

## Supporting Information

### *Molecular Orientation Calculations Based on Polarized IR Spectroscopy*

The orientation of a molecule can be defined by three Euler angles, which describe three rotations: *i*)  $\phi$ , a counter-clockwise rotation about the z-axis, *ii*)  $\theta$ , a counter-clockwise rotation about the x-axis, and *iii*)  $\psi$ , a counter-clockwise rotation again about the z-axis. The x- and y-axes have been defined as in the plane of the substrate, and the z-axis is perpendicular to the substrate surface. A rotation matrix can be used to describe these rotations mathematically as shown below.

$$A = \begin{pmatrix} \cos \psi \cdot \cos \phi - \sin \psi \cdot \cos \theta \cdot \sin \phi & -\cos \psi \cdot \sin \phi - \sin \psi \cdot \cos \theta \cdot \cos \phi & \sin \psi \cdot \sin \theta \\ \sin \psi \cdot \cos \phi + \cos \psi \cdot \cos \theta \cdot \sin \phi & -\sin \psi \cdot \sin \phi + \cos \psi \cdot \cos \theta \cdot \cos \phi & -\cos \psi \cdot \sin \theta \\ \sin \theta \cdot \sin \phi & \sin \theta \cdot \cos \phi & \cos \theta \end{pmatrix} \quad (1)$$

In this treatment of the data, the two in plane dipoles ( $\mu_{IN}$ ) are defined as parallel to the y and z-axes, and the out-of-plane dipole ( $\mu_{OUT}$ ) is defined as parallel to the x-axis. This defines a reference point for the Pc molecule (in the y-z plane), and a vector containing these dipole components can be multiplied by the rotation matrix A to determine how the dipoles will project onto each of the laboratory axes. Three equations can then be derived that relate the absorbance measured in the transmission and RAIRS experiments to the Euler angles. The transmission experiment leads to the following two equations:

$$R_{IN} = \frac{A_y^{IN}}{A_x^{IN}} = \frac{(-\sin \psi \cdot \sin \phi + \cos \psi \cdot \cos \theta \cdot \cos \phi - \cos \psi \cdot \sin \theta)^2}{(-\cos \psi \cdot \sin \phi - \sin \psi \cdot \cos \theta \cdot \cos \phi + \sin \psi \cdot \sin \theta)^2} \quad (2)$$

$$R_{OUT} = \frac{A_y^{OUT}}{A_x^{OUT}} = \frac{(\sin \psi \cdot \cos \phi + \cos \psi \cdot \cos \theta \cdot \sin \phi)^2}{(\cos \psi \cdot \cos \phi - \sin \psi \cdot \cos \theta \cdot \sin \phi)^2} \quad (3)$$

where  $A_y^{IN}$  and  $A_x^{IN}$  are the absorbance values of the in-plane transitions projecting onto the y and x-axes, respectively, and  $A_y^{OUT}$  and  $A_x^{OUT}$  are absorbance values for the out-of-plane transitions. The RAIRS experiment produces an equation:

$$r = \frac{A_Z^{IN} \cdot A_{bulk}^{OUT}}{A_Z^{OUT} \cdot A_{bulk}^{IN}} = \frac{(\sin \theta \cdot \cos \phi + \cos \theta)^2}{(\sin \theta \cdot \sin \phi)^2} \quad (4)$$

where  $A_Z^{IN}$  and  $A_Z^{OUT}$  are the in-plane and out-of-plane absorbance values measured along the z-axis on

the Au surface, and  $A_{\text{bulk}}^{\text{IN}}$  and  $A_{\text{bulk}}^{\text{OUT}}$  are the absorbance values for the isotropic sample in a KBr pellet. Equations 2-4 can be solved for the Euler angles to define the position of the molecule in space with respect to the reference position defined by the original position of the dipoles.

The in- and out-of-plane absorbances used in these experiments were  $\nu_{(\text{Pc-O-C, ip})}$  at  $1204\text{ cm}^{-1}$  and  $1283\text{ cm}^{-1}$  as the in-plane transitions (associated with the side-chain of the Pc), and  $\delta_{(\text{ring C-H, op})}$  at  $745\text{ cm}^{-1}$  as the out-of-plane transition. The peak at  $745\text{ cm}^{-1}$  is overlapped with another transition (most clearly seen in the KBr spectrum in Figure 7b), whose contribution is removed by peak fitting to isolate the contribution from the out-of-plane transition.

### ***Synthesis of 2,3,9,10,16,17,23,24-Octa(Cinnamyloxyethoxy)-phthalocyanato Copper (II)***

#### *2-Styryl-[1,3]dioxolane*

A solution of trans-cinnamyl aldehyde (Aldrich®) (40.0 g, 303 mmol), ethylene glycol (18.8 g, 303 mmol) and p-toluene sulfonic acid (0.6 g) in 150 mL of benzene was refluxed for 12 hours in a 250 mL round bottom flask outfitted with a Dean Stark trap. The reaction was then cooled to room temperature and excess  $\text{K}_2\text{CO}_3$  was added. The mixture was decanted and the benzene was removed in vacuo. The resulting liquid was vacuum distilled to yield 50.67 g of a clear liquid at  $120\text{ }^\circ\text{C}$  at 2.0 mm Hg (95% yield):  $R_f = 0.67$  (80:20 Hex/EtOAc), IR (KBr)  $1206$  and  $1127\text{ cm}^{-1}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.45-7.23 (m, 5H), 6.83-6.72 (d,  $J=15.9\text{ Hz}$ , 1H), 6.24-6.09 (doublet of doublets,  $J=9.0\text{ Hz}$ , 1H), 5.45-5.38 (d,  $J=7.1\text{ Hz}$ , 1H), 4.08-3.86 (m, 4H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  128.98, 128.46, 128.39, 128.24, 126.82, 125.06, 103.74, 64.94, Mass Spectral Analysis (GC-MS) MI 176 (Theoretical mass for  $\text{C}_{11}\text{H}_{12}\text{O}_2 = 176$ ).

#### *2-Cinnamyloxyethanol*

$\text{LiAlH}_4$  (2.0 g, 60 mmol) was suspended in 150 mL of anhydrous ethyl ether and cooled to  $0\text{ }^\circ\text{C}$ . A solution of  $\text{AlCl}_3$  (8.0 g, 60 mmol) in 20 mL of anhydrous ether was slowly added and the mixture was stirred at  $0\text{ }^\circ\text{C}$  for 15 minutes. 2-Styryl-[1,3]dioxolane (21.2 g, 120 mmol) was dissolved in 25

mL of ether and slowly added to the aluminum reagent solution. The solution was stirred for one hour and a 15% aqueous KOH solution was slowly added until gas evolution ceased. The white precipitate (lithium aluminate) was removed by suction filtration. The salt was washed with 50 mL of ether. The filtrate was partitioned between 200 mL of deionized (DI) water and 150 mL of ether. The aqueous layer was washed twice with 50 mL ether. The organic layer was then dried over  $\text{MgSO}_4$ , gravity filtered and the organic solvent was removed in vacuo. The resulting liquid was vacuum distilled to yield 20.95 g of a clear liquid at 135-138 °C at 2.0 mm Hg (98% yield):  $R_f = 0.35$  (80:20 Hex/EtOAc), IR (KBr)  $3445\text{ cm}^{-1}$ ,  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.45-7.19 (m, 5H), 6.73-6.57 (d,  $J=16.0$  Hz, 1H), 6.40-6.24 (doublet of triplets,  $J=7.0$  Hz, 1H), 4.23-4.16 (d,  $J=5.9$  Hz, 2H), 3.78-3.67 (t,  $J=4.76$ , 2H), 3.64-3.57 (t,  $J=5.14$ , 2H), 2.32-2.16 (broad singlet, 1 H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.11, 132.49, 128.92, 128.03, 126.77, 126.53, 71.93, 71.85, 62.13 Mass Spectral Analysis (GC-MS) MI 178 (Theoretical mass for  $\text{C}_{11}\text{H}_{14}\text{O}_2 = 178$ ). (R)

### *2-Cinnamyloxyethyl tosylate*

A solution of 2-cinnamyloxyethanol (5.0 g, 28.1 mmol) and tosyl chloride (6.0 g, 30.9 mmol) in 150 mL of ethyl ether was cooled to 0 °C and freshly pulverized NaOH (5.5 g, 112.4 mmol) was slowly added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was then partitioned between 100 mL DI water and 100 mL of ethyl ether; the aqueous layer was extracted and washed with two 50 mL portions of ethyl ether. The organic layer was then dried over  $\text{MgSO}_4$ , gravity filtered and the organic solvent was removed in vacuo. The resulting liquid was determined to be pure by thin layer chromatography (TLC), NMR, and mass spectroscopy; the yield was 9.00 g of a clear liquid (96% yield):  $R_f = 0.42$  (80:20 Hex/EtOAc),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.85-7.74 (d, 2H), 7.38-7.17 (m, 7H), 6.59-6.47 (d,  $J=15.8$  Hz, 1H), 6.24-6.07 (m,  $J=6.9$  Hz, 1H), 4.24-4.15 (t,  $J=6.32$  Hz, 2H), 4.14-4.07 (d,  $J=6.02$  Hz, 2H), 3.71-3.63 (t,  $J=6.9$ , 2 H), 2.42-2.37 (s, 3 H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  144.7, 136.4, 133.0, 129.7, 128.5, 127.9, 127.7, 126.4, 125.2, 71.7, 69.2, 67.3, 21.5, Mass

Spectral Analysis (FAB+) MI 332.2 (Theoretical mass for  $C_{18}H_{20}O_4S = 332.1$ ).

*2-Cinnamyloxyethyl bromide*

A solution of 2-cinnamyloxyethyl tosylate (14.50 g, 43.6 mmol) and dry LiBr (15.0 g, 174.4 mmol) in 100 mL of tetrahydrofuran (THF) was heated to 40 °C. The reaction was stirred under argon for 48 hours. The reaction was then partitioned between 100 mL DI water and 100 mL of ethyl ether; the organic layer was washed with 3x 50 mL portions of DI water. The organic layer was then dried over  $MgSO_4$ , gravity filtered and the organic solvent was removed in vacuo. The resulting liquid was vacuum distilled to yield 9.59 g of a clear liquid at 150-155 °C at 2.0 mm Hg (91% yield):  $R_f = 0.81$  (80:20 Hex/EtOAc), IR (KBr Plate)  $1121\text{ cm}^{-1}$ ,  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.45-7.17 (d, 5 H), 6.89-6.54 (d,  $J = 16.8\text{ Hz}$ , 1H), 6.34-6.17 (doublet of triplets,  $J = 6.7\text{ Hz}$ , 1H), 4.24-4.15 (d,  $J=6.22\text{ Hz}$ , 2H), 3.84-3.73 (t,  $J = 6.22\text{ Hz}$ , 2H), 3.53-3.43 (t,  $J = 6.26$ , 2 H),  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  136.4, 132.8, 128.5, 127.7, 126.4, 125.4, 71.6, 69.8, 30.4, Mass Spectral Analysis (FAB+) MI 241.0 (Theoretical mass for  $C_{11}H_{14}OBr = 241.1$ ).

*4,5- bis (Cinnamyloxyethoxy)-phthalic acid dimethyl ester*

A solution of dimethyl ester (2.50 g, 11.1 mmol), 2-cinnamyloxyethyl bromide (10.7 g, 44.2 mmol), KI (0.73 g, 4.42 mmol) and anhydrous  $K_2CO_3$  (12.2 g, 88.4 mmol) in 60 mL of acetonitrile was refluxed for 96 hours and then partitioned between 100 mL DI water and 150 mL ethyl ether. The organic layer was dried over  $MgSO_4$ , gravity filtered and the organic solvent was removed in vacuo. The resulting liquid was purified using chromatography on  $SiO_2$  with 1:1 hexanes/ethyl acetate giving the desired diether (5.62 g 93%) as a white solid upon removal of solvent:  $R_f = 0.51$  (1:1 Hex/EtOAc), IR (KBr)  $1722.7\text{ cm}^{-1}$ ,  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.41-7.17 (m, 12H), 6.67-6.54 (d,  $J= 15.92\text{ Hz}$ , 2H), 6.35-6.19 (m,  $J=5.9\text{ Hz}$ , 2H), 4.32-4.18 (m, 8H), 3.92-3.84 (m, 10H),  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  167.7, 150.5, 136.6, 132.6, 128.5, 127.7, 126.5, 125.8, 125.4, 113.9, 72.0, 69.0, 68.2, 52.5 Mass Spectral

Analysis (FAB+) MI 547.17 (Theoretical mass for  $C_{32}H_{34}O_8 = 547.23$ ).

*4,5-bis(Cinnamyloxyethoxy)-phthalic acid*

A solution of 4,5-bis (cinnamyloxyethoxy) phthalic acid dimethyl ester (5.50 g, 10.1 mmoles) in 50 mL of 15% KOH (aqueous) and 50 mL methanol was heated to reflux for 24 hours and then allowed to cool to room temperature. The solution was then concentrated in vacuo removing the methanol and a majority of the water. A 20 mL portion of DI water was added and the pH of the solution was slowly adjusted to 3.0 using 10% HCl. The solution was cooled to 5 °C and the desired 4,5-bis (cinnamyloxyethoxy) phthalic acid was collected by vacuum filtration and dried for 12 hours in a vacuum oven at 60 °C. The white crystalline solid collected weighed 4.75 g (91%): mp = 186-188 °C, IR (KBr) 2614 and 1712  $cm^{-1}$ ,  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  7.84-7.67 (s, 2H), 7.45-7.18 (m, 10H), 6.64-6.53 (d,  $J = 16.00$  Hz, 2H), 6.39-6.27 (m,  $J = 6.6$  Hz, 2H) 4.34-4.09 (m, 8H), 3.86-3.68 (m, 4H),  $^{13}C$  NMR ( $d_6$  DMSO)  $\delta$  167.6, 149.5, 149.0, 136.4, 131.3, 128.6, 128.4, 127.6, 126.5, 126.3, 116.4, 70.8, 68.1, 67.9, Mass Spectral Analysis (FAB+) MI 519.17 (Theoretical mass for  $C_{30}H_{31}O_8 = 519.20$ ).

*4,5-bis(Cinnamyloxyethoxy)-phthalimide*

4,5-bis(cinnamyloxyethoxy) phthalic acid (2.00 g, 3.9 mmoles) was heated to 160 °C under argon with constant stirring in a large test tube containing urea (0.60 g, 10.0 mmoles). The reaction was removed from the oil bath when the evolution of ammonia gas ceased, as followed using moistened pH paper. The resulting solid was dissolved in  $CH_2Cl_2$ /DI water and the organic layer was separated and dried over  $MgSO_4$ . Removal of the  $CH_2Cl_2$  in vacuo afforded 1.75 g of the desired 4,5-bis (cinnamyloxyethoxy) phthalimide (91%) as a white solid: mp 130-131 °C,  $R_f = 0.92$  (90:10  $CHCl_3$ /MeOH), IR (KBr) 3245, 1763 and 1719  $cm^{-1}$ ,  $^1H$  NMR (Solvent  $CD_2Cl_2$ )  $\delta$  8.10-7.95 (broad, 1H), 7.43-7.18 (m, 12H), 6.69-6.54 (d,  $J = 15.8$ , 2H), 6.38-6.21 (doublet of triplets,  $J = 5.9$ , 2H), 4.34-4.19 (q,  $J = 4.4$ , 8H), 3.94-3.85 (t,  $J = 4.4$  Hz, 4H),  $^{13}C$  NMR (Solvent  $CD_2Cl_2$ )  $\delta$  168.6, 154.0, 137.0, 132.7,

128.9, 128.0, 126.8, 126.5, 126.3, 107.2, 72.2, 69.6, 68.5, Mass Spectral Analysis (FAB+) MI 500.22 (MH<sup>+</sup>) (Theoretical mass for C<sub>30</sub>H<sub>30</sub>NO<sub>6</sub> = 500.21).

*4,5-bis(Cinnamyloxyethoxy)-phthalamide*

A mixture of 4,5-bis (cinnamyloxyethoxy) phthalimide (1.00 g, 2.0 mmoles) and 30 mL of 25% (wt. %) aqueous ammonia in a 50 mL round bottom flask was sealed with a rubber septum and stirred vigorously for 24 hours at room temperature. The mixture was then gravity filtered and washed with DI water. The solid collected was dried in a vacuum dessicator for 12 hours affording 0.98 g of the desired 4,5-bis (cinnamyloxyethoxy) phthalamide (95%) as a light tan solid. mp = 158-160 °C, R<sub>f</sub> = 0.33 (90:10 CHCl<sub>3</sub>/MeOH), IR (KBr) 3453, 1647, 1598 cm<sup>-1</sup>, <sup>1</sup>H (d<sub>6</sub>-DMSO) δ 7.80-7.68 (broad, 2H), 7.49-7.08 (m, 12H), 6.64-6.55 (d, J=15.9 Hz, 2H), 6.42-6.28 (doublet of triplets, J=5.4 Hz, 2H), 4.35-4.08 (m, 8H), 3.89-3.68 (m, 4H), <sup>13</sup>C NMR (d<sub>6</sub>-DMSO) δ 169.7, 149.5, 136.4, 131.3, 129.1, 128.6, 127.6, 126.5, 126.4, 113.463, 70.9, 68.5, 68.0, Mass Spectral Analysis (FAB+) MI 517.21 (MH<sup>+</sup>) (Theoretical mass for C<sub>30</sub>H<sub>33</sub>N<sub>2</sub>O<sub>6</sub> = 517.23).

*4,5-bis(Cinnamyloxyethoxy)-phthalonitrile*

Anhydrous dimethyl formamide (DMF) (1.20 mL, 15.5 mmoles) was added via syringe to 25 mL acetonitrile cooled to 0 °C, then oxalyl chloride (1.25 mL, 14.2 mmoles) was slowly added with formation of a white precipitate and gas evolution. When the evolution of gas ceased, 4,5-bis (cinnamyloxyethoxy) phthalamide (0.85 g, 1.65 mmoles) was added as a suspension in 5 mL of acetonitrile. Within a few minutes the reaction solution became homogeneous. Pyridine (2.30 mL, 28.4 mmoles) was then added and the reaction was stirred for an additional 45 minutes at 0 °C. The reaction was then quenched by the addition of 50 mL ethyl ether and 50 mL 10% HCl. The aqueous layer was extracted and washed with 50 mL of ethyl ether. The combined ether layers were then extracted with saturated NaCl and dried over MgSO<sub>4</sub>. The ether was removed in vacuo to yield a clear oil, which

solidified into white needle crystals. The resulting crystals were washed with 5 mL portions of cold pentane and dried in a vacuum dessicator. The weight of the 4,5-bis (cinnamyloxyethoxy) phthalonitrile was 0.75 g (95%): mp = 75-77 °C,  $R_f$  = 0.91 (90:10 CHCl<sub>3</sub>/MeOH), IR (KBr) 2228 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.42-7.18 (s, 12H), 6.68-6.53 (d, J=15.8 Hz, 2H), 6.37-6.17 (doublet of triplets, J=6.0 Hz, 2H), 4.39-4.18 (m, 8H), 3.96-3.84 (m, 4H), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 152.3, 136.3, 132.9, 128.5, 127.8, 126.4, 125.3, 116.8, 115.7, 107.1, 72.0, 69.4, 67.8, Mass Spectral Analysis (FAB+) MI 480.29 (MH<sup>+</sup>) (Theoretical mass for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub> = 480.23).

#### *2,3,9,10,16,17,23,24-Octa(Cinnamyloxyethoxy)-phthalocyanine*

A 10 ml round bottom flask containing a magnetic stirrer was charged with 1.5 ml of 1-pentanol, 4,5-bis (cinnamyloxyethoxy) phthalonitrile (0.25 g, 0.52 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.07 g, 0.56 mmol) was heated to reflux for 25 hours. The solid was vacuum filtered through a medium sintered glass crucible and the solid washed with DI water. The solid was purified by Soxhlet extraction with ethyl ether giving 0.054 g of the purified phthalocyanine (22%) as a green solid after removal of solvent in vacuo.  $R_f$  = 0.87 (95:5 CHCl<sub>3</sub>/MeOH), UV-Vis (CHCl<sub>3</sub>) 677.7 nm, Mass Spectral Analysis (MALDI) MI 1922.83 (Theoretical mass for C<sub>120</sub>H<sub>114</sub>N<sub>8</sub>O<sub>16</sub> = 1922.84).

#### *2,3,9,10,16,17,23,24-Octa(Cinnamyloxyethoxy)-phthalocyanato Copper (II)*

A 10 ml round bottom flask containing a magnetic stirrer was charged with 5 ml of 1-pentanol, 4,5-bis (cinnamyloxyethoxy) phthalonitrile (0.50 g, 1.0 mmol), copper (II) bromide (0.058 g, 0.25 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.16 g, 1.0 mmol) was heated to reflux for 25 hours. The solid was vacuum filtered through a medium sintered glass crucible and the solid washed with DI water. The solid was purified by Soxhlet extraction with ethyl ether giving 0.21 g of the purified phthalocyanine (42%) as a green solid after removal of solvent in vacuo.  $R_f$  = 0.87 (95:5 CHCl<sub>3</sub>/MeOH), UV-Vis (CHCl<sub>3</sub>) 677.7 nm, Mass Spectral Analysis (MALDI) MI 1984.7385

(Theoretical mass for  $\text{C}_{120}\text{H}_{112}\text{N}_8\text{O}_{16}\text{Cu} = 1984.7510$ ).