Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Methanofullerene reversibly switchable by photoexcitation and reduction

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Contents:

Reagents and solvents

4,4’-dimetoxybenzophenone (Sigma-Aldrich, 97%), tosyl hydrazine ($TsNHNH_2$) (Sigma-Aldrich, 97%), $TsOH*H_2O$ (Sigma-Aldrich, 98.5%), C_{70} (Fullerene-center, Russia, 99,8%), CF_3I (P&M Invest, Russia, 99%), pyridine (Acros Organics, 99+%), 18-crown-6 (Sigma-Aldrich, 99%) were used as received. K_2CO_3 was dried in vacuo at 120°C for 3 hours.

Toluene (Chimmed, 99%) was refluxed over Na for 2 h, and then distilled; fraction with b.p. 110.6 °C was collected. Hexane (Chimmed, 99%) was refluxed over P_2O_5 for 2 h, and then distilled; fraction with b.p. 69°C was collected.

o-Dichlorobenzene (Acros Organics, 99%) was refluxed over CaH_2 for 2 h, and then distilled under reduced pressure (12 mmHg); fraction with b.p. 64°C was collected.

Synthetic procedures

Synthesis of 4,4’-dimetoxybenzophenone tosyl hydrazone[1]. 4,4’-dimetoxybenzophenone (2.12 g, 8.7 mmol) was dissolved in methanol in a round bottom flask, then $TsNHNH_2$ (1.64 g, 8.8 mmol) and $TsOH{\cdot}H_2O$ (catalytic amount) was added. The reaction mixture was refluxed for 6 hours. After that, the reaction mixture was cooled down, the white precipitate was vacuum-filtrated and washed with cold methanol (3.30 g, 8.0 mmol, 91% yield).

Synthesis of C_s-$C_{70}(CF_3)_8$[2]. To obtain C_s-$C_{70}(CF_3)_8$, a two-step procedure was employed. Fullerene C_{70} (40 mg) was placed into a three-section glass ampoule, and the excess of CF_3I was condensed. The ampule was sealed and heated at 420 °C in a gradient furnace for 48 h to give a mixture of higher trifluoromethylfullerenes (146 mg), which was then thoroughly ground with pristine C_{70} (56 mg), put into two-section glass ampoule. Then the ampule was sealed and heated at 440 °C in a gradient furnace for 40 h. Individual trifluoromethylfullerenes were isolated by means of preparative HPLC.

Mixture of $C_{70}(CF_3)_n$ (n=18-20): MALDI MS m/z (I, %): 2082 (7%, $C_{70}(CF_3)_{18}^-$), 2152 (25%, $C_{70}(CF_3)_{19}^-$), 2220 (100%, $C_{70}(CF_3)_{20}^-$).

Mixture of $C_{70}(CF_3)_n$ (n=6-10): MALDI MS m/z (I, %): 840 (25%, C_{70}^-) 1254 (11%, $C_{70}(CF_3)_6^-$), 1392 (100%, $C_{70}(CF_3)_8^-$), 1530 (90%, $C_{70}(CF_3)_{10}^-$); HPLC (t_R, min, CB 4.6 mm i.d. × 250 mm , toluene, 1 mL·min^{-1}): 3.7 (C_1-p^7mp-$C_{70}(CF_3)_{10}$), 4.6 (C_s-p^7-$C_{70}(CF_3)_8$), 5.2 (C_2-$C_{70}(CF_3)_8$), 12.5 (C_{70}).

C_s-p^7-$C_{70}(CF_3)_8$: MALDI MS m/z (I, %): 1392 (M^-, $C_{70}(CF_3)_8^-$), 100%); HPLC (t_R, min, CB 4.6 mm i.d. × 250 mm, toluene 1 mL·min^{-1}): 4.6.

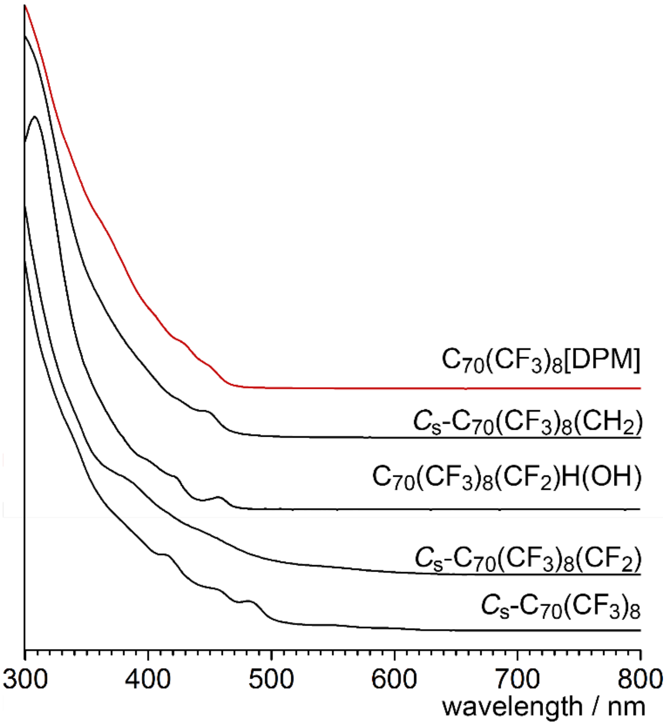


Figure S1. UV-vis spectrum of $C_{70}(CF_3)_8$[DPM] in comparison with parent $C_{70}(CF_3)_8$ and other related derivatives.

Experimental methods

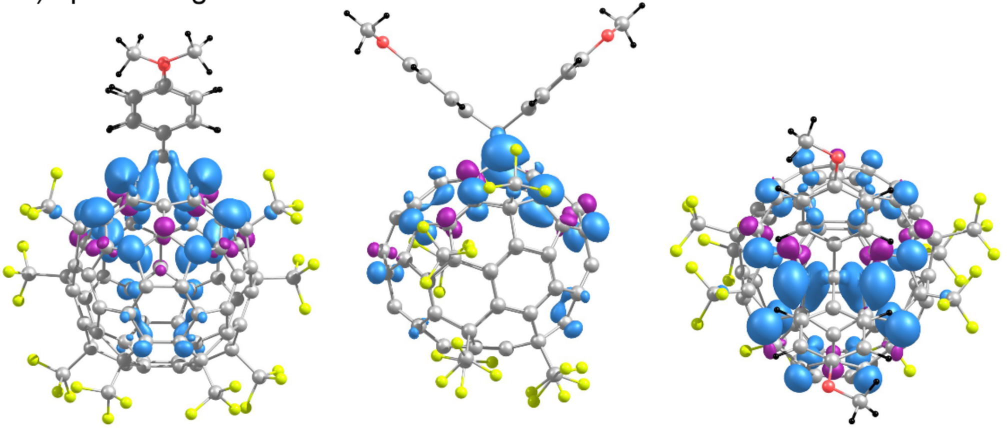
Mass spectrometry. MALDI mass spectra were recorded in the negative ions mode using a Bruker Autoflex II TOF-mass spectrometer (337 nm impulse nitrogen laser). Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Sigma Aldrich, ≥98%) was used as matrix.

Quantum chemical calculations

Vertical emission energy and excited state geometry optimization were computed by TDDFT approach with employment BHHLYP[3] and PBE0[4] hybrid functionals using Def2-SVP basis set[5] and the Firefly v. 8.2.0 package[6], partly based on the GAMESS(US) software code[7].

Molecular geometry optimization and relaxed PES scan were calculated at the DFT level of the theory using of the PRIRODA v.6 software implementing efficient RI approximation[8], PBE exchange-correlation functional[9] and a built-in basis set of triple zeta quality (TZ2p). Isotropic hyperfine coupling constants were calculated at the DFT-PBE level with quadruple zeta quality basis (QZ3p).

a) open configuration



b) closed configuration

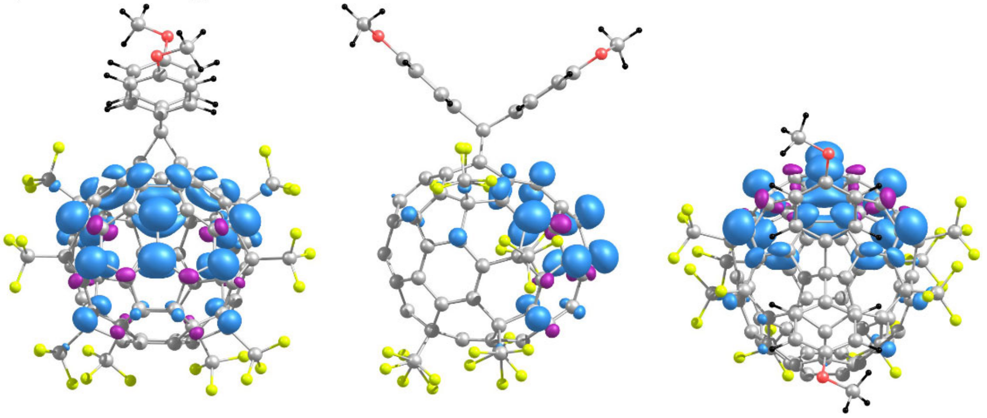


Figure S2. Spin density distribution in the (a) open and (b) closed configurations of $C_{70}(CF_3)_8[DPM]^{-\bullet}$.

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