Facile Synthesis of Shape and Size Tunable Porphyrinoid Coordination Polymers: From Copper Porphyrin Nanoplates to Microspindles

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Electronic Supplementary Information:

Experimental Section.

5,10,15,20-Tetrapyridylporphine (TPyP) (> 98%) was synthesized as previously reported.[1] A certain amount of acetic solution of TPyP (5 mM, 2 mL) was added into 60 mL aqueous solution of copper acetate ($CuAc_2 \cdot H_2O$ 0.10 g, 16 mM) in the presence of cetyltrimethylammonium bromide (CTAB, 10 mM) under stirring for 10 seconds at 20^{o}C. The obtained homogeneous solution was then left stand and it gradually turned turbid in one hour. The obtained product completely precipitated during one day. The obtained red purple precipitate was centrifugated and washed by deionized water to remove the remained surfactant. The obtained product at this condition (the solution concentrations are ca. [TPyP] equals 0.16 mM, [$CuAc_2$] equals 16 mM and [CTAB] equals 10 mM, respectively) is named as **Sample S**, FE-SEM images of which show that they are microspindles with ~1.2 μm in the lateral length (Fig. 1 in the text). While in the absence of CTAB, it produced a large quantity of suspending precipitates immediately when TPyP was fast added into the aqueous solution of $CuAc_2$ under stirring during the feed-in process. Nanoplates with ~50

nm-in-thick and 500 nm ~ 1 μm-in-diameter were obtained (Fig. 3). The condition of the other products with different size or shape was interpreted in their corresponding Figure caption part. UV–vis absorption spectra of the samples were conducted at a UV3600-NIR-Recording spectrophotometer operated at resolution of 2 nm (Shimadzu, Japan). XRD patterns were recorded on X' Pert Pro X-ray diffractometer (PAN analytical, the Netherland). SEM images were taken on a Hitachi S-4800 scanning electron microscope, or JEO-1500VP field emission scanning electron microscope or JSM-5600 scanning electron microscope. TEM images were taken on a JEOL JEM-2100 transmission electron microscope.

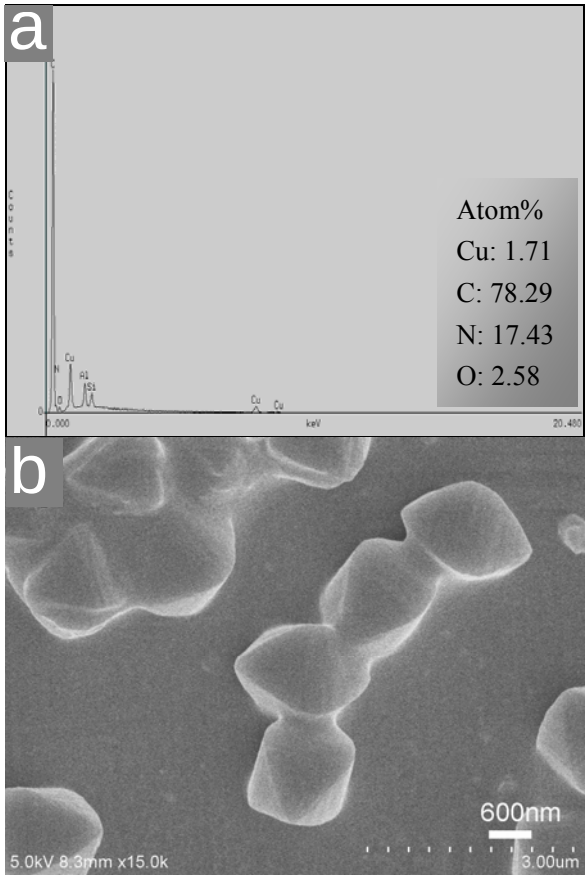


Fig. S1 (a) The energy dispersed X-ray (EDX) analysis of the microspindles of Sample S; (b) FE-SEM image of the obtained CuTPyP microspindles as Sample S after the treatment by sonication.

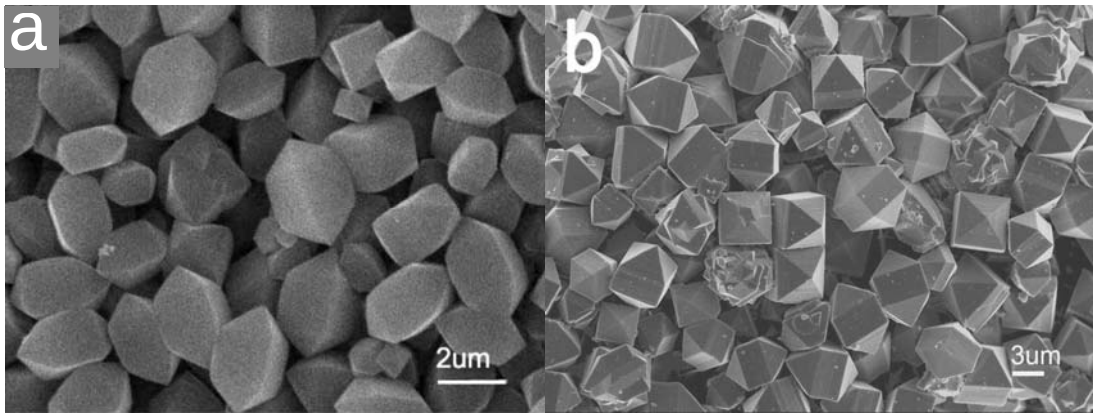


Fig. S2 The obtained CuTPyP at the condition of (a) [TPyP] = 0.32 mM, [$CuAc_2$] = 16 mM, [CTAB] = 10 mM. (b) [TPyP] = 0.32 mM, [$CuAc_2$] = 16 mM, [CTAB] = 50 mM.

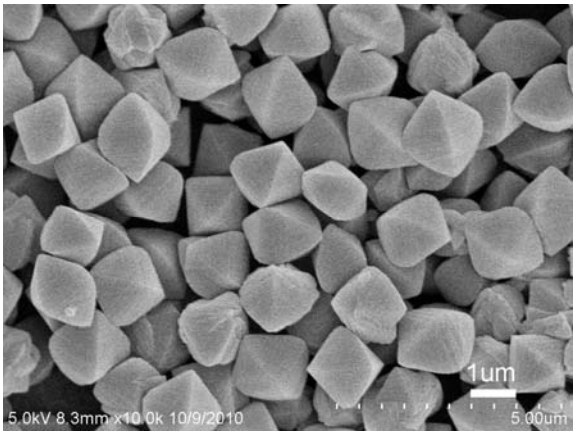


Fig. S3 FE-SEM image of the obtained structures at reaction for 10 minutes under the same condition as Sample S.

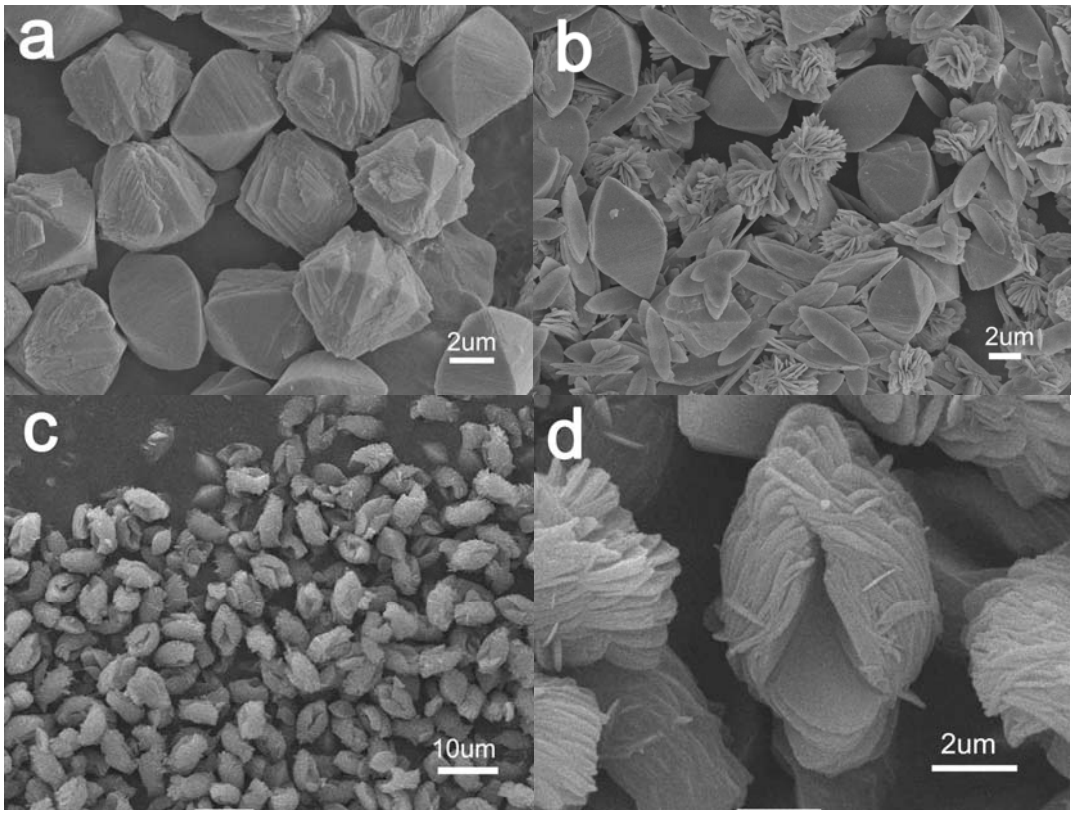
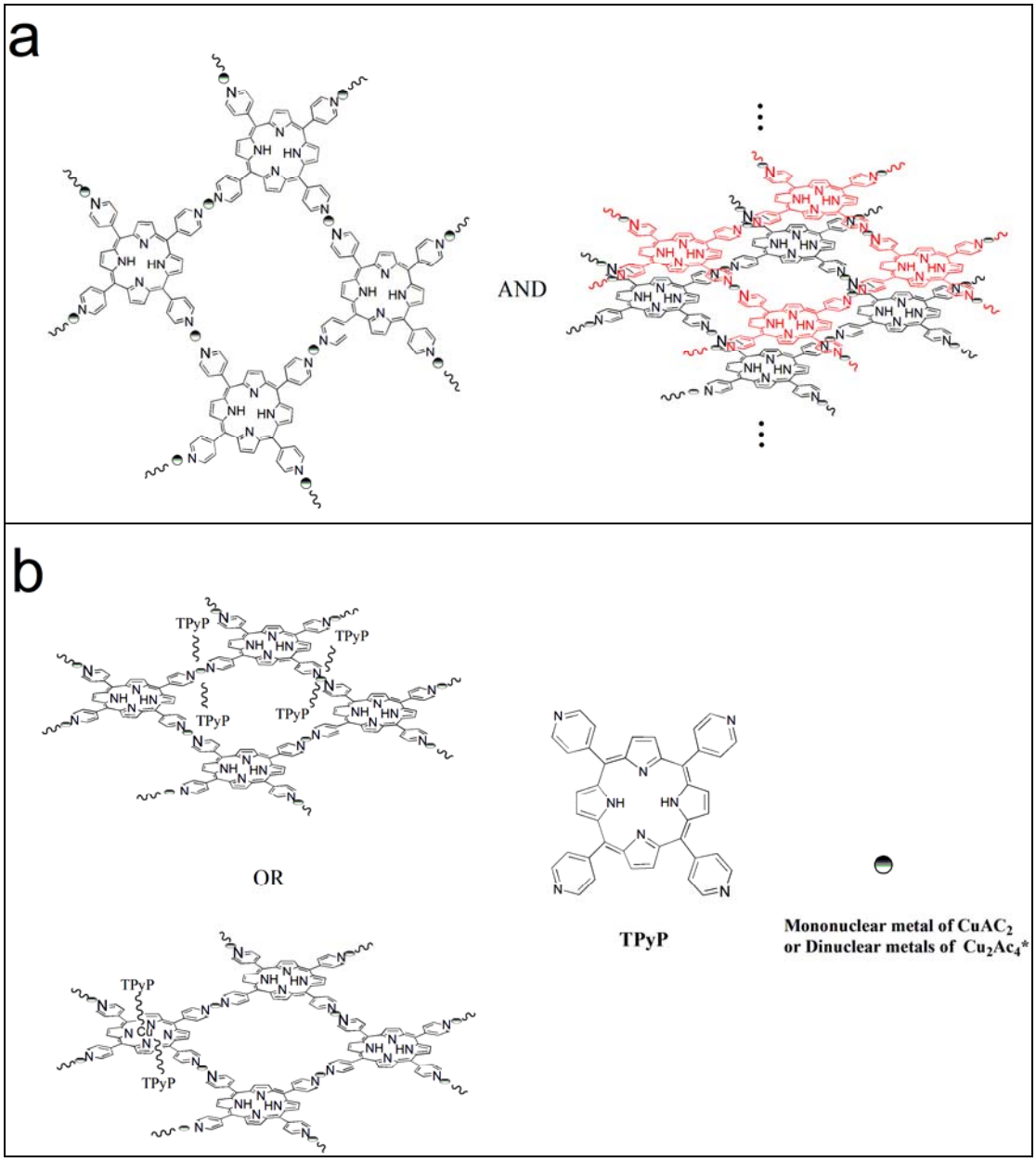


Fig. S4 (a) Low magnification SEM image of the obtained structures under the reactant concentration as Sample S at 18 ^{o}C; (b) Low magnification SEM image of the structures obtained under the reactant concentration as Sample S at 15 ^{o}C; (c) and (d) Low and High magnification image of the obtained CuTPyP at the condition of [TPyP] = 0.32 mM, [$CuAc_2$] = 16 mM, [CTAB] = 10 mM at 10 ^{o}C.



Scheme S1 The sketch of possible molecular aggregation modes in CuTPyP nanoplates and spindles. (a) 2-D coordination mode; (b) 3-D axis coordination mode (*Copper acetate can be present as dimeric species with paddle-wheel form in solution state[2]).

References.

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2 T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito and K. Tatsumi, *Inorg. Chem.*, 2006, **45**, 7988.