Supporting Information

Helical nano-structures self-assembled from dimethylaminoethyloxy-containing unsymmetrical octakis-substituted phthalocyanine derivatives

Pan Ma, Zhaopin Bai, Yingning Gao, Jinglan Kan, Yongzhong Bian and Jianzhuang Jiang*
Synthesis of unsymmetrical zinc

2,3,9,10,16,17,23-heptakis(butyloxy)-24-mono(dimethylaminoethoxy)-phthalocyanine Zn{Pc(OC₄H₉)₇[OC₂H₄N(CH₃)₂]} (2). Zn(OAc)₂·2H₂O (20 mg, 0.09 mmol), H₂{Pc(OC₄H₉)₇[OC₂H₄N(CH₃)₂]} (33 mg, 0.03 mmol) in 3 ml DMF was stirred for 4 h at 140°C. The solution containing the reaction mixture was concentrated and then chromatographed on a silica gel column with CHCl₃ as eluent. Repeated chromatography followed by recrystallization from CHCl₃ and methanol gave pure target compound Zn{Pc(OC₄H₉)₇[OC₂H₄N(CH₃)₂]} as a reddish purple powder (29 mg, 85%). MS (MALDI-TOF) an isotopic cluster peaking at m/z 1167.7 (Calc. for M⁺ 1167.5). Anal. Calc. for ZnC₆₄H₈₁N₉O₈: C, 65.71%; H, 6.98%; N, 10.78%. Found: C, 65.38%; H, 6.18%; N, 10.90%. UV-Vis (CHCl₃) [λ max/nm (log ε)] 366 (4.53), 613(4.08), 681(4.76), 692(4.84); UV-Vis (CHCl₃ + pyridine) [λ max/nm (log ε)] 362 (4.52), 613(4.07), 680(4.89). ¹H NMR[CDCl₃/pyridine-d5 (99:1), 300 MHz]: 8.93-8.89 (Ar-H), 4.568 (t, OCH₂), 2.98 [t, OCH₂CH₂N(CH₃)₂], 2.43[s, OCH₂CH₂N(CH₃)₂], 2.05(m, OCH₂CH₂CH₂CH₃), 1.68-1.70 (m, OCH₂CH₂CH₂CH₃), 1.06-1.11 (t, OCH₂CH₂CH₂CH₃).
Fig. S1. Experimental (a) and simulated isotopic patterns (b) for molecular ion of phthalocyaninato zinc complex Zn{Pe(OC₄H₉)₇[OC₂H₄N(CH₃)₂]} (2).
Fig. S2. The $^1$H NMR spectrum of Zn\{Pc(OC$_4$H$_9$)$_7$[OC$_2$H$_4$N(CH$_3$)$_2$]\} (2) in CDCl$_3$/pyridine-d$_5$ (99:1). The signals due to pyridine-d$_5$, residue CHCl$_3$ and water are denoted as $^+$, $^*$, and $^#$, respectively.
Fig. S3. IR spectra of H$_2$Pc(OC$_4$H$_9$)$_8$ (A), H$_2$Pc(OC$_4$H$_9$)$_2$[OC$_2$H$_4$N(CH$_3$)$_2$] (I) (B), and the aggregates of I formed in methanol (C) in the region 2750-3500 cm$^{-1}$ with 2 cm$^{-1}$ resolution.
Fig. S4. IR spectra of compound Zn{Pc(OC₄H₉)₈} (A), Zn{Pc(OC₄H₉)₇[OC₂H₄N(CH₃)₂]} (2) (B), and the aggregates of 2 formed in methanol (C) in the region 2750-3050 cm⁻¹ with 2 cm⁻¹ resolution.
Fig. S5. TEM image of tubular superstructure of $\text{H}_2\{\text{Pc(OC}_4\text{H}_9)\}_7[\text{OC}_2\text{H}_4\text{N(CH}_3)_2]\}$ (I).
Figure S6. SEM images of the two-electrode device fabricated on SiO$_2$: (A) nanostructures of H$_2$\{Pc(OC$_4$H$_9$)$_2$[OC$_2$H$_4$N(CH$_3$)$_2$]\} (1), (B) nanowire bundles of Zn\{Pc(OC$_4$H$_9$)$_2$[OC$_2$H$_4$N(CH$_3$)$_2$]\}(2).
Figure S7. *I-V* curves measured on $\text{H}_2\{\text{Pc(OC}_4\text{H}_9)_{2}[\text{OC}_2\text{H}_4\text{N(CH}_3)_2]\}\}$ drop-casting film (A) and $\text{Zn}\{\text{Pc(OC}_4\text{H}_9)_{2}[\text{OC}_2\text{H}_4\text{N(CH}_3)_2]\}\}$ drop-casting film (B): undoped (dash line), doped with iodine vapor (solid line). The inset is the *I-V* curve of undoped drop-casting film from –100 to 100V.
Table S1. Electronic absorption data for compounds $H_2\{Pc(OC_4H_9)\_7[OC_2H_4N(CH_3)\_2]\}$ (1) and $Zn\{Pc(OC_4H_9)\_7[OC_2H_4N(CH_3)\_2]\}$ (2) dissolved in CHCl$_3$ and their self-assemblies dispersed in methanol.

<table>
<thead>
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<th>Compound</th>
<th>λ$_{max}$/nm</th>
<th>CHCl$_3$</th>
<th>methanol</th>
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<td>362, 421, 680, 692</td>
<td>357, 409, 615</td>
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