Supporting Information for

Remarkably Bistable and Fast Reversible Calixarene Based Copper Centered Redox Molecular Switch

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General methods. Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography was performed using silica gel (Kieselgel-60, 0.040-0.063 nm, Merck). Reactions were monitored by TLC on POLYGAM® SIL G/UV$_{254}$ (Macherey-Nagel) silica gel plate and visualized by UV light. $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 and 75 MHz (CDCl$_3$) on a Bruker Avance DRX 300 spectrometer. Mass spectra were acquired on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive ions (+) or negative ions (-) in the ESI mode. Samples (in methanol:dichloromethane:water, 45:40:15, v/v/v) were infused directly into the source (5μL/min) using a syringe pump. The following source parameters were applied: spray voltage 3.0–3.5 kV, nitrogen sheath gas flow 5–20 arbitrary units. The heated capillary was held at 200°C. High resolution mass spectra were acquired on a THERMOQUEST Finnigan MAT 95 XL. Acetonitrile (Rathburn, HPLC grade) was used as received. Tetra-$n$-butylammonium PF$_6$ was purchased from Fluka and used as received. Electrochemical experiments were conducted in a conventional three-electrode cell. For analytical experiments, the counter electrode was a platinum wire. The reference electrode was a Ag/AgNO$_3$ (10 mM in CH$_3$CN containing 0.1 M TBAP) purchased from CH-instrument. Rotating disk electrode (RDE) voltammetry was carried out with a radiometer equipment at a rotation rate of 500 rpm using glassy carbon RDE tips ($\Theta$ = 2 mm). Cyclic voltammetry (CV) curves were recorded using a CH instrument CH-660 potentiostat. The CH-instrument vitreous carbon working electrodes (($\Theta$ = 2 mm). were polished with 1 μm diamond paste before each recording. Electrolyses were performed at controlled
potential using a Pt plate as working electrode as well as a large Pt counter electrode isolated through an ionic bridge.

**Synthesis of Di-quinoline calixarene 2**

Under nitrogen atmosphere, dibromo calixarene 1 (4.25 g; 4.62 mmol; 1 equiv) and K₂CO₃ (2.55 g; 18.5 mmol; 4 equiv) were dissolved in freshly distillate acetonitrile (80 mL). The suspension was stirring during 30 minutes at room temperature. 8-hydroxyquinoline (5.36 g; 37.0 mmol; 8 equiv) was then added and the reaction mixture was refluxing during 5 days. After allowing the mixture going back to room temperature, the solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane and wash with HCl 10% (100 mL), then with water until pH = 7. After dichloromethane extraction, drying, filtration and solvent evaporation, the resulting crude compound was purified by flash chromatography (methanol/dichloromethane 3/97) giving pure diquinoleine calixarene 2 (3.09 g, 64%) as pale beige solid: mp 190 °C dec; IR (CHCl₃) ν 3403, 2952, 1485, 1318, 1111, 745 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (s, 18 H, tBu), 1.22 (s, 18H, tBu), 2.17-2.22 (m, 4H, O-CH₂-CH₂-CH₂-O-quin), 2.28-2.34 (m, 4H, O-CH₂-CH₂-CH₂-C₄H₄-O-quino), 3.24 (d, 4H, J = 13 Hz, Ar-CH₂-OH ax), 4.00 (t, 4H, J = 6.2 Hz, O-CH₂-CH₂-CH₂-O-quin), 4.20 (d, 4H, J = 13 Hz, Ar-CH₂-OH eq), 4.31 (t, 4H, J = 5.9 Hz, O-CH₂-CH₂-CH₂-O-quin), 6.73 (s, 4H, ArHcalix), 6.98 (s, 4H, ArHcalix), 7.06 (s, 2H, Hquinoline), 7.29-7.38 (m, 6H, Hquinoline), 7.49 (s, 2H, OH); 8.10 (d, 2H, J = 7 Hz, Hquinoline), 8.91 (m, 2H, Hquinoline); ¹³C NMR (CDCl₃) δ 26.2, 27.3, 31.4, 32.1, 34.2, 34.3, 68.9, 76.5, 109.4, 119.8, 121.8, 125.5, 125.9, 127.2, 129.9, 133.0, 136.2, 140.8, 141.8, 147.2, 149.6, 150.3, 151.1, 155.2. HRMS (ESI-TOF) m/z : calcd for C₇₀H₈₃N₂O₆ [M + H]⁺: 1047.6251; Found: 1047.6244.

**Synthesis of [di-quo di-imidazole] calixarene 3**

Under nitrogen atmosphere, anhydrous THF was added to a mixture of di-quinoline calixarene 2 (2.00 g; 1.91 mmol) and NaH (60% in oil, 1.38 g, 34.5 mmol). The reaction mixture was stirred for one hour at room temperature and 2-chloromethyl-N-methylimidazole hydrochloride (1.92 g, 11.5 mmol) was introduced. After 18 h of refluxing, the solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane and washed with water until pH = 7. After dichloromethane extraction drying, filtration and solvent evaporation, the resulting crude compound was purified by flash chromatography (dichlorométhane/méthanol/triéthylamine : 88/10/2) giving pure di-imidazole di-quinoline calixarene 3 (1.13 g, 48%) as a white solid: mp 194 °C ; IR (CHCl₃) ν 2959, 1479, 1260, 1105, 791 cm⁻¹; ¹H NMR (CDCl₃) δ 0.79 (s, 18 H, tBu), 1.22 (s, 18H, tBu), 1.79-1.90 (m, 4H, O-CH₂-
CH₂-CH₂-CH₂-O-quin), 1.95-2.05 (m, 4H, O-CH₂-CH₂-CH₂-O-quin), 2.99 (d, 4H, J = 13 Hz, Ar-CH₂-Ar ax), 3.09 (s, 6H, NCH₃), 3.90 (t, 4H, J = 5.9 Hz, O-CH₂-CH₂-CH₂-CH₂-O-quin), 4.09 (t, 4H, J = 6.2 Hz, O-CH₂-CH₂-CH₂-CH₂-O-quin), 4.30 (d, 4H, J = 13 Hz, Ar-CH₂-Ar eq), 4.78 (s, 4H, CH₂Im), 6.44 (s, 4H, ArHcalix), 6.70 (s, 2H, ImH), 6.88 (s, 2H, ImH), 6.97 (s, 4H, ArHcalix), 7.02 (d, 2H, J = 7.0 Hz, Hquinoline), 7.20-7.34 (m, 6H, Hquinoline), 8.03 (d, 2H, J = 7 Hz, Hquinoline), 8.83-8.84 (m, 2H, Hquinoline); ¹³C NMR (CDCl₃) δ 26.2, 26.8, 31.3, 31.6, 32.1, 33.2, 34.1, 34.4, 67.7, 69.5, 75.0, 109.4, 119.7, 121.9, 125.1, 125.8, 125.8, 128.5, 129.9, 132.9, 135.5, 136.2, 140.8, 145.1, 145.3, 149.5, 151.8, 154.7, 155.3. HRMS (ESI-TOF) m/z: calcd for C₈₀H₉₅N₆O₆ [M + H]⁺: 1235.7313; Found: 1235.7313.

Synthesis of complex 3.Cu I
Under nitrogen, CHCl₃ (3 mL) was added to a mixture of di-quinzo di-midazole calixarene 3 (30.0 mg, 0.024 mmol) and [Cu(CH₃CN)₄]PF₆ (9.5 mg, 0.025 mmol). The resulting pale yellow solution was stirring for one hour at room temperature. After a removal of the solvent under reduces pressure, the obtained complex 3.Cu I was dry under vacuum. (31 mg, 88 %): mp 155 °C dec; IR (CHCl₃) ν 2953, 1571, 1502, 1479, 837 cm⁻¹; ¹H NMR (CDCl₃) δ 0.81 (s, 18 H, tBu), 1.37 (s, 18H, tBu), 1.90-2.20 (m, 8H, O-CH₂-CH₂-CH₂-O-quin), 3.02 (s, 6H, NC₃H₃), 3.11 (d, 4H, J = 13 Hz, Ar-CH₂-Ar ax), 3.70-3.80 (m, 4H, O-CH₂-CH₂-CH₂-O-quin), 3.95 (d, 4H, J = 13 Hz, Ar-CH₂-Ar eq), 4.30-4.40 (m, 4H, O-CH₂-CH₂-CH₂-CH₂-O-quin), 5.45-5.55 (m, 4H, CH₂Im), 6.36 (s, 4H, ArHcalix), 6.80-7.00 (m, 4H, ImH), 7.14 (s, 4H, ArHcalix), 7.18 (d, 2H, J = 8.4 Hz, Hquinoline), 7.30-7.55 (m, 6H, Hquinoline), 8.12 (d, 2H, J = 8.1 Hz, Hquinoline), 8.80 (d, 2H, J = 4.6 Hz, Hquinoline); ¹³C NMR (CDCl₃) δ 26.5, 27.8, 31.5, 31.7, 32.1, 34.0, 34.6, 71.0, 109.7, 120.1, 122.2, 124.9, 126.7, 127.6, 130.0, 131.6, 135.9, 136.6, 140.1, 145.0, 147.2, 149.7, 150.4, 153.8, 154.8. HRMS (ESI-TOF) m/z: calcd for C₈₀H₉₃N₆O₆ [M + H]⁺: 1235.7313; Found: 1235.7313.

Synthesis of complex 3.Cu II
Under nitrogen, CH₃CN (3 mL) was added to a mixture of di-quinzo di-midazole calixarene 3 (32.1 mg, 0.026 mmol) and Cu(ClO₄)₂·2H₂O (9.8 mg, 0.026 mmol). The resulting deep green solution was stirring for one hour at room temperature. After a removal of the solvent under reduces pressure, the obtained complex 3.Cu II was dry under vacuum. (32 mg, 82 %): mp 190 °C dec; IR (CHCl₃) ν 2954, 1585, 1509, 1479, 1083 cm⁻¹; HRMS (ESI-TOF) m/z: calcd for C₈₀H₉₄ClCuN₆O₁₀ [M-ClO₄]⁺: 1396.6016; Found: 1396.6018; UV-vis (λᵥₘₐₓ = 635 nm, ε = 62.4 M⁻¹.cm⁻¹). EPR: (9.44 GHz, 40K, CH₃CN/Toluene 1/1, v/v): Aᵥ = 172 10⁻⁴ cm⁻¹ gᵥ = 2.211 gᵥ = 2.004.
Crystallographic data

A suitable crystal was mounted on a Nonius KappaCCD diffractometer using Mo Kα radiation (\(\lambda = 0.71073 \, \text{Å}\)). Intensities were collected at 150(1) K for CCDC 727116 and 293(2) K for CCDC 727115 by means of the COLLECT software.[1] Reflection indexing, Lorentz-polarization correction, peak integration, and background determination were carried out with DENZO.[2] Frame scaling and unit-cell parameters refinement were made with SCALPEPACK.[2] A semi-empirical absorption correction was applied using the program DIFABS [3]. The structures were solved by direct methods with SIR97.[4] The remaining non-hydrogen atoms were located by successive difference Fourier map analyses. H-atoms were placed geometrically and included in the refinement using soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93-0.98 Å and O-H = 0.82 Å) and isotropic atomic displacement parameters (\(U(H)\) in the range 1.2-1.5 times \(U_{eq}\) of the adjacent atom). In the last cycles of the refinement, the hydrogen atoms were refined using a riding mode. The structure refinement was carried out with CRYSTALS.[5]

**Table S1.** Selected Crystal data for [3.Cu(H2O)](ClO4)2

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**Table S2.** Selected Crystal data for [3.Cu(I)]PF$_6$

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<td></td>
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<td></td>
<td>$c = 19.851(9)$ Å, $\gamma = 90^\circ$</td>
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<td>reflections</td>
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**Figure S1:** $^1$H NMR Spectrum of compound 2
Figure S2: $^{13}$C NMR Spectrum of compound 2
Figure S3: $^{13}$C-DEPT NMR Spectrum of compound 2
Figure S4: COSY-2D NMR Spectrum of compound 2
Figure S5: HSQC Spectrum of compound 2
Figure S6: Mass Spectrum of compound 2
Figure S7: IR Spectrum of compound 2
Figure S8: $^1$H NMR Spectrum of compound 3
Figure S9: $^{13}$C NMR Spectrum of compound 3
Figure S10: $^{13}$C-DEPT NMR Spectrum of compound 3
Figure S11: COSY NMR Spectrum of compound 3
Figure S12: HSQC NMR Spectrum of compound 3
Figure S13: Mass Spectrum of compound 3
Figure S14: IR Spectrum of compound 3
**Figure S15:** $^1$H NMR Spectrum of compound 3.CuI
Figure S16: $^{13}$C NMR Spectrum of compound 3.CuI
Figure S17: Mass Spectrum of compound 3. CuI
Figure S18: IR Spectrum of compound 3.CuI
Figure S19: UV-vis Spectrum of compound 3.Cul in an acetonitrile solution ($10^{-3}$ M)
Figure S20: EPR Spectrum of compound 3.CuII

EPR Spectrum, Freq. 9.44 GHz, Bruker EMX-plus spectrometer coupled with an Oxford Instrument Hélium cryostat. Frozen solution (1.45 mM) in CH$_3$CN/Toluène 1/1, v/v), T= 40K

$A_{//} = 172 \times 10^{-4}$ cm$^{-1}$
$g_{//} = 2.211$
$g_{\perp} = 2.004$
Figure S21: Mass Spectrum of compound 3.CuII
Figure S22: IR Spectrum of compound 3.CuII
Figure S23: UV-vis Spectrum of compound 3.CuII. Top: solid state, bottom: in acetonitrile solution (10-3 M)
**Figure S24:** Dual display of $^1$H NMR spectra of compounds 3 and 3.CuI
Figure S25: CV curves of [3.Cu(I)]⁺ in CH₃CN + 0.1 M TBAPF₆ (0.1 V.s⁻¹, 1 mM, vitr. Carbon ø 2 mm, E vs Ag/Ag⁺).
Figure S26: CV curves of [3.Cu(I)]⁺ in CH₃CN + 0.1 M TBAPF₆ (1 V.s⁻¹, 1 mM, vitr. carbon ø 2 mm, E vs Ag/Ag⁺).
Figure S27: CV curves of [3.Cu(I)]⁺ in CH₃CN + 0.1 M TBAPF₆ (5V.s⁻¹, 1 mM, vitr. carbon ø 2 mm, E vs Ag/Ag⁺).
**Figure S28:** (solid line) Voltamperogram of $[3.\text{Cu(I)}]^+$ recorded with a vitreous carbon rotating disk in CH$_3$CN + 0.1 M TBAPF$_6$ (500 rd. s$^{-1}$, 10 mV.s$^{-1}$, 1 mM, vitr. carbon ø 2 mm, $E$ vs Ag/Ag$^+$).

(crosses) Voltamperogram recorded with a vitreous carbon rotating disk after bulk oxidation (carbon working electrode, $E_{\text{app}} = 0.8$ V) of $[3.\text{Cu(I)}]^+$ in CH$_3$CN + 0.1 M TBAPF$_6$ (500 rd. s$^{-1}$, 10 mV.s$^{-1}$, 1 mM, vitr. carbon ø 2 mm, $E$ vs Ag/Ag$^+$).
**Figure S29:** (solid line) CV curve of [3.Cu(I)]⁺ recorded in CH₃CN + 0.1 M TBAPF₆ (100 mV.s⁻¹, 1 mM, vitr. carbon ø 2 mm, E vs Ag/Ag⁺).
(crosses) CV curve recorded after bulk oxidation (carbon working electrode, E_app = 0.8 V) of [3.Cu(I)]⁺ in CH₃CN + 0.1 M TBAPF₆ (100 mV.s⁻¹, 1 mM, vitr. carbon ø 2 mm, E vs Ag/Ag⁺).
Figure S30: CV curve recorded after bulk oxidation (carbon working electrode, $E_{\text{app}} = 0.8$ V) of $[3.\text{Cu(I)}]^+$ in CH$_3$CN + 0.1 M TBAPF$_6$ (100 mV.s$^{-1}$, 1 mM, vitr. carbon ø 2 mm, $E$ vs Ag/Ag$^+$)
Figure S31: CV curves of [3,Cu(II)]^{2+} in CH_{3}CN + 0.1 M TBAPF_{6} (0.1 V.s^{-1}, 1 mM, vitr. carbon ø 2 mm, E vs Ag/Ag^+).
Figure S32: CV curves of $[3.\text{Cu(II)}]^2+ \text{ in CH}_3\text{CN} + 0.1 \text{ M TBAPF}_6$ (1 V.s$^{-1}$, 1 mM, vitr. carbon ø 2 mm, $E$ vs Ag/Ag$^+$).
Figure S33: CV curves of [3.Cu(II)]^{2+} in CH_3CN + 0.1 M TBAPF_6 (10 V.s^{-1}, 1 mM, vitr. Carbon ø 2 mm, E vs Ag/Ag^+).
**Figure S34:** Voltamperogram recorded with a vitreous carbon rotating disk on [3.Cu(II)]^{2+} in CH$_3$CN + 0.1 M TBAPF$_6$ (500 rd. s$^{-1}$, 10 mV.s$^{-1}$, 1 mM, vitr. carbon ø 2 mm, $E$ vs Ag/Ag$^+$).
**Figure S35:** Reduction/oxidation cycles followed by UV-Vis spectroscopy (absorbance recorded at $\lambda = 635$ nm). Successive electrolysies ($Q = 0.16$ C) were carried out in a 1cm quartz cell starting from LCuI (1x10^{-3} M in DMF, 0.1 M TBAP) upon switching the working electrode potential (1 cm² vitreous carbon) between +0.6 and -0.6 V vs Ag/Ag⁺.