

## An original self-assembly using a tetrathiafulvalene-based molecular clip for the recognition of fullerene C<sub>60</sub>

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**Figure S1.** Cyclic voltammogram and deconvoluted cyclic voltammogram of molecular clip **1** :  $2.5 \times 10^{-4}$  M in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (9/1) in *n*-Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M. Pt as the working and counter electrode, Ag/Ag<sup>+</sup> reference electrode, scan rate 100 mV s<sup>-1</sup>. Values are given vs. SCE, the couple Fc/Fc<sup>+</sup> (0.405 V vs. SCE) being used as an internal reference

**Figure S2.** UV-Visible absorption spectra of clip **1** ( $10^{-4}$  M, ODCB) upon titration with C<sub>60</sub> (from 0 to  $4.55 \times 10^{-4}$  M).

**Figure S3.** Cyclic voltammograms of clip **1** upon titration with C<sub>60</sub>, Cathodic shift of the quinone moieties: [**1**] =  $2.5 \times 10^{-4}$  mol.L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (9/1, v/v), TBAPF<sub>6</sub> (0.1 M),  $\nu = 100$  mV/s, Ref = AgNO<sub>3</sub>/Ag 0.01M in CH<sub>3</sub>CN

**Figure S4.** Cyclic voltammograms of clip **1** upon titration with C<sub>60</sub>, Anodic shift of the TTF moieties: [**1**] =  $2.5 \times 10^{-4}$  mol.L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (9/1, v/v), TBAPF<sub>6</sub> (0.1 M),  $\nu = 100$  mV/s, Ref = AgNO<sub>3</sub>/Ag 0.01M in CH<sub>3</sub>CN

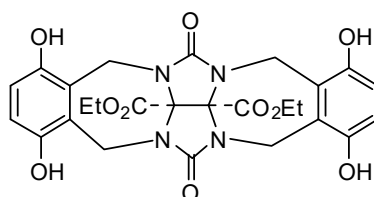
**Figure S5.** Binding isotherm at 600 nm obtained from the titration of **1** ( $10^{-4}$  M) by C<sub>60</sub> ( $4 \times 10^{-3}$  M) in ODCB at constant host concentration. The data were fitted according to a 2:1 stoichiometry to evaluate K1 and K2. Simulations are also included with varying K1, K2 couples.

## General procedures.

The following chemicals were obtained commercially and were used without any purification. Dry solvents were obtained by distillation over suitable desiccants (THF from Na/benzophenone). Reactions were monitored by thin-layer chromatography on aluminium sheets coated with silica gel 60 F254. Flash chromatography was performed with silica gel 60A (40–60  $\mu\text{m}$ ).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance III 300 ( $^1\text{H}$ : 300 MHz;  $^{13}\text{C}$ : 75 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to residual  $\text{CHCl}_3$ , DMSO or  $\text{CH}_2\text{Cl}_2$ . IR spectra were performed on a Bruker Vertex 70 spectrophotometer. UV-Visible absorption spectroscopy was performed on a Perkin Elmer Lambda 19 NIR and 950 spectrometers. Matrix-assisted laser-desorption/ionization mass spectrometry was performed on a Bruker Daltonics BIFLEX III spectrometer by using dithranol as the matrix. High resolution mass spectrum (HRMS) was recorded with a LTQ Orbitrap (Thermo Scientific) under electrospray ionization (ESI) in positive ionization mode. Cyclic voltammetry measurements were carried out in a three-electrode cell equipped with a platinum electrode as working electrode, a platinum wire counter electrode and a silver wire in a 0.01 M solution of  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$  as a reference electrode. The electrolytic media involved a 0.1 M solution of tetra-*n*-butylammonium-hexafluorophosphate (TBAHP – puriss quality) in  $\text{CH}_3\text{CN}$ . The ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ) was used as internal reference and the potentials were expressed versus the saturated calomel electrode (SCE) as a reference. All experiments were performed in a glove box containing dry, oxygen-free (< 1 ppm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat.

## Synthetic details and characterizations.

### Compound 3

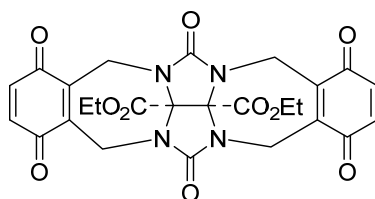


Glycoluril **2**<sup>1</sup> (300 mg, 0.81 mmol) and *p*-toluenesulfonic acid (614 mg, 3.24 mmol) were dissolved in 1,2-dichloroethane (30 mL). The mixture was heated under reflux using a Dean-Stark trap for 10 min. Hydroquinone (357 mg, 3.24 mmol) was then added and the mixture was heated at reflux for 24 h. After cooling to room temperature, the reaction mixture was concentrated. The residue was dissolved in methanol and the product was precipitated by adding diethyl ether. The solid was filtrated, washed with water to remove *p*-toluenesulfonic acid then additional diethyl ether. Compound **3** was isolated as a brown powder (265 mg, 59%).

$^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  = 8.82 (br s, 4H, OH), 6.51 (s, 4H,  $\text{H}_{\text{hydroquinone}}$ ), 5.09 (d, 4H,  $J$  = 15.6 Hz,  $\text{CH}_2\text{-N}$ ), 4.16 (q, 4H,  $J$  = 7.2 Hz,  $\text{CH}_2$ ), 4.01 (d, 4H,  $J$  = 15.6 Hz,  $\text{CH}_2\text{-N}$ ), 1.21 (t, 6H,  $J$  = 7.2 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  = 165.8 (C=O), 155.4 (N-C=O), 147.0 (C-OH), 124.1 ( $\text{C}_{\text{arom}}$ ), 115.4 ( $\text{C}_{\text{arom}}$ ), 80.1 ( $\text{C}_{\text{glycoluril}}^{\text{IV}}$ ), 63.1 ( $\text{CH}_2$ ), 36.8 ( $\text{CH}_2\text{-N}$ ), 13.7 ( $\text{CH}_3$ ); IR (neat)  $\nu$  = 3319, 1754, 1700, 1009  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_{10}$  554.1649, found 554.1638.

<sup>1</sup> C. A. Burnett, J. Lagona, A. Wu, J. A. Shaw, D. Coady, J. C. Fettinger, A. I. Day and L. Isaacs, *Tetrahedron*, 2003, **59**, 1961-1970.

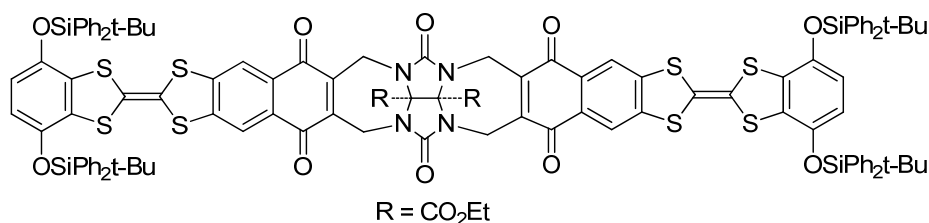
#### Compound 4



To a solution of compound **3** (80 mg, 0.14 mmol) in DMF (10 mL) was added DDQ (145 mg, 0.64 mmol) under argon atmosphere. The mixture was stirred at room temperature for 2 h. DCM was added, and the organic layer was washed three times with water. The organic phase was dried over  $\text{MgSO}_4$ , filtered and evaporated. Methanol was added and the product was precipitated by addition of  $\text{Et}_2\text{O}$ . The solid was filtrated and compound **4** was isolated as a brown solid (46 mg; 58%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 6.75 (s, 4H,  $\text{H}_{\text{quinone}}$ ), 5.51 (d, 4H,  $J$  = 17.0 Hz,  $\text{CH}_2\text{-N}$ ), 4.32 (q, 4H,  $J$  = 6.9 Hz,  $\text{CH}_2$ ), 3.94 (d, 4H,  $J$  = 17.0 Hz,  $\text{CH}_2\text{-N}$ ), 1.34 (t, 6H,  $J$  = 6.9 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 185.2 ( $\text{C}=\text{O}_{\text{quinone}}$ ), 164.8 ( $\text{C}=\text{O}$ ), 155.2 ( $\text{N}-\text{C}=\text{O}$ ), 141.5 ( $\text{C}_{\text{arom}}$ ), 136.2 ( $\text{C}_{\text{arom}}$ ), 77.4 ( $\text{C}^{\text{IV}}_{\text{glycoluril}}$ ), 64.0 ( $\text{CH}_2$ ), 36.8 ( $\text{CH}_2\text{-N}$ ), 14.2 ( $\text{CH}_3$ ); IR (neat)  $\nu$  = 1750, 1711, 1654, 1080  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_{10}$  550.1336, found 550.1338.

#### Compound 1



To a solution of compound **4** (82.5 mg, 0.15 mmol) in anhydrous THF (15 mL) were successively added at  $0^\circ\text{C}$  a solution of 2,3-bis(bromomethyl)TTF **5**<sup>2</sup> (290 mg, 0.3 mmol) in anhydrous THF (10 mL), 18-crown-6 (569 mg, 2.15 mmol) (freshly recrystallized in  $\text{CH}_3\text{CN}$ ), anhydrous KI (116 mg, 0.70 mmol). The reaction mixture was stirred for 36 h at room temperature under argon atmosphere. After addition of  $\text{EtOAc}$ , the solvent was partially evaporated under vacuum. The residue was purified by chromatography on silica gel (eluent  $\text{CH}_2\text{Cl}_2$ , then  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  97/3) to give compound **1** as a green powder (80 mg, 25%).

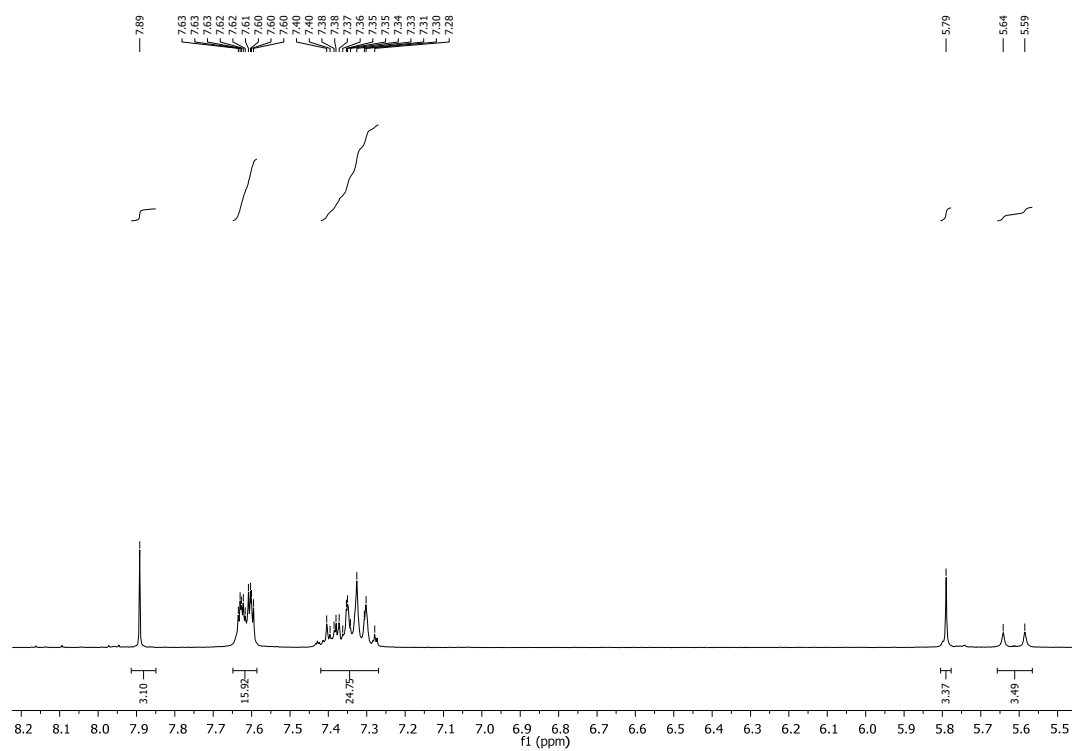
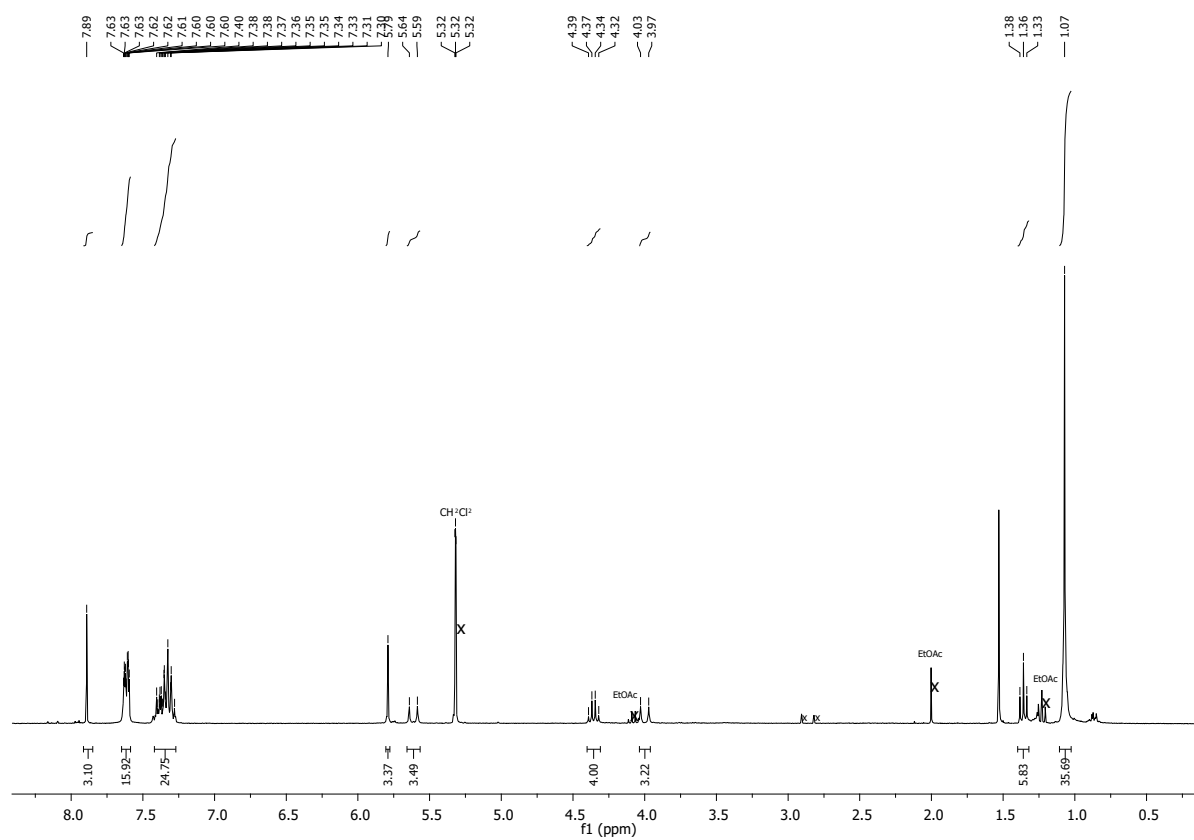
$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 7.89 (s, 4H,  $\text{H}_{\text{arom}}$ ), 7.62 (m, 16H,  $\text{H}_{\text{arom}}$ ), 7.40-7.30 (m, 24H,  $\text{H}_{\text{arom}}$ ), 5.79 (s, 4H,  $\text{H}_{\text{hydroquinone}}$ ), 5.62 (d, 4H,  $J$  = 17.0 Hz,  $\text{CH}_2\text{-N}$ ), 4.35 (q, 4H,  $J$  = 7.2 Hz,  $\text{CH}_2$ ), 4.00 (d, 4H,  $J$  = 17.0 Hz,  $\text{CH}_2\text{-N}$ ), 1.36 (t, 6H,  $J$  = 7.2 Hz,  $\text{CH}_3$ ), 1.07 (s, 36H,  $\text{tBu}$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 182.1 ( $\text{C}=\text{O}_{\text{quinone}}$ ), 165.4 ( $\text{CO}_2$ ), 155.5 ( $\text{N}-\text{C}=\text{O}$ ), 145.6, 144.1, 144.0, 135.8, 132.4, 132.3, 130.5, 129.7, 128.2, 119.6, 116.4, ( $\text{C}=\text{C}_{\text{TTF}}$  and  $\text{C}_{\text{arom}}$ ), 106.9 ( $\text{C}=\text{C}_{\text{hydroquinone}}$ ), 80.2 ( $\text{C}^{\text{IV}}_{\text{glycoluril}}$ ), 64.4 ( $\text{CH}_2_{\text{ester}}$ ), 36.9 ( $\text{CH}_2\text{-N}$ ), 26.6 ( $\text{C}^{\text{IV}}_{\text{tBu}}$ ), 19.6 ( $\text{CH}_3_{\text{tBu}}$ ), 14.2 ( $\text{CH}_3_{\text{ester}}$ ); IR (neat)  $\nu$  = 1734, 1662, 1257, 1017  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{114}\text{H}_{102}\text{N}_4\text{O}_{14}\text{S}_8\text{Si}_4$ : C, 64.21; H, 4.95; N, 2.32. Found: C, 64.56; H, 4.85; N, 2.64; HRMS (negative mode) calcd 2118.4235, found 2118.4186.

<sup>2</sup> J. Baffreau, F. Dumur and P. Hudhomme, *Org. Lett.*, 2006, **8**, 1307-1310.

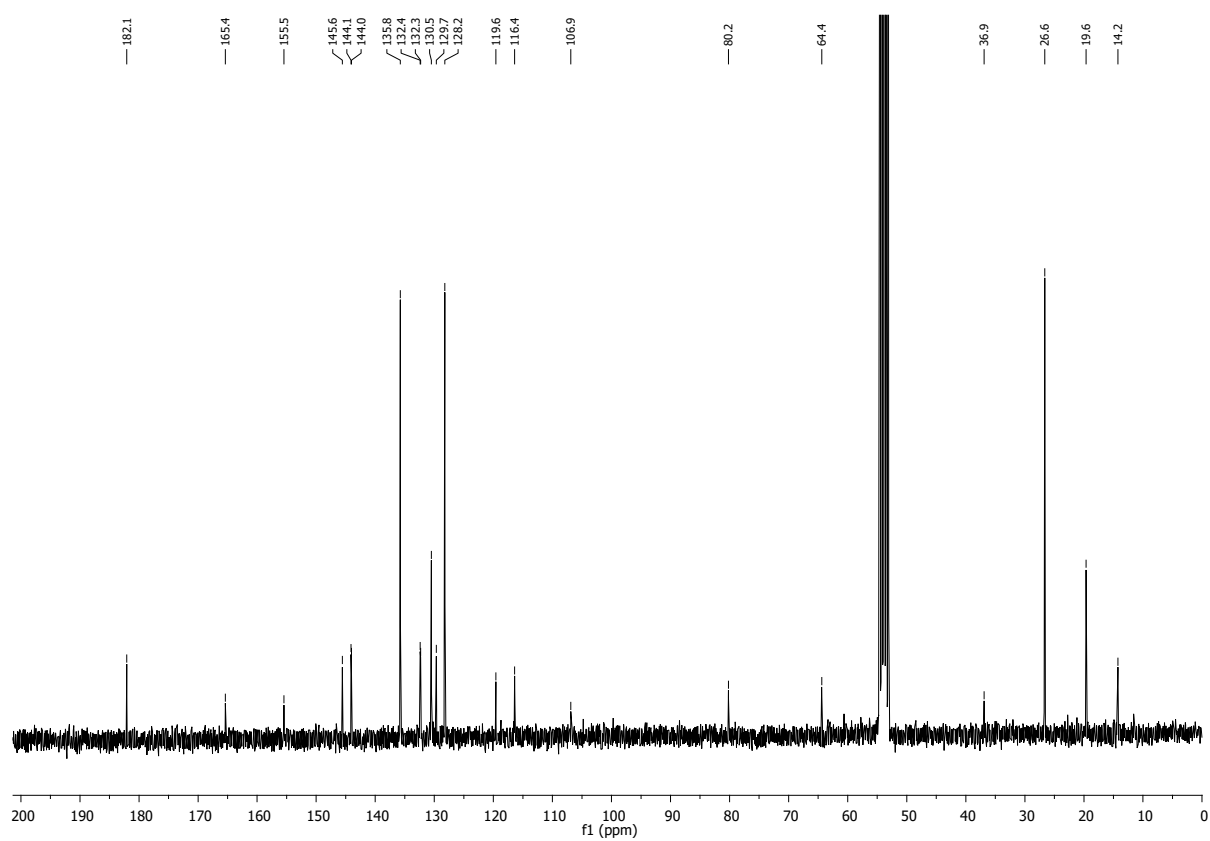
# $^1\text{H}$ and $^{13}\text{C}$ Spectra.

## Compound 1

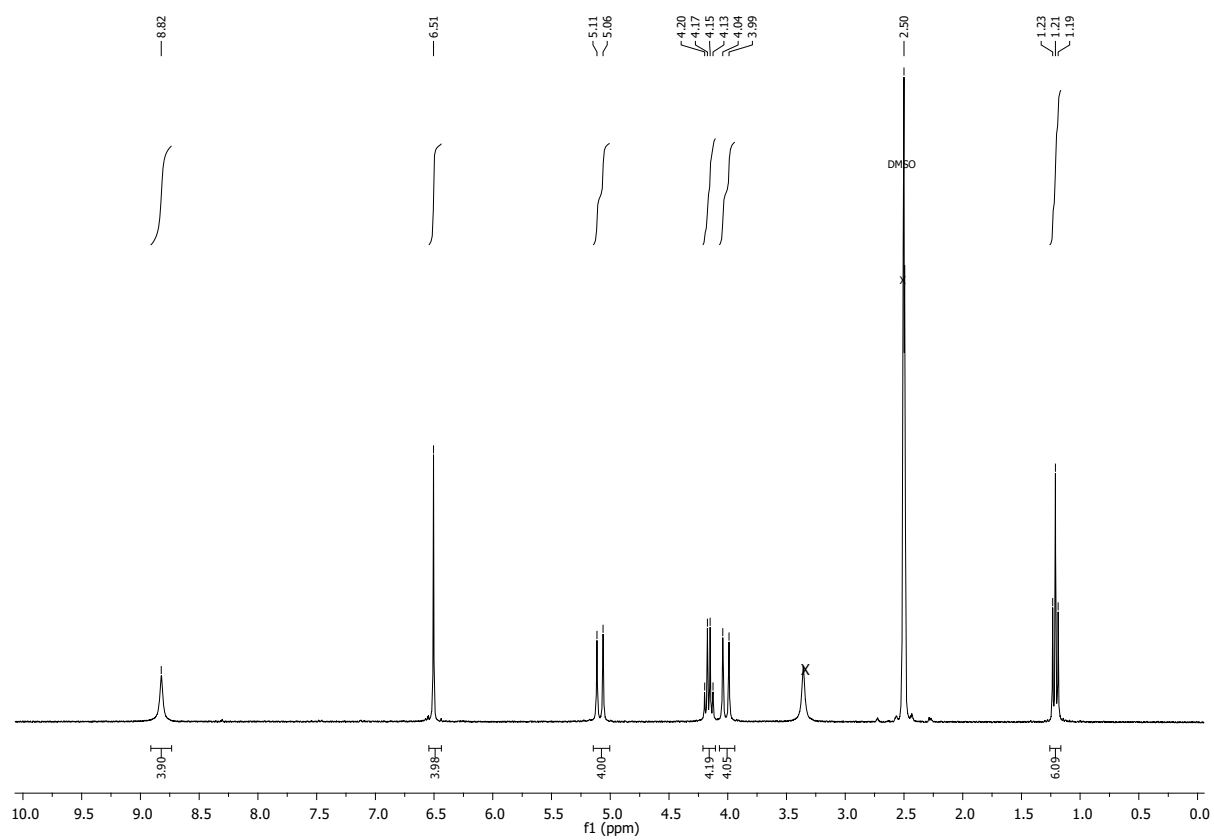
$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )



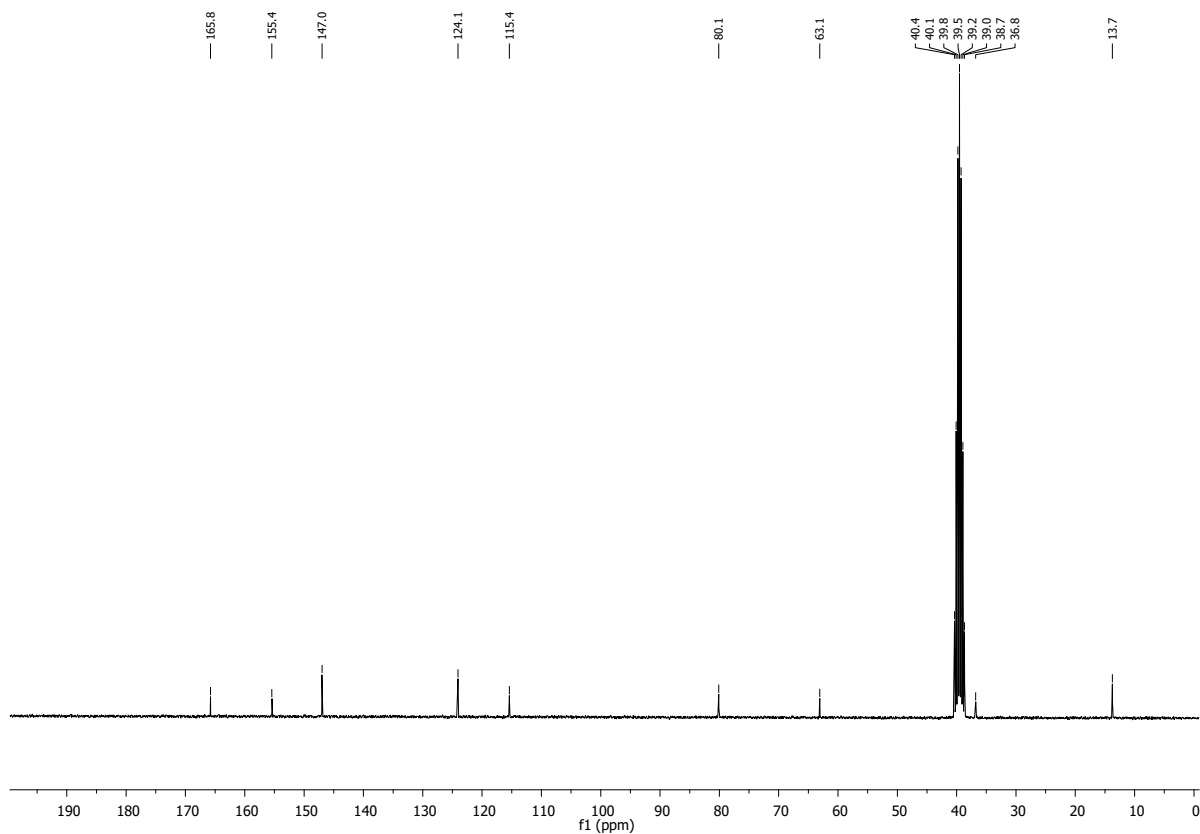
$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )



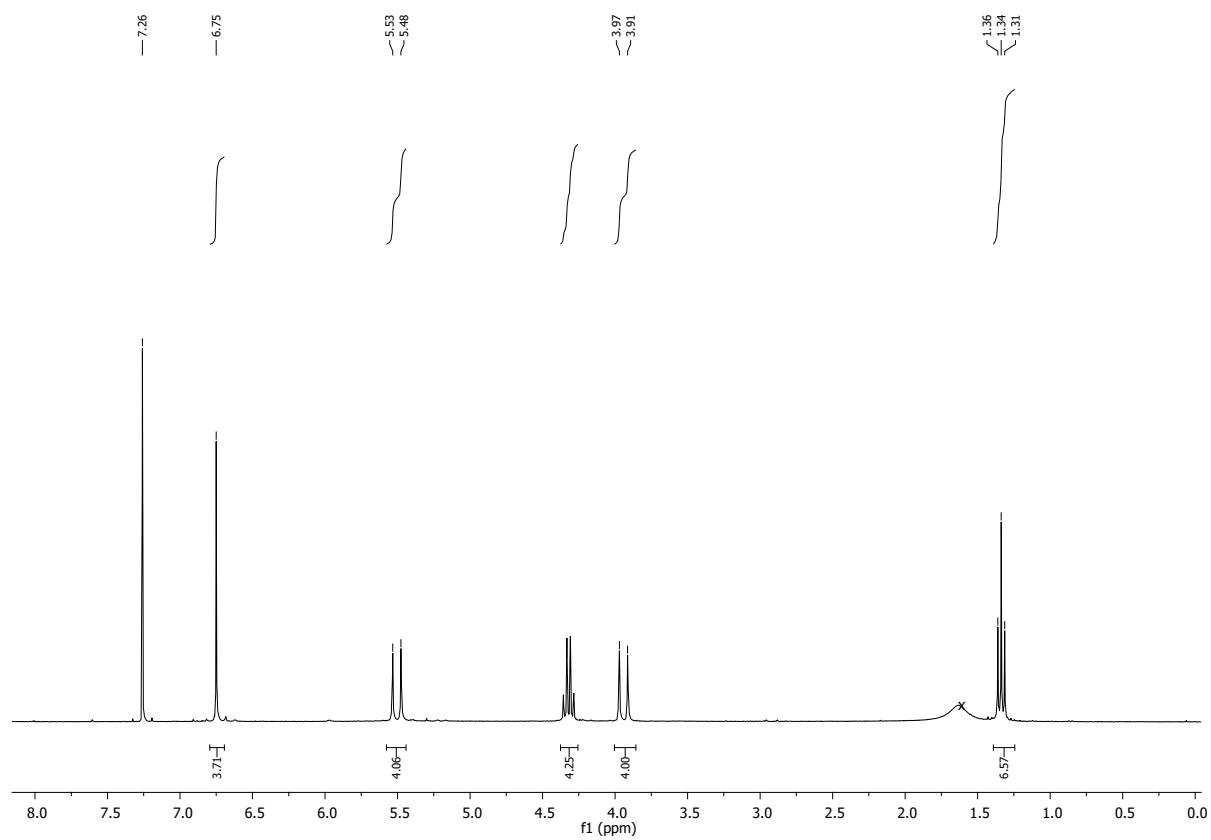
Compound 3  
<sup>1</sup>H NMR (DMSO-d6)



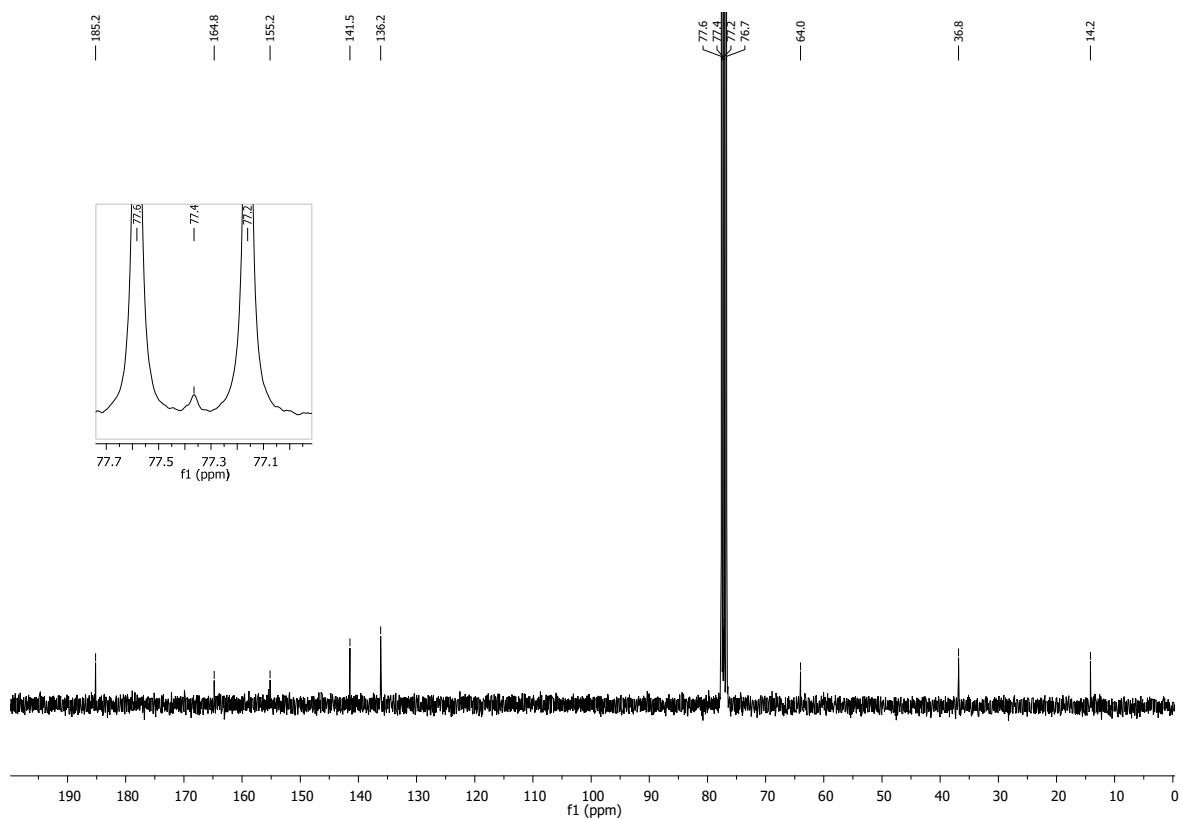
<sup>13</sup>C NMR (DMSO-d6)



Compound 4  
<sup>1</sup>H NMR (CDCl<sub>3</sub>)



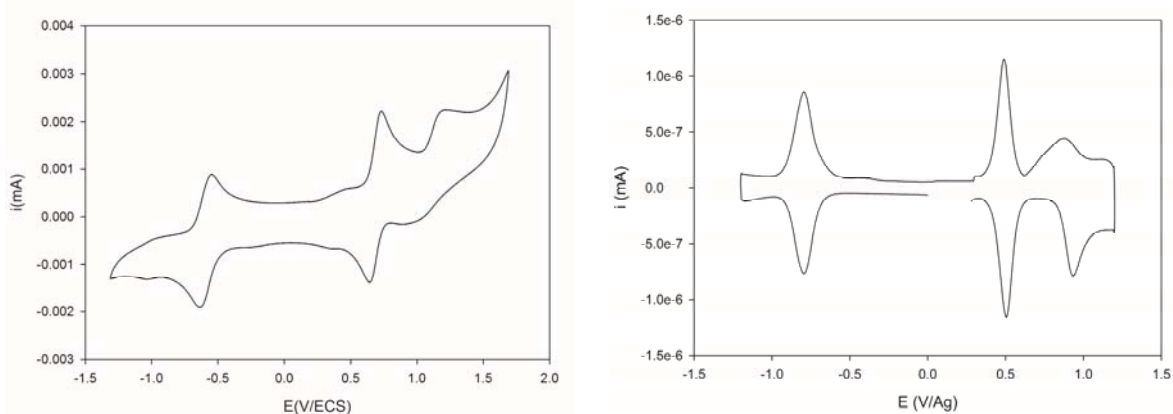
<sup>13</sup>C NMR (CDCl<sub>3</sub>)



### Cyclic voltammetry:

Cyclic voltammetry was performed in a three-electrode cell equipped with a platinum millielectrode as working electrode, a platinum wire counter electrode and a silver wire in a 0.01 M solution of  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$  as a reference electrode.

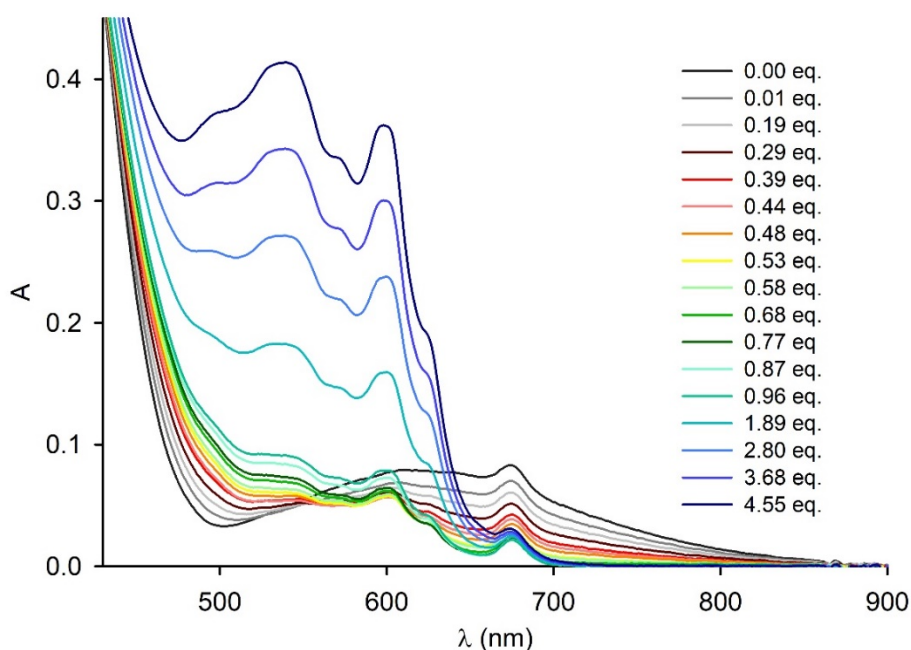
**Figure S1.** Cyclic voltammogram and deconvoluted cyclic voltammogram of molecular clip **1** :  $2.5 \times 10^{-4}$  M in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (9/1) in  $n\text{-Bu}_4\text{NPF}_6$  0.1 M. Pt as the working and counter electrode,  $\text{Ag}/\text{Ag}^+$  reference electrode, scan rate  $100 \text{ mV s}^{-1}$ . Values are given vs. SCE, the couple  $\text{Fc}/\text{Fc}^+$  ( $0.405 \text{ V vs. SCE}$ ) being used as an internal reference



### Determination of equilibrium constants

UV-Visible titrations were performed in a quartz cell (1 cm) at room temperature. A solution of **1** ( $10^{-4}$  M) was prepared in ODCB and was titrated with a solution of  $\text{C}_{60}$  ( $4 \cdot 10^{-3}$  M) solubilized in the solution of **1** allowing for constant host concentration. Binding isotherms were obtained by plotting the absorbance at a given wavelength against the  $\text{C}_{60}$  concentration and the fitting process was performed through least square method.

**Figure S2.** UV-Visible absorption spectra of clip **1** ( $10^{-4}$  M, ODCB) upon titration with  $\text{C}_{60}$  (from 0 to  $4.55 \times 10^{-4}$  M).

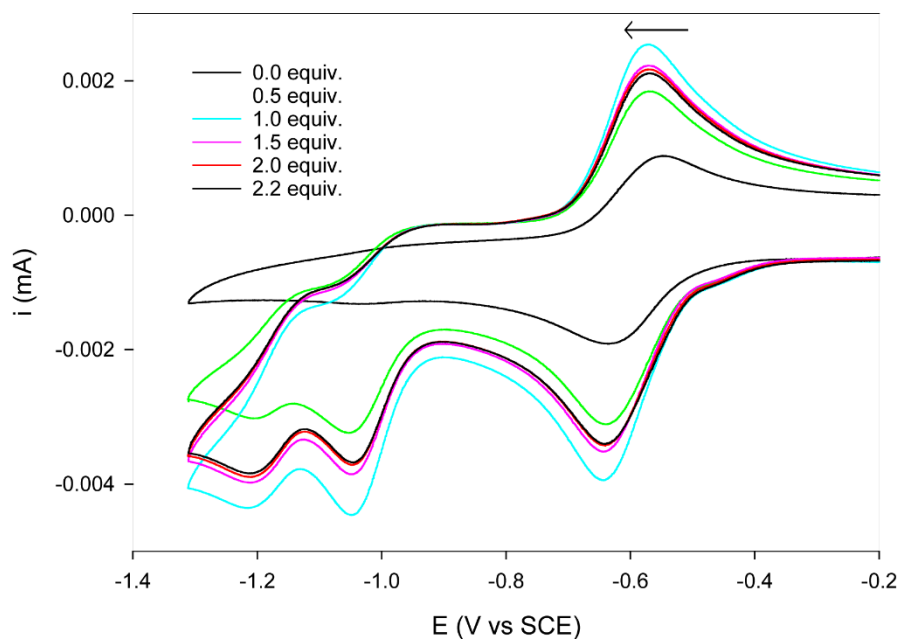




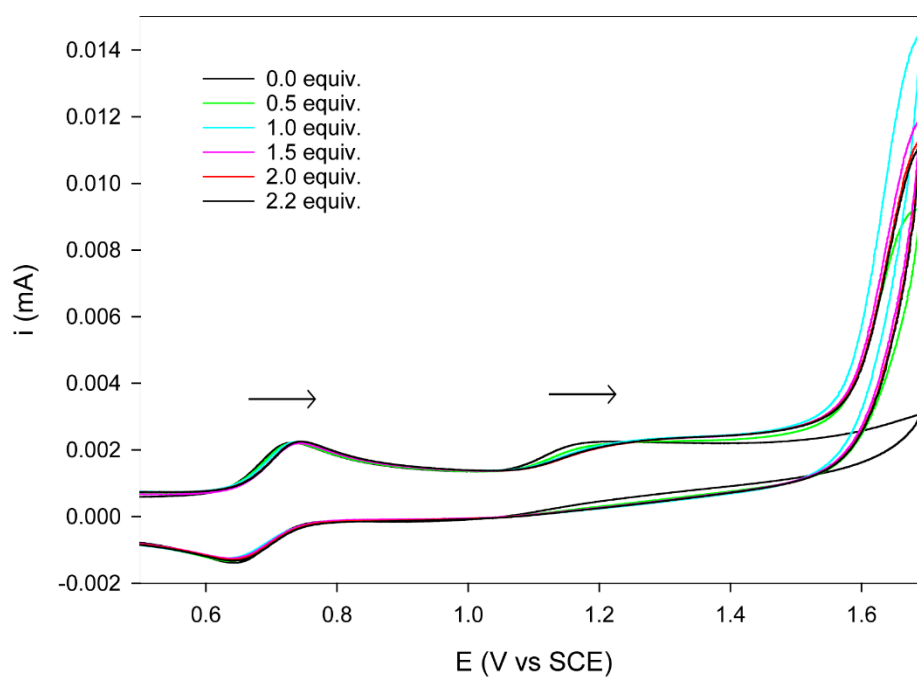
### Cyclic voltammograms of clip 1 upon titration with C<sub>60</sub>

Experimental conditions: [1] =  $2.5 \times 10^{-4}$  mol.L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (9/1, v/v), TBAPF<sub>6</sub> (0.1 M),  $\nu = 100$  mV/s, Ref = AgNO<sub>3</sub>/Ag 0.01M in CH<sub>3</sub>CN

**Figure S3.** Cathodic shift of the quinone moieties



**Figure S4.** Anodic shift of the TTF moieties



**Figure S5.** Binding isotherm at 600 nm obtained from the titration of **1** ( $10^{-4}$  M) by  $C_{60}$  ( $4 \cdot 10^{-3}$  M) in ODCB at constant host concentration. The data were fitted according to a 2:1 stoichiometry to evaluate  $K_1$  and  $K_2$  (solid line). Simulations are also included with varying  $K_1$ ,  $K_2$  couples (dashed lines).

