## SUPPORTING INFORMATION

# Trapping fullerenes with jellyfish-like subphthalocyanines

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#### **Supporting Information**

#### **General Remarks**

Synthesis and Characterization: UV-vis spectra were recorded with a JASCO V-660 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F-NMR spectra were recorded with a Bruker AC-300 equipment. Chemical shifts,  $\delta$ , are indicated in ppm, using the solvent as a reference. MALDI spectra were obtained with a ULTRAFLEX III (Bruker) spectrometer; TCNQ was chosen as matrix. Electrochemistry was measured with an Autolab equipment, using carbon electrode (work electrode), Ag/Ag<sup>+</sup> electrode (Reference electrode) and Pt electrode (Counterelectrode. Ferrocene was employed as internal reference. E is given in volts, vs Fc/Fc<sup>+</sup>. Column chromatographies were carried out on sílica gel Merck-60 (230-400 mesh, 60 Å), and TLC on aluminium sheets coated with silica gel 60 F<sub>254</sub> (Merck). Chemicals were purchased from Aldrich Chemical Co and Alfa Aesar and used as received without further purification.

General method for the synthesis of 4,5-dialkylthiophthalonitriles<sup>[1]</sup>: 4,5dichlorophthalonitrile (1g, 5.08 mmol),  $K_2CO_3$  (2.1 g, 15.24 mmol) and degassed *N*,*N*dimethylacetamide (13 ml) were placed in a round bottomed flask under argon atmosphere. The corresponding thiol (12 mmol) was added and the mixture was stirred at 90°C for 12 h. Characteristics of **2c** and **d** are identical to those previously described.

<sup>[1]</sup> a)A.G. Gürek, Ö. Bekâroglü, *J. Chem. Soc. Dalton Trans.* **1994**, 1419; b) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **1998**, *120*, 12808.

#### 4,5-diethylthiophthalonitrile



**Synthesis**: 4,5-dichlorophthalonitrile (212 mg, 1.08 mmol),  $K_2CO_3$  (5,5 g, 3.6 mmol) and 5 mL of degassed DMA were placed in a 25mL-round-bottomed flask. Ethanethiol (187 µL, 2.69 mmol) was added trough a syringe and the reaction was stirred at 80°C for 4 h. Then, 20 mL of dichloromethane were added and the solution was extracted with bleach (2x15), water (5x15) and brine (1x15). The organic layer was dried with MgSO<sub>4</sub> and evaporated. The resulting brown solid was dissolved in diethyl ether and filtered off. The colourless solution was concentrated and left in the fridge. The precipitate was filtered and washed with cold diethyl ether. The desired compound was obtained as a white solid (206 mg, 63%). If non-substituted or mono-substituted product remains, 4,5-diethylthiophthalonitrile can be isolated with column chromatography in silica gel (Hexane/AcOEt 7:1).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.4 (s, 2H, H*a*), 3.06 (q, *J* = 7.3 Hz 4H, H*b*), 1.42 ppm (t, *J* = 7.3 Hz, 4H, H*c*).



4,5-dibuthylthiophthalonitrile



**Synthesis**: 4,5-dichlorophthalonitrile (1g, 5.08 mmol), K<sub>2</sub>CO<sub>3</sub> (2.1 g, 15.24 mmol) and degassed *N*,*N*-dimethylacetamide (13 ml) were placed in a round bottomed flask under argon atmosphere. Buthanethiol (1,36 mL, 12 mmol) was added through a syringe and the mixture was stirred for 6 h at 90°C. CH2Cl2 (20 ml) was added and the solution was extracted with bleach (2 x 10 ml), water (4 x 10 ml) and brine. The organic layer is dried over MgSO4 and the solvent was evaporated. The resulting brown solid was washed with methanol and filtered off. 4,5-dibuthylthiophthalonitrile was obtained as a white solid (1.04 g, 68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 7.40 (s, 2H, H*a*), 3.01 (t, *J* = 7.2 Hz, 4H, H*b*), 1.73 (q, *J* = 7.0, 4H, H*c*), 1.50 (m, *J* = 7.4, 4H, H*d*), 0.97 ppm (t, *J* = 7.3 Hz, 6H, H*e*).



General method for the Synthesis of Subphthalocyanines 1-6b: In a 25-ml round bottomed flask, BCl<sub>3</sub> (0.3 mmol, 1M solution in p-xylene) was added to the corresponding phthalonitrile (0.6 mmol) under an argon atmosphere. The reaction mixture was stirred under reflux for 2 h and then flushed with argon to remove volatiles. Subsequent axial substitution was carried out without isolation of chlorosubphthalocyanines intermediate. 4-tert-buthylphenol (1.8 mmol) and toluene (1 ml) were added and the mixture was refluxed till reaction was completed (check by TLC; see eluent below). Reaction was cooled down to room temperature, the solvent was evaporated under reduced pressure and the resulting purple-green solid was washed with a 4:1 mixture of methanol and water. Finally, compounds 1-6b were purified by column chromatography in silica gel using as eluent: hexane/toluene (1:2.5) for 3 and **4b**, hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:1) for **5b**, hexane/ethyl acetate (20:1) for **6b**, toluene/THF (20:1) for 2b and hexane/CHCl<sub>3</sub> (2:1) for 1b. Characteristics of compounds 1c-f are identical to those previously described<sup>[16,2]</sup></sup>

 <sup>&</sup>lt;sup>[2]</sup> a) Díaz, D. D.; Bolink, H. J.; Capelli, L.; Claessens, C. G.; Coronado, E.; Torres, T. *Tetrahedron Lett*, 2007, 48, 4657; b) Claessens, C. G.; Torres, T. *Angew. Chem. Int. Ed.* 2002, 41, 2561.

### **Compound 3b**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 8.60$  (s, 6H, Ha), 6.79 (d, J = 8.5 Hz, 2H, He), 5.33 (d, J = 8.5 Hz, 2H, Hd), 3.25 (t, J = 7.6 Hz, 12H, Hb), 1.50 (t, J = 7.5 Hz, 18H, Hc), 1.07 ppm (s, 9H, Hd).



<sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  = 140.04, 127.23, 126.42, 125.49, 120.06, 119.72, 118.87, 114.76, 58.54, 31.53, 27.59, 13.69 ppm. IR (KBr) *ν* = 3057, 2297, 2195, 1587, 1481, 1436, 1223, 825, 750, 692 cm<sup>-1</sup>; UV/vis (Toluene) :  $\lambda_{max}$  (log( $\varepsilon$ ))= 302 (4.67), 385 (4.41), 597 nm (4.80). MALDI (DCTB): 904.26 [M<sup>+</sup>], 755.42 [M-tBufenoxy]<sup>+</sup> Electrochemistry (CH<sub>2</sub>Cl<sub>2</sub>, 200 mV/s, E vs Fc/Fc<sup>+</sup>): E = 0.52 (irrev), 1.08 (irrev), -1.19 (rev), -1.45 (rev), -1.73 (rev), -2.18 V (irrev). Elemental Analysis: Calculated for C<sub>46</sub>H<sub>49</sub>BN<sub>6</sub>OS<sub>6</sub>: C, 61.04; H, 5.46; N, 9.28; S, 21.26. Found: C, 61.69; H, 5.88; N, 7.29; S, 16.38.





IR (KBr)



UV-Vis (toluene, 5·10<sup>-5</sup>M)



MALDI (DCTB)



### **Compound 1b**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K):  $\delta = 8.57$  (s, 6H, Ha), 6.71 (d, J = 8.1 Hz, 2H, Hg), 5.27 (d, J = 8.1 Hz, 2H, Hf), 3.23 (m, 12H, Hb), 1.81 (m, 12H, Hc), 1.59 (m, 12H, Hd), 1.05 (s, 9H, Hh), 0.98 ppm (t, J = 7.24 Hz, 18H, He).





<sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ = 150.79, 147.22, 140.34, 136.35, 128.34, 125.62, 119.60, 117.74, 33.76, 33.30, 28.74, 27.19, 22.18, 13.68 ppm. IR (KBr) : v = 3060, 2691, 1662, 1437, 1252, 1029, 692, 638 cm<sup>-1</sup>. MALDI (DCTB) : 1072.42 [M<sup>+</sup>], 923.28 [M-tBufenoxy] UV/vis (Toluene) :  $λ_{max}$  (log(ε))= 286 (4.67), 385 (4.09), 598 nm (4.49). Electrochemistry (CH<sub>2</sub>Cl<sub>2</sub>, 200 mV/s, E vs Fc/Fc<sup>+</sup>): E = 0.86 (irrev), -1.07 (rev), -1.44 V (rev). Elemental Analysis: Calculated for C<sub>58</sub>H<sub>73</sub>BN<sub>6</sub>OS<sub>6</sub>: C, 64.90; H, 6.85; N, 7.83; S, 17.92.

Found: C, 63.03; H, 6.87; N, 6.25; S, 14.18.

<sup>13</sup>C-NMR



UV-Vis (toluene, 5·10<sup>-5</sup>M)



### MALDI (DCTB)



*S11* 



Figure S1. Job Plots of SubPcs **1b** and **3b** with  $C_{60}$  and of SubPcs **1-6b** with  $C_{70}$ .

**Titrations:** 

SubPc + Fullerene Ÿ Complex1:1 Complex1:1 + SubPc Ÿ Complex2:1

The equation employed for fitting is:

 $\Delta A = (\varepsilon_{HG} \cdot K_1 \cdot [H] + \varepsilon_{H2G} \cdot K_1 \cdot K_2 \cdot [H]^2) [G]_t / (1 + K_1 \cdot [H] + K_1 \cdot K_2 \cdot [H]^2)$ 

[H] = [SubPc]; [G] = [fullerene];  $\varepsilon_{HG}$  = absorption coefficient of 1:1 complex;  $\varepsilon_{H2G}$  = coefficient of 2:1 complex;  $K_1$  = binding constant for the first SubPc;  $K_2$  = binding constant for the second SubPc.

**3b** (data sign was changed)



**4b** 





**6b** 



5b



Figure S2: Fitting of titrations data, considering stepwise formation of 2:1 complex, for SubPcs **3-6b** with  $C_{60}$ .

4b



**5b** (data sign was changed)



**6b** (data sign was changed)



Figure S3: Fitting of titrations data, considering stepwise formation of 2:1 complex, for SubPcs **3-6b** with  $C_{70}$ .





Figure S4: Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (540 nm) of **4b** (2.5 x  $10^{-5}$  M) and C<sub>70</sub> (7.5 x  $10^{-5}$  M) in toluene with several time delays between 0.1 and 2800 ps at room temperature – see Figure Legend for details. Lower part – time absorption profiles of the spectra at 675 (black spectrum) and 1250 nm (red spectrum) monitoring the energy transfer dynamics.



Figure S5: Upper part – differential absorption spectra (visible and nearinfrared) obtained upon femtosecond pump probe experiments (540 nm) of **6b** (2.5 x  $10^{-5}$  M) and **C**<sub>70</sub> (7.5 x  $10^{-5}$  M) in toluene with several time delays between 0.1 and 2800 ps at room temperature – see Figure Legend for details. Lower part – time absorption profiles of the spectra at 675 (black spectrum) and 1250 nm (red spectrum) monitoring the energy transfer dynamics.