NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

Monitoring the length-controlled synthesis of one-dimensional metalloporphyrin-containing coordination polymer particles and their Photocatalytic Properties[†]

Yu Sun[a], Bongyoung Yoo[a*]

In this study, we investigated the length-controlled synthesis of one-dimensional (1D) metalloporphyrin coordination polymer particles (CPPs) through a bottom-up strategy assisted by an anion surfactant. We achieved the formation of 1D nanorod and nanowire structures, which showed efficient photocatalytic ability towards methylene blue (MB) decomposition under visible light illumination.

One-dimensional (1D) nanomaterials, including nanowires, nanotubes, nanobelts, etc., are important classes of nanomaterials due to their uniquely anisotropic structures, which make them very promising as the functional materials for nano-scale device fabrication, energy storage, chemical catalysis, and photonics.[1] However, most relevant research has been focused on 1D inorganic nanomaterials,[2] although organic counterparts have also played important roles in various fields.[3,4] As one of the most promising materials based on organic molecules, coordination polymer particles (CCPs) with various shapes and morphologies have received a great deal of attention due to use in various electronics, gas storage, optics, catalysis, recognition, and separation applications.[5-7] Therefore, substantial research efforts have been directed towards the synthesis of CPPs. Oh and co-workers prepared a variety of CPPs based on In(Ⅲ) and O, N-donor ligands with controlled morphologies and functionalities.[8] The Mirkin group reported the synthesis of nano-scale infinite coordination polymers by using bis-metallo-tridentate Schiff base ligands and metal acetates.[4(c)] In our previous work, metalloporphyrin, zinc 5, 10, 15, 20-tetra(4-pyridyl)-21*H*, 23*H*-porphine (ZnTPyP) was chosen as the building blocks in the construction of CPPs for various applications. Nano/micro-scale CPPs with diverse structures, such as four-petal flower structures, hexagonal nanorod structures, and nano/micro-octahedron structures, were synthesized by a bottom-up method

assisted by surfactants.[9] Nevertheless, several reports including our work[9, 10] have documented the synthesis of 1D metalloporphyrin-containing CPPs, but few of them were contributed to diverse applications of 1D CPPs in multidisciplinary fields.

Here, we extended our methods and concepts aimed at synthesizing 1D metalloporphyrin-containing CPPs in a controlled manner and employed the synthesized 1D CPPs for the dye decomposition under visible light illumination. As ZnTPyP does not readily dissolve in water, a homogeneous ZnTPyP stock solution was prepared by acidifying its pyridyl group to form soluble tetrapyridine zinc cations (ZnTPyPH$_4^{4+}$). The ZnTPyPH$_4^{4+}$ cations can be deprotonated through an acid-base neutralization reaction when they are injected into a basic stock solution of surfactants, producing insoluble ZnTPyP aggregates within the micelle interiors of the surfactants. Therefore, cationic surfactants (CTAB, MTAB, etc…)[10] and non-ionic surfactants (PF-127, cyclodextrin, etc…)[9] were used instead of anionic surfactants in order to avoid the combination of anionic surfactants with ZnTPyPH$_4^{4+}$ cations. In our typical synthesis,[9] when 250 μL of a ZnTPyP stock solution (0.01 M) was injected into 5 mL of a basic stock solution, which was prepared by dissolving different amounts of surfactants and NaOH (concentration: < 0.0125 M) in solvents, the mixture immediately turned cloudy, suggesting the formation of aggregated particles. However, except for short-nanorod structures with an average length in the range of 150 to190 nm, no other 1D ZnTPyP-containing CPPs (Z-CPPs) were synthesized.

There have been many works reporting that the micelles formed by sodium dodecyl sulphate (SDS) could facilitate the formation of 1D nano/micro-structures.[11] However, a transparent solution rather than a cloudy one was obtained after injecting 250 μL of the ZnTPyP stock solution (0.01 M) into 5 mL of the basic SDS stock solution,

which was prepared by dissolving 0.05 M SDS and 0.0125 M NaOH in 100 mL pure water solvent, indicating that $ZnTPyPH_4^{4+}$ cations are combined with SDS anions through electrostatic interactions instead of with OH^- anions. As the combination of $ZnTPyPH_4^{4+}$ cations with SDS anions is a competitive interaction compared to that of $ZnTPyPH_4^{4+}$ cations with OH anions, we assume that a higher concentration of OH^- anions could be favourable for ZnTPyP aggregation. Therefore, we prepared the basic stock solution with a high NaOH concentration by dissolving 0.1 M NaOH and 0.05 M SDS in 100 mL of a pure water solvent (BSS-1 solution). A trace amount of Z-CPPs was formed after 3 h of vigorous stirring, illustrating that the formation of Z-CPPs accelerated by increasing the NaOH concentration. The external morphologies of the Z-CPPs synthesized by injecting 250 μL of the ZnTPyP stock into 5 mL of the basic stock solution under mild stirring for 3 h and 24 h were characterized by scanning electron microscopy (SEM). As shown in Fig. 1(A) and 1(B), nanorod structures with an average length of ~380 nm and width of ~40 nm were synthesized with a the reaction time of 3 h. Continuous growth was obtained when the reaction time was increased to 24 h, forming nanorod structures with an average length of ~800 nm and width of ~40 nm. Furthermore, the controlled synthesis of various nanorod structures with varying lengths and widths was successfully achieved by adjusting the reaction time, initial ZnTPyP concentration, and NaOH concentration in the basic stock solution. (See the ESI,[†] Fig. S1)
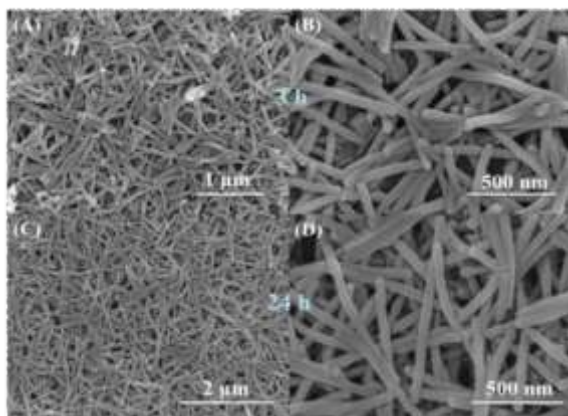

Fig. 1 ((A), (C)) Low-magnification and ((B), (D)) high magnification SEM images of nanorod structures obtained under mild stirring for ((A), (B)) 3 h and ((C), (D)) 24 h.

Inspired by the fact that nanorod structures with a longer length can be synthesized by increasing the reaction time, we carried out the experiment by injecting 250 μL of a ZnTPyP stock solution into 5 mL of a BSS-1 solution under mild stirring for 72 h. The mixture was centrifuged and repeatedly washed with pure water to remove the surfactants. Fig. 2 shows the low-magnification and high-magnification SEM images and corresponding TEM image of the obtained Z-CPPs. It is clearly seen that nanowire structures were massively synthesized with an average length and width of *ca.* 1.2 μm and 28 nm, respectively. The ratio of the average length to the average width of the nanowire structures increased to ~41, compared to that (~6.5) of the nanorod structures (Fig. 1(A)).
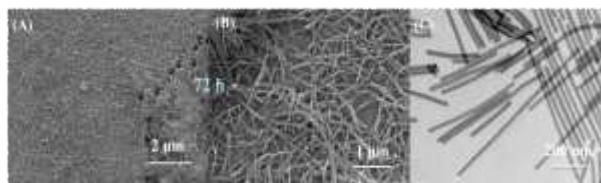

Fig. 2 (A) Low-magnification and (B) high-magnification SEM images, and a (C) TEM image of nanowire structures synthesized under mild stirring for 72 h.

As reported in our previous work, the electronic absorption properties of (metallo)-porphyrins can be determined from their by UV-visible spectra due to their characteristic color derived from the highly conjugated π–electron systems.[9] Therefore, the formation of CPPs based on (metallo)-porphyrins and their aggregation type can be detected based on the spectrum changes of the degenerated Soret band by comparing it with those of the (metallo)-porphyrin monomers. The details of the UV-vis spectra measurements including the sample preparation are described in the ESI.[†] As a reference, the electronic absorption spectrum of the ZnTPyP monomer was determined, showing a single Soret band at 426 nm and two weak Q bands at 565 nm and 593 nm (Fig. 3(A)). The spectra obtained with aging times of 20 s and 20 min are shown in Fig. 3(B) and 3(C), respectively. The Soret band at 426 nm was strongly weakened and blue-shifted to 443 nm, indicating that monomeric ZnTPyP molecules are the majority species within 20 min. The Soret band slightly split into one sharp peak at 443 nm and one wide band with a peak position at 428 nm when the reaction time was increased to 2 h (Fig. 3(D)). Similar cases were observed with reaction times of 4 h (Fig. 3(E)), 7 h (Fig. 3(F)), and 13 h (Fig. 3(G)). As a result, we confirmed that the ZnTPyP aggregation type is J-aggregation as the single Soret band was split to one blue-shifted absorption band and one red-shifted absorption band.[9] However, monomeric ZnTPyP molecules are still the majority species based on the observation of the wide Soret band. When the reaction time was increased to 24 h (Fig. 3(H)), the Soret band clearly split into two bands with a relatively weaker intensity appearing at 417 nm (blue-shifted) and one with a stronger intensity appearing at 447 nm (red-shifted). The shoulder peak was also observed near the red-shifted Soret band. The former and latter split Soret bands were ascribed to the transition moments parallel and perpendicular to the aggregates axis, respectively. Above a reaction time of 36 h (Fig. 3(I), 3(J), 3(K)), the Soret band was clearly split and no shoulder peak was observed, indicating that the aggregated Z-CPPs are the majority species and no further aggregation proceeded after 36 h. Therefore, we monitored the aggregation process by measuring the electronic absorption spectra, confirming that the J-type aggregation existed in both the nanorod and nanowire structures.

The Z-CPPs were also characterized by fluorescent spectroscopy (FS) and fluorescent microscopy (FM). The photoluminescence (PL) emission spectra of the Z-CPPs with nanorod (Fig. 1(A, B)) and nanowire (Fig. 2) structures are shown in Fig. S2†. As can be seen, upon excitation at the ZnTPyP Sort band wavelength (~ 425 nm), one broad emission band was observed for the ZnTPyP monomers (Fig. S2(A)†). By contrast, two intense emission bands in the wavelength region from 600 to 700 nm were

obtained for both the Z-CPPs with nanorod structures (Fig. S2(A)†) and nanowire structures (Fig. S2(B)†), which is in good agreement with the UV-vis experimental results described above. The fluorescent microscopy (FM) images (insets, Fig. S2†) further confirmed the FS results, demonstrating the fluorescent property in the red region of the spectrum.
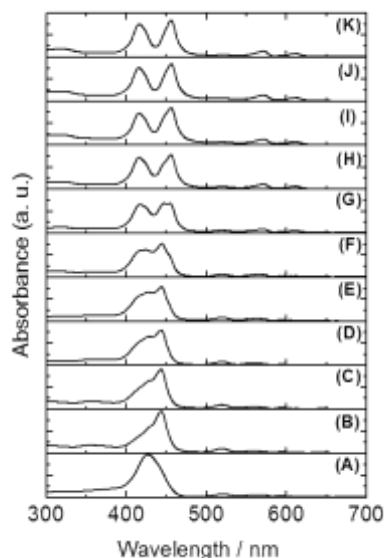

Fig. 3 UV-vis spectra of the (A) ZnTPyP monomer and those obtained as a function of reaction time: (B) 20 s, (C) 20 min, (D) 2 h, (E) 4 h, (F) 7 h, (G) 13 H, (H) 24 h, (I) 36 h, (J) 48 h, and (K) 72 h.

The internal structures of the as-prepared Z-CPPs were investigated by X-ray diffraction (XRD). As shown in Fig. S3†, both the Z-CPPs with nanorod (Fig. 1(A, B)) and nanowire (Fig. 2) structures exhibited similar XRD patterns, which correspond well to the simulated pattern on the basis of the crystal structure of ZnTPyP, indicating that both nanorod and nanowire structures have the $R3$ space group.[12] An interlattice distance of 1.632 nm can be derived from the diffraction peaks at $2\theta = 5.19^{o}$ and 10.55^{o}. Furthermore, the characteristic peaks attributed to (110) and (220) are remarkably intense for both the nanorod and nanowire structures. However, the other peaks attributed to (101) and (011 overbar) are much weaker than those attributed to (110) and (220). A similar XRD pattern has been obtained in our previous report, showing that the intensity of the diffraction peak at (220) was stronger than that of other peaks in ZnTPyP hexagonal nanorod structures but was strongly weakened in other nano/micro-structures. These features indicate that ZnTPyP molecules prefer to grow along the crystallographic c axis in one-dimensional nanostructures.[12(a)]

The best known porphyrins, chlorophyll in light-harvesting complexes and heme in red blood cells, play important roles in many biological energy transduction processes upon which all life forms on this planet depend. ZnTPyP, as a member of the porphyrin family, shares a similar molecular structure to its photoactive counterparts such as chlorophyll and heme, which offers analogous abilities to convert light energy into electron motion to facilitate photocatalytic reactions.[13] Therefore, we investigated the photocatalytic ability of the Z-CPPs with nanorod (Fig. 1(A, B)) and nanowire (Fig. 2) structures for methylene blue (MB) photo-degradation under visible light irradiation. Fig. S4† shows the photocatalytic degradation

of MB dye as a function of time in the presence of Z-CPPs determined by measuring the UV-vis absorption spectra. For a better comparison, MB decomposition without catalysts and with P25 TiO$_2$ catalysts was also investigated. As shown in Fig. S4(A) and (B)†, the absorption spectra without catalyst and with P25 TiO$_2$ catalyst did not change significantly as a function of time, indicating that P25 TiO$_2$ does not act as a photo-catalyst for the decomposition of MB under light illumination even after 5 h of illumination because of its poor visible light absorption capability due to its large band gap (~3.2 eV). However, irradiating the reaction slurry with visible light results in a gradual and steady decrease of the absorption peak formed at $\lambda_{max} = 664$ nm in the presence of both Z-CPPs nanorods and Z-CPPs nanowires. The percentage of dye degradation, η was calculated as follows

$$\eta = \frac{(A_0 - A)}{A} \times 100\%$$

where A_0 is the initial absorbance of the dye and A is the time dependent absorbance. Therefore, we plotted the percentage of dye residue (1-η) after 5 h of light illumination without catalysts and with P25 TiO$_2$ and 1D Z-CPPs catalysts. As shown in Fig. 6, ~64% and ~87% of MB dye was decomposed by the Z-CPPs nanorods and Z-CPPs nanowires, respectively, compared to ~12% MB degradation in the presence of no catalyst or P25 TiO$_2$. The colour changes of MB dye after 5 h illumination (Fig. 4, inset) were also compared, which further confirmed that the synthesized 1D Z-CPPs are effective for MB photo-decomposition under visible light illumination.
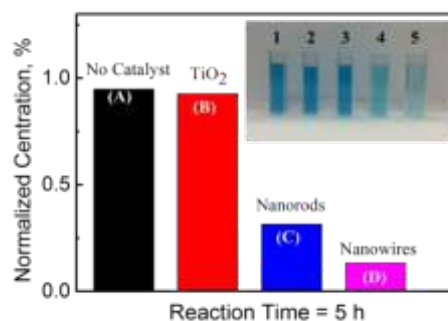

Fig. 4 Comparison of photocatalytic decomposition of MB (A) without catalysts and with (B) P25 TiO$_2$, (C) Z-CPPs with nanorod structures, and (D) Z-CPPs with nanowire structures as catalysts under visible light illumination with a reaction time of 5 h. The color fading of the MB dye solution after 5 h of illumination is shown in the inset: (1) 10 ppm MB, (2) 5 h reaction without catalyst, (3) 5 h reaction with TiO$_2$, (4) 5 h reaction with Z-CPPs nanorods, and (5) 5 h reaction with Z-CPPs nanowires as catalysts.

The aggregation and dimerization of (metallo)porphyrins influence their spectral and energetic characteristics as well as their efficacy in several applications.[14] In addition, it was reported that the J-type aggregation in ZnTPyP-containing nanoparticles favours the electron transfer, which may explain the morphological dependence of photocatalytic properties.[15] As shown in Figure 3(E) and 3(K), the extend of J-type aggregation differed in nanorod

structures and nanowire structures, which could probably influence the surface structure of Z-CPPs and the corresponding energetic and photocatalytic properties. More experiments are under way to study the size- and shape-dependent photocatalytic property.

In conclusion, we investigated the length controlled synthesis of 1D metalloporphyrin-containing CPPs (Z-CPPs) through a bottom-up strategy assisted by an anion surfactant (SDS). Diverse nanorod structures with various lengths and widths were synthesized by tuning the aging time, initial reactant concentration, and NaOH concentration in the basic stock solution. Nanowire structures of Z-CPPs were morphologically transformed from nanorod structures by increasing the aging time. The ZnTPyP aggregation process to form 1D Z-CPPs was monitored by measuring UV-vis spectra as a function of time, confirming that the continuous aggregation took place within 36 h and all 1D nanostructures of the Z-CPPs were formed through an edge-to-edge molecular arrangement, which is J-type aggregation. The further characterization by fluorescence microscopy revealed that the synthesized 1D Z-CPPs are fluorescent in the red region of the spectrum, which matches well with the results obtained by fluorescence spectroscopy, where intense emission bands were observed in the wavelength range from 580 to 680 nm upon excitation at the ZnTPyP Soret band wavelength (~425 nm). The photocatalytic abilities of Z-CPPs with nanorod and nanowire structures were also investigated by monitoring the degradation of MB dye, which demonstrated that all 1D Z-CPPs were effective towards MB photo-decomposition under visible light illumination. The further improvement of the photocatalytic ability of 1D Z-CPPs by loading other materials to form a hybrid system is under investigation.

Experimental

Typically, 250 μL of a ZnTPyP stock solution was injected into 5 mL of a basic stock solution under vigorous stirring at room temperature. After certain reaction time, the mixture was centrifuged and repeatedly washed with pure water in order to remove the surfactants.

Acknowledgements

Notes and references

1   (a) J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435; (b) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353; (c) Z. L. Wang, *Adv. Mater.*, 2003, **15**, 432; (d) R. Könenkamp, R. C. Word and M. Godinez, *Nano Lett.*, 2005, **5**, 2005; (e) J. Goldberger, A. Hochbaum, R. Fan and P. Yang, *Nano Lett.*, 2006, **6**, 973; (f) M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, **4**, 455.

2   Y. S. Zhao, H. Fu, A. Peng, Y. Ma, Q. Liao and J. Yao, *Acc. Chem. Res.*, 2010, **43**, 409.

3   A. Peng, D. Xiao, Y. Ma, W. Yang and J. Yao, *Adv. Mater.*, 2005, **17**, 2070.

4   (a) Y. S. Zhao, J. Wu and J. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 3158; (b) B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410; (c) B. K. An, S. K. Kwon and S. Y. Park, *Angew. Chem., Int. Ed.*, 2007, **46**, 1978.

5   (a) W. Cho, H. J. Lee and M. Oh, *J. Am. Chem. Soc.*, 2008, **130**, 16943; (b) M. Oh and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2006, **45**, 5492; (c) M. Oh and C. A. Mirkin, *Nature*, 2005, **438**, 651.

6   L. H. Wee, S. R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C. E. A. Kirschhock and J. A. Martens, *Chem. Commun.*, 2010, **46**, 8186.

7   P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle and G. Ferey, *Angew. Chem., Int. Ed.*, 2006, **45**, 5974.

8   H. J. Lee, W. Cho and M. Oh, *CrystEngComm*, 2010, **12**, 3959.

9   Y. Sun and B. Y. Yoo, *CrystEngComm*, 2014, **16**, 8950.

10   (a) F. Bai, H. M. Wu, R. E. Haddad, Z. C. Sun, S. K. Schmitt, V. R. Skocypec and H. Y. Fan, *Chem. Comm.*, 2010, **46**, 4941; (b) F. Bai, Z. C. Sun, H. M. Wu, R. E. Haddad, E. N. Coker, J. Y. Huang, M. A. Rodriguez and H. Y. Fan, *Nano Lett.*, 2011, **11**, 5196.

11   (a) S. Gorai, D. Ganguli and S. Chaudhuri, *Mater. Chem. Phys.*, 2004, **88**, 383; (b) M. G. Han and S. H. Foulger, *Small*, 2006, **2**, 1164.

12   (a) W. Sun, H. L. Wang, D. D. Qi, L. Wang, K. Wang, J. L. Kan, W. J. Li, Y. L. Chen and J. Z. Jiang, *CrystEngComm*, 2012, **14**, 7780; (b) S. H. Im, U. Jeong and Y. Xia, *Nat. Mater.*, 2005, **4**, 671; (c) H. Krupitsky, Z. Stein, I. Goldberg and C. E. J. Strouse, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **18**, 177; (d) K. J. Lin, *Angew. Chem., Int. Ed.*, 1999, **38**, 2730.

13   Y. F. Qiu, P. L. Chen and M. H. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 9644.

14   (a) V. E. Yushmanov, T. T. Tominaga, I. E. Bobrissevitch, H. Imasato and M. Tabak, *Magn. Reson. Imaging*, 1996, **14**, 255; (b) K. Komagoe and T. Katsu, *Anal. Sci.*, 2006, **22**, 255.

15   P. Guo, P. Chen, W. Ma, and M. Liu, *J. Mater. Chem.*, 2012, **22**, 20243.