-4}$ for most of the investigated monoadducts[10]), has been established as a sensitive and useful marker for probing excited state interactions. In an effort to characterise the switch behaviour of **2a**–**c** a series of time-resolved and steady-state experiments were conducted in different solvents (toluene: $\varepsilon = 2.38$; benzonitrile: $\varepsilon = 24.8$) and at variable temperature (24–80 °C).

The fullerene fluorescence in **2a**–**c** is, in line with our previous studies on a series of (π-extended)TTF units linked either to a methanofullerene[11] or a pyrrolidinofullerene,[12] subject to strong quenching relative to the fullerene reference. Importantly, the pattern of the C_{60} fluorescence with strong *0–0 maxima around 715 nm is, despite the overall quenching, fully preserved. A closer inspection of the fluorescence quantum yields (see Table 1) reveals two main trends regarding the magnitude of fluorescence quenching. First, the quenching relates well with the oxidation strength of the (π-extended)TTF donor and, secondly, it increases progressively with the solvent polarity. Extreme scenarios are benzonitrile as a solvent and H-substitution on the (π-extended)TTF donor yielding fluorescence quantum yields as low as 0.18×10^{-4}. A rationalisation for these qualitative values infer that the fullerene singlet excited state (1.76 eV) is readily deactivated by an intramolecular electron transfer event to yield the relatively long-lived $C_{60}{}^{\bullet-}$-(π-extended)$TTF^{\bullet+}$ (~1.2 eV), for which we determined lifetimes of the order of ~200 ns in benzonitrile.

Increasing the reaction temperature in 10 °C intervals from room temperature to 80 °C led to a gradual reactivation of the excited state fluorescence. Instead of seeing, however, the characteristic fullerene fluorescence of a monoadduct, the weak fluorescence of pristine C_{60} ($\Phi = 2 \times 10^{-4}$) and that of the anthracene moiety in 5,14-bis(1,3-dithiol-2-ylidene)-5,14-dihydropentacene (**1a**–**c**) ($\Phi = 1.0 \times 10^{-2}$) are registered in the low- and high-energetic region of the emission spectrum, respectively. In Fig. 2 we compare the fluorescence spectra of dyad **2a** before and after heating at 80 °C with that of **1a** at room temperature. Since the fluorescence quantum yields of both constituents at 80 °C are comparable to those of the reference compounds, we reach the conclusion that dyads **2a**–**c** fragmentize nearly quantitatively and that the dissociated donor and acceptor moieties do not interact on the time scale of excited state fluorescence.

In retrospect, we have shown a fluorescing switch, whose status, that is, ON *versus* OFF is controlled by an electron transfer scenario. The mode of action is temperature, initiating the reversible switching between the two states. Singlet excited state fluorescence quenching (*i.e.*, activated electron transfer) refers to the ON-state, while strong reactivation of the emission features indicate the OFF-state (*i.e.*, deactivated electron transfer). This level of control is the incentive for work in progress, characterising the ON *versus* OFF sequence in C_{60}-(π-extended)TTF dyads **2a**–**c**, incorporated, for example, into an inert polymer matrix.

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Table 1 Electrochemical and fluorescence properties of **2a**–**b**

Compd.	Solvent	$10^4\Phi^a$	$E_{red}{}^b$/V	$E_{ox}{}^b$/V
2a	Toluene	0.50	−0.68, −1.08, −1.66, −2.20	0.52
	Benzonitrile	0.18		
2b	Toluene	0.88	−0.65, −1.00, −1.72, −2.33	0.60
	Benzonitrile	0.29		
2c	Toluene	0.63	−0.66, −1.02, −1.64, —[d]	0.60
	Benzonitrile	0.20		
C_{60}	Toluene	2.0	−0.60, −1.07, −1.64, −1.93	—
3[c]	—	—	—	0.45

[a] Fluorescence quantum yield. [b] $Bu_4N^+ClO_4^-$ (0.1 M); toluene : acetonitrile (4 : 1 *v*/*v*); 200 mV s^{-1}; values quoted relative to SCE. [c] **3**: 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene; GCE; $Bu_4N^+ClO_4^-$ (0.1 M); CH_2Cl_2; 200 mV s^{-1}. [d] Not observed.

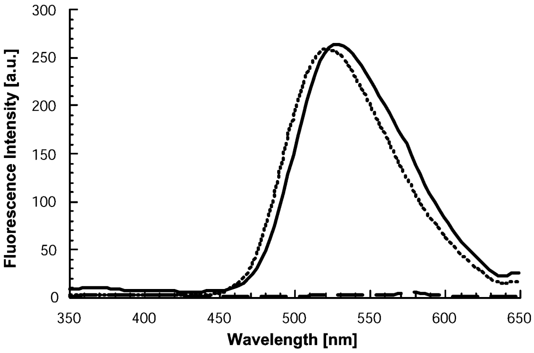

Fig. 2 Fluorescence spectra of dyad **2a** in *ortho*-dichlorobenzene at 20 °C (dashed line) and at 80 °C (dotted line) and of reference **1a** at 20 °C (solid line). All samples were adjusted to display identical absorption at the 320 nm excitation wavelength (*i.e.*, $OD_{320\,nm} = 0.5$).

Notes and references

† Selected spectroscopic data. **2a**: 11% yield (22% based on recovered C_{60}); ν_{max} (KBr)/cm^{-1} 1636, 1542, 1507, 1461, 1430, 1262, 1113, 800, 751, 701, 652, 591, 575, 560, 554, 527; δ_H ($CDCl_3$, 300 MHz) 8.07 (1H, s), 7.86–7.81 (2H, m), 7.73–7.70 (2H, m), 7.57–7.54 (2H, m), 7.48–7.46 (2H, m), 6.34–6.25 (4H, m), 5.85 (2H, s); δ_C ($CDCl_3/CS_2$ 1/1, 125 MHz) 155.3, 155.2, 155.0, 147.3, 146.2, 146.0, 145.4, 145.1, 144.4, 142.9, 142.8, 142.3, 142.1, 141.8, 141.5, 141.0, 139.8, 139.0, 138.9, 137.1, 135.4, 135.2, 134.5, 134.4, 134.2, 131.9, 129.9, 128.0, 127.3, 127.2, 126.1, 126.0, 125.9, 125.6, 125.5, 125.3, 125.2, 125.1, 124.8, 123.7, 122.4, 122.3, 117.2, 117.1, 72.4, 58.3; λ_{max} (CH_2Cl_2)/nm (log ε) 256 (5.40), 316 (5.06), 370 (4.88), 422 (4.76), 438 (4.79); *m*/*z* (MALDI-TOF) 1202 (M^+, 45), 720 (C_{60}, 100), 480 (M^+-C_{60}, 50).

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