

## A Phthalocyanine Dendrimer Capable of Forming Spherical Micelles

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**Abstract:** A novel and intrinsically spherical micelle has been prepared by utilizing a silicon phthalocyanine ((WG3)SiPc) that has a thin hydrophobic alkyl chain and a bulky hydrophilic poly(aryl ether) dendrimer with terminal carboxyl groups, as its two axial ligands. Gel-permeation chromatography and cryo-transmission electron mi-

croscopic experiments indicate that (WG3)SiPcs self-assemble to form a spherical micelle at very low concentrations in aqueous solution. Depending

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on the pH of the aqueous phase, (WG3)SiPc shuttles between aqueous and organic phases. In the presence of hydrophobic molecules, this transfer is accompanied by the inclusion of these (guest) molecules, indicating that the micelle acts as a molecular capsule with a nanospace surrounded by functional phthalocyanine planes.

### Introduction

Phthalocyanine (Pc) molecules have received great attention as a result of their diverse electronic, optical, and structural properties, which enable application to numerous areas, such as dyes, pigments, catalysis for controlling sulfur effluents, photoconducting agents in photocopiers, chemical sensors, optical disks, deodorants, photovoltaic cells, molecular electronics, and photodynamic therapy of cancer.<sup>[1–3]</sup> Novel Pc derivatives have been realized by McKeown et al., who obtained Pc-centered aryl ether dendrimers, by Kraus et al., who obtained a dendrimer with Pc units surrounding a central core;<sup>[4–6]</sup> the interiors of such dendritic molecules, with a hierarchy of branched structures and in which the surface is denser than the core, display a number of interesting properties.<sup>[7–12]</sup> These include inhibiting energy deactivation,<sup>[13,14]</sup> chambers for chemical reactions,<sup>[15]</sup> molecular inclusion,<sup>[16,17]</sup> unimolecular micelles,<sup>[18–28]</sup> or biomimetic models.

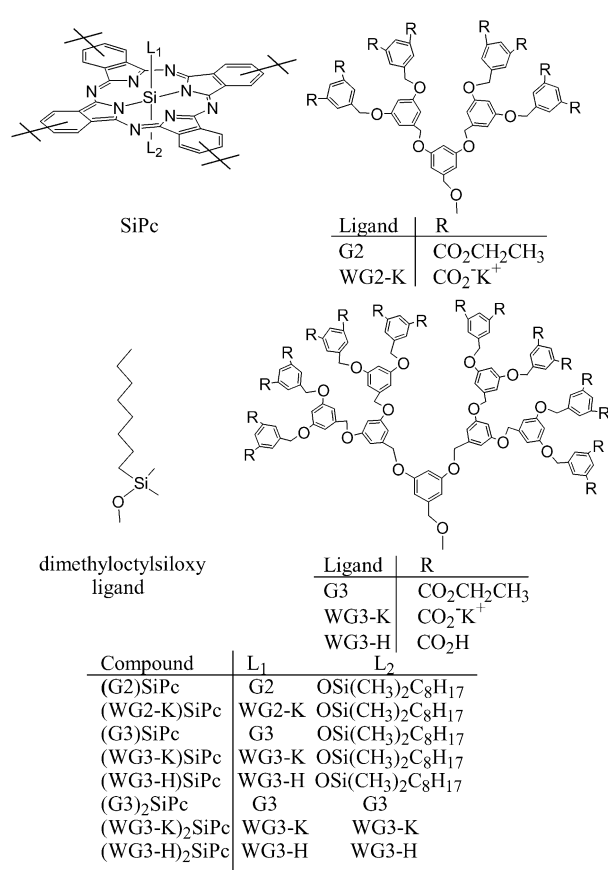
Recently, self-assembly of dendrimers has generated considerable interest, since this could potentially achieve the rapid construction of giant architectures.<sup>[29–36]</sup> These studies have shown that the shape and directionality of the den-

drimers are the most important factors that control the states and properties of aggregates, for example, spherical shape,<sup>[32–34]</sup> hydrogel properties,<sup>[35]</sup> and liquid crystals.<sup>[32–34,36]</sup> Spherical micelles of self-assembled dendrimers, corresponding to intermediates between unimolecular micelles and self-assembled surfactants, should include molecules in the attractive dendritic nanospace, accompanied by drastic conformational changes, which are expected to give several advantages compared with unimolecular micelles of dendrimers or copolymers.<sup>[18–28,37–39]</sup> However, few spherical micelles of self-assembled dendrimers have been reported, in contrast to micelles of self-assembled copolymers.<sup>[40,41]</sup> For example, Hawker et al. prepared a hybrid dendrimer, whose constitution resembles conventional surfactants (half of the macromolecule had 16 hydrophilic terminal carboxylate groups, while the other half had 16 hydrophobic terminal phenyl groups), but this hybrid dendrimer only formed an emulsion of water and dichloromethane.<sup>[42]</sup>

In this report, we describe the spherical micelle formation of self-assembled Pc dendrimers that act as molecular capsules. The key to our strategy is the use of tetra-*tert*-butylphthalocyaninosilicon (SiPc) plane to make a directionally ordered dendrimer.<sup>[43,44]</sup> One axial ligand of SiPc was substituted with a thin hydrophobic alkyl chain, while a hydrophilic poly(aryl ether) dendrimer with terminal carboxyl groups was utilized as the other axial ligand. The spherical micelle formation of self-assembled dendrimers in aqueous solution can be likened to the opening of an umbrella of the dendrimer surrounded by carboxylic acid. This self-assembly originates from the mushroom shape of the molecule, in which the hydrophobic alkyl chain is only slightly longer than the radius of the Pc plane.

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## Results and Discussion

Gel-permeation chromatography (GPC) experiments were carried out to confirm the state of self-assembly. It was found through the use of a Bio-Beads S-X1 column that the elution volume of solutions in toluene increases in the order, (G3)<sub>2</sub>SiPc (molecular weight ( $M_r$ ) = 6257) < (G3)SiPc ( $M_r$  = 3698) < SiPc(OH)<sub>2</sub> ( $M_r$  = 799) (Figure 1A), and has good linearity with the logarithm of  $M_r$  (Figure 1B); this strongly suggests that these compounds exist as monomers in organic solvents. The GPC behavior of the water-soluble dendrimers WG3SiPc and (WG3)<sub>2</sub>SiPc in aqueous solution was examined by using a Sephadex G-100 column, and compared with those of several well-known proteins, that is, myoglobin ( $M_r$  =  $1.2 \times 10^4$ ), ovalbumin ( $M_r$  =  $4.3 \times 10^4$ ), serum albumin ( $M_r$  =  $6.8 \times 10^4$ ), and yeast alcohol dehydrogenase (ADH,

$M_r$  =  $1.4 \times 10^5$ ).<sup>[45]</sup> The elution volume exhibited a good linear relationship with log  $M_r$  except for (WG3-K)SiPc (Figure 1C and D). The elution volume of (WG3-K)SiPc is almost identical to that of ovalbumin, which evidently indicates aggregation of (WG3-K)SiPc. The  $M_r$  of the aggregates is evaluated as  $3\text{--}5 \times 10^4$ .

To observe the self-assembled (WG3)SiPcs directly, cryo-transmission electron microscopic (Cryo-TEM) measurements were carried out. In the TEM images, a spherical shape is seen in the frozen vitreous ice, even though the noise level is high and the images granular (Figure 2). In the images, atoms in the dendrimers are densely packed in projections along the electron beam direction, so that they exhibit darker ringlike contrasts. The radius was estimated to be about 3.5 nm, which is almost identical to the Stokes radius (~3.5 nm) of ovalbumin. Given the  $M_r$  observed by GPC and the spherical shape determined by the TEM images, the number of aggregates,  $N$ , was estimated to be  $10 \pm 3$ .<sup>[46]</sup> In this model, the radius of the micelle is 3.6–3.9 nm, consistent with the Cryo-TEM image (~3.5 nm).

This self-assembled Pc dendrimer micelle has the following features with respect to conventional anionic surfactants: 1) our spherical micelle can be formed by only ~10 (WG3-K)SiPcs, while several tens of surfactants are required to generate spherical micelles;<sup>[47]</sup> and 2) the concentration of (WG3-K)SiPc eluted from the Sephadex G-100 column is very low ( $10^{-7}$ – $10^{-6}$  M), in contrast to the high critical micelle concentration of conventional anionic surfactants ( $10^{-1}$ – $10^{-3}$  M).<sup>[47]</sup> That is, this self-assembly of dendrimers is prone to form a spherical micelle much more readily than general anionic surfactants, and is intermediate between unimolecular micelles and self-assembled surfactants. This originates from the mushroom-type molecular shape of (WG3)SiPc and demonstrates a distinct relationship between the self-assembly and the molecular shape of the constituents.<sup>[48]</sup>

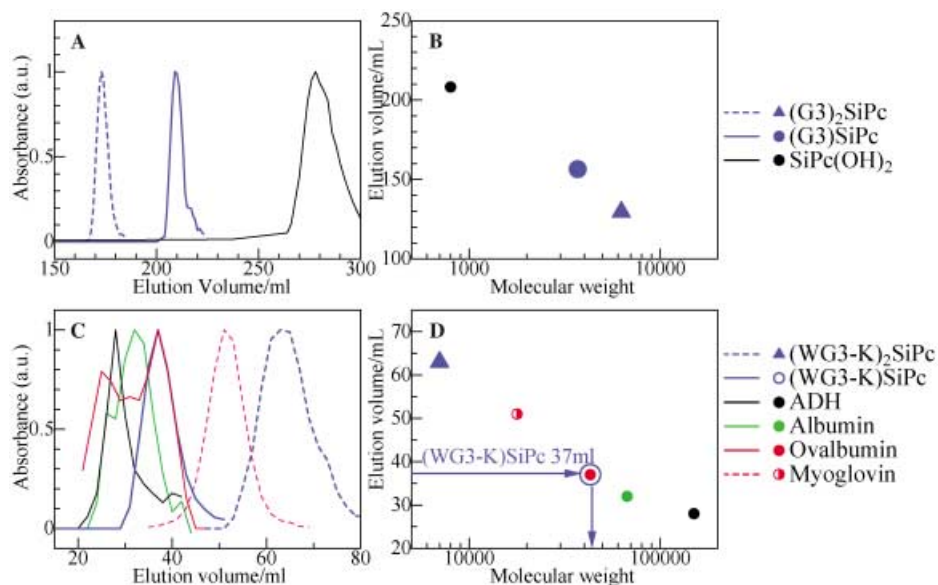


Figure 1. Gel-permeation chromatograms from Bio-Beads S-X1 (A) and Sephadex G-100 (C) columns. Figures B and D show the relationships of molecular weight versus elution volume in our Bio-Beads S-X1 and Sephadex G-100 columns, respectively. Experimental details are given in the text.

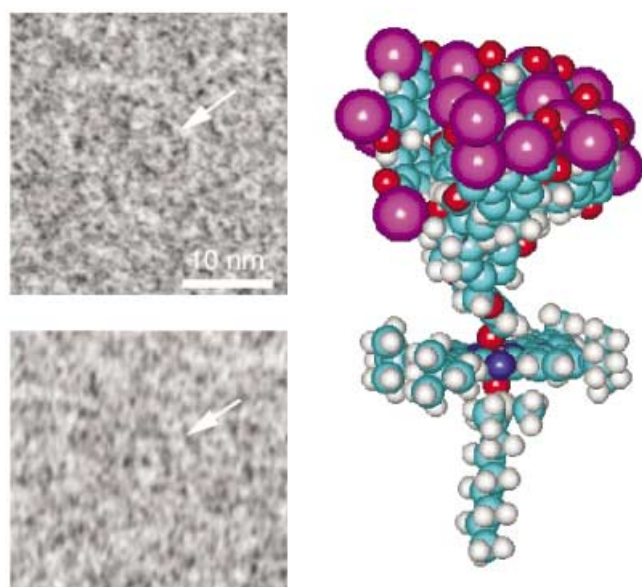


Figure 2. TEM images of (WG3-K)SiPc in frozen aqueous solution at 4 K (left), and a space-filling model of (WG3-K)SiPc constituting the micelle (right).

The hydrophobic environment around the Pcs was studied using fluorescence spectroscopy. While fluorescence quantum yields ( $\Phi_F$ ) in  $\text{CH}_2\text{Cl}_2$  are independent of the dendrimers,<sup>[49]</sup> those of (WG3-K)SiPc, (WG3-K)<sub>2</sub>SiPc, and (WG2-K)SiPc in aqueous solution are 0.38, 0.37, and 0.02, respectively. The very small  $\Phi_F$  value of (WG2-K)SiPc can be interpreted by assuming that the WG2 dendrimer cannot form a hydrophobic environment effectively. It is worth noting that the  $\Phi_F$  value of (WG3-K)SiPc is almost identical to that of (WG3-K)<sub>2</sub>SiPc, although in the case of (WG3-K)<sub>2</sub>SiPc the SiPc plane is protected both above and below. This also indicates the micelle formation of the self-assembled (WG3-K)SiPcs, with a hydrophobic environment which is similar to that of (WG3-K)<sub>2</sub>SiPc.

Since (WG3)SiPc forms a micelle in aqueous solution in contrast to a monomeric form of (G3)SiPc in organic solvents, transfers of (WG3)SiPc between organic (ethyl acetate) and aqueous phases were investigated for controlling the self-assembly. Figure 3A shows the transfer of (WG3)SiPc between the organic and aqueous phases. When the aqueous phase was alkaline, (WG3-K)SiPc dissolved as a result of the formation of  $\text{CO}_2^- \text{K}^+$  terminal groups (Figure 3A1). By adding excess acetic acid, the aqueous phase became acidic, resulting in the formation of (WG3-H)SiPc with  $\text{CO}_2\text{H}$  terminal groups and transferred into the organic phase (Figure 3A2).<sup>[50]</sup> After subsequent addition of a KOH aqueous solution and vigorous stirring, the water-soluble (WG3-K)SiPc was again formed and transferred into the aqueous phase (Figure 3A3). Therefore, together with the above-described results of GPC, Cryo-TEM, and fluorescence experiments, we can conclude that (WG3)SiPc transfers between the organic and aqueous phases, accompanied by the open–close behavior of the supramolecular micelle (Figure 3B).

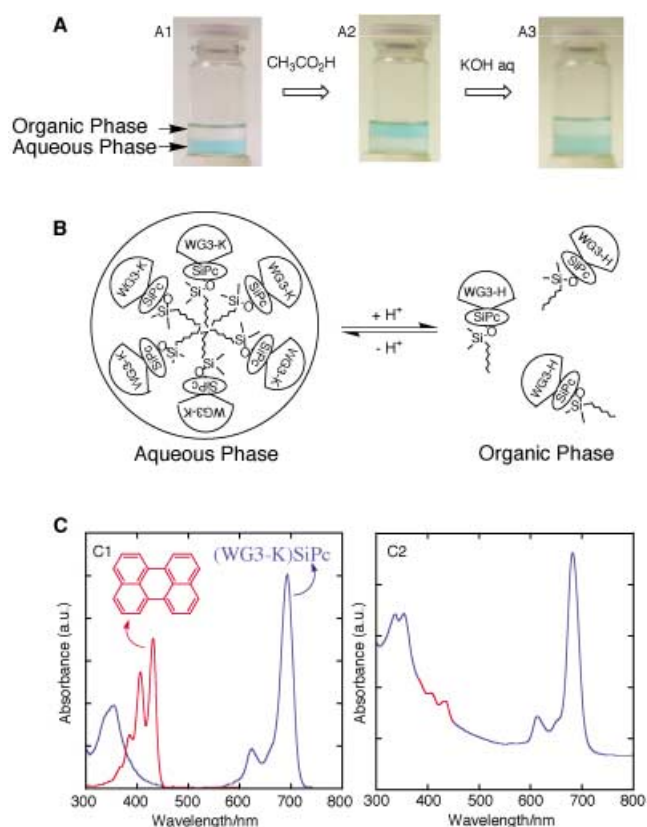


Figure 3. Transfer of (WG3)SiPc between aqueous and organic (ethyl acetate) phases. Figure A shows photographs of (WG3)SiPc in aqueous/organic phases. (WG3)SiPc dissolved in aqueous phase (A1) transferred into the organic phase when an excess  $\text{CH}_3\text{CO}_2\text{H}$  was added (A2). Subsequent addition of aqueous KOH and vigorous stirring yielded the water-soluble (WG3-K)SiPc again in the aqueous phase (A3). Figure B (left and right) shows the proposed conformations in aqueous and organic phases, respectively. Figure C shows electronic absorption spectra of (WG3-K)SiPc in aqueous solution (blue solid line, C1), perylene in ethyl acetate (red solid line, C1), and (WG3-K)SiPc including perylene in aqueous solution (solid line, C2).

Utilizing this open–close behavior, molecular inclusion was examined. Initially, the inclusion of perylene was investigated by electronic absorption spectroscopy (Figure 3C1). After the transfer of (WG3)SiPc from an aqueous phase to an ethyl acetate phase containing pre-dissolved perylene, (WG3)SiPc was transferred back into the aqueous phase by adding a KOH aqueous solution. This aqueous solution clearly showed absorption bands due to perylene at around 400–450 nm (Figure 3C2). Although the same experiment was carried out for (WG3)<sub>2</sub>SiPc that contained two dendrimers above and below the Pc plane, no absorption bands due to perylene could be detected in the aqueous solution. These results show that perylene is captured when (WG3)SiPcs self-assemble to form a supramolecular micelle, and that it cannot be included from the dense dendritic side. Furthermore, the inclusion of 1,4-benzoquinone (BQ) was investigated by fluorescence measurements. Here, aqueous solutions were prepared by adding a large amount of water to a small amount of  $\text{CH}_2\text{Cl}_2$  that contained BQ and (WG3-K)SiPc (or (WG3-K)<sub>2</sub>SiPc) ( $[\text{BQ}]/[\text{SiPc}] = 50$ ). While the  $\Phi_F$  value of (WG3-K)<sub>2</sub>SiPc was not influenced by BQ, the  $\Phi_F$

value of (WG3-K)SiPc decreased by ~20% in the presence of BQ, originating from photoinduced electron transfer. In CH<sub>2</sub>Cl<sub>2</sub>, fluorescence of (G3)SiPc and (G3)<sub>2</sub>SiPc was barely quenched by BQ. These results indicate that BQ is also trapped in the supramolecular micelle of (WG3-K)SiPc, and that photoinduced electron transfer is more efficient in the micelle than in the CH<sub>2</sub>Cl<sub>2</sub> solution.

## Conclusion

In summary, we have realized a supramolecular spherical micelle consisting of self-assembled Pc dendrimers by directionally ordering the dendritic unit. In addition, we have demonstrated that, in contrast to general surfactants, the large functional Pc molecule can be employed as the constituting unit of a spherical micelle by utilizing a cone-shaped dendritic umbrella. Since this spherical micelle acts as a molecular capsule, it provides an attractive nanospace surrounded by the Pc planes, which exhibit photonic and redox activity. In addition, since selective adsorption of Pcs to cancer cells has been used for photodynamic therapy, the micelle formed by dendrimers in this study has potential as a novel drug delivery system in this field.

## Experimental Section

**Measurements:** The 400 MHz <sup>1</sup>H NMR spectral measurements were made with a JEOL GSX-400 instrument. Mass spectra were obtained using a Perspective Biosystem Voyager-DE-PRO (MALDI-TOF mass) or a Micromass LCT (ESI-TOF mass) spectrometer. Electronic absorption spectra were recorded with a Hitachi 330 LC or a Hitachi U-3410 spectrophotometer. Fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. The  $\Phi_F$  values were determined by the use of SiPc(OH)<sub>2</sub> ( $\Phi_F=0.57$ ).<sup>[51]</sup> GPC was carried out with a Bio-Beads S-X1 column (Bio-Rad, toluene, 20  $\phi$  × 1100 mm, 0.75 mL min<sup>-1</sup>) or a Sephadex G100 column (Pharmacia Fine Chemicals, 0.75 M-tris-HCl buffer solution, 20  $\phi$  × 320 mm, 0.15–0.19 mL min<sup>-1</sup>). Cryo-TEM measurements were performed at 4 K using a JEOL JEM-4000EX.<sup>[52]</sup> An aqueous solution of (WG3-K)SiPc (10<sup>-4</sup> M) on a grid was immediately quenched into liquid propane (at 100 K), after which the frozen solution was observed at a relatively low magnification of 50000 so as to avoid radiation damage.

**Synthesis:** Fréchet's poly(aryl ether) dendrimers with ethoxycarbonyl terminal groups were prepared by the convergent method, as follows.<sup>[53]</sup> Coupling of the diethyl 5-(bromomethyl)isophthalate end group with the 3,5-dihydroxybenzyl alcohol monomer was performed in refluxing acetone in the presence of K<sub>2</sub>CO<sub>3</sub> and [18]crown-6, to afford (EtO<sub>2</sub>C)<sub>4</sub>[G-1]-OH (this notation describes the dendrimer chain functionality, followed by the generation number, followed by the focal point group functionality). Conversion to the corresponding benzylic bromide was then undertaken by reaction with PPh<sub>3</sub> and CBr<sub>4</sub> in THF. The coupling reaction of the first-generation bromide (EtO<sub>2</sub>C)<sub>4</sub>[G-1]-Br (or the second-generation bromide (EtO<sub>2</sub>C)<sub>8</sub>[G-2]-Br) with the 3,5-dihydroxybenzyl alcohol monomer to give the second-generation alcohol (EtO<sub>2</sub>C)<sub>8</sub>[G-2]-OH (or the third-generation alcohol (EtO<sub>2</sub>C)<sub>16</sub>[G-3]-OH) was carried out in acetone at 40–45 °C in the presence of K<sub>2</sub>CO<sub>3</sub> and a high concentration (0.65–0.8 equiv) of [18]crown-6.

Monosilylated SiPc, SiPc(OH)(OSi(CH<sub>3</sub>)<sub>2</sub>C<sub>8</sub>H<sub>17</sub>) (L<sub>1</sub>=OH, L<sub>2</sub>=O-Si(CH<sub>3</sub>)<sub>2</sub>C<sub>8</sub>H<sub>17</sub>), was prepared by reaction of SiPc(OH)<sub>2</sub> and chlorodimethylsilyl silane in pyridine at 60 °C.<sup>[54]</sup> Dendrimer units were linked to the axial positions of SiPc by reaction with SiPc(OH)<sub>2</sub> or SiPc(OH)(O-Si(CH<sub>3</sub>)<sub>2</sub>C<sub>8</sub>H<sub>17</sub>) in refluxing toluene.<sup>[4]</sup> Typical experimental conditions are given for (G3)SiPc below.

**(G3)SiPc:** SiPc(OH)(OSi(CH<sub>3</sub>)<sub>2</sub>C<sub>8</sub>H<sub>17</sub>) (27 mg) and (EtO<sub>2</sub>C)<sub>16</sub>[G-3]-OH (31 mg) were refluxed in a dry toluene (1.5 mL) for 10 h. After removal of the solvent by evaporation, the residue was purified by alumina (toluene) and gel-permeation (Bio-Beads S-X1, Bio-Rad, toluene/ACoEt 40:1 v/v) chromatography and preparative TLC on silica (toluene/ACoEt 40:1 v/v), to give the desired compound (9.4 mg, 9.2%). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (10<sup>-4</sup>ε)=680.0 (23.8), 650.5 (3.07), 612.0 (3.62), 355.5 (7.66), 278.0 nm (4.68); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ =9.97 (m, 4H; arom H), 9.74 (m, 4H; arom H), 8.96 (s, 8H; arom H), 8.35 (s, 16H; arom H), 8.17 (m, 4H; arom H), 6.73–6.52 (m, 18H; arom H), 6.06 (s, 1H; arom H), 4.81 (s, 8H; benzylic), 4.54 (s, 16H; benzylic), 4.14 (s, 4H; benzylic), 4.09 (q, 32H; OCH<sub>2</sub>), 3.94 (d, 2H; arom H), 1.55 (m, 36H; CCH<sub>3</sub>), 1.34 (s, 2H; benzylic), 1.17 (m, 2H; CH<sub>2</sub>), 0.98 (t, 48H; CH<sub>3</sub>), 0.88 (t, 3H; CH<sub>3</sub>), 0.80 (q, 2H; CH<sub>2</sub>), 0.43 (m, 2H; CH<sub>2</sub>), -0.05 (m, 2H; CH<sub>2</sub>), -0.19 (m, 2H; CH<sub>2</sub>), -1.03 (m, 2H; CH<sub>2</sub>), -2.01 (m, 2H; SiCH<sub>2</sub>), -2.52 ppm (s, 6H; SiCH<sub>3</sub>); ESI-TOF MS: *m/z* calcd for C<sub>211</sub>H<sub>227</sub>O<sub>48</sub>N<sub>8</sub>Si<sub>2</sub>: 3698.5 [M+H]<sup>+</sup>; found: 3698.5; elemental analysis calcd (%) for C<sub>211</sub>H<sub>226</sub>O<sub>48</sub>N<sub>8</sub>Si<sub>2</sub>: C 68.55, H 6.13, N 3.03; found: C 68.82, H 6.30, N 2.75.

(G2)SiPc and (G3)<sub>2</sub>SiPc were synthesized by a method similar to that described for (G3)SiPc, purified by GPC, and characterized by electronic absorption, 400 MHz <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), ESI- or MALDI-TOF MS, and elemental analysis as follows.

**(G2)SiPc:** Yield 61%; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (10<sup>-4</sup>ε)=680.5 (30.5), 651.0 (4.08), 613.0 (4.79), 357.0 (9.96), 283.0 nm (4.91); <sup>1</sup>H NMR:  $\delta$ =9.97 (m, 4H; arom H), 9.79 (m, 4H; arom H), 9.03 (s, 4H; arom H), 8.40 (s, 8H; arom H), 8.18 (m, 4H; arom H), 6.48 (s, 4H; arom H), 6.46 (m, 2H; arom H), 6.15 (m, 1H; arom H), 4.48 (s, 8H; benzylic), 4.10 (q, 16H; OCH<sub>2</sub>), 4.10 (s, 4H; benzylic), 4.00 (s, 2H; arom H), 1.54 (m, 36H; CCH<sub>3</sub>), 1.34 (s, 2H; benzylic), 1.21 (m, 2H; CH<sub>2</sub>), 0.99 (t, 24H; CH<sub>3</sub>), 0.91 (t, 3H; CH<sub>3</sub>), 0.81 (m, 2H; CH<sub>2</sub>), 0.45 (m, 2H; CH<sub>2</sub>), 0.025 (m, 2H; CH<sub>2</sub>), -0.86 (m, 2H; CH<sub>2</sub>), -0.95 (m, 2H; CH<sub>2</sub>), -1.91 (m, 2H; SiCH<sub>2</sub>), -2.44 ppm (s, 6H; SiCH<sub>3</sub>); ESI-TOF MS: *m/z* calcd for C<sub>131</sub>H<sub>148</sub>O<sub>25</sub>N<sub>8</sub>Si<sub>2</sub>: 2290 [M+H<sub>2</sub>O]<sup>+</sup>; found: 2290.6; elemental analysis calcd (%) for C<sub>131</sub>H<sub>146</sub>O<sub>24</sub>N<sub>8</sub>Si<sub>2</sub>: C 69.23, H 6.47, N 4.93; found: C 68.56, H 6.85, N 4.43.

**(G3)<sub>2</sub>SiPc:** Yield 17%; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (10<sup>-4</sup>ε)=685.0 (21.5), 616.5 (3.57), 357.5 (7.07), 283.5 nm (7.40); <sup>1</sup>H NMR:  $\delta$ =9.90 (m, 4H; arom H), 9.69 (m, 4H; arom H), 8.92 (s, 16H; arom H), 8.33 (m, 32H; arom H), 8.17 (d, 4H; arom H), 6.73–6.53 (m, 36H; arom H), 6.04 (s, 2H; arom H), 4.82 (s, 16H; benzylic), 4.60 (s, 32H; benzylic), 4.13 (s, 8H; benzylic), 4.09 (q, 64H; OCH<sub>2</sub>), 3.95 (m, 4H; arom H), 1.55 (m, 36H; CCH<sub>3</sub>), 1.34 (s, 4H; benzylic), 1.17 (m, 2H; CH<sub>2</sub>), 0.99 ppm (t, 96H; CH<sub>3</sub>); MALDI-TOF MS: *m/z* calcd for C<sub>354</sub>H<sub>358</sub>O<sub>94</sub>N<sub>8</sub>Si<sub>2</sub>: 6252.4 [M]<sup>+</sup>; found: 6259.14; elemental analysis calcd (%) for C<sub>354</sub>H<sub>358</sub>O<sub>94</sub>N<sub>8</sub>Si<sub>2</sub>: C 67.96, H 5.77, N 1.79; found: C 68.83, H 5.99, N 1.66.

Ethoxycarbonyl groups were converted into carboxylates by hydrolysis in a mixed solution (0.45 M KOH aqueous solution/methanol/tetrahydrofuran=1:1:2 v/v/v) at ambient temperature (reaction times were 3, 14, and 20 h for (G2)SiPc, (G3)SiPc, and (G3)<sub>2</sub>SiPc, respectively), yielding water-soluble (WGn-K)SiPc or (WG3-K)<sub>2</sub>SiPc.

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