

On the interest of ambipolar materials for gas sensing

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Supplementary material

Chemicals. Dimethylformamide (DMF, RPE), methanol (RPE), absolute ethanol (RPE), CHCl₃ (RPE), CH₂Cl₂ (technical grade) and nitrobenzene (technical grade) were purchased from Carlo Erba. Pyromellitic dianhydride, urea, ammonium molybdate tetrahydrate and cobalt(II) acetate tetrahydrate were purchased from Sigma Aldrich and used as received. Sulfuric acid (analaR normapur) was purchased from VWR. Dicyclohexylcarbodiimide, Bu₄NPF₆, activated alumina (58 Å pore size) and n-hexanol were purchased from Sigma Aldrich.

Syntheses

The cobalt 2,3,9,10,16,17,23,24-octacarboxylic acid phthalocyanine was obtained by reaction of cobalt(II) acetate tetrahydrate (0.624 g, 2.5x10⁻³ mol), pyromellitic dianhydride (2.18 g, 10⁻² mol), urea (10 g, 16.65 10⁻² mol) and ammonium molybdate tetrahydrate (50 mg, 4.04 10⁻⁵ mol) in nitrobenzene (20 mL). The mixture was heated at 210 °C for 6 h. The precipitate was filtered off and washed with ethanol and boiling water successively. The dark blue solid was purified using soxhlet, with toluene, ethanol, methanol and acetone, successively, for 48 h each. The product was heated at 50 °C in hydrochloric acid (4 N) and washed with water, then with NaOH, HCl, and water and finally with acetone to yield a deep blue (738 mg, 32 %).

The cobalt 2,3,9,10,16,17,23,24-octa(hexyloxycarbonyl) phthalocyanine, Co((hexylo₂C)₈Pc), **2**, was obtained by reaction of cobalt 2,3,9,10,16,17,23,24-octacarboxylic acid phthalocyanine (50 mg, 5.42 mmol) in the presence of dicyclohexylcarbodiimide (0.188 mL, 0.87 mmol), in n-hexanol (5 mL). The mixture was heated at 160 °C under argon for 15 h. After cooling to room temperature, the crude product was precipitate at ca. 4 °C in 100 mL of cold methanol kept in the fridge (1 h) and separated by centrifugation at 3500 rpm (10 min). After removing the supernatant, 10 mL of CHCl₃ was added in order to solubilize **1**. The filtrate was evaporated

and the product was washed with methanol (2x10 mL), by stirring in an ultrasonic bath (10 min) and filtering off through a millipore membrane (nylon, 10.0 μm). The product was dried at 100 $^{\circ}\text{C}$ under reduced pressure for 2 h to yield a blue solid (45.5 mg, 52 %).

λ_{max} (chloronaphthalene)/nm 699 ($\log \epsilon = 4.97$), 631 ($\log \epsilon = 4.3$). FTIR (KBr pellet): $\nu \text{ cm}^{-1}$ 2927 and 2855 (C-H), 1765 and 1708 (C=O), 1521 and 1453 (Ar C=C), 1361 and 1345 (CH_2/CH_3), 1272 (C-O), 1095.

m/z (negative ions) 1467.80 $[\text{M}-\text{CO}_2\text{C}_6\text{H}_{13}]^-$

Electronic absorption spectroscopy

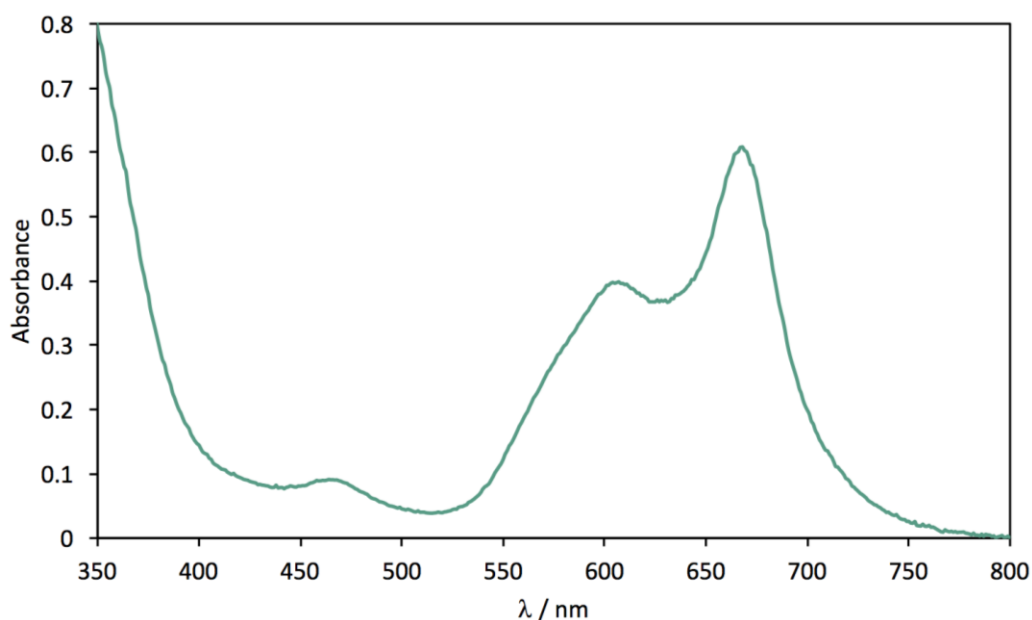


Figure S1. Electronic absorption spectrum of a $\text{Cu}(\text{F}_8\text{Pc})/\text{LuPc}_2$ MSDI (MSDI 1).

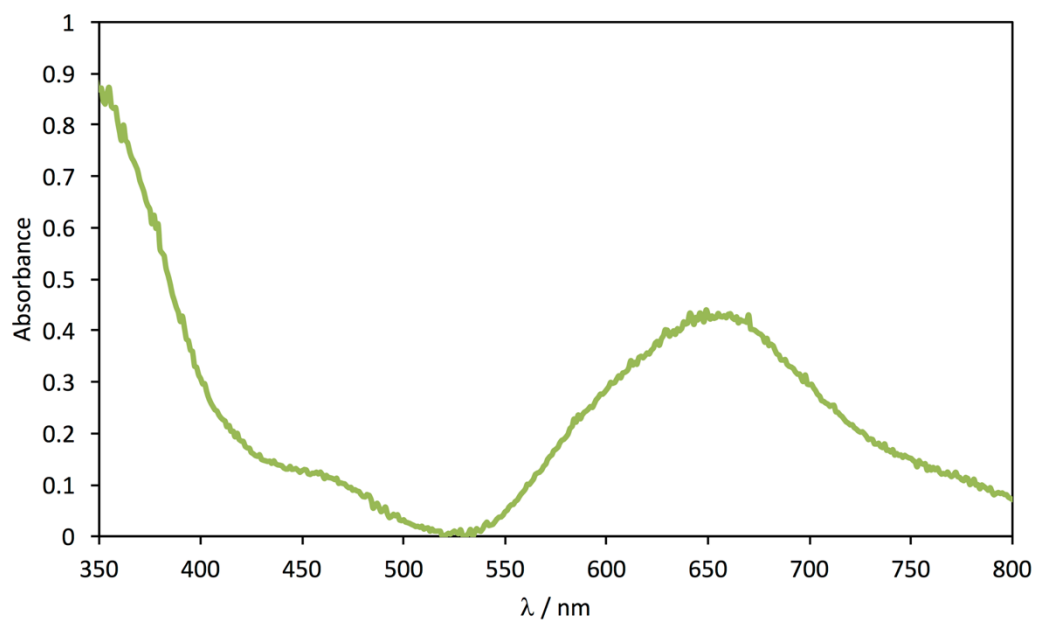


Figure S2. Electronic absorption spectrum of a $\text{Co}((\text{COOC}_6\text{H}_{13})_8\text{Pc})/\text{LuPc}_2$ MSDI (MSDI 2).

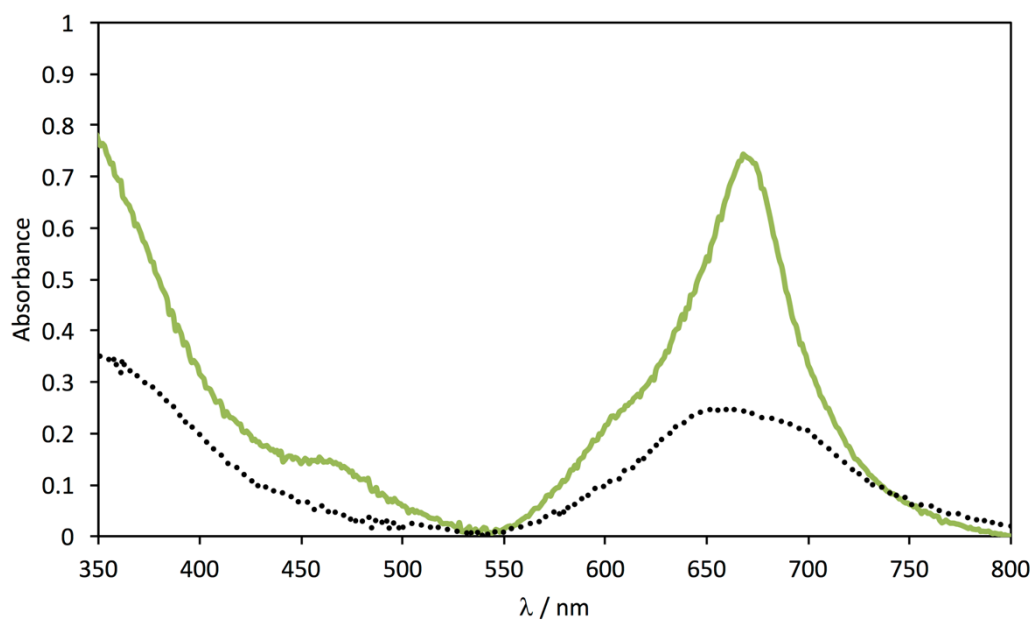


Figure S3. Electronic absorption spectrum of a $\text{Zn}(\text{T}_4\text{F}_{12})\text{Pc}/\text{LuPc}_2$ MSDI (MSDI 3, solid line) compared to this of a $\text{Zn}(\text{T}_4\text{F}_{12})\text{Pc}$ resistor (dotted line).

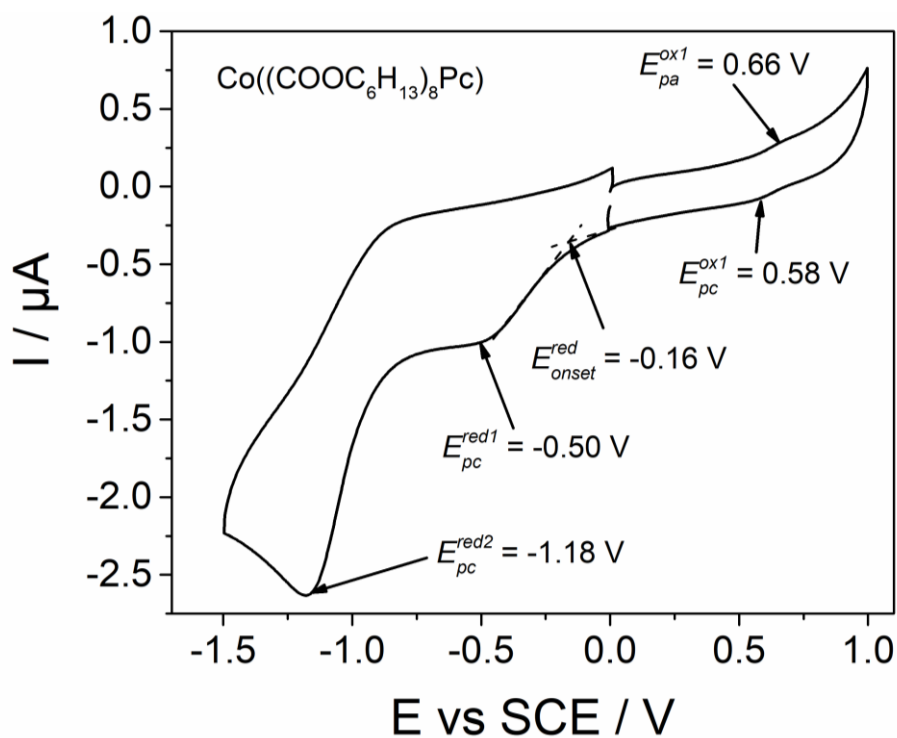


Figure S4. Cyclic voltammogram of **2**, on Pt disc electrode, in DMF containing 0.1 M Bu_4NPF_6 , at a scan rate of 0.1 V s^{-1} , at a concentration of $10^{-3} \text{ mol L}^{-1}$.

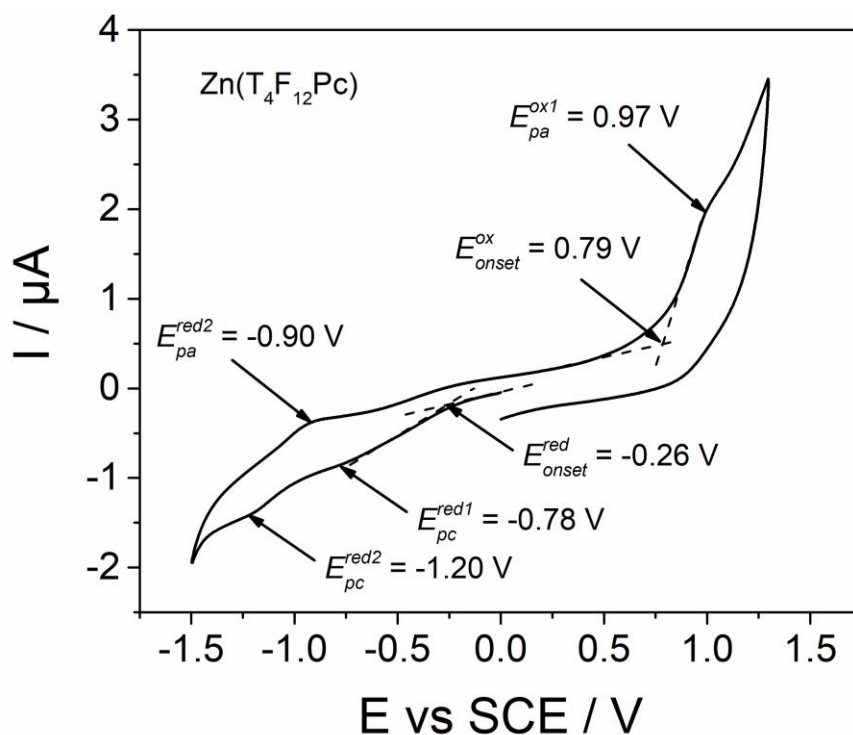


Figure S5. Cyclic voltammogram of **3**, on Pt disc electrode, in DMF containing 0.1 M Bu_4NPF_6 , at a scan rate of 0.1 V s^{-1} , at a concentration of $10^{-3} \text{ mol L}^{-1}$.

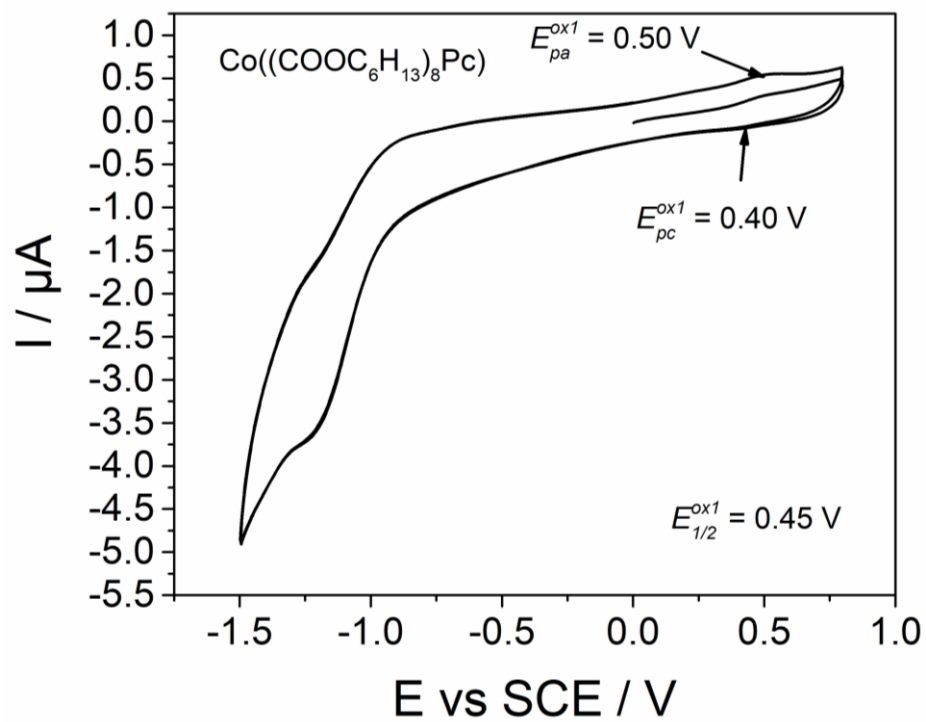


Figure S6. Cyclic voltammogram of **2**, on Pt disc electrode, in CH₂Cl₂ containing 0.1 M Bu₄NPF₆, at a scan rate of 0.1 V s⁻¹, at a concentration of 10⁻³ mol L⁻¹.