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New low bandgap molecules based on ethylene-separated benzothiadiazoles: synthesis and bandgap comparison

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ABSTRACT

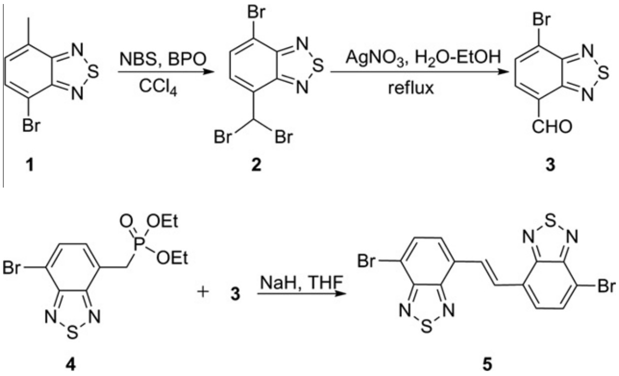
New ethylene-separated benzothiadiazoles were synthesized for the first time by using a facile procedure, and they showed lower bandgaps than the reported benzothiadiazole-containing compounds. This new benzothiadiazole-containing unit could be introduced into the backbone of the π-conjugated small molecules or polymers to develop new materials with a low bandgap that may have potential applications in optoelectronic fields.

Among the aryl heterocyclic compounds, those containing a 2,1,3-benzothiadiazole unit have received much attention in the past decades because of their interesting properties and potential applications in many areas such as biology,[1] iatrology[2] and optoelectronic devices.[3] In particular, the ability of this unit to tune the bandgap of the compounds has gathered much interest in the field of organic solar cells.[4] Some examples such as those incorporating this unit to fluorene, carbazole, thiophene to obtain small molecules or polymers with low bandgap had been reported.[5,6] Usually, a 2,1,3-benzothiadiazole unit is called as a low bandgap unit or a bandgap tuner. Theoretically, such an ability to tune bandgap is derived from the strong electron affinity of the 2,1,3-benzothiadiazole unit.[7] Hence, to prepare the materials with a lower bandgap, many efforts to enhance the electron affinity have been carried out, including the synthesis of the compounds with a bisbenzothiadiazole unit,[8a] a benzobisthiadiazole unit,[9] and a thiadiazoloquinoxaline unit.[10] The obtained materials showed a very low bandgap and can be used in photovoltaic cells (PVCs),[9f,10b] near-infrared organic light-emitting diodes (NIR OLEDs),[9d,e] and near-infrared liquid crystal (NIR LC) display.[9c]

However, the above-mentioned efforts were unsatisfactory because the inconvenient procedures for the preparation of the thiadiazole-based compounds were employed.[8] Moreover, in some cases, introducing some thiadiazole units into the backbone of the other compounds cannot greatly decrease the bandgap of the molecules. Are there any facilely prepared thiadiazole derivatives that can greatly decrease the bandgap of the molecules? This motivates us to design new thiadiazole derivatives. We found that the compounds based on ethylene-separated benzothiadiazoles were more easily prepared and showed a lower bandgap, compared to the reported benzothiadiazole-containing compounds.[8,11] In this contribution, we report the synthesis and properties of these new compounds, as shown in Scheme 1[15] and Scheme 2.[16,17]

As can be seen from Scheme 1, the ethylene-separated bromobenzothiadiazole **5** was prepared via the Horner–Wittig reaction from **3** and **4** in a yield of 84%. The precursors, **1** and **4** were synthesized according to the literature,[12] and **2** was prepared in high yield by bromination of **1** with a controlling equivalence ratio of **1** and NBS (*N*-bromosuccinimide). The precursor, 7-bromo-2,1,3-benzothiadiazole-4-carbaldehyde **3** was prepared by a modified procedure. In comparison with the reported methods that 4-bromo-7-(bromomethyl)-2,1,3-benzothiadiazole was oxidized to obtain the aldehyde **3**,[13] the modified method gave high yield and a product which can be easily purified. The FT-IR spectrum of **5** shows an absorption at 968 cm^{-1}, suggesting the existence of a double band with trans configuration in this compound.

The UV–vis spectrum of **5** in THF is presented in Figure 1. For comparison, the spectrum of 4,7-dibromobenzothiadiazole (**BT**) is also given in Figure 1. Obviously, the absorption maximum (λ_{max})



Scheme 1. Synthesis of the ethylene-separated benzothiadiazole **5**.

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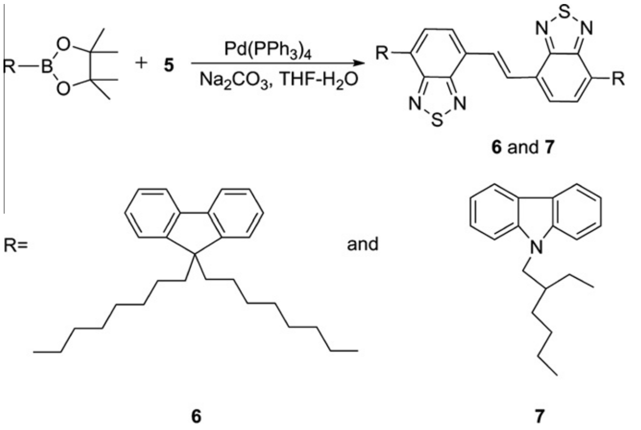

Scheme 2. The procedure for the preparation of the new low bandgap molecules **6** and **7**.

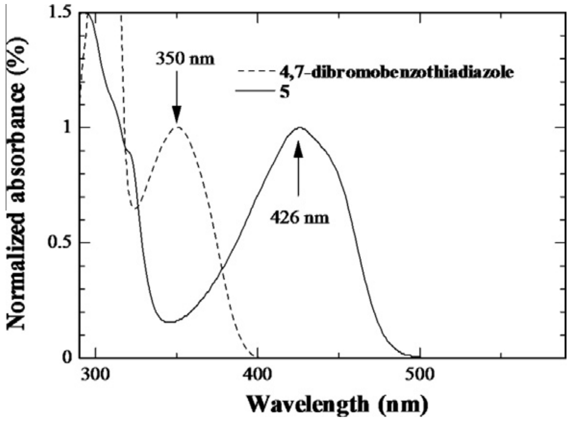

Figure 1. Normalized absorption spectra of compounds **5** and 4,7-dibromobenzothiadiazole in THF.

of **5** exhibits a 76 nm red shift as compared to **BT**. This shift is also observed for the bandgap. The onset of the absorption spectrum of **5** is at 478 nm which corresponds to a band gap (E_g^{opt}) of 2.59 eV, while for **BT** the absorption edge is at 387 nm, corresponding to a band gap (E_g^{opt}) of 3.20 eV. Surprisingly, the E_g^{opt} of **5** is even lower than 2.99 eV, which is that of bisbenzothiadiazole.[8a] It is noted that the molecules with muti-benzothiadiazole units are regarded as a new class of low bandgap compounds, whereas they are prepared with difficulty.[8] In our case, the lower E_g^{opt} shown by **5** suggests that the ethylene-separated benzothiadiazole unit may be used as a new unit for tuning the bandgap of the compounds.

To further confirm the ability of the ethylene-separated benzothiadiazole unit to tune the bandgap, two new compounds **6** and **7** were prepared by using the standard Suzuki coupling reaction, as shown in Scheme 2. The chemical structure of **6** and **7** was confirmed by ^1H NMR, ^{13}C NMR spectra, elemental analysis and mass spectrometry (MALDI-TOF).

Figure 2 depicts the UV–vis spectra of **6** and **7** in THF, which indicate a big red shift for **6** (λ_{max} = 474 nm) and **7** (λ_{max} = 495 nm), compared to that of **5** (λ_{max} = 426 nm). This behavior is attributed to the charge transfer between a donating group (fluorene or carbazole) and an accepting ethylene-separated benzothiadiazole unit. Due to the electron-donating ability of carbazole unit is stronger than that of fluorene group, the absorption maximum (λ_{max}) of **7** exhibits a bathochromic shift of 21 nm, compared to that of **6**. From their UV–vis absorption onset wavelength, the E_g^{opt} of **6** and **7** are estimated as 2.31 and 2.20 eV, respectively. Such results are lower than both E_g^{opt} of a compound with a configuration of fluorene-benzothiadiazole-fluorene (**FBF**)[11] ($E_g^{opt} = 2.70$ eV) and a molecule containing fluorene-bisbenzothiadiazole-fluorene (**FDBF**) structure ($E_g^{opt} = 2.50$ eV),[8a] indicating that the ethylene-separated benzothiadiazole unit with higher conjugation possesses greater electron-accepting ability, and is a new potential bandgap tuner. In many cases, the bandgap of π-conjugated compounds may become narrow with the increase of the conjugated units. For example, poly(fluorene-*co*-benzothiadiazole) shows an E_g^{opt} of 2.34 eV,[11,14] which is lower than that of above-mentioned **FBF**. This means that the polymers would show lower bandgap if the ethylene-separated benzothiadiazole unit would be introduced into the backbone of the conjugated polymers.

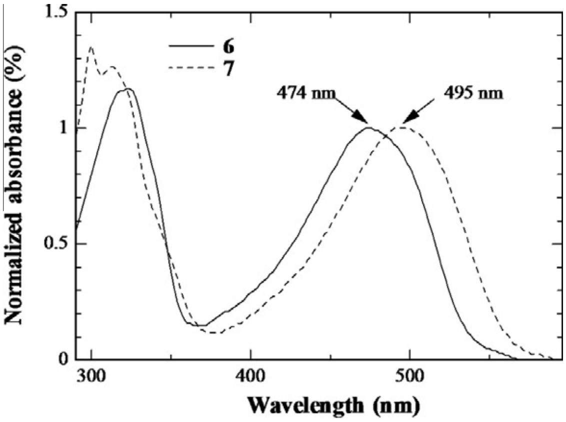

Figure 2. Normalized absorption spectra of compounds **6** and **7** in THF.

The photoluminescent (PL) spectra of **6** and **7** are shown in Figure 3. As can be seen from Figure 3, **6** and **7** show a maximum emission peak (λ_{em}) at 563 and 585 nm, respectively. Compared to that of the above-mentioned **FDBF** (λ_{em} = 531 nm, in THF),[8a] the λ_{em} of **6** has a red shift of about 32 nm, suggesting that the ethylene-separated benzothiadiazole unit has a higher conjugated level than the bisbenzothiadiazole unit.

The fluorescent quantum yields (φ_f) of solutions of **6** and **7** in THF were determined to be 2.52 and 1.09, respectively, by using an acetonitrile solution of DCM as a reference.[18] Such φ_f values are over 100%, indicating that the compounds show good photoluminescent emission behavior.

The electrochemical properties of **6** and **7** were observed in a CH_2Cl_2 solution containing $[Bu_4N]ClO_4$ (0.10 M, Bu = *n*-butyl) using an Ag/AgCl and a platinum disk as the reference and counter electrodes, respectively. Figure 4 shows the cyclic voltammograms of compounds **6** and **7**. Electrochemical oxidations of **6** and **7** start

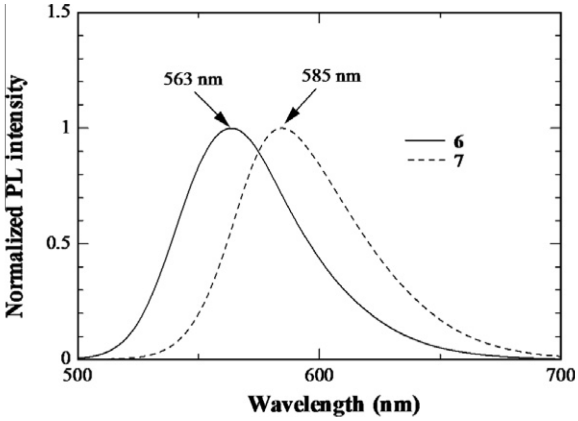

Figure 3. Normalized emission spectra of compounds **6** and **7** in THF.

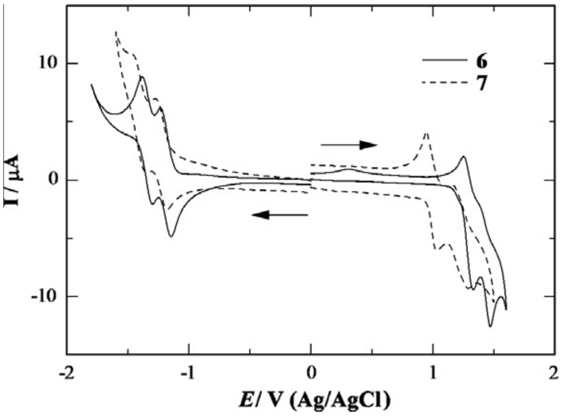

Figure 4. CV charts of **6** and **7** measured in a solution of dichloromethane containing 0.1 M Bu_4NClO_4 at a scan rate of 50 mV/s.

at about 1.25 and 0.92 V versus Ag/AgCl, respectively, and both **6** and **7** show two oxidation peaks (**6**: 1.33 and 1.47 V; **7**: 1.04 and 1.29 V). Compared with those of poly(fluorene-*co*-benzothiadiazole) and poly(carbazole-*co*-benzothiadiazole),[6,11] the two oxidation peaks are attributed to the oxidation of the carbazole unit and the fluorene unit in **6** and **7**. According to the relationship between oxidation onset potential (E^{ox}_{onset}) and the highest occupied molecular orbital (HOMO) energy, HOMO $= -(E^{ox}_{onset} + 4.4)$, the HOMO values of **6** and **7** are estimated as -5.65 eV and -5.32 eV, respectively. The electrochemical reductions of **6** and **7** start at about -1.12 and -1.22 V versus Ag/AgCl, respectively, which agree with the reported results for poly(2,1,3-benzothiadiazole)[19] and poly(fluorene).[20] The reduction potential peaks for **6** and **7** are at -1.23, -1.38 and -1.28, -1.49 V versus Ag/AgCl, respectively. From the reduction onset potentials, the lowest unoccupied molecular orbital (LUMO) values of **6** and **7** can be estimated as -3.28 eV and -3.18 eV, respectively, using the equation LUMO $= -(E^{red}_{onset} + 4.4)$. These results also agree with those reported on poly(2,1,3-benzothiadiazole) and poly(fluorene).

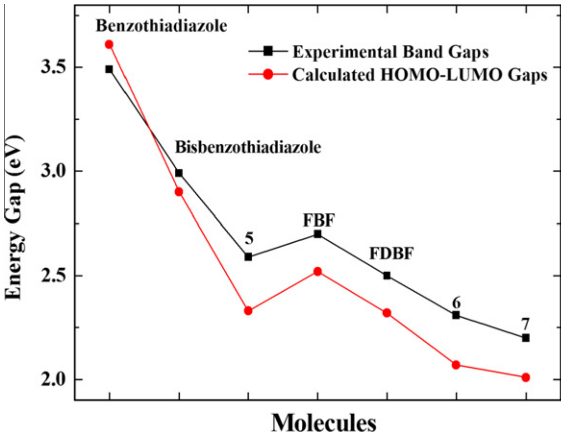

Figure 5. The experimental band gaps and the calculated HOMO–LUMO energy gaps (eV). Calculated at B3LYP/6-31G* level.

Based on the above-mentioned electrochemical results, the electrochemical bandgaps for **6** and **7** are obtained as 2.37 and 2.14 eV, respectively, which are close to the E^{opt}_{g} of **6** and **7**. Such electrochemical bandgaps are also lower than those of above-mentioned **FBF** (e.g., about 2.70 eV),[11] further confirming that the ethylene-separated benzothiadiazole unit can efficiently tune the bandgap of these compounds.

To better understand why the compounds with ethylene-separated benzothiadiazole unit showed good bandgap-tuning ability, a theoretical calculation using density functional theory (DFT) was carried out.[21] The calculation was carried out with the GAUSSIAN03 program employing the B3LYP[22] method and 6-31G* basis set. In the calculation models, the side chains in the fluorene and carbazole units were simplified to methyl groups. The calculated HOMO–LUMO gaps along with the experimental values are shown in Figure 5, and the optimized structures are listed in Figure 6. For benzothiadiazole, bisbenzothiadiazole, and compound **5**, the

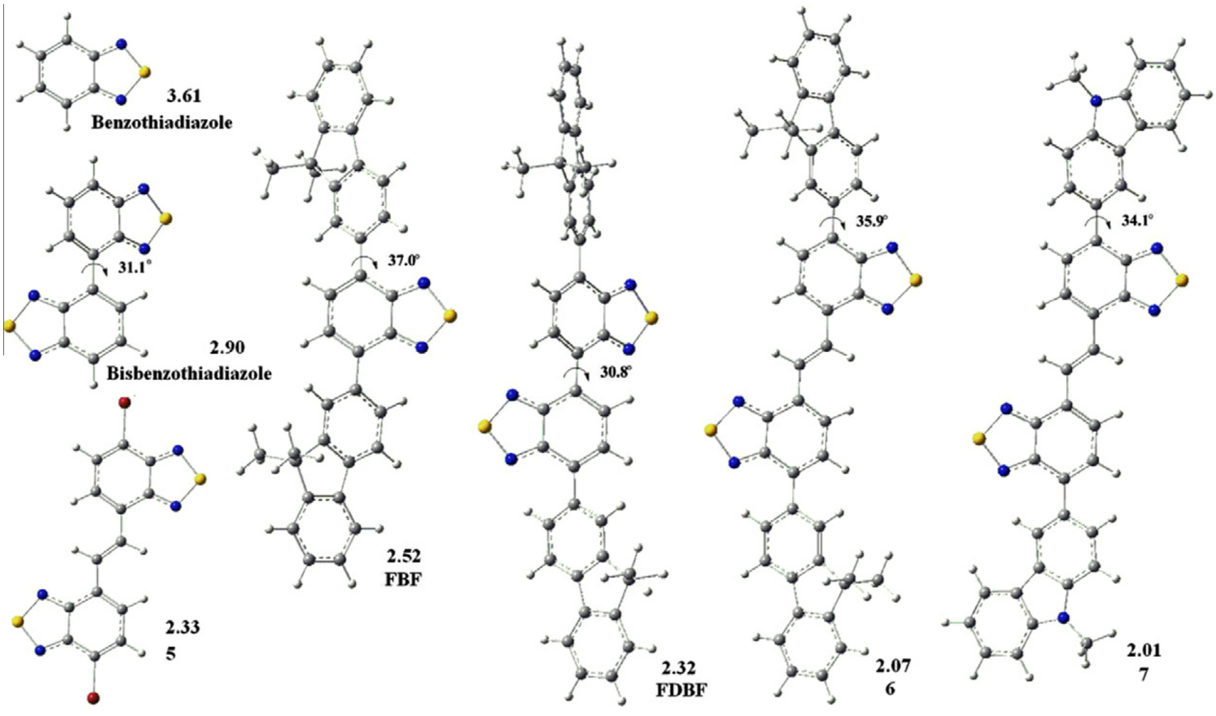

Figure 6. The optimized structures with calculated HOMO–LUMO energy gaps (eV). All structures have C_2 symmetry except for the benzothiadiazole. Calculated at B3LYP/6-31G* level.

calculations on the 6-311+G** basis set were also performed, and the calculated energy gaps were 3.59, 2.90, and 2.32 eV, respectively, which are very close to the results of 6-31G* basis set (3.61, 2.90, and 2.33 eV), suggesting that the 6-31G* basis set is suitable for this calculation.

As shown in Figure 6, the two benzothiadiazole units in bisbenzothiadiazole are staggered with a dihedral angle of 31.3°, whereas the ethylene unit in **5** releases the steric repulsion between the adjacent benzothiadiazole units and brings about the whole molecule to be nearly coplanar. As a result, the conjugated level increases, and subsequently, the energy gap decreases. The same situation can be found in **6** and **FDBF**. Thus, except for extending the conjugated system, the insertion of the ethylene units changes the molecule from staggered to coplanar, resulting in the increase of the conjugated level.

In summary, two new compounds with an ethylene-separated benzothiadiazole unit have been synthesized using a simple method. Compared with the reported compounds containing bisbenzothiadiazole unit, the molecules with an ethylene-separated benzothiadiazole unit can greatly decrease the bandgap of the compounds, and such a unit can be introduced into the backbone of π-conjugated small molecules or polymers to develop new materials with low bandgap that may have potential applications in optoelectronic fields. The investigation on the synthesis and properties of the polymers containing this unit used in organic light-emitting diodes (OLED) and organic photovoltaic cells is carried out.

Acknowledgments

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15. *Compound* **5**: Under argon atmosphere, a mixture of NaH in THF (15 mL) was added to a solution of compound **4** (2.191 g, 6 mmol) in THF (15 mL), and the resulting mixture was stirred for 1 h at room temperature. Then a solution of **3** in THF (15 mL) was added to the reaction mixture. The resulting mixture was kept at room temperature for 2 h. The solvent was evaporated under reduced pressure, and the residue was washed with water (2 × 30 mL), ethanol (2 × 30 mL), ethyl acetate (2 × 30 mL), and CH_2Cl_2 (2 × 30 mL), and dried in vacuo to yield **5** as a yellow solid (2.315 g, 5.1 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 2H), 7.90 (d, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H). IR (KBr, cm^{-1}): 3048, 3025, 1571, 1508, 1479, 1340, 968, 937, 885, 850, 829, 773, 632. MS (EI, *m/z*): 452. Elemental Anal. Calcd for $C_{14}H_6Br_2N_4S_2$: C, 37.02; H, 1.33; Br, 35.19; N, 12.34; S, 14.12. Found: C, 37.02; H, 1.52; Br, 35.16; N, 12.27; S, 14.03.
16. *Characterization data of compound* **6**: ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 2H), 8.03 (d, 7.6 Hz, 2H), 7.98 (s, 3H), 7.97 (s, 1H), 7.87–7.84 (m, 4H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.40–7.32 (m, 6H), 2.10–1.97 (m, 8H), 1.25–1.02 (m, 40H), 0.82–0.69 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 154.2, 151.4, 151.2, 141.5, 140.7, 136.1, 134.0, 129.5, 129.2, 128.2, 128.0, 127.9, 127.4, 126.9, 123.9, 123.0, 120.0, 119.8, 55.3, 40.3, 31.8, 30.1, 29.3, 23.9, 22.6, 14.1. IR (KBr, cm^{-1}): 3036, 3015, 2953, 2923, 2850, 1637, 1561, 1541, 1375, 975, 894, 858, 829, 738. MS (MALDI-TOF, *m/z*): 1072.4. Elemental Anal. Calcd for $C_{72}H_{88}N_4S_2$: C, 80.55; H, 8.26; N, 5.22; S, 5.97. Found: C, 80.72; H, 8.41; N, 5.04; S, 5.83.
17. *Characterization data of compound* **7**: ^1H NMR (400 MHz, DMSO-d_6): δ 8.88 (s, 2H), 8.70 (s, 2H), 8.27 (d, $J = 7.6$ Hz, 2H), 8.20 (m, 4H), 8.09 (d, $J = 7.6$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 7.6$ Hz, 2H), 4.35 (d, $J = 6.8$ Hz, 4H), 2.03–2.10 (m, 2H), 1.61–1.18 (m, 16H), 0.90 (t, $J = 7.2$ Hz, 6H), 0.81 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 154.2, 141.4, 141.0, 134.2, 128.8, 128.7, 128.2, 127.9, 127.6, 127.1, 125.9, 123.2, 123.1, 121.2, 120.6, 119.1, 109.2, 109.0, 47.6, 39.5, 31.1, 28.9, 24.5, 23.1, 14.1, 11.0. IR (KBr, cm^{-1}): 3048, 2955, 2925, 2856, 1625, 1597, 1535, 1480, 1464, 1379, 1350, 1328, 1260, 1024, 968, 806, 746, 728. MS (MALDI-TOF, *m/z*): 850.4. Elemental Anal. Calcd for $C_{54}H_{54}N_6S_2$: C, 76.20; H, 6.39; N, 9.87; S, 7.53. Found: C, 76.33; H, 6.46; N, 9.62; S, 7.59.
18. DCM, (4-(dicyanomethylene)-2-methyl 6-[*p*-(dimethylamino) styryl]-4*H*-pyran, $\varphi_f = 65\%$ in acetonitrile. See: Thomas, K. R. J.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *Adv. Mater.* **2002**, *14*, 822.
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