

Supporting Information

A smart and visible way to switch aromaticity of silicon(IV) phthalocyanines

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Reference

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1. Experimental Procedures

1.1 Materials

4-nitrophenol and 4-nitrobenzoic acid were purchased from Innochem Co., Ltd, China. Sodium hydride and 1,3-diphenylisobenzofuran (DPBF) were purchased from Acros organics (Belgium). All reactions were carried out under an atmosphere of nitrogen. *N,N*-dimethylformamide (DMF) and toluene were dried over molecular sieves and further distilled under reduced pressure before using for reaction. Chromatographic purifications were performed on silica gel columns (100-200 mesh, Qingdao Haiyang Chemical Co., Ltd, China) with the indicated eluents. All other solvents and reagents were analytical grade and employed as received.

SiPcs 1-5 and **ZnPc 1** were synthesized according to previous procedure.¹⁻⁶

1.2 Instruments

Fluorescence emission and electronic absorption spectra were measured on an Edinburgh FL900/FS900 spectrofluorometer and GENESYS 150 UV-vis spectrometer, respectively. ¹H NMR spectra were determined on a JEOL 500 spectrometer (500 MHz) in DMSO-*d*₆ or CDCl₃. Chemical shifts were relative to internal SiMe₄ ($\delta = 0$ ppm). High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Exactive Plus Orbitrap LC/MS spectrometer.

1.3 Synthesis of SiPc 6

A mixture of silicon(IV) phthalocyanine dichloride (SiPcCl₂) (50 mg, 0.08 mmol), 4-nitrophenol (56.87 mg, 0.40 mmol), and NaH (2.40 mg, 0.10 mmol) in anhydrous toluene (15 mL) was refluxed at 110 °C for 24 h. After brief cooling, the reaction mixture was filtered, and the filter was evaporated in vacuo to give dark blue residue, which was purified by silica gel column chromatography using dichloromethane and methanol (V:V = 1:1) as eluents. A blue band was

collected, and the volatiles were evaporated to give dark blue solid **SiPc 6** (20.14 mg, 30.16%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.66-9.68 (m, 8H), 8.43-8.45 (m, 8H), 6.53 (dd, *J* = 9.5 Hz, 3.0 Hz, 4H), 2.48 (dd, *J* = 9.5 Hz, 3.0 Hz, 4H). HRMS (ESI): *m/z* calcd for C₄₄H₂₄N₁₀O₆Si [M+H]⁺, 817.1722; found 817.1733. Relative error: 1.35 ppm. The ¹³C NMR datum was not obtained because of its low solubility.

1.4 Synthesis of SiPc 7

A mixture of SiPcCl₂ (50 mg, 0.08mmol), 4-nitrobenzoic acid (68.32 mg, 0.40 mmol) and NaH (2.40 mg, 0.10 mmol) in anhydrous toluene (15 mL) was refluxed at 110 °C for 24 h. After brief cooling, the reaction solution was filtered, and the filter was evaporated in vacuo. The dark blue residue was purified by a silica gel column chromatography with dichloromethane as eluents. A blue band was collected, and the volatiles was evaporated to give the product **SiPc7** (47.63 mg, 66.74%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.76 – 9.72 (m, 8H), 8.46 – 8.42 (m, 8H), 7.09 (dt, *J* = 9.0 Hz, 2.5 Hz, 4H), 5.26 (dt, *J* = 9.5 Hz, 2.0 Hz, 4H). HRMS (ESI): *m/z* calcd for C₄₆H₂₄N₁₀O₈Si [M]⁻, 872.1553; found 872.1573. Relative error: 2.29 ppm. ¹³C NMR (126 MHz, CDCl₃, ppm) δ 157.50, 150.36, 148.80, 135.68, 135.35, 131.86, 128.41, 124.23, 121.95.

1.5 Allochroic reaction monitored by absorption and fluorescence spectra

SiPcs (or **ZnPc 1**) were dissolved in DMF to give 1 mM solutions, which were diluted in DMF to 10 μM. Then the solutions were titrated with alkali stock solutions (NaOH in H₂O, NaOCH₃ in CH₃OH, Na₂S in CH₃OH, [NaOH] = [NaOCH₃] = [Na₂S] = 0.5 M, 2 μL for each time). After mixing, the absorption and fluorescence spectra of the solutions were recorded on a GENESYS 150 UV-vis spectrometer and an Edinburgh FL900/FS900 spectrofluorometer (excited at 610 nm), respectively.

The alkali-treated SiPc solution ($[\text{NaOH}] = [\text{NaOCH}_3] = 4 \text{ mM}$) was titrated with HCl aqueous solution (1 M, 2 μL for each time). After mixing, the absorption and fluorescence spectra of the solutions were recorded on a GENESYS 150 UV-vis spectrometer and an Edinburgh FL900/FS900 spectrofluorometer (excited at 610 nm), respectively.

1.6 Allochroic reaction monitored by ^1H NMR spectra

SiPcs were dissolved in DMSO- d_6 (0.5 mL) for ^1H NMR measurement, and then saturated NaOH solution in D $_2$ O (1 μL) was added to the solution for ^1H NMR measurement again, followed by treating with trifluoroacetic acid (TFA) (1 μL) for another ^1H NMR measurement.

1.7 $^1\text{O}_2$ detection

The $^1\text{O}_2$ generation efficiency of the solutions of **SiPc 1**, **SiPc 1** + NaOCH $_3$ and **SiPc 1** + NaOCH $_3$ + HCl were assessed using DPBF as the scavenger. The stock solutions of DPBF (10 mM) and **SiPc 1** (1 mM) in DMF, and NaOCH $_3$ (1 M) in CH $_3$ OH were first prepared. The solution of **SiPc 1** (1 mM) was diluted with DMF to 10 μM , and then NaOCH $_3$ solution (10 μL) was added to give the solution of **SiPc 1** + NaOCH $_3$ ($[\text{SiPc 1}] = 10 \mu\text{M}$, $[\text{NaOCH}_3] = 5 \text{ mM}$), which was further treated with HCl solution (10 μL) to give the solution of **SiPc 1** + NaOCH $_3$ + HCl ($[\text{HCl}] = 5 \text{ mM}$). All the three solutions were mixed with DPBF ($[\text{DPBF}] = 65 \mu\text{M}$), respectively, and then was immediately treated with alternate UV-vis spectral measurement (300-800 nm) and light irradiation ($\lambda > 610 \text{ nm}$, 10 s, 1 mW cm $^{-2}$) with a total irradiation time of 40 s. The light source consisted of a 150 W halogen lamp, a water tank for cooling, and a color glass filter cut-on 610 nm.

The $^1\text{O}_2$ generation of **ZnPc 1** in the presence of NaOCH $_3$ was performed with the same procedure as **SiPc 1**.

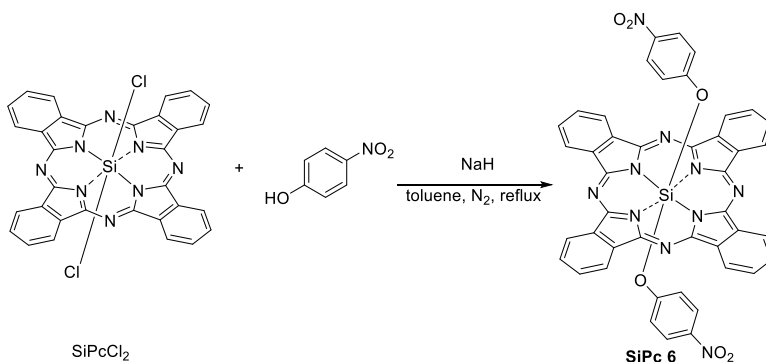
1.8 Photothermal conversion ability

The solutions of **SiPc 1**, **SiPc 1** + NaOCH₃, and **SiPc1** + NaOCH₃ + HCl ([**SiPc 1**] = 10 μM, [NaOCH₃] = [HCl] = 5 mM, 200 μL) in DMSO were added to 96-well plates, respectively. Each solution was continuously irradiated with a laser (660 nm for **SiPc 1**, and **SiPc1** + NaOCH₃ + HCl and 808 nm for **SiPc 1** + NaOCH₃) at a power of 1 W·cm⁻² for 2 min, and the temperature was recorded with a near-infrared thermal imaging camera (TiX520, Fluke, USA).

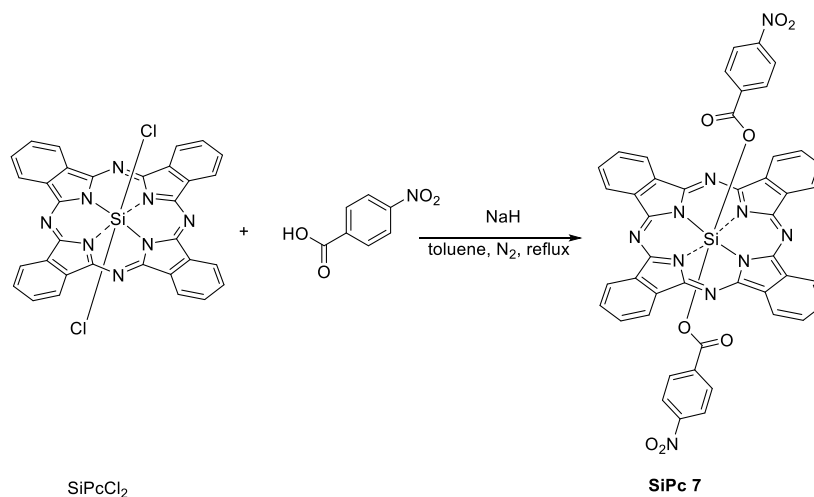
1.9 Theoretical calculations

All calculations were performed by using Gaussian 16 program at the density functional theory (DFT) level with the B3LYP functional.⁷⁻⁹ Zn atom was described using the Stuttgart-Dresden (SDD) pseudopotential, and the 6-31G (d) basis set was used for the other atoms.

2. Supplementary Schemes, Figures, and Tables



Scheme S1. Synthesis of **SiPc 6**.



Scheme S2. Synthesis of **SiPc 7**.

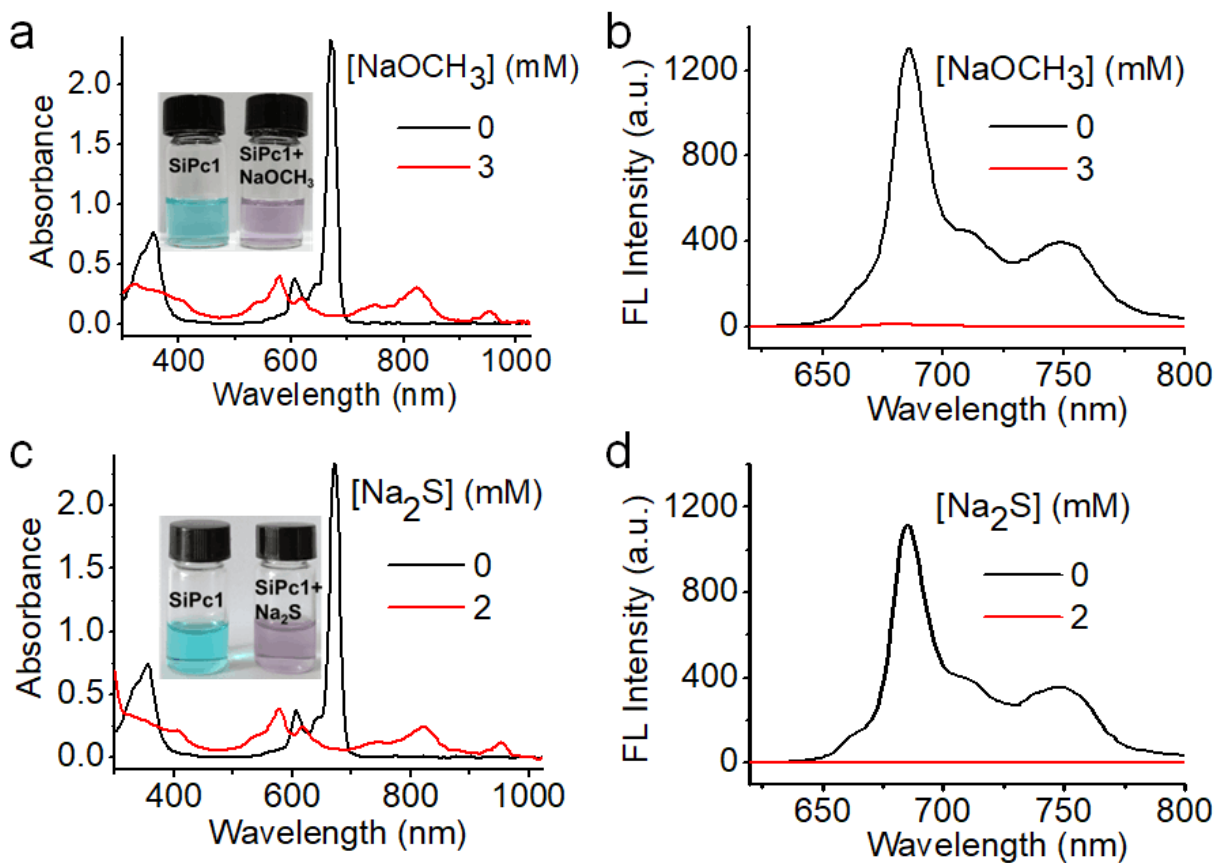


Fig. S1 Changes in (a, c) absorption and (b, d) fluorescence spectra of **SiPc 1** in DMF ($[\text{SiPc 1}] = 10 \mu\text{M}$) upon titration of NaOCH₃ or Na₂S solution.

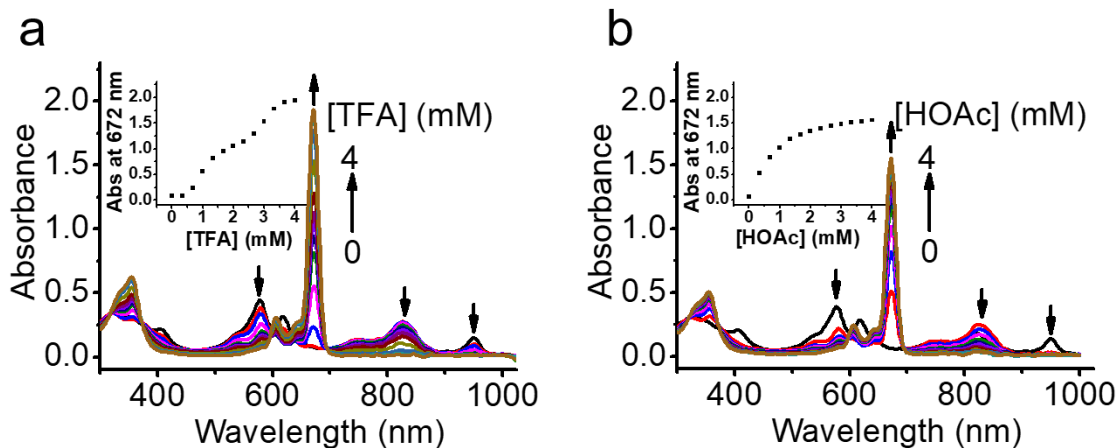


Fig. S2 Absorption spectra of **SiPc 1** in DMF ($[\text{SiPc 1}] = 10 \mu\text{M}$) upon addition of NaOH solution (4 mM) and further treated with (a) TFA and (b) acetic acid (HOAc) solution (0-4 mM).

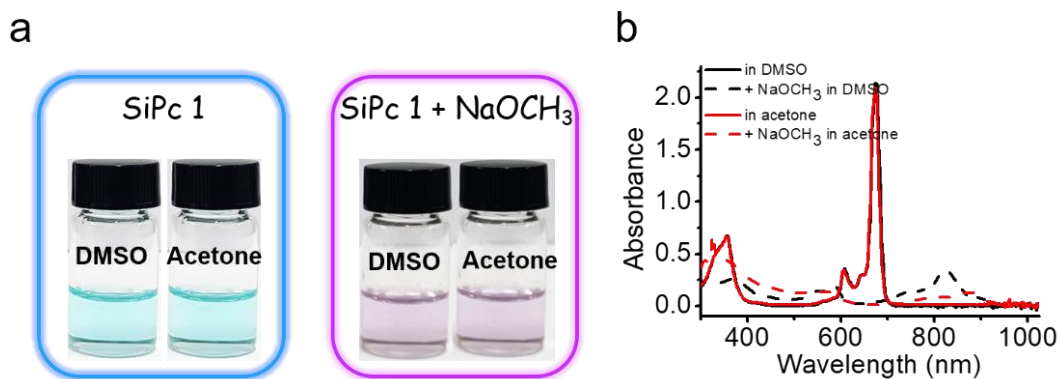


Fig. S3 (a) Photos and (b) corresponding spectra of **SiPc 1** in DMSO or acetone ($[\text{SiPc 1}] = 10 \mu\text{M}$) in the absence and presence of NaOCH₃ ($[\text{NaOCH}_3] = 5 \text{ mM}$).

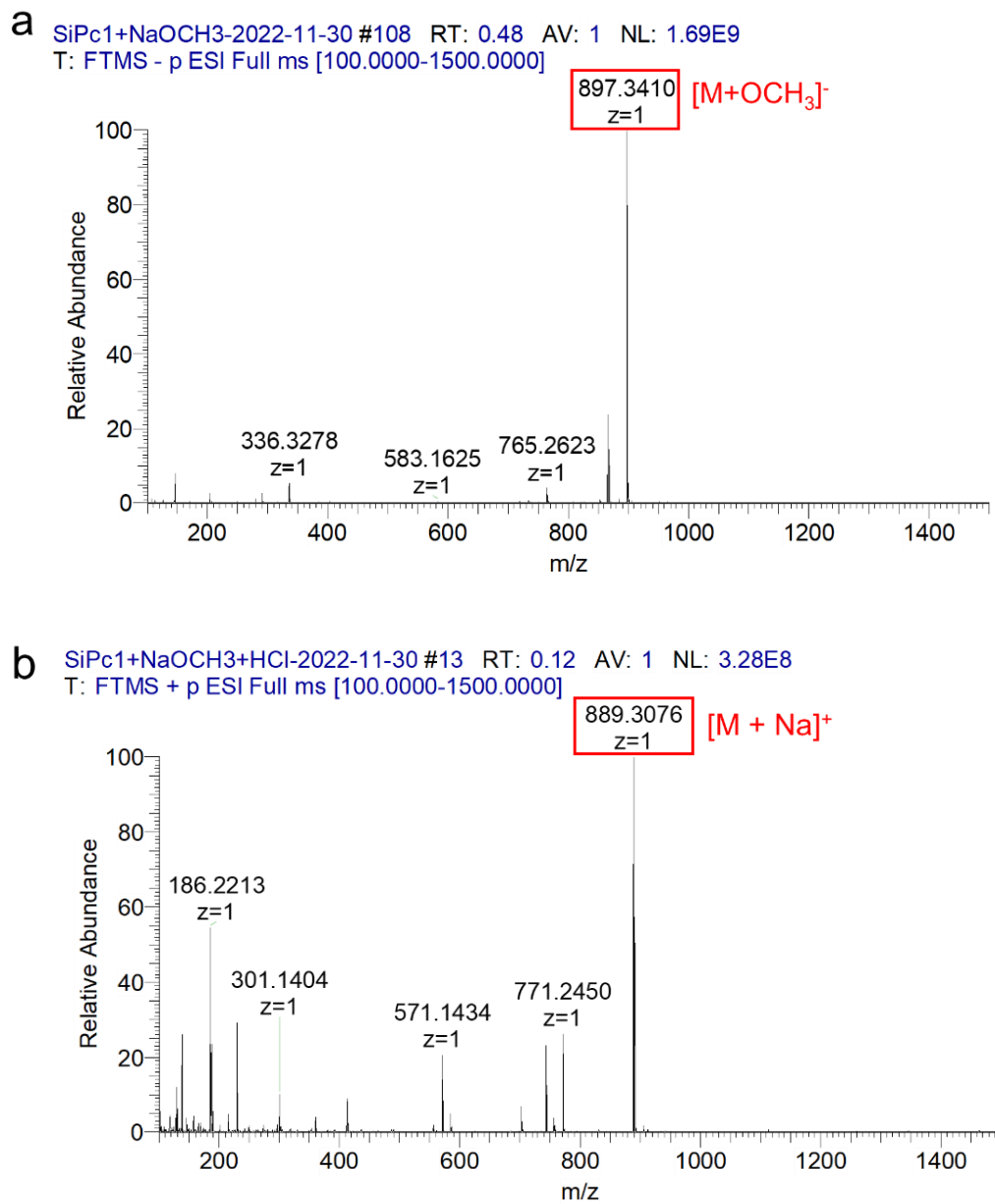


Fig. S4 HRMS of **SiPc 1** treated with (a) NaOCH₃ and (b) followed by HCl solution.

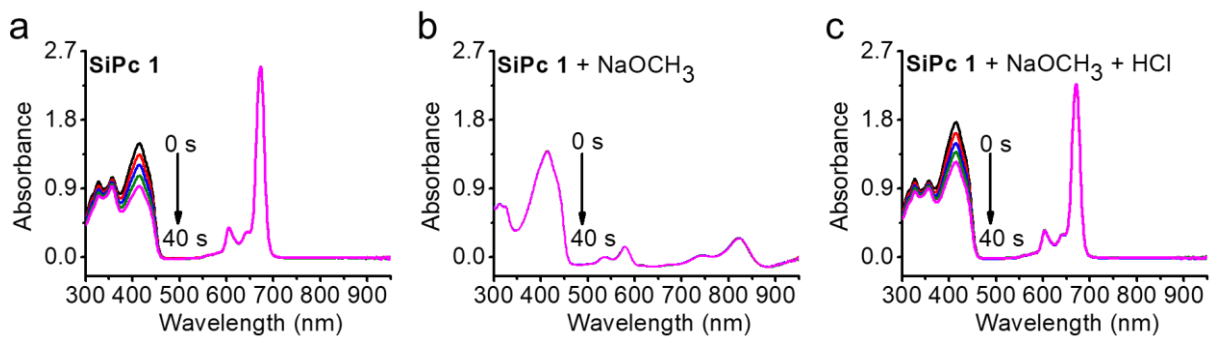


Fig. S5 Absorption spectra of DPBF treated with (a) **SiPc 1**, (b) **SiPc 1** + NaOCH₃, and (c) **SiPc 1** + NaOCH₃ + HCl in DMF upon light irradiation ($\lambda > 610$ nm, 1 mW cm⁻²) ([**SiPc 1**] = 10 μ M, [NaOCH₃] = 5 mM, [HCl] = 5 mM).

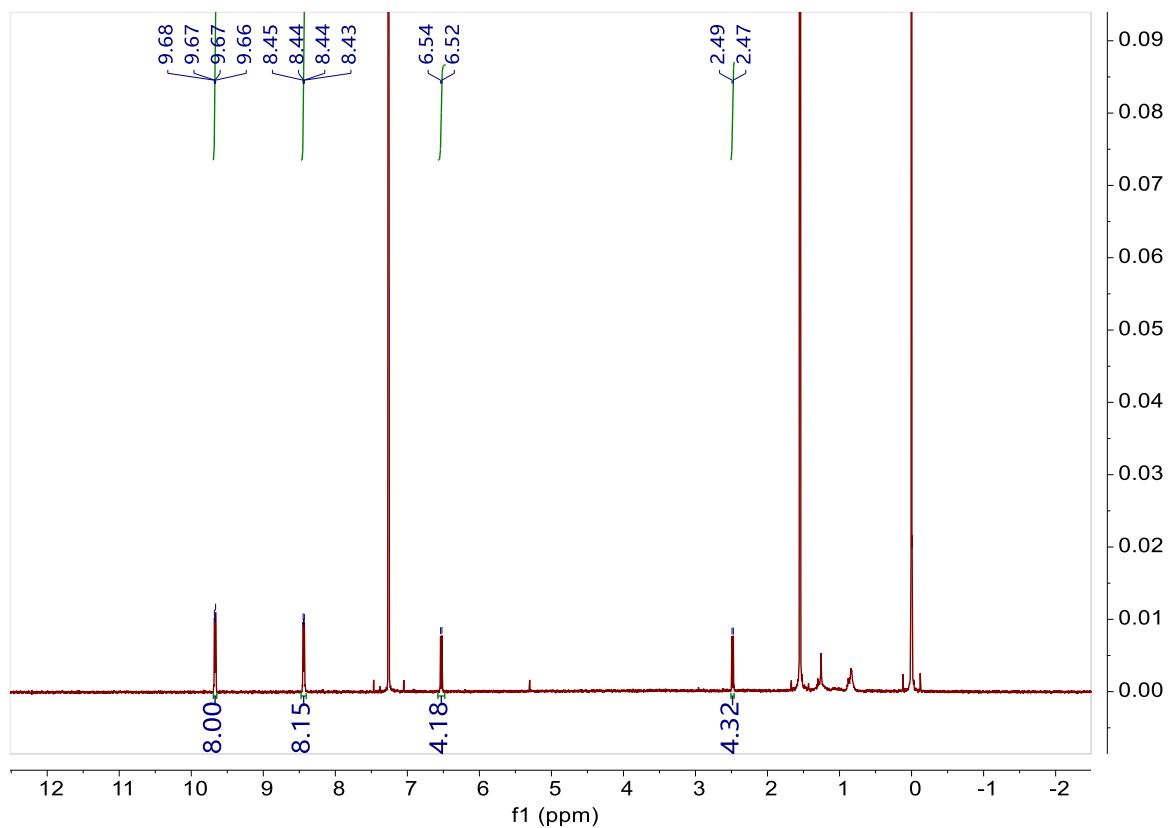


Fig. S6 ¹H NMR spectrum of **SiPc 6** in CDCl₃.

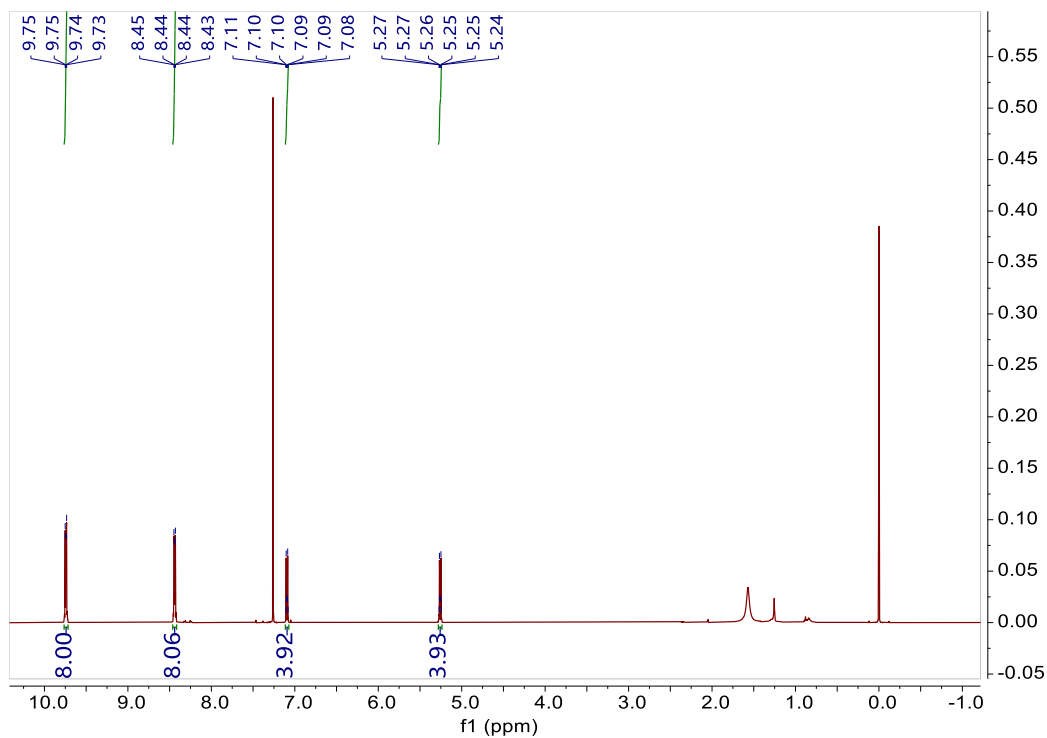


Fig. S7 ^1H NMR spectrum of **SiPc 7** in CDCl_3 .

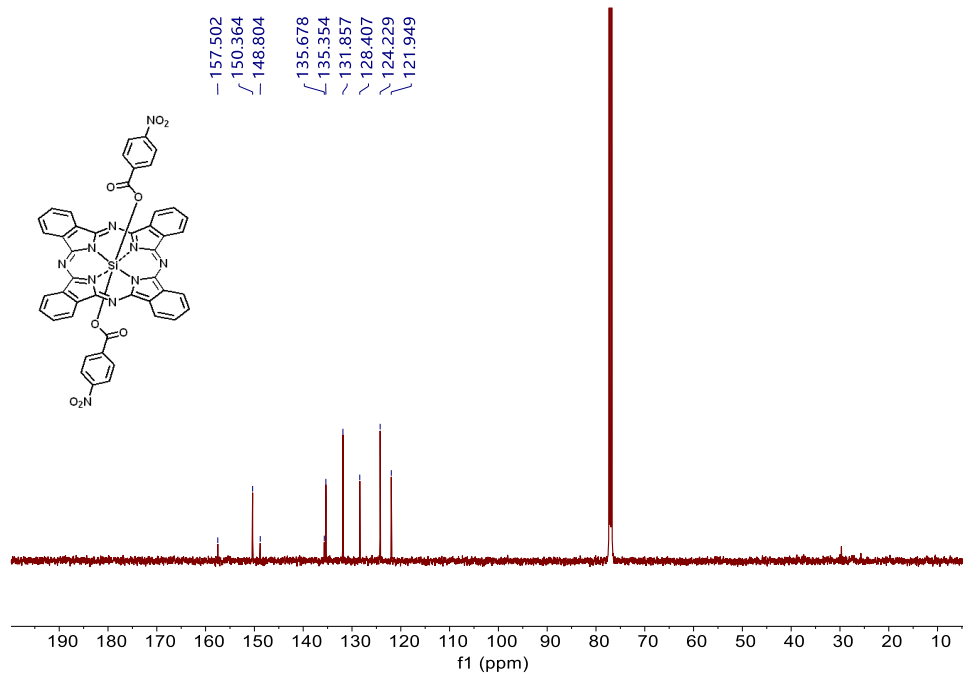


Fig. S8 ^{13}C NMR spectrum of **SiPc 7** in CDCl_3 .

SiPcono20221019APCI #11 RT: 0.12 AV: 1 NL: 4.78E6
T: FTMS + p APCI corona Full ms [1

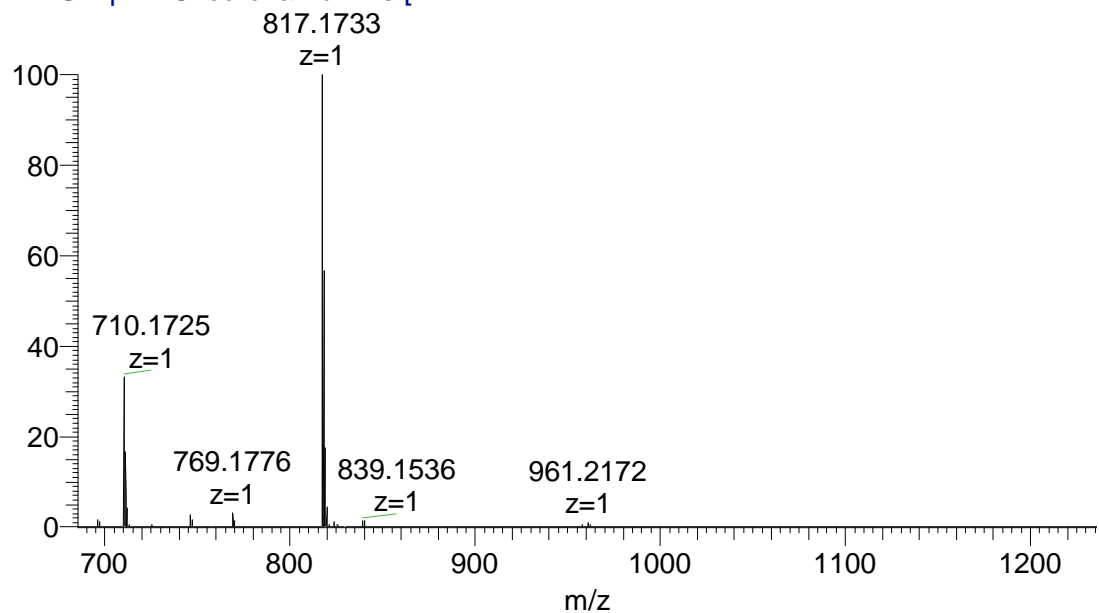


Fig. S9 HRMS of SiPc 6.

SiPcOCONO2 #20 RT: 0.19 AV: 1 NL: 1.84E6
T: FTMS - p ESI Full ms [200.0000-2000

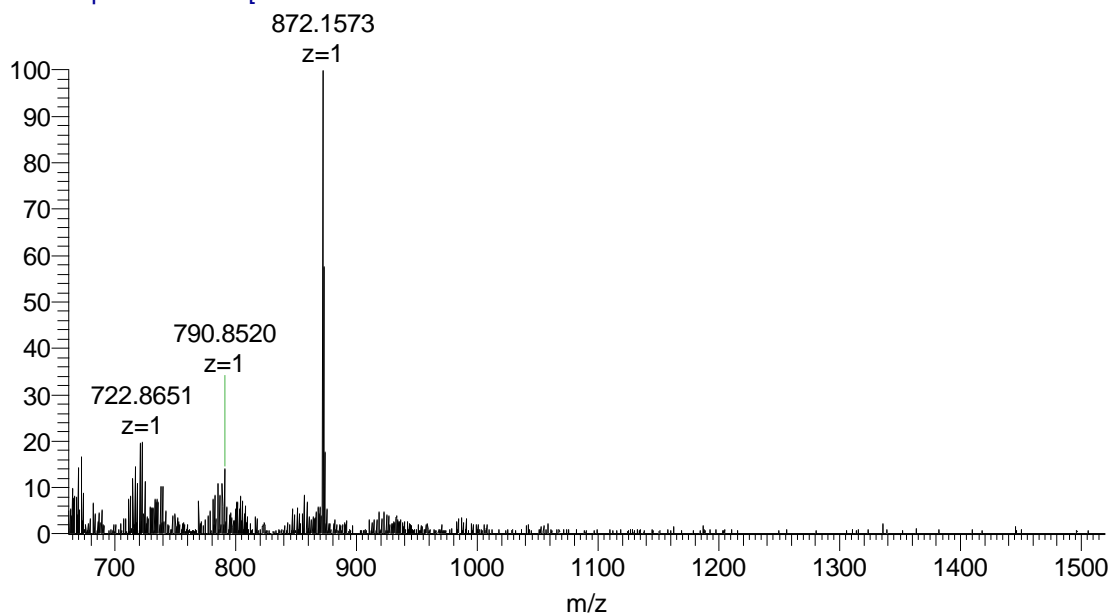


Fig. S10 HRMS of SiPc 7.

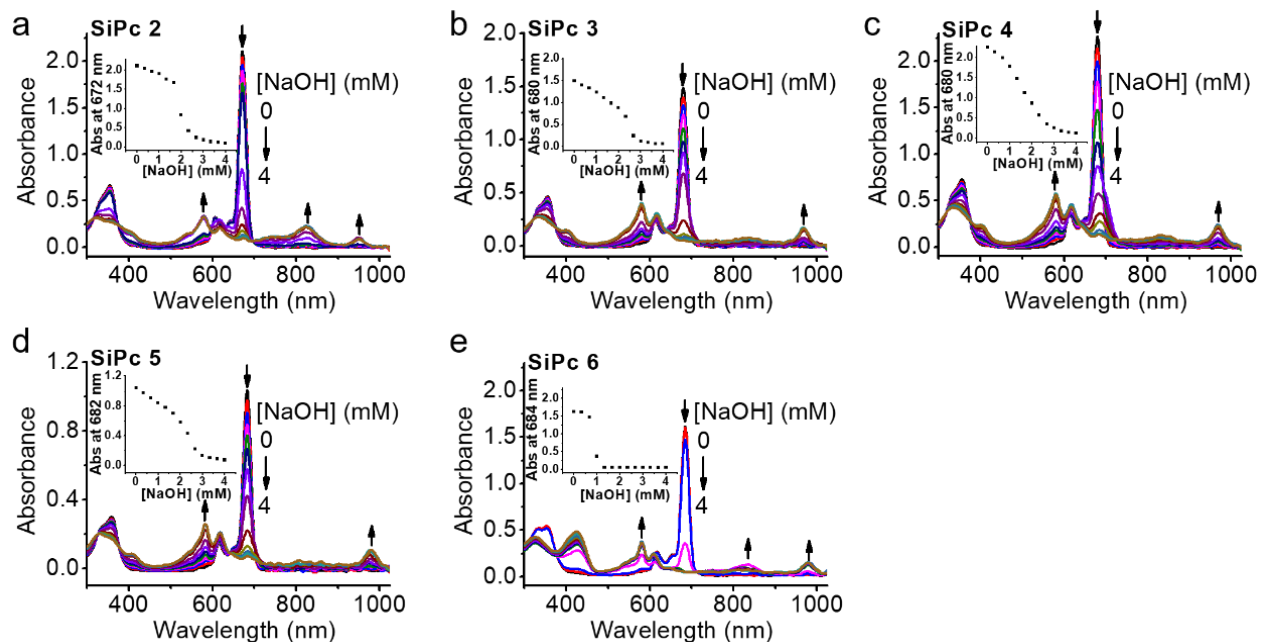


Fig. S11 Changes in absorption spectra of SiPcs 2-6 in DMF ($[\text{SiPcs}] = 10 \mu\text{M}$) upon titration of NaOH solution (0-4 mM).

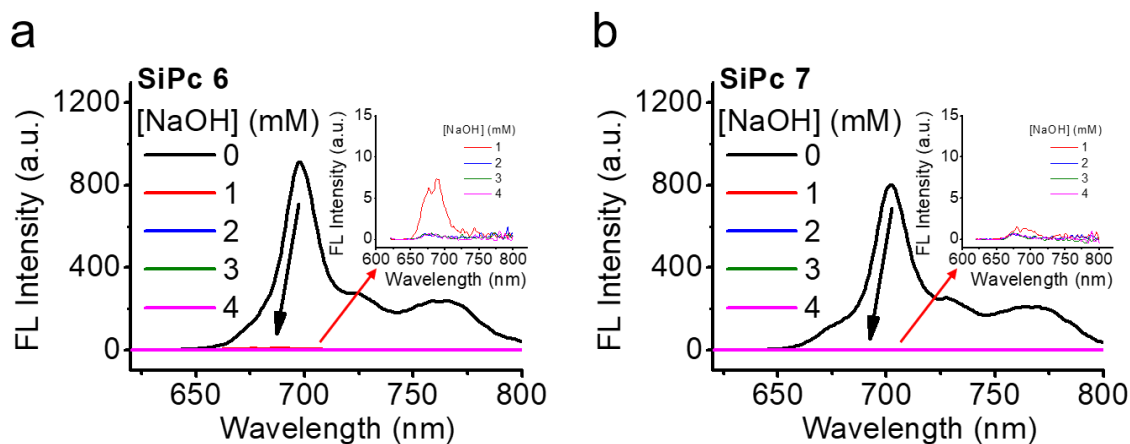


Fig. S12 Fluorescence spectra of (a) SiPc 6 and (b) SiPc 7 in DMF (both at 10 μM) upon titration of NaOH solution (0-4 mM).

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