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Fabrication and morphology control of the electrostatic self-assembled system containing porphyrin electrolytes and sulfonated fullerene derivatives

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Fabrication and morphology control of the electrostatic self-assembled system containing porphyrin electrolytes and sulfonated fullerene derivatives

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A series of water-soluble porphyrin electrolytes with quaternary ammonium ions side chains (TEMZnPN and THMZnPN) and sulfonated fullerene derivatives were synthesised and characterised. The self-assembled system was fabricated through the electrostatic interaction between the quaternary ammonium ions on the porphyrin derivatives and the sulfonic ions on the fullerene derivatives. The optical properties of the self-assembled system in aqueous solution were recorded by ultraviolet–visible and fluorescence spectroscopy. Scanning electron microscopy indicated that the morphology of the self-assembled films was highly relative to the distance between the quaternary ammonium ions and the porphyrin core, which could be easily adjusted by changing the length of the alkyl chain in the porphyrin derivatives.

Keywords: porphyrin; fullerene; electrostatic; self-assembled; electrolyte

Introduction

Self-assembly of organic molecules is one of the most efficient approaches to obtain supramolecular nanostructures with controlled dimensions and specific functions (*1–5*). The as-prepared supramolecular materials can be used in many fields, such as optoelectronic devices (*6*, *7*), drug delivery systems (*8*), hydrogels (*9*, *10*) and sensors (*11–14*). The assembly strategies of the supramolecular systems rely on the presence of many different types of weak interactions, including magnetic force (*15–17*), host–guest coordination (*18*), van der Waals force (*19–22*), hydrogen bonding (*23–27*), electrostatic (*28–32*) and hydrophilic–hydrophobic interactions (*33*, *34*). Among these various interactions, electrostatic force is one of the most versatile interactions to mediate the structure of self-assembled systems (*35*). The electrostatic self-assembled system could be fabricated through not only alternating deposition of oppositely charged rigid planar molecules on the surface of the substrates (*36*), but also mixing the molecules with opposite charges in solution (*37*). Furthermore, the morphology and the physical properties of the electrostatic self-assembled systems could be tuned by means of modifying the chemical structures of the charged components or changing the external environment of the system (*38*). For example, Grohn's group reported a variety of electrostatic assemble systems with different shapes ranging from spheres to rods, networks and vesicles (*39*), and the formation of nano assemblies could respond to external stimuli such as the change of the PH value in the solution environment (*40*) or the wavelength of the excitation light (*41*). Ouyang's group reported the fabrication and enhanced nonlinear optical properties of electrostatic self-assembled film containing water-soluble chiral poly(phenylenevinylene)s and oligo-thiophene derivatives (*42*).

The supramolecular system containing porphyrins and fullerenes, owing to their characteristic structural features, have always attracted great interest in the formation of self-assembled complex (*43–47*). However, the studies on the electrostatic self-assembled system containing porphyrin and fullerene derivatives are relatively rare (*48*). Herein, we investigated an electrostatic self-assembled system utilising porphyrin electrolytes with quaternary ammonium salts side chains and fullerene sulfonic sodium salts. As shown in Figure 1, the porphyrin and fullerene derivatives could form the electrostatic complex through the interaction of the side chains with opposite charges. Specifically, the distance between the quaternary ammonium groups and the porphyrin core could be tuned by changing the length of the alkyl-connecting chain. So that the optical properties and the expected morphology of the electrostatic self-assembled system would be adjusted. This could be approved by the different titration curves of absorption and fluorescence spectra and the scanning electron microscopy (SEM) images of the supramolecular systems.

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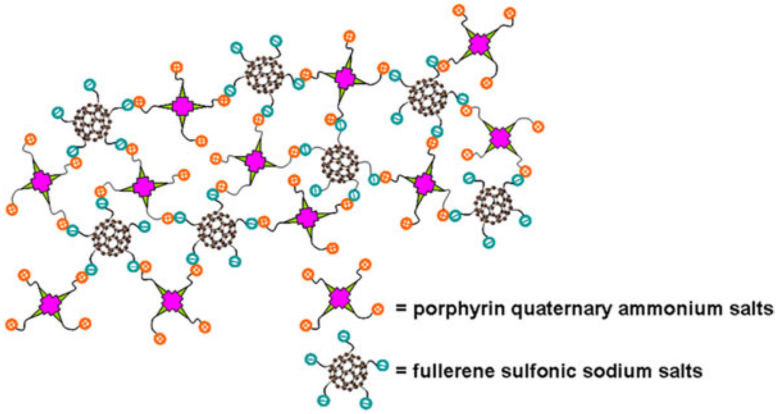
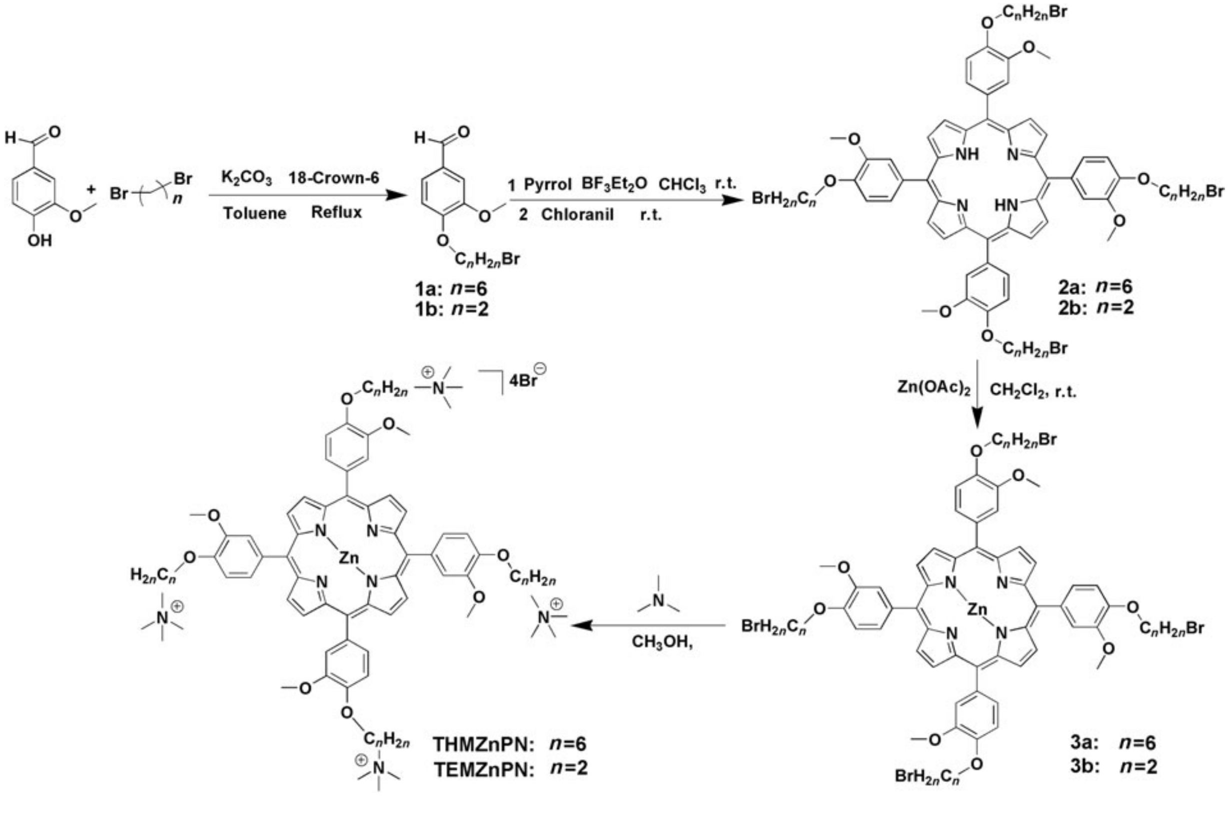


Figure 1. (Colour online) Formation of the electrostatic self-assembled system based on the porphyrin electrolytes and fullerene sulfonic sodium salts.

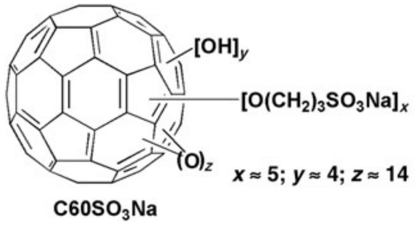
Results and discussion

Synthesis

As shown in Scheme 1, vanillin was reacted with three times equivalent of 1,2-dibromoehtane and 1,6-dibromohexane catalysed by potassium carbonate and 18-crown-6 to afford compounds **1a** and **1b**, respectively (*49*). The porphyrin derivatives **2a** and **2b** were conveniently synthesised through condensation of **1a** and **1b** with pyrrole at the aid of catalysed amount of borontrifluoride diethyl etherate in chloroform, respectively (*18*). The porphyrin electrolytes with quaternary ammonium salts side chains THMZnPN and TEMZnPN were prepared based on the typical reaction between the alkyl bromides and amine (*50*). The quaternisation reaction was completed which was proved by the ^{1}H NMR of the products (Figures S1 and S2). The fullerene Sulfonic Sodium Salts C60SO$_3$Na (Scheme 2) were synthesised referring to the reported procedure (*51*). The products were characterised by ^{1}H NMR, ^{13}C NMR and high-resolution



Scheme 1. Synthesis route of porphyrin derivatives.



Scheme 2. The chemical structure of fullerene derivatives.

mass spectra (HRMS). Both the porphyrin and the fullerene electrolytes had good solubility in aqueous solution.

Optical properties

Figure 2 shows the absorption spectra change of porphyrin derivatives in aqueous solution upon adding different ratios of C60SO$_3$Na at room temperature. As shown in Figure 2(a), the absorption spectrum of TEMZnPN without C60SO$_3$Na had one strong Soret band at 426 nm and two Q-band peaks at 560 and 601 nm. The maximum for the Soret band shifted to longer wavelength and the absorbance reduced with the addition of C60SO$_3$Na. Meanwhile, a shoulder peak at 443 nm appeared and the absorbance enhanced with the increasing concentration of the C60SO$_3$Na in the solution. Consequently, a tight isobestic point at 434 nm was displayed. A similar changing trend of absorption spectra was found in the case of THMZnPN, except that a relatively smaller change amplitude was found compared with that of TEMZnPN while adding the same amount of C60SO$_3$Na (Figure 2 (b)). The plots of the absorption change at 426 nm versus C60SO$_3$Na concentration indicating the existence of the limiting values for both TEMZnPN and THMZnPN (see Figure S3). In the case of TEMZnPN, the curve was convergent at 0.21 when 1.2 equiv. of C60SO$_3$Na was added; in the case of THMZnPN, the curve was convergent at 0.33 when 2.4 equiv. of C60SO$_3$Na was added. The above results indicated the existence of interaction between the porphyrin electrolytes and the fullerene sulfonic sodium salts in the ground state (*52*).

As shown in Figure 3(a), the fluorescence spectrum of pure compound **TEMZnPN** in aqueous solution showed maximum peak at 614 nm with a shoulder peak at around 660 nm. On addition of C60SO$_3$Na, the fluorescence intensity of the TEMZnPN decreased, which confirmed the formation of electrostatic self-assembled complex (*18*). The similar fluorescence quench was found in the case of THMZnPN (Figure 3(b)). Interestingly, the quench of TEMZnPN was much more efficient than that of THMZnPN with adding the same amount of C60SO$_3$Na in the solution, which was well consistent with the changing trend of the absorption spectra.

The Stern–Volmer plots constructed from the fluorescence quenching data are shown in Figure 3(c). For both the porphyrin electrolytes with different lengths of side chains, the Stern–Volmer plots were linear at low quencher concentrations ($<0.8\ \mu$M), which suggested that the excited-state porphyrin was deactivated upon a diffusive encounter with fullerene (*53*). It should be noted that the static quenching constant (K_{sv}) for TEMZnPN was $6.32 \times 10^5\ \mathrm{M}^{-1}$, which was 3.7 times larger than K_{sv} for THMZnPN (Figure 3(c), inset). The result meant that the TEMZnPN/C60SO$_3$Na complex had higher stability than that of THMZnPN/C60SO$_3$Na (*54*). Considering the only difference between the two electrostatic systems that was the distance between the porphyrin core and the quaternary ammonium function groups, we could conclude that the length of the alkyl-connecting chain played a key role in affecting the Ksv of our self-assembled system. The length of TEMZnPN side chain was shorter than that of THMZnPN, thus TEMZnPN was more exposed to fullerene, while with a longer side chain the steric effect would prevent fullerene from approaching THMZnPN.

As the concentration of the C60SO$_3$Na increased, the Stern–Volmer plots (Figure 3(c)) for both TEMZnPN and

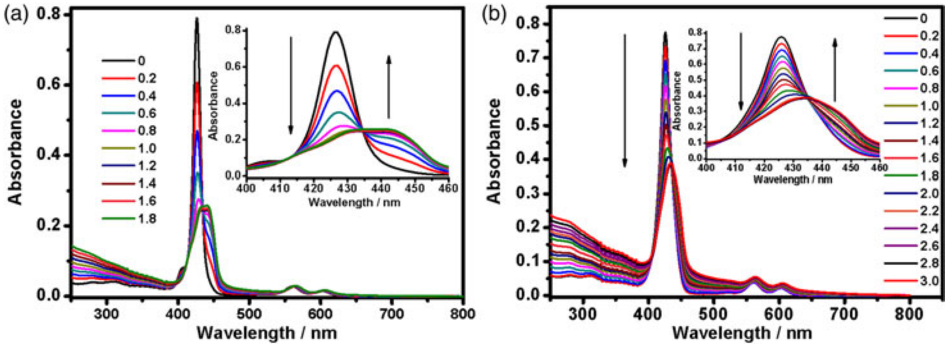


Figure 2. (Colour online) (a) Changes in the UV–vis absorption spectra of TEMZnPN upon adding different ratio of C60SO$_3$Na in aqueous solution (0.2–1.8 equiv.). (b) Changes in the UV–vis absorption spectra of THMZnPN upon adding different ratio of C60SO$_3$Na in aqueous solution (0.2–3.0 equiv.). [TEMZnPN or THMZnPN] $= 2.0 \times 10^{-6}$ M. [C60SO$_3$Na] $= 2.0 \times 10^{-4}$ M.

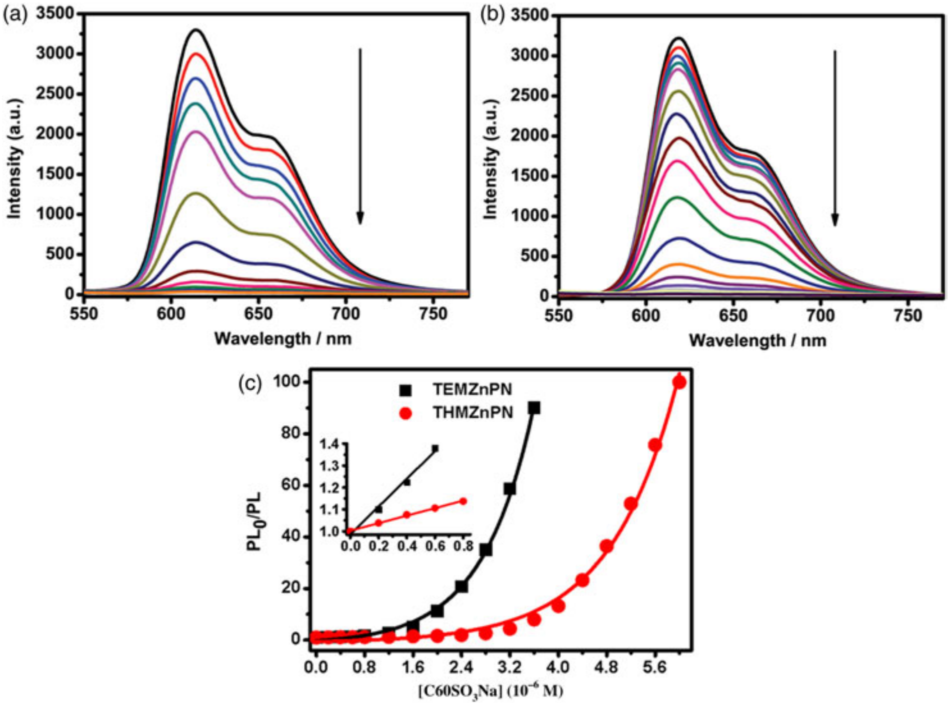


Figure 3. (Colour online) (a) Steady-state fluorescence spectra of TEMZnPN (2.0×10^{-6} M) with the increasing addition of $C60SO_3Na$ (2.0×10^{-7}–3.6×10^{-6} M). (b) Steady-state fluorescence spectra of THMZnPN (2.0×10^{-6} M) with the increasing addition of $C60SO_3Na$ (2.0×10^{-7}–6.0×10^{-6} M). (c) Stern–Volmer plots for the fluorescence quenching of TEMZnPN (square) at 614 nm and THMZnPN (circle) at 618 nm by $C60SO_3Na$ (curves are fitted using the modified Stern–Volmer equation, PL represents the fluorescence intensity at a given quencher concentration; PL_0 represents the initial fluorescence intensity in the absence of quencher); inset: low quencher concentration region and linear static Stern–Volmer fittings.

THMZnPN become superlinear. The upward deviation of the plots indicated that the quenching was more effective with a dramatically increased K_{sv} value, which reflected a contribution of static quenching to the dynamic quenching of the porphyrin by fullerene according to the previous similar reported study on the electrostatic self-assembled systems (*55–57*). As the concentration of fullerene increased, a network of stronger electrostatic complex was formed, leading to an additional increase in the quenching constant (K_{SV}), which was the reason for the deviation from the Stern–Volmer relationship. It should also be noted that the quenching constant (K_{SV}) for TEMZnPN was still larger than that for THMZnPN, which should be also attributed to that a shorter side chain could assist the rapid exciton diffusion from porphyrin core to fullerene more effectively, thus facilitating the static quenching.

The control experiments with 1,6-naphthalenedisulfonic acid disodium salt as the reference compound. The titration curves of absorption (Figure S4) and fluorescence spectra (Figure S5) proved the formation of electrostatic self-assembled systems while adding the aqueous solution of 1,6-naphthalenedisulfonic acid disodium salt; however, the change amplitude of the spectra was much lower than that with $C60SO_3Na$ as quencher, which was due to the lack of fullerene moiety and the decreased number of sulfonic acid sodium salt in the reference compound.

The morphologies of self-assembled films

Figure 4(a) and (b) presented the morphology of the film prepared through dropping the aqueous solution containing TEMZnPN and $C60SO_3Na$ on the silicon wafer substrate. A flower-like morphology was obtained with diameters in the range of 50–200 nm. Interestingly, under the same experimental conditions, the film containing THMZnPN and $C60SO_3Na$ showed a fibre-like morphology with diameters in the range of 50–100 nm (Figure 4(c) and (d)). These results indicated that the morphology of the electrostatic self-assembled system could be tuned by altering the length of the alkyl-connecting chain in the porphyrin electrolyte. The morphology change could be ascribed to the binding constant difference between the porphyrin electrolytes with different side chains and fullerene sulfonic sodium salts.

Conclusion

A series of porphyrin derivatives with quaternary ammonium salts groups have been synthesised and

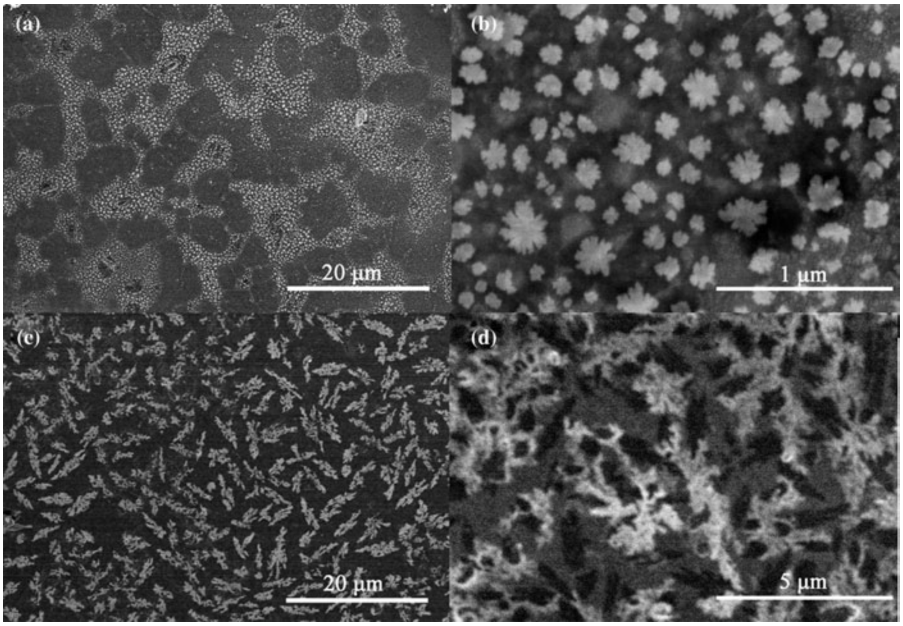


Figure 4. SEM images of the self-assembled film containing the fullerene derivatives $C60SO_3Na$ and the porphyrin derivatives TEMZnPN in large scale (a) and small scale (b). FE-SEM images of the self-assembled film containing the fullerene derivatives $C60SO_3Na$ and the porphyrin derivatives THMZnPN in large scale (c) and small scale (d).

characterised. The electrostatic self-assembled system containing the porphyrin electrolytes and the fullerene sulfonic sodium salts was fabricated. The absorption spectra results indicated the existence of interaction between the two chromophores in the ground state. On addition of $C60SO_3Na$ to the aqueous solution containing porphyrin derivatives, the fluorescence intensity of both TEMZnPN and THMZnPN decreased. The different quenching rate of the two porphyrin electrolytes indicated that the length of the alkyl-connecting chain between the porphyrin chromophore core and the quaternary ammonium functional groups played a key role in affecting the binding constant of self-assembled system. The SEM results indicated that the morphology of the electrostatic self-assembled system could also be tuned by altering alkyl-connecting chain in the porphyrin electrolyte. Our work provided a strategy to tune the optical property and morphology of the electrostatic self-assembled system.

Experimental

Materials

All reagents were bought from commercial sources and were used without further purification. The solvents were purified with standard methods. Silica gel (200–300 mesh) was used for column chromatography. The products were characterised by ^1H NMR, ^{13}C NMR and electrospray ionisation (ESI) HRMS.

Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer (Bruker, Bremen, Germany). ESI mass spectrometric measurements were carried out on AB SCIEX 4000 QTRAP in positive ion mode (Agilent, Santa Clara, CA, USA). Ultraviolet–visible (UV–vis) spectra were measured on a Varian Cary 50 spectrophotometer (Varian, Palo Alto, CA, USA). Fluorescence spectra were recorded on a HJY-FluoroMax-4-NIR spectrofluorometer (Horiba, Bensheim, Germany). The emission spectra (500–800 nm) were taken with excitation at 426 nm. The optical titration experiment was carried out as follows: TEMZnPN or THMZnPN was dissolved in distilled water to prepare the aqueous solution of porphyrin derivatives, in which the concentration of the solution was 2.0×10^{-6} M. For each addition in the absorption spectra measurement, 5 μL of aqueous solution of $C60SO_3Na$ (2.0×10^{-4} M) was added into 2.5 mL of aqueous solution of TEMZnPN or THMZnPN (the adding ratio is 0.2 equiv. of $C60SO_3Na$ to 1 equiv. of TEMZnPN or THMZnPN for each addition, respectively). The similar procedure was followed in the fluorescence spectra measurement except that 2.5 μL of aqueous solution of $C60SO_3Na$ (2.0×10^{-4} M) was added to the anterior four times additions to investigate the quenching of fluorescence at low concentration of $C60SO_3Na$. Field emission scanning electron microscopy (FE-SEM) images were taken on a JSM 6700F NT instrument (Hitachi, Tokyo, Japan). The sample was prepared as follows: 0.1 mL of the aqueous solution containing porphyrin electrolyte and $C60SO_3Na$ was dropped on the surface of silicon wafer substrate ([porphyrin electrolyte, $C60SO_3Na$] = 2.0×10^{-6} M). The sample was dried in oven at room temperature for 48 h before measurement.

Synthesis of 4-(6-bromohexyloxy)-3-methoxybenzaldehyde (1a)

Vanillin (15.2 g, 0.1 mol), 1,6-dibromohexane (72.3 g, 0.3 mol), potassium carbonate (13.8 g, 0.1 mol) and 18-crown-6 (2.64 g, 10 mmol) were added in 500 mL of toluene and refluxed for 48 h. The reactant mixture was allowed to cool to the room temperature and filtered. The filtrate was evaporated to remove the 1,6-dibromohexane and toluene. The residue was purified by a silica column (chloroform as eluent) to afford **1a** as white solid (23.7 g, 75.5%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 9.86 (s, 1H), 7.46 (dd, $J_1 = 8.17$ Hz, $J_2 = 1.75$ Hz, 1H), 7.43 (d, $J = 1.75$ Hz, 1H), 6.98 (d, $J = 8.17$ Hz, 1H), 4.13 (t, $J = 6.60$ Hz, 2H), 3.95 (s, 3H), 3.44 (t, $J = 6.60$ Hz, 2H), 1.95–1.89 (m, 4H), 1.58–1.51 (m, 4H).

Synthesis of 4-(2-bromoethoxy)-3-methoxybenzaldehyde (1b)

Vanillin (15.2 g, 0.1 mol), 1,2-dibromoethane (55.8 g, 0.3 mol), potassium carbonate (13.8 g, 0.1 mol) and 18-crown-6 (2.64 g, 10 mmol) were combined under experimental conditions identical to that for the synthesis of **1a** to get **1b** as white solid (21.0 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 9.89 (s, 1H), 7.48–7.45 (m, 2H), 7.01 (d, $J = 7.90$ Hz, 1H), 4.44 (t, $J = 6.60$ Hz, 2H), 3.96 (s, 3H), 3.72 (t, $J = 6.60$ Hz, 2H).

Synthesis of 5,10,15,20-tetra(4-(6-bromohexyloxy)-3-methoxyphenyl)porphyrin (2a)

A solution of compound **1a** (3.14 g, 10 mmol) and pyrrole (670 mg, 10 mmol) in dry $CHCl_3$ (260 mL) was purged with nitrogen for 30 min, and then 64 µL of borontrifluoride diethyl etherate was added. The solution was stirred for 2 h at room temperature, and chloranil (487 mg, 2 mmol) was added. The mixture was stirred overnight, and then the solvent was removed. Column chromatography on silica gel with chloroform as the eluent afforded the pure product as purple solid (457 mg, 12.6%). ^{1}H NMR (600 MHz, $CDCl_3$):δ 8.92 (s, 8H), 7.80 (s, 4H), 7.75 (d, $J = 7.90$ Hz, 4H), 7.25 (d, $J = 7.90$ Hz, 4H), 4.35 (t, $J = 6.60$ Hz, 8H), 3.99 (s, 12H), 3.53 (t, $J = 6.60$ Hz, 8H), 2.13–1.99 (m, 16H), 1.75–1.65 (m, 16H), −2.72 (s, 2H). 1^{13}C NMR ($CDCl_3$):δ 155.3, 150.6, 147.1, 144.3, 131.8, 125.7, 122.1, 117.5, 115.2, 113.6, 102.5, 61.4, 56.5, 33.1, 32.0, 30.4, 27.3, 24.5.

Synthesis of 5,10,15,20-tetra(4-(2-bromoethoxy)-3-methoxyphenyl)porphyrin (2b)

Compound **1b** (2.60 g, 10 mmol), pyrrole (670 mg, 10 mmol), borontrifluoride diethyl etherate (64 µL) and chloranil (487 mg, 2 mmol) were reacted in $CHCl_3$ (260 mL) following the experimental conditions identical to that for the synthesis of **2a** to obtain **2b** as purple solid (436 mg, 14.3%). ^{1}H NMR (600 MHz, $CDCl_3$):δ 8.91 (s, 8H), 7.82 (s, 4H), 7.77 (d, $J = 7.90$ Hz, 4H), 7.31 (d, $J = 7.90$ Hz, 4H), 4.67 (t, $J = 6.60$ Hz, 8H), 4.00 (s, 12H), 3.92 (t, $J = 6.60$ Hz, 8H), −2.75 (s, 2H). ^{13}C NMR ($CDCl_3$):δ 155.4, 150.8, 147.2, 144.5, 131.9, 125.7, 122.0, 117.7, 115.6, 113.5, 102.5, 61.5, 56.7, 27.2.

Synthesis of zinc complex of 5,10,15,20-tetra(4-(6-bromohexyloxy)-3-methoxyphenyl)porphyrin (3a)

Saturated zinc acetate dihydrate solution in methanol (10 mL) was added to a solution of compound **2a** (400 mg, 0.28 mmol) in chloroform (60 mL). The mixture was stirred at room temperature for 3 h and then was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed to afford **3a** as purple powder. (407 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$):δ 9.02 (s, 8H), 7.80 (s, 4H), 7.75 (d, $J = 7.90$ Hz, 4H), 7.25 (d, $J = 7.90$ Hz, 4H), 4.35 (t, $J = 6.60$ Hz, 8H), 3.98 (s, 12H), 3.53 (t, $J = 6.60$ Hz, 8H), 2.13–2.00 (m, 16H), 1.73–1.55 (m, 16H). ^{13}C NMR ($CDCl_3$):δ 155.1, 150.4, 146.1, 142.0, 132.5, 125.8, 120.9, 117.5, 112.9, 113.6, 102.5, 61.4, 56.4, 33.2, 32.7, 30.3, 27.2, 24.5.

Synthesis of zinc complex of 5,10,15,20-tetra(4-(2-bromoethoxy)-3-methoxyphenyl) porphyrin (3b)

Compound **2b** (400 mg, 0.33 mmol), zinc acetate dihydrate solution in methanol (10 mL) and $CHCl_3$ (60 mL) were combined under the experimental conditions identical to that for the synthesis of **3a** to obtain **3b** as purple powder (413 mg, 97%). ^{1}H NMR (600 MHz, $CDCl_3$):δ 9.02 (s, 8H), 7.82 (s, 4H), 7.77 (d, $J = 7.90$ Hz, 4H), 7.31 (d, $J = 7.90$ Hz, 4H), 4.68 (t, $J = 6.60$ Hz, 8H), 3.99 (s, 12H), 3.92 (t, $J = 6.60$ Hz, 8H). ^{13}C NMR ($CDCl_3$):δ 155.1, 150.6, 146.1, 142.1, 132.8, 125.9, 120.8, 117.5, 112.3, 111.1, 101.3, 61.5, 56.5, 27.1.

Synthesis of porphyrin derivatives with quaternary ammonium salts THMZnPN

Compound **3a** (60.4 mg, 0.04 mmol) was dissolved in 15 mL of THF and then the mixture was cooled to 0^{o}C. The water solution trimethylamine (50%, 6 mL) was added to the above mixture with vigorous stirring. The reaction mixture was allowed to stir at room temperature for 24 h. The solvent was removed and the residue was washed with dichloromethane for several times to get product THMZnPN as purple solid (70.1 mg, 98%). ^{1}H NMR (600 MHz, CD_3OD): 8.90 (s, 8H), 7.83 (s, 4H), 7.74 (d, $J = 7.55$ Hz, 4H), 7.35 (d, $J = 7.55$ Hz, 4H), 4.34 (t, $J = 6.06$ Hz, 8H), 3.97 (s, 12H), 3.44 (t, $J = 6.06$ Hz, 8H), 3.20 (s, 36H), 2.37–2.16 (m, 16H), 1.95–1.68 (m, 16H). ^{13}C NMR (CD_3OD): 158.2, 154.3, 149.1, 144.0, 137.7, 125.8, 121.2, 117.5, 119.4, 114.7, 102.6, 64.3, 61.4, 56.4, 55.4, 34.2, 32.7, 30.2, 27.5. HRMS (ESI): calcd for $C_{84}H_{116}N_8O_8Zn^{4+}$, $m/z = [M - 4Br]^{4+}/4 = 357.2603$, found 357.2625.

Synthesis of porphyrin derivatives with quaternary ammonium salts TEMZnPN

Compound **3b** (51.6 mg, 0.04 mmol), THF (15 mL) and 6 mL of 50% trimethylamine solution in water were combined under the experimental conditions identical to that for the synthesis of THMZnPN to obtain TEMZnPN as purple powder (61.3 mg, 98%). ^{1}H NMR (600 MHz, CD_3OD): 8.90 (s, 8H), 7.89 (s, 4H), 7.79 (d, $J = 7.90$ Hz, 4H), 7.49 (d, $J = 7.90$ Hz, 4H), 4.79 (t, $J = 6.09$ Hz, 8H), 3.98 (s, 12H), 3.96 (t, $J = 6.09$ Hz, 8H). 3.47 (s, 36H). ^{13}C NMR (CD_3OD): 159.1, 154.3, 149.2, 145.4, 137.5, 124.4, 121.2, 119.6, 113.1, 112.6, 101.6, 67.2, 64.2, 57.5, 55.1. HRMS (ESI): calcd for $C_{68}H_{84}N_8O_8Zn^{4+}$, $m/z = [M-4Br]^{4+}/4 = 301.1398$, found 301.1436.

Funding

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