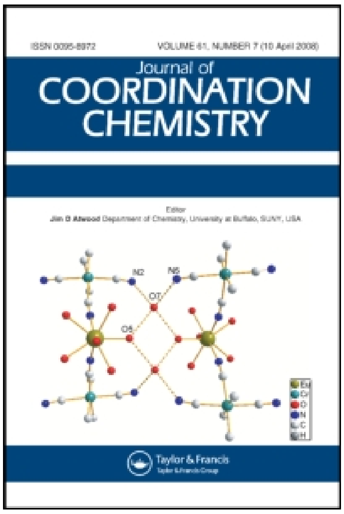

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Threefold exTTF-based Buckycatcher

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Threefold exTTF-based Buckycatcher

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Charge-transfer complex formation by a tuning-fork shaped π-extended tetrathiafulvalene-based molecule, which acts as molecular catcher for C_{60} in a variety of solvents upon photoexcitation, has been explored. An increase in 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole unit creates an easy-chair like conformation accommodating C_{60}, which leads to a binding constant and lifetime of radical ion pair state of $2.23 \times 10^4\,(\mathrm{mol\,L^{-1}})^{-1}$ and 4.8 ps in *ortho*-dichlorobenzene.

Keywords: Charge transfer; exTTF, Tuning-fork; Molecular receptor; Photoexcitation; C_{60}

1. Introduction

Exploitation of weak non-covalent interactions such as π–π interactions [1], hydrogen bonds [2], electrostatic interactions [3], hydrophobic interactions [4], and coordination of metal bonds [5] have given rise to a variety of supramolecular self-assemblies. The traditional paradigm using π–π interactions to lock a concave surface to a convex surface has continued to see a variety of macromolecular receptors [6] and has further gained importance since Whitlock [7] coined the term "molecular tweezers" to describe an aromatic tether with pincer-like structure which is capable of gripping another π-structure. The ultimate goal is supramolecular assemblies with the preeminent target; molecular electronics – solar energy harnessing. Fullerenes and their derivatives have been widely employed in photovoltaic devices [8]. Myriad compounds have been chosen as electron donors, with both electro and photoactive nature [9]. Owing to their electronic and structural characteristics, tetrathia fulvalene (TTF) derivatives are versatile building blocks which are widely employed to form macromolecular

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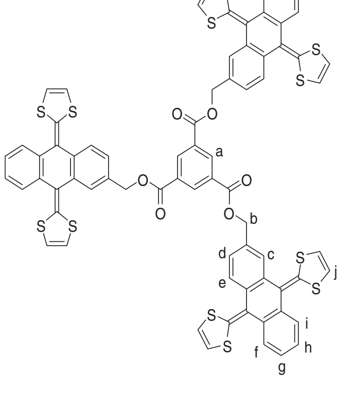
assemblies with interesting conducting properties [10]. Thus, TTFs are good electron donors that form stable open-shell species by transferring one π-electron from the HOMO, that is, it can undergo aromatization upon oxidation leading to the formation of thermodynamically stable mono- or di-cationic radical species at relatively low oxidation potentials. The aromatic species formed upon oxidation is accompanied by dramatic geometrical changes, stabilizing the resultant radical ions [10, 11]. One such example is the *p*-quininoid analogue of TTF, 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole, abbreviated as exTTF, which serves as an excellent electron donor [12]. We have recently reported the synthesis of exTTF tweezer with pincer-like structure and macrocycles capable of capturing fullerenes in solution [13]. In the present work, we investigate the influence of a third unit of exTTF, giving rise to a tuning-fork shaped structure, on the recognition abilities of our receptors, and on the photophysical properties of the assembly. Thus, absorption and fluorescence titrations, complemented by transient absorption measurements, were carried out using toluene, anisole, *ortho*-dichlorobenzene, and benzonitrile as solvents.

2. Experimental

All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh, or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum-coated Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 500 spectrometers at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in hertz and chemical shifts (δ) in parts per million. Matrix-assisted laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer.



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3. Synthesis of the tuning-fork-shaped 1

To a solution of (9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-yl)methanol (0.100 g, 0.243 mmol) and 4-dimethylaminopyridine (0.036 g, 0.292 mmol) in 5 mL of dry CH_2Cl_2, a solution of benzene-1,3,5-tricarbonyl trichloride (0.021 g, 0.079 mmol) in 5 mL of dry CH_2Cl_2 was added dropwise [14]. The resulting solution was stirred for 2 h and then diluted with 50 mL of CH_2Cl_2, washed with aqueous HCl (1 mol L^{-1}, 2 × 50 mL), $NaHCO_3$ (saturated aqueous solution, 2 × 50 mL) and brine (2 × 50 mL). The organic layer was dried over $MgSO_4$ and filtered; the filtrate was evaporated under reduced pressure and purified by recrystallization from DMSO/CH_3OH to yield 0.219 (65%) of the desired compound as a yellow solid. m.p. > 300°C; ^1H NMR (300 MHz, DMSO-d_6, 298 K) δ 8.84 (bs, 3H, H_a), 7.86–7.24 (bm, 22H, $H_d + H_e + H_f + H_g + H_i$), 6.80–6.52 (bm, 12H, H_j), 5.47 (bs, 6H, H_b); ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ 164.9, 137.8, 135.8, 135.4, 134.8, 134.4, 134.2, 131.9, 127.1, 126.5, 125.6, 125.5, 125.0, 121.2, 118.9, 118.8, 107.7, 67.6. MS *m*/*z*: Calcd for $C_{72}H_{42}O_6S_{12}$ [M^+] 1385.96, found (MALDI-TOF) 1385.93.

4. Analytical instrumentation

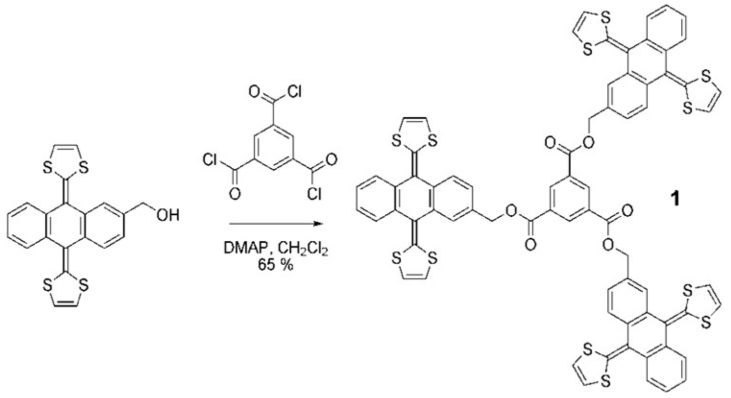
UV-Vis experiments were carried out on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The fluorescence studies were performed on a Fluoromax 3 (Horiba) using 434 nm as excitation wavelength.

Cyclic voltammetry was performed using an Autolab PGStat 30. A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (0.3 µm) for 1 min, and platinum wire was used as counter electrode and Ag/$AgNO_3$ electrode was used as a reference. Tetrabutylammonium perchlorate (0.1 mol L^{-1}) was used as supporting electrolyte and *ortho*-dichlorobenzene as solvent. The samples were purged with argon prior to measurements. The scan rate was 100 mV s^{-1}.

Femtosecond transient absorption studies were performed using 387 nm laser pulses of 150 fs pulse width, generated by a *beta*-barium borate crystal upon higher order non-linear processes from an amplified Ti : Sapphire laser system (CPA 2001 Laser, Clark–MXR Inc.). For the generation of 484 nm excitation wavelength – a wavelength of 775 nm of pulse width of 150 fs is split into two by a beam splitter: one is used to generate the desired wavelength (484 nm) with the help of noncollinear optical parametrical amplifier (NOPA, Clark MXR) and the other runs along a delay line and passes through a 2-mm Sapphire crystal, where white light was generated. With the help of a delay line, a time delay between the pump and the probe beams was created with high precision. Finally, the change in optical density (ΔOD) is measured against the wavelength in both visible and near-infrared regions.

5. Results and discussion

The synthesis of the tuning-fork-shaped **1** was carried out in a single synthetic step from readily available exTTF methyl alcohol and commercially available trimesic



Scheme 1. Synthesis of the tuning-fork shaped exTTF molecule **1**.

acid chloride in 65% yield as shown in scheme 1 [14]. The identity and purity of **1** were unambiguously established by standard spectroscopic and spectrometric techniques.

The formation of the $\mathbf{1}:C_{60}$ complex in solution was initially investigated through absorption titrations at room temperature. In these assays, $7 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ solutions of **1** in different solvents – toluene, anisole, *ortho*-dichlorobenzene, and benzonitrile – were titrated against variable C_{60} concentrations (i.e., from 2.5×10^{-7} to $8 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) at room temperature. The spectral changes as seen in figure 1 are analogous to our previous studies on the exTTF tweezer compounds [13]. We note the evolution of a new broad transition at 490 nm in benzonitrile at the expense of the 438 nm absorption maximum. Another notable feature is two clearly defined isosbestic points, at 396 and 459 nm, which confirm the clean formation of only one kind of associate. The low-energy isosbestic point around 459 nm reveals considerable hypsochromic shifts when going from polar benzonitrile (459 nm) to non-polar toluene (451 nm) showing that the solvent polarity dependence on the complexes formed. Similar hypsochromic shifts were noted for the charge transfer absorption, which was found, for example, in benzonitrile to be at 490 nm while in toluene at 480 nm. We evoke charge transfer transitions – $C_{60}^{\delta-}/\mathrm{exTTF}^{\delta+}$ – to be responsible for these new features. Importantly, the energies of the charge transfer bands follow the trend seen in the electrochemically derived radical ion pair energies – *vide infra*. Such charge transfer features are primarily a consequence of strong electronic coupling between **1** and fullerene of $285.77\,\mathrm{cm^{-1}}$ in benzonitrile, which is comparable to our previously reported data for tweezer compounds.

Fluorescence spectra (figure 1), as recorded for **1** in the presence of C_{60}, also confirm mutual interactions with the electron-accepting C_{60}. More precisely, the exTTF-excited state (2.6 eV) with an emission quantum yield of 10^{-3} and an emission lifetime of less than 100 ps, which maximizes at 475 nm, diminishes concomitantly with the rise of a new feature centered around 558 nm (2.2 eV). Again, we postulate the facile formation of a charge transfer complex. These rather strong charge transfer features are discernable in non-polar as well as polar solvents with emission quantum yields of about 10^{-3} and emission lifetimes shorter than our time-resolution of 100 ps. A large red shift of ~33 nm, from 525 nm in toluene to 558 nm in benzonitrile, reflects solvent

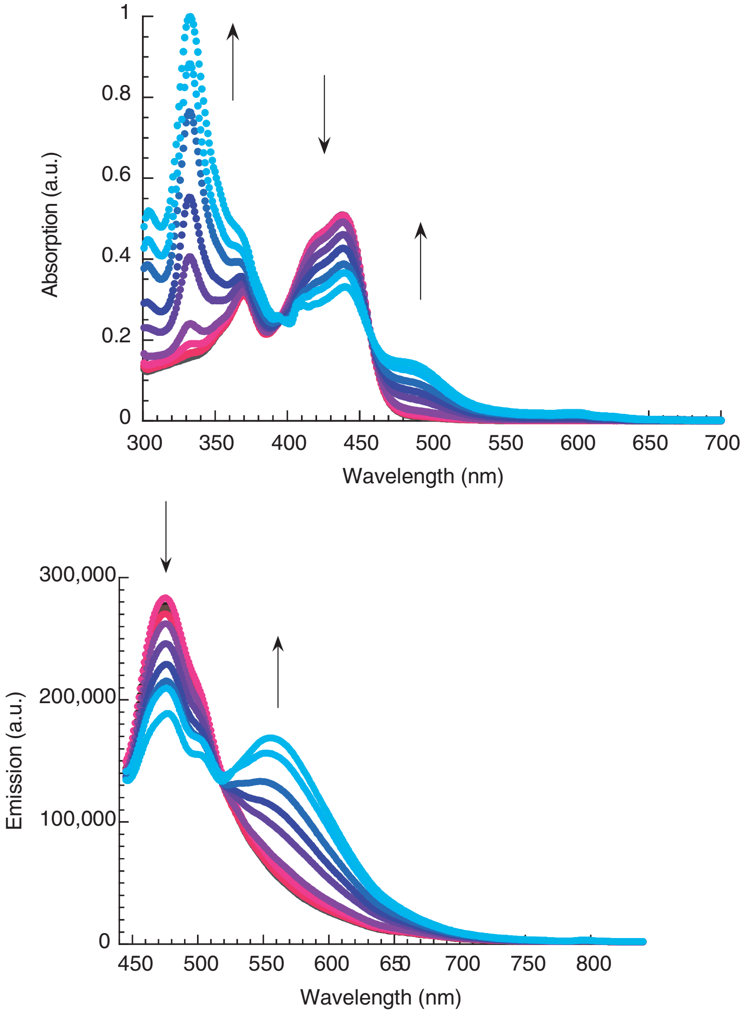


Figure 1. Absorption spectra (upper part) and emission spectra upon 435 nm excitation (lower part) of benzonitrile solution of **1** ($7.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$) with variable concentrations of C_{60} (0; 2.5×10^{-7}; 7.5×10^{-7}; 1.25×10^{-6}; 2×10^{-6}; 5×10^{-6}; 1.5×10^{-5}; 2.5×10^{-5}; 4×10^{-5}; 6×10^{-5}; 8×10^{-5}). Arrows indicate the progression of the titration.

stabilization of the charge transfer state. Considering a 1 : 1 stoichiometry, we calculated the binding constants according to [15]:

$$\frac{I_F}{I_O} = 1 - \frac{1}{2C_F}\left[\left(C_P + C_O + \frac{1}{K}\right) - \sqrt{\left(C_P + C_O + \frac{1}{K}\right)^2 - 4C_O C_P}\right]$$

where K is the binding constant, C_O is the concentration of **1**, and C_P is the concentration of the C_{60} added. Overall, the binding constants were on the order of $10^4\,(\mathrm{mol\,L^{-1}})^{-1}$ (table 1). The values obtained were comparable to that of the exTTF

Table 1. Binding constants from the emission data of **1** in various solvents fit to a 1 : 1 complex.

Solvent	K (mol L^{-1})$^{-1}$
Benzonitrile	0.61 (±0.09) × 10^4
ortho-Dichlorobenzene	2.23 (±0.44) × 10^4
Chlorobenzene	3.16 (±0.01) × 10^4
Toluene	1.21 (±0.19) × 10^4

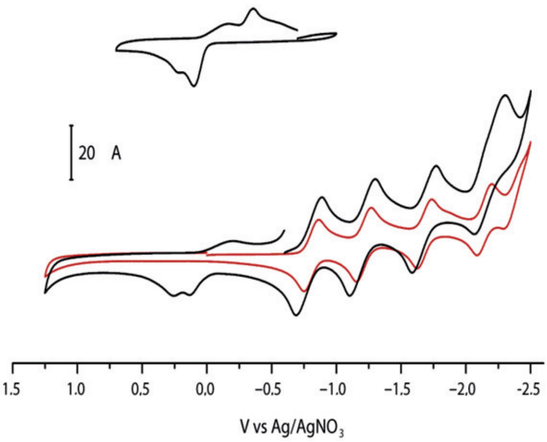


Figure 2. Cyclic voltammograms of **1** (top, black), **1 :** C_{60} (bottom, black), and C_{60} (bottom, red). Experimental conditions: 298 K, scan rate 100 mV s^{-1}, Bu_4NClO_4 as electrolyte, glassy carbon as working electrode, Ag/AgNO$_3$ as reference electrode.

Table 2. Reduction and oxidation potentials of C_{60}, **1**, and **1** : C_{60}.

	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}	E^1_{OX}	E^2_{OX}
C_{60}	−0.87	−1.27	−1.74	−2.20	–	–
1 : C_{60}	−0.88	−1.30	−1.77	−2.30	0.13	0.26
1	–	–	–	–	0.10	0.23

tweezers, but the increase is not as significant as might have been expected, indicating that the contribution of the third exTTF unit to the stability of the complex is limited, perhaps due to the entropic reasons.

Apart from the ground state absorption and the emission spectral evidence, support for the charge-transfer came from electrochemical measurements as seen in figure 2. Initially, **1** was characterized by cyclic voltammetry with 1 × 10^{-3} mol L^{-1} solutions of **1** in deareated *ortho*-dichlorobenzene. Compound **1** shows two distinct oxidation waves, the first one of which ($E^1_{OX} = 0.10$ V) is significantly more intense than the second ($E^2_{OX} = 0.23$ V). Upon addition of C_{60}, these oxidation processes undergo anodic shifts of approximately 35 mV. Meanwhile, the first reduction wave of C_{60} is shifted cathodically by *ca* 10 mV (table 2). Notable, similar shifts have previously been observed in exTTF tweezers upon complexing C_{60}.

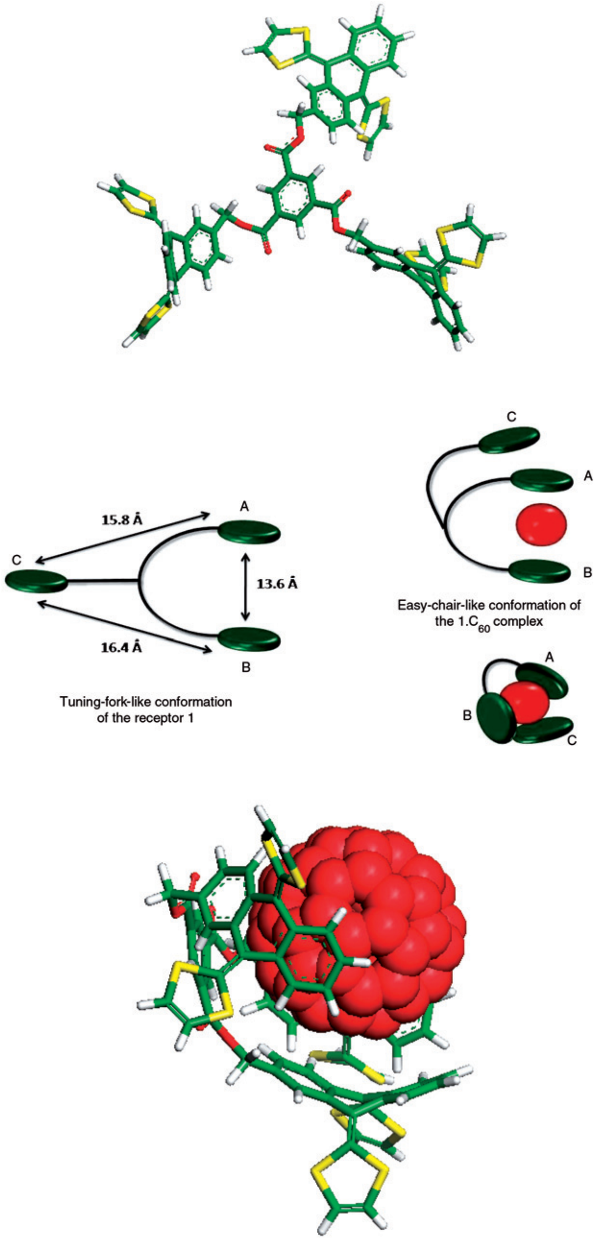


Figure 3. Structure of tuning-fork shaped exTTF **1** and its complex with C_{60} as obtained from the DFT calculations. Upper part: top view; middle part: a cartoon representation of the systems under study; bottom part: **1** : C_{60} complex.

Molecular mechanics and semiempirical (AM1) calculations were employed to shine light on the **1** : C_{60} complexes. These calculations provided indisputable evidence for favorable interactions between the tweezers and C_{60}. Density functional theory (DFT) calculations using BH&H 3-21G helped to corroborate these findings. Figure 3 shows the energy-minimized structure of **1** and its complex with C_{60}. The receptor displays a tuning-fork-shaped conformation, in which the exTTF units adopt butterfly-shaped conformations consistent with our previous report on the exTTF tweezer molecules [13b]. The concave form adopted by the anthracene moieties is a perfect match to the convex surface of C_{60}. Specifically, the distances between the centers of the exTTF moieties range from 13.6 to 16.4 Å, thus creating a molecular cavity that can adequately host C_{60}. Importantly, this distance also corroborates with typical Buckycatcher distances reported in the literature [6b, 6d].

This tuning-fork like structure of the molecule led us to speculate the type of binding that C_{60} could undergo during complexation – could **1** still have a tweezer-like conformation or would it adopt a bowl-shape conformation? To confirm this, molecular dynamics were performed *in vacuo* using the forcite molecular dynamics package implemented in Materials Studio 4.2 [16] and its Universal Force Field [17]. To run the molecular dynamics, the above energy minimized molecule **1** was used. The fullerene was placed at an arbitrary distance of ~6 Å to the central phenyl ring of **1** taking the van der Waals' interaction into consideration. The simulations with a time step of 1 fs for 500 ps were performed using a microcanonical (NVE, MN, USA) ensemble *in vacuo*. An equilibration time of 150 ps was considered sufficient and thus the resulting configurations were used for further investigations. The complexation with C_{60} leads to an easy-chair like conformation of **1**, in which C_{60} resides, with distances between the exTTF moieties A, B, and C (figure 3) shortened – AB = 8.26 Å, AC = 12.67 Å, BC = 18.80 Å.

In transient absorption measurements (i.e., visible and near-infrared region) with an exTTF compound previously reported [13b], only one transient evolved centering on exTTF and appeared simultaneously with the conclusion of the 387 nm laser pulse. It was characterized by absorptions around 609 nm in the visible and 850 nm in the near-infrared and decayed rapidly with a lifetime of only 1.2 ps. The short lifetime was rationalized by the presence of the sulfurs, with a strong second-order vibronic spin-orbit coupling [18].

Figure 4 shows the differential absorption changes obtained upon photoexciting **1** and C_{60} mixture in *ortho*-dichlorobenzene (i.e., 1 : 100) into the charge transfer features at 484 nm. In fact, the spectral features clearly reveal instantaneous (i.e., $>10^{12}\,s^{-1}$) formation of a fully $C_{60}^{\bullet-}$/exTTF$^{\bullet+}$ radical ion pair state. We assign the transient centered at 662 nm to the one-electron oxidized radical cation of the tripod in accordance with previous studies one exTTF tweezers and photolytic as well as radiolytic measurements [13b]. The one-electron reduced radical anion of C_{60}, on the other hand, surfaces in the near-infrared (i.e., 1100 nm). Importantly, the instantaneous appearance of the radical ion pair state confirms intimate interactions between **1** and C_{60}. The radical ion pair state lifetimes, as determined from the 662 and 1100 nm decay, were in general very short. In *ortho*-dichlorobenzene, a lifetime of 4.8 ps is derived owing to the charge stabilization, further confirming the fact that the third exTTF unit contributes to the limited stability of the complex. This can be further corroborated from dynamics calculations; the easychair-like conformation formed by **1** cannot clutch the C_{60} completely and hence its movements are not arrested by the presence of the third exTTF group.

To conclude, the ability of the tuning-fork shaped molecule **1** to catch a Buckyball has been demonstrated. The stable discrete supramolecular complex of **1** with C_{60}, in a variety of solvents, convert into fully charge-separated states,

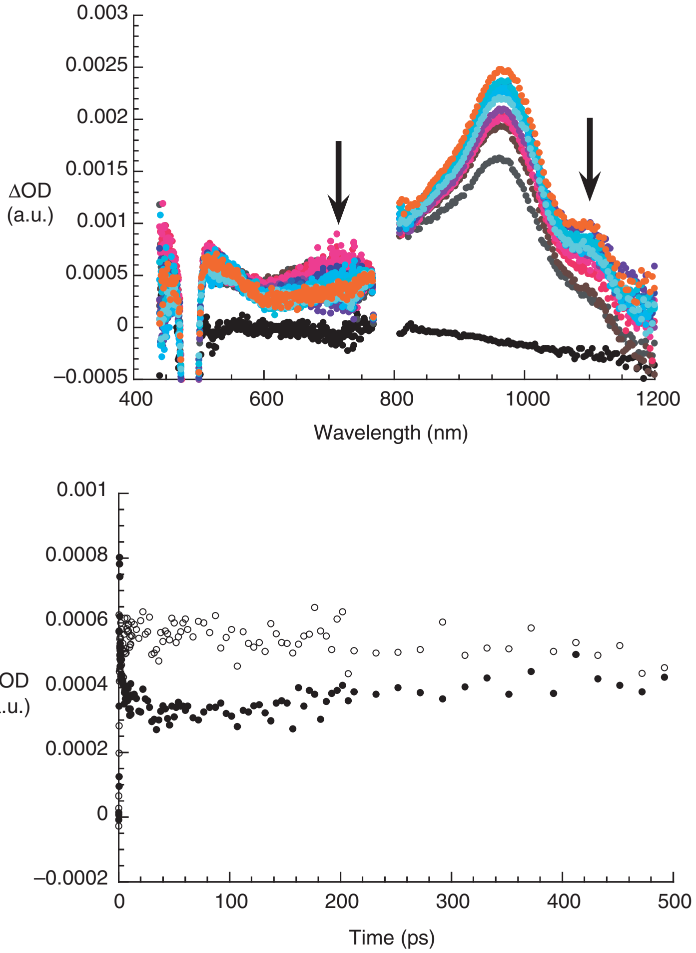


Figure 4. Upper part: differential absorption spectra (visible and near-infrared regions) obtained upon femtosecond flash photolysis (484 nm) of **1**:C_{60} (**1**: 2.5×10^{-5} mol L^{-1}; C_{60}: 2.5×10^{-3} mol L^{-1}) in *ortho*-dichlorobenzene with various time delays at room temperature. Lower part: time absorption profiles at 662 nm (●) and 540 nm (o), which reflect the charge-separation and charge-recombination dynamics.

$C_{60}^{\bullet-}$/exTTF$^{\bullet+}$, upon photoexcitation. While the addition of a third exTTF moiety to the previously reported tweezers did not result in drastic changes in the donor–acceptor interactions, with the radical ion pair state lifetime of 4.8 ps in the place of 9–12 ps [13b]. This suggests that the two-coordinate tweezer-like systems are better than the three-coordinate systems and thus can be further tailored with a variety of donors to achieve the desired Buckycatcher systems.

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