JOC The Journal of Organic Chemistry

NOTE

pubs.acs.org/joc

Organic Dye Bearing Asymmetric Double Donor-π-Acceptor Chains for Dye-Sensitized Solar Cells

Yanping Hong,[†,∥] Jin-Yun Liao,[‡] Derong Cao,[*,†,§] Xufeng Zang,[†] Dai-Bin Kuang,[*,‡] Lingyun Wang,[†] Herbert Meier,[⊥] and Cheng-Yong Su[‡]

[†]School of Chemistry and Chemical Engineering and [§]State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

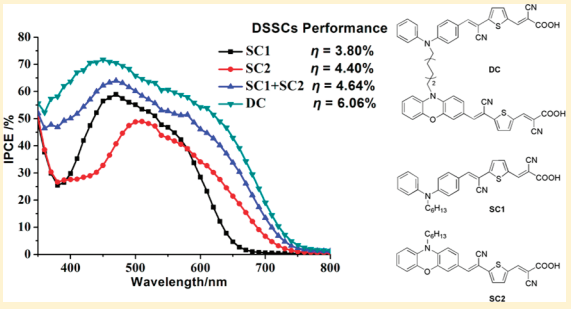
[‡]MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

[∥]College of Food Science and Engineering, Jiangxi Agricultural University, Nanchang 330045, China

[⊥]Institute of Organic Chemistry, University of Mainz, 55099 Mainz, Germany

Supporting Information

ABSTRACT: A novel efficient metal free sensitizer containing asymmetric double donor-π-acceptor chains (**DC**) was synthesized for dye-sensitized solar cells (DSSCs). Comparing to 3.80%, 4.40% and 4.64% for the DSSCs based on the dyes with single chain (**SC1**, **SC2**) and cosensitizers (**SC1** + **SC2**), the overall conversion efficiency reaches 6.06% for **DC**-sensitized solar cells as a result of its longer electron lifetime and higher incident monochromatic photon-to-current conversion efficiency.



Dye-sensitized solar cells (DSSCs) as one of the most promising alternatives to crystalline Si-based photovoltaics for converting clean, inexhaustible sunlight to electricity have received significant research interest due to their low fabrication cost and relatively high power conversion efficiency (η) since the first cell reported by Grätzel et al. in 1991.[1] As a critical component in DSSCs, the sensitizer plays a vital role in the light-harvesting efficiency, providing electron injection into the conduction band of an oxide semiconductor (e.g., TiO_2) upon light excitation. Nowadays, the photoelectric conversion efficiency of DSSCs sensitized by Ru-complex dyes has achieved maximum power conversion efficiencies of more than 11%.[2−4] In recent years, metal-free organic dyes have been investigated intensely as an alternative to noble Ru-complexes owing to their advantages of high molar extinction coefficients, flexibility in structure tailoring, low-cost preparation process, and compliance with environmental issues.[5] Many efficient metal-free dyes have been explored for DSSCs showing good performance.[6−20]

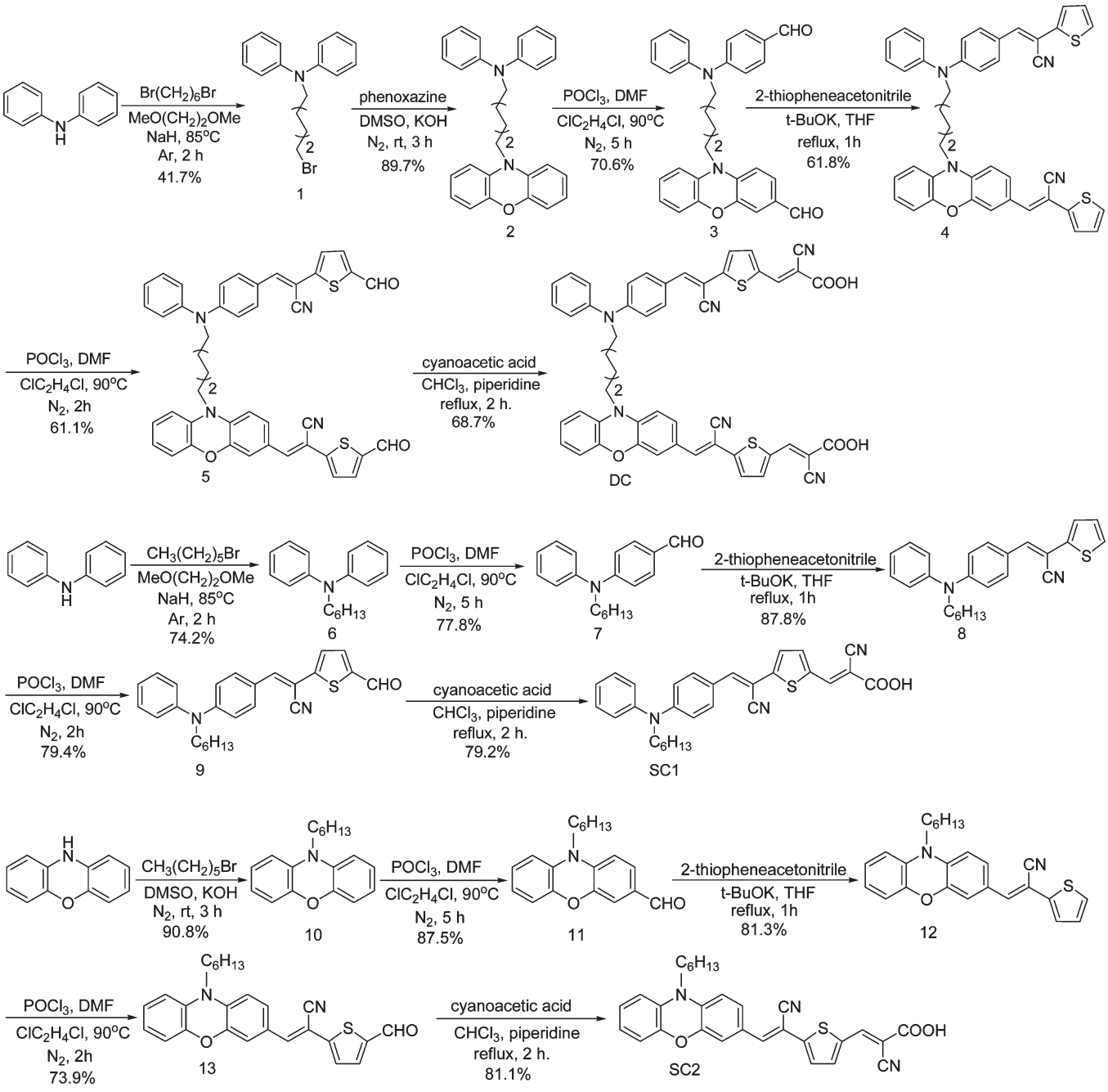
Organic dyes possessing a rod-like configuration with donor and acceptor moieties bridged by a π-conjugated unit (called D-π-A structure) are considered as one of the most promising classes of organic sensitizers. It is found that the photoinduced intramolecule electron transfer takes place easily and the photophysical properties can be easily tuned by varying donor, spacer, and acceptor moieties in these dyes.[21−23] DSSCs with these dyes show a better perfomance.[24,25]

As is well-known, organic dyes bearing a single D-π-A system often afford only one absorption peak in the visible region. Hence, there will be much interest to design and synthesize novel dyes containing two different D-π-A systems, which show two different absorption bands in the visible light range.

In our previous work, it was demonstrated that organic dyes containing two symmetric D-π-A chains (**DB**) could increase η of DSSCs compared to the corresponding single D-π-A dye because one molecule of **DB** contained two light-harvesting units.[26] However, **DB** did not broaden the absorption range because the two chains are the same and absorb in the same range of the sunlight. In this work, in order to increase the light-harvesting units and broaden the absorption range of organic dyes, we designed a novel organic dye containing two asymmetric D-π-A chains that are linked by a nonconjugated *n*-hexane chain. The resulting **DC** has two separate light-harvesting systems. In one D-π-A chain, diphenylamine (**DPA**) was introduced as the donor, and it would form the starburst structure similar to triphenylamine (**TPA**), which could contribute to depress the aggregation of dyes on the TiO_2 surface. In the other D-π-A chain, phenoxazine (**POZ**) was introduced as donor because of its good light-havesting property in the visible region.[27,28] Owing to two different light-harvesting units in one dye molecule, **DC**

Received: June 3, 2011
Published: August 22, 2011

Scheme 1. Synthesis of Dyes DC, SC1, and SC2



might be expected to exhibit a stronger and broader absorption range, resulting in higher conversion efficiency of DSSC compared to the reference dyes **SC1** and **SC2** with a single D-π-A unit each.

The synthesis of the dyes **SC1**, **SC2** and **DC** is shown in Scheme 1. Well-known organic reactions including alkylation, Vilsmeier and Knoevenagel reactions were used for this purpose.

The absorption spectra of the dyes in MeOH/CH_2Cl_2 (1:1) solutions are shown in Figure 1, and the photophysical data are collected in Table 1. All of these dyes have a relatively broad and strong absorption in the ultraviolet and visible region. The absorption bands at 220−400 nm are ascribed to the $\pi-\pi^*$ transitions of the conjugated systems, while the bands in the range of 400−650 nm are assigned to the intramolecular charge transfer (ICT) between donor and acceptor. The major absorption peaks for **SC1**, **SC2**, and **DC** are at 463/343 nm, 513/376 nm and 511/437/373 nm, respectively. In comparison to **SC1** and **SC2**, **DC** possesses a broader and more intensive absorption in the ultraviolet and visible region, which could produce a higher short-circuit current in the DSSCs. The molar absorption coefficient (ε) of **DC** is much higher (ε_{max} > 18043 M^{-1} cm^{-1}) than those of **SC1** and **SC2** in the range of 400−553 nm, indicating that **DC** has a good light-harvesting ability. It is worthy to note that the **DC** dye has two absorption bands compared to the one absorption band of the **SC1** and **SC2** dyes between 400−600 nm. The absorption of **DC** is not just the

dx.doi.org/10.1021/jo201057b |*J. Org. Chem.* 2011, 76, 8015–8021

sum of the absorption bands of **SC1** and **SC2** (Figure 1). The distinctive and stronger absorption of **DC** may be attributed to the absorption overlap of the two independent D-π-A units.

Cyclic voltammetry (CV) was employed to estimate the first oxidation potential (E_{ox}) corresponding to the HOMO level of the dyes (Table 1). The HOMO energy levels of the three dyes are more positive than the I^-/I_3^- redox couple (0.4 V vs NHE), ensuring regeneration of the oxidized dyes by I^- after electron injection. The LUMO levels of the three dyes (calculated by $E_{ox} - E_{0-0}$, Table 1) are sufficiently more negative than the fermi level of TiO_2 (−0.5 V vs NHE),[29] and provided that an energy gap of 0.2 eV is necessary for efficient electron injection.[30,31] Hence the electron injection process is energetically favorable.

The J−V curves and all essential photovoltaic properties of DSSCs based on these dyes are demonstrated in Figure 2 and summarized in Table 2, respectively. As shown in Figure 2 and Table 2, under the standard AM 1.5 G (100 mW cm^{-2}) irradiation, the cosensitized (**SC1** + **SC2**) solar cell shows a higher photocurrent than the cells with individual dyes **SC1** and **SC2**. A higher power conversion efficiency is due to a better utilization of sunlight. Furthermore, the **DC**-sensitized cell exhibits an overall conversion efficiency (η) of 6.06% accompanied a short circuit photocurrent density (J_{sc}) of 12.75 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 691 mV and a fill factor (FF) of 0.69. The η value is much higher than those of DSSCs based on **SC1** (3.80%), **SC2** (4.40%), and cosensitizers (**SC1** + **SC2**, 4.64%) because of its relatively higher J_{sc} and V_{oc}.

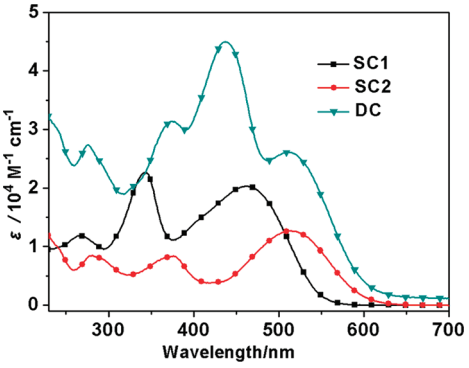


Figure 1. Absorption spectra of the dyes in CH_2Cl_2/MeOH.

Figure 3 shows the IPCE as a function of the wavelength for the DSSCs based on the three new dyes as sensitizers. There are two characteristic peaks at 470 and 550 nm that were clearly observed in the IPCE spectrum of the cosensitized cell, which proved that the two organic dyes (**SC1** + **SC2**) were efficiently coadsorbed to the surface of TiO_2, resulting in increase of the photocurrent density compared to the single dye (Table 2). Moreover, the IPCE of **DC** based DSSC exceeds 50% in a broad spectral region from 350 to 630 nm and reaches its maximum of 72% at 450 nm. In contrast, the IPCE of cosensitizers (**SC1** + **SC2**)- and **SC1**-based DSSCs also exceed 50% in a narrow range of 400−580 nm and 440−530 nm and give relatively low values with maxima of 65% and 58% at 470 nm, respectively. The higher and broader spectra response of the **DC**-based cell within the whole visible region might contribute to a higher photocurrent,

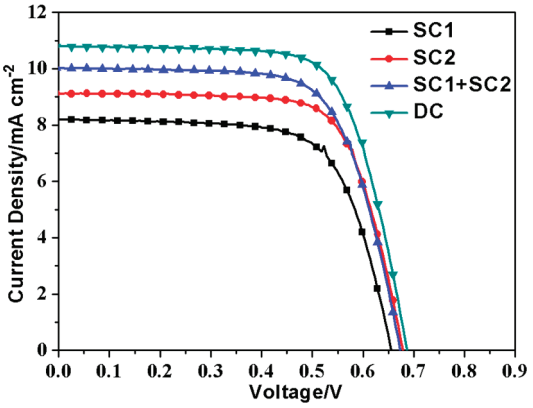


Figure 2. J−V curves of DSSCs sensitized by **SC1**, **SC2**, cosensitizers (**SC1** + **SC2**) and **DC**.

Table 2. Photovoltaic Performance of DSSCs Based on the Dyes SC1, SC2, Cosensitizers (SC1 + SC2) and DC

dye	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
SC1	8.20	655	0.71	3.80
SC2	9.13	679	0.71	4.40
SC1 + SC2	10.02	674	0.69	4.64
DC	12.75	691	0.69	6.06

Table 1. Absorption, Emission, and Electrochemical Properties of Dyes SC1, SC2, and DC

	absorption		emission	oxidation potential data				
dye	λ_{max} in CH_2Cl_2/MeOH (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	E_{ox} (V, vs NHE)	E_{0-0} (V)[a]	$E_{ox} - E_{0-0}$ (V, vs NHE)	E_{gap}[b] (V, vs NHE)	E_{HOMO}/ E_{LUMO}[c] (eV)
SC1	343	22633	599 (463)	0.73	2.31	−1.58	1.08	−5.33/−2.75
	463	20311						
SC2	376	8374	676 (513)	0.62	2.09	−1.47	0.97	−5.12/−2.91
	513	12667						
DC	373	31371	568 (511)	0.66	2.29	−1.63	1.13	−5.44/−2.75[d]
	437	44976						−5.31/−2.94[e]
	511	26103						

[a] E_{0-0} were estimated from the intersection of the normalized absorption and emission spectra (see Supporting Information). [b] E_{gap} is the energy gap between the $E_{ox} - E_{0-0}$ of the dye and the conductive band level of TiO_2 (−0.5 V vs NHE). [c] Calculated at the B3LYP-31G(d) level in vacuum. [d] Calculated for the **SC1** side of **DC**. [e] Calculated for the **SC2** side of **DC**.

dx.doi.org/10.1021/jo201057b |J. Org. Chem. 2011, 76, 8015–8021

which can be confirmed by the amount of dyes adsorbed on TiO_2 films (1.72×10^{-7} mol cm^{-2} for **SC1**, 1.23×10^{-7} mol cm^{-2} for **SC2**, ($0.95 \times 10^{-7} + 0.52 \times 10^{-7}$ mol cm^{-2}) for cosensitizers (**SC1** + **SC2**), and 1.56×10^{-7} mol cm^{-2} for **DC**) according to the UV−vis absorption measurement. Compared to the cells based on **SC1** and **SC2**, the cosensitizers (**SC1** + **SC2**)-based cell exhibits the higher IPCE due to the broader absorption range initiated from the two dyes coadsorbed on the TiO_2 film. The IPCE of the **DC**-based cell is higher than that of the cosensitizers (**SC1** + **SC2**)-based cell because the adsorbed amount of the dyes in the former cell is higher, which results in a higher short-circuit current density.

To further elucidate the photovoltaic results and display more dynamic information of interfacial charge transfer process in DSSCs sensitized by **SC1**, **SC2**, cosensitizers (**SC1** + **SC2**), and **DC**, electrochemical impedance spectroscopy (EIS) was also performed in dark under a forward bias of 0.65 V. The Nyquist plots and Bode phase plots for **SC1**, **SC2**, cosensitized (**SC1** + **SC2**), and **DC** sensitized cells are shown in Figure 4a and b, respectively. Two semicircles, including a small one at higher frequency (10^3−10^5 Hz) and a large semicircle at lower frequency (1−10^2 Hz), are observed in the Nyquist plots. Usually, the smaller semicircle corresponds to the high-frequency peaks of Bode plots, which represents mainly the electron transfer process from the Pt counter electrode to the oxidized species in the electrolyte. The larger semicircle corresponding to the low frequency peaks of Bode plots is ascribed to the recombination resistance and chemical capacitance across the TiO_2/redox electrolyte interface. The recombination resistance of the **DC**-based cell is smaller than those of other cells obtained from the Z-view software (Supporting Information). However, the largest chemical capacitance will result in the longest lifetime for the cell based on **DC**. The electron lifetime values derived from the Nyquist curves for the cells of **SC1**, **SC2**, cosensitizers (**SC1** + **SC2**), and **DC** are 52.7, 61.2, 53.8, and 61.7 ms, respectively (see Supporting Information). The longer electron lifetime observed for **DC** indicates a more effective suppression of the back reaction of the injected electron with the I_3^- in the electrolyte, reflecting in the improvement of the photocurrent and photovoltage yielding a substantially enhanced overall conversion efficiency. The Bode phase plots (Figure 4b) likewise support the differences in the electron lifetime (fitting from Nyquist plots) for TiO_2 films based on these dyes. The middle-frequency peak of the DSSC based on **DC** shifts to lower frequency relative to **SC1**, **SC2**, and cosensitizers (**SC1** + **SC2**), indicating a longer lifetime for the former dye.

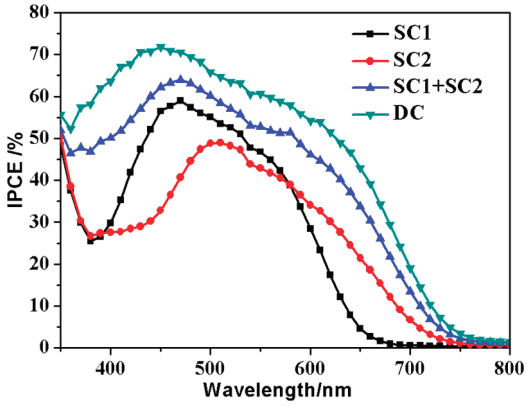


Figure 3. IPCE spectra of DSSCs based on the dyes.

Density functional theory (DFT) calculations were performed on a B3LYP/6-31+G(d) level with Gaussian 03.[27] The electron distribution of the HOMO and LUMO of the dyes are shown in the Supporting Information. The HOMOs of the dyes are localized in the **DPA** and **POZ** units and the LUMOs are localized in the cyanoacrylic unit and thiophene. The results indicated that the HOMO−LUMO excitation induced by light moved the high electron density from the **DPA** and **POZ** units to the cyanoacrylic acid moieties, thus allowing an efficient photoinduced electron transfer from the dye to the TiO_2 electrode.

In summary, a new efficient organic dye (**DC**) with double asymmetric D-π-A chains and two corresponding reference dyes containing single D-π-A chains [**SC1**, **SC2**, and cosensitizers (**SC1** + **SC2**)] were investigated. It was found that not only did the dye with double D-π-A chains exhibit a broader and more intense absorption than the reference dyes, but the incident monochromatic photon-to-electron conversion efficiency (IPCE), short-circuit current density, open-circuit voltage, and overall conversion efficiency (η) of the DSSCs based on **DC** were superior to the other dyes systems. The electron lifetime of **DC** was the longest among these dyes. These results confirm that the dyes containing two asymmetric D-π-A chains with different donors might enhance significantly the photoelectrical performance of DSSCs.

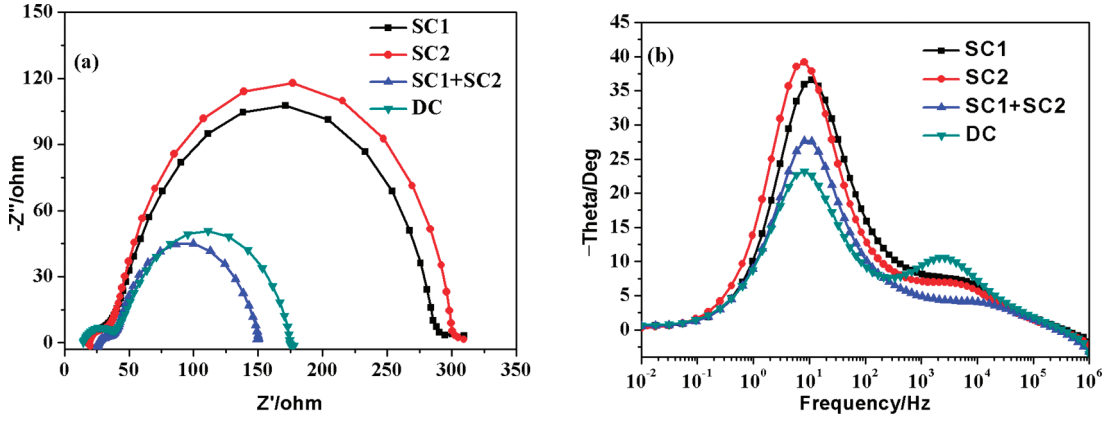


Figure 4. Electrochemical impedance spectra for DSSCs sensitized by **SC1**, **SC2**, cosensitizers (**SC1** + **SC2**) and **DC**, respectively: (a) Nyquist plots and (b) Bode phase plots.

dx.doi.org/10.1021/jo201057b |*J. Org. Chem.* 2011, 76, 8015–8021

EXPERIMENTAL SECTION

General. All reactions were carried out under an inert gas atmosphere (nitrogen or argon). All solvents and chemicals were reagent grade, and the solvents were dried by standard procedures. The column chromatography was performed with 200−300 mesh silica gel as stationary phase. The ^{1}H and ^{13}C NMR spectra were measured by using a 400 MHz spectrometer. The absorption, emission spectra were measured in CH_2Cl_2/MeOH solution (2×10^{-5} M) at room temperature. The electrochemical impedance spectra of the DSSCs were measured at a forward bias voltage of 0.65 V in the dark between 10 mHz and 1 MHz with an alternate current (AC) amplitude of 10 mV. The E_{ox} was measured in dry acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte (work electrolyte FTO/TiO_2/dye; reference electrode Ag/Ag^+; calibrated with ferrocenium/ferrocene (Fc/Fc^+) as an external reference and converted to NHE by addition of 0.65 mV; counter electrode Pt). DSSCs were constructed by building a sandwich configuration with an electrolyte composed of 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate (GuSCN), 0.03 M I_2, 0.5 M *tert*-butylpyridine in acetonitrile and valeronitrile (85:15).

(6-Bromohexyl)-diphenyl-amine (1). A solution of diphenylamine (5.07 g, 30 mmol), NaH (1.8 g, 45 mmol) in $MeO(CH_2)_2OMe$ (30 mL) was stirred at room temperature for 0.5 h under argon. Then 1,6-dibromohexane (8.79 g, 36 mmol) was poured into the mixture and heated at 85 °C for 2 h. After cooling, the reaction mixture was filtered, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography with petroleum ether as eluent to give **1** (4.16 g, 41.7% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (m, 2H), 1.44 (m, 2H), 1.67 (m, 2H), 1.83 (m, 2H), 3.37 (t, 2H), 3.68 (t, 2H), 6.95 (m, 6H), 7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 27.3, 27.9, 32.6, 33.7, 52.1, 120.8, 121.1, 129.2, 148.0; MS (*m*/*z*, ESI) calcd for $C_{18}H_{22}BrN$ 331.1, found 330.3 $[M - H]^+$. Anal. Calcd for $C_{18}H_{22}BrN$: C, 65.06; H, 6.67; N, 4.22. Found: C, 65.12; H, 6.69; N, 4.21.

Hexyl-diphenyl-amine (6). Prepared as colorless liquid (5.64 g, 74.2% yield) from diphenylamine by using the method established for **1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H), 1.29 (m, 6H), 1.65 (m, 2H), 3.67 (t, 2H), 6.92 (m, 2H), 6.97 (m, 4H), 7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 26.8, 27.5, 31.7, 52.4, 120.9, 121.1, 129.3, 148.2.

(6-Phenoxazin-10-yl-hexyl)diphenyl-amine (2). Phenoxazine (0.915 g, 5.0 mmol) was added to a suspension of potassium hydroxide (0.336 g, 6.0 mmol) in DMSO (12 mL) under nitrogen. The mixture was stirred for 30 min after which time **1** (1.83 g, 5.5 mmol) was added. The reaction was stirred for 3 h at room temperature. Water (30 mL) was added, the mixture was extracted with dichloromethane (3 × 30 mL), and the organic fraction was then washed with brine, dried with anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography with CH_2Cl_2/petroleum ether (v/v = 1/7) as the eluent to give **2** (1.95 g, 89.7%) as a colorless solid, mp 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (m, 4H), 1.63 (m, 2H), 1.70 (m, 2H), 3.42 (t, 2H,), 3.69 (t, 2H), 6.41 (m, 2H), 6.62 (m, 4H), 6.75 (m, 2H), 6.93 (m, 2H), 6.97 (m, 4H), 7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 26.8, 26.9, 27.6, 43.9, 52.2, 111.3, 115.4, 120.7, 120.9, 121.2, 123.6, 129.3, 133.4, 145.0, 148.1; MS (*m*/*z*, ESI) calcd for $C_{30}H_{30}N_2O$ 434.2, found 457.3 $[M + Na]^+$. Anal. Calcd for $C_{30}H_{30}N_2O$: C, 82.91; H, 6.96; N, 6.45. Found: C, 83.03; H, 7.01; N, 6.46.

10-{6-[(4-Formyl-phenyl)-phenyl-amino]-hexyl}-10*H*-phenoxazin-3-carbaldehyde (3). To a solution of **2** (1.74 g, 4 mmol) and dry DMF (1.76 g, 24 mmol) in 1,2-dichloroethane (20 mL) phosphorus oxychloride (3.69 g, 24 mmol) was added slowly at 0 °C in an ice−water bath. Then the bath was heated to 90 °C and maintained for 5 h. Dilute aqueous solution of sodium hydroxide was added, and the mixture was extracted three times with CH_2Cl_2. The combined organic fractions were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography with CH_2Cl_2/petroleum ether (v/v = 5/1) as the eluent to give **3** (1.38 g, 70.6% yield) as a yellow solid, mp 48−49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (m, 4H), 1.66 (m, 2H), 1.75 (m, 2H), 3.50 (t, 2H,), 3.75 (t, 2H), 6.45 (m, 1H), 6.48 (m, 1H), 6.64 (m, 1H), 6.69 (m, 2H), 6.73 (m, 1H), 6.79 (m, 1H), 7.06 (m, 1H), 7.21 (m, 2H), 7.29 (m, 2H), 7.44 (m, 2H), 7.65 (m, 2H), 9.65 (s, 1H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 26.6, 26.8, 27.3, 44.0, 52.5, 110.4, 112.0, 113.3, 114.3, 115.8, 122.6, 123.9, 126.5, 126.5, 127.5, 128.6, 129.9, 130.2, 131.3, 131.8, 139.2, 144.7, 145.1, 145.7, 153.3, 189.6, 190.2; MS (*m*/*z*, ESI) calcd for $C_{30}H_{30}N_2O$ 490.2, found 513.2 $[M + Na]^+$. Anal. Calcd for $C_{32}H_{30}N_2O_3$: C, 78.34; H, 6.16; N, 5.71. Found: C, 78.32; H, 6.18; N, 5.73.

(*E*)-3-[4-({6-[3-((*E*)-2-Cyano-2-thiophen-2-yl-vinyl)phenoxazin-10-yl]hexyl}phenyl-amino)phenyl]-2-thiophen-2-yl-acrylonitrile (4). To a stirred solution of *t*-BuOK (0.112 g, 1.0 mmol) and 2-thiopheneacetonitrile (0.985 g, 8.0 mmol) in THF (20 mL) was added **3** (0.98 g, 2.0 mmol) at room temperature under nitrogen. The reaction mixture was refluxed for 1 h and cooled to room temperature, and then the mixture was concentrated under reduced pressure. The resulting residue was purified by column chromatography with ethyl acetate/petroleum ether (v/v = 1/10) as the eluent to give **4** (0.866 g, 61.8%) as a scarlet solid, mp 68−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (m, 4H), 1.64 (m, 2H), 1.73 (m, 2H), 3.43 (t, 2H,), 3.73 (t, 2H), 6.38 (m, 1H), 6.44 (m, 1H), 6.62 (m, 1H), 6.67 (m, 1H), 6.74 (m, 2H), 6.78 (m, 1H), 6.84 (s, 2H), 7.01 (m, 2H), 7.04 (s, 1H), 7.21 (m, 8H), 7.40 (m, 2H), 7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 26.7, 26.8, 27.5, 43.9, 52.3, 100.4, 101.8, 110.9, 111.7, 114.7, 114.8, 115.7, 117.6, 118.1, 122.0, 122.9, 123.9, 124.8, 125.3, 125.5, 125.6, 126.0, 126.1, 126.7, 126.9, 128.0, 130.0, 130.9, 131.7, 135.6, 138.6, 139.9, 140.3, 144.7, 146.2, 150.1, 153.8; MS (*m*/*z*, ESI) calcd for $C_{44}H_{36}N_4OS_2$ 700.2, found 723.4 $[M + Na]^+$. Anal. Calcd for $C_{44}H_{36}N_4OS_2$: C, 75.40; H, 5.18; N, 7.99; S, 9.15. Found: C, 75.49; H, 5.20; N, 8.01; S, 9.14.

(*E*)-3-{4-[(6-{3-[(*E*)-2-Cyano-2-(5-formylthiophen-2-yl)-vinyl]phenoxazin-10-yl}-hexyl)phenylamino]phenyl}-2-(5-formylthiophen-2-yl)acrylonitrile (5). To a solution of **4** (0.841 g, 1.2 mmol) and dry DMF (0.53 g, 7.2 mmol) in 1,2-dichloroethane (15 mL) was slowly added phosphorus oxychloride (1.11 g, 7.2 mmol) at 0 °C in an ice−water bath. Then the bath was heated to 90 °C and maintained for 2 h. A aqueous solution of dilute sodium hydroxide was added, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography with acetone/petroleum ether (v/v = 1/10) as the eluent to give **5** (0.556 g, 61.1%) as a red-black solid, mp 63−65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (m, 4H), 1.66 (m, 2H), 1.76 (m, 2H), 3.48 (t, 2H), 3.84 (t, 2H), 6.41 (m, 1H), 6.47 (m, 1H), 6.64 (m, 1H), 6.71 (m, 1H), 6.79 (m, 1H), 6.99 (m, 2H), 7.07 (m, 1H), 7.22 (m, 4H), 7.29 (m, 1H), 7.32 (s, 1H), 7.34 (m, 2H), 7.65 (m, 1H), 7.74 (m, 2H), 7.86 (m, 2H), 9.81 (s, 1H,), 9.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 26.6, 26.8, 27.5, 43.9, 52.3, 100.5, 104.8, 110.9, 111.9, 115.0, 115.9, 116.8, 117.1, 117.3, 122.5, 123.9, 124.1, 125.4, 126.1, 126.3, 127.0, 128.2, 128.3, 128.8, 129.2, 130.8, 131.2, 131.7, 136.9, 137.1, 138.5, 139.3, 141.8, 142.2, 144.6, 144.8, 147.9, 149.3, 152.3, 182.4, 190.3; MS (*m*/*z*, ESI) calcd for $C_{46}H_{36}N_4O_3S_2$ 756.2, found 779.7 $[M + Na]^+$. Anal. Calcd for $C_{46}H_{36}N_4O_3S_2$: C, 72.99; H, 4.79; N, 7.40; S, 8.47. Found: C, 72.94; H, 4.81; N, 7.42; S, 8.46.

4-(Hexyl-phenyl-amino)-benzaldehyde (7). Prepared as light yellow liquid (0.875 g, 77.8% yield) from **6** by using the method established for **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H), 1.31 (m, 6H), 1.69 (m, 2H), 3.71 (t, 2H), 6.69 (m, 2H), 7.20 (m, 2H), 7.27 (m, 1H), 7.42 (m, 2H), 7.65 (m, 2H), 9.72 (s, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 13.9, 22.5, 26.4, 27.2, 31.4, 52.5, 113.1, 126.2, 126.3, 127.4, 130.0, 131.6, 145.6, 153.2, 190.0; MS (m/z, ESI) calcd for $C_{19}H_{23}NO$ 281.2, found 282.1 $[M + H]^+$. Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.93; H, 8.27; N, 4.99.

10-Hexyl-phenoxazine (10). Prepared as colorless liquid (1.21 g, 90.8% yield) from phenoxazine by using the method established for **2**. ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, 3H), 1.42 (m, 6H), 1.67 (m, 2H), 3.47 (t, 2H), 6.47 (m, 2H), 6.63 (br. s, 4H), 6.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ14.1, 22.7, 24.9, 26.6, 31.6, 44.1, 111.3, 115.3, 120.7, 123.6, 133.5, 145.0.

(*E*)-3-[4-(Hexyl-phenyl-amino)-phenyl]-2-thiophen-2-yl-acrylonitrile (8). Prepared as yellow liquid (0.678 g, 87.8% yield) from **7** by using the method established for **4**. ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, 3H), 1.21 (m, 6H), 1.59 (m, 2H), 3.61 (t, 2H), 6.65 (m, 2H), 6.92 (m, 1H), 7.11 (m, 5H), 7.16 (m, 1H), 7.30 (m, 2H), 7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 26.8, 27.4, 31.7, 52.6, 100.3, 114.7, 118.1, 122.8, 124.8, 125.5, 125.6, 126.8, 128.0, 130.0, 130.9, 140.1, 140.5, 146.3, 150.3; MS (m/z, ESI) calcd for $C_{25}H_{26}N_2S$ 386.2, found 387.1 $[M + H]^+$. Anal. Calcd for $C_{25}H_{26}N_2S$: C, 77.68; H, 6.78; N, 7.25; S, 8.30. Found: C, 77.58; H, 6.80; N, 7.26; S, 8.29.

(*E*)-2-(5-Formyl-thiophen-2-yl)-3-[4-(hexyl-phenyl-amino)-phenyl]acrylonitrile (9). Prepared as red liquid (0.394 g, 79.4% yield) from **8** by using the method established for **5**. ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, 3H), 1.18 (m, 6H), 1.63 (m, 2H), 3.65 (t, 2H), 6.64 (m, 2H), 7.14 (m, 2H), 7.22 (m, 2H), 7.32 (s, 1H); 7.36 (m, 2H), 7.60 (m, 1H), 7.70 (m, 2H), 9.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 26.7, 27.3, 31.6, 52.7, 98.4, 114.1, 117.4, 121.7, 125.6, 126.4, 127.3, 130.1, 131.9, 137.2, 141.6, 143.3, 145.7, 150.3, 151.3, 182.4; MS (m/z, ESI) calcd for $C_{26}H_{26}N_2OS$ 414.2, found 415.2 $[M + H]^+$. Anal. Calcd for $C_{26}H_{26}N_2OS$: C, 75.33; H, 6.32; N, 6.76; S, 7.73. Found: C, 75.31; H, 6.34; N, 6.77; S, 7.74.

10-Hexyl-phenoxazine-3-carbaldehyde (11). Prepared as yellow liquid (1.03 g, 87.5% yield) from **10** by using the method established for **3**. ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, 3H), 1.36 (m, 6H), 1.64 (m, 2H), 3.46 (t, 2H), 6.45 (m, 1H), 6.49 (m, 1H), 6.60 (m, 1H), 6.69 (m, 1H), 6.79 (m, 1H), 7.02 (m, 1H), 7.25 (m, 1H), 9.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.0, 26.6, 31.6, 44.4, 110.5, 112.1, 114.1, 115.7, 122.5, 124.0, 128.8, 129.8, 131.4, 139.3, 144.7, 145.1, 189.6; MS (m/z, ESI) calcd for $C_{19}H_{21}NO_2$ 295.2, found 318.2 $[M + Na]^+$. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.19; H, 7.20; N, 4.73.

(*E*)-3-(10-Hexyl-10*H*-phenoxazin-3-yl)-2-thiophen-2-yl-acrylonitrile (12). Prepared as red liquid (0.651 g, 81.3% yield) from **11** by using the method established for **4**. ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, 3H), 1.26 (m, 6H), 1.51 (m, 2H), 3.31 (t, 2H), 6.28 (m, 1H), 6.34 (m, 1H), 6.50 (m, 1H), 6.55 (m, 1H), 6.66 (m, 1H), 6.90 (m, 2H), 7.06 (m, 1H), 7.10 (m, 2H), 7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.0, 26.6, 31.6, 44.1, 101.6, 110.9, 111.7, 114.7, 115.6, 117.6, 121.9, 123.8, 125.2, 125.9, 126.9, 128.0, 131.8, 135.7, 138.6, 140.0, 144.7; MS (m/z, ESI) calcd for $C_{25}H_{24}NO_2S$ 400.2, found 401.1 $[M + H]^+$. Anal. Calcd for $C_{25}H_{24}N_2OS$: C, 74.97; H, 6.04; N, 6.99; S, 8.01. Found: C, 74.94; H, 6.05; N, 7.00; S, 7.99.

(*E*)-2-(5-Formyl-thiophen-2-yl)-3-(10-hexyl-10*H*-phenoxazin-3-yl)acrylonitrile (13). Prepared as red-black solid (0.380 g, 73.9% yield) from **12** by using the method established for **5**, mp 143−144 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, 3H), 1.39 (m, 6H), 1.66 (m, 2H), 3.49 (t, 2H), 6.45 (m, 1H), 6.50 (m, 1H), 6.64 (m, 1H), 6.70 (m, 1H), 6.81 (m, 1H), 7.22 (s, 1H), 7.27 (m, 1H), 7.29 (m, 1H), 7.34 (m, 1H), 7.66 (m, 1H), 9.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.8, 25.2, 26.6, 31.6, 44.3, 100.3, 111.0, 112.1, 114.9, 115.8, 116.9, 122.5, 124.0, 125.3, 126.3, 128.6, 131.4, 137.1, 141.9, 142.1, 144.7, 144.8, 149.5, 182.4; MS (m/z, ESI) calcd for $C_{26}H_{24}N_2O_2S$ 428.2, found 451.3 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{24}N_2O_2S$: C, 72.87; H, 5.64; N, 6.54; S, 7.48. Found: C, 72.81; H, 5.65; N, 6.53; S, 7.46.

(*E*)-3-{5-[(*E*)-2-(4-{[6-(3-{(*E*)-2-[5-((*E*)-2-Carboxy-2-cyanovinyl)thiophen-2-yl]-2-cyanovinyl}phenoxazin-10-yl)-hexyl]-phenylamino}phenyl)-1-cyanovinyl]thiophen-2-yl}-2-cyanoacrylic Acid (DC). A solution of **5** (0.493 g, 0,65 mmol) in $CHCl_3$ (15 mL) was condensed with 2-cyanoacetic acid (0.552 g, 6.5 mmol) in the presence of piperidine (0.35 mL, 3.55 mmol). The mixture was refluxed for 2 h under nitrogen. After cooling to room temperature, the mixture was poured into a mixture of CH_2Cl_2 and 2 M aqueous HCl. The organic layer was separated and dried over anhydrous Na_2SO_4. After removal of the solvent at reduced pressure, the crude product was purified by column chromatography with CH_2Cl_2/methanol/acetic acid (v/v = 100/10/1) as the eluent to give **DC** (0.398 g, 68.7%) as a black solid, mp 182−184 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 1.41 (br. s, 4H), 1.52 (br. s, 2H), 1.63 (br. s, 2H), 3.54 (br. s, 2H,), 3.87 (br. s, 2H), 6.76 (m, 5H), 7.08 (m, 2H), 7.15 (s, 1H), 7.38 (m, 6H), 7.62 (m, 2H), 7.69 (s, 1H), 7.88 (m, 5H), 8.08 (s, 1H), 8.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 24.4, 25.6, 25.9, 27.0, 42.9, 51.4, 99.0, 102.7, 111.8, 112.7, 113.6, 115.3, 117.2, 117.3, 117.5, 117.8, 122.3, 123.3, 123.4, 124.3, 125.3, 125.3, 126.3, 127.4, 128.4, 129.2, 130.7, 130.9, 132.7, 135.7, 136.2, 138.6, 138.8, 139.3, 141.6, 143.4, 143.8, 146.3, 147.4, 150.4, 152.0, 163.3, 164.3. MS (m/z, ESI) calcd for $C_{52}H_{38}N_6O_5S_2$ 890.2; found 889.3 $[M - H]^+$. Anal. Calcd for $C_{52}H_{38}N_6O_5S_2$: C, 70.09; H, 4.30; N, 9.43; S, 7.20. Found: C, 70.04; H, 4.29; N, 9.41; S, 7.19.

(*E*)-2-Cyano-3-(5-{(*E*)-1-cyano-2-[4-(hexyl-phenyl-amino)-phenyl]vinyl}thiophen-2-yl)acrylic Acid (SC1). Prepared as black solid (0.247 g, 79.2% yield) from **9** by using the method established for **DC**, mp 73−74 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 0.82 (t, 3H), 1.23 (m, 4H), 1.30 (m, 2H), 1.58 (m, 2H), 3.75 (t, 2H), 6.77 (m, 2H), 7.27 (m, 2H), 7.30 (m, 1H), 7.49 (m, 3H), 7.79 (s, 1H), 7.84 (m, 2H), 7.93 (m, 1H), 8.42 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9, 22.1, 25.9, 26.9, 31.1, 51.8, 96.8, 99.1, 114.0, 116.7, 117.7, 121.6, 125.2, 126.3, 127.0, 130.2, 132.0, 134.4, 140.9, 143.6, 145.2, 145.9, 148.9, 151.1, 163.6. MS (m/z, ESI) calcd for $C_{29}H_{27}N_3O_2S$ 481.1, found 435.7 $[M - COOH]^+$. Anal. Calcd for $C_{29}H_{27}N_3O_2S$: C, 72.32; H, 5.65; N, 8.72; S, 6.66. Found: C, 72.39; H, 5.67; N, 8.73; S, 6.65.

(*E*)-2-Cyano-3-{5-[(*E*)-1-cyano-2-(10-hexyl-10*H*-phenoxazin-3-yl)vinyl]thiophen-2-yl}acrylic Acid (SC2). Prepared as black solid (0.261 g, 81.1% yield) from **13** by using the method established for **DC**, mp 248−249 °C. ^1H NMR (400 MHz, C_5H_5N-d_5) δ 0.84 (t, 3H), 1.21 (m, 4H), 1.29 (m, 2H), 1.53 (m, 2H), 3.46 (t, 2H), 6.67 (m, 1H), 6.70 (m, 1H), 6.79 (m, 2H), 6.89 (m, 1H), 7.41 (m, 1H), 7.50 (m, 1H), 7.52 (d, 1H), 7.58 (s, 1H), 7.61 (m, 1H), 7.73 (m, 1H); ^{13}C NMR (100 MHz, C_5H_5N-d_5) δ 14.2, 22.9, 25.3, 26.6, 31.7, 44.1, 100.6, 102.6, 111.9, 112.9, 115.1, 116.0, 117.6, 117.8, 122.8, 124.6, 126.2, 126.7, 129.2, 131.9, 136.1, 136.2, 137.2, 138.9, 142.1, 145.0, 145.2, 148.4, 165.5. MS (m/z, ESI) calcd for $C_{29}H_{25}N_3O_3S$ 495.1, found 449.7 $[M - COOH]^+$. Anal. Calcd for $C_{29}H_{25}N_3O_3S$: C, 70.28; H, 5.08; N, 8.48; S, 6.47. Found: C, 70.32; H, 5.10; N, 8.49; S, 6.46.

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra, normalized absorption and emission spectra, frontier molecular orbitals, and the calculated electron lifetime of all of the dyes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: drcao@scut.edu.cn, kuangdb@mail.sysu.edu.cn.

■ ACKNOWLEDGMENT

We thank the National Natural Science Foundation of China (20872038, 20873183, 21072064), Jiangxi Province Natural

Science Foundation of China (2009GQC0055), and the Natural Science Foundation of Guangdong Province, China (10351064-101000000) for financial support.

REFERENCES

(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(2) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Bessho, T.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
(3) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M. K.; Jing, X. Y.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720.
(4) Grätzel, M. *Prog. Photovoltaics: Res. Appl.* **2006**, *14*, 429.
(5) Li, G.; Jiang, K. J.; Li, Y. F.; Li, S. L.; Yang, L. M. *J. Phys. Chem. C* **2008**, *112*, 11591.
(6) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 569.
(7) Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256.
(8) Wang, Z. S.; Koumura, N.; Cui, Y.; Takahashi, M.; Sekiguchi, H.; Mori, A.; Kubo, T.; Furube, A.; Hara, K. *Chem. Mater.* **2008**, *20*, 3993.
(9) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. C. *Chem. Commun.* **2006**, 2245.
(10) Hwang, S.; Lee, J. H.; Park, C.; Lee, H.; Kim, C.; Lee, M. H.; Lee, W.; Park, J.; Kim, K.; Park, N. G. *Chem. Commun.* **2007**, 4887.
(11) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Pechy, P.; Graetzel, M. *Chem. Commun.* **2008**, 5194.
(12) Kuang, D.; Uchida, S.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 1923.
(13) Kim, S.; Kim, D.; Choi, H.; Kang, M. S.; Song, K.; Kang, S. O.; Ko, J. *Chem. Commun.* **2008**, 4951.
(14) Choi, H.; Baik, C.; Kang, S. O.; Ko, J.; Kang, M. S.; Nazeeruddin, M. K.; Grätzel, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 327.
(15) Zhang, X. H.; Cui, Y.; Katoh, R.; Koumura, N.; Hara, K. *J. Phys. Chem. C* **2010**, *114*, 18283.
(16) Wang, Z.; Cui, Y.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Hara, K. *J. Phys. Chem. C* **2008**, *112*, 17011.
(17) Zeng, W. D.; Cao, Y. M.; Bai, Y.; Wang, Y. H.; Shi, Y. S.; Zhang, M.; Wang, F. F.; Pan, C. Y.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915.
(18) Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299.
(19) Kolemen, S.; Cakmak, Y.; Erten-Ela, S.; Altay, Y.; Brendel, J.; Thelakkat, M.; Akkaya, E. U. *Org. Lett.* **2010**, *12*, 3812.
(20) Kolemen, S.; Bozdemir, O. A.; Cakmak, Y.; Barin, G.; Erten-Ela, S.; Marszalek, M.; Yum, J.-H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M.; Akkaya, E. U. *Chem. Sci.* **2011**, *2*, 949.
(21) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903.
(22) Chen, Z. G.; Li, F. Y.; Huang, C. H. *Curr. Org. Chem.* **2007**, *11*, 1241.
(23) Fischer, M. K. R.; Wenger, S.; Wang, M. K.; Mishra, A.; Zakeeruddin, S. M.; Grätzel, M.; Bauerle, P. *Chem. Mater.* **2010**, *22*, 1836.
(24) Hagberg, D. P.; Yum, J. H.; Lee, H.; De Angelis, F.; Marinado, T.; Karlsson, K. M.; Humphry-Baker, R.; Sun, L. C.; Hagfeldt, A.; Grätzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2008**, *130*, 6259.
(25) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550.
(26) Cao, D.; Peng, J.; Hong, Y.; Fang, X.; Wang, L.; Meier, H. *Org. Lett.* **2011**, *13*, 1610.
(27) Tian, H. N.; Yang, X. C.; Cong, J. Y.; Chen, R. K.; Liu, J.; Hao, Y.; Hagfeldt, A.; Sun, L. C. *Chem. Commun.* **2009**, 6288.
(28) Tian, H. N.; Yang, X. C.; Chen, R. K.; Hagfeldt, A.; Sun, L. C. *Energy Environ. Sci* **2009**, *2*, 674.
(29) Grätzel, M. *Nature* **2001**, *414*, 338.
(30) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Pechy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202.
(31) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597.