Supporting Information

SELF ORGANIZED THIN FILMS OF HYDROGEN-BONDED PHTHALOCYANINES: CHARACTERIZATION OF STRUCTURE AND ELECTRICAL PROPERTIES ON NANO METER LENGTH SCALES

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1) SYNTHESIS AND MASS SPECTRAL, NMR ANALYSIS OF INTERMEDIATES AND FINAL PRODUCTS

General Information: All non-aqueous reactions were carried out under an argon atmosphere unless stated otherwise. Reagents and solvents were purchased from Aldrich®, Fluka®, or TCI® and were used as received unless specified otherwise. All NMR data was collected with a Varian Unity 200 MHz or Gemini 300 MHz system. Column chromatography was performed using 300 mesh SiO₂ unless otherwise specified.

Scheme S1. Synthetic pathway to 2,3,9,10,16,17,23,24-octakis(2-(4-octylbenzamide ethylsulfanyl)) phthalocyanine(1).
2,3,9,10,16,17,23,24-octakis(2-(4-octylbenzamide ethylsulfanyl)) phthalocyanato copper (II) (Pc (1)).

A procedure from Shirashi and coworkers\(^4\) was modified as follows: 4,5-bis (2-(4-octylbenzamide) ethylsulfanyl) phthalonitrile (5) (0.71 g, 0.94 mmoles), copper (II) bromide (0.06 g, 0.24 mmoles), and DBU (0.15 g, 1.1 mmoles) were suspended in 10 mL of 1-pentanol and the mixture was refluxed under argon for 12 h. The reaction was cooled to room temperature and was then placed in a freezer overnight to allow the product to crystallize out of solution. The phthalocyanine was collected by suction filtration and the blue-green solid was washed (2 x 30 mL) with DI water and (2 x 30 mL) with ether. The solid was placed in a Soxhlet thimble and was extracted for 48 h with boiling ether, followed by 48 hours with methanol, and finally 48 hours with acetone. The solid weighed 0.51 g of the blue green solid, 71 % yield.

**Elemental Analysis of Pc (1):**

Multiple elemental (C,H,N,S) analyses were done by Columbia Analytical Services with less precision than we have seen in prior Pc syntheses, involving non-H-bonding materials. The average results, however, coupled with the MALDI mass spectral data, suggest that the final product is within acceptable limits of the elemental compositions expected:

<table>
<thead>
<tr>
<th>Element</th>
<th>Actual (±)</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>67.20 % (+/- 0.21 %)</td>
<td>69.40 %</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.15 % (+/- 0.02 %)</td>
<td>7.48 %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>7.62 % (+/- 0.02 %)</td>
<td>7.70 %</td>
</tr>
<tr>
<td>Sulfur</td>
<td>8.01 % (+/- 0.12 %)</td>
<td>8.8 %</td>
</tr>
</tbody>
</table>
Mass Spectral Analysis of Pc (1):

(HR-MALDI) 2905.5179 (22%), 2906.4873 (43%), 2908.4482 (100%), 2909.4326 (69%), 2910.4440 (46%) (Theoretical mass with isotope distribution (with relative intensities) for C₁₆₈H₂₁₆CuN₁₆O₈S₈ = 2905.4127 (33%), 2906.4158 (67%), 2907.4164 (94%), 2908.4171 (100%), 2909.4177 (85%), 2910.4182 (60%), 2911.4186 (37%), 2912.4190 (20%), 2913.4192 (10%), 2914.4195 (4%), 2915.4197 (1%).

Figure S1. MALDI Spectrum of Pc (1)
2) UV-VISIBLE SPECTROSCOPY OF SOLUTIONS OF Pc (1)

Figure S2. (upper panel) UV-Vis spectra in THF, with increasing amounts of trifluoromethanesulfonic acid (TA). The Pc is co-facially aggregated in THF as evidenced by the broad, blue-shifted absorbance from 600-800 nm. At 3% TA, the Q-band absorbance for the monomeric species was observed at 800nm. All solutions were 4.8 X 10⁻⁶ M; (lower panel) UV-vis spectrum of a thin film of Pc (1) ca. 4 monolayers showing the blue-shifted Q-band spectrum suggestive of H-aggregation of the Pc.
3) **FT-IR SPECTROSCOPY OF POWDERS OF Pc (I)**

![FTIR spectrum of Pc (I) as a KBr pellet.](image)

**Figure S3.** FTIR of Pc (I) as a KBr pellet.

IR (KBr pellet, cm\(^{-1}\)) 3398 (N-H stretching, free), 3298 (N-H stretching, H-bonded), 3037 (C-H, aromatic), 2923 (CH\(_2\) asym. stretch), 2853 (CH\(_2\) sym. stretch), 1654 (C=O, amide I), 1539 (N-H in-plane bending, amide II), 1503 (C=N, pyrole stretch) 1305 (C-N amide III), 954 (Pc ring vibration).
### 4) 2-D NMR SPECTROSCOPY OF Pc (1)

Table S1. Chemical Shift assignment from 2D-HSQC

<table>
<thead>
<tr>
<th>Position</th>
<th>$^1$H (δ ppm, mult., J Hz)</th>
<th>$^{13}$C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^Z$^a</td>
<td>$^E$^a</td>
</tr>
<tr>
<td></td>
<td>$^Z$^b</td>
<td>$^E$^b</td>
</tr>
<tr>
<td>1'</td>
<td>3.735 t, 5.4 3.634 t, 5.2</td>
<td>44.35 42.47</td>
</tr>
<tr>
<td>2'</td>
<td>3.802 q, 5.6 4.438 t, 5.2</td>
<td>41.63 63.66</td>
</tr>
<tr>
<td>NH</td>
<td>6.469 br. t 8.354 br. s</td>
<td>7.971 d, 8.1</td>
</tr>
<tr>
<td>5'</td>
<td>7.693 d, 8.1 7.971 d, 8.1</td>
<td>126.98 129.78</td>
</tr>
<tr>
<td>6'</td>
<td>7.248 7.185</td>
<td>128.69 128.64</td>
</tr>
<tr>
<td>8'</td>
<td>2.639 t, 7.6</td>
<td>35.93</td>
</tr>
<tr>
<td>9'</td>
<td>1.606</td>
<td>31.23</td>
</tr>
<tr>
<td>10'</td>
<td>1.247</td>
<td>31.90</td>
</tr>
<tr>
<td>11'</td>
<td>1.244</td>
<td>29.72$^c$</td>
</tr>
<tr>
<td>12'</td>
<td>1.298</td>
<td>29.38$^c$</td>
</tr>
<tr>
<td>13'</td>
<td>1.255</td>
<td>29.23$^c$</td>
</tr>
<tr>
<td>14'</td>
<td>1.278</td>
<td>22.68</td>
</tr>
<tr>
<td>15'</td>
<td>0.868 t, 7.0</td>
<td>14.16</td>
</tr>
</tbody>
</table>

Figure S4. Numbering scheme for Pc (1). Only one side chain is shown for simplicity.
Footnotes for Table S1:

a) $^1$H and $^{1}$H-$^{13}$C{ HSQC spectra were acquired with about 40 $\mu$g of sample in 0.5 mL of CDCl$_3$ using a Varian Inova-600 spectrometer ($^1$H frequency 599.70 MHz, $^{13}$C frequency 150.80 MHz) equipped with a 5mm cryogenic HCN probe. The gradient-selected HSQC spectrum was acquired with 1024 complex data points in $t_2$ and 375 complex data points in $t_1$, using echo-antiecho phase encoding in $t_1$. For each FID, 48 transients were acquired with a spectral width of 5286 Hz in $F_2$ and 22573 Hz in $F_1$. Data were zero-filled to a final matrix size of 2048 ($F_2$) x 1024 ($F_1$) data points and a skewed, 45°-shifted sine-bell window was applied in both dimensions. Chemical shifts are referenced to residual CHCl$_3$ at 7.25 ppm ($^1$H) and 77.21 ppm ($^{13}$C).

b) For nuclei near the amide linkage two signals were observed in approximate intensity ratio 3:1. This was assumed to be due to amide rotation which is slow on the NMR time scale, with the major rotamer being the Z configuration.

c) Overlapped in HSQC spectrum.

Discussion of NMR data:

The NMR data were consistent with the structure assigned to compound 1. Due to the very low solubility, only 1D $^1$H and 2D $^{1}$H-$^{13}$C-HSQC spectra could be obtained. HSQC intensities were lower near the phthalocyanine core, presumably due to slow relaxation due to limited mobility of C-H bonds. In fact, the phthalocyanine aromatic C-H pairs were not observed at all. Cis-trans isomerization of the amide linkages led to doubling of the nearby $^1$H and $^{13}$C resonances, with a Z:E ratio of about 3:1. In the E (minor) form, exchange of the NH proton is more rapid and J coupling is not observed to the vicinal CH$_2$ protons. The n-octyl assignments were made by comparison to $^1$H and $^{13}$C chemical shifts of n-octyl benzene.
Figure S5. [$^1$H – $^{13}$C] HSQC NMR spectrum of Pc (1).
Figure S6. $^1$H NMR Spectrum of Pc (1).
5). Thin Film Morphologies:

**Figure S7.** AFM images of (a) spin cast film on silicon wafer from $10^{-3}$ M Pc (1) solution; high molecular aggregation was observed (b). drop cast film on silicon from $10^{-5}$ M Pc (1) solution; inset in the high resolution image of a micro crystallite. (c) LB film deposited on silicon from $10^{-3}$ M Pc (1) solution; long fibers were observed (d) drop cast film on HOPG from $10^{-3}$ M Pc solution (e) chemisorbed film on HOPG from $10^{-3}$ M Pc solution; a net worked layers formed (f) chemisorbed film on HOPG from $10^{-6}$M Pc solution; inset is the high resolution image of layered structure.
6) Scheme 2 – Amide fictionalization of gold through diimide coupling of propylamine to self-assembled 11-mercaptonodecanoic acid and face-on assembly of Pc (1) through hydrogen bonding interactions.
**Figure S8.** Schematic illustration of layer-by-layer assembly of Pc molecules on amide functionalized gold. The arrows indicate the direction of transition dipole moments of amide I (C=O stretch), along z-axis and amide II (C-N stretch and N-H in-plane bend) vibrational modes on the x-y plane in the layered structure.
Figure S9. (a) AFM image of bare ITO surface. (b) AFM image of Pc (1) layers on ITO showing net-worked layers. (c) Section analysis of the layers illustrates presence of layers with an average thickness of ca 4.2 Å on ITO surface. (d) AFM image of PEDOT: PSS modified ITO. (e) Pc (1) layers adsorbed on PEDOT: PSS modified ITO. (f). Section analysis showing layers with thickness of ca. 4.4 Å on PEDOT: PSS modified ITO.
7) Nano-Scale Electrical Properties:

**Figure S10.** The left column is the height images, middle column is the current images, and the right column is $I-V$ curves obtained by point contact method in conducting probe AFM. (a), (b), and (c) are the height image, current image and $I-V$ curves of Pc (1) on HOPG respectively. (d), (e), and (f) are the height image, current image and $I-V$ curves of Pc (1) on amide functionalized gold respectively. (g), (h), and (i) are the height image, current image and $I-V$ curves of Pc (1) on ITO respectively. (j), (k), and (l) are the height image, current image and $I-V$ curves of Pc (1) on PEDOT: PSS modified ITO respectively. The bright areas in the height image are Pc layers, whereas the bright areas in the current images are substrates (because more current is conducted through the substrate than that of the Pc layers). Each of these $I-V$ curves are an average of ten curves obtained from same sample.
Figure S11. Current density-voltage plot acquired by point contact method on CAFM from the Pc layers assembled on ITO, HOPG, amide functionalized gold, and PEDOT: PSS modified ITO. During the positive scanning the Pt tip serves as the hole injecting electrode and in the negative scan the substrate is the hole injecting electrode.
Figure S12. The plots are fittings of the $I$-$V$ curves in the negative (a) and positive (b) bias regions. During the negative bias region, $\ln$ (current density) shows linear relationship with voltage. Hole injection from the substrate is controlled by thermionic emission. In the positive bias region, Pt tip and Pc contact shows ohmic current ($I \propto V$) in the low bias region, as the voltage increases, the current is limited by the bulk, where space charge limited current is observed, $I \propto V^2$. 
8) REFERENCES