# Hyperchromic Effect of Silyl Groups on the UV–Visible Spectrum of 5,10,15,20-Tetraphenylporphyrin

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UV–visible spectra of 5,10,15,20-tetrakis(4-silylphenyl)-porphyrins and 5,10,15,20-tetrakis(3,5-disilylphenyl)porphyrins were measured. Silyl groups were found to have a hyperchromic effect on the Soret band and the Q band of 5,10,15,20-tetraphenylporphyrin.

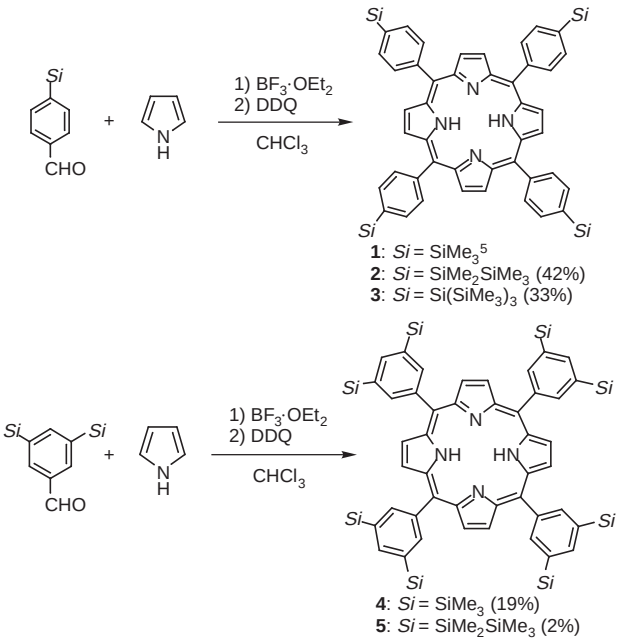
5,10,15,20-Tetraphenylporphyrin (TPP) and its derivatives have been extensively studied.[1] For example, they have been used as analytical reagents for the detection of trace amounts of metals,[1] photosensitizers for photodynamic therapy,[2] and dyes for dye-sensitized solar cells.[3] In these photochemical applications, effective absorption of light is especially important to improve light sensitivity of these reagents. For this purpose, appropriate molecular design of TPP is desired, but such methods have not been well established.

In the course of our studies on organosilicon compounds containing aromatic rings, we found that silyl groups increase the molecular extinction coefficients of aromatic compounds.[4] These results led us to use silyl groups for improvement of the light sensitivity of 5,10,15,20-tetraphenylporphyrin. We report herein that silyl groups have a hyperchromic effect on the UV–visible spectrum of TPP.

5,10,15,20-Tetrakis(4-trimethylsilylphenyl)porphyrin (**1**) has been reported to be synthesized by the reaction of 4-trimethylsilylbenzaldehyde with pyrrole in the presence of boron trifluoride diethyl etherate, followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[5] According to this method, **2**–**5** were successfully synthesized (Scheme 1).[6–9]

The structure of **2** was analyzed by X-ray crystallography (Figure 1).[10] The porphyrin ring has an almost planar structure with the features of 18$\pi$ aromaticity.[11] The C(1)–C(2) and C(3)–C(4) bonds (1.437(2) and 1.429(2) Å) are significantly shorter than the C(6)–C(7) and C(8)–C(9) bonds (1.458(2) and 1.455(2) Å), while the C(2)–C(3) bond (1.362(2) Å) is longer than the C(7)–C(8) bond (1.348(2) Å). As bond alternation in the N(1)–C(1)–C(2)–C(3)–C(4) ring is reduced compared with the N(2)–C(6)–C(7)–C(8)–C(9) ring, 18$\pi$ aromaticity is present along the black bonds shown in Figure 1. The dihedral angles between the porphyrin ring and the benzene rings are 63.6 and 60.3°. The dihedral angles between the silicon–silicon bonds and the benzene rings are 52.4 and 62.4°. These values show that conjugation between the porphyrin ring and the benzene rings and $\sigma$–$\pi$ conjugation[12] between the silicon–silicon $\sigma$ bonds and the benzene rings are partially effective.

TPP has been known to show an intense Soret band at ca. 400–430 nm and a Q band at ca. 500–700 nm.[1] The Soret bands and the Q bands of **1**–**3** and TPP are shown in Figure 2. The Soret band and the Q band show a slight bathochromic shift in the order of TPP, **1**, **2**, and **3**. In addition, the molecular extinction coefficients of the Soret band and the Q band gradually increase




**Scheme 1.**

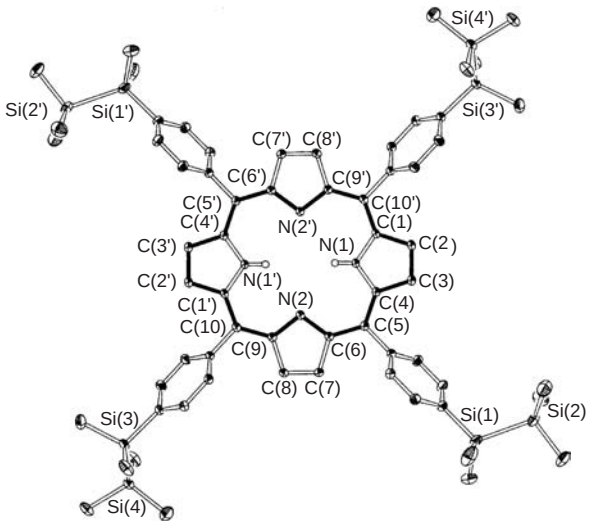



**Figure 1.** Molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level.

in this order. The molecular extinction coefficient ($\varepsilon$) of the Soret band of **3** is 540000 $M^{-1}$ $cm^{-1}$ which is remarkably larger than that of TPP ($\varepsilon$ 420000 $M^{-1}$ $cm^{-1}$). To the best of our knowledge, the largest value of the molecular extinction coefficient of the Soret band is 550000 $M^{-1}$ $cm^{-1}$ of 5,10,15,20-tet-

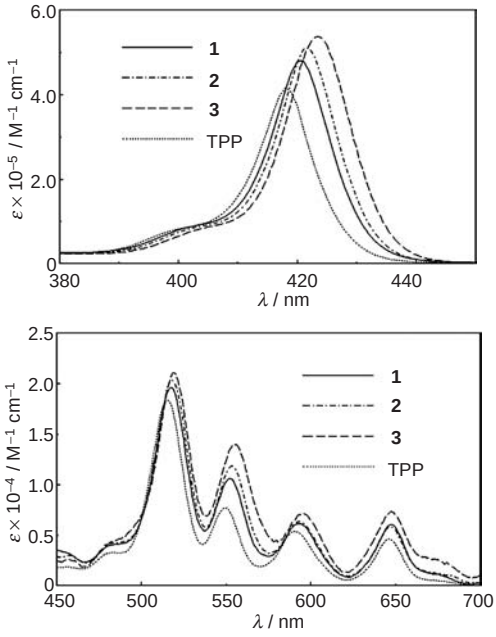



**Figure 2.** The Soret bands (top) and the Q bands (bottom) of the UV–visible spectra of **1**–**3** and TPP in chloroform at room temperature.

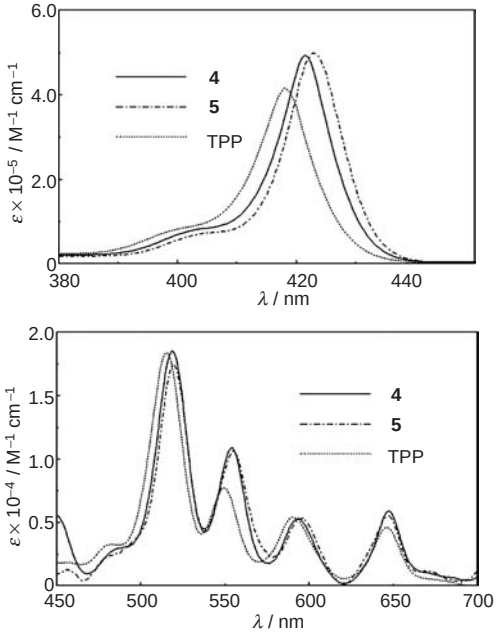



**Figure 3.** The Soret bands (top) and the Q bands (bottom) of the UV–visible spectra of **4**, **5**, and TPP in chloroform at room temperature.

rakis(3′,5′-di-*tert*-butylbiphenyl-4-yl)porphyrin.[13] These results show that silyl groups effectively increase the molecular extinction coefficient of TPP.

The Soret bands and the Q bands of **4** and **5** show a slight bathochromic shift compared with those of TPP (Figure 3). The molecular extinction coefficients of **4** and **5** are larger than those of TPP. As the molecular extinction coefficients of the Soret bands of **4** ($\varepsilon$ 490000 $M^{-1}$ $cm^{-1}$) and **5** ($\varepsilon$ 500000 $M^{-1}$ $cm^{-1}$) are almost equal to those of **1** ($\varepsilon$ 480000 $M^{-1}$ $cm^{-1}$) and **2** ($\varepsilon$ 510000 $M^{-1}$ $cm^{-1}$), respectively, the hyperchromic effect of two silyl groups at the meta positions corresponds to that of a silyl group at the para position.

**References and Notes**

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6 **2**: mp > 300 °C; $^1$H NMR ($CDCl_3$): $\delta$ −2.75 (s, 2H), 0.23 (s, 36H), 0.57 (s, 24H), 7.81 (d, 8H, $J$ = 7.9 Hz), 8.19 (d, 8H, $J$ = 7.9 Hz), 8.86 (s, 8H); $^{13}$C NMR ($CDCl_3$): $\delta$ −3.8, −2.1, 120.2, 132.0, 134.1, 138.8, 142.0; $^{29}$Si NMR ($CDCl_3$): $\delta$ −21.2, −19.2; IR (KBr) 3320, 3060, 3010, 2950, 2890, 1560, 1470, 1400, 1250, 1100, 970, 830, 800 $cm^{-1}$; UV–vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/$M^{-1}$ $cm^{-1}$) 422 (510000), 518 (20000), 553 (12000), 593 (6400), 647 nm (5900); ESI-MS $m/z$ (%) 1135.4 $[M + H]^+$ (100); Anal. Calcd for $C_{64}H_{86}N_4Si_8$: C, 67.66; H, 7.63; N, 4.93%. Found: C, 67.54; H, 7.88; N, 4.90%.

7 **3**: mp > 300 °C; $^1$H NMR ($CDCl_3$): $\delta$ −2.79 (s, 2H), 0.37 (s, 108H), 7.78 (d, 8H, $J$ = 8.1 Hz), 8.09 (d, 8H, $J$ = 8.1 Hz), 8.85 (s, 8H); $^{13}$C NMR ($CDCl_3$): $\delta$ 1.3, 120.2, 134.1, 134.7, 135.0, 141.1; $^{29}$Si NMR ($CDCl_3$): $\delta$ −76.7, −12.6; IR (KBr) 3320, 3060, 3020, 2950, 2890, 1560, 1470, 1400, 1250, 970, 870, 840, 800 $cm^{-1}$; UV–vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/$M^{-1}$ $cm^{-1}$) 424 (540000), 519 (21000), 555 (14000), 595 (7200), 648 nm (7400); ESI-MS $m/z$ (%) 1599.6 $[M + H]^+$ (100); Anal. Calcd for $C_{80}H_{134}N_4Si_{16}$: C, 60.00; H, 8.43; N, 3.50%. Found: C, 60.09; H, 8.43; N, 3.50%.

8 **4**: mp > 300 °C; $^1$H NMR ($CDCl_3$): $\delta$ −2.71 (s, 2H), 0.38 (s, 72H), 7.99 (t, 4H, $J$ = 0.9 Hz), 8.34 (d, 8H, $J$ = 0.9 Hz), 8.85 (s, 8H); $^{13}$C NMR ($CDCl_3$): $\delta$ −0.9, 121.0, 137.1, 137.5, 140.0, 140.6; $^{29}$Si NMR ($CDCl_3$): $\delta$ −3.5; IR (KBr) 3320, 3020, 2950, 2900, 1560, 1470, 1400, 1380, 1340, 1250, 1140, 1030, 980, 860, 840, 800, 750 $cm^{-1}$; UV–vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/$M^{-1}$ $cm^{-1}$) 422 (490000), 518 (18000), 554 (11000), 594 (5200), 648 nm (5800); ESI-MS $m/z$ (%) 1191.5 $[M + H]^+$ (100); Anal. Calcd for $C_{68}H_{94}N_4Si_8$: C, 68.51; H, 7.95; N, 4.70%. Found: C, 68.76; H, 8.05; N, 4.73%.

9 **5**: mp 315 °C; $^1$H NMR ($CDCl_3$): $\delta$ −2.70 (s, 2H), 0.16 (s, 72H), 0.45 (s, 48H), 7.90 (t, 4H, $J$ = 1.0 Hz), 8.26 (d, 8H, $J$ = 1.0 Hz), 8.83 (s, 8H); $^{13}$C NMR ($CDCl_3$): $\delta$ −4.0, −2.1, 121.0, 136.5, 138.2, 140.0, 140.8; $^{29}$Si NMR ($CDCl_3$): $\delta$ −21.1, −18.9; IR (KBr) 3320, 3020, 2950, 2890, 1560, 1480, 1400, 1340, 1250, 1130, 1030, 980, 840, 800, 760 $cm^{-1}$; UV–vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/$M^{-1}$ $cm^{-1}$) 423 (500000), 520 (18000), 555 (11000), 597 (5300), 647 nm (5600); ESI-MS $m/z$ (%) 1655.7 $[M + H]^+$ (100); Anal. Calcd for $C_{84}H_{142}N_4Si_{16}$: C, 60.87; H, 8.64; N, 3.38%. Found: C, 60.68; H, 8.54; N, 3.36%.

10 Crystallographic data reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-718841. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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