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## ARTICLE

# Self-Assembled Core-Shell Nanospheres and Dendritic Nanostructure of Novel Tetra-(3-phenyprop-2-allyloxy) phthalocyanine in Different Solvents

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Novel metal-free Tetra-(3-phenyprop-2-allyloxy) phthalocyanine (TPAO-Pc) was synthesized and characterized by Nuclear magnetic resonance spectrum ( $^1\text{H}$  NMR), MALDI-TOF MS, Fourier-transform infrared (FT-IR) and UV-Visible absorption (UV-Vis) spectra. The effects of concentrations and solvents on the properties of self-assembly were investigated via absorption and fluorescence spectra, transmission electron microscopy (TEM). TPAO-Pc was stable in most organic solvents, such as toluene, acetone and dimethylsulfoxide. However, the TPAO-Pc exhibits the tendency of forming “face-to-face” stacking mode self-assemblies (H-aggregate) in DMSO/water and acetone/water mixed solutions. Self-assembly of the TPAO-Pc has also been demonstrated by fluorescence spectra. The TEM images display the core-shell nanospheres and dendritic nanostructure of TPAO-Pc formed in the DMSO/water and acetone/water mixed solutions, respectively. The mechanism of the self-assemblies growth was proposed on the basis of the experimental results. The morphology of the TPAO-Pc self-assemblies was related with the selected solvent conditions and the aggregation time. H-bond,  $\pi$ - $\pi$  interaction may be the main driving force for the formation of core-shell nanospheres and dendritic nanostructure.

## Introduction

The aromatic macrocycle phthalocyanines (Pc) containing an extended aromatic  $18\text{-}\pi$  electron system are one of the best known synthetic porphyrin analogues that have received considerable attention in recent years.<sup>1,2</sup> The phthalocyanine structure with smart modification has been shown to improve its properties of photochemistry and photophysics, and usually enhance their solubility effectively. Because of their excellent chemical and thermal stability, phthalocyanine compounds have been used in various potential applications such as chemical sensors,<sup>3</sup> electrocatalyst, data storage systems, nonlinear optics, liquid crystals<sup>4</sup> and photosensitizers for photodynamic therapy.<sup>5</sup> These advanced technological applications often require the aggregates of phthalocyanine for functional materials because the supramolecular assemblies of phthalocyanine possess more advantageous electrical, chemical, physical and optical properties than dispersed monomer molecular.<sup>6-9</sup>

Molecular materials and machines, based on supramolecular self-assembly, perform some special functions such as electrical conductivity, chemical sensing,<sup>10</sup> and mechanical movement.<sup>11</sup> The supramolecular self-assembly of phthalocyanines can be achieved through the cooperation of intermolecular interactions such as metal coordination, donor-acceptor, hydrogen-bond,

acid-base interactions, and  $\pi$ - $\pi$  stacking.<sup>12-15</sup> In general, great progress has been made in the self-assembly of phthalocyanines that forms various morphology nanostructures has been extensively investigated.<sup>16</sup> Recently, Zhu and coworkers<sup>17</sup> have reported the design and synthesis of two phthalocyanine compounds with optical activity. And their self-assembly properties was comparatively investigated. The metal-free and Zn phthalocyanine self-assembled to nanosheets and helical nanofibers, respectively. Kim et al.<sup>18</sup> have reported the phthalocyanine nanospheres with a very thin shell and hollow interior via rational design and synthesis, without using any templates or emulsifiers. In general, many developments have been made in the design and synthesis of phthalocyanine derivatives. However, these studies were focused on the formation of aggregates and aggregated structures, few studies have reported the effect of solvent on the structure and morphology of aggregates.

In the present paper, we report the synthesis and an unexpected solvent effect of dimethylsulfoxide/water (DMSO/water) and acetone/water on the self-assembly of novel tetra-(3-phenyprop-2-allyloxy) phthalocyanine (TPAO-Pc) (Scheme 1). TPAO-Pc forms core-shell nanospheres in a mixture of DMSO/water (1:4, v/v), whereas in acetone/water it self-assembles into dendritic nanostructure without using any templates or emulsifiers. The process of core-shell nanospheres

and dendritic nanostructure growth was also studied by TEM. For TPAO-Pc,  $\pi$ - $\pi$  stacking in cooperation with hydrogen bonding results in the formation of self-assembly in DMSO/water and acetone/water.

## Experimental

### Materials

Cinnamic alcohol (compound 1) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aladdin. All solvents were dried and purified as described by Perrin and Armarego.<sup>19</sup> All reactions were carried out under nitrogen atmosphere. The progress of the reactions was monitored by TLC (SiO<sub>2</sub>). Column chromatography was carried out on silica gel (Haiyang, Kieselgel 60, 200–300 mesh) with the indicated eluents. 4-Nitrophthalonitrile (compound 2) was prepared according to the literature procedures.<sup>20</sup>

### Synthesis of 4-(3-phenylprop-2-allyloxy) phthalonitrile (compound 3)

4-nitrophthalonitrile (compound 2) (0.5 g, 2.888 mmol) and cinnamic alcohol (compound 1) (0.775g, 5.78 mmol) were added to dry DMF (20 mL) successively with stirring and the mixture was stirred under N<sub>2</sub> stream at 55 °C. Then the powdered anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (0.8 g, 5.80 mmol) was added in eight equal portions for two hours and the mixture was stirred vigorously at 55 °C for 24 h. Then, the crude product was precipitated by adding 150 mL ice-water. The precipitate was collected by filtration. Then, the precipitate was washed successively with water and methanol several times. Finally, the crude product was crystallized repeatedly from ethanol to give light brown crystalline powder. Yield: 0.462 g, 61.5 %, MA=260.3 g/mol, M.p.=136 °C. IR  $\nu_{\max}$ /(cm<sup>-1</sup>): 2924-2880  $\nu$ (Aliph. CH), 3091  $\nu$ (Ar-H), 2229  $\nu$ (C≡N), 1588-1479  $\nu$ (Ar C=C), 1095-1010  $\nu$ (C-O-C), 995  $\nu$ (CH). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): ( $\delta$ : ppm): 7.71 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.41 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.35 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.30 (dd, *J* = 14.0, 2H, Ar-H), 7.27 – 7.21 (m, 1H, Ar-H), 6.75 (d, *J* = 16.0 Hz, 1H, =CH), 6.35 (dt, *J* = 16.0, 1H, CH=), 4.80 (dd, *J* = 5.9, 0.9 Hz, 2H, -CH<sub>2</sub>). MS (ESI), (*m/z*): 260.52 [M]<sup>+</sup>. For C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O Anal. Calc.: C, 78.46; H, 4.62; N, 10.77. Found: C, 78.28; H, 4.63; N, 10.74.

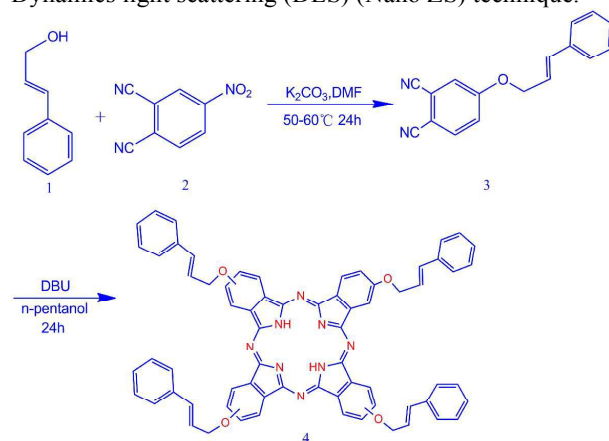
### Synthesis of tetra-(3-phenylprop-2-allyloxy) phthalocyanine (TPAO-Pc) (compound 4)

4-(3-phenylprop-2-allyloxy) phthalonitrile (compound 3) (0.205 g, 0.79 mmol) was dissolved in dry n-pentanol (5 mL). The reaction mixture was heated at 90 °C under N<sub>2</sub>, and then 0.44 mL DBU (0.80 mmol) was added to the mixture. The reaction mixture was refluxed for over night under N<sub>2</sub>. After cool down to room temperature, n-hexane (30 mL) was added to the mixed solution. The resulting precipitate was filtrated and washed successively with methyl alcohol, alcohol and ether, and then the product was dried. The raw product was purified with column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH (20/1, v/v) mixtures for elution to give dark green solid. Yield: 0.24 g, (29.1%), mp >300 °C. IR  $\nu_{\max}$ /(cm<sup>-1</sup>): 3475-3280 (-NH), 3090  $\nu$ (Ar-CH), 2965-2868  $\nu$ (Aliph. CH), 1721-1610  $\nu$ (C=C), 1602  $\delta$ (-NH), 1132  $\delta$ (C-N), 1093-1001  $\delta$ (C-O-C), 985  $\delta$ (CH), 758  $\delta$ (Ar-H). UV/Vis (dichloromethane):  $\lambda_{\max}$  nm (log  $\epsilon$ ) 730 (3.93), 693 (3.81). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): ( $\delta$ : ppm): 7.74-7.08 (m, 32H, Ar-H), 6.89– 6.67 (m, 4H, =CH), 6.36 (dt, 4H, CH=), 5.03 – 4.81 (m, 8H, -CH<sub>2</sub>). MALDI-TOF MS:

Calculated: 1043.22 [M]; Found: 1044.58 [M+H]<sup>+</sup>. For C<sub>68</sub>H<sub>50</sub>N<sub>8</sub>O<sub>4</sub> Anal. Calc.: C, 78.29; H, 4.83; N, 10.74. Found: C, 78.56; H, 4.81; N, 10.78.

### Characterization

The <sup>1</sup>H NMR (600 MHz) spectra were performed in CDCl<sub>3</sub> on a Bruker AVANCE III 600. MALDI-TOF mass spectrum was taken on a Bruker BIFLEX III ultra-high resolution. Elemental analysis was recorded on an Elementar Vario EL III instrument. The FT-IR spectra were recorded with a Nicolet 6700 Fourier transform infrared (FT-IR, Thermo Scientific) instrument using potassium bromide pellets. The UV-Vis spectra were measured on Hitachi U-3900H spectrophotometer. Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. TEM images of the aggregates were performed on a JEOL 1200EX electron microscopy (Japan). The size measurements of nanoaggregates were made by Dynamics light scattering (DLS) (Nano ZS) technique.



**Scheme 1** Synthetic route of novel tetra-(3-phenylprop-2-allyloxy) phthalocyanine (TPAO-Pc).

## Results and discussion

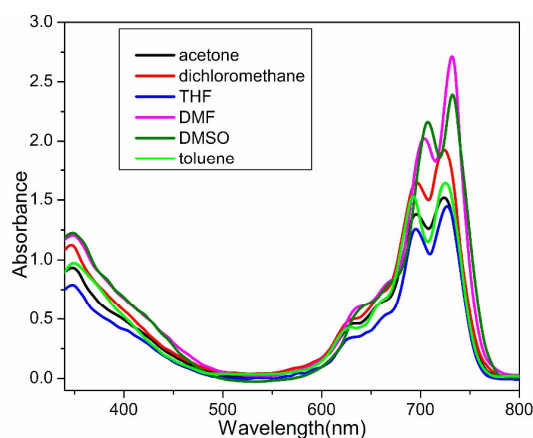
### Synthesis and Characterization of TPAO-Pc

The synthetic route of novel tetra-(3-phenylprop-2-allyloxy) phthalocyanine is depicted in Scheme 1. Nucleophilic aromatic nitro displacement reaction of 4-nitrophthalonitrile in dry DMF in the presence of K<sub>2</sub>CO<sub>3</sub> as base catalyst under N<sub>2</sub> atmosphere at about 60 °C for 24h has been carried out by many scientists.<sup>20,21</sup> This is accomplished by nucleophilic substitution of 4-nitrophthalonitrile in the presence of base as catalyst in dipolar aprotic solvent, such as DMF or DMSO.<sup>21,22</sup> In this respect, initial 4-(3-phenylprop-2-allyloxy) phthalonitrile (compound 3) was obtained from reaction between cinnamic alcohol (compound 1) and 4-nitrophthalonitrile (compound 2) in dry DMF at 55 °C. TPAO-Pc was synthesized based on typical procedures by processing the 4-(3-phenylprop-2-allyloxy) phthalonitrile in the existence of DBU in dry n-pentanol under N<sub>2</sub> atmosphere at 138 °C for 24h. In each case, the product was obtained as a mixture of four different possible isomers and purified by extraction and column chromatography.<sup>23</sup> The pure metal-free TPAO-Pc was obtained in a good yield. The MALDI-TOF mass spectra of TPAO-Pc exhibited intense signal corresponding to the molecular ion [M+H]<sup>+</sup>. The characterization of the compounds was also carried out by some other methods, including <sup>1</sup>H NMR, UV-Vis and FT-IR spectra. The proposed structures of the compounds were confirmed by

the results of these analyses.<sup>24</sup> The TPAO-Pc is soluble in lots of organic solvents, such as dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, acetone, ethanol, dichloromethane, dimethylsulfoxide (DMSO), pyridine, toluene and acetic ether.

### UV-Vis spectra of the TPAO-Pc

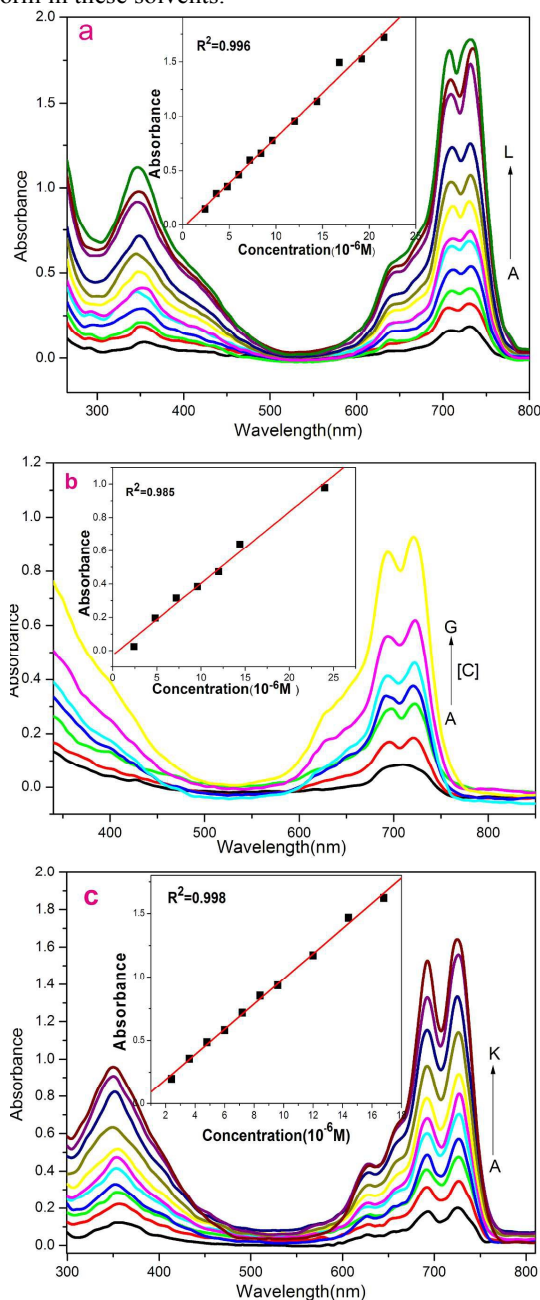
Phthalocyanines display typical two distinct regions in absorption spectra, one of them is called as the “B” or Soret band at about 300 nm and the other one is called as the “Q” band at 600-750 nm.<sup>25,26</sup> The Q band of the metal-free phthalocyanine was observed as splitted two bands due to  $D_{2h}$  symmetry, as  $Q_x$  and  $Q_y$  bands.<sup>27,28</sup> Fig.1 depicts the absorption spectra of metal-free TPAO-Pc in acetone, dichloromethane, THF, DMF, DMSO and toluene at the concentration of 24  $\mu\text{M}$ . The TPAO-Pc in these organic solvent exhibits splitting Q-bands with absorption maxima ( $\lambda_{\text{max}}$ ) at about 690 and 730 nm which is characteristic for metal-free phthalocyanines. The B or Soret absorption band for TPAO-Pc at near UV region is observed at  $\lambda_{\text{max}}$  342 nm. All these absorption spectra indicate that the monomeric phthalocyanines present in the above solution.



**Fig. 1** Absorption spectra of TPAO-Pc in dimethylformamide (DMF), tetrahydrofuran(THF), acetone, dichloromethane, DMSO and toluene. The measured concentration is 24  $\mu\text{M}$ .

Aggregation is usually described as a progressing of the compounds with coplanar association of rings from monomer to dimer and higher order complexes.<sup>29</sup> It depends on the property of the substituents, solvents and concentration, environmental temperature and type of coordinate metal ions.<sup>30-32</sup> The aggregation or self-assembly behavior of phthalocyanines in solution indicates the presence of interactions between the aromatic macrocycles and substituents. The formation of Pc aggregation could be investigated by the electronic absorption spectrum effectively.<sup>33</sup> For the formation of phthalocyanine aggregates, the maximum absorption peak exhibits a blue-shift or red-shift of the Q band with some decrease in intensity.<sup>34</sup> In this study, the self-assembly behavior of the TPAO-Pc was firstly investigated at different concentrations in dichloromethane, acetone, DMSO, ethanol, toluene and ethyl acetate. For examples, with the concentration range of  $2.4 \times 10^{-6} \sim 21.6 \times 10^{-6}$  M in DMSO, acetone and toluene (Fig. 2a, 2b and 2c), the intensity of the Q band increased with the increasing of the concentration and no new bands appeared due to the aggregates for the studied TPAO-Pc.<sup>30,33</sup> This indicated that the TPAO-Pc did not show aggregation in DMSO, acetone and

toluene in this concentration range. Beer-Lambert law was obeyed for TPAO-Pc in the concentrations range of  $2.4 \times 10^{-6} \sim 21.6 \times 10^{-6}$  M as shown in the inserts of Fig. 2. In the other organic solvents, Beer-Lambert law was also obeyed for TPAO-Pc in the measured concentration range (Fig. S3). It indicated that the presence of TPAO-Pc is mainly a monomeric form in these solvents.<sup>35</sup>

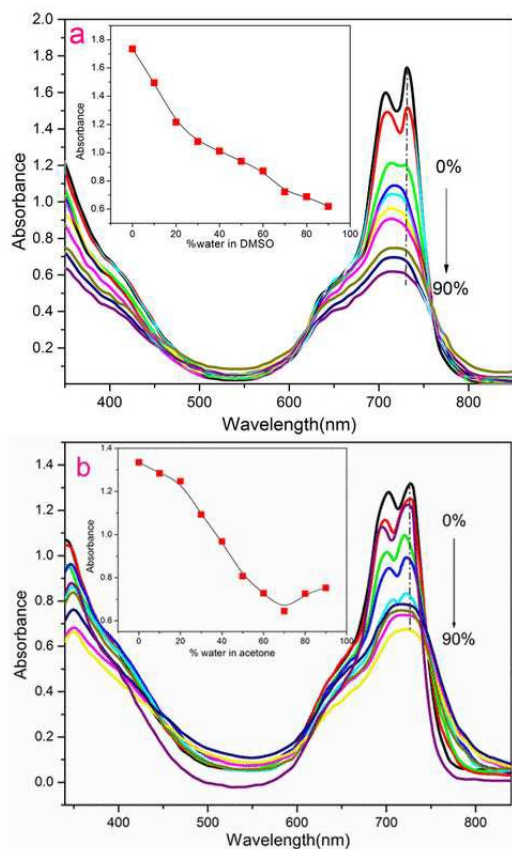


**Fig. 2** Absorption spectra changes of TPAO-Pc in DMSO (a), acetone (b) and toluene (c) at different concentrations:  $2.4 \times 10^{-6}$  (A),  $3.6 \times 10^{-6}$  (B),  $4.8 \times 10^{-6}$  (C),  $6.0 \times 10^{-6}$  (D),  $7.2 \times 10^{-6}$  (E),  $8.4 \times 10^{-6}$  (F),  $9.6 \times 10^{-6}$  (G),  $12 \times 10^{-6}$  (H),  $14.4 \times 10^{-6}$  (I),  $16.8 \times 10^{-6}$  (J),  $19.2 \times 10^{-6}$  (K),  $21.6 \times 10^{-6}$  M (L). (Insets: Plot of absorbance versus concentration in Q-band.)

The aggregation behavior of TPAO-Pc was subsequently studied by mixing the DMSO and acetone solutions of TPAO-Pc with water in various volume ratios (10:0~1:9(v/v)). As a



result of solvent effect, the electronic spectra of the TPAO-Pc in mixed solutions showed some differences with those in DMSO and acetone. As shown in Fig. 3a, the absorption intensity at 728 nm decreased with an increase in water volume percent in DMSO/water mixed solutions (concentration of the solutions was kept constant at  $19.2 \times 10^{-6}$  M for all tested ratios) and a blue-shift of the Q-band. However, in acetone/water mixed solutions, the absorption intensity at 723 nm decreased with the increasing water percentage from 0 to 70% and increased when the water percentage was larger than 70% (Fig. 3b). The Q band of TPAO-Pc in acetone/water mixed solutions also showed a slight blue-shift. In DMSO/water and acetone/water mixed solutions, the well-defined Q bands of TPAO-Pc at about 705 and 725 nm disappeared, while a broad absorption band appeared,<sup>36</sup> which was promoted by the addition of water.<sup>37</sup> On the basis of Kasha's rule,<sup>38</sup> a blue-shift in the Q bands of TPAO-Pc upon aggregation, which is a sign of the effective intermolecular interaction of TPAO-Pc, typically. This indicates the formation of the H-aggregate and revealing face-to-face molecular self-assembly in DMSO/water and acetone/water.

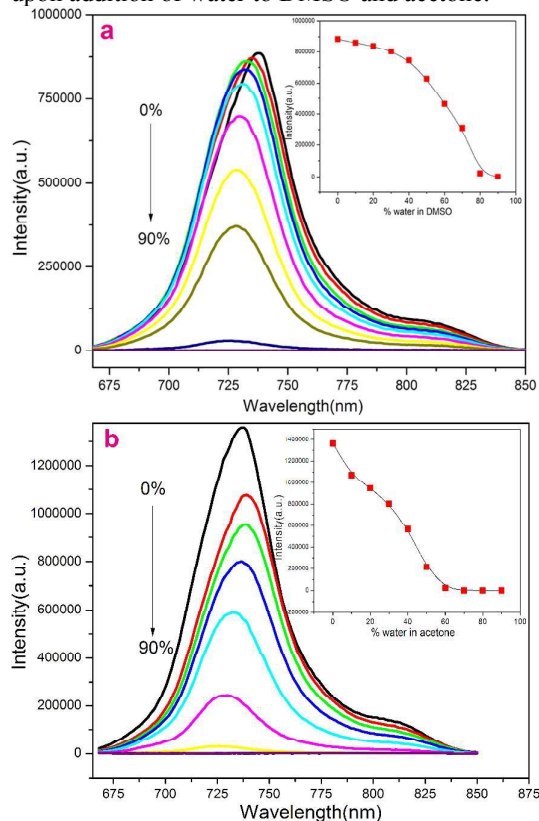


**Fig. 3** Absorption spectra of TPAO-Pc in DMSO/water (a) and acetone/water (b) mixed solvent with different volume ratios (10:0 ~ 1:9 (v/v)). Concentration of the sample was kept at  $19.2 \times 10^{-6}$  M. Inset: Dependence of absorption intensity in Q-band on the percentage of water.

#### Fluorescence spectroscopy of the TPAO-Pc

Fluorescence spectroscopy can also be used as a method to investigate the formation of aggregates in phthalocyanine systems, since the formation of aggregate results in significant quenching of fluorescence.<sup>39,40</sup> The fluorescence emission

spectrum of TPAO-Pc was monitored as increasing the percentage of water in the DMSO/water and acetone/water mixtures. The fluorescence spectra of TPAO-Pc in DMSO/water (a) and acetone/water (b) obtained at an excitation wavelength of 660 nm and 658 nm are displayed in Fig. 4. Concentration of the sample was kept at  $19.2 \times 10^{-6}$  M. The fluorescence band with a maximum at 735 nm (a) and 737 nm (b) is observed. And the intensity decreases down to baseline without the appearance of a new emission band,<sup>37</sup> which suggests that the new species formed is non-fluorescent. The emission bands of TPAO-Pc in DMSO/water and acetone/water (v/v, 1/9) are broadened and blue-shifted about 10 nm compared to those from TPAO-Pc in DMSO and acetone (DMSO/water and acetone/water, v/v, 1/0). Fluorescence quantum yields ( $\Phi_f$ ) are determined by using zinc phthalocyanine ( $\Phi_f=0.3$ ) in DMF as a standard.<sup>41</sup>  $\Phi_f$  for TPAO-Pc decreased dramatically to 0.0015, 0.0012 in DMSO/water, acetone/water (1/9, v/v) from 0.20, 0.25 in DMSO and acetone, respectively. The significant fluorescence quenching and emission bands blue-shift is observed for TPAO-Pc in DMSO/water and acetone/water, indicating the formation of H-aggregates with strong intermolecular interactions of the phthalocyanine molecules. These observations are consistent with the investigation of absorption spectra on the H-aggregates upon addition of water to DMSO and acetone.



**Fig. 4** Changes in the emission spectrum of TPAO-Pc ( $19.2 \times 10^{-6}$  M) seen upon the addition of different content of water in DMSO (a) and acetone (b) (the ratio of DMSO/water and acetone/water is from 10:0 to 1:9 (v/v)); excitation at 660 nm (a) and 658 nm (b). Inset: Dependence of fluorescence intensity on the content of water in the mixed solutions.

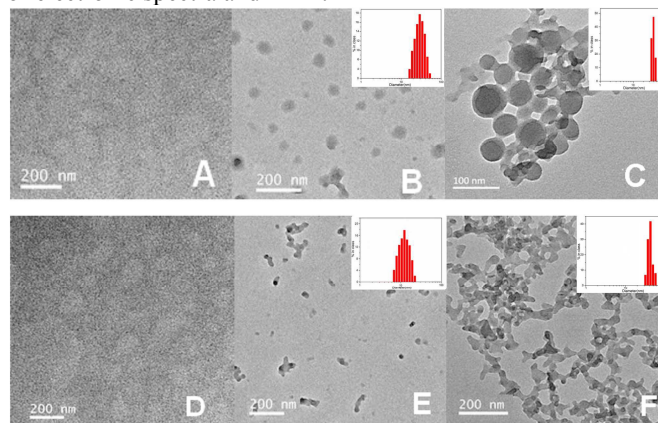
#### Morphology of Self-Assembled TPAO-Pc in Solution

The absorption and fluorescence spectra of TPAO-Pc in DMSO/water and acetone/water mixed solvents are indicative of its strong tendency of aggregation. It is interesting to know whether these microscopic intermolecular interaction patterns that result in the aggregation of TPAO-Pc are really reflected by the macroscopic superstructures.<sup>42</sup> Using Transmission Electron Microscopy (TEM) and Scanning electron microscopy (SEM) could investigate directly the morphology of self-assembled TPAO-Pc in solution. As seen from the TEM image (Fig. 5C), the TPAO-Pc molecules assemble into core-shell nanospheres with a diameter of ca.  $50 \pm 10$  nm in DMSO/water after 12 hour of aggregation, and the SEM image in Fig. S4a shows that the TPAO-Pc molecules assemble into non-solid nanospheres. When the solvent is changed to acetone/water, further change in the morphology of the nanostructure of self-assembled is observed, revealing the solvent effect on the formation of self-assembled nanoscale aggregates. As shown in TEM and SEM image (Fig. 5F and Fig. S4b), after 12 hour of aggregation, molecules of TPAO-Pc self-assemble into nanostructures with dendritic morphology with a length from 600 to 200 nm and a width from 40 to 20 nm. To investigate the process of self-assemble nanostructure growth in more detail, the TPAO-Pc self-assemblies formed in DMSO/water (from Fig. 5A to 5C) and acetone/water (from Fig. 5D to 5F) with different aggregation time was studied by TEM. As shown in Fig. 5A, there are no distinct nano-aggregates formed in DMSO/water and acetone/water after five minutes of aggregation. As the self-assembly time was increased to 1 h, the spherical-like nano-aggregates were formed in DMSO/water with an average diameter of  $40 \pm 10$  nm (Fig. 5B). And the small belt-like nano-aggregates was formed in acetone/water (Fig. 5E) with about 20–30 nm in length and 10–20 nm in width. The  $\pi$ - $\pi$  stacking and H-bond promotes the growth of aggregates. Along with aggregation time prolonged to 12 h, the core-shell nano-spherical and dendritic structure was formed in DMSO/water and acetone/water, respectively. DLS was also used for characterization of the diameter sizes of the TPAO-Pc nano-aggregates formed in DMSO/water and acetone/water. The spectra were analyzed for particle size distribution using the CONTIN algorithm<sup>43</sup>. The corresponding size intensity weighted size distribution was shown in the insets of Fig. 5B, 5C, 5E and 5F. The distribution of nano-aggregates formed in DMSO/water showed the diameter in the range of 19–55 nm and 35–55 nm with the center at 30 and 40 nm (Fig. 5B and 5C). And the distribution of nano-aggregates formed in acetone/water showed the diameter in the range of 8–22 nm and 30–55 nm with the center at 12 and 45 nm (Fig. 5E and 5F). These results were along with those by TEM measurements. Accordingly, the morphology and size of the TPAO-Pc core-shell nanospheres and dendritic self-assemblies was related with the selected solvent conditions and the aggregation time.

#### FT-IR spectra of TPAO-Pc and Self-Assemblies

The TPAO-Pc and its self-assembled nanostructures formed in DMSO/water and acetone/water was also studied by FT-IR spectra.<sup>42</sup> As shown in Fig. S5, most vibration bands observed in the FT-IR spectra of the nanoscale aggregates can be found in the spectrum of TPAO-Pc, which unambiguously confirms the formation of corresponding aggregates. In the FT-IR spectrum of monomeric TPAO-Pc (Fig. S5A in the Supporting Information), two absorptions at approximately 1134 and 1032  $\text{cm}^{-1}$  are assigned to  $\delta$  (C-N) and  $\delta$  (C-O-C) bending vibration, respectively. Similar absorption peaks at 1131, 1132  $\text{cm}^{-1}$  and 1044, 1025  $\text{cm}^{-1}$  are also observed in the FT-IR spectra of self-

assemblies fabricated from TPAO-Pc in DMSO/water and acetone/water mixed solutions (see Fig. S5B and 5C in the Supporting Information). It is worth noting that the broad absorption peak appeared at about 3475  $\text{cm}^{-1}$  for TPAO-Pc (Fig. S5A) due to the -NH stretching vibration, which is clearly broadened and shifted lower frequency (3372 and 3385  $\text{cm}^{-1}$ ) in the self-assembled nanostructures formed in acetone/water and DMSO/water.<sup>44-46</sup> This indicates the formation of H-bonds between the -NH in one TPAO-Pc molecule and =N- in other one TPAO-Pc molecule in the nanostructure. In particular, the FT-IR spectrum of TPAO-Pc self-assemblies formed in DMSO/water has some difference with self-assemblies in acetone/water. It is also revealed that the solvents have a great influence on the formation of TPAO-Pc self-assembled nanostructures and these results are consistent with the results of electronic spectra and TEM.

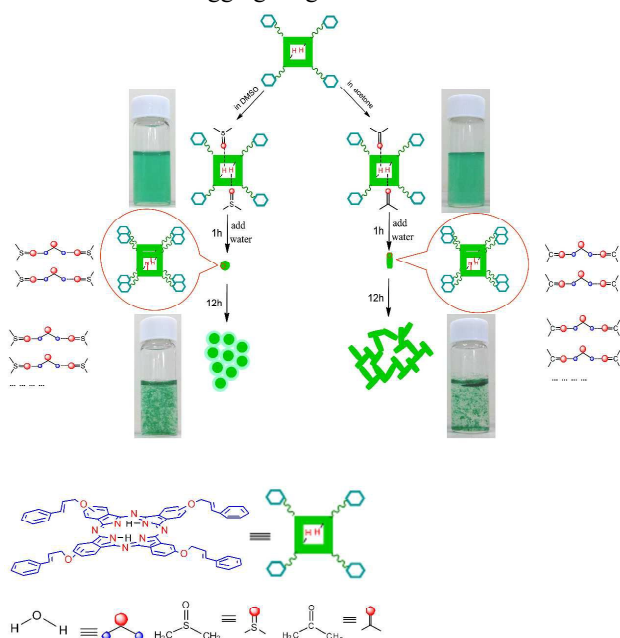


**Fig. 5** TEM images of the morphologies self-assembled from DMSO/water after (A) 5 min, (B) 1h, (C) 12 h, and acetone/water after (D) 5 min, (E) 1h, (F) 12 h. The sample was prepared by dripping a drop of DMSO/water and acetone/water mixed solution on copper grid, and then the solvent was quickly evaporated under vacuum. Inset: DLS results for TPAO-Pc in DMSO/water and acetone/water (B, C, E and F).

#### Mechanism of Self-Assemblies

Based on the results of UV-Vis, fluorescence and TEM described above, the formation process of the core-shell nanospheres in DMSO/water and dendritic nanostructure in acetone/water was illustrated (Fig. 6). The UV-Vis depended on the concentration of TPAO-Pc did not show the self-assemblies formed in DMSO and acetone, which was possibly caused by the formation of intermolecular hydrogen bonding between the molecules of TPAO-Pc and DMSO, acetone. Each TPAO-Pc molecule was possibly bound with two DMSO or acetone molecules via hydrogen bonding, leading to a relatively large intermolecular distance for the formation of self-assemblies. Therefore, TPAO-Pc was stable in DMSO and acetone. After mixing the DMSO and acetone solutions of TPAO-Pc with water, the water molecules would be linked with the DMSO and acetone molecules to form more stable hydrogen bonding, thus resulting in the disruption of the hydrogen bonding existing in the TPAO-Pc and DMSO, acetone molecules. As a result, TPAO-Pc molecules connect adjacent TPAO-Pc molecules into a face-to-face stacking supramolecular structure

(H-aggregates) depending on the H-bond and  $\pi$ - $\pi$  interaction. After 1 h aggregation, the intermolecular interaction and the accumulation of surface free energy promoted to the growth of the small nano-aggregates. With increasing of the aggregation time, adjacent small nano-aggregates attached together gradually. Finally, the small nano-aggregates would construct well-defined core-shell nanospheres and dendritic nanostructure after 12 h, which were the most stable morphology as shown in Fig. 5C and 5F. Accompanied by the information deduced from the UV-Vis, fluorescence and IR spectra, the formation of nanoscale self-assemblies morphological transitions were mainly due to the influence of hydrogen bonding and  $\pi$ - $\pi$  stacking formed in neighboring phthalocyanine molecules. The formation process of TPAO-Pc core-shell nanospheres in DMSO/water was the same as dendritic nanostructure in acetone/water, while the morphologies of the synthesized phthalocyanine nanoaggregates were affected by the selected solvent and/or the aggregating time.



**Fig. 6** Schematic illustration for the formation process of core-shell nanospheres and dendritic nanostructure of TPAO-Pc self-assemblies in DMSO/water and acetone/water.

## Conclusions

In summary, the novel metal-free Tetra-(3-phenylprop-2-allyloxy) phthalocyanine (TPAO-Pc) was successfully synthesized and the self-assembly properties was also investigated. TPAO-Pc exhibits excellent solubility in most organic solvents without aggregation. But TPAO-Pc shows aggregation tendency in DMSO/water and acetone/water mixed solutions in the concentration range of about  $10^{-6}$ M, indicating the formation of “face-to-face” stacking mode self-assemblies. Further comparative investigation on the self-assembly behavior of TPAO-Pc reveals the formation of core-shell nanospheres self-assemblies in DMSO/water. However, TPAO-Pc self-assembles into dendritic nanostructure in acetone/water. These results imply the solvent effect on the morphology of nanoscale self-assemblies. The driving force for the formation

of nano-aggregates is proposed to be the intermolecular H-bond in cooperation with  $\pi$ - $\pi$  interaction between TPAO-Pc molecules. In addition, the core-shell nanospheres and dendritic nanostructure described in this work may be used to design nanostructured materials with excellent catalytic, electric and organic properties.

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## Notes and references

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