

Electronic Supplementary Information

Ionic manipulation of charge-transfer and photodynamics of [60]fullerene confined in pyrrolo-tetrathiafulvalene cage

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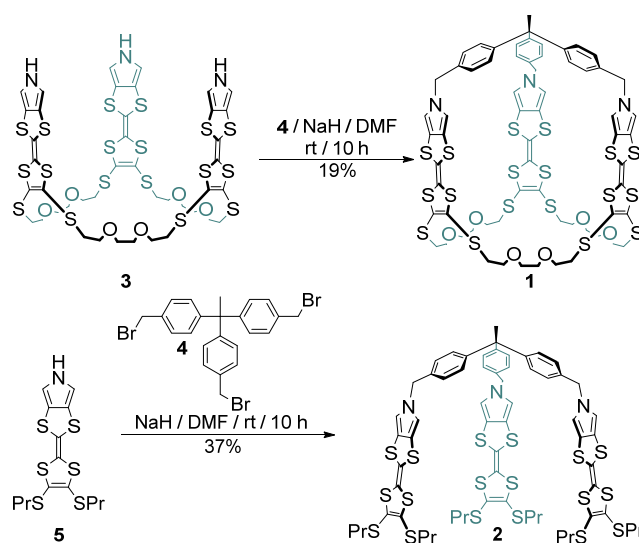
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Experimental Section

General Methods: Chemicals were purchased from Sigma-Aldrich or Fluka and were used as received. Compounds **3**^{S1}, **4**^{S2}, and **5**^{S3} were prepared according to literature procedures. All reactions were carried out under an atmosphere of anhydrous nitrogen unless otherwise stated. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days prior to use, while CH₂Cl₂ was distilled before use. Thin-layer chromatography (TLC) was carried out using aluminium sheets precoated with silica gel 60F (Merck 5554). The plates were inspected under UV light (254 nm) and, if required, developed by I₂ vapour. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). ¹H NMR were recorded at room temperature at 400 MHz and 300 MHz, on a Bruker ADVANCED III spectrometer and a Varian Gemini spectrometer, respectively, using residual solvent as the internal standard. ¹³C NMR spectra were recorded at room temperature at 100 MHz and 75 MHz, on a Bruker ADVANCED III spectrometer and a Varian Gemini spectrometer, respectively, using residual solvent as the internal standard. The solvent signals were assigned according to Nudelman *et al.*^{S4} All chemical shifts are quoted on a δ scale, and all coupling constants (*J*) are expressed in Hertz (Hz). The following abbreviations are used in listing the NMR spectra: s = singlet, bs = broad singlet d = doublet, t = triplet, q = quartet, sext = sextet, bs = broad singlet, and m = multiplet. Samples were prepared using CDCl₃ purchased from Cambridge Isotope Labs or Sigma-Aldrich. Matrix assisted laser-desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Autoflex III Smartbeam mass spectrometer, utilising a 2,5-dihydroxybenzoic acid matrix. UV–Vis–NIR spectroscopic data were recorded on a Shimadzu UV–1601PC spectrophotometer or a JASCO V–670 spectrophotometer. Elemental analyses were performed by the Atlantic Microlabs, Inc., Atlanta, Georgia.



Scheme S1 Synthesis of cage molecule **1** and semi-cage **2**.

Synthesis of Cage (1): A solution of compound **3** (96 mg, 0.076 mmol) and compound **4** (51 mg, 0.095 mmol) in anhydrous DMF (20 mL) was degassed (N_2) for 15 min and transferred to a syringe, which was placed in a perfuser pump. NaH (55–65% v/v in mineral oil, 18.5 mg, 0.46 mmol) was dissolved in anhydrous DMF (10 mL) and degassed (N_2) and then cooled to 0 °C. The mixture of **3** and **4** was then added with a rate of 2 mL h⁻¹ to the solution of NaH at 0 °C. After addition was completed, the reaction mixture was allowed to reach room temperature and stirred for 5 h at room temperature, where after a saturated aqueous solution of NaCl (60 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 60 mL) and the combined organic phases were washed with a saturated aqueous solution of NaCl (2 × 60 mL), H_2O (60 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified by column chromatography (SiO_2 , CH_2Cl_2 :MeOH 199:1 v/v) providing the cage molecule **1** as a yellow solid (222 mg, 19%). M.p. 210–212 °C; ¹H NMR (300 MHz, $CDCl_3$, 298 K) δ 2.12 (s, 3H, Ph_3CH_3), 3.00–3.10 (m, 6H, SCH_2), 2.90–2.99 (m, 6H, SCH_2), 3.66 (s, 12H, OCH_2CH_2O), 3.69–3.72 (m, 12H, SCH_2CH_2), 4.95 (bs, 6H, NCH_2), 6.48 (s, 6H, α -H pyrrole), 6.98 (s, 12H, (Ph-H)₃); ¹³C NMR (75 MHz, $CDCl_3$, 298 K) δ 14.1, 22.7, 35.5, 70.1, 70.5, 110.2, 113.0, 119.4, 126.4, 127.7, 128.9, 135.4, 148.3 (two lines are missing/overlapping); MS (MALDI-TOF) m/z 1582 ($[M + Na]^+$), 1559 (M^+); MS (Hi-Res-FT-ESI) calcd. for $C_{65}H_{63}N_3O_6S_{18}^{*+}$ 1556.9684; found 1556.9623; Anal. Calcd. for $C_{65}H_{63}N_3O_6S_{18}$: C, 50.06; H, 4.07; N, 2.69; S, 37.01. Found: C, 50.24; H, 4.09; N, 2.80; S 36.84.

Synthesis of Semi-Cage (2): A solution of compound **5** (510 mg, 1.30 mmol) in anhydrous DMF (15 mL) was degassed (N_2) for 15 min before NaH (55–65% v/v in mineral oil, 260 mg, 6.5 mmol) was added. After 15 min, a solution of **4** (200 mg, 0.372 mmol) in anhydrous DMF (4 mL) was added dropwise over 10 min. After 2 h, the brown reaction mixture was quenched by addition of a saturated aqueous solution of NaCl (125 mL). The solution was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic phases were washed with a saturated aqueous solution of NaCl (100 mL), H_2O (100 mL), and dried ($MgSO_4$). Removal of the solvent gave a yellow oil, which was purified by column chromatography (SiO_2 , CH_2Cl_2 :petroleum ether 1:1 v/v) providing the semi-cage molecule **2** as a yellow solid (202 mg, 37%). Recrystallization from CH_2Cl_2 /MeOH afforded **2** as a fine yellow powder. M.p. 75.8–77.5 °C; ¹H NMR (400 MHz, $CDCl_3$, 298 K) δ 1.01(t, 18H, CH_2CH_3), 1.66 (sext, 12H, CH_2CH_3), 2.09 (s, 3H, Ph_3CH_3), 2.80 (t, 12H, SCH_2), 4.95 (bs, 6H, NCH_2), 6.48 (s, 6H, α -H pyrrole), 7.00 (s, 12H, (Ph-H)₃); ¹³C NMR (100 MHz, $CDCl_3$, 298 K) δ 13.2, 23.2, 30.4, 38.3, 52.1, 54.0, 113.0, 119.6, 126.7, 127.5, 129.0, 135.1, 148.5 (two lines are missing/overlapping). A comparison of the integrals of the H_2O resonances the pure $CDCl_3$ and that of **4** recorded in $CDCl_3$ showed additional water content of 0.79× H_2O per molecule of **4**. MS (MALDI-TOF) m/z 1468 ($[MH]^+$); Anal. Calcd. for $C_{65}H_{69}N_3S_{18}$: C, 53.13; H, 4.73; N, 2.86; S, 39.27. Anal. Calcd. for $C_{65}H_{69}N_3S_{18} + 0.79 \times H_2O$: C, 52.62; H, 4.80; N, 2.83; O, 0.85; S, 38.90. Found: C, 52.70; H, 4.82; N, 2.87; S 38.78.

¹H NMR Spectroscopic Investigation

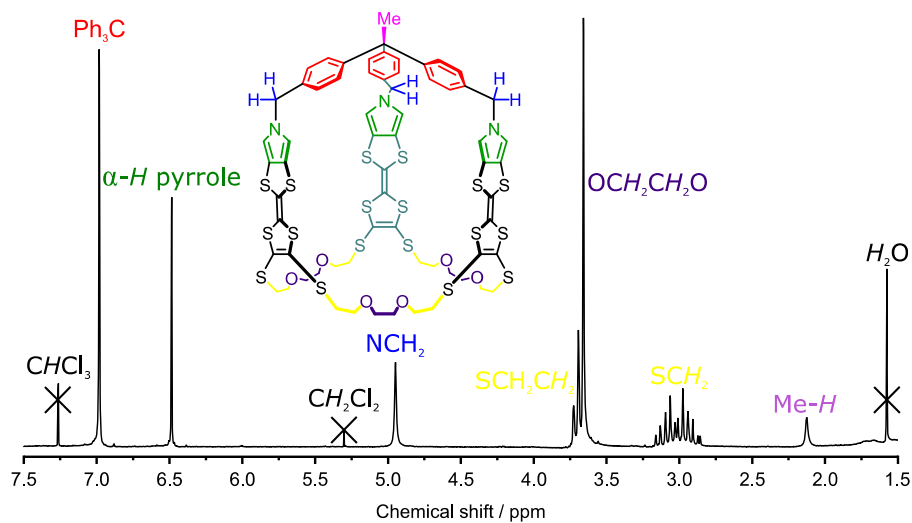


Fig. S1 ¹H NMR (300 MHz, CDCl₃, 298 K) spectrum of **1**.

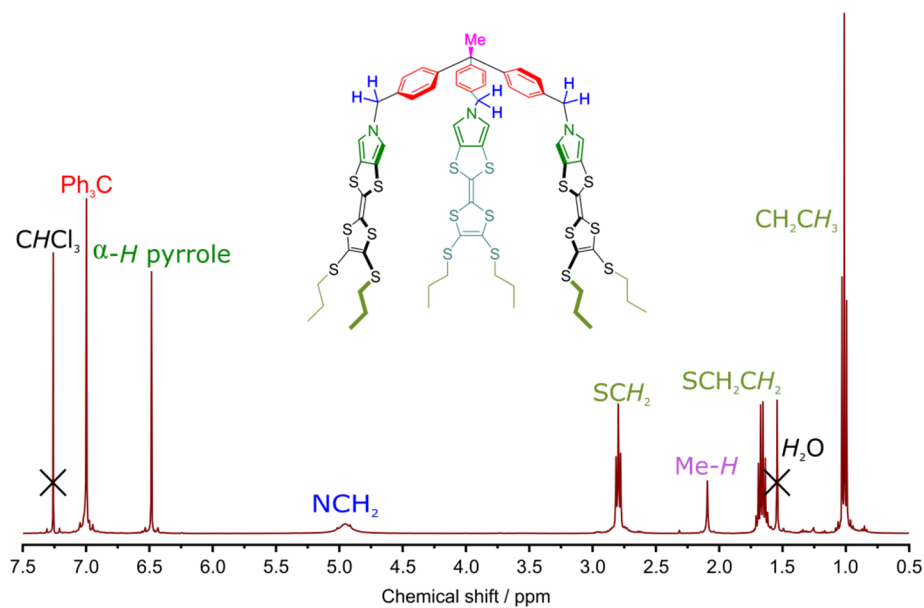


Fig. S2 ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of **2**.

Determination of Binding Constant by ^1H NMR Spectroscopy

The MPTTF cage molecule **1** was observed to be in slow exchange with its C_{60} complex $\text{C}_{60}\text{C1}$ on the ^1H NMR time scale (300 MHz, 298 K), allowing the binding constant to be determined using the single-point method.^{S5} Both the α -pyrrole protons, NCH_2 protons, and the protons from the methyl group show significant shifts in their resonances upon complexation with C_{60} (Fig. S3). This makes it possible to determine the binding constants K_a by the single-point method. If I_c and I_u are the integrals of a specific proton in the complexed and uncomplexed case and if C_1 and $C_{\text{C}_{60}}$ are the initial molar concentrations of the uncomplexed species, **1** and C_{60} , respectively, K_a can be determined by $K_a = \frac{I_c}{I_u(C_1 - \frac{I_c}{I_u + I_c}C_{\text{C}_{60}})}$

Three independent ^1H NMR spectra were recorded and the α -pyrrole, NCH_2 , and the CH_3 protons were used as probes. This resulted in 9 K_a values which are listed in Table S1.

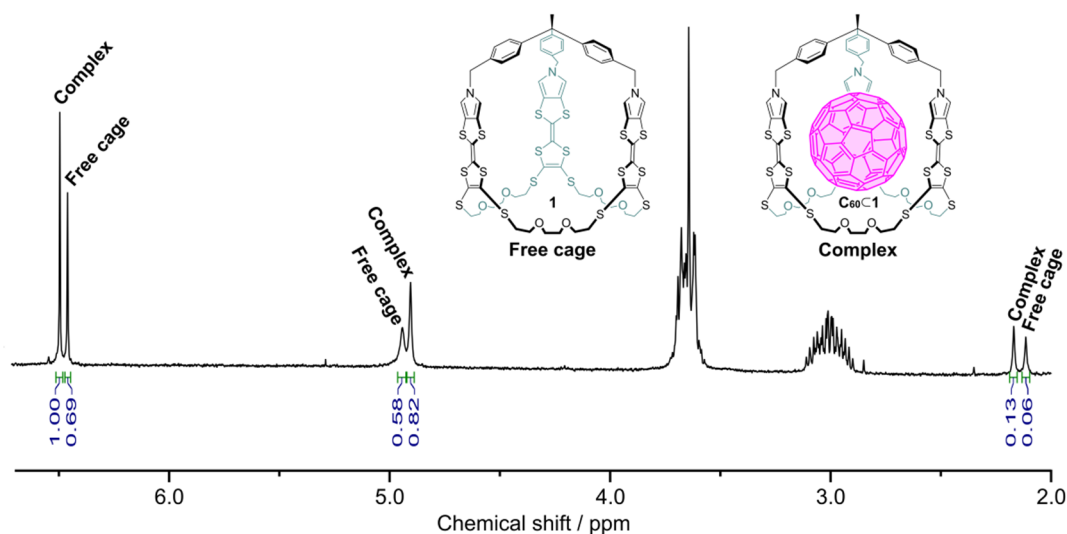


Fig. S3 Partial ^1H NMR spectrum (300 MHz) recorded of a 1:1 mixture (1.6 mM) **1** and C_{60} in $\text{CDCl}_3/\text{CS}_2$ (85:15) at 298 K.

Table S1 Binding constants between the MPTTF cage **1** (1.43 mM) and C_{60} (1.43 mM) obtained using the ^1H NMR (300 MHz) single-point method in $\text{CDCl}_3/\text{CS}_2$ at 298 K using the α -pyrrole, NCH_2 , and the CH_3 protons as probes.

	α -H pyrrole			NCH_2			CH_3		
	I_u	I_c	K_a / M^{-1}	I_u	I_c	K_a / M^{-1}	I_u	I_c	K_a / M^{-1}
1	0.70	1.00	2426	0.66	0.89	2275	0.26	0.34	2110
2	0.69	1.00	2482	0.58	0.83	2432	0.05	0.10	4195
3	0.65	1.00	2730	0.43	0.68	2854	0.13	0.19	2515

UV–vis–NIR Absorption Spectroscopic Investigations

Qualitative Analysis

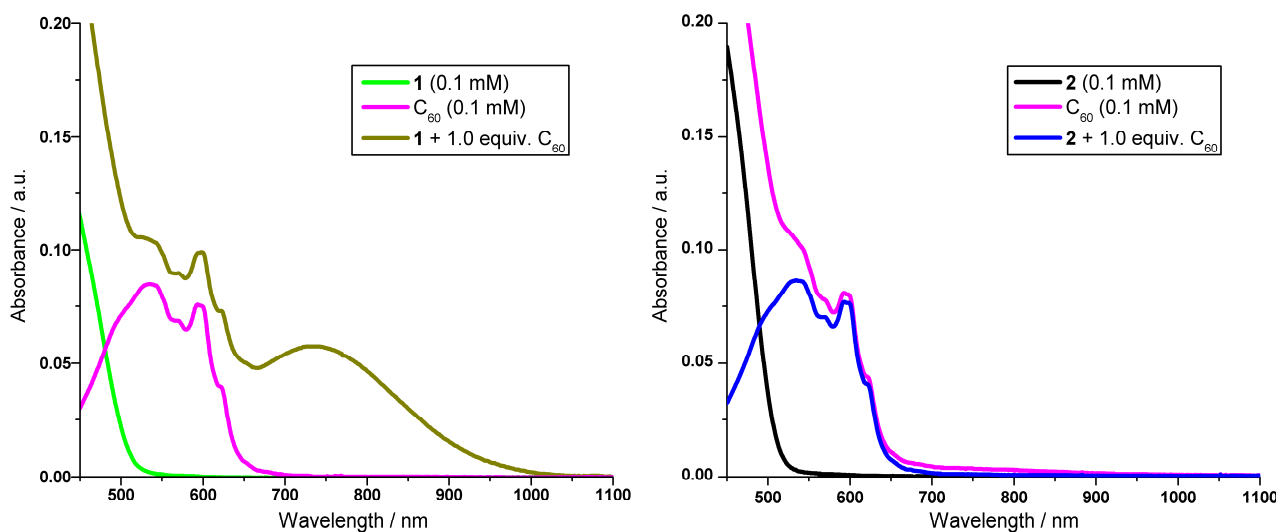


Fig. S4 UV–vis–NIR absorption (CH_2Cl_2 , 298 K) of left: **1** (0.1 mM), C_{60} (0.1 mM) and **1** (0.1 mM) + C_{60} (0.1 mM); right: **2** (0.1 mM), C_{60} (0.1 mM) and **2** (0.1 mM) + C_{60} (0.1 mM).

Job Plot

The Job plot^{S6} titration was carried out at 298 K in CH_2Cl_2 . The initial concentrations are $[1] = 0.1$ mM and $[C_{60}] = 0.1$ mM. The maximum of the CT band at $\lambda = 735$ nm was used as the probe.

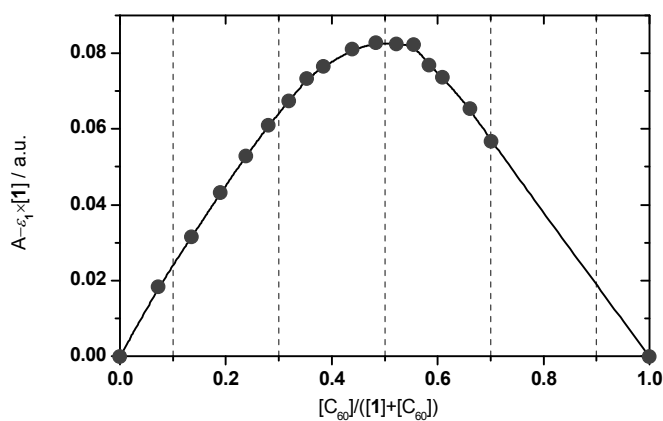


Fig. S5 Job Plot obtained between **1** and C_{60} in CH_2Cl_2 with $[1] = [C_{60}] = 0.1$ mM, at $\lambda = 735$ nm.

Determination of Binding Constants

A solution of **1** (5.6 μM in CH_2Cl_2 at 295 K) was titrated by adding quantities of a known concentrated solution of either C_{60} or $\text{Li}^+\text{@C}_{60}$. The solution used to effect the titration contained the cage **1** at the same concentration as the cage solution into which they were being titrated so as to obviate a need to account for dilution.

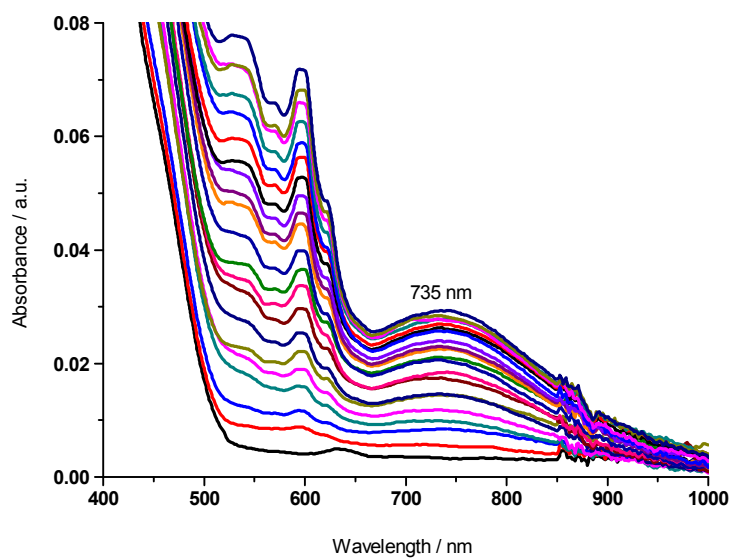


Fig. S6 UV-vis-NIR absorption (CH_2Cl_2 , 298 K) spectroscopic titration of **1** with C_{60} .

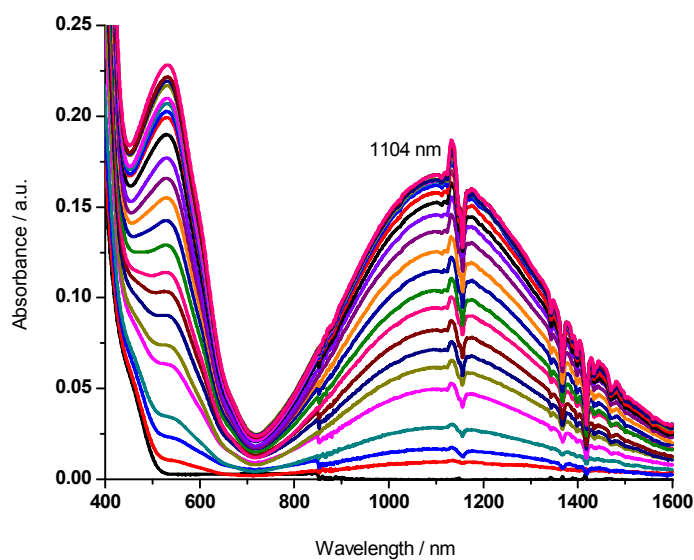


Fig. S7 UV-vis-NIR Absorption (CH_2Cl_2 , 298 K) spectroscopic titration of **1** with $\text{Li}^+\text{@C}_{60}$.

The change in absorbance at $\lambda = 735$ nm (C_{60}) and 1104 nm ($Li^+@C_{60}$) was used to derive the binding constants for the complexation of **1** with C_{60} and $Li^+@C_{60}$, respectively. The data was fitted to Connors 1:1 UV-vis-NIR equation:⁵⁷

$$A = A_0 + \frac{A_{lim} - A_0}{2 \times C_0} \times \sqrt{C_0 + G + K^{-1} - (C_0 + G + K^{-1})^2 - 4 \times C_0 \times G}$$

where A_0 is the initial absorbance, A_{lim} is the maximum absorbance, C_0 is the host (i.e., **1**) concentration, G is the guest (i.e., C_{60} or $Li^+@C_{60}$) concentration, and K is the binding constant.

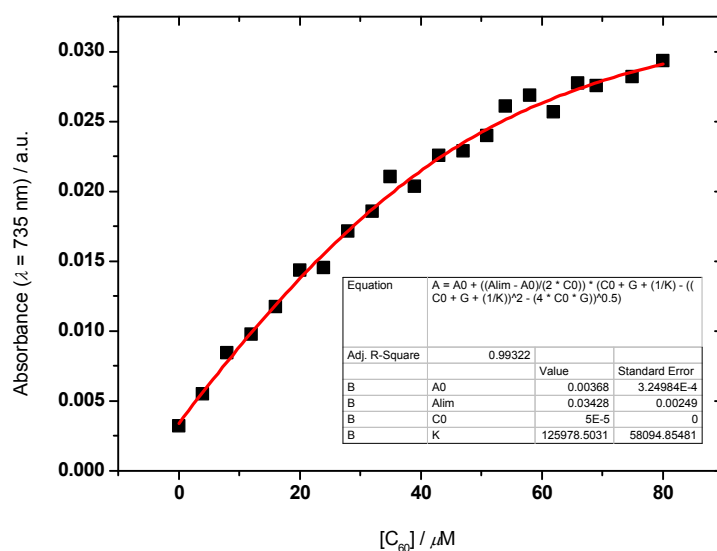


Fig. S8 Binding curves obtained from absorption spectroscopic titration of the MPTTF cage **1** (50 μ M) with increasing amounts of C_{60} in CH_2Cl_2 at 298 K together with the calculated binding isotherm derived by using Connors 1:1 equation.⁵⁷

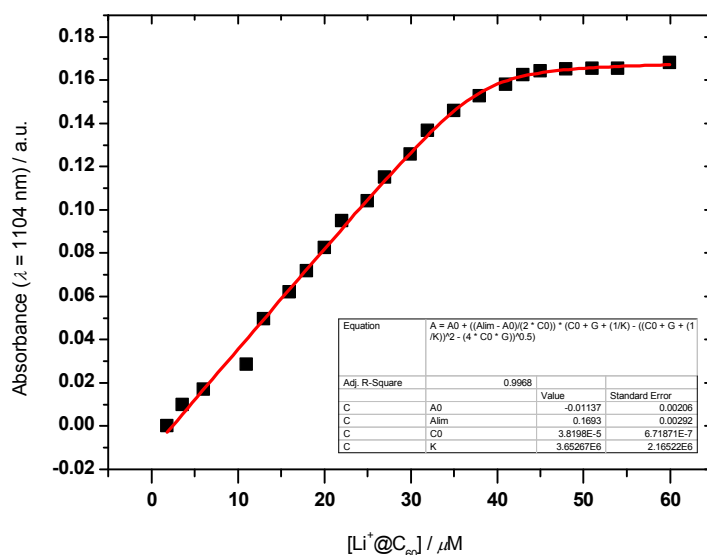


Fig. S9 Binding curves obtained from absorption spectroscopic titration of the MPTTF cage **1** (50 μ M) with increasing amounts of $Li^+@C_{60}$ in CH_2Cl_2 at 298 K together with the calculated binding isotherm derived by using Connors 1:1 equation.⁵⁷

Electrochemical Measurements

Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated solvents containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with ALS polishing alumina suspension (0.05 μ m) and rinsed with water and acetone before use. The measured potentials were recorded with respect to a saturated calomel electrode (SCE). All electrochemical measurements were carried out under an atmospheric pressure of N₂.

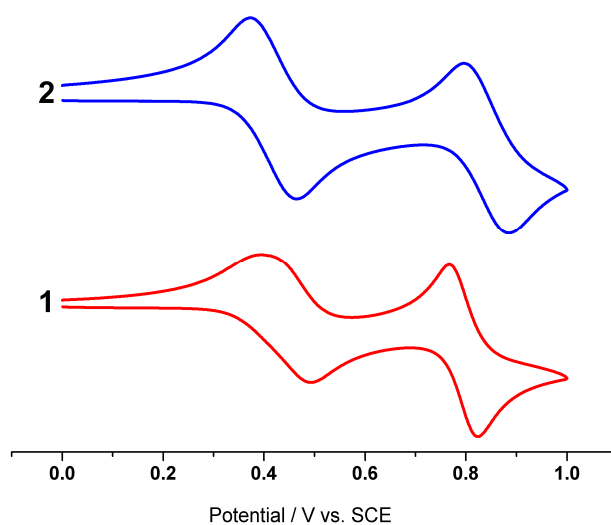


Fig. S10 Cyclic voltammograms of semi-cage **2** and cage **1** in deaerated CH₂Cl₂ containing 0.1 M TBAPF₆ (scan rate: 0.1 mV s⁻¹).

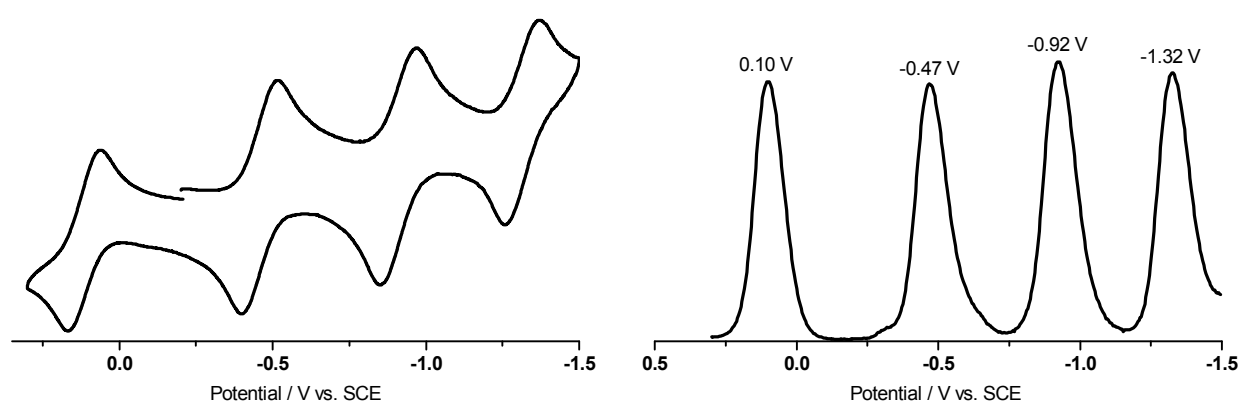


Fig. S11 Cyclic (left) and differential pulse (right) voltammograms of Li⁺@C₆₀ in dichlorobenzene containing 0.1 M TBAPF₆ (scan rate: 0.1 mV s⁻¹).

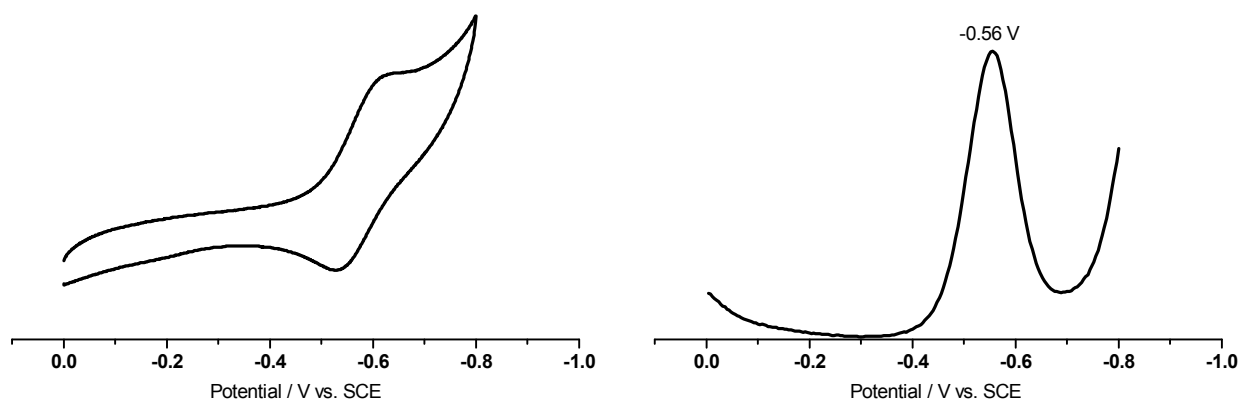


Fig. S12 Cyclic (left) and differential pulse (right) voltammograms of C_{60} in dichlorobenzene containing 0.1 M $TBAPF_6$ (scan rate: 0.1 mV s^{-1}).

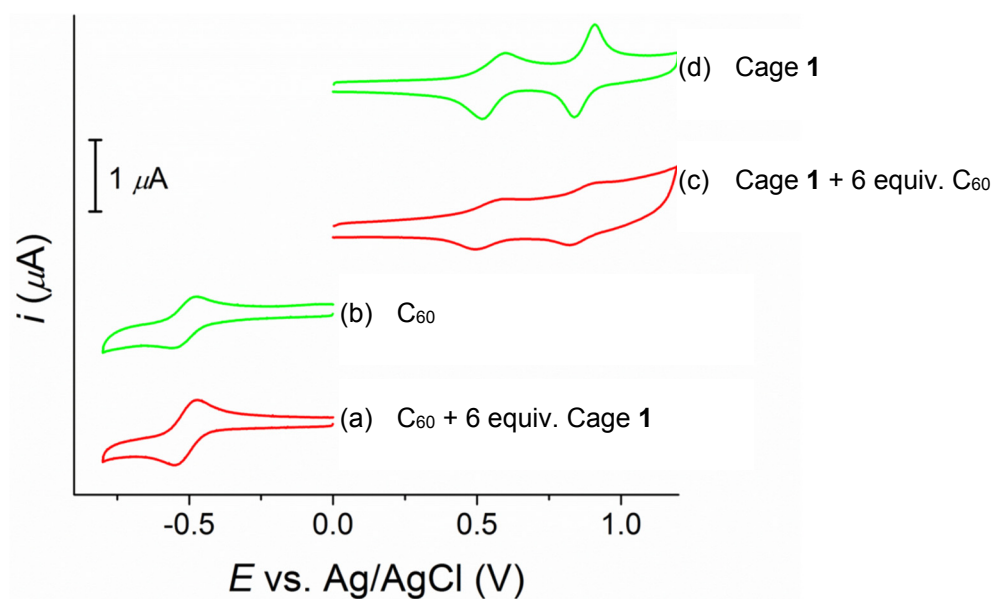


Fig. S13 Cyclic voltammetry of (a) 0.1 mM cage molecule **1**, (b) 0.1 mM cage molecule **1** with 6 equiv. C_{60} , (c) 0.1 mM C_{60} , and (d) 0.1 mM C_{60} with 6 equiv. cage molecule **1**. 1:1 $CH_2Cl_2:CS_2$ with 0.1 M $TBAPF_6$ supporting electrolyte, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl, scan rate: 0.2 mV s^{-1} .

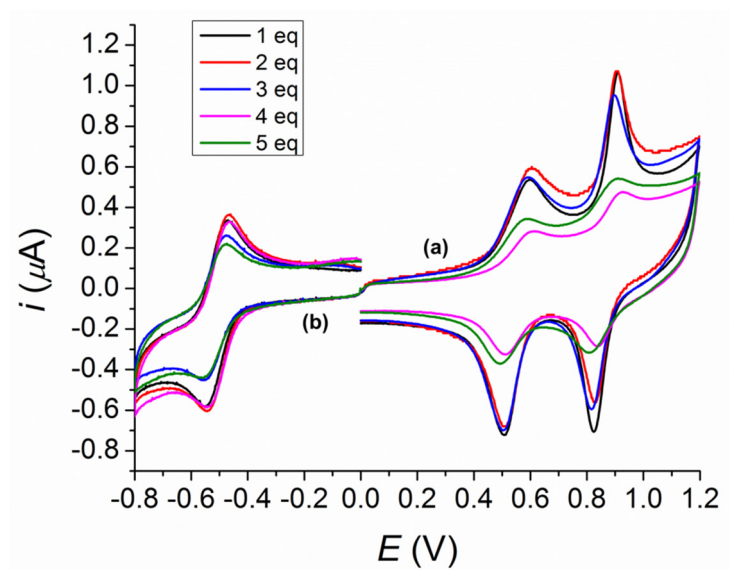


Fig. S14 CV of (a) empty cage **1** titrated with aliquots of C_{60} and (b) free C_{60} titrated with aliquots of cage molecule **1**. 1:1 $CH_2Cl_2:CS_2$ with 0.1 M $TBAPF_6$ supporting electrolyte, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: $Ag/AgCl$, scan rate: 0.2 mV s^{-1} .

Time-Resolved Transient Absorption and Electron Paramagnetic Resonance Measurements

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses was derived from the fundamental output of Integra-C (780 nm, 2 mJ per pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS, which has optical frequency mixers resulting in a tunable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 s to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at 298 K.

For nanosecond transient absorption measurements, deaerated solutions of the compounds were excited with a Panther optical parametric oscillator (OPO) equipped with a Nd:YAG laser (Continuum, SLII-10, fwhm = 4–6 ns) with a power of 10–15 mJ per pulse. The photochemical reactions were monitored by continuous exposure to a Xe lamp (150 W) as a probe light and a detector (SpectraPro 300i). The transient spectra were recorded using fresh solutions in each laser excitation. Solutions were deoxygenated by N₂ purging for about 15 min prior to the transient spectral measurements. All measurements were carried out at 298 K.

The electron paramagnetic resonance (EPR) spectrum was determined using a JEOL X-band spectrometer (JES-RE1XE) under photoirradiation with a high-pressure mercury lamp (USH-1005D) through a water filter by focusing the sample cell in the EPR cavity at 4 K.

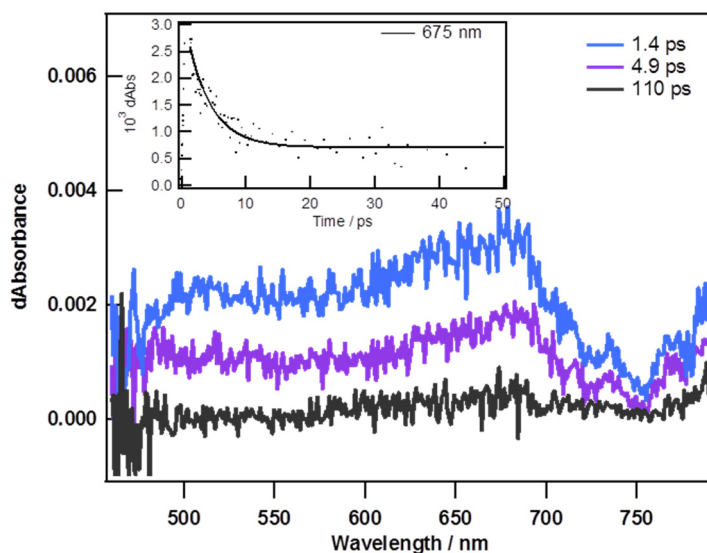


Fig. S15 Femtosecond transient absorption spectra of the cage molecule **1** recorded in deaerated CH₂Cl₂ at indicated time delays. Inset: Time profile at 675 nm ($\lambda_{\text{exc}} = 390$ nm).

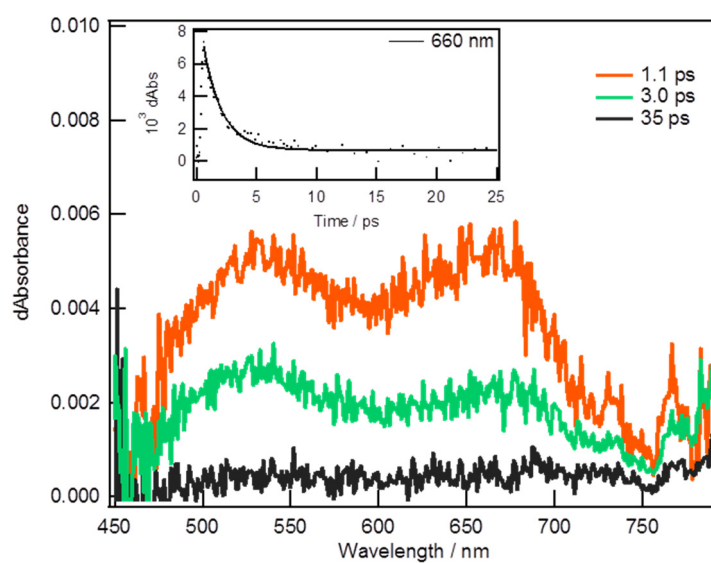


Fig. S16 Femtosecond transient absorption spectra of the $C_{60}C1$ complex (0.23 mM) recorded in deaerated CH_2Cl_2 at indicated time delays. Inset: Time profile at 660 nm ($\lambda_{exc} = 390$ nm).

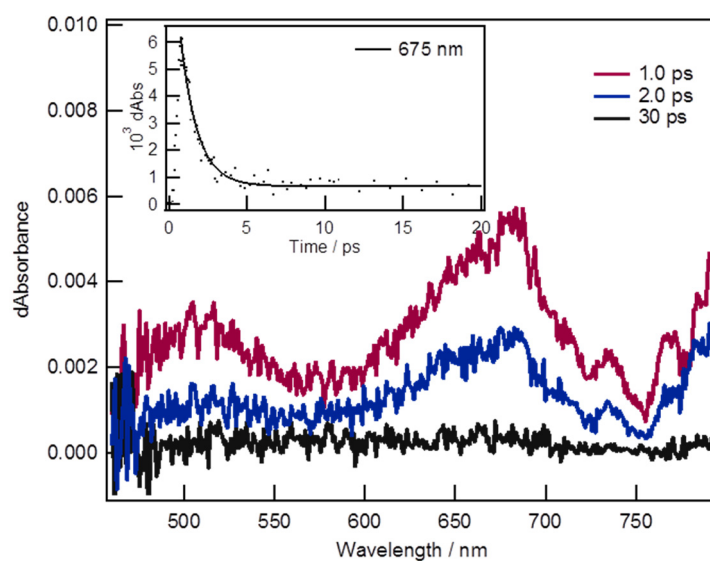


Fig. S17 Femtosecond transient absorption spectra of the $Li^+@C_{60}C1$ complex (0.28 mM) recorded in deaerated CH_2Cl_2 at indicated time delays. Inset: Time profile at 675 nm ($\lambda_{exc} = 390$ nm).

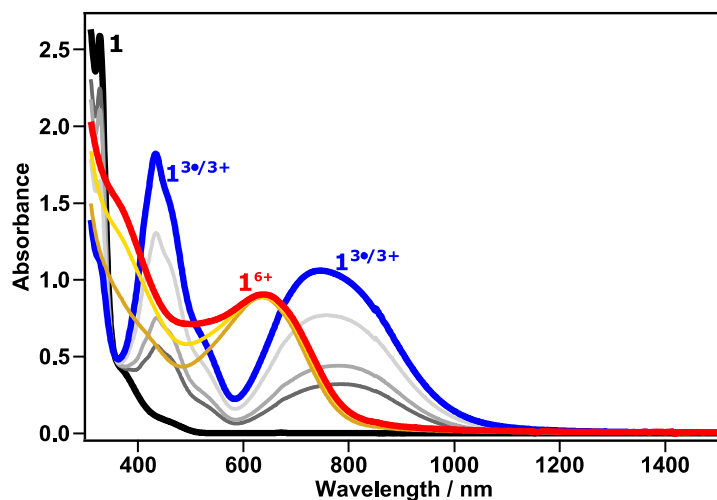


Fig. S18 Absorption spectra of the oxidised states of **1** (0.10 mM in deaerated CH_2Cl_2 at 298 K). The oxidised species were generated by titrating with nitrosonium hexafluoroantimonate (NOSbF_6) as oxidising agent.

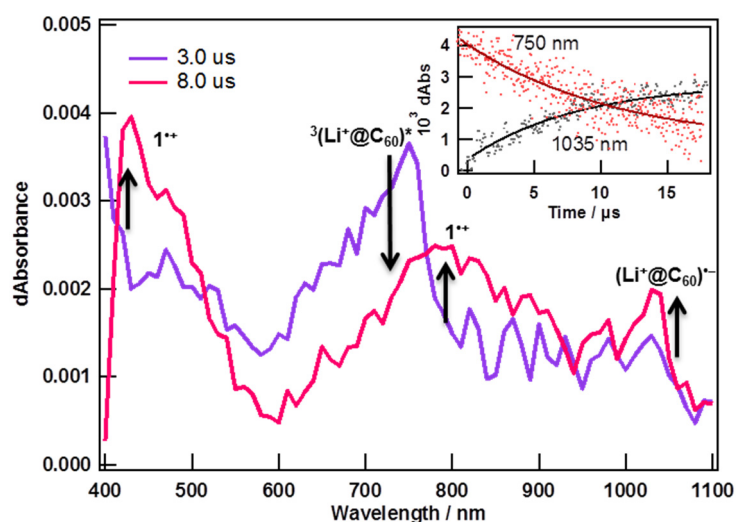


Fig. S19 Nanosecond transient absorption spectra of **1** (0.19 mM) and $\text{Li}^+\text{@C}_{60}$ (0.02 mM) recorded in CH_2Cl_2 at indicated time delays, showing the decay of $^3(\text{Li}^+\text{@C}_{60})^*$ yielding the CS products. Insets: The decay of $^3(\text{Li}^+\text{@C}_{60})^*$ at 750 nm and the rise of radical anion of $\text{Li}^+\text{@C}_{60}$ at 1035 nm ($\lambda_{\text{exc}} = 355 \text{ nm}$).

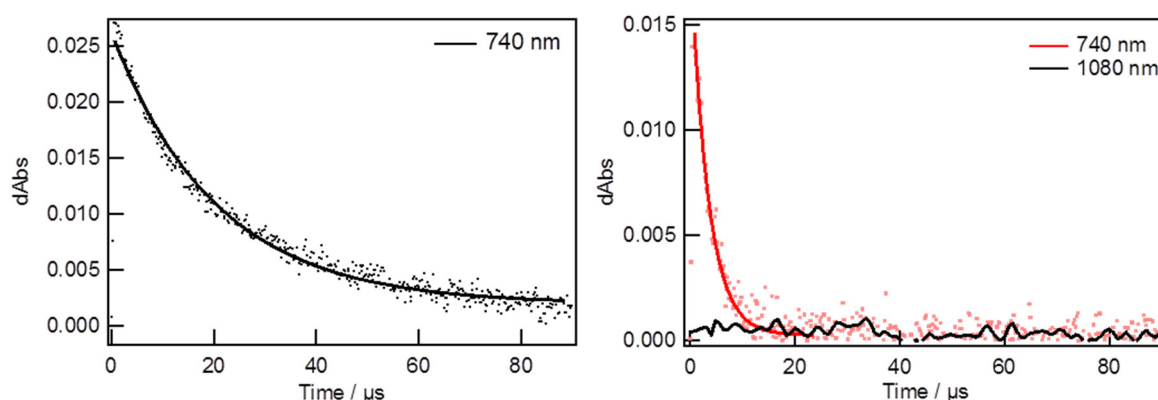


Fig. S20 Time profiles of 0.16 mM C₆₀ (left) and 0.16 mM C₆₀C₁ (right) at indicated wavelengths in deaerated CH₂Cl₂ ($\lambda_{\text{exc}} = 355$ nm).



Fig. S21 EPR spectrum of Li⁺@C₆₀C₁ recorded in PhCN at 4 K after photoexcitation showing the triplet signal of Li⁺@C₆₀^{•-} at $g = 2.001$ and $g = 4.29$. The signal at $g = 2.001$ shows the formation of radicals as the result of a photoinduced electron transfer in the host-guest system, while the feature at $g = 4.29$ arise from the triplet excited states of Li⁺@C₆₀. Although the latter signal is weak, it supports the conclusion that the charge separated state is driven by triplet excited states of Li⁺@C₆₀, which was indeed directly monitored in the nanosecond transient spectra in Fig. S19, in which the radical species form at $\lambda = 450, 800$ and 1035 nm while the triplet states of Li⁺@C₆₀ decay at $\lambda = 750$ nm (Fig. S19, inset). The EPR spectra were used as supporting data in similar ET processes of Li⁺@C₆₀ with electron donors.^{S8,S9}

Crystallographic Information

A single crystal with a dimension of 0.8 x 0.15 x 0.08 mm³ was used for X-ray diffraction studies. Data for C₆₀-**1** were collected with a Rigaku Raxis-RAPID imaging plate using Mo K α radiation (λ = 0.71075 Å) at 100 K. The space group was assigned to be *P*2₁/*a* and the structure was solved by direct methods using the Shelxs 2016^{S10} suite of programs and refined by full-matrix least squares on *F*₂ using Shelxl 2016.^{S11} Thermal parameters were refined anisotropically for all non-hydrogen atoms. All hydrogen atoms were placed geometrically and refined using a riding model.

Crystal data for C₆₀-**1**: C₁₂₆H₆₅Cl₂N₃O₆S₁₈, space group *P*2₁/*a*, *a* = 16.902(3) Å, *b* = 26.870(5) Å, *c* = 21.474(4) Å, β = 92.102(7)°, *V* = 9746(3) Å³, *Z* = 4, 21689 reflections collected, the final *R* is 0.0938, and *wR* is 0.2605.

It was found that seven sulfur atoms on two of the pyrrole-fused TTF unit as well as the crystal solvent (CH₂Cl₂) are disordered. By a population analysis, the ratio of disordered atoms was determined. Following the disorder, the thermal factor of one sulfur atom becomes large, and the corresponding C-S bond length becomes too short, which is over the criteria.

CCDC 1545616 contains the supplementary crystallographic data for C₆₀-**1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

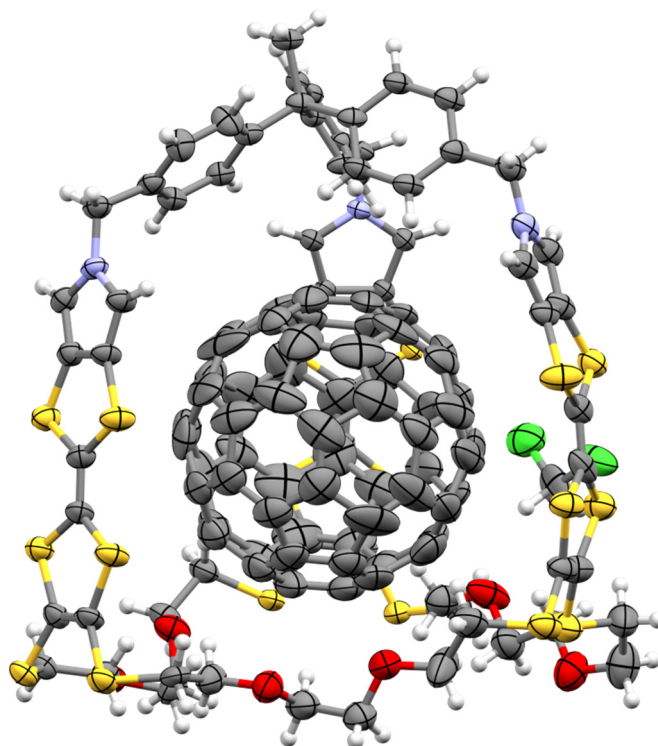


Fig. S22 Single-crystal X-ray structure of the complex C₆₀-**1**. Thermal ellipsoids are scaled at the 50% probability level.

References

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