The N=S=N Link as Electron Accepting Moiety for Stable, Solution-Processable Conjugated Oligomers

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ABSTRACT: New conjugated oligomers, oligo(9,9-didodecyl-fluorene-bis-sulphurdiimide), consisting of 9,9-didodecylfluorene separated by —N=S=N— moieties, are reported. These oligomers are stable purple solids under ambient conditions with absorption covering a broad spectral window in the UV-vis range and a main broad peak centered at 555 nm with onset extending to 700 nm. These oligomers show an obviously longer conjugation length than its dimeric analogue, bis-9,9-didodecyl-fluorene-2-sulfurdiimide that shows a band-edge absorption centered at 484 nm with onset at 590 nm. The dimer and oligomers are soluble in a variety of organic solvents. Moreover, we found that the oligomer with an average repeating-unit number of six could significantly quench the photoluminescence (PL) of poly[2-methoxy-5-(2′-ethyl-hexy-loxy)-1,4-phenylene vinylene] (MEH-PPV) or poly(3-hexylthiophene) (P3HT) in the solid state. More importantly, the composites of this oligomer with P3HT showed a nearly 10-fold enhancement of the photocurrent, compared with that of P3HT itself. In addition, the PL of this oligomer could be quenched by the presence of phenyl-C_{61}-butyric acid methyl ester (PCBM) in toluene. These results suggest the presence of photoinduced charge transfer in composites of these oligomers blended with an electronic partner that either donates or accepts electrons. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 441–451, 2011

KEYWORDS: charge transfer; conjugated polymers; oligomers; photovoltaics; sulphurdiimide

INTRODUCTION The advance in solution-processed organic photovoltaics (OPV) requires new processable materials with good charge-carrier mobility and broad absorption that matches the solar spectrum. These properties are essential for organic solar cells to achieve high power conversion efficiency.[1] To reach this goal, it is clearly important to explore low-band-gap molecules as well as new acceptor molecules for small molecule OPV as well as polymeric OPV.[2]

Recently, the N=S=N moiety has become the mainstay of the family of low-band-gap donor-acceptor polymers, where the NSN component, in the form of thiadiazole units, imparts electron accepting character to its molecules.[2,3] Another outstanding member of the NSN family is (SN)x,[4] the only superconducting polymer and truly intrinsically conducting polymer known. Though some attempts have been made to incorporate NSN in the backbone of organic polymers,[5] it was long time ago when the paradigm of the day was improved conductivity, rather than organic electronics. Moreover, these polymers to date had rather limited solubility in common solvents, raising a significant challenge for characterization and solution-processing.

In a previous report,[6] we presented our exploration on the synthesis and characterization of a conjugated polymer (denoted as PBSDDT), based on alternating 1-alkyl-1,2,4-triazole and N=S=N links. For PBSDDT, 4,4-dimethylamino pyridine (DMAP) is an effective reagent for the polymerization of bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole. This polymer, showing a broad absorption band in the range of 400 to 600 nm, is easily soluble in a range of nonpolar solvents including tetrahydrofuran (THF), chloroform, dichloromethane (DCM), and chlorobenzene. It is stable under inert atmosphere but hydrolyzes easily upon exposure to air. The poor stability of PBSDDT under ambient conditions is unacceptable for optoelectronic devices.

Herein we describe the design and synthesis of oligo(9,9-didodecylfluorene-bis-sulphurdiimides), a new type of conjugated oligomers consisting of alternating N=S=N moieties separated by 9,9-didodecylfluorene. In contrast to PBSDDT, these oligomers show remarkable chemical stability under ambient conditions. Moreover, these oligomers exhibit good solubility in a wide range of organic solvents and broad absorption in the UV-vis spectral window.

In the following sections, we start by describing the synthetic design of these new oligomers. The body of results and discussion mainly includes two parts. The first presents the synthesis and the characterization of a model compound (compound **5**, Scheme 1) that is composed of two 9,9-didodecylfluorene linked
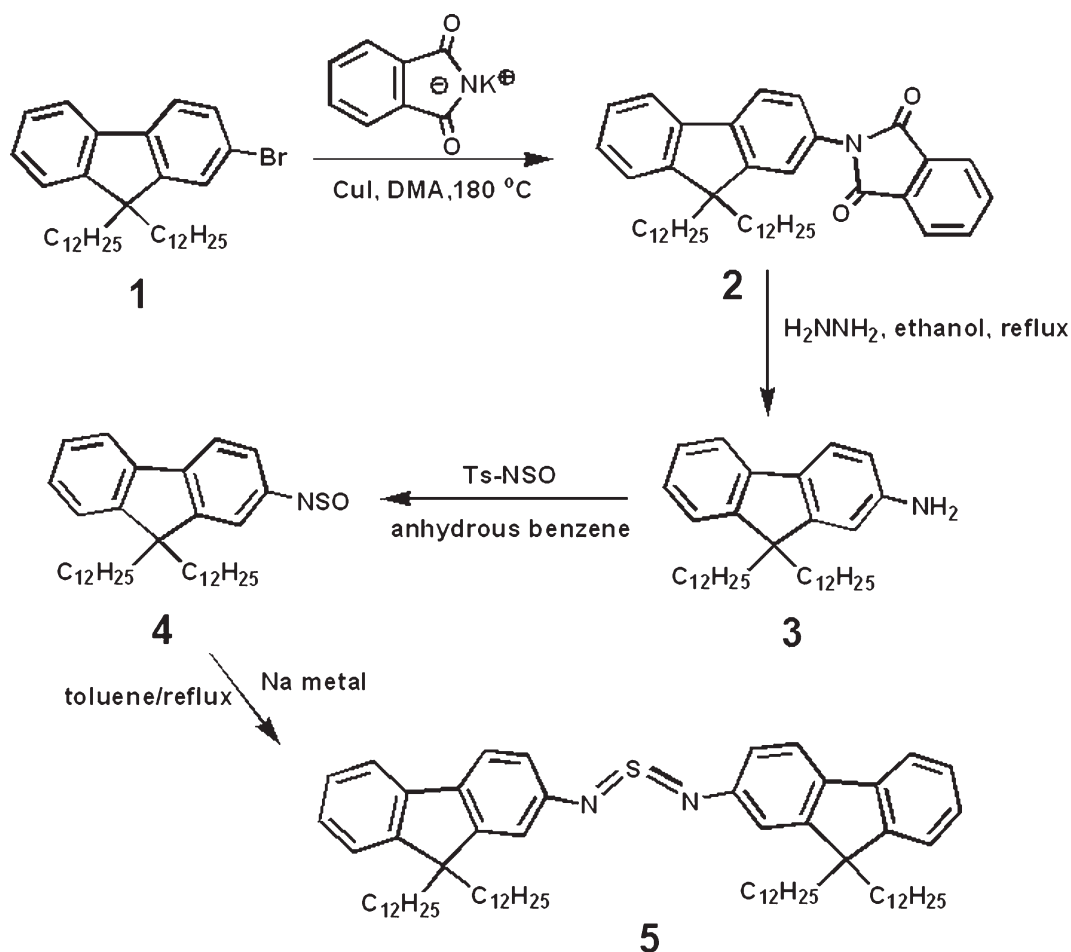
SCHEME 1 The synthetic route to bis-9,9-didodecyl-fluorene-2-sulphurdiimide.

in between by one N=S=N moiety. This dimer, owing to its well-defined molecular structure, gives us a good reference to understand the molecular characteristics of the oligomers described in the second part of this article. Specifically, the second part starts by describing the synthesis and characterization of bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine that serves as the monomer, followed by discussion of its polymerization under different reaction conditions. Finally, we present results of photoluminescence (PL) quenching and photoconductivity (PC) measurements in composites of oligo(9,9-didodecylfluorene-bis-sulphurdiimides) with MEH-PPV and P3HT in the solid states, to investigate the photoinduced charge transfer in these systems.

EXPERIMENTAL

Materials and Instruments
Chemicals were purchased from Sigma-Aldrich or Across Organics and used as received without further purification. All dry solvents were freshly distilled under argon over an appropriate drying agent prior to use. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Inova 500 MHz spectrometer and referenced to the solvent peak. Mass spectrometry was performed by UC Santa Barbara Mass Spectrometry Laboratory. UV-Vis spectra were recorded on an Agilent 8453 spectrophotometer using either 1 cm quartz cuvettes

for solution or glass slides for films at room temperature. PL spectra were measured using a SPEX Fluorolog spectrofluorometer (Jobin Yvon/SPEX, Edison, New Jersey).

Films used for the PC measurement were spin-cast onto alumina substrates from a 1 wt % dichlorobenzene solution, comprising pure P3HT or P3HT: **10c** at 1:0.8 weight ratio, resulting in a film thickness of ~100 nm. The Auston switch sample geometry was used, with a 50 μm gap between the evaporated gold electrodes. Steady-state PC measurements were carried out using monochromatic light generated from a tungsten lamp source; the incident light beam was mechanically chopped at 170 Hz to enable the use of the standard lock-in amplifier modulation technique. The applied electric field was $F = 2.0 \times 10^4$ V cm^{-1}. Samples were kept under dynamic vacuum ($<10^{-4}$ mbar) during the measurements. The spectral dependence of the incident beam was determined after each measurement using a calibrated Si photodiode also used to normalize the PC data.

Synthesis of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2, 7-diamine (9)
The fluorene derivative **8** (1.0 g, 1.88 mmol) was dissolved in anhydrous benzene (24 mL) in a Schlenk round-bottom flask (100 mL) and treated with *N*-sulfinyl-*p*-toluenesulfonamide
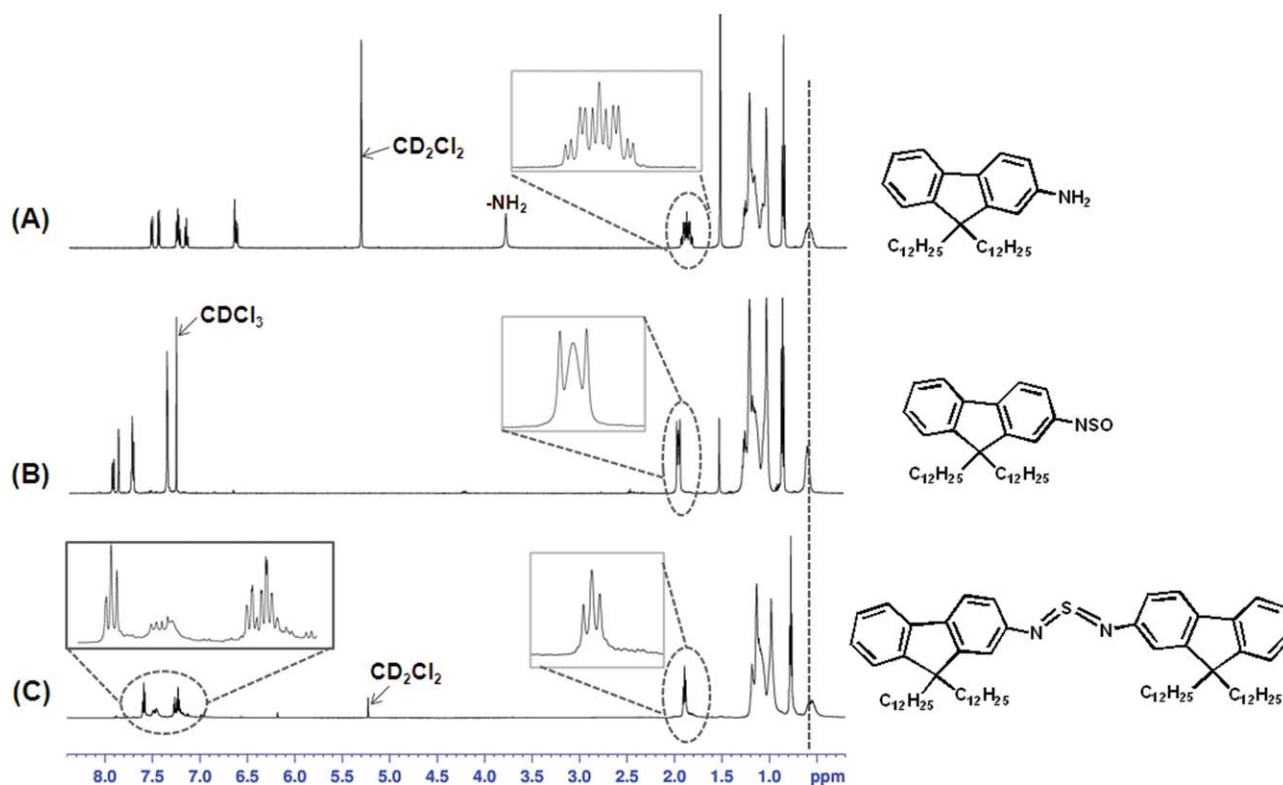
FIGURE 1 ^{1}H NMR spectra of compound **3** (A), **4** (B), and **5** (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

(1.22 g, 5.64 mmol) quickly under N_2 atmosphere. The mixture turned from light brown to orange immediately after addition of *N*-sulfinyl-*p*-toluenesulfonamide. The mixture was stirred at room temperature for 22 h, followed by filtration, drying under vacuum and the residue redissolved in anhydrous pentane (ca., 15 mL) and filtered. The procedure was repeated twice to completely remove the pentane-insoluble *p*-toluenesulfona-mide. A dark yellow solid was obtained after drying the filtrate under vacuum. Yield: 1.15 g (98%). $T_m = 36 \pm 1\ °C$. ^{1}H NMR (CDCl$_3$, 500 MHz): δ (ppm) = 7.97–7.93 (d, 2H), 7.89–7.87 (s, 2H), 7.78–7.74 (d, 2H), 2.02–1.95 (m, 4H), 1.70–1.00 (m, 36H), 0.90–0.85 (t, 6H), 0.68–0.58 (broad signal, 4H). ^{13}C NMR (CDCl$_3$, 500 MHz): δ (ppm) = 153.27, 143.28, 142.45, 127.46, 122.35, 121.30, 56.11, 40.32, 32.25, 30.19, 29.95, 29.88, 29.85, 29.67, 29.56, 24.11, 23.03, 14.46. IR: max 3476, 3388, 2926, 2846, 1621, 1592, 1460, 1352, 1286, 1136, 1024, 814, 719 cm^{-1} +ESI-TOF MS: MW = 624.38 (calculated), m/z 624.47 (measured). Elemental analysis: Calculated C (71.1), H (9.1), N (4.5), S (10.2). Found C (71.9), H (8.9), N (4.6), S (9.56).

Reaction of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine with Dimethylamino Pyridine

The monomer **9** (0.72 g, 1.17 mmol) was dissolved in 4 mL of dry CH$_2$Cl$_2$ and to this mixture was added DMAP (143 mg, 1.17 mmol), and the mixture was stirred at room temperature for 24 h. After this period, more DMAP (143 mg, 1.17 mmol) and 1 mL more of dry CH$_2$Cl$_2$ was added. After being stirred for 6 days at room temperature, the mixture was dried under vacuum. The residue was washed with dry

CH$_3$CN and filtered. (Note: the filtrate was dark red.) The resulting solid was washed again with dry CH$_3$CN (30 mL/portion, twice) and dried under vacuum. The ^{1}H NMR, FTIR, and UV-vis spectra of this final product are shown in the Supporting Information.

Reaction of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine using SmI$_2$

The monomer **9** (126 mg, 0.2 mmol) was charged in a Schlenk flask (50 mL) and to it was added SmI$_2$ (0.1 M THF solution, 2.0 mL) quickly, resulting in a dark red solution. The mixture was stirred at room temperature, but no obvious color change was observed even after 2-days stirring. The mixture was dried under vacuum, resulting in a dark-red, CDCl$_3$ insoluble, solid.

Polymerization of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine using Sodium Metal

The monomer **9** (0.40 g, 0.6 mmol) was dissolved in dry toluene (6 mL) in a Schlenk flask (50 mL) and to it was added sodium metal (27.6 mg, 1.2 mmol) quickly under N_2 atmosphere. The mixture was bubbled with dry N_2 for ~10 min and then heated at 120–130 °C under N_2 atmosphere, resulting in a deeper color with increasing heating time. After 43 h, the mixture was diluted with 20 mL of dry toluene and then bubbled with dry air for 2 h, resulting in a purple mixture. The mixture was filtered and washed with distilled water (50 mL/portion, three times) and brine (50 mL/portion, three times). The organic layer was isolated, dried over anhydrous Na$_2$SO$_4$, filtered and dried under vacuum at room
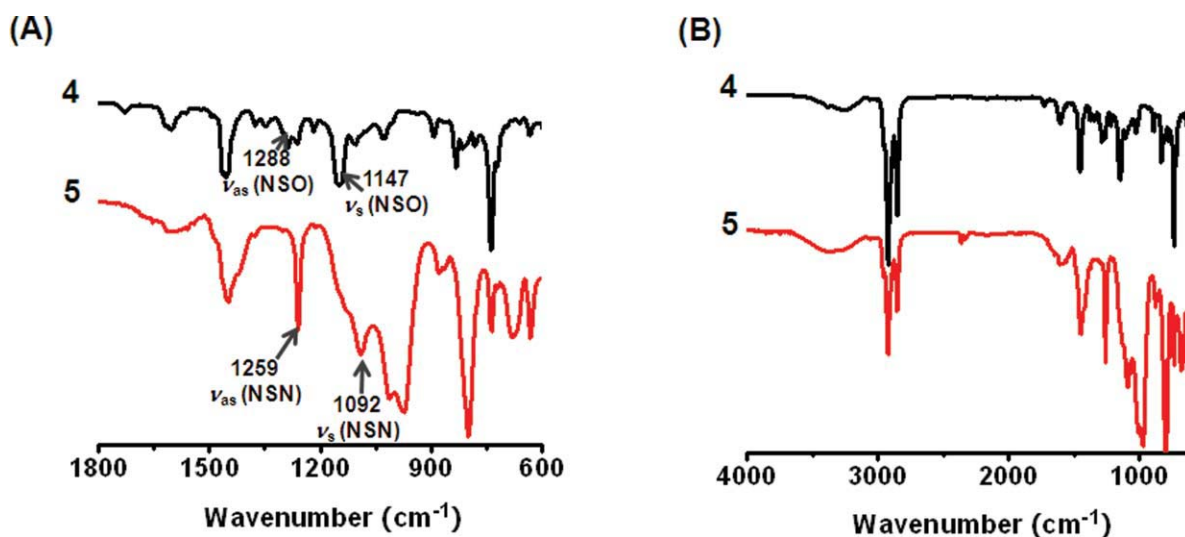
FIGURE 2 FTIR spectra of compound **4** and **5** in solid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

temperature to afford a deep purple solid. The solid was easily soluble in pentane, hexane, toluene, chloroform, DCM, THF, ethyl acetate, and diethyl ether but insoluble in either methanol or acetonitrile. Yield: 0.32 g (95%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ (ppm) = 7.85–7.32 (m, 5H), 6.68–6.60 (d, 1H), 3.90–3.65 (s, end group), 2.15–1.70 (m, 4H), 1.40–1.00 (m, 36H), 0.90–0.80 (t, 6H), 0.80–0.60 (broad signal, 4H). ^{13}C NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) = 180.06, 169.03, 163.50, 153.32, 152.46, 151.29, 150.76, 146.81, 144.46, 140.76, 131.45, 123.27, 121.17, 120.60, 119.99, 118.81, 118.25, 116.09, 113.88, 113.76, 109.78, 109.44, 102.75, 40.51, 29.62, 23.87, 22.67, 13.86. IR: max 3356, 2926, 2848, 1613, 1585, 1460, 1264, 1186, 1122, 1064, 1035, 928, 814, 752, 719 cm^{-1}.

Synthesis of Bis-9,9-didodecyl-fluorene-2-sulfurdiimide

The synthesis of dimer **5** was similar to that described above for **10b–c** except that 1:1 equivalent ratio of fluorene/reactants was used for **5** instead of a 2:1 equivalent ratio of fluorene/reactants for **10b–c**. The synthetic details are described in Supporting Information.

RESULTS AND DISCUSSION

The [SN]x polymer is remarkably inert. It does not react with water or acidic solutions but slowly decomposes in alkaline solutions.[4(b)] Kresze and coworkers[7] reported that small molecules of sulphur diimides linked to *n*-alkyl groups or strongly electron-withdrawing groups such as tosyl are extremely sensitive to hydrolysis and are very reactive. This result is consistent with the low stability of our previous polymer (PBSDDT) consisting of alternating 1-decyl-1,2,4-triazole and N=S=N links, in which the electron-withdrawing nature of triazole may contribute to the easy hydrolysis of PBSDDT.[6] In contrast, Ph—N=S=N—Ph synthesized from the reaction of Ph—N=S=O and sodium metal is stable against hydrolysis.[8]

Based on the facts described above, we proposed a new conjugated polymer consisting of alternating 9,9-didodecylfluor-ene and N=S=N links. Our hypothesis is that the neutral-to-electron-donating nature of 9,9-didodecylfluorene may lead to a conjugated polymer chain with enhanced chemical stability. While our initial objective was to obtain such conjugated polymers with relatively high molecular weights that could benefit both the electronic and the mechanical properties for device applications, our several attempts to optimize the polymerization conditions resulted in oligomers with relatively short chain lengths. The focus of this article is to describe the synthesis and characterization of these oligomers and to investigate photoinduced charge transfer in blends of these oligomers with their electronic partners.

Synthesis and Characterization of Bis-9,9-didodecyl-fluorene-2-sulphurdiimide

The synthetic route to bis-9,9-didodecyl-fluorene-2-sulphur-diimide (compound **5**) is shown in Scheme 1. The synthesis of 9,9-didodecylfluorene-2-phthalimide (compound **2**) and 9,9-didodecylfluorene-2-amine (compound **3**) followed a procedure reported by Neuteboom et al.[9] The reaction of **3** with *N*-sulfinyl-*p*-toluenesulfonamide in anhydrous benzene at room temperature led to complete conversion of —NH$_2$ into —NSO, as demonstrated by the ^{1}H NMR spectra in Figure 1.

While exploring reaction conditions to convert the —NSO into —NSN— bonds, we first repeated the reaction reported by Oakley and coworkers[8] by refluxing thionylaniline with one equivalent of sodium metal in toluene. This reaction led to formation of a stable red compound—PhNSNPh. Under similar reaction conditions, refluxing of *N*-sulfinyl-1-amino-9,9-didodecylfluorene (compound **4**) with 1 equivalent sodium metal[8] followed by purification resulted in a stable red solid (compound **5**), insoluble in CH$_3$CN but readily soluble in a variety of nonpolar solvents such as pentane, hexane, toluene, and midpolar solvents such as dichloromethane, chloroform, THF, and diethyl ether.
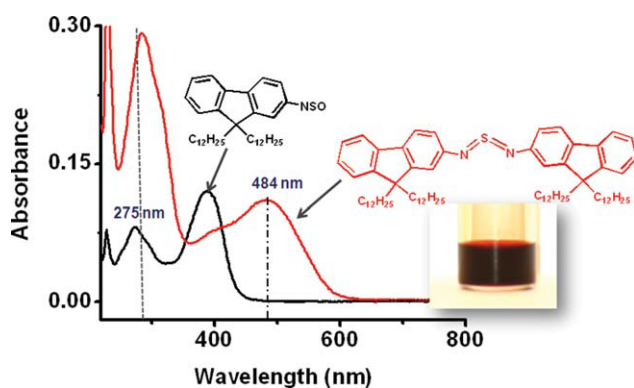
FIGURE 3 UV-vis absorption spectra of compound **4** and **5** in CH$_2$Cl$_2$. The digital photograph shows the solution of **5** in CH$_2$Cl$_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

The ^{1}H NMR spectra of compounds **3–5** are shown in Figure 1. The conversion of —NH$_2$ into —NSO led to obvious down-field shifts for the aromatic protons (δ = 6.0–8.0 ppm) from the fluorene unit) and the proton from the first —CH$_2$ (δ = 1.7–2.0 ppm) linked to the fluorene, whereas no significant shift was observed for other aliphatic protons (δ = 0.4–1.3

ppm). Compared with the spectrum of **4** [Fig. 1(B)], all of the aromatic proton signals of **5** shifted up-field.

To confirm the conversion of —NSO into —N=S=N— bonds, the monomer **4** and the dimer **5** were characterized by FTIR. The spectra (Fig. 2) show that the characteristic peaks of —NSO units at 1288 and 1147 cm^{-1} disappeared after the reaction of **4** with sodium metal, accompanied by strong peaks at 1259 and 1092 cm^{-1}, corresponding to v_{as}(N=S=N) and v_s(N=S=N), respectively.

UV-vis absorption spectra (Fig. 3) show a dramatic red shift for the band-edge absorption peak of **4** from 387 to 484 nm after its reaction with sodium metal. There was also a relatively small red-shift (10 nm) for the absorption peak of **4** at 275 nm.

The results described above indicate that —NSO is a viable precursor for the formation of —N=S=N— group. Moreover, the neutral-to-electron-donating nature of 9,9-didodecylfluorene leads to a stable N=S=N-linked 9,9-didodecylfluorene dimer (**5**) that is easily soluble in nonpolar solvents.

Synthesis and Characterization of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine

A "transsulfinylation" reaction between 9,9-didodecylfluorene-2,7-diamine (**8**) and *N*-sulfinyl-*p*-toluenesulfonamide in
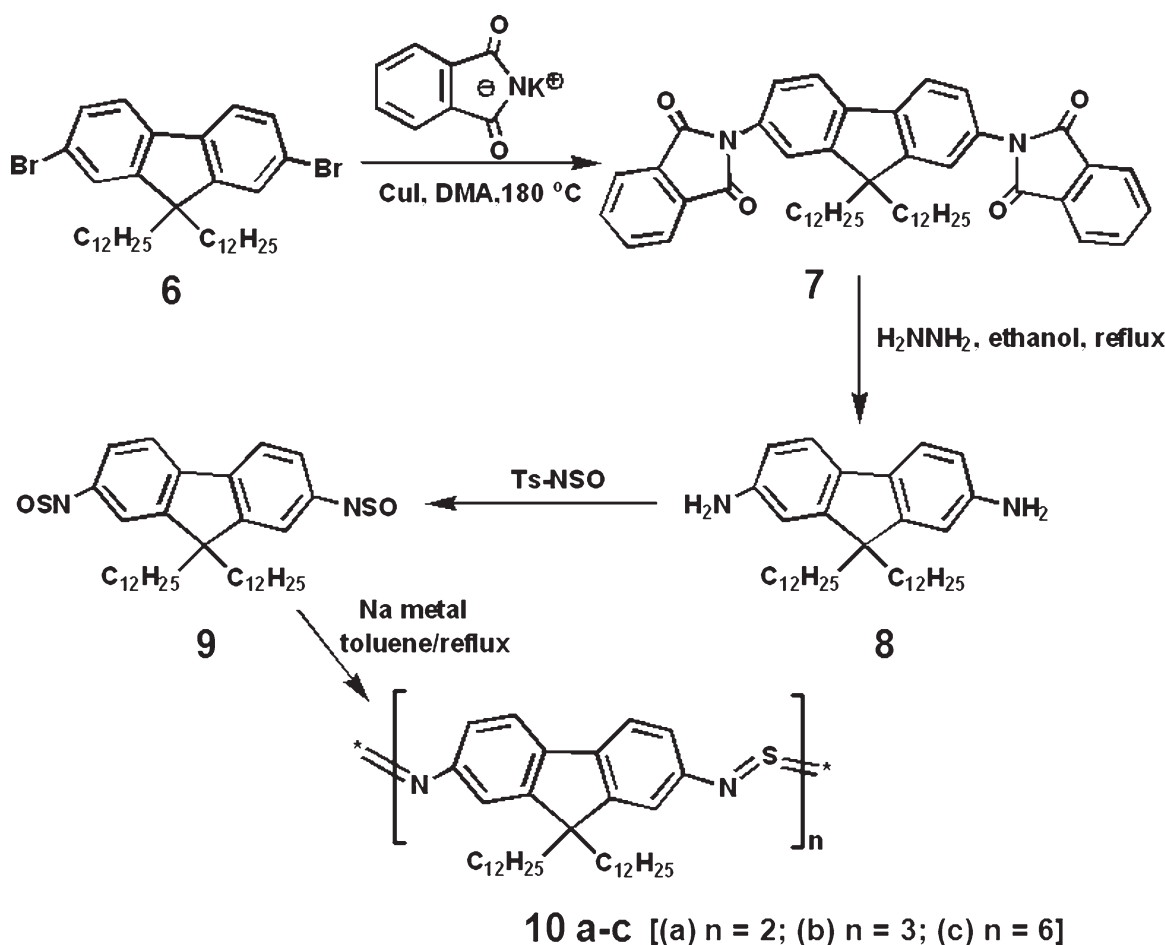
SCHEME 2 The synthetic route to oligo(9,9-didodecylfluorene-bis-sulphurdiimide).
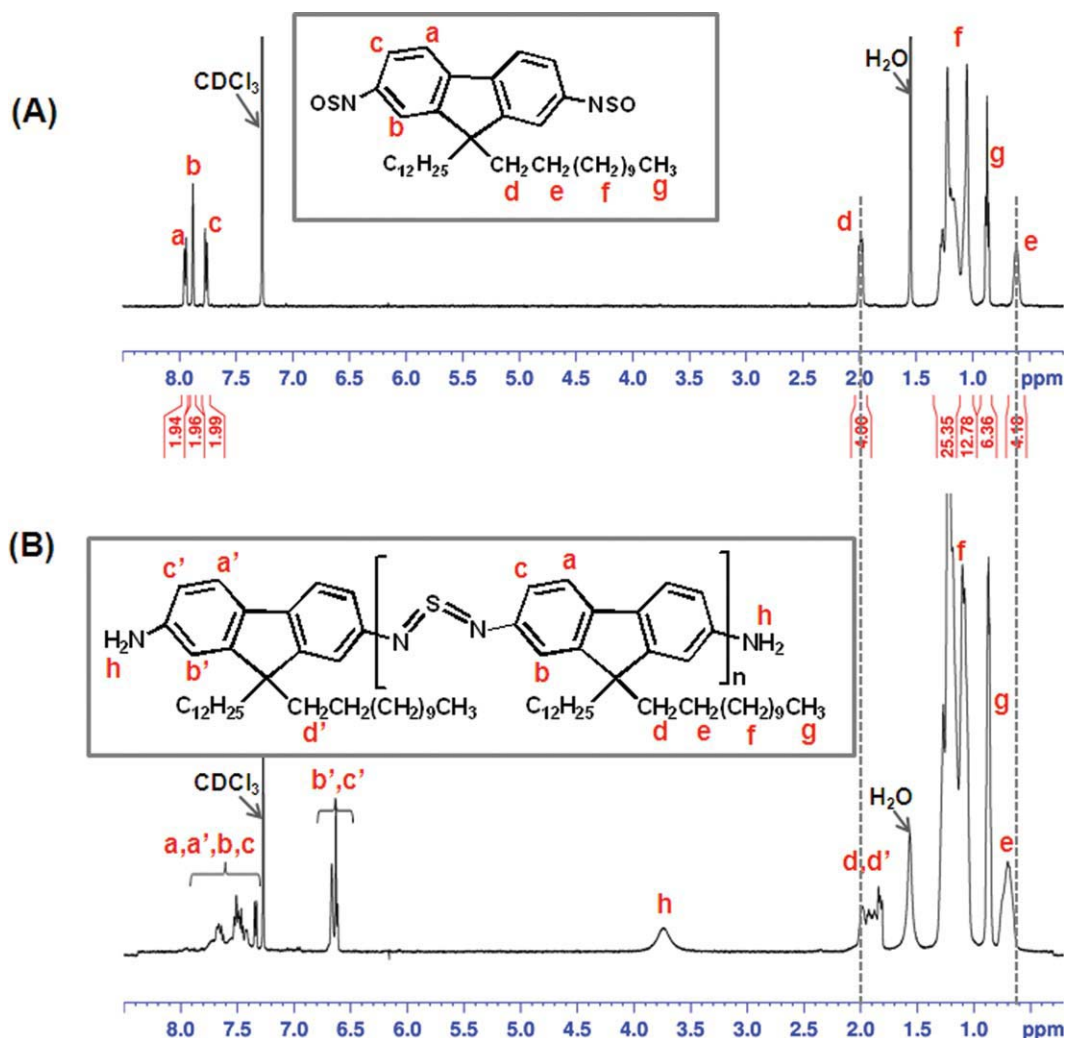
FIGURE 4 ^{1}H NMR (CDCl$_3$) spectra of compound **9** (A) and **10b** (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

anhydrous benzene resulted in the formation of bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine (**9**) and the insoluble *p*-toluenesulfonamide that could be removed by filtration (Scheme 2). Monomer **9** was further purified by drying the filtrate under vacuum and re-dispersing the residue in anhydrous pentane, followed by filtration. This process was repeated twice until no more solid was visible in the pentane solution. The ^{1}H NMR spectrum [Fig. 4(A)] of purified **9** showed no existence of *p*-toluenesulfonamide in the final product. This sulfinylamine exhibits remarkably higher stability compared with bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole.[6] The ^{1}H NMR spectrum did not exhibit any hydrolysis of **9** after standing in CDCl$_3$ for at least 3 days under ambient condition. The composition of **9** was further confirmed by EI-mass spectrometry (Supporting Information Figure S6) where the measured value (624.47 m/z) matches the calculated value (624.38 g mol^{-1}) very well. The FTIR spectrum of **9** will be discussed in Section "Polymerization of bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine with Sodium Metal."

Polymerization of Bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine

Refluxing **9** with metallic sodium in toluene, followed by purification, resulted in a stable purple solid that showed a broad absorption band with an onset around 700 nm. In contrast, the reaction of **9** with DMAP only resulted in **10a** with short conjugating length (*n* = 2), while the reaction of **9** with SmI$_2$ in THF did not lead to any color change. Also

TABLE 1 Comparison of Compound 5 with 10a–c

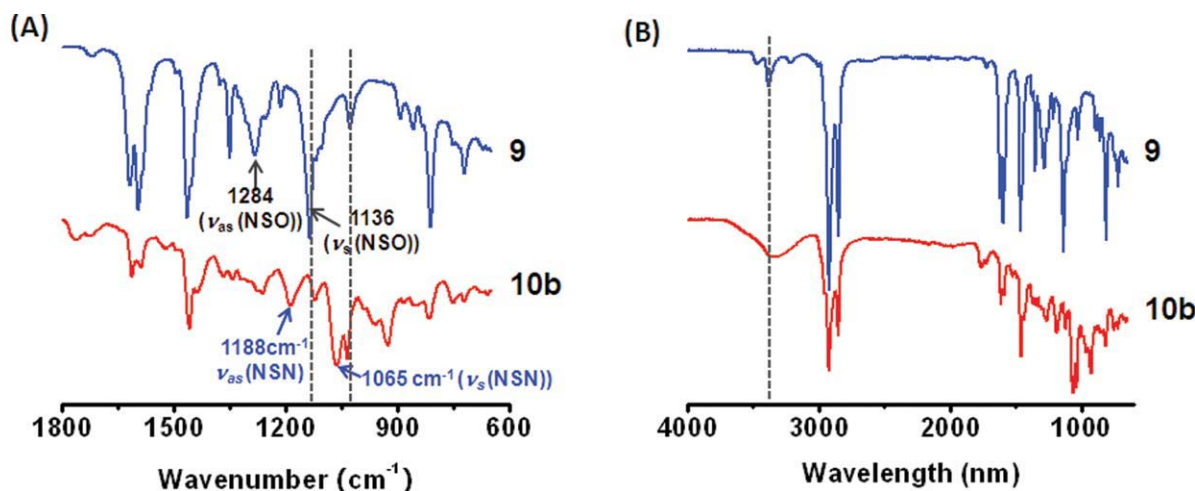| Compound	Catalyst	*n* (Average Number of Repeating Units)	$\lambda_{abs,max}$ (nm) (in THF)	$\lambda_{abs,onset}$ (nm) (in THF)
5	Sodium metal	2	481	592
10a	DMAP	2	429	530
10b	Sodium metal	3	555	680
10c	Sodium metal	6	555	680

FIGURE 5 FTIR spectrum of compound **10b** from the reaction of **9** with sodium metal. For comparison, the FTIR spectrum of **9** is also presented here. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

described below are our studies of PL quenching and steady-state PC measurements to investigate the photoinduced charge transfer in composite films of **10c** (n = 6) blended with MEH-PPV and P3HT. In addition, the PL quenching of **10c** with PCBM has been examined in solution.

Reaction of Bis-N-*sulfinyl-9,9-didodecylfluorene-2,7-diamine with Dimethylamino Pyridine*

In our previous report,[6] we found that DMAP is an effective reagent for the polymerization of bis-*N*-sulfinyl-3,5-diamino-1-decyl-1,2,4-triazole. Therefore, we first examined whether DMAP was also able to initiate the polymerization of **9**. The reaction of **9** with 1 equivalent of DMAP in dry CH_2Cl_2 at room temperature for 24 h did not result in any obvious color change. The increase of **9**/DMAP molar ratio to 1:2 and the extension of the reaction time up to 6 days only led to a slightly deeper color (deep red) of the mixture. In contrast with the purification of poly(1-decyl-1,2,4-triazole-bis-sulphurdiimide) (PBSDDT), when a large excess of dry CH_3CN was added to the concentrated reaction mixture, only a small portion of material (brownish red) precipitated, while significant amount of material remained in the red filtrate. The precipitate was washed twice with dry CH_3CN, followed by drying under vacuum before characterization.

The ^{1}H NMR spectrum (Supporting Information Figure S7) of the purified precipitate (denoted as **10a**) in $CDCl_3$ did show new peaks in the aromatic range (7.92–7.88, 7.83–7.81, 7.58–7.55 ppm) that could be ascribed to the protons of the phenyl rings connected by —N=S=N— links. At the same time, the proton signals belonging to **8** and **9** could also be discerned. While the presence of —NH_2 end group was proved by the presence of a broad singlet peak at 4.2–3.9 ppm, the signal of **9** could be either from some unreacted monomer **9** or from the product with an NSO end-group. All of these proton signals in the aromatic range appear well resolved (i.e., narrow and sharp), an implication of the low molecular weight of the product. The integration ratio of the peak at 7.83–7.81 ppm over that at 7.97–7.93

ppm indicates that the majority of **10a** is a dimer linked by —N=S=N— in between, that is, n = 2. In addition, the first —CH_2— group next to the fluorene ring showed an obviously broader peak at 2.02–1.82 ppm compared with that of **9**. In this range, again, a new signal appeared at 1.96–1.90 ppm, corresponding to the first —CH_2— group next to the (N=S=N)-linked fluorene ring, besides the signals from **9** (2.02–1.96 ppm) and **8** (1.90–1.82 ppm).

The FTIR spectrum (Supporting Information Figure S8) of **10a**, in comparison with the spectra of **8** and **9**, shows a new peak with strong absorption at 1032 cm^{-1}, accompanied by a shoulder at 1102 cm^{-1}. At the same time, one can see that the peak at 1136 cm^{-1}, corresponding to the v_s(N=S=O),[7,8,10] still remained in the product of **10a**.

The UV-vis spectra (Supporting Information Figure S9) show that the absorption onset of **10a** had red-shifted to 570 nm, compared with that of **9** (absorption onset around 500 nm). This relatively small red-shift implies that the conjugation length in **10a** is relatively short, consistent with the ^{1}H NMR result described above.

Attempts at heating neat **9** with DMAP around 40 °C or by refluxing **9** and DMAP in toluene did not lead to products with a longer conjugation length than that of **10a** described above.

Polymerization of Bis-N-*sulfinyl-9,9-didodecylfluorene-2, 7-diamine with Sodium Metal*

In a reaction similar to the synthesis of **5** (Section "Materials and Instruments") using **9** and 2 equivalents of sodium metal, the color of the mixture in toluene became darker with increasing reflux time. After the reaction mixture was quenched with air and washed with water, followed by drying under vacuum, a deep purple solid (denoted as **10b**) was obtained.

The ^{1}H NMR spectrum [Fig. 4(B)] of this product in $CDCl_3$ showed multiple broad peaks in the aromatic region as well as in the 2.03–1.80 ppm range. The integration ratio of the peak at 2.03–1.80 ppm over that of the peak at 6.75–6.60 ppm gives an average value of 3 for the degree of polymerization.
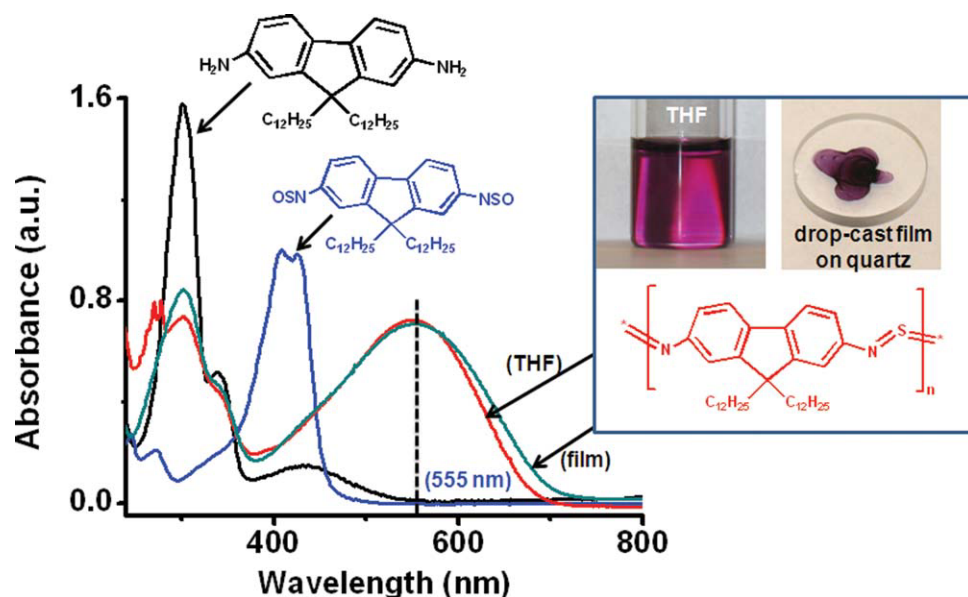
FIGURE 6 UV-vis absorption spectrum of **10b** from the reaction of **9** with sodium metal. For comparison, the absorption spectra of **8** and **9** are also presented here. The inset shows the photograph of **10b** in THF and in the solid film drop-cast on a quartz slide.

The FAB-mass spectrum (Supporting Information Figure S10) of **10b** indicates the coexistence of trimers and dimers, both of which are terminated by —NH₂ groups at both ends. This result is consistent with an average of $n = 3$ (based on the number of fluorene groups) as estimated by ^{1}H NMR above (Table 1).

Figure 5 shows the FTIR spectrum of **10b** in comparison with that of **9**. One can see that there is a new peak at 1188 cm^{-1} corresponding to υ_{as}(N=S=N) in **10b** and another one at 1065 cm^{-1} corresponding to υ_s(N=S=N) [Fig. 5(A)]. Compared with the FTIR spectrum of **5** (Fig. 2), both υ_{as}(N=S=N) and υ_s(N=S=N) of **10b** shifted to lower wavenumbers due to the increased electron delocalization in **10b** in comparison with **5**. Similar phenomena of lowering in energy of υ_{as}(N=S=N) were also observed by Kuyper and Street[11] in R(SN)$_n$R (R = aryl) when n was increased. In addition, the IR signals in the range of 3500–3000 cm^{-1} became broader and featureless in **10b**, compared with those in **9** [Fig. 5(B)], indicating H-bonded N—H stretching.

The UV-vis spectra of **10b** are shown in Figure 6. Compared with the absorption of **8** and to that of **9**, **10b** exhibits a remarkable red-shift in THF solution, with an onset extended to 700 nm. Moreover, the absorption of **10b**, with a main band centered at 555 nm, covers a broad window in the UV-vis range. In the solid state, **10b** shows a slight red-shift (ca., 20 nm), mainly on the red edge. In addition, the component of the absorption belonging to **9** is not significant in **10b**, while the absorption feature of **8** can be discerned clearly in THF solution and solid film of **10b**. These results, together with the ^{1}H NMR spectrum shown in Figure 4, imply that the end-group of **10b** is essentially —NH₂.

Efforts Toward Increasing the M_w of oligo(9,9-didodecyl-fluorene-bis-sulphurdiimide)

To increase the molecular weight of oligo(9,9-didodecylfluorene-bis-sulphurdiimide), we optimized the polymerization

condition by doubling the monomer (**9**) concentration to 70 mg/mL in the reaction medium and by quenching the reaction mixture with dry air.

The ^{1}H NMR spectrum (Supporting Information Figure S11) of this product (denoted as **10c**) in CDCl₃ indicates that the average number of the repeating units can be increased to 6 (based on the number of fluorene groups) after the optimization of the polymerization reaction. Nevertheless, the UV-vis absorption (Supporting Information Figure S13) of **10c**, in the range of 400–700 nm, is essentially the same as that of **10b**. In addition, one can see that the absorbance of **10c** in the range of 280–350 nm (corresponding to the end group) decreased compared with that of **10b**. This result is consistent with the higher M_w in **10c** than **10b** as also demonstrated by ^{1}H NMR (Supporting Information Figure S11).

Several factors may limit the M_w of oligo(9,9-didodecylfluorene-bis-sulphurdiimide). First, the present reaction mixture was a heterogeneous system due the insolubility of sodium metal in toluene. The progress of the polymerization was relatively slow due to the low surface-contact-area between the monomer and the sodium metal. A new homogeneous catalyst would help to optimize the polymerization in the future. Second, Bestari et al.[8] found that the presence of a catalytic quantity of alkali metal (Na, K) could induce rapid scrambling in mixtures of RNSNR and R′NSNR′, which led to formation of RNSNR′. Similarly, one can imagine that the skeletal scrambling of sulfur diimide radical anions during the polymerization of monomer **9** may break longer polymer chains into shorter ones, thus placing an upper limit for the average M_w of the oligomer. Third, the stability of very long thiazyl chains remains questionable.[4(b)] For example, Zibarev et al. reported that reaction of ArS₄N₄SiMe₃ [Ar = o-NO₂C₆H₄ or 2,4-(NO₂)₂C₆H₃] with SCl₂ did not lead to the 17-heteroatom chain, ArS₉N₈Ar, but rather to the isolation of the decomposition products, ArS₅N₄Ar.[11,12] This result implies that the aromatic nitro groups inhibit spontaneous
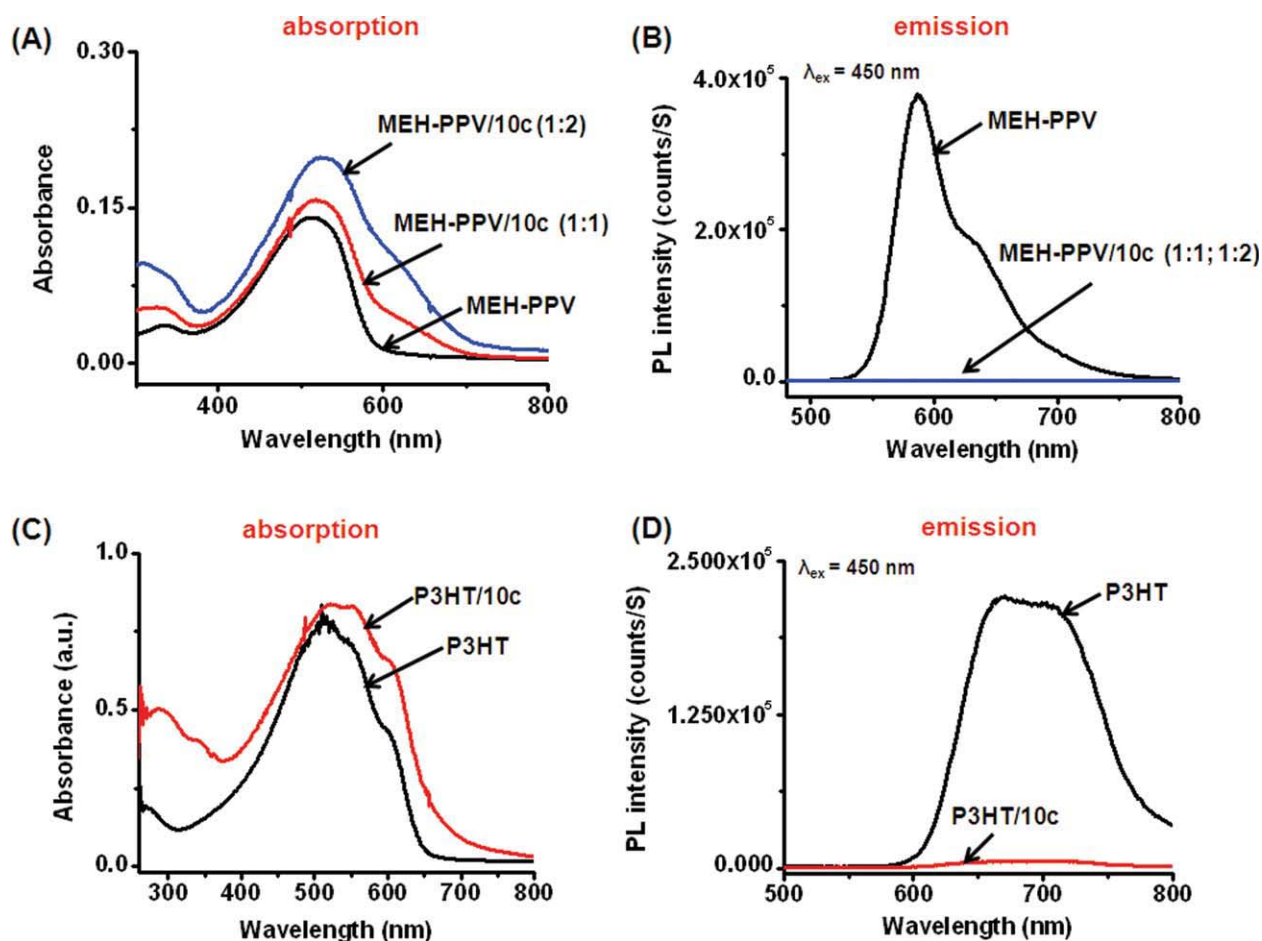
FIGURE 7 UV-vis absorption (A,C) and PL (B,D) spectra of the composites of MEH-PPV/**10c** (A,B) and P3HT/**10c** (C,D) in the solid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

shortening of thiazyl chains of $(ArSN=S=N)_2S$, but they do not stabilize the compounds containing a chain of 17 alternating nitrogen and sulphur atoms. Nevertheless, the authors did not discuss the stability of ArS_5N_4Ar [Ar = o-$NO_2C_6H_4$ or 2,4-$(NO_2)_2C_6H_3$] against moisture.[12]

Photoinduced Charge Transfer

The UV-vis absorption and PL spectra of **10c** in toluene (Supporting Information Figure S14A) and in the solid film (Supporting Information Figure S14B) drop cast on a quartz slide are presented in Supporting Information. In toluene, **10c** shows relatively weak fluorescence with a peak centered at 515 nm. The mechanism for this negative Stokes shift remains unclear to us. In the solid state, the PL of **10c** was dramatically quenched, whereas the absorption appears similar to that in solution.

We note that **5** and **10b** ($n = 3$) also showed weak fluorescence in toluene, while the emission peaks of both of them appeared broader than that of **10c** ($n = 6$) (Supporting Information Figure S15). This result implies that the fluorescence of **10c** observed in toluene could not be exclusively from relatively short chains in the product.

To ascertain the HOMO and the LUMO levels of **10c**, we carried out cyclic voltammetry and ultraviolet photoelectron spectroscopy (UPS) measurements. The cyclovoltagram of **10c** in CH_2Cl_2 (containing 0.1 M tetrabutylamonium hexafluorophosphate) shows two quasi reversible peaks at -1.43 and -1.66 V, respectively (Supporting Information Figure S16). The onset of the reduction potential is located at -1.12 V, giving a LUMO level of -3.4 eV versus ferrocene. Given this LUMO level and the optical band gap of 1.8 eV, the HOMO level of **10c** is -5.2 eV, which is close to the value of the HOMO (-5.3 eV) measured by UPS (Supporting Information Figure S17).

MEH-PPV, due to its strong PL in the solid state, was first chosen to study the PL quenching with **10c**. Figure 7 shows that, at a weight ratio of MEH-PP/**10c** from 1:1 to 1:2, the PL of MEH-PPV was completely quenched in the solid state, while the absorption [Fig. 7(A)] shows the features of both MEH-PPV and **10c**.

We also examined the PL quenching of regioregular P3HT by **10c**. In dilute toluene solution, **10c** quenches the PL of P3HT as effectively as PCBM (Supporting Information Figure S19). Again, dramatic (ca. 90%) PL quenching occurred in
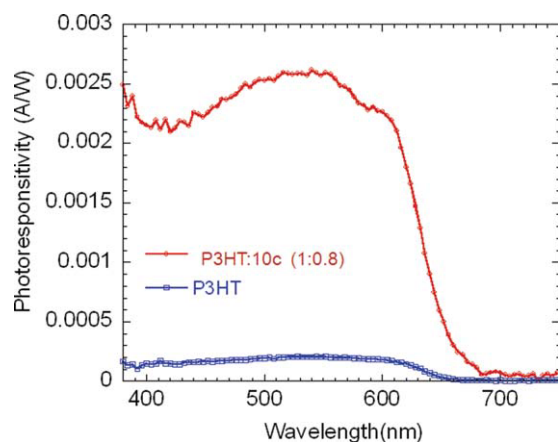
FIGURE 8 Steady-state photoresponse of the composites of P3HT/**10c** in comparison to P3HT itself in the solid states. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

the solid film of P3HT by **10c** [Fig. 7(C,D)]. For comparison, only 65% of the PL intensity of P3HT was quenched by the dimer, **5**, in the solid films (Supporting Information Figure S20).

Figure 8 shows the PC data obtained from thin films of pristine P3HT and P3HT:**10c** (1:0.8, by wt.), respectively. The steady state PC spectral profiles of the pristine P3HT and the composite films shown in Figure 8 are similar to the corresponding absorption spectra. The PC is strongly sensitized in the blend; the photocurrent increases over that in pristine P3HT by about one order of magnitude. The data are in agreement with results obtained from typical polymer:fullerene BHJ materials, where electron-transfer from the polymer donor to the fullerene acceptor quenches the PL with a corresponding increase in the yield of photogenerated mobile charge-carriers.

All results described above demonstrate efficient photoinduced charge transfer in the composites of **10c** with MEH-PPV or P3HT, due to the electron acceptor **10c**, similar to PCBM, in these systems.

To know the potential of **10c** as an electron donor in photoinduced charge transfer systems, we studied the PL quenching of **10c** mixed with PCBM in dilute solution. At a weight ratio of **10c**/PCBM 1:2.5 in toluene ($C_{10c} = 0.012$ mg/mL), the absorption [Fig. 9(A)] shows additive feature of these two components, whereas the PL [Fig. 9(B)] of **10c** was quenched by 20% compared with **10c** itself with the same concentration in toluene.

SUMMARY

Refluxing of *N*-sulfinyl-2-amino-9,9-didodecylfluorene (**4**) with sodium metal in toluene led to formation of bis-9,9-didodecyl-fluorene-2-sulphurdiimide (**5**). This *N*=S=N linked dimeric fluorene appears as a stable red solid under ambient conditions. Compound **5** is easily soluble in a variety of midpolar to nonpolar solvents in which the band-edge absorption of **5** is centered at 484 nm while the absorption onset is at 590 nm.

Reaction of bis-*N*-sulfinyl-9,9-didodecylfluorene-2,7-diamine (**9**) with sodium metal under similar conditions led to formation of oligomeric 9,9-didodecylfluorene-bis-sulphurdiimide (**10b–c**). This material, appearing as a stable purple solid, shows good solubility in a variety of organic solvents such as pentane, hexane, toluene, chlorobenzene, THF, chloroform, and DCM. Moreover, the absorption of these oligomers covers a broad spectral window in the UV-vis range, with a main broad peak centered at 555 nm and an onset extended to 700 nm.

We found that oligomer **10c** ($n = 6$) significantly quenched the PL of MEH-PPV or P3HT in the solid state. In addition, this oligomer showed stronger quenching effect to the PL intensity of P3HT than the dimeric analogue (**5**). Furthermore, the composites of **10c** with P3HT showed a nearly 10-fold enhancement of the photocurrent compared with that of P3HT itself. On the other hand, the PL of **10c** was quenched
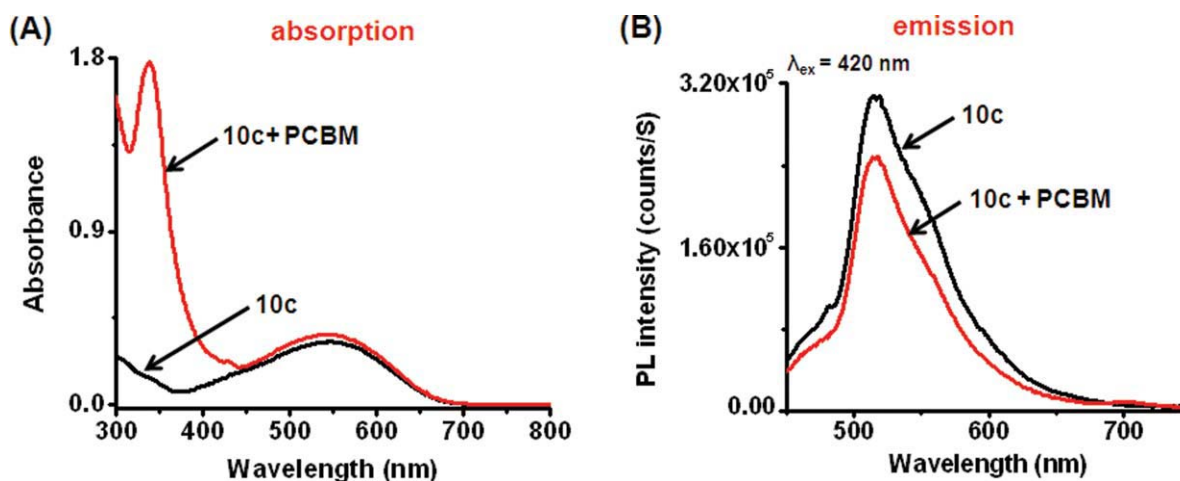

FIGURE 9 UV-vis absorption (A) and PL (B) spectra of **10c**/PCBM in toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

by PCBM in toluene. A quenching experiment with **10c** and PCBM in films is difficult because of the extremely weak fluorescence of both **10c** and PCBM in the solid state. These results suggest the presence of photoinduced charge transfer in composites of **10c** blended with an electronic partner that either donates or accepts electrons.

Finally, we note that the —NH_2 group at the chain end of oligo(9,9-didodecylfluorene-bis-sulphurdiimides) provides an opportunity to incorporate other functionalities into this molecule for a variety of applications.

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