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Synthesis, optical and electrochemical properties of regioisomeric methanofullerene derivatives of C_s-$C_{70}(CF_3)_8$

Sofia V. Gracheva, Nadezhda B. Tamm, Maria P. Kosaya, Alexey V. Rybalchenko, Nikita M. Belov, Natalia S. Lukonina and Alexey A. Goryunkov

Contents

General information

High-Performance Liquid Chromatography. Analyses of samples by means of HPLC were performed using Agilent 1100 system (diode array detector operated at 190–950 nm) equipped with a Cosmosil Buckyprep column (4.6 mm i.d. × 25 cm) at 23°C. Isolation of the compounds was performed using Waters Breeze series system (UV/vis λ2 detector operated at 190–700 nm) equipped with a Cosmosil Buckyprep semi-preparative column (10 mm i.d. × 25 cm) at 25°C. Mixtures of toluene and hexane were used as eluents.

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 a matrix, the analyte-to-matrix ratio was ca 1:1000.

Fluorescence spectroscopy. Absorption and emission spectra were recorded using ULS2048x64TEC SensLine fiber-optic spectrometer equipped with AvaLight-DHc light source (200–2500 nm range, deuterium and halogen lamps). Spectrometer working range is 190–1100 nm. Optical resolution is 0.04 nm. Solutions of the samples in cyclohexane were measured at the 355 nm excitation wavelength using light-emitting diode source AvaLight-LED355 (FWHM=10 nm). Fluorescence quantum yields were determined by relative method toward standard quinine sulfate (QS (≥98%, BioReagent, Sigma-Aldrich) in 0.5M H_2SO_4 (Φ_F 0.546)).[S1]

NMR spectroscopy. NMR spectra were registered using Bruker Avanve-600 spectrometer operated with 600.3 MHz (^1H) and 564.7 MHz (^{19}F) in $CDCl_3$ at 25°C. $CHCl_3$ and C_6F_6 were employed as internal standards with δ_H= 7.27 ppm and δ_F= –162.9 ppm.

Electrochemistry. The voltammetry experiments were carried out in a glovebox MBRAUN LabStar under argon atmosphere with $p(O_2) < 0.1$ ppm, $p(H_2O) < 0.1$ ppm. The *ortho*-dichlorobenzene (*o*-DCB) used as a solvent was purified by refluxing in the presence of CaH_2 followed by distillation under the reduced pressure of argon. CVA curves were registered at room temperature in a three-electrode cell with a platinum disk working electrode (WE), a platinum coil counter electrode (CE), and an $Ag/AgNO_3$ reference electrode (RE) using an Elins Pi-50Pro-3 potentiostat (Russia). The RE was made of a silver wire immersed in a solution of $AgNO_3$ (0.01 mol L^{-1}) and n-Bu_4NBF_4 (0.1 mol L^{-1}) in acetonitrile. n-Bu_4NBF_4 (for electrochemical analysis, 99+%, Fluka, 0.2 mol L^{-1}) in *o*-DCB was used as the supporting electrolyte (prepared and stored in the glovebox). The scan rate was 100 mV s^{-1}. The potential *iR*-drops were corrected during the experiment using the hardware positive feedback method. After the experiment, ferrocene (Fc) was added to the cell as an internal redox system after each experiment. The potential of the $Fc^{+/0}$ couple in *o*-DCB was 0.204 V vs the $Ag/AgNO_3$ couple.

The energies of the LUMO and HOMO levels were estimated from the electrochemical data using the equations of $E_{LUMO}{}^{EC} = -(E_{[onset,red\ vs\ Fc(+/0)]} + 5.1)$ eV and $E_{HOMO}{}^{EC} = -(E_{[onset,ox\ vs\ Fc(+/0)]} + 5.1)$[S2] where $E_{[onset,red\ vs\ Fc(+/0)]}$ and $E_{[onset,ox\ vs\ Fc(+/0)]}$ values are the onsets of the first reduction and oxidation potentials (V) of the compound referenced to $Fc^{+/0}$ couple; the value of –5.1 V is the formal potential of the $Fc^{+/0}$ redox couple in the Fermi scale assuming its value of 0.40 V versus SCE in acetonitrile (neglecting the $Fc^{+/0}$ couple changing for ca 0.03 V in acetonitrile and *o*-DCB).[S3]

Synthetic procedures

Trifluoromethylated fullerene C_s-$C_{70}(CF_3)_8$ was synthesized according to the two-step typical procedure previously described in refs.[S4,S5]. Isomerically pure C_s-$C_{70}(CF_3)_8$ was isolated by means of preparative HPLC using Cosmosil Buckyprep 10 mm i.d. × 25 cm column toluene as an eluent. **4,4'-Dimetoxybenzophenone tosyl hydrazone** was synthesized according to standard procedure.[S6]

Reaction of C_s-$C_{70}(CF_3)_8$ and 4,4'-dimetoxybenzophenone tosyl hydrazone: to the solution of C_s-$C_{70}(CF_3)_8$ (25 mg, 18 μmol) in *o*-DCB (20 mL) were added 4,4'-dimetoxybenzophenone tosyl hydrazone (11 mg, 27 µmol), K_2CO_3 (ca 50 mg), pyridine (200 µL) and catalytic amount of 18-crown-6 (ca 10%mol). The reaction mixture was refluxed under inert atmosphere for 3.5 h. Then it was quenched by adding trifluoroacetic acid (300 µl), and filtered through a short plug of silica with toluene as an eluent. Then the semi-preparative HPLC (Cosmosil Buckyprep 10 mm i.d. × 25 cm column and toluene:hexane=1:1 as an eluent) product mixture separation was employed to isolate fractions with individual compounds. Yields of compounds were estimated according to the HPLC trace integration registered at wavelength of 290 nm. The molecular composition of the isolated fractions was established by means of MALDI mass spectrometry. Spectral identification of the compounds was performed using ^{19}F and ^{1}H NMR as well as UV/Vis data. The spectral data for the early eluted fraction of $C_{70}(CF_3)_8$DPM (**1**) is fully consisted with those for the major monoadduct at the near-equatorial bond ***d*** which was previously reported.[S4]

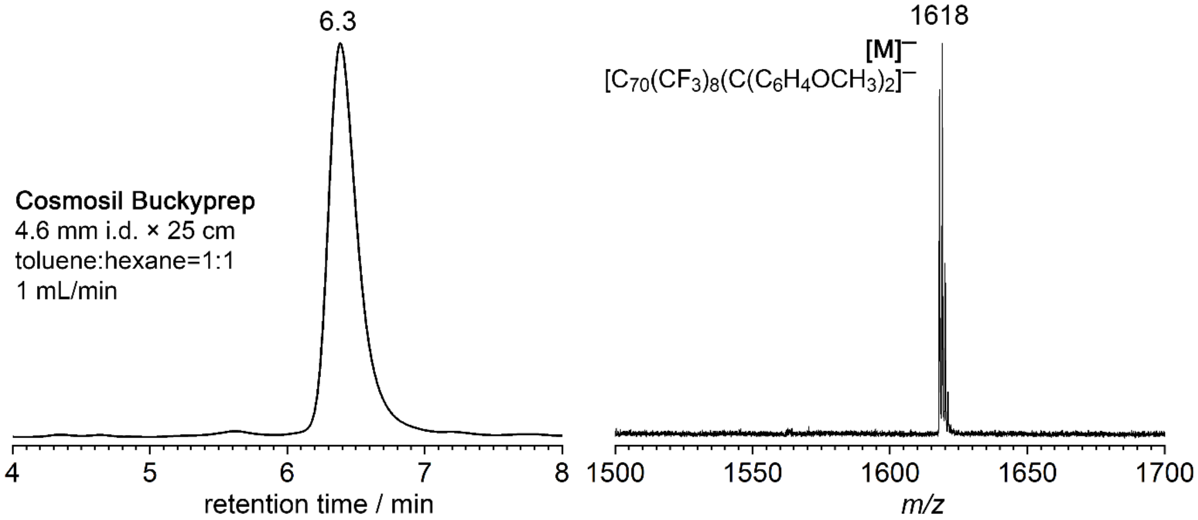
$C_{70}(CF_3)_8$DPM (2), *C*$_s$-symmetrical adduct at the bond *a*: Yield: 12%; HPLC (t_R, min; CB, toluene:hexane 1:1, 1 mL/min): 6.32; MALDI MS m/z (*I*, %): 1618 (100%, M^-, $C_{70}(CF_3)_8DPM^-$); UV (λ_{max}, nm): 324, 330, 358, 378, 422, 450, 482, 498; NMR ^{1}H ($CDCl_3$, δ_H, ppm, *J*, Hz): 3.78 (s, 6H, OCH_3); 6.87 (m. 4H); 7.70 ppm (m, 4H); NMR ^{19}F ($CDCl_3$, $-\delta_F$, ppm, *J*, Hz): 61.47 (m, 6F, CF_3), 61.87(m, 6F, CF_3), 62.40 (m, 6F, CF_3), 66.13 ppm (q, 6F, J_{FF}=16.5 Hz, CF_3).

$C_{70}(CF_3)_8DPM_2$ (3): Yield: 11%; HPLC (t_R, min; CB, toluene:hexane 1:1, 1 mL/min): 6.75; MALDI MS m/z (*I*, %): 1845 (100%, M^-, $C_{70}(CF_3)_8DPM_2^-$);UV (λ_{max}, nm): 364, 398, 430, 460, 488, 516, 556.

$C_{70}(CF_3)_8$DPM (4): Yield: 10%; HPLC (t_R, min; CB, toluene:hexane 1:1, 1 mL/min): 7.49; MALDI MS m/z (*I*, %): 1618 (100%, M^-, $C_{70}(CF_3)_8DPM^-$); UV (λ_{max}, nm): 328, 390, 450, 480, 514, 552.

$C_{70}(CF_3)_8$DPM (5), adduct at the bond *b'*: Yield: 16%; HPLC (t_R, min; CB, toluene:hexane 1:1, 1 mL/min): 8.18; MALDI MS m/z (*I*, %): 1618 (100%, M^-, $C_{70}(CF_3)_8DPM^-$), 1562.3 (12%, $[M-CF_3]^{*-}$, metastable $C_{70}(CF_3)_7DPM^{*-}$), 1549 (3%, $[M-CF_3]^-$, $C_{70}(CF_3)_7DPM^-$); UV (λ_{max}, nm): 306, 352, 382, 430, 460, 496, 534; NMR ^{1}H ($CDCl_3$, δ_H, ppm, *J*, Hz) 3.74 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3); 6.81 (m, 2H, Ar); 6.95 (m, 2H, Ar), 7.42 (m, 2H, Ar), 7.75 ppm (m, 2H, Ar); NMR ^{19}F ($CDCl_3$, $-\delta_F$, ppm, *J*, Hz): 61.09 (m, 6F, CF_3), 61.63 (m, 3F, CF_3), 61.83 (m, 3F, CF_3), 62.01 (m, 3F, CF_3), 62.26 (m, 3F, CF_3); 64.61 (q, 3F, J_{FF}=13.9 Hz, CF_3); 66.78 (q, 3F, J_{FF}=16.0 Hz, CF_3).

$C_{70}(CF_3)_8$DPM (2), adduct at the bond *a*



$C_{70}(CF_3)_8$DPM (5), adduct at the bond *b'*

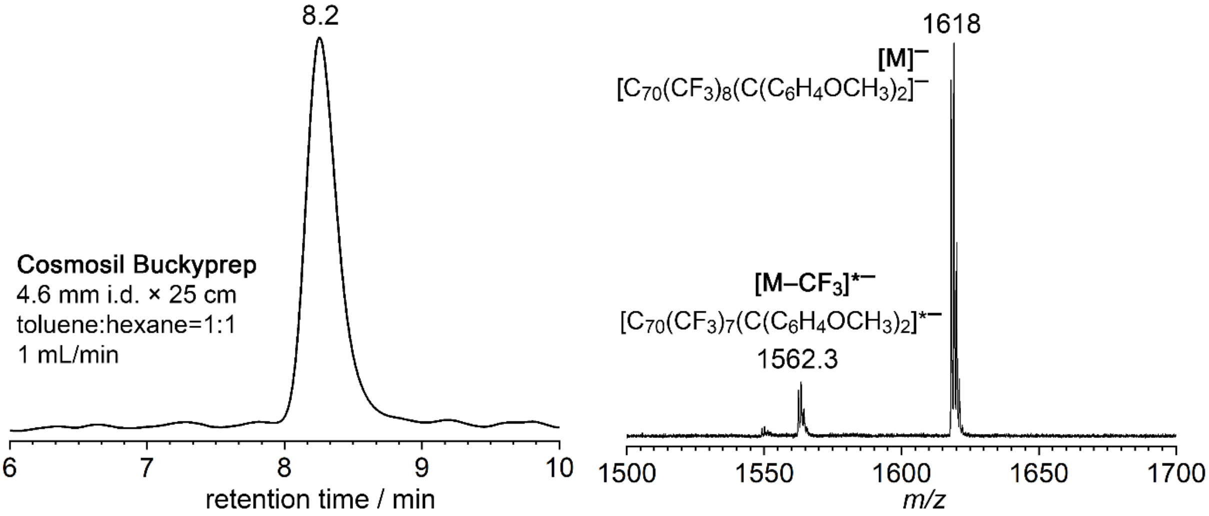


Figure S1. The HPLC traces and the negative ions MALDI mass spectra for isomeric methanofullerenes $C_{70}(CF_3)_8$DPM **2** and **5**.

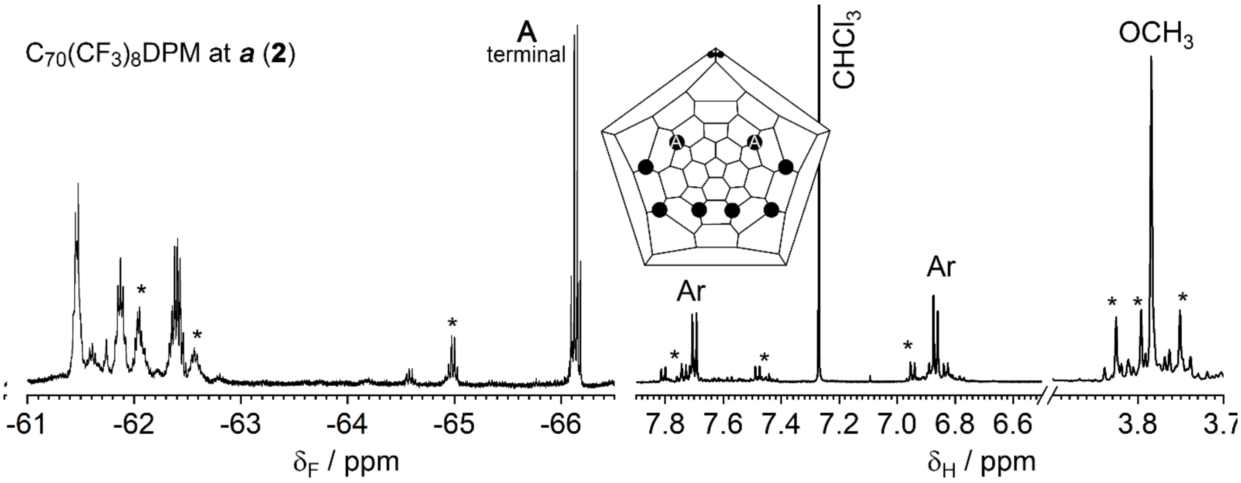


Figure S2. The ^{19}F and ^{1}H NMR spectra of methanofullerene **2** (signals from admixture via oxidation in solution at 2 weeks are marked by asterisk).

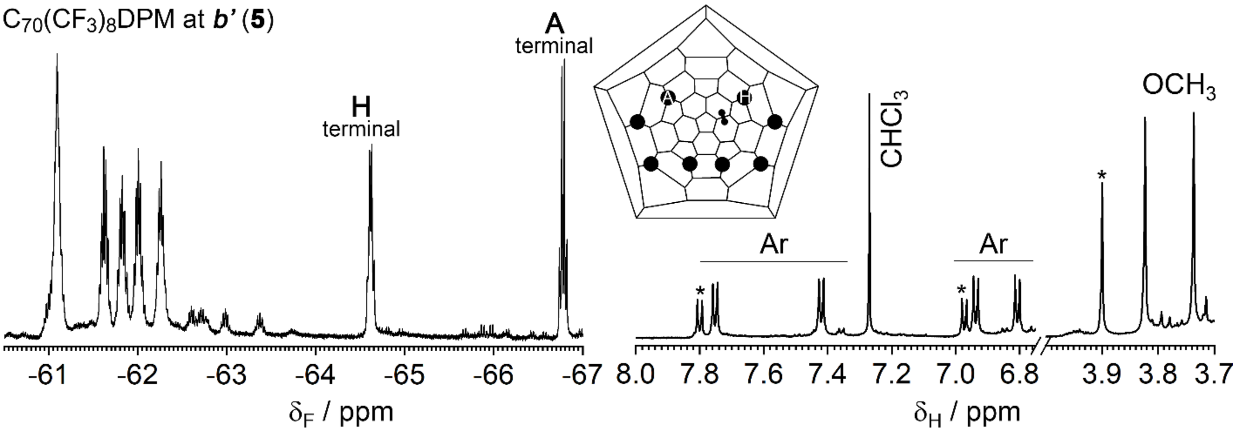


Figure S3. The ^{19}F and ^{1}H NMR spectra of methanofullerene **5** (signals from admixture via oxidation in solution at 2 weeks are marked by asterisk).

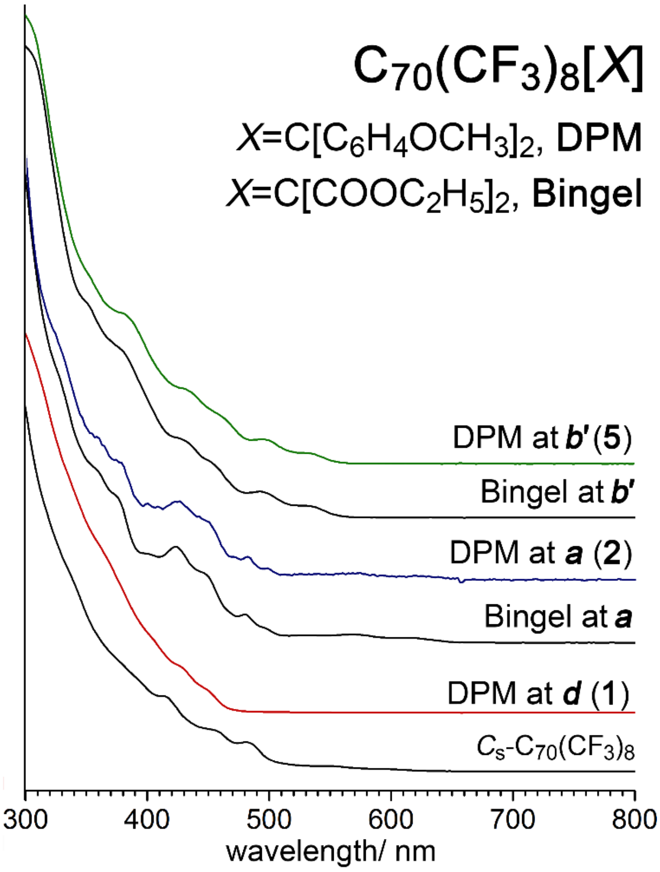


Figure S4. The UV/Vis spectra of C_s-$C_{70}(CF_3)_8$ and its monocyclopropanated adducts $C_{70}(CF_3)[X]$, where X=DPM for derivatives **1**[S4], **2** and **5** under study and X=$C(CO_2Et)_2$ obtained via the Bingel-Hirsch reaction[S7] (toluene, wavelength range of 300–800 nm).

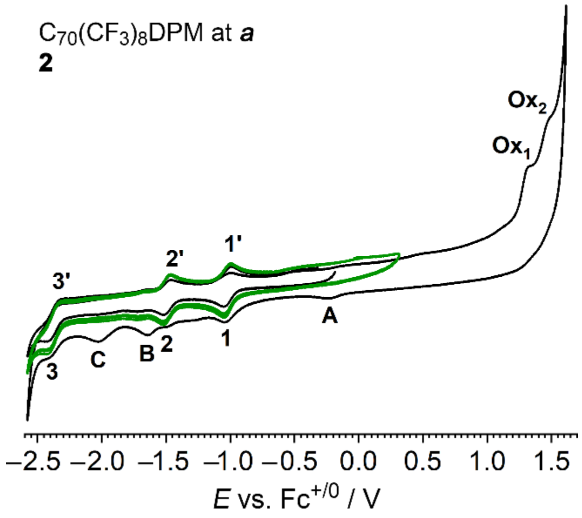


Figure S5. The CVA curve for methanofullerene **2** (Pt, *o*DCB, 0.2 M *n*-Bu_4NBF_4, 100 mV s^{-1}).

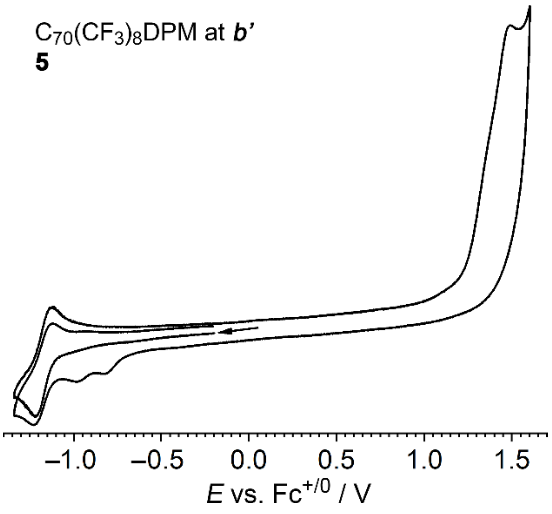


Figure S6. The CVA curve for methanofullerene **5** (Pt, oDCB, 0.2 M *n*-Bu_4NBF_4, 100 mV s^{-1}).

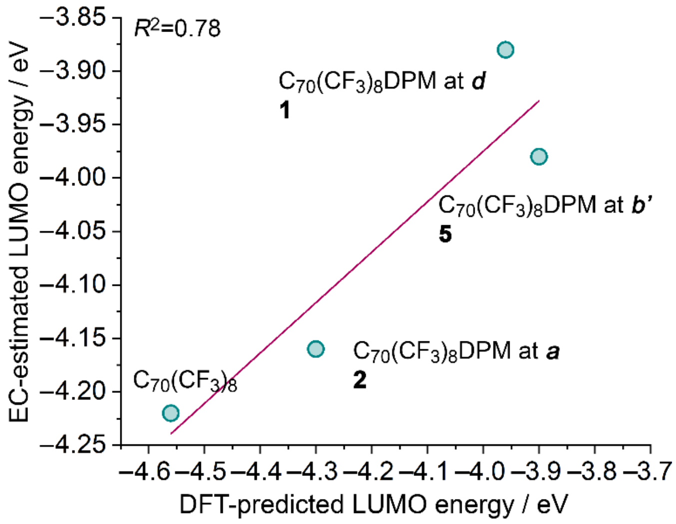


Figure S7. The correlation of LUMO energies estimated from CVA and calculated at the DFT level of theory (PBE/TZ2p).

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