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Synthesis of Multidentate Squaraines

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Abstract: To search for more better sensitizer of organic solar cell, a series of multidentate squaraines (**Sq1~6**) were synthesized, the structures were determined by elemental analysis, IR, UV-vis, ^{1}H NMR and MS spectroscopies. The squaraines have good solubility in polar solvents such as EtOH, CH_3COCH_3, $CHCl_3$,*etc*. as well as strong absorption band over 600～700 nm spectral range.

Keywords: Multidentate squaraines, synthesis.

A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO_2 films was described by Brian O'Regan and Michael Gratzel in 1991[1-3]. But the Ruthenium bipyridyl complex has the maximum absorption wavelength around 500 nm. It is unable to make full use of solar spectrum due to its weak absorption in the red visible region above 600 nm, which is a vital factor restricting the photoelectric conversion efficiency of the cell.

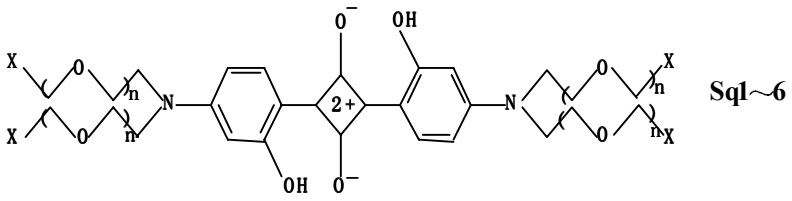
One of the important criteria for an efficient photosensitization is to adsorb dyes on the semiconductor surface with an electrostatic, hydrophobic, or chemical interaction. Squaric acid has unique charge separation in the molecular, and carries two positive electronic charges within the four membered ring framework. Its derivatives, squaraines, have high extinction coefficients in the visible region.

In order to search for more better sensitizer to improve the photoelectric conversion efficiency of "Gratzel solar cell", we synthesized a series of multidentate squaraines **Sq1~6**, whose structures were determined by the elemental analysis, IR, UV-vis, ^{1}H NMR and MS spectroscopies. **Sq1~6**, possess a good solubility in polar solvents, and have strong absorption band over 600~700 nm spectral range. Addition of TiO_2 colloids to a solution of **Sq1** resulted in the increase of optical density, fluorescence quenching and shorter fluorescence lifetime. All of these indicated that **Sq1** was strongly adsorpted on TiO_2 surface. With attaching carboxy group leads to build up suitable electric coupling between the excited state of photosensitizer and the conduction band of TiO_2 electrode. This is beneficial to electron injection process. The apparent association constant of 1517mol • L^{-1} with nanoparticle TiO_2 was determined from the data of **Sq1** fluorescence quenching by TiO_2 colloids. The full data and experimental details will be reported elsewhere. Herein, we report on the synthesis of these new compounds[4].

Experiment

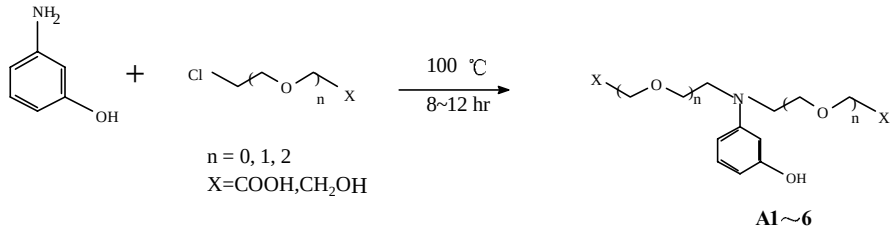
Elemental analysis. IR, UV-vis, ^{1}H NMR, MS spectra of **Sq1~6** were measured using a Carlo Erba 1106 elemental analyzer, FX-IR 170SX infrared spectro- photometer, P-E Lambda 4B ultraviolet spectrometer, JNM-FX90G NMR spectrometer, Finnigan-4510 mass spectrometer, respectively. All the solvents were analytical grade and were purified before use. **Scheme 1** lists the chemical structures of the multidentate squaraines. The synthesis of multidentate squaraines (**Sq1~6**) was performed as shown in **Scheme 2**.

Scheme 1 Chemical structures of multidentate squaraines



	Sq1	Sq2	Sq3	Sq4	Sq5	Sq6
n	0	1	2	0	1	2
X	COOH	COOH	COOH	CH_2OH	CH_2OH	CH_2OH

Scheme 2 The synthetic routes of multidentate squaraines



	A1	A2	A3	A4	A5	A6
n	0	1	2	0	1	2
X	COOH	COOH	COOH	CH_2OH	CH_2OH	CH_2OH

The description of synthetic route starts with squaric acid prepartion. Squaric acid was prepared from hexachlorobutadiene and morpholine according to Ref. [5] *via* a one-pot method in two-step reaction of substitution cyclization (intramolecular '2+2' addition) and hydrolysis. **Sq1~6** were synthesized by condensation of 3-N, N-bis (2-carboxymethyl) aminophenol or its analogs **A1~6** with squaric acid in butanol at 117°C. **A1~6** were synthesized by condensation *m*-aminophol with chloracetic acid or its analogs.

A1 Yellow crystal, mp 122~3°C, yield 56.5%. υ (KBr): 3400~2559 (-OH,

COOH), 1708 (C=O), 1600, 1502 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 13.00 (s, 2H, COOH), 8.01 (s, 1H, Ar-OH), 6.94 (t, 1H, J=5.30 Hz, Ar-H), 6.52 ~6.00 (m, 3H, Ar-H), 3.84 (s, 4H, 2 × CH_2). *m/z* %: 225 (M^+, 20).

A2 Yellow crystal, mp 114~6°C, yield 45.2%. υ (KBr): 3400~2520 (-OH, COOH), 1702 (C=O), 1600, 1520 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 13.00 (s, 2H, COOH), 8.95 (s, 1H, Ar-OH), 7.00 ~6.25 (m, 4H, Ar-H), 3.90 (s, 4H, 2×CH_2), 3.15~3.01 (m, 8H, 2×-CH_2CH_2-). *m/z*%: 313 (M^+, 18).

A3 Yellow crystal, mp 102~3°C, yield 47.2%. υ (KBr): 3400~2520 (-OH, COOH), 1700 (C=O), 1620, 1500 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 12.80 (s, 2H, COOH), 8.09 (s, 1H, Ar-OH), 7.21~6.50 (m, 4H, Ar-H), 3.85 (s, 4H, 2×CH_2), 3.20~3.00 (m, 16H, 4×-CH_2CH_2-). *m/z* %: 401 (M^+, 10).

A4 Yellow crystal, mp 68~69°C, yield 55.0%. υ (KBr): 3343 (-OH), 1610, 1570 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 8.90 (s, 1H, Ar-OH), 6.05 (m, 3H, Ar-H), 6.88 (t, 1H, J=2.38 Hz, ArH), 4.17~3.12 (m, 10H, NCH_2, OCH_2, CH_2OH). *m/z* %: 197 (M^+, 2 0).

A5 Yellow crystal, mp 70~71°C, yield 40.5%. υ (KBr): 3339 (-OH), 1620, 1570 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 8.88 (s, 1H, Ar-OH), 6.37 (m, 3H, Ar-H), 7.20 (t, 1H, J=6.05 Hz, ArH), 4.20~3.09 (m, 18H, NCH_2, OCH_2, CH_2OH). *m/z* %: 285(M^+,32).

A6 Yellow crystal, mp 78~79°C, yield 31.0%. υ (KBr) 3340 (-OH), 1615, 1572 (Ar) cm^{-1}. ^1H NMR (DMSO-d_6, δppm, TMS): 8.91 (s, 1H, Ar-OH), 6.40 (m, 3H, Ar-H), 7.15 (t, 1H, J=6.12 Hz, ArH), 4.20~3.00 (m, 26H, NCH_2, OCH_2, CH_2OH). *m/z*%: 374(M^++1, 61).

Sq1 Greenish blue crystal, mp>330°C, yield 85.0%. Anal. Calcd (%) for $C_{24}H_{20}N_2O_{12}$: C, 54.54; H, 3.75; N, 5.30. Found (%): C, 54.59; H, 3.72; N, 5.80. υ (KBr): 3600~2500 (br, -COOH and -OH), 1797 (s, C=O), 1623 (s, C=O), 1500, 1460 (s, Ar), 1213, 1159 (s, OCH_2 , NCH_2) cm^{-1}. $\lambda_{Ex\ max}^{ETOH}$: 600.0 nm , $\lambda_{EM\ max}^{ETOH}$ (lgε): 655.0 nm (5.48). λ_{max}^{ETOH} (lgε): 626.6 nm (5.35). ^1H NMR (DMSO- d_6, δppm, TMS): 12.08 (s, 4H, -COOH), 11.68 (d, 2H, J=5.30 Hz, ArOH), 7.90 (d, 2H, J=7.89 Hz, ArH), 6.25 (m, 4H, ArH), 4.08~3.10 (m, 8H, NCH_2). *m/z* (%); 528 (M^+, 20).

Sq2 Greenish blue crystal, mp>330°C, yield 81.0%, Anal. Calcd (%) for $C_{32}H_{36}N_2O_{16}$: C, 54.54; H, 5.11; N, 3.98. Found (%): C, 54.60; H, 5.58; N, 4.39. υ (KBr): 3600~2500 (br, -COOH and -OH), 1780 (s, C=O), 1620 (s, C=O), 1520, 1465 (s, Ar), 1223, 1180 (s, OCH_2, NCH_2) cm^{-1}. λ_{max}^{ETOH} (lgε): 621.0 nm (5.42). ^1H NMR (DMSO-d_6, δppm, TMS): 11.98 (s, 4H, -COOH), 10.95 (d, 2H, J=4.95 Hz, ArOH), 7.98 (d, 2H, J=8.10 Hz, ArH), 6.28 (m, 4H, ArH), 4.18~3.03 (m, 24H, NCH_2, OCH_2). *m/z* (%): 704 (M^+, 18).

Sq3 Greenish blue crystal, mp>330°C, yield 75.0%, Anal. Calcd (%) for $C_{40}H_{52}N_2O_{20}$: C, 54.54; H, 5.91; N, 3.18. Found (%): C, 54.50; H, 3.53; N, 3.23. υ (KBr): 3600~2500 (br, -COOH and -OH), 1785 (s, C=O), 1611 (s, C=O), 1515, 1439 (s, Ar), 1220, 1150 (s, OCH_2, NCH_2) cm^{-1}. λ_{max}^{ETOH} (lg ε) 630.0 nm (5.14). ^1H NMR (DMSO-d_6, δppm, TMS): 11.59 (s, 4H, -COOH), 10.48 (d, 2H, J=4.70 Hz, ArOH), 7.90 (d, 2H, J=8.90 Hz, ArH), 6.28(m, 4H, ArH), 4.18~3.03 (m, 4OH, NCH_2, OCH_2) . *m/z* (%): 880 (M^+,15).

Sq4 Greenish crystal, mp>308~309°C (dec), yield 67.0%, Anal. Calcd (%) for $C_{24}H_{28}N_2O_8$: C, 61.01; H, 5.93; N, 5.93. Found (%): C, 61.19; H, 5.74; N, 5.86. υ (KBr): 3376 (br, -OH), 1610 (s, C=O) cm^{-1}. λ_{max}^{ETOH} (lg ε) 646.8 nm (5.14). ^1H NMR (DMSO-d_6, δppm, TMS): 11.68 (d, 2H, J=5.05 Hz, ArOH), 7.90 (d, 2H, J=8.13 Hz, ArH), 6.28 (m, 4H, ArH), 4.08~3.00 (m, 20H, NCH_2, OCH_2, CH_2OH). *m/z* (%): 273 (M^+/2+1, 15), 206 (M^+/2-CH_2, 85).

Sq5 Greenish crystal, mp 201~202°C (dec), yield 56.0%, Anal. Calcd (%) for $C_{32}H_{44}N_2O_{12}$: C, 59.26; H, 6.79; N, 4.32. Found (%): C, 59.02; H, 6.81; N, 4.58. υ (KBr): 3360 (br, -OH), 1620 (s, C=O) cm^{-1}. λ_{max}^{ETOH} (lg ε) 634.2 nm (5.05). ^1H NMR (DMSO-d_6, δppm, TMS): 10.98 (d, 2H, J=4.81 Hz, ArOH), 7.98 (d, 2H, J=7.92 Hz, ArH), 6.16 (d, 2H, J=8.80 Hz, ArH), 5.98 (d, 2H, J=2.75 Hz, ArH), 3.86~3.04 (m,36H, NCH_2, OCH_2, CH_2OH). *m/z* (%): 647 (M^+-1,20).

Sq6 Greenish crystal, mp 129.5~130°C (dec), yield 52.0%, Anal. Calcd (%) for $C_{40}H_{60}N_2O_{16}$: C, 58.24; H, 7.28; N, 3.40. Found (%): C, 58.39; H, 7.12; N, 3.65. υ (KBr): 3361(br, -OH), 1620 (s, C=O) cm^{-1}. λ_{max}^{ETOH} (lg ε) 641.0 nm (5.42). ^1H NMR (DMSO-d_6, δppm, TMS): 11.71 (d, 2H, J=5.01 Hz, ArOH), 7.98 (d, 2H, J=7.89 Hz, ArH), 6.26 (d, 2H, J=7.51 Hz, ArH), 6.00 (d, 2H, J=2.90 Hz, ArH), 4.08~3.00 (m, 52H, NCH_2, OCH_2,CH_2OH). *m/z* (%): 824 (M^+, 5), 703 (M^+-1, -4CH_2O), 414 (M^+/2+2, 75).

References and Notes

1. B. O'Regan , M.A. Gratzel , *Nature*, **1991**, *353* (24) ,737.
2. E.M. Thomas , *Nature*, **1991**, *353* (24) , 698.
3. M.A. Gratzel , *Chemie Ingenieur Technick* , **1995**, *67*, 1300.
4. Fluorescence spectra of **Sq1** have been deposited in the editorial office of CCL.
5. L.S. Heng., D.S. Peng , Y.Z. Chen, J.C. Li, W.Z. Yu, H.M. Zhao , *J.Sichuan Univ (Natural Sci.Ed.)* , **1995** , *32*, 566.

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