

Electronic supplementary information

Morphology Controlled Nano-structures of an Octa(phenoxy)- substituted Phthalocyaninato Zinc complex: Solvent Effect on the Self-assembly Behavior

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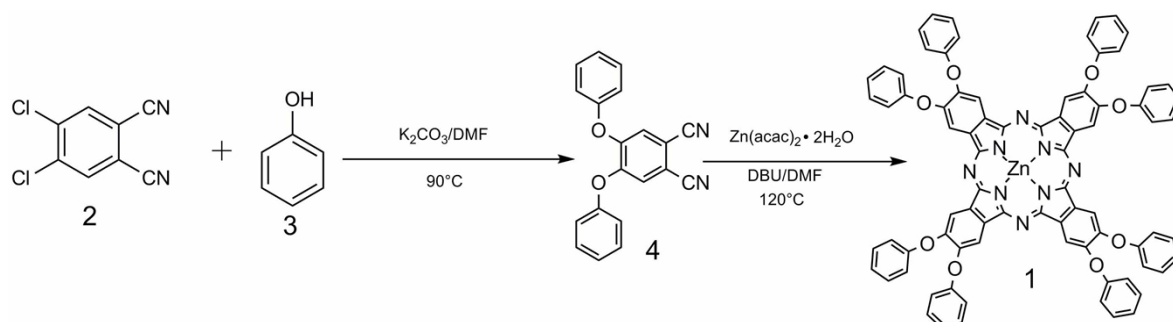
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Preparation of Zn[Pc(OPh)₈]



Scheme S1. Preparation of 2,3,9,10,16,17,24,25-octakis (phenoxy) phthalocyanine (Zn[Pc(OPh)₈])

Preparation of 4,5-di(phenoxy)phthalonitrile (4) : Compound 4 was prepared according to a general procedure.¹ 4,5-Dichloro-1,2-dicyanobenzene (2) (1.97g, 10 mmol) and 60 mmol of a phenol compound (3) were heated at 90°C in DMF (20 mL) with stirring under N₂. K₂CO₃ powder (2.76 g, 20 mmol) was added in portions (8 × 20 mmol) every 5 min. The mixture was heated for a further 30 min. After cooling the mixture was added to 200 mL of cold water, filtered and the product was recrystallised from MeOH.

Preparation of 2,3,9,10,16,17,24,25-octakis(phenoxy)phthalocyaninato zinc (1) :

Compound 1 was synthesized and purified according to published procedures.² A mixture of 4 (55 mg, 0.1 mmol), Zn(OAc)₂·2H₂O (55 mg, 0.25 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 50 mg) in DMF (5 mL) was heated at 120°C under a slow stream of nitrogen overnight. After cooling to room temperature, the volatiles were removed in vacuum. The residue was dissolved in CHCl₃ and subjected to chromatography on a silica gel column with CHCl₃/CH₃OH (9:1, v/v) as eluent. The first green band containing 1 was collected. Yield 70%, mp >275°C (Found: C, 73.59%, H, 3.68%; N, 8.70%. requires C, 73.70%; H, 3.70%; N, 8.72%); ν_{\max} (KBr)/cm⁻¹ 748, 891, 1087, 1207, 1273, 1450, 1489, 1593, 1628; M⁺(m/z)

(Experimental value)1313.95, M⁺ (m/z) (Calculated value) 1313.29.

References

- 1 X. Yang, X. Xu, and H. F. Ji, *Journal of Physical Chemistry B*, 2008, **112**, 7196-7202.
- 2 S. E. Maree and T. Nyokong, *Journal of Porphyrins and Phthalocyanines*, 2001, **5**, 782-792.

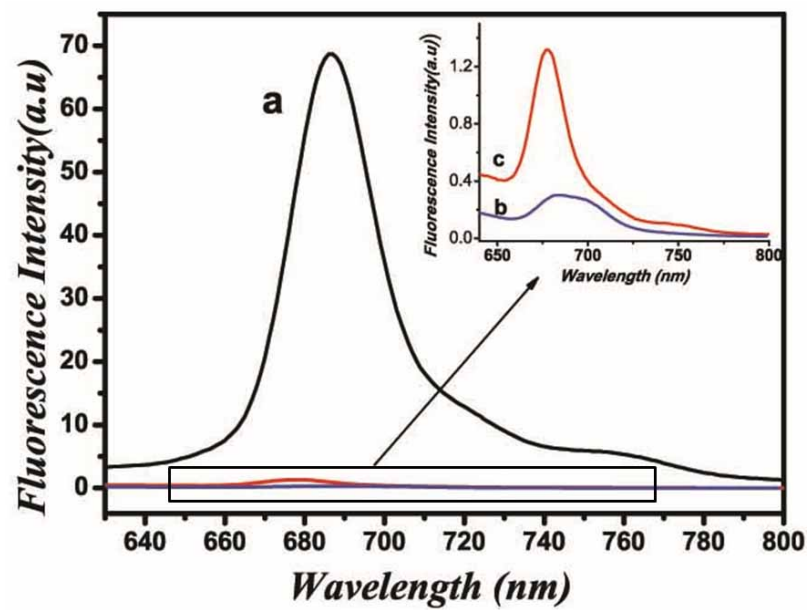


Fig. S1. Fluorescence spectra of Zn[Pc(OPh)₈] in chloroform (a), its self-assembled nanostructures formed in *n*-hexane (b) and in methanol (c) ($\lambda_{\text{ex}} = 590 \text{ nm}$)

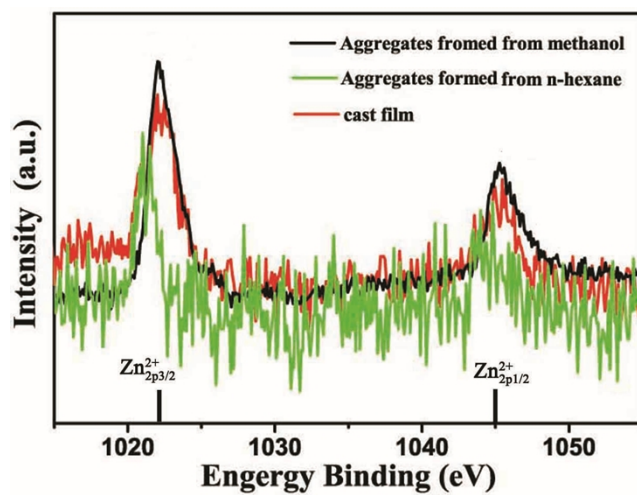


Fig.S2. X-ray photoelectron spectra of Zn[Pc(OPh)₈] aggregates in methanol (black line), in *n*-hexane (green line) and the cast film (red line) deposited on silicon surface.

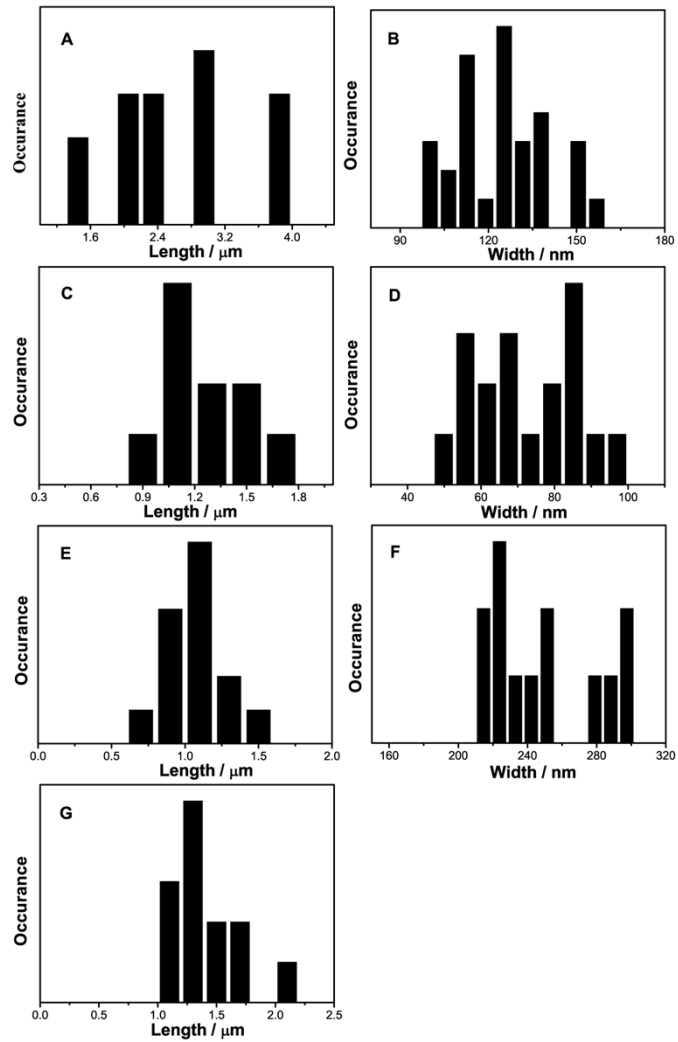


Fig. S3. The length and width distribution of the belts (A-B) and soft sticks (C-D), the diameter distribution of mushrooms in needle mushroom-like structures (E), the length distribution of needle mushrooms (F), and pine leaves (G).

