An original self-assembly using a tetrathiafulvalene-based molecular clip for the recognition of fullerene C₆₀

Yoann Cotelle, Marie Hardouin-Lerouge, Elise Lemasson, Yohann Morille, David Canevet, Stéphanie Legoupy* and Piétrick Hudhomme*

Laboratoire MOLTECH-Anjou, UMR CNRS 6200, UNIV Angers, SFR MATRIX, 2 Bd Lavoisier, 49045 Angers Cedex, France. E-mail: stephanie.legoupy@univ-angers.fr, pietrick.hudhomme@univ-angers.fr

Supporting information

General procedures 2

Synthetic details and characterizations 2

Collection of spectra

Figure S1. Cyclic voltammogram and deconvoluted cyclic voltamogramm of molecular clip 1: 2.5 × 10⁻⁴ M in CH₂Cl₂/CH₃CN (9/1) in n-Bu₄NPF₆ 0.1 M. Pt as the working and counter electrode, Ag/Ag⁺ reference electrode, scan rate 100 mV s⁻¹. Values are given vs. SCE, the couple Fc/Fc⁺ (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 C₆₀ (from 0 to 4.55 × 10⁻⁴ M).

Figure S3. Cyclic voltammograms of clip 1 upon titration with C₆₀, Cathodic shift of the quinone moieties: [1] = 2.5 × 10⁻⁴ mol.L⁻¹ in CH₂Cl₂/CH₃CN (9/1, v/v), TBAPF₆ (0.1 M), v = 100 mV/s, Ref = AgNO₃/Ag 0.01M in CH₃CN

Figure S4. Cyclic voltammograms of clip 1 upon titration with C₆₀, Anodic shift of the TTF moieties: [1] = 2.5 × 10⁻⁴ mol.L⁻¹ in CH₂Cl₂/CH₃CN (9/1, v/v), TBAPF₆ (0.1 M), v = 100 mV/s, Ref = AgNO₃/Ag 0.01M in CH₃CN

Figure S5. Binding isotherm at 600 nm obtained from the titration of 1 (10⁻⁴ M) by C₆₀ (4.10⁻³M) 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 dessicants (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 60 A (40–60 μm). 1H NMR and 13C NMR spectra were recorded on Bruker Avance III 300 (1H: 300 MHz; 13C: 75 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to residual CHCl3, DMSO or CH2Cl2. 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 (Thero 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 AgNO3 in CH3CN as a reference electrode. The electrolytic media involved a 0.1 M solution of tetra-n-butylammonium-hexafluorophosphate (TBAHP – puriss quality) in CH3CN. The ferrocene/ferrocenium couple (Fc/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

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\begin{align*}
\text{Glycoluril 2}^1 &\quad (300 \text{ mg, 0.81 mmol}) \text{ and } p\text{-toluenesulfonic acid (614 mg, 3.24 mmol)} \text{ 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%).}
\end{align*}
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\[ ^1\text{H NMR (DMSO-d6) } \delta = 8.82 \text{ (br s, 4H, OH), 6.51 (s, 4H, } \text{H}_{\text{hydroquinone}}\text{), 5.09 (d, 4H, } J = 15.6 \text{ Hz, CH}_2\text{-N), 4.16 (q, 4H, } J = 7.2 \text{ Hz, CH}_2\text{), 4.01 (d, 4H, } J = 15.6 \text{ Hz, CH}_2\text{-N), 1.21 (t, 6H, } J = 7.2 \text{ Hz, CH}_3\text{); } ^{13}\text{C NMR (DMSO-d6) } \delta = 165.8 \text{ (C=O), 155.4 (N-C=O), 147.0 (C-OH), 124.1 (C}_{\text{arom}}\text{), 115.4 (C}_{\text{arom}}\text{), 80.1 (C}_{\text{glycoluril}}\text{), 63.1 (CH}_3\text{), 36.8 (CH}_3\text{-N), 13.7 (CH}_3\text{); IR (neat) } \nu = 3319, 1754, 1700, 1009 \text{ cm}^{-1}; \text{ HRMS calcd for } C_{26}H_{26}N_4O_{10} 554.1649, \text{ found 554.1638.}
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Compound 4

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\text{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 MgSO}_4\text{, filtered and evaporated. Methanol was added and the product was precipitated by addition of Et}_2\text{O. The solid was filtrated and compound 4 was isolated as a brown solid (46 mg; 58%).}
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^1\text{H NMR (CDCl}_3\text{)} \delta = 6.75 \text{ (s, 4H, Hquinone), 5.51 \text{ (d, 4H, J = 17.0 Hz ,CH}_2\text{-N), 4.32 \text{ (q, 4H, J = 6.9 Hz, CH}_2\text{), 3.94 \text{ (d, 4H, J = 17.0 Hz ,CH}_2\text{-N), 1.34 \text{ (t, 6H, J = 6.9 Hz, CH}_3\text{); }^{13}\text{C NMR (CDCl}_3\text{)} \delta = 185.2 \text{ (C=O quinone), 164.8 \text{ (C=O), 155.2 \text{ (N-C=O), 141.5 \text{ (C=O arrom), 136.2 \text{ (C=O arrom), 77.4 \text{ (C=O glycoluril), 64.0 \text{ (CH}_2\text{), 36.8 \text{ (CH}_2\text{-N), 14.2 \text{ (CH}_3); IR (neat) } \nu = 1750, 1711, 1654, 1080 \text{ cm}^{-1\text{-1}; HRMS calcld for C}_{26}\text{H}_{22}\text{N}_4\text{O}_{10}: 550.1336, found 550.1338.}}
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Compound 1

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\text{To a solution of compound 4 (82.5 mg, 0.15 mmol) in anhydrous THF (15 mL) were successively added at 0°C a solution of 2,3-bis(bromomethyl)TTF 5\text{2 (290 mg, 0.3 mmol) in anhydrous THF (10 mL), 18-crown-6 (569 mg, 2.15 mmol) (freshly recrystallized in 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 EtOAc, the solvent was partially evaporated under vacuum. The residue was purified by chromatography on silica gel (eluents CH}_2\text{Cl}_2\text{, then CH}_2\text{Cl}_2\text{/EtOAc 97/3) to give compound 1 as a green powder (80 mg, 25%).}
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^1\text{H NMR (CD}_2\text{Cl}_2\text{)} \delta = 7.89 \text{ (s, 4H, H arom), 7.62 \text{ (m, 16H, H arom), 7.40-7.30 \text{ (m, 24H, H arom), 5.79 \text{ (s, 4H, H hydroquinone), 5.62 \text{ (d, 4H, J =17.0 Hz, CH}_2\text{-N), 4.35 \text{ (q, 4H, J = 7.2 Hz, CH}_2\text{), 4.00 \text{ (d, 4H, J = 17.0 Hz ,CH}_2\text{-N), 1.36 \text{ (t, 6H, J = 7.2 Hz, CH}_3\text{), 1.07 \text{ (s, 36H, tBu); }^{13}\text{C NMR (CD}_2\text{Cl}_2\text{)} \delta = 182.1 \text{ (C=O quinone), 165.4 \text{ (CO}_2\text{), 155.5 \text{ (N-C=O), 145.6, 144.1, 144.0, 135.8, 132.4, 132.3, 130.5, 129.7, 128.2, 119.6, 116.4, (C=CTTF and C=CTTF), 106.9 \text{ (C=hydroquinone), 80.2 \text{ (C=O glycoluril), 64.4 \text{ (CH}_2\text{ ester), 36.9 \text{ (CH}_2\text{-N), 26.6 \text{ (C=O 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\text{-1; Anal. Calcld for 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) calcld 2118.4235, found 2118.4186.}}}
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\[^2\text{ J. Baffreau, F. Dumur and P. Hudhomme, Org. Lett., 2006, 8, 1307-1310.}\]
$^1$H and $^{13}$C Spectra.

Compound 1
$^1$H NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)
Compound 3

$^1$H NMR (DMSO-d6)

$^{13}$C NMR (DMSO-d6)
Compound 4

$^1$H NMR (CDCl$_3$)

$^1$H NMR (CDCl$_3$)

$^13$C NMR (CDCl$_3$)

$^13$C NMR (CDCl$_3$)
**Cyclic voltammetry:**

Cyclic voltammetry was performed in a three-electrode cell equipped with a platinium millielectrode as working electrode, a platinium wire counter electrode and a silver wire in a 0.01 M solution of AgNO₃ in CH₃CN as a reference electrode.

**Figure S1.** Cyclic voltammogram and deconvoluted cyclic voltammogram of molecular clip 1 : 2.5 × 10⁻⁴ M in CH₂Cl₂/CH₃CN (9/1) in n-Bu₄NPF₆ 0.1 M. Pt as the working and counter electrode, Ag/Ag⁺ reference electrode, scan rate 100 mV s⁻¹. Values are given vs. SCE, the couple Fc/Fc⁺ (0.405 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 C₆₀ (4.10⁻³ M) solubilized in the solution of 1 allowing for constant host concentration. Binding isotherm were obtained by plotting the absorbance at a given wavelength against the C₆₀ 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 C₆₀ (from 0 to 4.55 × 10⁻⁴ M).
Cyclic voltammograms of clip 1 upon titration with C_60

Experimental conditions: [1] = 2.5 × 10^{-4} mol.L⁻¹ in CH₂Cl₂/CH₃CN (9/1, v/v), TBAPF₆ (0.1 M), v = 100 mV/s, Ref = AgNO₃/Ag 0.01M in CH₃CN

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 C₆₀ (4.10⁻³M) in ODCB at constant host concentration. The data were fitted according to a 2:1 stoichiometry to evaluate K₁ and K₂ (solid line). Simulations are also included with varying K₁, K₂ couples (dashed lines).