

Supplementary information

Fulleropyrrolidine Molecular Dumbbells Act as Multi-Electron-Acceptor Triads. Spectroscopic, Electrochemical, Computational and Morphological Characterizations

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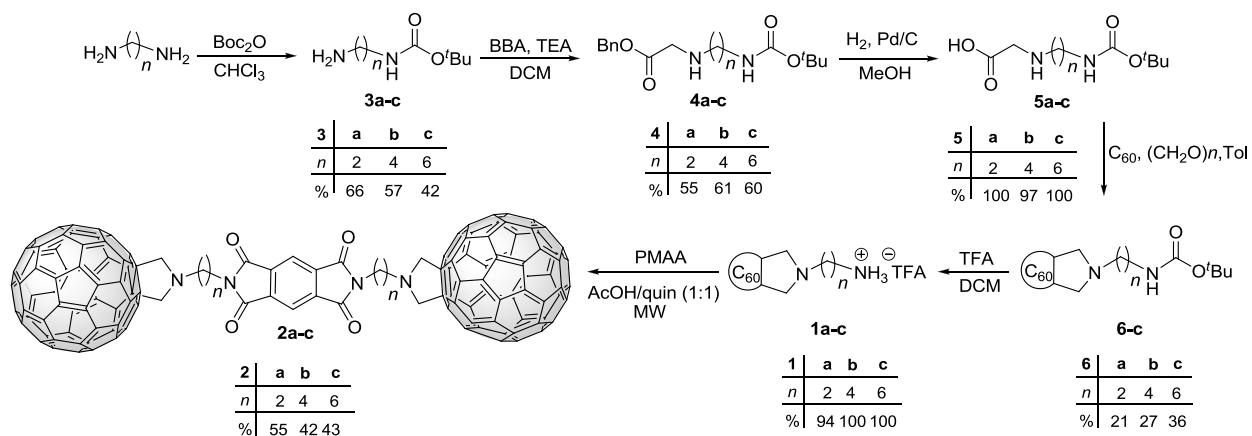
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General

FTIR spectra were recorded on Perkin-Elmer-FT-IR 1725X spectrophotometer; values are given in cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 and Bruker Avance III 500 spectrometers at 200/50 and 500/125 MHz, respectively. The chemical shifts were measured to residual nondeuterated solvent resonances or TMS. Fullerenic carbons, presented as Cf, were numbered in a simplified way, according to the literature.¹ Mass spectra were obtained on Agilent technologies 6210 TOF LC/MS instrument; MALDI/TOF spectra were recorded on Shimadzu Biotech Axima Confidence with DCTB used as matrix. UV spectra were recorded on a GBC-Cintra 40 spectrophotometer. Fluorescence spectra were obtained on FluoroMax®-4, HORIBA Jobin Yvon Inc. Reactions were monitored by TLC using plates precoated with silica gel 60 F254. Column chromatography was performed on Silica, 10-18, 60A, ICN Biomedicals. Standard techniques were used for the purification of reagent and solvents. Reactions induced by microwave irradiation were performed in a Milestone MultiSynth microwave multimode oven, using a MedCHEM kit and MonoPREP kit. Investigations of samples morphology were carried out with scanning electron microscopy, using a JEOL JSM-840A instrument, at an acceleration voltage of 30 kV. A several drops of a dilute solution (1 mg/mL in toluene, toluene/dioxane (2:1), toluene/*iso*-propanol (2:1); chloroform, chloroform/dioxane (2:1), chloroform/*iso*-propanol (2:1) and ODCB, ODCB/dioxane (2:1), ODCB/ *iso*-propanol (2:1)) of fullero-pyromellitic imide triads were deposited on the surface of glass plates and then slowly evaporated in a glass petri dish (diameter 10 cm) under toluene atmosphere at the room temperature. The investigated samples were gold sputtered in a JFC 1100 ion sputterer and then subjected to SEM observations. Cyclic voltammograms (CV) were recorded using an CHI760B instrument (CHIInstruments, USA). The cell was equipped with Boron-doped diamond electrode (Windsor Scientific) an accessory platinum electrode of larger area (Model CHI221, cell top including Pt wire counter electrode) and non-aqueous Ag/AgCl reference electrode (Model CHI111). Prior to each measurement the electrodes were mechanically polished. CV potentials were measured relative to the standard potential of redox system ferrocene/ferrocenium ion, using $n\text{Bu}_4\text{NPF}_6$ (TBA-HFP) as supporting electrolyte in ODCB/DMF (2/1) mixture at room temperature. Transmission electron microscopy (TEM) images were recorded on FEI Tecnai G2 Spirit TEM microscope working at 80 kW.



Scheme S1. Synthetic route to dumbbell **2a-c**

The optimization of coupling conditions was conducted on **1a** and PMAA as test substrates and results are outlined in Table 1. In the first experimental set, target compound **2a** was synthesized from corresponding starting compounds by refluxing the reaction mixture for 24 h, whereas in the second set MWI was used as a heating source. According to the literature methods pyromellitic diimides are relatively easy to obtain, in high yields from PMAA and corresponding amine, in refluxing solvent.^{2, 3} Major drawback when fulleropyrrolidines ammonium salts are used instead of regular amines, is their insolubility as well its decomposition when exposed to high temperatures for prolonged time. Hence, compound **2a** was isolated in low yields (3-29 %) when conventional 24 h heating of the reaction mixture was applied. By dramatically shortening the reaction time, on 30 min in MWR two to tenfold higher yields were obtain for the same solvent or solvents mixture.

Table S1. Optimization of reaction conditions for the synthesis of **2a**

Conditions	Yield % ^a	Yield % ^b
1. AcOH	18	25
2. Quinoline, ZnOAc	3	34
3. AcOH/Pyr (3/2)	29	34
4. AcOH/ Quinoline (1/1)	15	55

^a Reflux, 24 h. ^b Microwave irradiation, 30 min.

General procedure for preparation of compounds 2a-c

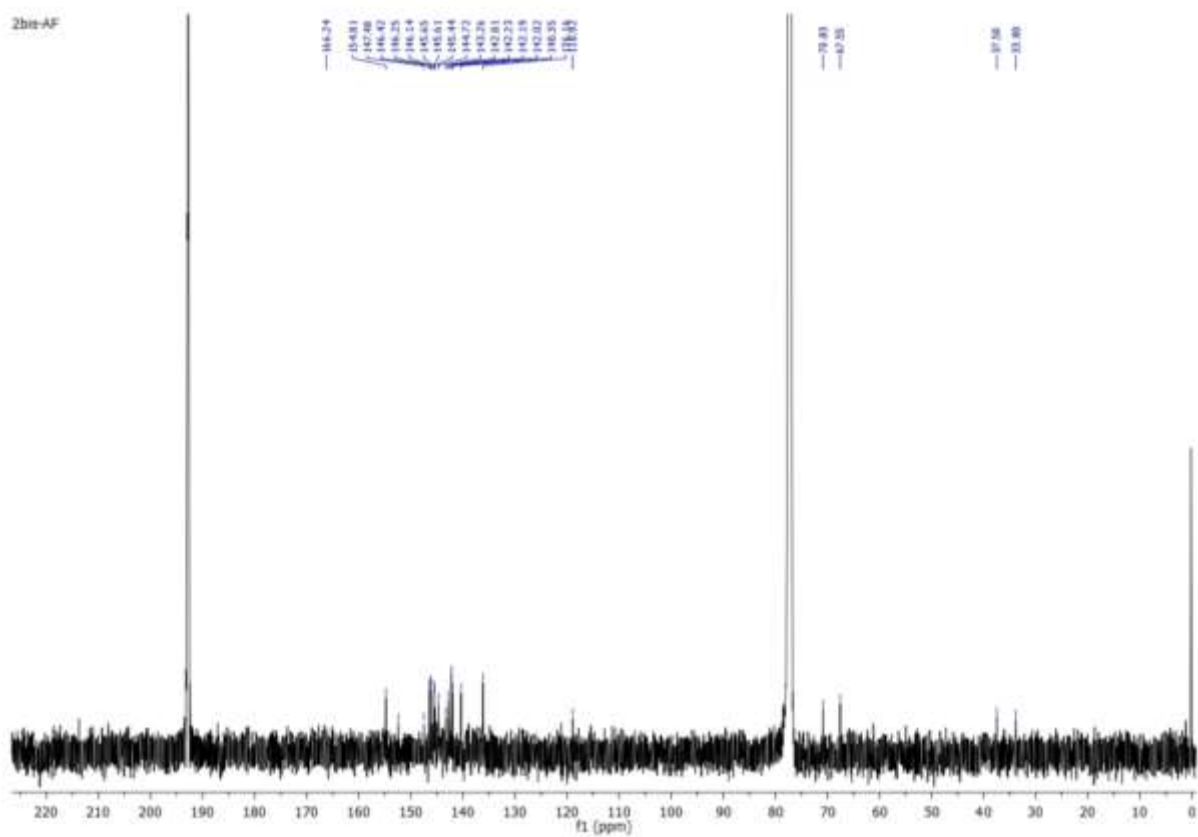
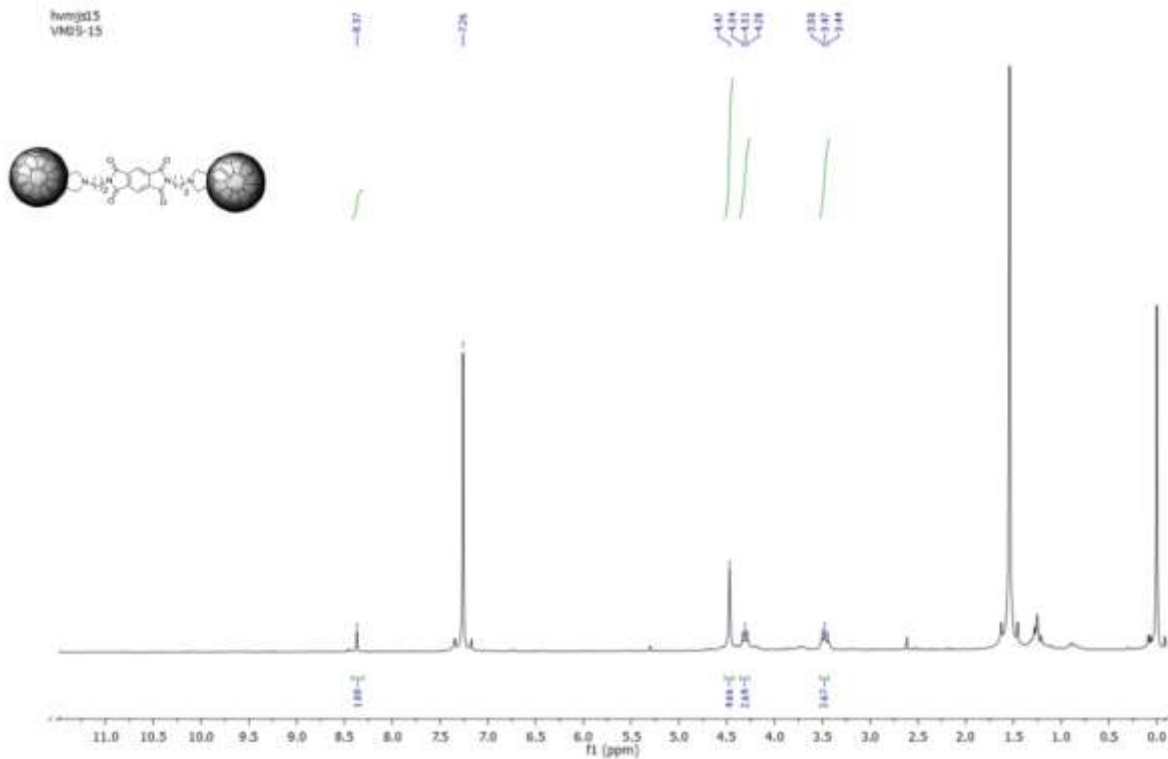
A suspension of **1a-c** (0.0052 mmol) and pyromellitic acid anhydride (0.0026 mmol) in AcOH/quinoline (1:1) mixture (1.2 mL) was irradiated in a microwave reactor for 30 min with an inner temperature of 130°C and applied pulse of 300 W. Crude product was precipitated by the addition of methanol in the reaction mixture and purified by column chromatography on SiO₂ with EtOAc-toluene (1/9) mixture as an eluent. Subsequent precipitation, from highly concentrated solution in CHCl₃ gave pure products **2a-c** as brown powders in 42-55% yields.

2a: Yield 2.5 mg (55%). IR (ATR) $\tilde{\nu}$: 2930, 1719, 1370, 1093, 760, 481 cm⁻¹. UV-VIS (CHCl₃) λ (ϵ , M⁻¹cm⁻¹): 430 (4200), 704 (380). ¹H (CDCl₃, 500 MHz) δ 8.37 (s, 2H); 4.48 (s, 8H); 4.47 (s, 4H), 4.34-4.28 (m, 4H), 3.50-3.44 (m, 4H). ¹³C (CDCl₃, 125 MHz) δ 166.2 (4C); 154.8 (Cf-12); 147.5 (Cf-17); 146.4 (Cf-7); 146.1 (Cf-11); 145.6 (Cf-16); 145.5 (Cf-5); 144.7 (Cf-9); 143.3 (Cf-15); 142.8 (Cf-8); 142.2 (Cf-6); 142.1 (Cf-14); 142.0 (Cf-4); 141.8 (Cf-12,13); 141.1 (Cf-10); 140.3 (Cf-3); 138.8 (4C), 136.2 (4 C); 118.9 (2CH); 70.8 (4C); 67.5 (4CH₂); 37.5 (2CH₂); 33.8 (2CH₂). MALDI/TOF: m/z calcd for [C₁₃₈H₁₈N₄O₄+H]⁺ 1796, measured 1796.

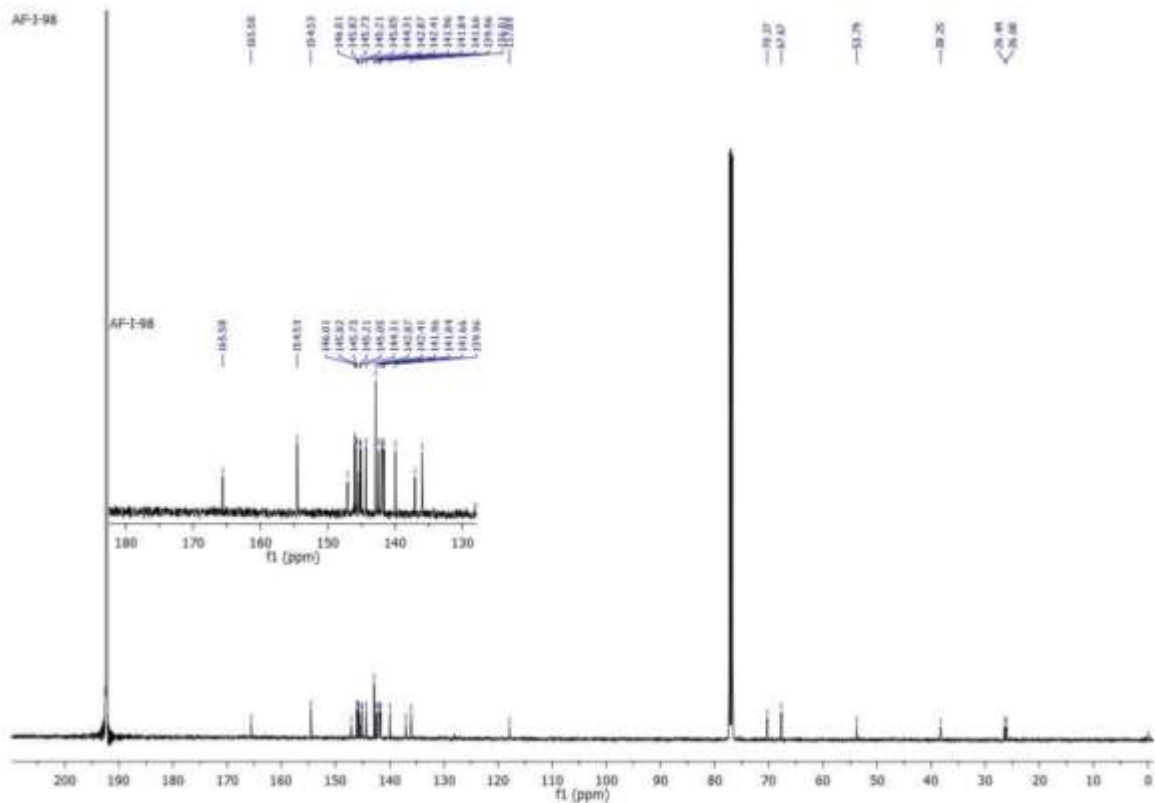
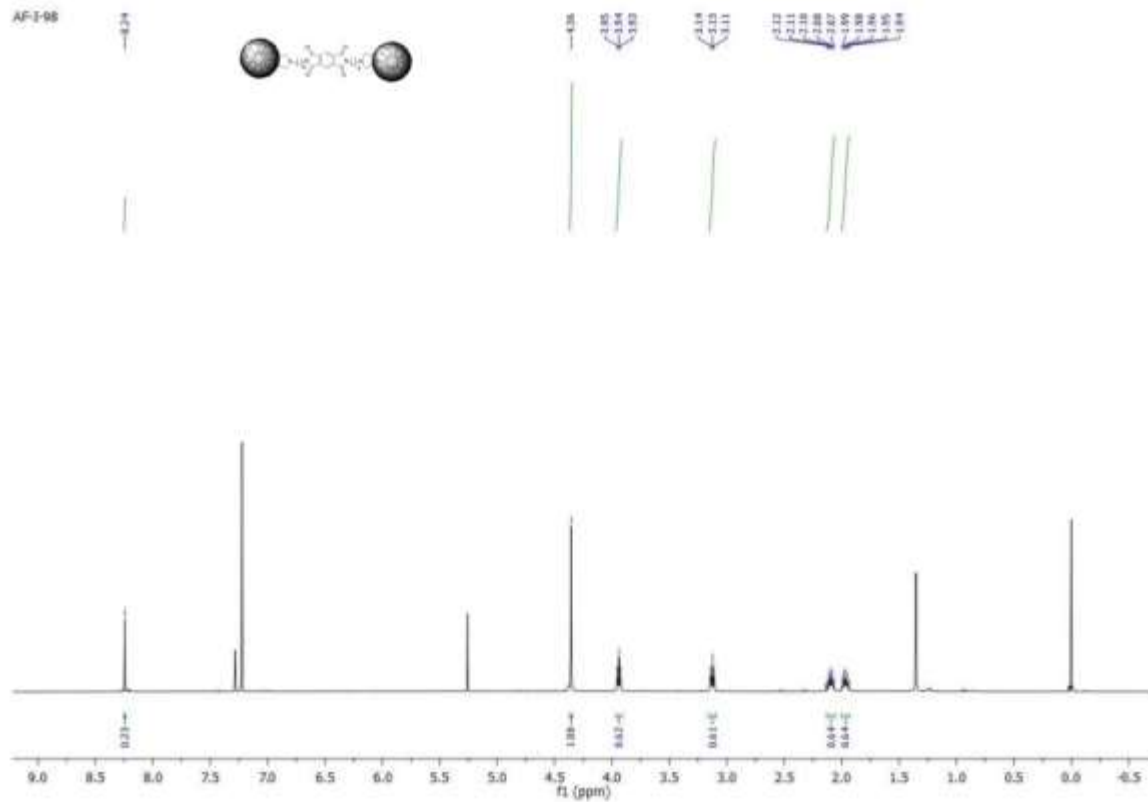
2b: Yield 2.0 mg (42%). IR (ATR) $\tilde{\nu}$: 2925, 1719, 1368, 1118, 728, 526 cm⁻¹. UV-VIS (CHCl₃) λ (ϵ , M⁻¹cm⁻¹): 430 (5200), 704 (380). ¹H (CDCl₃, 500 MHz) δ 8.24 (s, 2H); 4.36 (s, 8H); 3.94 (t, 4H, *J*=5); 3.13 (t, 4H, *J*=5); 2.12-2.07 (m, 4H); 1.99-1.94 (m, 4H). ¹³C (CDCl₃, 125 MHz): δ 165.6 (4C); 154.5 (Cf-12); 147.0 (Cf-17); 146.0 (Cf-7); 145.8 (Cf-11); 145.7 (Cf-16); 145.4 (Cf-5); 145.2 (Cf-9); 145.0 (Cf-15); 144.3 (Cf-8); 142.9 (Cf-6); 142.4 (Cf-14); 142.0 (Cf-4); 141.9 (Cf-12,13); 141.7 (Cf-10); 140.0 (Cf-3); 137.0 (4C); 136.0 (4C); 117.9 (2CH); 70.3 (4C); 67.7 (4CH₂); 53.8 (2CH₂); 38.2 (2CH₂); 26.4 (2CH₂); 26.1 (2CH₂). MALDI/TOF: m/z calcd for [C₁₄₂H₂₆N₄O₄+H]⁺ 1853, measured 1853.

2c: Yield 2.1 mg (43%). IR (ATR) $\tilde{\nu}$: 2933, 1721, 1365, 1118, 731, 525 cm⁻¹. UV-VIS (CHCl₃) λ (ϵ , M⁻¹cm⁻¹): 430 (6600), 704 (380). ¹H (CDCl₃, 500 MHz) δ 8.21 (s, 2H); 4.37 (s, 8H); 3.79 (t, 4H, *J*=5); 3.07(t, 4H, *J*=5); 1.96-1.90 (m, 4H); 1.86-1.79 (m, 4H); 1.74-1.71 (m, 4H); 1.69-1.52 (m, 4H). ¹³C (CDCl₃, 125 MHz) δ 165.6 (4C); 154.7 (Cf-12); 147.0 (Cf-17); 146.0 (Cf-7); 145.8 (Cf-11); 145.8 (Cf-16); 145.4 (Cf-5); 145.2 (Cf-9); 145.1 (Cf-15); 144.3 (Cf-8); 142.9 (Cf-6); 142.4 (Cf-14); 142.0 (Cf-4); 141.8 (Cf-12,13); 141.7 (Cf-10); 140.0 (Cf-3); 137.0 (4C); 136.0 (4C); 117.8 (2CH); 70.4 (4C); 67.8 (4CH₂); 54.6 (2CH₂); 38.4 (2CH₂); 28.7 (2CH₂); 28.5 (2CH₂); 27.1 (2CH₂); 26.8 (2CH₂). MALDI/TOF: m/z calcd for [C₁₄₆H₃₄N₄O₄+H]⁺ 1909, measured 1909.

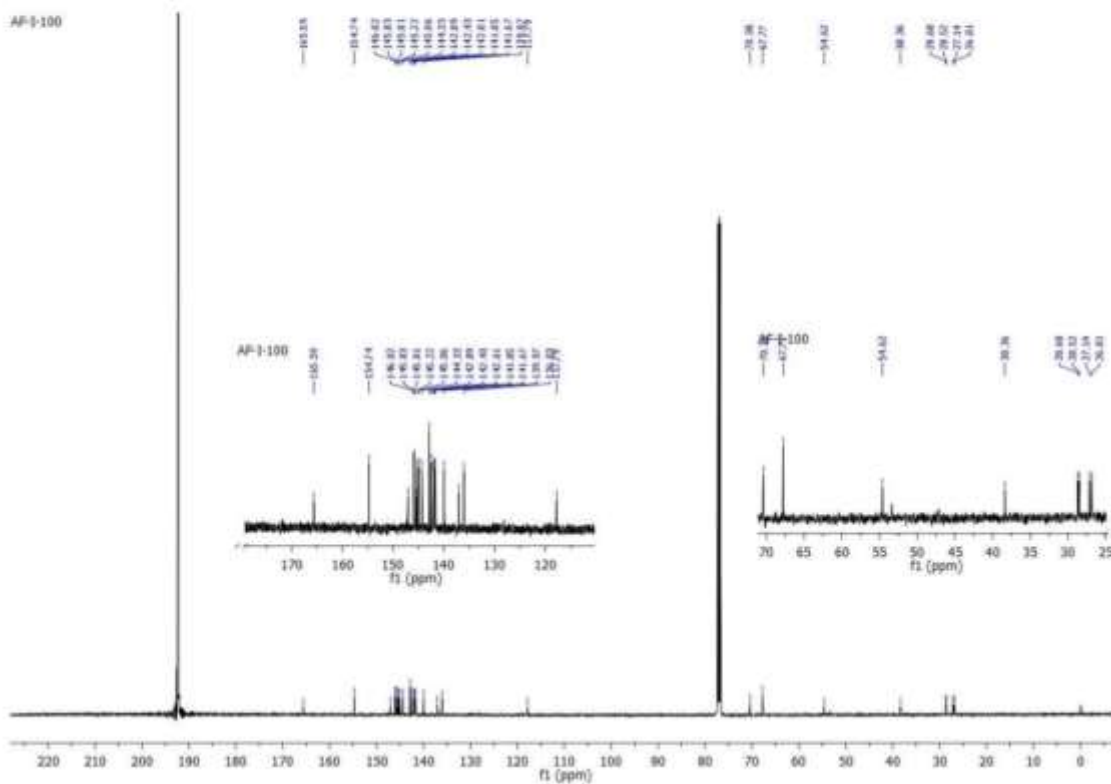
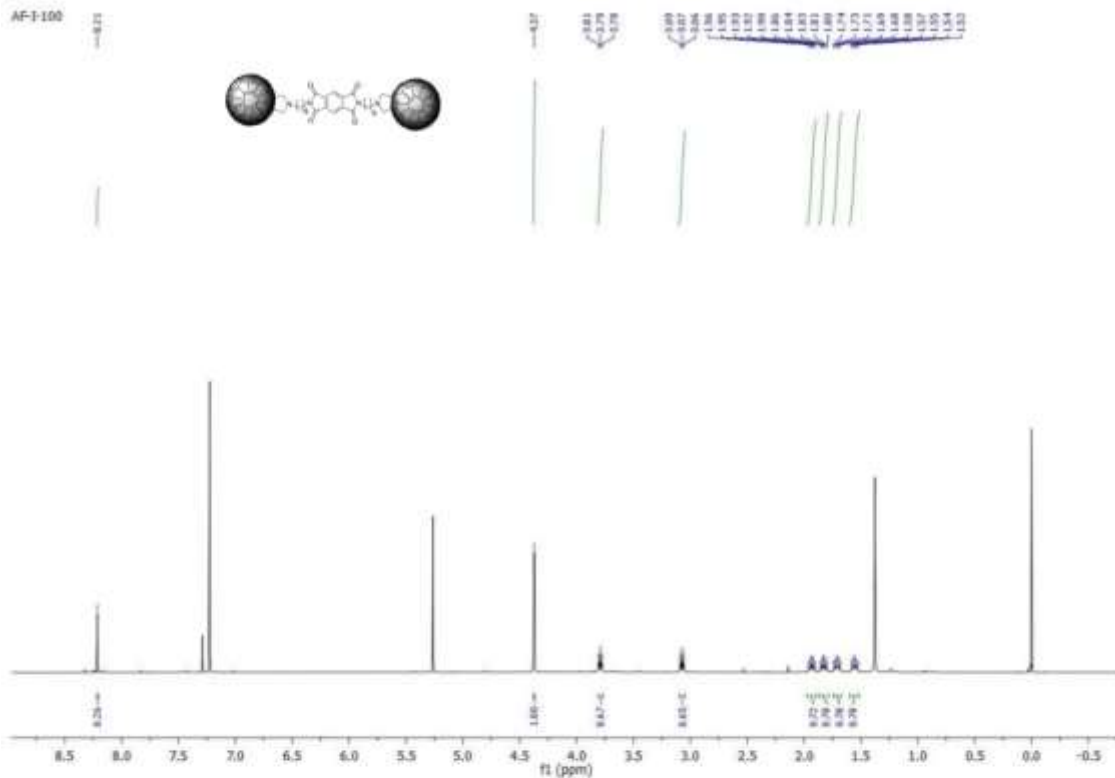
Scanned NMR spectra of 2a



Scanned NMR spectra of **2b**



Scanned NMR spectra of 2c



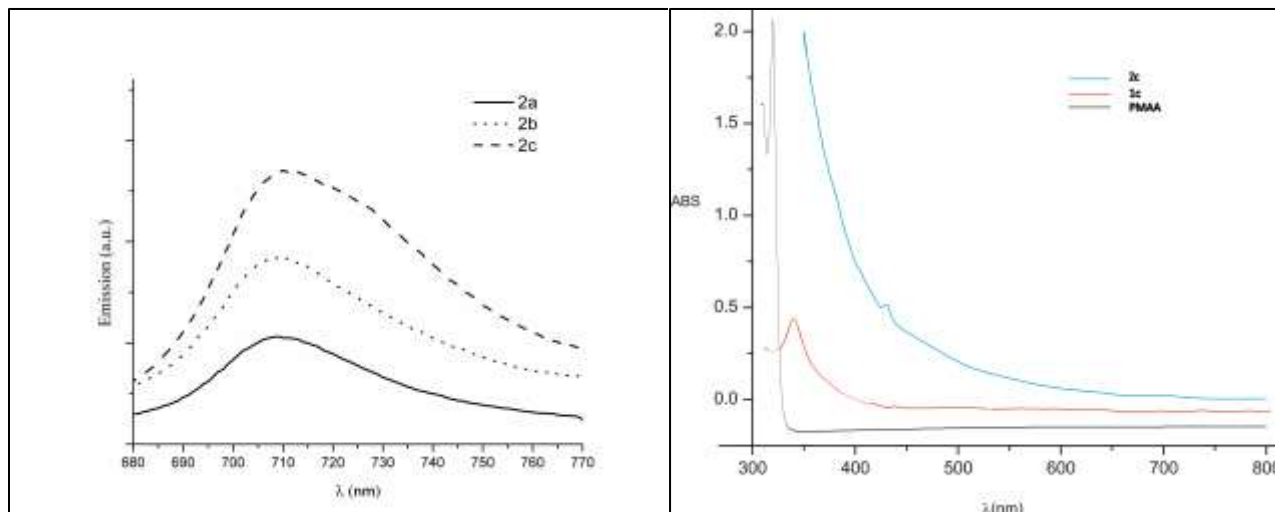


Fig S1. Emission spectra of compounds **2a-c**, C₆₀

Fig S2. Superimposed UV-vis spectra of the synthesized molecules with the reactants

Cyclic Voltammetry spectra of dumbbells 2a-c

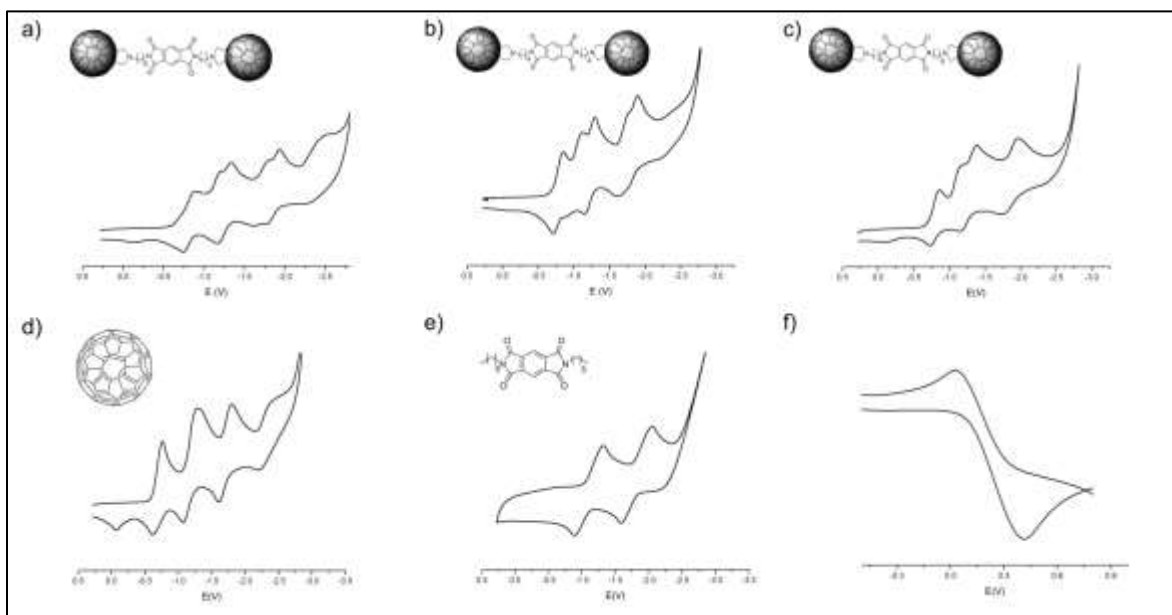


Fig S3. Cyclic voltammograms of a) **2a**, b) **2b**, c) **2c**, d) C₆₀, e) DHPMDI, f) ferrocene at scan rate 50 mV s⁻¹ in ODCB:DMF (2:1) mixture, containing 0.1m nBu₄NPF₆.

Table S2. Calculated molecular properties for C_{60} and conformers of compound **2a**.

Molecular property	C_{60}	Extended	Single folded	Double folded
HOMO (eV)	-5.867	-5.575	-5.447	-5.417
Egap (eV)	1.686	1.341	1.209	1.16
LUMO (eV)	-4.181	-4.234	-4.238	-4.257
Ionization potential (I)	5.867	5.575	5.447	5.417
Electron affinity (A)	4.181	4.234	4.238	4.257
Electronegativity (χ)	5.024	4.9045	4.8425	4.837
Global hardness (η)	0.843	0.6705	0.6045	0.58
Global softness (S)	1.186	1.491	1.654	1.724
Chemical potential (μ)	-5.024	-4.9045	-4.8425	-4.837
Global electrophilicity (ω)	14.97	17.94	19.40	20.17

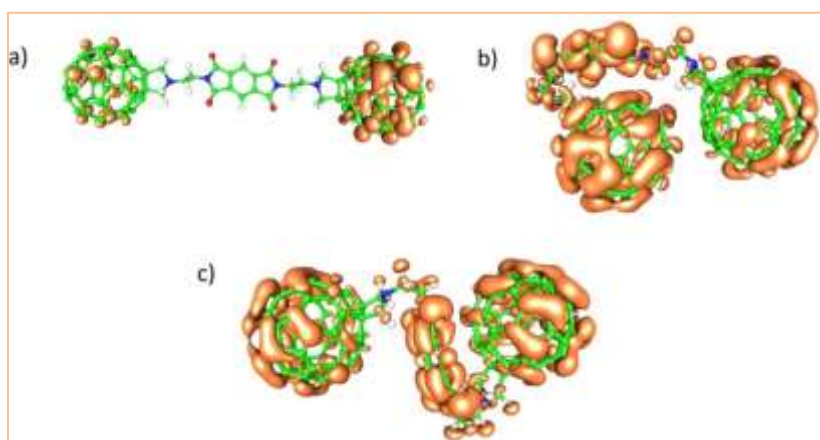


Fig S4. Calculated Fukui functions for a) extended, b) single folded and c) double folded conformer of compound **2a**. Orange lobes represent electrophilic parts of the molecule.

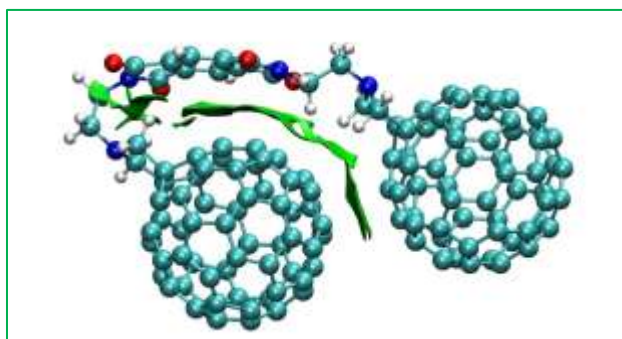


Figure S5. NCI visualization index of single folded conformer of compound **2a**. Green surface represents an area of C–H \cdots π , C–H \cdots O and π – π interactions.

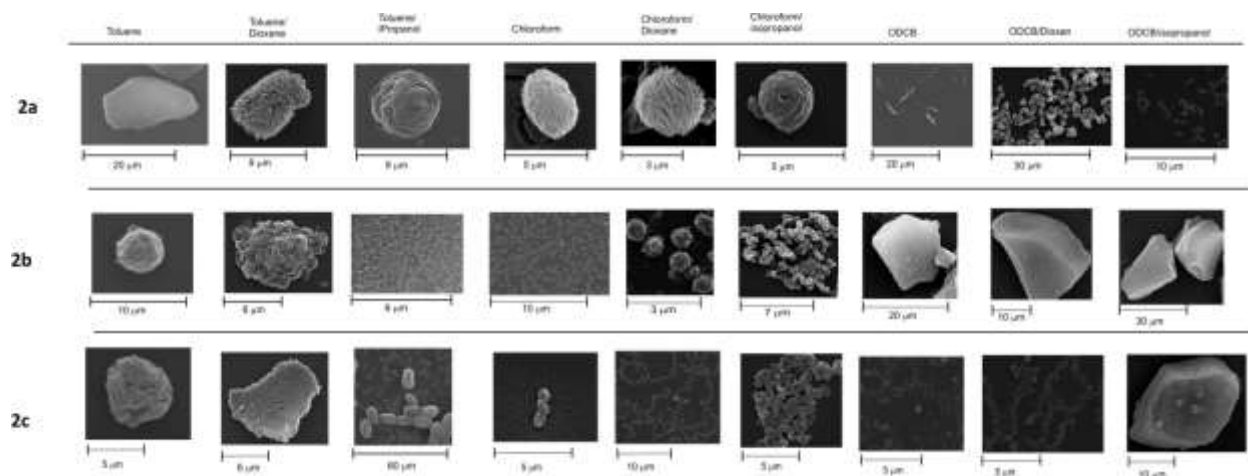


Fig S6. SEM images of compounds **2a-c**

References

1. M. S. Meier, H. P. Spielmann, R. G. Bergosh and M. C. Tetreau, *J.Org. Chem.*, 2003, **68**, 7867–7870.
2. N. Barooah and J. B. Baruah, *Journal of Molecular Structure*, 2008, **872**, 205–211.
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