

## **Orthogonally bifunctionalised polyacrylamide nanoparticles: a support for the assembly of multifunctional nanodevices**

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**Scheme S.I.1:** Preparation of phthalocyanine **17**.

**4-(2-(2-(2-(2-tosylethoxy)ethoxy)ethoxy)ethoxy)phthalonitrile B**

To a solution of phthalonitrile **A**<sup>1,2</sup> (1 g, 3.12 mmol) in pyridine (20 mL) cooled to 4 °C, a solution of tosyl chloride (0.71 g, 3.74 mmol) in pyridine was added dropwise. The reaction mixture was stirred overnight at room temperature, then it was diluted with dichloromethane (100 mL) and washed three times with 1 M aqueous HCl (50 mL). The organic phase was dried (sodium sulfate), concentrated and loaded on a silica gel column. Elution with hexan/ethyl acetate 1/1 and ethyl acetate, afforded 1.48 g of **B** (90%). Colourless oil. C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>7</sub>S, MW 474.53 g/mol. ATR-IR (ν<sub>max</sub>/cm<sup>-1</sup>) 3064 (ArCH), 2987–2937 (-CH), 2231 (C≡N), 1598, 1563, 1351, 1312, 1256, 1176 ve 1097 (-SO<sub>2</sub>). ESI-MS: isotopic cluster peaking at *m/z* 497.16 [M+Na]<sup>+</sup>; <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ: 7.60 (3H, m, aromatics), 7.20 (2H, d, aromatics), 7.13 (2H, m, aromatics), 3.41–4.12 (16H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 3.89 (2H, m, *H*-6 and *H*-7), 2.28 (3H, s); <sup>13</sup>C NMR: (CDCl<sub>3</sub>) δ: 170.26, 161.59, 144.42, 134.81, 132.31, 129.40, 127.28, 119.47, 119.29, 116.39, 115.40, 114.95, 106.28, 70.14, 69.97, 69.94, 69.83, 69.03, 68.56, 68.29, 67.96, 59.67, 20.99, 20.40, 13.66. Anal. Calcd. for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>7</sub>S: C, 58.22; H, 5.52; N, 5.90%. Found: C, 58.25; H, 5.53; N, 5.89%.

**4-(2-(2-(2-(2-azidoethoxy)ethoxy)ethoxy)ethoxy)phthalonitrile D:** A solution of phthalonitrile **C** (1.5 g, 3.16 mmol) and  $\text{NaN}_3$  (820 mg, 12.6 mmol) in DMF (15 mL) was stirred overnight at 90 °C. The reaction mixture was filtered, diluted with dichloromethane (50 mL) and washed with water (3 x 50 mL). The organic phase was dried (sodium sulphate), concentrated and loaded on a silica gel column. Elution with hexane/ethyl acetate 2/1 afforded the title compound (95%, 1.09 g). Colourless oil.  $\text{C}_{16}\text{H}_{19}\text{N}_5\text{O}_4$ , MW 345.35 g/mol. ATR-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ) 2922 (-CH), 2229 ( $\text{N}_3$ ), 2201 ( $\text{C}\equiv\text{N}$ ), 1672, 1597, 1492, 1254, 1045, 838. ESI-MS: isotopic cluster peaking at  $m/z$   $[\text{M}+\text{H}]^+$  344.13.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ : 7.63 (1H, d, Ar), 7.25 (1H, d, Ar), 7.16 (dd, 1H, HAr), 3.31-4.16 (m, 12H, 3  $\text{OCH}_2\text{CH}_2\text{O}$ ), 2.89, 2.82 (s, 4H,  $-\text{CH}_2\text{CH}_2\text{N}_3$ ).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ : 161.61, 134.92, 127.28, 119.37, 119.29, 116.46, 115.40, 114.88, 70.14, 69.94, 69.83, 69.82, 69.03, 68.56, 68.29, 67.96, 53.40. Anal. Calcd for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_7\text{S}$ : C, 58.22; H, 5.52; N, 5.90%. Found: C, 58.22; H, 5.54; N, 5.88%.

**3-[[2,3-bis-(tert-butyldimethylsilyloxy)propyl-1-oxy]phthalonitrile E:** A solution of phthalonitrile **D**<sup>1,2</sup> (3.1 g, 11.9 mmol) in 80 % acetic acid was stirred overnight at room temperature. The solvent was evaporated and the resulting white solid was dissolved in ethyl acetate and filtered through a short silica column. Elution with ethyl acetate afforded 3-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]phthalonitrile as a white solid (2.2 g, 85%). The solid obtained was dissolved in DMF (50 mL) and the resulting solution was treated with *tert*-butyldimethylsilyl chloride (3.65 g, 24.3 mmol) and imidazole (3.4 g, 50.5 mmol). The mixture was stirred overnight at room temperature, then it was diluted with dichloromethane (150 mL) and washed with water (3 x 250 mL). The organic phase was dried (sodium sulfate), concentrated and purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8/1). The desired compound was obtained as a waxy white solid (4.45 g, 95 %).  $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}_2$ , MW 432.70 g/mol. ATR-IR ( $\nu_{\text{max}}/\text{cm}^{-1}$ ) 2954, 2929, 2231, 1585, 830, 776. ESI-MS: isotopic cluster peaking at  $m/z$   $[\text{M}+\text{Na}]^+$  469.29;  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ : 7.61 (1H, t, aromatic), 7.34 (1H, d, aromatic), 7.30 (1H, d, aromatic), 4.28 (1H, m, CH), 4.11, 3.66 (4H, 2 m, 2  $\text{OCH}_2$ ), 0.91 (m, 18H, 2  $\text{C}(\text{CH}_3)_3$ ), 0.05 (m, 12H, 2  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ : Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}_2$ : C, 61.07; H, 8.39; N, 6.47%. Found: C, 61.05; H, 8.40; N, 6.45%.

**[1(4),8(11),15(18)-tri-( 2,3-dihydroxypropyloxy)-23-(12-azido-(1,4,7,10 tetraoxadodecyl)] phthalocyaninato Zn(II) (17).**

Phthalonitrile **C** (42 mg, 0.12 mmol), phthalonitrile **E** (500 mg, 1.16 mmol) and anhydrous  $\text{Zn}(\text{OAc})_2$  (100 mg, 0.54 mmol) were heated at 130 °C for two hours. The mixture quickly became blue, then green, and then it turned into a waxy solid. The mixture was allowed to cool at room temperature and then it was loaded on a precolumn and eluted with dichloromethane. The resulting mixture of phthalocyanines was concentrated and purified on a silica gel column chromatography. The desired TBDMS-protected phthalocyanine **17** was eluted (hexane/ethyl acetate=5/1) after the symmetric

derivative (hexane/ ethyl acetate=8/1). The green waxy solid (25 mg, 12%) was identified by MS-MALDI-TOF,  $m/z$  1752.25 (M+H)<sup>+</sup>. 20 mg (11 nmol) of the solid obtained were treated with *n*-Bu<sub>4</sub>NF (200 mg) in tetrahydrofuran (3 mL). The mixture was stirred overnight, then it was concentrated and purified on silica, (eluent: dichloromethane/ethanol=1/1), yielding **17** (9.6 mg, 82%). C<sub>49</sub>H<sub>49</sub>N<sub>11</sub>O<sub>13</sub>Zn, MW 1065.39. MS-MALDI-TOF,  $m/z$  1066.37 (M+H)<sup>+</sup>. UV-vis (DMSO)  $\lambda_{\max}$  (log  $\epsilon$ ): 698 (4.12). HRMS-ESI:  $m/z$  calcd for C<sub>49</sub>H<sub>50</sub>N<sub>11</sub>O<sub>13</sub>Zn, 1064.2876; found 1064.2835. HPLC  $t_R$ : 8.77 min.

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