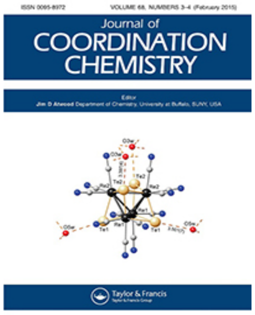

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Xiuqin Chen, Dongdong Ma, Kaicong Cai, Sujuan Pan, Yuhua Wang, Tiantian Zhang, Zheng Huang, Hongqin Yang & Yiru Peng (2015) Effect of axial ligands on the photophysical properties of new silicon(IV) phthalocyanines, Journal of Coordination Chemistry, 68:4, 732-740, DOI: 10.1080/00958972.2014.998658

To link to this article: http://dx.doi.org/10.1080/00958972.2014.998658

Journal of Coordination Chemistry, 2015
Vol. 68, No. 4, 732–740, http://dx.doi.org/10.1080/00958972.2014.998658

Effect of axial ligands on the photophysical properties of new silicon(IV) phthalocyanines

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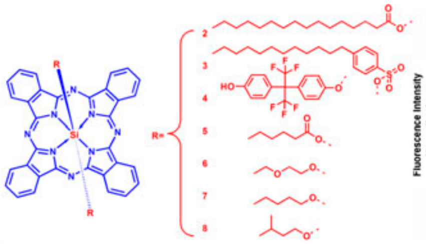
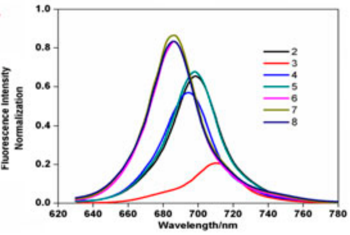
(*Received 21 July 2014; accepted 21 November 2014*)





A series of axial di-substituted silicon(IV) phthalocyanines with electron-donating and electron-withdrawing properties were synthesized. The compounds were characterized by elemental analysis, ^{1}H NMR, IR, and ESI-MS. The effect of axial ligands on the photophysical properties of silicon phthalocyanines was studied by UV/Vis, steady-state and time-resolved fluorescence spectroscopic analyses. Compared with silicon phthalocyanines with electron-donating properties, silicon phthalocyanines with electron-withdrawing properties could expand the π-conjugation in the dyes, resulting in a redshift of Q bands, lower fluorescence emission intensity and fluorescence quantum yields, but increasing fluorescence lifetimes. These results strongly suggest that the molecular design of phthalocyanines is essential for construction of photoactive materials.

Keywords: Silicon(IV) phthalocyanine; Photophysical property; Electron-donating and electron-withdrawing groups

1. Introduction

Phthalocyanines (Pcs) have attracted attention for their applications in material science [1, 2]. They have been used in electro-optical devices [3, 4], solar cells [5], liquid crystals [6], optical data storage [7, 8], electrochromic display [9], and photodynamic therapy [10, 11].

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However, many applications are restrained by their limited solubility in common organic solvents and water. Moreover, because of the π–π interaction between planar aromatic structures, Pcs have a strong tendency to form insoluble aggregates [12, 13].

Aggregation is an unfavorable property of Pcs, since it can cause difficulties in purification and characterization [14]. One of the strategies employed to prevent the formation of aggregates is the introduction of substituents on the axial position of phthalocyanines. The substituent groups on axial positions can strongly influence essential parameters of a phthalocyanine, such as its solubility, aggregation behavior, and electronic absorption, thus ultimately increasing the amount of monomer in solution. For example, substitution on axial positions with bulky groups [15], long alkyl chains [16], crown ethers [17, 18], or phenoxy groups [19] can lead to phthalocyanine derivatives soluble in common organic solvents, and with quaternized amino, sulfonate, or carboxylic groups can result in phthalocyanine derivatives soluble in water [20–22]. Ishii and Kobayashi [23] provided photophysical data of a range of substituted and unsubstituted metal phthalocyanine complexes. Nyokong [24–26] reviewed some photophysical data of silicon phthalocyanines including the work from her group. However, to date, the relationship between the ligand structure and photophysical property of axially di-substituted silicon(IV) phthalocyanines has not been reported. In this article, we designed and synthesized a series of axial substituents on silicon phthalocyanines with changed electron-donating or electron-withdrawing properties. The effect of axial groups on the photophysical properties of silicon phthalocyanines were investigated by UV/Vis, steady-state and time-resolved fluorescence spectroscopic methods.

2. Experimental

2.1. *Materials and equipment*

All reagents and solvents were of reagent grade and obtained from commercial suppliers. Compounds $SiPcCl_2$**1** and unsubstituted zinc(II) phthalocyanine (**n-ZnPc**) were obtained according to the literature [27].

IR spectra were recorded on a Perkin Elmer PE-983G FT-IR spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer using TMS as an internal standard. Mass spectra were performed on a Finnigan (USA) LCQ Deca XP MAX spectrometer. The elemental analyses were performed on an Elementar Vario EL III elemental analyzer. UV/Vis spectra were recorded on a Varian Cary 50 spectrophotometer. Steady-state and time-resolved fluorescence spectra were measured on a FL900/FS920 fluorescence spectrophotometer.

2.2. *Determination of photophysical parameters*

Fluorescence quantum yields were determined according to equation (1) [28, 29],

$$\Phi_X = \Phi_{ZnPc} \times \frac{F_X}{F_{ZnPc}} \times \frac{A_{ZnPc}}{A_X} \tag{1}$$

where Φ_{ZnPc} is the fluorescence quantum yield of **n-ZnPc** in DMF ($\Phi_{\mathbf{n\text{-}ZnPc}}$ = 0.28) [30], where F_X and F_{ZnPc} are the integrals of fluorescence emission intensity of the silicon phthalocyanines **2–8** and the **n-ZnPc**, respectively. A_X and A_{ZnPc} are the absorbances of the silicon phthalocyanines **2–8** and the **n-ZnPc** at the specific excitation wavelength, respectively.

The fluorescence decay curves were fitted using an iterative nonlinear least squares method and analyzed by a reconvolution of the instrumental response function.

2.3. *Synthesis and characterization*

2.3.1. Synthesis of bis-pentadecylcarboxylate silicon phthalocyanine (2). A mixture of palmitic acid (0.21 g, 0.7 mM), **1** (0.20 g, 0.33 mM), and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) was refluxed at 110 °C for 48 h. The reaction mixture was then cooled to room temperature and the solvent was evaporated to dryness under reduced pressure. The solid product was purified for 24 h by Soxhlet extraction using dichloromethane (DCM) as an extracting agent. The extracted material was recrystallized. The obtained crystal was washed three times with methanol and water ($v:v = 1:1$). The silicon phthalocyanine **2** was obtained as a blue solid. Yield: 72.5 mg (21.1%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.67–9.70 (m, 8H; Pc-αH), 8.36–8.38 (m, 8H; Pc-βH), −0.66 (t, 4H; CH_2), −0.98 (q, 4H; CH_2), −0.76 (q, 4H; CH_2), 0.05 (q, 4H; CH_2), 0.52 (q, 4H; CH_2), 0.81 (q, 4H; CH_2), 1.03 (q, 4H; CH_2), 1.14 (q, 4H; CH_2), 1.26–1.30 (m, 24H; CH_2), 0.89 (t, 6H; CH_3). IR (KBr, cm^{-1}): 2923, 2849 (CH_3, CH_2), 1682 (C=O), 1612, 1528, 1432, 739 (Pc ring), 1288, 1125 (C–O), 1082 (Si–O). ESI-MS *m*/*z*: 1051$[M]^+$. Anal. Calcd for $C_{64}H_{78}N_8O_4Si$: C, 73.11; H, 7.48; N, 10.66. Found: C, 73.05; H, 7.46; N, 10.61%.

2.3.2. Synthesis of bis-4-dodecyl-phenyl sulfonate silicon phthalocyanine (3). According to the procedure described for synthesis of silicon phthalocyanine **2**, treatment of **1** (0.20 g, 0.33 mM) with sodium dodecylbenzene sulfonate (0.24 g, 0.70 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **3** as a blue solid. Yield: 22.6 mg (5.8%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.63–9.64 (m, 8H; Pc-αH), 8.45–8.46 (m, 8H; Pc-βH), 6.15 (d, 4H; Ar–H), 4.91 (d, 4H; $ArCH_2$-H), 1.30–0.89 (m, 50H; $–CH_2–$, $–CH_3$). IR (KBr, cm^{-1}): 2958, 2925, 2854, 1470 (CH_3, CH_2), 1615, 1529, 1431, 736 (Pc ring), 1292, 1124 (C=O), 1082 (Si–O). ESI-MS *m*/*z*: 1183$[M\text{-}CH_2CH_3 + H_2O]^+$. Anal. Calcd for $C_{68}H_{74}N_8O_6S_2Si$: C, 68.54; H, 6.26; N, 9.40. Found: C, 68.52; H, 6.30; N, 9.36%.

2.3.3. Synthesis of bis-2,2-bis (4-hydroxyphenyl) hexafluoropropane silicon phthalocyanine (4). According to the procedure described for **2**, treatment of **1** (0.20 g, 0.33 mM) with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (0.24 g, 0.7 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **4** as a blue solid. Yield: 62.1 mg (15.7%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.61–9.62 (m, 8H; Pc-αH), 8.37–8.38 (m, 8H; Pc-βH), 2.39 (d, 4H; Ar–H), 5.58 (d, 4H; Ar–H), 6.47 (d, 4H; Ar–H), 6.64 (d, 4H; Ar–H). IR (KBr, cm^{-1}): 3439 (–OH), 1612, 1514, 1429, 736 (Pc ring), 1251, 1207, 1172, 1127 (C–F), 1080 (Si–O). ESI-MS *m*/*z*: 1209 $[M-H]^+$, 1246 $[M + 2H_2O]^+$. Anal. Calcd for $C_{62}H_{34}F_{12}N_8O_4Si$: C, 61.49; H, 2.83; N, 9.25. Found: C, 61.44; H, 2.80; N, 9.23%.

2.3.4. Synthesis of bis-pentyl-carboxylate silicon phthalocyanine (5). According to the procedure described for synthesis of silicon phthalocyanine **2**, treatment of **1** (0.20 g, 0.33 mM) with hexanoic acid (0.5 mL, 3.99 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **5** as a blue solid. Yield: 61.5 mg (24.4%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.70–9.72 (m, 8H; Pc-αH), 8.38–8.40 (m, 8H; Pc-βH), −0.64 (t, 4H; CH_2), −0.93 (q, 4H; CH_2), −0.73 (q, 4H; CH_2), 0.12 (q, 4H; CH_2), 0.22 (q, 6H; CH_3). IR (KBr, cm^{-1}): 2927, 2853, 1470 (CH_3, CH_2), 1684(–C=O), 1081(Si–O), 1612, 1529, 1431, 736 (Pc ring). ESI-MS *m/z*: 771 $[M]^+$. Anal. Calcd for $C_{44}H_{38}N_8O_4Si$: C, 68.55; H, 4.97; N, 14.54. Found: C, 68.50; H, 4.93; N, 14.53%.

2.3.5. Synthesis of bis-2-ethoxylated silicon phthalocyanine (6). According to the procedure described for synthesis of silicon phthalocyanine **2**, treatment of **1** (0.20 g, 0.33 mM) with 2-ethoxyethanol (0.5 mL, 5.16 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **6** as a blue solid. Yield: 39.5 mg (16.8%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.55 (m, 8H; Pc-αH), 8.33 (m, 8H; Pc-βH), −1.91 (t, 4H; CH_2), 0.31 (t, 4H; CH_2–O), 1.66 (t, 4H; CH_2–O), 0.12 (t, 6H; CH_3). IR (KBr, cm^{-1}): 2965, 2881 (CH_3, CH_2), 1615, 1520, 1427, 735 (Pc ring), 1289, 1261, 1119 (C–O), 1080 (Si–O). ESI-MS *m/z*: 719 $[M]^+$. Anal. Calcd for $C_{40}H_{34}N_8O_4Si$: C, 66.83; H, 4.77; N, 15.59. Found: C, 66.74; H, 4.72; N, 15.56%.

2.3.6. Synthesis of bis-pentyloxy silicon phthalocyanine (7). According to the procedure described for synthesis of silicon phthalocyanine **2**, treatment of **1** (0.20 g, 0.33 mM) with n-pentanol (0.5 mL, 4.60 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **7** as a blue solid. Yield: 44.7 mg (19.1%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.65–9.66 (m, 8H; Pc-αH), 8.35–8.36 (m, 8H; Pc-βH), −2.07 (t, 4H; CH_2), −1.68 (q, 4H; CH_2), −1.40 (q, 4H; CH_2), −0.38 (q, 4H; CH_2), −0.13 (t, 6H; CH_3). IR (KBr, cm^{-1}): 2948, 2923, 2851 (CH_3, CH_2), 1612, 1518, 1427, 736 (Pc ring), 1080 (Si–O). ESI-MS *m/z*: 715 $[M]^+$. Anal. Calcd for $C_{42}H_{38}N_8O_2Si$: C, 70.56; H, 5.36; N, 15.67. Found: C, 70.55; H, 5.34; N, 15.68%.

2.3.7. Synthesis of bis-3-methyl-butoxy silicon phthalocyanine (8). According to the procedure described for synthesis of silicon phthalocyanine **2**, treatment of **1** (0.20 g, 0.33 mM) with isoamyl alcohol (0.09 g, 1.02 mM) and anhydrous K_2CO_3 (0.14 g, 1.01 mM) in dried toluene (30 mL) gave the silicon phthalocyanine **8** as a blue solid. Yield: 58.5 mg (25.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.65–9.67 (m, 8H; Pc-αH), 8.34–8.36 (m, 8H; Pc-βH), –2.08 (t, 4H; CH_2), −1.85 (t, 4H; CH_2), −1.22 (t, 2H; CH), −0.79 (t, 12H; CH_3). IR (KBr, cm^{-1}): 2953, 2920, 2867, 1468 (CH_3, CH_2), 1610, 1518, 1428, 739 (Pc ring), 1080 (Si–O). ESI-MS *m/z*: 715$[M]^+$. Anal. Calcd for $C_{42}H_{38}N_8O_2Si$: C, 70.56; H, 5.36; N, 15.67. Found: C, 70.48; H, 5.30; N, 15.63%.

3. Results and discussion

3.1. *Syntheses and characterization*

The synthesis scheme of **2–8** is shown in scheme 1. Reaction of **1** with different acids such as palmitic acid, caproic acid, dodecyl benzene sulfonic acid sodium, and

2,2-bis(4-hydroxyphenyl)hexafluoropropane gave **2–5** bearing ester groups with electron-withdrawing properties, respectively. Reaction of **1** with different alcohols (*e.g.* amyl alcohol, isoamyl alcohol, ethylene glycol monomethyl ether) gave **6–8** bearing ether groups with electron-donating properties.

The structures of new compounds were characterized by elemental analysis, UV/Vis, IR, ^{1}H NMR, and ESI-MS spectral methods. They were compatible with the proposed structures. The detailed characterization data are shown in section 2 and the characteristic figures in Supplementary material.

Each compound gave a satisfactory elemental analysis. Intense singly charged molecular ion peaks were observed in the ESI-MS of all silicon-phthalocyanines **2–8**.

The silicon-phthalocyanines **2–8** were found to be pure by ^{1}H NMR with both the axial groups and phthalocyanine ring protons in their respective aromatic and alkyl regions. Two sets of resonances were observed at 9.60 and 8.40 ppm integrating for eight protons each, making a total of 16 protons expected for the αH and βH of phthalocyanine protons. The resonances at 6.64–5.58 ppm were contributed to the signals of the aromatic protons for **3** and **4**. The resonance at 4.91 ppm was assigned to the signals of the methylene linked with the aromatic ring for **3**. As the strong ring current of phthalocyanine ring, the signals of aliphatic protons exhibited higher values of δ between −2.08 and 0.22 ppm. These silicon phthalocyanines have good solubility in solvents such as chloroform, DCM, acetone, DMF, DMSO, THF, and ethyl acetate.

3.2. *Photophysical properties*

The UV/Vis spectra of **2–8** in DCM are shown in figure 1. Silicon phthalocyanines **2–8** mainly existed as monomers in DCM. They exhibited a B-band at 350 nm and a strong Q-band ranging from 671 to 696 nm. Noticeably, **4** had a strong UV band at 270 and 290 nm, assigned to the absorption of 2,2-bis(4-hydroxyphenyl)hexafluoropropane group. Furthermore, the electron-withdrawing and electron-donating nature of ligands on the axial position can strongly influence the position of Q-bands. The Q-bands of **6–8** with

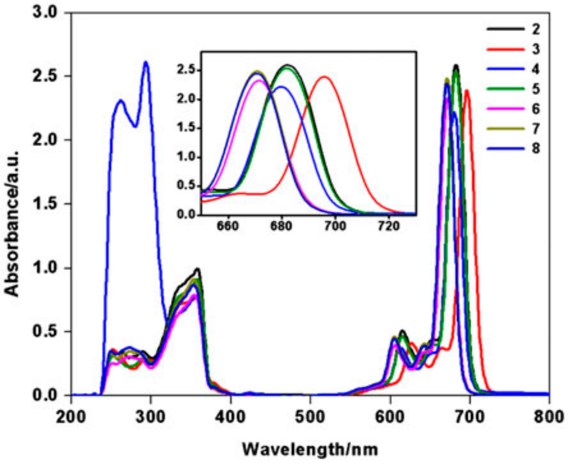


Figure 1. UV/Vis spectra of **2–8** in DCM (concentration = 1 × 10^{-5} M L^{-1}).

electron-donating ether groups mainly existed at 671 nm, whereas the Q-bands of **2**, **4,** and **5** with electron-withdrawing ester groups were at 680–682 nm. Compared with **6–8**, the Q-bands of silicon phthalocyanines with electron-withdrawing ester groups were redshifted about 10 nm. More obvious, the Q-band of **3** with dodecyl benzene sulfonic ether groups was observed at 696 nm, about 25 nm redshifted relative to **6–8**. This result indicated that the substituted groups of **2–5** linking with Si through ester bonds could form an expanded π conjugation system in the dyes, which decreased the electron density of phthalocyanine ring and reduced the LUMO and HOMO energy level differences, therefore leading to the red-shift of Q-bands. As the electron-withdrawing ability of dodecyl benzene sulfonic ether was stronger than other ligands with ester bonds, the increased redshift of the Q-band for **3** was observed.

The fluorescence spectra of **2–8** in DCM are shown in figure 2. Upon excitation at 610 nm, these compounds exhibited a fluorescence emission at 685–710 nm. The fluorescence decay curves of **2–8** in DCM are shown in figure 3. The fitting fluorescence lifetimes (τ_S) of **2–8** are listed in table 1. The fluorescence quantum yields (Φ_F) were determined using n-ZnPc as a reference standard.

Changes in the nature of axial ligands for silicon phthalocyanines also exerted effect on the position and intensity of fluorescence spectra, fluorescence lifetimes and fluorescence quantum yields. Silicon phthalocyanines **6–8** containing two electron-donating groups via ether linkages exhibited emission at 686 nm, while **2–5** with electron-withdrawing groups via ester linkages exhibited a redshift emission between 694 and 698 nm. The emission of **3** with stronger electron-withdrawing dodecyl benzene sulfonic sodium ester was observed at 710 nm. For the silicon phthalocyanines with electron-donating groups, higher fluorescence intensity was observed than those with electron-withdrawing groups.

The fluorescence lifetimes are 7.24–9.45 ns, which did not vary too much with change of axial ligands. There was a trend of increasing τ_s value from **6** to **8** containing electron-donating groups to **2–5** comprising electron-withdrawing groups. The differences in the lifetimes could be explained in that **6–8** via ether linkage with silicon could not form a conjugated π system with the macromolecular system and reduced the interaction possibility between the substituted groups and phthalocyanine ring, thus resulting in lower fluorescence lifetimes.

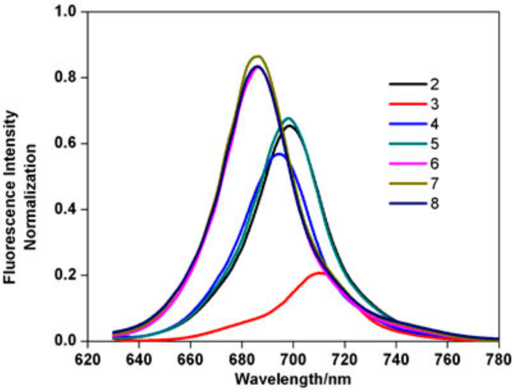


Figure 2. Fluorescence spectra of **2–8** in DCM (concentration = 1 × 10^{-5} M L^{-1}).

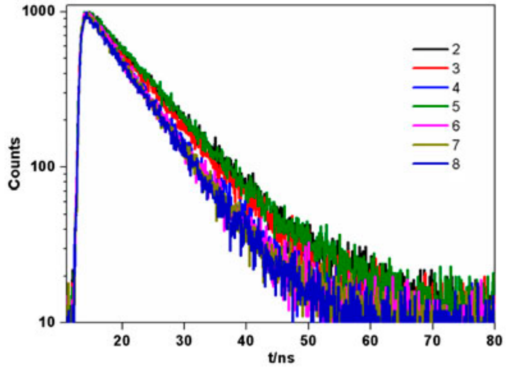
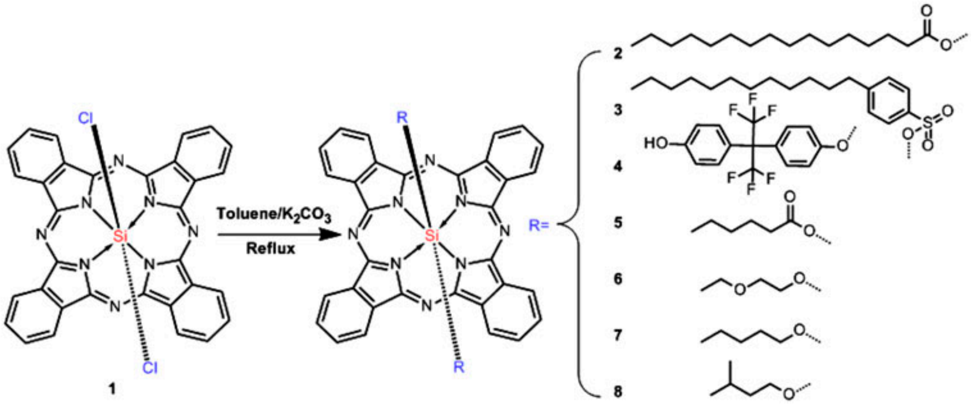


Figure 3. Fluorescence decay curves of silicon(IV) phthalocyanines in DCM (λ_{ex} = 405 nm; concentration = 1×10^{-5} M L^{-1}).



Scheme 1. The scheme for synthesis of **2–8**.

Table 1. The spectral data of **2–8**.[b]

Complexes	λ_{abs} (nm)	λ_{em} (nm)	τ_s (ns)	Φ_F[a]
2	358, 682	698	9.45 ± 0.95	0.24
3	358, 696	710	8.89 ± 0.89	0.30
4	262, 293, 355, 680	694	7.82 ± 0.78	0.25
5	358, 682	698	9.33 ± 0.93	0.27
6	354, 672	686	7.41 ± 0.74	0.34
7	354, 671	686	7.43 ± 0.74	0.34
8	353, 671	686	7.38 ± 0.74	0.30

[a] Unsubstituted zinc(II) phthalocyanine (**n-ZnPc**) in DMF as the reference (Φ_F = 0.28).
[b] λ_{ex} = 610 nm.

The change of nature of axial ligands within silicon phthalocyanines also does not exert significant effect on the fluorescence quantum yields. The fluorescence quantum yields of **2–8** are 0.24–0.34 (see table 1). The Φ_F values for **2–5** with electron-withdrawing groups were relatively lower than those with electron-donating groups. This observation is consistent with the notion that electron-withdrawing groups are part of the phthalocyanine π system and thus, can increase the possibility of intersystem crossing [26].

4. Conclusion

A series of axially substituted silicon phthalocyanines **2–8** containing electron-donating and electron-withdrawing groups were synthesized. Their structures were unambiguously characterized by elemental analysis, ESI-MS, and ^{1}H NMR. The photophysical properties of silicon phthalocyanines were studied by UV/Vis, steady–state, and time-resolved spectroscopic methods. Results showed that the Q-band position, emission intensity and position, fluorescence lifetimes, and fluorescence quantum yields were affected by the nature of electron-withdrawing and electron-donating abilities. As **2–5** with electron-withdrawing groups could form conjugated π system with the phthalocyanine ring, they exhibited a redshift of Q-band absorption, lower fluorescence intensity, and fluorescence quantum yield, but longer fluorescence lifetimes.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21274021, 61335011, and 81471703), and the college students' innovative and entrepreneurial training program of Fujian Province (hxhg-21).

Funding

This work was supported by the National Natural Science Foundation of China [grant number 21274021], [grant number 61335011], and [grant number 81471703].

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.998658].

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