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

Bruno Grimm, Helena Isla, Emilio M. Pérez, Nazario Martín, and Dirk M. Guldi

Supporting Information

General Information: All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. 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-backed Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded with Bruker Avance 300 spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet. FT-IR spectra were recorded with a Perkin-Elmer 781 spectrometer. UV/Vis spectra were recorded with Varian Cary 50. Steady state fluorescence studies were carried out on a Fluoromax 3 (Horiba) instrument and all the spectra were corrected for the instrument response. The femtosecond transient absorption studies were performed with laser pulses (1KHz 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Mass spectra were recorded with a HP 5989A spectrometer.
Synthesis of macrocyclic host (1): This host was synthesized as reported in *J. Am. Chem. Soc.* 2010, 132, 1772–1773. Specifically:

Anthraflavic acid 3.33 g (12.5 mmol) was dissolved with sonication in 450 mL of dry DMF. Then, 1.73 g (12.5 mmol) of dry K₂CO₃, 2.21 g (12.5 mmol) of 7-bromo-1-heptene, and a catalytic amount of NaI were added and the mixture heated to reflux for 2 h. The crude reaction was poured into ice-cold 1 M aqueous HCl, and filtrated. The solid was redissolved in CH₂Cl₂ and washed with water (2x), the organic fraction was dried over MgSO₄, the solvent evaporated, and the resulting product subjected to column chromatography (CH₂Cl₂ to CH₂Cl₂:CH₃OH 2%) to obtain the pure product as a light yellow solid in 47% yield.

1H NMR (d₆-DMSO, 300 MHz) δ 11.02 (brs, 1H, Hₐ), 8.09 (d, J = 8.5 Hz, 1H, H₉), 8.06 (d, J = 8.1 Hz, 1H, Hₐ), 7.54 (d, J = 2.7 Hz, 1H, Hₙ), 7.48 (d, J = 2.7 Hz, 1H, H₉), 7.36 (dd, J = 2.7 Hz, J = 8.5 Hz, 1H, Hₘ), 5.81 (m, 1H, Hₘ), 4.98 (m, 2H, Hₙ), 4.16 (t, J = 6.7 Hz, 2H, Hₙ), 2.04 (m, 2H, Hₙ), 1.77 (m, 2H, Hₙ), 1.44 (m, 4H, Hₙ). 13C NMR (d₆-DMSO, 75 MHz) δ 182.26, 181.90, 164.33, 164.09, 139.53, 136.35, 130.71, 130.27, 127.20, 126.07, 121.94, 121.26, 115.68, 113.10, 111.48, 69.22, 33.98, 29.13, 28.81, 25.77. MS m/z: calcd. for C₂₁H₁₉O₄ [M-H+ 335.1 found ESI (neg.) [M-H+ O]

1.23 g (8.91 mmol) of dry K₂CO₃, 1.17 g (4.46 mmol) of α-α′ dibromo-p-xylene, and a catalytic amount of sodium iodide were added to a solution of 2.69 g (8.0 mmol) of the monoalkylated anthraflavic acid in 20–25 mL of dry N,N-dimethylformamide. The solution was heated to 60 °C for 4 h, and the resulting suspension was filtered. The solid obtained was washed successively with methanol and diethylether to remove unreacted starting materials, to yield pure compounds without further purification (y = 67%). The insolubility of this compound at room temperature forced us to characterize it at 353 K in C₂D₂Cl₄.
**mp** 275-278 °C; \(^1\)H NMR (CD\(_2\)Cl\(_2\), 500 MHz, 353 K) δ 8.28 (d, J = 8.3 Hz, 2H, H\(_{\text{h}}\)), 8.25 (d, J = 8.3 Hz, 2H, H\(_{\text{e}}\)), 7.86 (d, J = 2.6 Hz, 2H, H\(_{\text{f}}\)), 7.75 (d, J = 2.5 Hz, 2H, H\(_{\text{c}}\)), 7.56 (s, 4H, H\(_{\text{a}}\)), 7.37 (dd, J = 2.6 Hz, J = 8.3 Hz, 2H, H\(_{\text{g}}\)), 7.28 (dd, J = 2.5 Hz, J = 8.3 Hz, 2H, H\(_{\text{d}}\)), 5.89 (m, 2H, H\(_{\text{n}}\)), 5.32 (brs, 4H, H\(_{\text{b}}\)), 5.05 (m, 4H, H\(_{\text{o}}\)), 4.21 (t, J = 6.6 Hz, 4H, H\(_{\text{i}}\)), 2.16 (m, 4H, H\(_{\text{m}}\)), 1.91 (m, 4H, H\(_{\text{j}}\)), 1.55 (m, 8H, H\(_{\text{k+l}}\)). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 125 MHz, 353 K) δ 181.85, 181.72, 164.02, 163.41, 138.46, 136.93, 136.79, 136.00, 129.06, 128.06, 126.99, 126.57, 120.91, 120.69, 120.21, 114.39, 111.35, 111.03, 70.24, 68.80, 33.26, 28.74, 28.39, 25.25. MS m/z: calcd. for C\(_{50}\)H\(_{47}\)O\(_8\) [M+H] \(^+\) found MALDI-TOF 775.32.

A solution of dimethyl 1,3-dithiol-2-ylphosphonate 0.343 mg (1.62 mmol) in 5 mL of dry THF was cooled to –78 °C, and then BuLi (0.85 mL, 2 M in hexane, 1.70 mmol) was added. The solution was left to stir at –78 °C for 25 min, with appearance of a yellow precipitate. In the meantime, a suspension of 0.105 g of the anthraquinone precursor (0.135 mmol) in 5 mL of dry THF was dispersed with sonication for ca. 30 min. The resulting suspension was added to the phosphorous ylide suspension, and the cooling bath immediately removed. The mixture was allowed to warm to room temperature and left to stir for 2 h. The resulting deep red solution was quenched with CH\(_3\)OH, with precipitation of a yellow solid. The solid was filtrated, redissolved in CH\(_2\)Cl\(_2\), and subjected to column chromatography (Hex:CH\(_2\)Cl\(_2\) 3:1 to Hex:CH\(_2\)Cl\(_2\) 2:1) to obtain the pure product as a bright yellow solid (y = 37%).

**mp** 172–175 °C; \(^1\)H NMR (CDCl\(_3\), 500 MHz) δ 7.60 (d, J = 8.5 Hz, 2H, H\(_{\text{h}}\)), 7.57 (bd, 2H, H\(_{\text{e}}\)), 7.50 (s, 4H, H\(_{\text{a}}\)), 7.26 (bs, 2H, H\(_{\text{i}}\)), 7.22 (bs, 2H, H\(_{\text{c}}\)), 6.90 (bd, J = 8.5 Hz, 2H, H\(_{\text{g}}\)), 6.81 (bm, 2H, H\(_{\text{d}}\)), 6.23 (m, 8H, H\(_{\text{n}}\)), 5.87 (m, 2H, H\(_{\text{o}}\)), 5.17 (m, 4H, H\(_{\text{b}}\)), 5.01 (m, 4H, H\(_{\text{i}}\)), 4.03 (bt, 4H, H\(_{\text{j}}\)), 2.12 (m, 4H, H\(_{\text{k}}\)), 1.84 (m, 4H, H\(_{\text{m}}\)), 1.51 (m, 8H, H\(_{\text{l+m}}\)). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) δ 157.10, 156.57, 156.35, 138.93, 138.79, 136.93, 136.79, 136.57, 136.35, 133.99, 133.80, 128.71, 128.69, 127.75, 126.12, 126.04, 122.05, 121.79, 117.16, 117.05, 114.47, 112.45, 112.37, 112.04, 111.97, 111.20, 111.15, 110.93, 110.90, 69.87, 68.12, 33.73, 29.15, 28.69, 25.70, 25.59. MS m/z: calcd. for C\(_{62}\)H\(_{54}\)O\(_4\)S\(_8\) [M+H] \(^+\) found MALDI-TOF 1118.15.
A catalytic amount of Grubb's 1st generation catalyst was added to a solution of the linear precursor 1 in dry and degassed CH₂Cl₂. The solution was stirred at room temperature and its progress monitored by TLC (Hex:CH₂Cl₂ 2:1). The reaction proceeds spot to spot until it is close to completion, when unidentified polar spots start to appear on the TLC. The reaction is then stopped, filtered through a pad of Celite, the solvent evaporated under reduced pressure, and the crude subjected to column chromatography on silica gel (Hex:CH₂Cl₂ 2:1) to yield the product as an inseparable mixture of E/Z isomers ($\gamma = 90\%$).

The product shows complicated $^1$H NMR, consistent with an asymmetric molecule in several conformations in slow chemical exchange at NMR timescale. We have obtained a sufficiently well-resolved spectrum on a Bruker AvanceII 700 MHz in chlorobenzene-$d_6$, and fully assigned it based on COSY and TOCSY experiments (see below). Lettering corresponds to that shown above. No distinction between isomers or conformers has been made.

$^1$H NMR (chlorobenzene-$d_6$, 700 MHz, 298 K) $\delta$ 7.64 (d, J = 8.4 Hz, 0.25H, Hₙ), 7.36 (d, J = 8.4 Hz, 0.75H, Hₕ), 7.31 (d, J = 8.4 Hz, 0.50H, Hₗ), 7.29 (d, J = 8.4 Hz, 0.50H, Hₕ), 7.23 (s, 0.25H, Hₖ), 7.19 (d, J = 8.4 Hz, 0.75H, Hₖ), 7.16 (d, J = 8.4 Hz, 0.25H, Hₙ), 7.09 (d, J = 8.4 Hz, 0.50H, Hₗ), 7.04 (s, 3H, Hₗ), 7.02 (s, 1H, Hₙ), 7.00 (d, J = 2.3 Hz, 0.50H, Hₗ), 6.99 (s, 0.50H, Hₖ), 6.86 (s, 0.25H, Hₖ), 6.85 (d, J = 2.3 Hz, 0.75H, Hₗ), 6.83 (m, 0.25H, Hₗ), 6.79 (dd, J = 8.3 Hz, J = 2.4 Hz, 0.50H, Hₗ), 6.77 (s, 0.25H, Hₖ), 6.66 (dd, J = 8.4 Hz, J = 2.4 Hz, 0.50H, Hₗ), 6.63 (s, 0.25H, Hₖ), 6.60 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H, Hₗ), 6.51 (m, 1.5H, Hₗ), 6.33 (dd, J = 8.4 Hz, J = 2.3 Hz, 0.50H, Hₗ), 6.26 (dd, J = 8.5 Hz, J = 2.3 Hz, 0.50H, Hₗ), 5.63 (d, J = 6.6 Hz, 0.50H, Hₗ), 5.57 (m, 1H, Hₗ), 5.47 (m, 1H, Hₗ), 5.24 (d, J = 6.6 Hz, 0.50H, Hₗ), 5.19 (d, J = 6.6 Hz, 0.50H, Hₗ), 5.16 (m, 0.75H, Hₗ), 5.13 (m, 1.25H, Hₗ), 5.09 (d, J = 6.6 Hz, 0.50H, Hₗ), 4.98-4.87 (m, 4H, Hₗ), 3.59 (m, 4H, Hₗ), 1.79 (m, 4H, Hₗ), 1.44 (m, 4H, Hₗ), 1.19 (m, 8H, Hᵢ₋ₘ). $^{13}$C
NMR (chlorobenzene-\textit{d}_5, 175 MHz, 298 K) \( \delta \) 157.52, 156.49, 156.25, 156.02, 138.90, 137.56, 137.49, 137.39, 137.31, 137.09, 136.95, 132.47, 130.89, 130.65, 127.28, 127.21, 127.10, 121.84, 121.43, 117.20, 117.09, 117.00, 116.93, 116.72, 116.66, 116.57, 114.31, 113.70, 112.83, 112.33, 111.89, 111.84, 111.76, 111.66, 111.39, 111.20, 111.01, 110.52, 69.21, 69.07, 68.23, 68.02, 37.91, 34.55, 34.17, 33.21, 32.63, 29.84, 29.63, 29.41, 29.14, 27.69, 27.23, 27.02, 25.38, 25.32. MS \( m/z \): calcd. for C\textsubscript{60}H\textsubscript{50}O\textsubscript{4}S\textsubscript{8} [M\textsuperscript{+}] 1090.1 found MALDI-TOF 1090.2 HRMS \( m/z \): calcd. for C\textsubscript{60}H\textsubscript{50}O\textsubscript{4}S\textsubscript{8} [M\textsuperscript{+}] 1090.1475 [M\textsuperscript{2+}] 545.0738 found ESI (pos.) 1090.1372; 545.0732.

**UV/Vis Titrations:** Binding constants were evaluated by titrating a fixed concentration solution of 1 with variable amounts of fullerene C\textsubscript{60} or C\textsubscript{70} (from 0 to \( 2 \times 10^{-5} \) M\textsuperscript{-1}) using toluene, chlorobenzene, or benzonitrile as solvent. The resulting solutions were measured by UV/Vis spectroscopy at room temperature. Some spectra were corrected by background substraction. \( \Delta \text{Abs} \) of 1 at 470 nm was plotted against the total concentration of the fullerene. The resulting curve was fitted using Microcal Origin 7.5 software. The association constant \( K_S \) was evaluated using the equation:\textsuperscript{1}

\[
\Delta \text{Abs} = \Delta \text{Abs}_{\text{max}} (1 + K_s[C_{60}] + K_s[1]_0) - \left( (1 + K_s[C_{60}] + K_s[1]_0)^2 - 4 K_s[C_{60}][1]_0 \right)^{1/2} / (2 K_s[1]_0)
\]
**Fig. S1** Absorption spectra of 1 (1.56 x 10^{-5} M) in benzonitrile with variable concentrations of C_{60} (0; 3.36 x 10^{-7} M; 6.72 x 10^{-7} M; 9.96 x 10^{-7} M; 1.48 x 10^{-6} M; 1.96 x 10^{-6} M; 2.59 x 10^{-6} M; 3.22 x 10^{-6} M; 4.13 x 10^{-6} M; 5.28 x 10^{-6} M; 6.67 x 10^{-6} M; 8.28 x 10^{-6} M; 1.00 x 10^{-5} M; 1.2 x 10^{-5} M; 1.39 x 10^{-5} M and 1.60 x 10^{-5} M). C_{60} absorptions were subtracted. Insert: binding isotherm that displays the absorption changes at 470 nm as a function of C_{60} concentration.
Fig. S2 Upper part – absorption spectra of 1 (1.82 \times 10^{-5} \text{M}) in toluene with variable concentrations of C_{60} (0; 7.5 \times 10^{-7} \text{M}; 1.48 \times 10^{-6} \text{M}; 2.19 \times 10^{-6} \text{M}; 2.88 \times 10^{-6} \text{M}; 4.22 \times 10^{-6} \text{M}; 5.50 \times 10^{-6} \text{M}; 7.89 \times 10^{-6} \text{M}; 1.01 \times 10^{-5} \text{M}; 1.21 \times 10^{-5} \text{M}; 1.48 \times 10^{-5} \text{M}; 1.80 \times 10^{-5} \text{M} and 2.08 \times 10^{-5} \text{M}). C_{60} absorptions were subtracted. Lower part – binding isotherm that displays the absorption changes at 470 nm as a function of C_{60} concentration.

\[
y = \frac{(M1^*M2^*M3^*)0}{(1+M2^*M0)}
\]

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Fig. S3 Upper part – absorption spectra of 1 (2.88 x 10⁻⁵M) in chlorobenzene with variable concentrations of C₆₀ (0; 2.99 x 10⁻⁶M; 5.95 x 10⁻⁶M; 9.81 x 10⁻⁶M; 1.36 x 10⁻⁵M; 1.73 x 10⁻⁵M; 2.10 x 10⁻⁵M; 2.46 x 10⁻⁵M; 2.81 x 10⁻⁵M; 3.15 x 10⁻⁵M; 3.49 x 10⁻⁵M; 3.99 x 10⁻⁵M and 4.47 x 10⁻⁵M). C₆₀ absorptions were subtracted. Lower part – binding isotherm that displays the absorption changes at 470 nm as a function of C₆₀ concentration.
Fig. S4 Charge transfer absorption in 1•C₆₀ (red spectrum) and exTTF bis-crown ether•C₆₀³ (black spectrum) in benzonitrile at room temperature.
Fig. S5 Absorption spectra of 1 (1.56 x 10⁻⁵ M) in benzonitrile with variable concentrations of C₇₀ (0; 3.36 x 10⁻⁷ M; 6.67 x 10⁻⁷ M; 9.96 x 10⁻⁷ M; 1.48 x 10⁻⁶ M; 1.96 x 10⁻⁶ M; 2.59 x 10⁻⁶ M; 3.22 x 10⁻⁶ M; 4.13 x 10⁻⁶ M; 5.28 x 10⁻⁶ M; 6.67 x 10⁻⁶ M; 8.28 x 10⁻⁶ M; 1.00 x 10⁻⁵ M; 1.2 x 10⁻⁵ M; 1.39 x 10⁻⁵ M and 1.60 x 10⁻⁵ M).
Fig. S6 Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (480 nm) of $1\cdot C_{70}$ in Ar-saturated benzonitrile with time delays between 0.1 and 5750 ps at room temperature. Lower part - time-absorption profile at 950 nm, reflecting the transformation of $C_{70}^{\delta-}/exTTF^{\delta+}$ into the fully $C_{70}^{-}/exTTF^{+}$ charge separated state and charge recombination kinetics yielding the triplet excited state of $C_{70}$. 
**Fluorescence titrations:** Complementary fluorescence titration experiments were carried out in line with earlier work. The fluorescence of 1 was monitored while the variable amounts of fullerenes ($C_{60}$ and $C_{70}$) were added. The gradual quenching at 462 nm was used to estimate the association constants $K_a$ according to the following equation:

$$\frac{I_r}{I_0} = 1 - \frac{1}{2K_a} \left[ \frac{1}{K_a + c_0 + c_D} - \sqrt{\left(\frac{1}{K_a + c_0 + c_D}\right)^2 - 4c_0c_D} \right]$$

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