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Synthesis, Characterization, and Photophysical Properties of Bodipy-Spirooxazine and -Spiropyran Conjugates: Modulation of Fluorescence Resonance Energy Transfer Behavior via Acidochromic and Photochromic Switching

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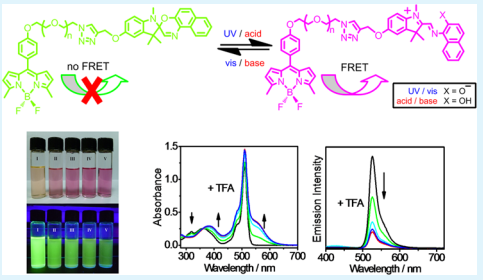
Supporting Information

ABSTRACT: Two series of Bodipy-containing photochromic spirooxazine and spiropyran derivatives have been designed, synthesized and characterized by ^{1}H NMR, ESI mass spectrometry and elemental analysis. Their electrochemical and photochromic properties were investigated. The photophysical, ultrafast transient absorption, and fluorescence resonance energy transfer (FRET) properties from Bodipy (donor) to the ring-opened merocyanine (acceptor) were also studied. Upon photoexcitation, all the photochromic spirooxazine- and spiropyran-containing compounds exhibited reversible photochromism. Computational studies have been performed to provide further insights into the nature of the electronic transitions for the two classes of compounds. The rate constants and activation parameters for thermal bleaching reactions of compounds SO, SP-alkyne, **1**−**3**, and **8**−**10** were determined through kinetic studies in acetonitrile. The thermal bleaching reaction rate of the spiropyran-containing compounds is found to be much slower than that of the spirooxazine-containing counterparts.



KEYWORDS: *fluorescence resonance energy transfer, acidochromism, spirooxazine, spiropyran, Bodipy, photochromism*

INTRODUCTION

During the past few decades, 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (Bodipy) has received much attention in many research areas owing to its rich photophysical properties.[1−4] Bodipy-containing molecular materials are very versatile and have been utilized as dyes in a variety of different fields, such as in light harvesting materials[5−8] and as sensitizers for solar energy conversion,[9−12] probes and cation sensors,[13−17] and fluorescence labels.[18,19] However, Bodipy dyes have some drawbacks including the relatively small energy gap between the absorption and emission maxima; in other words, small Stokes' shifts. Currently, a number of fluorescence probes are suffering from poor selectivity and stability, and their emissions in the visible region may be interfered by the fluorescence of other proteins in the biological samples.[20] To address this problem, one approach would be to employ energy transfer strategies to increase the Stokes' shift. As a result, there have been a number of studies on the energy transfer properties of Bodipy-containing molecular devices.[21,22]

Fluorescence resonance energy transfer (FRET) is an excited-state energy transfer process from the initially excited donor chromophore to an acceptor moiety via long range dipole−dipole interactions.[23] The efficiency of FRET strongly depends on the degree of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, the distance between the donor and the acceptor, and their orientation.[24,25] In recent years, there have been many fluorescence probes based on FRET[26−30] where most of them are confined to systems containing two organic fluorophores of high fluorescence quantum yields. In addition, acid- and photoresponsive spirooxazines or spiropyrans,[31−34] which show distinctive absorption characteristics upon photoexcitation or variation in pH, were also employed to investigate the energy transfer in nanoparticles, nanotube, and various other nanostructures.[35−39] Incorporation of acidochromic and photochromic spirooxazines or spiropyrans into energy transfer systems not only could modulate the luminescence properties of the donor but also might result in interesting photochromic and photophysical properties in response to light and variation of pH environments.

Spirooxazines and spiropyrans are interesting classes of materials that are known to show photochromic and acid-

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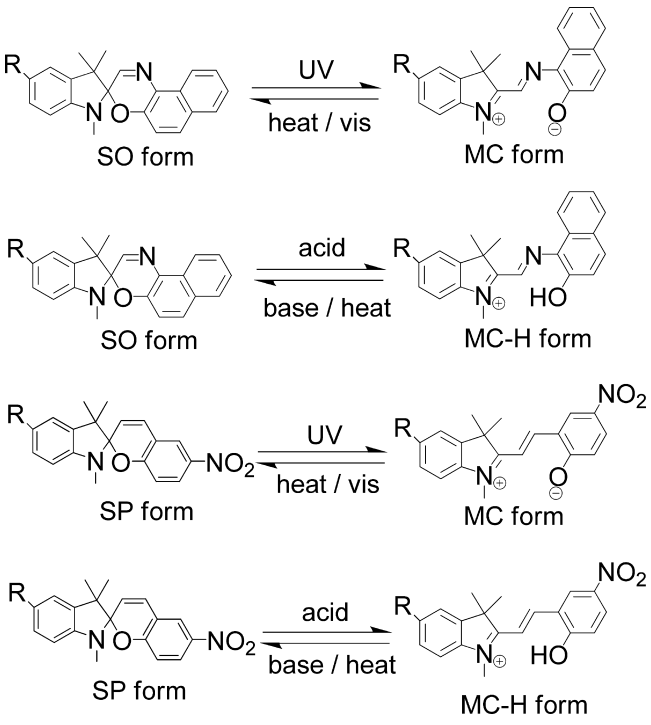
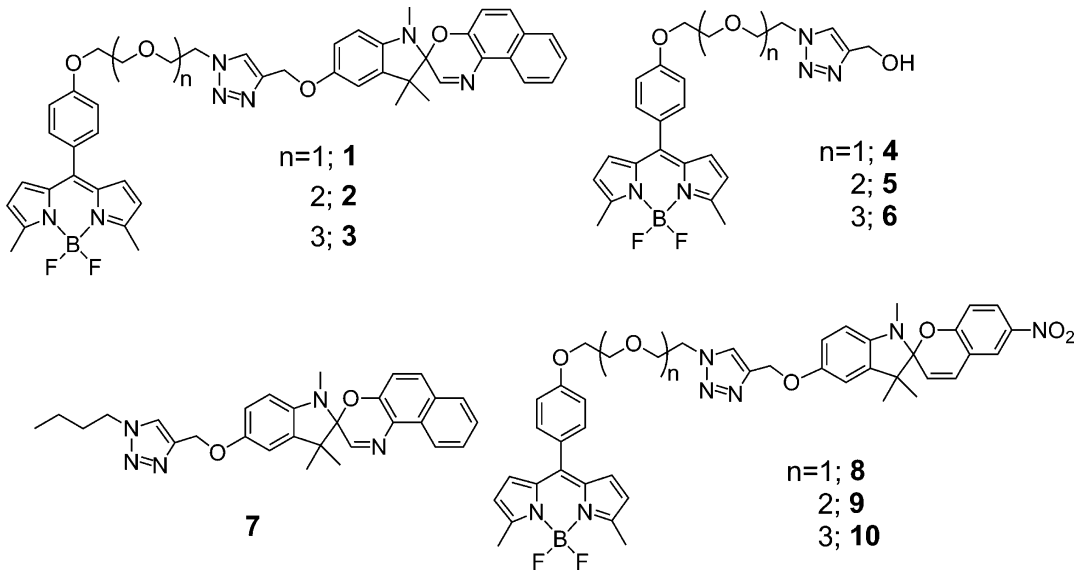
ochromic properties.[40−46] Due to their high fatigue resistance and excellent photostability, their photochromic behavior[47] has been extensively studied for potential applications in the development of molecular switching devices, optical information storage, and various other applications.[48−51] The photochromism of spirooxazines and spiropyrans is based on photoinduced isomerization between the closed form and the ring-opened merocyanine (MC) form (Scheme 1). The photochemical cleavage of spiro carbon−oxygen bond results in the extension of π-conjugation in the ring-opened structure. In addition, the spiro carbon−oxygen bond could also be cleaved by acid to form another type of ring-opened structure (MC-H) (Scheme 1).

Scheme 1. Photoinduced and Proton-Induced Ring-Opening Reactions of Spirooxazine and Spiropyran



There are a number of reports on photochromic behaviour of organic spirooxazines and spiropyrans,[52−54] and several photochromic Bodipy-containing derivatives are also reported.[55−61] However, most of them are confined to photocontrolled fluorescence systems,[62−71] with corresponding studies on acid-induced spirooxazine- and spiropyran-containing energy transfer systems being very rare.[72,73] Therefore, it is envisaged that the combination of the strong luminescence properties of Bodipy moieties and the acidochromic and photochromic behaviour of spirooxazine and spiropyran moieties, together with the possibility of switchable FRET properties, may provide attractive multifunctional features for the development of multifunctional switchable materials. The linking of fluorescent Bodipy to the photochromic SO/SP may also allow one to explore the sensitization of SO/SP by Bodipy using lower energy visible light as well as the possible modulation of the fluorescence properties of Bodipy by energy transfer to the ring-opened merocyanine form via the photo- and acid-responsive ring-opening processes. This would also allow the systematic study of the influence of Bodipy on SP/SO as well as the influence of the photochromic SP/SO unit in switching on and off the fluorescence property of Bodipy, which would provide important insights into the future design of multifunctional switches and materials. Herein are described the design and synthesis of two series of spirooxazine- and spiropyran-containing Bodipy derivatives. Their spectroscopic, electrochemical, and photo- or acid-induced FRET behaviors have been investigated. Efficient energy transfer process was observed in the presence of TFA. In addition, computational studies have been performed to provide a deeper insight into the nature of the electronic transitions for the two classes of compounds. In order to provide further insights regarding the energy transfer properties of spirooxazine-containing Bodipy derivatives upon addition of TFA, femtosecond transient absorption spectroscopy has also been performed in dichloromethane solution (0.1 M $^{n}Bu_4NPF_6$) with and without the presence of 40 equiv of TFA at room temperature. To the best of our knowledge, the present work represents the first

Scheme 2. Structure of Spirooxazine- and Spiropyran-Containing Bodipy Derivatives and Reference Molecules



systematic study using ultrafast transient absorption spectroscopy to probe the energy transfer processes in acid-induced energy transfer system. Furthermore, the photochromic properties of two series of spirooxazine- and spiropyran-containing Bodipy derivatives have been studied systematically in acetonitrile. The rate constants and activation parameters for the thermal bleaching reactions of these compounds have also been determined through kinetic studies. A common bleaching reaction mechanism has been found for the spirooxazine-containing Bodipy derivatives as well as the spiropyran-containing Bodipy derivatives. The synthesis, electrochemical, photophysical, photochromic, and energy transfer properties of two series of spirooxazine- and spiropyran-containing Bodipy derivatives (Scheme 2) are described.

EXPERIMENTAL SECTION

Materials and Reagents. Propargyl bromide and propargyl alcohol were purchased from Aldrich Chemical Co. 1,3,3-Trimethyl-5-hydroxy-spiroindolenaphthoxazine[74] (SO), 1,3,3-trimethyl-5-hydroxy-spiropyran[74] (SP-OH), 4,4-difluoro-3,5-dimethyl-8-{4-(2-[2-(*p*-toluenesulfonyloxy)ethoxy]ethoxy)phenyl}-4-bora-3*a*,4*a*-diaza-*s*-indacene (Bodipy-EO_2-OTs), 4,4-difluoro-3,5-dimethyl-8-{4-[2-(2-[2-(*p*-toluenesulfonyloxy)ethoxy]ethoxy)-ethoxy]phenyl}-4-bora-3*a*,4*a*-diaza-*s*-indacene (Bodipy-EO_3-OTs), and 4,4-difluoro-3,5-dimethyl-8-{4-(2-[2-(2-[2-(*p*-toluenesulfonyloxy)ethoxy]ethoxyl)ethoxy]ethoxy)-phenyl}-4-bora-3*a*,4*a*-diaza-*s*-indacene (Bodipy-EO_4-OTs)[75,76] were synthesized according to modifications of the methods described in the literature. All solvents were purified and distilled by using standard procedures before use. All other reagents were of analytical grade and were used as received.

Synthesis. *Bodipy-EO_2-N_3.* A mixture of Bodipy-EO_2-OTs (400 mg, 0.72 mmol) and NaN_3 (300 mg, 4.6 mmol) in acetonitrile was heated to reflux for 2 days with stirring under nitrogen. The mixture was cooled to room temperature, and the solvent was removed under vacuum after filtration. The obtained crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1 v/v) as the eluent to give the desired product. Yield: 180 mg, 59%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.45 (d, J = 8.4 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.02 (d, J = 8.4 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.74 (d, J = 3.9 Hz, 2H; pyrrole protons at 1,7-position), 6.26 (d, J = 3.9 Hz, 2H; pyrrole protons at 2,6-position), 4.22 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.92 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.78 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2N_3$), 3.44 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2N_3$), 2.65 (s, 6H; $-CH_3$).

Bodipy-EO_3-N_3. The procedure was similar to that described for the synthesis of Bodipy-EO_2-N_3 except Bodipy-EO_3-OTs (400 mg, 0.67 mmol) was used instead of Bodipy-EO_2-OTs. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1 v/v) as the eluent to give the desired product. Yield: 163 mg, 52%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.44 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.02 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.74 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.27 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 4.22 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.93 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.68–3.79 (m, 6H; $-OCH_2CH_2-$), 3.41 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N_3$), 2.65 (s, 6H; $-CH_3$).

Bodipy-EO_4-N_3. The procedure was similar to that described for the synthesis of Bodipy-EO_2-N_3 except Bodipy-EO_4-OTs (550 mg, 0.86 mmol) was used instead of Bodipy-EO_2-OTs. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:1 v/v) as the eluent to give the desired product. Yield: 220 mg, 50%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.44 (d, J = 8.4 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.01 (d, J = 8.4 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.74 (d, J = 3.9 Hz, 2H; pyrrole protons at 1,7-position), 6.27 (d, J = 3.9 Hz, 2H; pyrrole protons at 2,6-position), 4.21 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.91 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.64–3.79 (m, 10H; $-OCH_2CH_2-$), 3.39 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2N-$), 2.64 (s, 6H; $-CH_3$).

SO-Alkyne. 3-Bromo-1-propyne (1.5 mL) was added to a solution of SO (770 mg, 2.24 mmol) in the presence of potassium carbonate (928 mg, 6.72 mmol) in acetone, and the mixture was heated to reflux for overnight under N_2. After filtration, the solvent was removed under reduced pressure. The obtained crude product was purified by column chromatography on silica gel with petroleum ether/diethyl ether (4:1 v/v) as the eluent to give the desired product. Yield: 700 mg, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 8.55 (d, J = 8.4 Hz, 1H; naphthoxazinic proton at 10′-position), 7.72–7.77 (m, 2H; naphthoxazinic proton at 2′,7′-position), 7.66 (d, J = 8.7 Hz, 1H; naphthoxazinic proton at 6′-position), 7.54–7.61 (m, 1H; naphthoxazinic proton at 9′-position), 7.36–7.44 (m, 1H; naphthoxazinic proton at 8′-position), 7.02 (d, J = 8.7 Hz, 1H; naphthoxazinic proton at 5′-position), 6.77–6.86 (m, 2H; indolinic proton at 4,6-position), 6.48 (d, J = 8.4 Hz, 1H; indolinic proton at 7-position), 4.66 (d, J = 2.4 Hz, 2H; $-CH_2-$), 2.71 (s, 3H; $-NCH_3$), 2.53 (t, J = 2.4 Hz, 1H; alkyne proton), 1.36 (s, 3H; $-C(CH_3)_2$), 1.33 (s, 3H; $-C(CH_3)_2$).

SP-Alkyne. The procedure was similar to that described for the synthesis of SO-alkyne except SP-OH (300 mg, 0.89 mmol) was used instead of SO. The crude product was purified by column chromatography on silica gel using petroleum ether/diethyl ether (4:1 v/v) as the eluent to give the desired product. Yield: 270 mg, 84%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.99–8.06 (m, 2H; phthoxazinic protons at 5′,7′-position), 6.92 (d, J = 10.5 Hz, 1H; phthoxazinic proton at 4′-position), 6.75–6.88 (m, 3H; indolinic protons at 4,6-position and phthoxazinic proton at 8′-position), 6.46 (d, J = 8.4 Hz, 1H; indolinic proton at 7-position), 5.85 (d, J = 10.5 Hz, 1H; phthoxazinic proton at 3′-position), 4.66 (d, J = 2.4 Hz, 2H; $-CH_2-$), 2.70 (s, 3H; $-NCH_3$), 2.53 (t, J = 2.4 Hz, 1H; alkyne proton), 1.27 (s, 3H; $-C(CH_3)_2$), 1.19 (s, 3H; $-C(CH_3)_2$).

Compound 1. To a solution of Bodipy-EO_2-N_3 (180 mg, 0.42 mmol) and SO-alkyne (178 mg, 0.47 mmol) in dichloromethane (4.5 ml) were added sodium ascorbate (50 mg, 0.26 mmol) and $CuSO_4 \cdot 5H_2O$ (140 mg, 0.56 mmol) in water (3 mL). The mixture was stirred at room temperature under N_2 for overnight. Dichloromethane and water were then added to the mixture, and the organic phase was separated and washed with water for two times, and then was dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (3:2 v/v) as the eluent to give the desired product. Yield: 240 mg, 71%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 8.55 (d, J = 8.4 Hz, 1H; naphthoxazinic proton at 10′-position), 7.86 (s, 1H; triazole proton), 7.71–7.76 (m, 2H; naphthoxazinic proton at 2′,7′-position), 7.65 (d, J = 9.0 Hz, 1H; naphthoxazinic proton at 6′-position), 7.54–7.62 (m, 1H; naphthoxazinic proton at 9′-position), 7.36–7.45 (m, 3H; Bodipy protons at 8-*o*-Ar-position and naphthoxazinic proton at 8′-position), 6.96–7.03 (m, 3H; Bodipy protons at 8-*m*-Ar-position and naphthoxazinic proton at 5′-position), 6.78–6.85 (m, 2H; indolinic protons at 4,6-position), 6.72 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.44 (d, J = 8.1 Hz, 1H; indolinic proton at 7-position), 6.25 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 5.15 (s, 2H; $-CH_2O-$), 4.62 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.16 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.99 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 3.86 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 2.68 (s, 3H; $-NCH_3$ of SO), 2.64 (s, 6H; $-CH_3$ of Bodipy), 1.32 (s, 3H; $-C(CH_3)_2$), 1.29 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.54, 157.45, 153.26, 150.90, 144.88, 144.42, 142.68, 142.56, 137.88, 134.79, 132.40, 131.16, 130.56, 129.56, 128.10, 127.43, 127.31, 124.48, 124.23, 123.23, 121.82, 119.56, 119.54, 117.06, 114.59, 113.34, 110.73, 107.63, 99.22, 70.04, 69.98, 67.69, 63.39, 52.20, 50.70, 30.25, 25.63, 20.99, 15.21. ESI-MS: m/z 808.4 $[M+H]^+$. Anal. Calcd (%) for $C_{46}H_{44}BF_2N_7O_4$: C, 68.40; H, 5.49; N, 12.14. Found: C, 68.16; H, 5.44; N, 11.85.

Compound 2. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_3-N_3 (150 mg, 0.32 mmol) was used instead of Bodipy-EO_2-N_3. The crude product was purified

by column chromatography on silica gel using ethyl acetate/petroleum ether (2:1 v/v) as the eluent to give the desired product. Yield: 181 mg, 67%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si) / ppm: δ = 8.55 (d, J = 8.7 Hz, 1H; naphthoxazinic proton at 10′-position), 7.85 (s, 1H; triazole proton), 7.72−7.75 (m, 2H; naphthoxazinic protons at 2′,7′-position), 7.65 (d, J = 8.7 Hz, 1H; naphthoxazinic proton at 6′-position), 7.55−7.60 (m, 1H; naphthoxazinic proton at 9′-position), 7.37−7.43 (m, 3H; Bodipy protons at 8-*o*-Ar-position and naphthoxazinic proton at 8′-position), 6.94−7.02 (m, 3H; Bodipy protons at 8-*m*-Ar-position and naphthoxazinic proton at 5′-position), 6.78−6.84 (m, 2H; indolinic protons at 4,6-position), 6.72 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.45 (d, J = 8.1 Hz, 1H; indolinic proton at 7-position), 6.25 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 5.16 (s, 2H; $-CH_2O-$), 4.58 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N$-), 4.18 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.92 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 3.86 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.64−3.73 (m, 4H; $-OCH_2CH_2O-$), 2.69 (s, 3H, $-NCH_3$ of SO), 2.64 (s, 6H; $-CH_3$ of Bodipy), 1.33 (s, 3H; $-C(CH_3)_2$), 1.30 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.70, 157.34, 153.26, 150.88, 144.72, 144.39, 142.77, 142.53, 137.86, 134.76, 132.33, 131.12, 130.54, 129.53, 128.08, 127.41, 127.08, 124.47, 124.19, 123.20, 121.79, 119.51, 119.49, 117.02, 114.60, 113.23, 110.77, 107.58, 99.20, 71.04, 70.93, 69.94, 69.80, 67.88, 63.32, 52.17, 50.65, 30.24, 25.62, 20.96, 15.18. ESI-MS: m/z 852.2 $[M+H]^+$. Anal. Calcd (%) for $C_{48}H_{48}BF_2N_7O_5$: C, 67.69; H, 5.68; N, 11.51. Found: C, 67.55; H, 5.66; N, 11.21.

Compound ***3***. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_4-N_3 (220 mg, 0.43 mmol) was used instead of Bodipy-EO_2-N_3. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (5:2 v/v) as the eluent to give the desired product. Yield: 240 mg, 62%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 8.55 (d, J = 8.4 Hz, 1H; naphthoxazinic proton at 10′-position), 7.85 (s, 1H; triazole proton), 7.72−7.76 (m, 2H; naphthoxazinic protons at 2′,7′-position), 7.65 (d, J = 9.0 Hz, 1H; naphthoxazinic proton at 6′-position), 7.54−7.60 (m, 1H; naphthoxazinic proton at 9′-position), 7.34−7.46 (m, 3H; Bodipy protons at 8-*o*-Ar-position and naphthoxazinic proton at 8′-position), 6.96−7.01 (m, 3H; Bodipy protons at 8-*m*-Ar-position and naphthoxazinic proton at 5′-position), 6.79−6.87 (m, 2H; indolinic protons at 4,6-position), 6.72 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.46 (d, J = 8.4 Hz, 1H; indolinic proton at 7-position), 6.25 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 5.17 (s, 2H; $-CH_2O-$), 4.56 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.17 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.85−3.92 (m, 4H; $-OCH_2CH_2-$), 3.71−3.75 (m, 2H; $-OCH_2CH_2O-$), 3.62−3.69 (m, 6H; $-OCH_2CH_2O-$), 2.70 (s, 3H; $-NCH_3$ of SO), 2.64 (s, 6H; $-CH_3$ of Bodipy), 1.35 (s, 3H; $-C(CH_3)_2$), 1.32 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) / ppm: δ = 160.78, 157.38, 153.32, 150.92, 144.74, 144.43, 142.83, 142.55, 137.90, 134.82, 132.34, 131.16, 130.57, 129.57, 128.11, 127.45, 127.09, 124.50, 124.25, 123.25, 121.82, 119.53, 119.51, 117.07, 114.64, 113.29, 110.81, 107.61, 99.25, 71.23, 70.99, 70.94, 70.90, 69.98, 69.81, 67.93, 63.36, 52.22, 50.67, 30.30, 25.68, 21.01, 15.21. ESI-MS: m/z 896.4 $[M+H]^+$. Anal. Calcd (%) for $C_{50}H_{52}BF_2N_7O_6$: C, 67.04; H, 5.85; N, 10.95. Found: C, 67.32; H, 5.81; N, 10.69.

Compound ***4***. The procedure was similar to that described for the synthesis of compound **1** except propargyl alcohol (40 mg, 0.71 mmol) was used instead of SO-alkyne. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate/ethanol (10:10:1 v/v/v) as the eluent to give the desired product. Yield: 270 mg, 79%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.74 (s, 1H; triazole proton), 7.46 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.00 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.74 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.27 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 4.77 (d, J = 4.8 Hz, 2H; $-CH_2OH$), 4.60 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.16 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.98 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 3.86 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 2.65 (s, 6H; $-CH_3$ of Bodipy). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.52, 157.42, 147.93, 142.68, 134.78, 132.38, 130.54, 127.27, 123.22, 119.56, 114.56, 70.00, 69.93, 67.71, 56.79, 50.62, 15.18. ESI-MS: m/z 482.5 $[M+H]^+$. Anal. Calcd (%) for $C_{24}H_{26}BF_2N_5O_3$: C, 59.89; H, 5.44; N, 14.55. Found: C, 59.59; H, 5.51; N, 14.26.

Compound ***5***. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_3-N_3 (440 mg, 0.94 mmol) and propargyl alcohol (53 mg, 0.94 mmol) were used instead of Bodipy-EO_2-N_3 and SO-alkyne, respectively. The crude product was purified by column chromatography on silica gel using petroleum ether-ethyl acetate-ethanol (8:8:1 v/v/v) as the eluent to give the desired product. Yield: 385 mg, 78%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.76 (s, 1H; triazole proton), 7.45 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.01 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.74 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.27 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 4.77 (d, J = 5.7 Hz, 2H; $-CH_2OH$), 4.57 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.21 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.85−3.93 (m, 4H; $-OCH_2CH_2-$), 3.64−3.74 (m, 4H; $-OCH_2CH_2O-$), 2.65 (s, 6H; $-CH_3$ of Bodipy). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.70, 157.41, 147.82, 142.78, 134.83, 132.37, 130.56, 127.20, 123.21, 119.55, 114.64, 71.07, 70.94, 69.98, 69.85, 67.95, 57.01, 50.62, 15.21. ESI-MS: m/z 526.3 $[M+H]^+$. Anal. Calcd (%) for $C_{26}H_{30}BF_2N_5O_4$: C, 59.44; H, 5.76; N, 13.33. Found: C, 59.13; H, 5.75; N, 13.02.

Compound ***6***. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_4-N_3 (420 mg, 0.82 mmol) and propargyl alcohol (46 mg, 0.82 mmol) were used instead of Bodipy-EO_2-N_3 and SO-alkyne, respectively. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate/ethanol (8:8:1 v/v/v) as the eluent to give the desired product. Yield: 383 mg, 82%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.80 (s, 1H; triazole proton), 7.45 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 7.01 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.75 (d, J = 4.2 Hz, 2H; pyrrole protons at 1,7-position), 6.28 (d, J = 4.2 Hz, 2H; pyrrole protons at 2,6-position), 4.80 (d, J = 6.0 Hz, 2H; $-CH_2OH$), 4.54 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.21 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.82−3.94 (m, 4H; $-OCH_2CH_2-$), 3.70−3.80 (m, 2H; $-OCH_2CH_2O-$), 3.60−3.70 (m, 6H; $-OCH_2CH_2O-$), 2.65 (s, 6H; $-CH_3$ of Bodipy). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.73, 157.38, 148.02, 142.82, 134.82, 132.34, 130.57, 127.13, 123.32, 119.51, 114.65, 71.23, 70.92, 70.87, 70.83, 69.97, 69.77, 67.93, 57.09, 50.59, 15.20. ESI-MS: m/z 570.2 $[M+H]^+$. Anal. Calcd (%) for $C_{28}H_{34}BF_2N_5O_5$: C, 59.06; H, 6.02; N, 12.30. Found: C, 58.94; H, 6.11; N, 11.98.

Compound ***7***. The procedure was similar to that described for the synthesis of compound **1** except azidobutane (63 mg, 0.64 mmol) was used instead of Bodipy-EO_2-N_3. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1 v/v) as the eluent to give the desired product. Yield: 240 mg, 78%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 8.55 (d, J = 8.4 Hz, 1H; naphthoxazinic proton at 10′-position), 7.73−7.76 (m, 2H; naphthoxazinic protons at 2′,7′-position), 7.66 (d, J = 9.0 Hz, 1H; naphthoxazinic proton at 6′-position), 7.54−7.61 (m, 2H; naphthoxazinic proton at 9′-position and triazole proton), 7.36−7.43 (m, 1H; naphthoxazinic proton at 8′-position), 7.01 (d, J = 9.0 Hz, 1H; naphthoxazinic proton at 5′-position), 6.79−6.87 (m, 2H; indolinic protons at 4,6-position), 6.48 (d, J = 8.4 Hz, 1H; indolinic proton at 7-position), 5.19 (s, 2H; $-CH_2O-$), 4.37 (t, J = 7.2 Hz, 2H; $-CH_2CH_2N-$ of alkyl chain), 2.71 (s, 3H; $-NCH_3$), 1.86−1.96 (m, 2H; $-CH_2CH_2-$ of alkyl chain), 1.32−1.43 (m, 8H; $-CH_2CH_3$ of alkyl chain and $-C(CH_3)_2$), 0.97 (t, J = 7.2 Hz, 3H; $-CH_3$ of alkyl chain). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 153.26, 150.94, 144.91, 144.45, 142.56, 137.86, 131.15, 130.56, 129.55, 128.10, 127.43, 124.48, 123.23, 122.67, 121.81, 117.09, 113.34, 110.83, 107.61, 99.24, 63.50, 52.21, 50.47, 32.58, 30.29, 25.65, 20.99, 20.04, 13.79. ESI-MS: m/z 482.2 $[M+H]^+$. Anal. Calcd (%) for $C_{29}H_{31}N_5O_2$: C, 72.33; H, 6.49; N, 14.54. Found: C, 72.62; H, 6.38; N, 14.45.

Compound ***8***. The procedure was similar to that described for the synthesis of compound **1** except SP-alkyne (150 mg, 0.40 mmol) was used instead of SO-alkyne. The crude product was purified by column chromatography on silica gel with ethyl acetate-petroleum ether (2:1 v/v) as the eluent to give the desired product. Yield: 240 mg, 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.97−8.02 (m, 2H; phthoxazinic proton at 5′,7′-position), 7.87 (s, 1H; triazole proton), 7.40 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 6.99 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.90 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 4′-position), 6.78−6.83 (m, 2H; indolinic protons at 4,6-position), 6.70−6.74 (m, 3H; pyrrole protons at 1,7-position and phthoxazinic proton at 8′-position), 6.42 (d, J = 8.7 Hz, 1H; indolinic proton at 7-position), 6.25 (d, J = 3.9 Hz, 2H; pyrrole protons at 2,6-position), 5.82 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 3′-position), 5.14 (s, 2H; $-CH_2O-$), 4.61 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.16 (t, J = 4.5 Hz, 2H; $-OCH_2CH_2O-$), 3.99 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 3.86 (t, J = 4.5 Hz, 2H; -OCH_2CH_2O-), 2.66 (s, 3H; -NCH_3), 2.64 (s, 6H; $-CH_3$ of Bodipy), 1.23 (s, 3H; $-C(CH_3)_2$), 1.14 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.54, 160.14, 157.48, 153.22, 144.90, 142.70, 141.25, 138.14, 134.80, 132.41, 130.55, 128.57, 127.31, 126.19, 124.27, 123.02, 121.85, 119.54, 119.01, 115.75, 114.60, 113.10, 110.85, 107.53, 107.09, 70.04, 69.98, 67.69, 63.38, 52.71, 50.71, 29.47, 26.10, 20.19, 15.22. ESI-MS: m/z 802.5 $[M+H]^+$. Anal. Calcd (%) for $C_{43}H_{42}BF_2N_7O_6$: C, 64.43; H, 5.28; N, 12.23. Found: C, 64.71; H, 5.30; N, 11.95.

Compound ***9***. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_3-N_3 (240 mg, 0.52 mmol) and SP-alkyne (196 mg, 0.52 mmol) were used instead of Bodipy-EO_2-N_3 and SO-alkyne, respectively. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (5:2 v/v) as the eluent to give the desired product. Yield: 266 mg, 61%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.96−8.01 (m, 2H; phthoxazinic proton at 5′,7′-position), 7.86 (s, 1H; triazole proton), 7.40 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 6.97 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.90 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 4′-position), 6.79−6.84 (m, 2H, indolinic protons at 4,6-positions), 6.70−6.75 (m, 3H; pyrrole protons at 1,7-position and phthoxazinic proton at 8′-position), 6.42 (d, J = 8.7 Hz, 1H; indolinic proton at 7-position), 6.25 (d, J = 3.9 Hz, 2H; pyrrole protons at 2,6-position), 5.82 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 3′-position), 5.15 (s, 2H; $-CH_2O-$), 4.57 (t, J = 4.8 Hz, 2H; -OCH_2CH_2N-), 4.17 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.92 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 3.86 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.64−3.74 (m, 4H; $-OCH_2CH_2O-$), 2.66 (s, 3H; $-NCH_3$), 2.63 (s, 6H; $-CH_3$ of Bodipy), 1.24 (s, 3H; $-C(CH_3)_2$), 1.14 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.71, 160.12, 157.38, 153.23, 144.75, 142.79, 142.67, 141.23, 138.12, 134.78, 132.34, 130.53, 128.55, 127.10, 126.15, 124.20, 123.00, 121.82, 119.52, 119.00, 115.72, 114.61, 113.03, 110.90, 107.48, 107.08, 71.05, 70.95, 69.97, 69.82, 67.91, 63.34, 52.70, 50.67, 29.46, 26.10, 20.18, 15.19. ESI-MS: m/z 846.3 $[M+H]^+$. Anal. Calcd (%) for $C_{45}H_{46}BF_2N_7O_7$: C, 63.91; H, 5.48; N, 11.59. Found: C, 64.18; H, 5.46; N, 11.30.

Compound ***10***. The procedure was similar to that described for the synthesis of compound **1** except Bodipy-EO_4-N_3 (230 mg, 0.45 mmol) and SP-alkyne (25 mg, 0.45 mmol) were used instead of Bodipy-EO_2-N_3 and SO-alkyne, respectively. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (3:1 v/v) as the eluent to give the desired product. Yield: 270 mg, 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si)/ppm: δ = 7.98−8.03 (m, 2H; phthoxazinic proton at 5′,7′-position), 7.84 (s, 1H; triazole proton), 7.42 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*o*-Ar-position), 6.98 (d, J = 8.7 Hz, 2H; Bodipy protons at 8-*m*-Ar-position), 6.90 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 4′-position), 6.81−6.85 (m, 2H, indolinic protons at 4,6-position), 6.71−6.77 (m, 3H; pyrrole protons at 1,7-position and phthoxazinic proton at 8′-position), 6.44 (d, J = 8.4 Hz, 1H; indolinic proton at 7-position), 6.26 (d, J = 4.5 Hz, 2H; pyrrole protons at 2,6-position), 5.83 (d, J = 10.2 Hz, 1H; phthoxazinic proton at 3′-position), 5.17 (s, 2H; $-CH_2O-$), 4.56 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2N-$), 4.17 (t, J = 4.8 Hz, 2H; $-OCH_2CH_2O-$), 3.85−3.92 (m, 4H; $-OCH_2CH_2O-$), 3.71−3.75 (m, 2H; $-OCH_2CH_2O-$), 3.63−3.68 (m, 6H; $-OCH_2CH_2O-$), 2.68 (s, 3H; $-NCH_3$), 2.64 (s, 6H; $-CH_3$ of Bodipy), 1.26 (s, 3H; $-C(CH_3)_2$), 1.17 (s, 3H; $-C(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K)/ppm: δ = 160.77, 160.14, 157.38, 153.25, 144.72, 142.81, 142.66, 141.24, 138.11, 134.80, 132.32, 130.54, 128.57, 127.08, 126.17, 124.24, 123.02, 121.84, 119.52, 119.01, 115.74, 114.64, 113.06, 110.93, 107.48, 107.10, 71.22, 70.98, 70.93, 70.89, 69.97, 69.80, 67.93, 63.32, 52.72, 50.66, 29.50, 26.13, 20.20, 15.20. ESI-MS: m/z 890.3 $[M+H]^+$. Anal. Calcd (%) for $C_{47}H_{50}BF_2N_7O_8 \cdot 0.5C_6H_{14}$: C, 64.38; H, 6.16; N, 10.51. Found: C, 64.28; H, 5.94; N, 10.61.

Physical Measurements and Instrumentation. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian 300 (300 MHz) or a Bruker DRX 500 (500 MHz) spectrometer with chemical shifts reported relative to tetramethylsilane, Me_4Si. All positive ion ESI-MS were recorded on QTRAP 2000 mass spectrometer. Elemental analysis of compounds were performed on a Flash EA 1112 elemental analyzer at Jilin University.

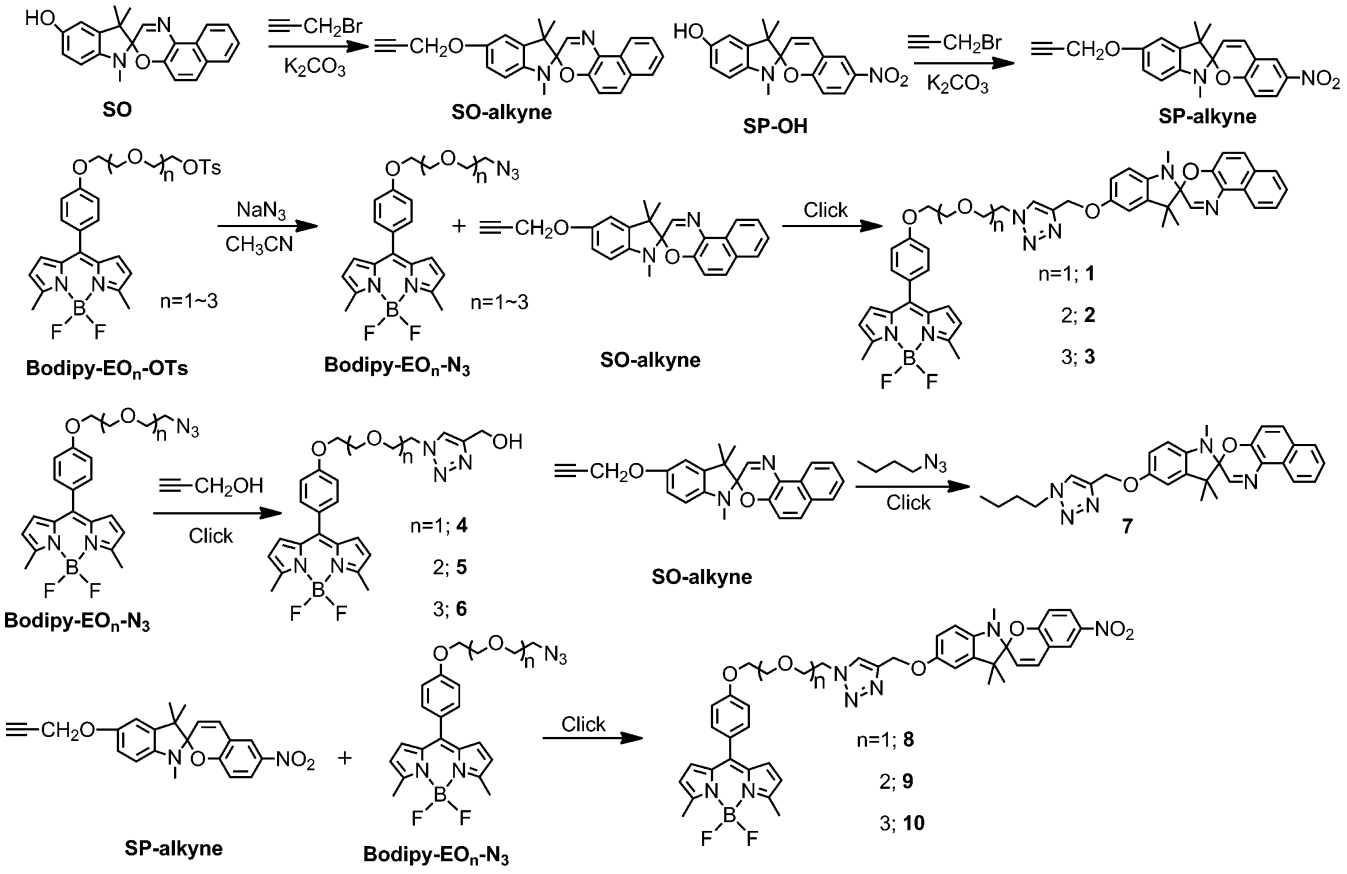
Cyclic voltammetric measurements were performed by using a CH instruments Inc. model CHI 660C electrochemical analyzer. Electrochemical measurements were performed in dichloromethane solution with 0.1 mol dm^{-3} $^nBu_4NPF_6$ (TBAH) as supporting electrolyte at room temperature. The reference electrolyte was an $Ag/AgNO_3$ (0.1 mol dm^{-3} in acetonitrile) electrode and the working electrode was a glassy carbon electrode (CH instruments) with a platinum wire as the counter electrode. The working electrode surface was first polished with 1 μm alumina slurry. It was then rinsed with ultrapure deionized water and sonicated in a beaker containing ultra-pure water for five minutes. The polishing and sonication steps were repeated twice and then the working electrode was finally rinsed under a stream of ultrapure deionized water. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference. All solutions for electrochemical studies were deaerated with prepurified argon gas prior to measurements.

UV-vis absorption spectra were obtained using a Varian Cary 50 UV-vis spectrophotometer or a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission spectra at RT were recorded on a Spex Fluorolog-2-model F111 fluorescence spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube or a Horiba-Jobin-Yvon Fluorolog-3 fluorescence spectrofluorometer equipped with a R928P PMT detector. For the determination of emission quantum yields φ in dichloromethane, Rhodamine 6G in water (φ = 0.78) was used as the reference standard. All solutions for energy transfer studies were prepared at the concentration of 1.6×10^{-5} M in dichloromethane containing 0.1 M $^nBu_4NPF_6$ and subjected to sonicating for 2 mins. Subsequently photophysical measurements were carried out.

A commercial femtosecond Ti:Sapphire regenerative amplifier laser system equipped with a Helios transient absorption spectrometer and automated data acquisition system (Ultrafast Systems, Helios) was used to perform the ultrafast transient absorption experiments. The amplifer was seeded with the 120 fs output from the oscillator (Spectra Physics, Maitai). The sample solutions were excited by a 400 nm pump beam. The probe pulse was obtained by using approximately 5 % of the amplified 800 nm output from the Spitfire to generate a white-light continuum (350-800 nm). The intrinsic temporal resolution is 7 fs. The instrument response function was determined to be 150 fs. The sample solutions were stirred to reduce charging effects. Signals, one for spectra without pump excitation and one with a variable probe-pump delay from 0 to 2860 ps were focused into a pair of monochromators and dispersed onto CMOS sensor that had a 1.5 nm intrinsic resolution. All the measurements were performed at room temperature.

The thermal bleaching reactions of spirooxazines and spiropyrans were known to follow first-order kinetics at various temperature. The kinetics for the bleaching reaction were determined by measurement of the UV-vis spectral changes at various temperature with the use of a Hewlett-Packard 8452A diode array spectrophotometer with temper-

Scheme 3. Synthetic Routes for the Preparation of Compounds 1−10



ature controlled by a Lauda RM6 compact low-temperature thermostat. Photoirradiation was carried out by using a 300 W Xe (ozone-free) lamp (Oriel model 6258) and monochromatic light was obtained by passing the light through an Applied Photophysics F 3.4 monochromator. The first-order rate constants were obtained by taking the negative value of the slope of a linear least-squares fit of $\ln[(A - A_\infty)/(A_0 - A_\infty)]$ against time according to eq 1:

$$\ln[(A - A_\infty)/(A_0 - A_\infty)] = -kt \quad (1)$$

where A, A_0, and A_∞ are the absorbance at the absorption wavelength maximum of the open form at times t, 0, and infinity, respectively, and k is the rate constant of the reaction. The kinetic parameters were obtained by a linear least-squares fit of $\ln(k/T)$ against $1/T$ according to the linear expression of the Eyring eq 2, $\ln k$ against $1/T$ according to the Arrhenius eq 3, and the changes in Gibbs free energy of activation ($\Delta G^{\ddagger}$) at 298 K were determined according to eq 4:

$$\ln(k/T) = -(\Delta H^{\ddagger}/R)(1/T) + \ln(k_B/h) + (\Delta S^{\ddagger}/R) \quad (2)$$

$$\ln(k) = -E_a/RT + \ln A \quad (3)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (4)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the changes in enthalpy of activation and entropy of activation, respectively, E_a is the activation energy, T is the temperature, and k_B, R, h, and A are the Boltzmann's constant, the universal gas constant, the Planck constant, and the frequency factor, respectively.

Computational Details. Calculations were performed by using the Gaussian 09 software package.[77] The ground-state geometries for the open and closed forms of compounds **1** and **8** were fully optimized in CH_2Cl_2 by using density functional theory (DFT) calculations with the hybrid Perdew, Burke, and Ernzerhof functional (PBE0)[78−80] in conjunction with the conductor-like polarizable continuum model (CPCM).[81,82] Vibrational frequencies were calculated for all stationary points to verify that each was a minimum (NIMAG=0) on the potential energy surface. On the basis of the ground state optimized geometries, time-dependent density functional theory (TDDFT) calculations[83−85] were performed to compute the singlet−singlet transitions using CAM-B3LYP functional[86] associated with the CPCM (CH_2Cl_2). The 6-31G** basis set[87,88] was used for the geometry optimization, whereas a larger basis set (6-311++G**)[89,90] was employed for the TDDFT calculation.

RESULTS AND DISCUSSION

Synthesis. Scheme 3 summarizes the synthetic routes of compounds **1−10** in this study. Compounds **1−3** and compounds **8−10** were synthesized by the click reaction of azido-functionalized Bodipy with alkyne in CH_2Cl_2−H_2O (3:2 v/v) mixed solvent in the presence of sodium ascorbate and $CuSO_4 \cdot 5H_2O$. Similarly, compounds **4−6** were prepared by the reaction of azido-functionalized Bodipy and propargyl alcohol in THF−H_2O (3:1 v/v). On the other hand, compound **7** was synthesized from the reaction of 1,3,3-trimethyl-5-hydroxyspiroindolinenaphthoxazine-containing alkyne (SO-alkyne) and azidobutane in CH_2Cl_2−H_2O (3:2 v/v) mixed solvent. The identities of the target molecules were confirmed by ^{1}H NMR spectroscopy, ESI mass spectrometry, and elemental analysis.

Electrochemistry. Compounds **1−3** and **8−10** each display two irreversible oxidation waves at about +0.84 to +0.90 V and +1.28 to +1.32 V versus SCE in the oxidative scan of their cyclic voltammograms in dichloromethane (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$), while one quasi-reversible reduction wave at about −1.01 to −1.04 V versus SCE is observed in the reductive scan. Compounds **8−10** also show an irreversible reduction wave at about −1.22 to −1.27 V versus SCE. The

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electrochemical data for compounds **1**−**10** are summarized in Table 1.

Table 1. Electrochemical Data for Compounds 1−10 in Dichloromethane Solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) at 298 K[a]

compd	oxidation E_{pa}[b] [V] vs SCE	reduction $E_{1/2}$[c] [V] vs SCE (ΔE_p [mV])[d]
1	+0.90, +1.32	−1.03 (73)
2	+0.88, +1.32	−1.04 (70)
3	+0.89, +1.31	−1.02 (71)
4	+1.30	−1.02 (87)
5	+1.29	−1.03 (84)
6	+1.29	−1.03 (79)
7	+1.02	−[e]
8	+0.86, +1.30	−1.01 (70), −1.22[f]
9	+0.85, +1.29	−1.03 (77), −1.27[f]
10	+0.84, +1.28	−1.04 (75), −1.27[f]

[a]Working electrode, glassy carbon; scan rate, 100 mVs^{-1}. [b]E_{pa} is reported for the irreversible oxidation wave. [c]$E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively. [d]$\Delta E_p = (E_{pa} - E_{pc})$. [e]No reduction wave was observed. [f]E_{pc} is reported for irreversible reduction wave.

According to previous electrochemical studies on spiropyrans[91] and spirooxazines[92] as well as the resemblance of the potentials of the first irreversible oxidation wave to that of compound **7**, the first oxidative wave is tentatively assigned to the oxidation of the spiropyran or spirooxazine, arising from the indoline-centered oxidation. The second irreversible oxidation wave in compounds **1**−**3** and **8**−**10** at about +1.28 to +1.32 V versus SCE is similar to those of the first irreversible oxidation wave of compounds **4**−**6**, which is tentatively assigned to the oxidation of Bodipy.

The first quasi-reversible reduction couple in compounds **1**−**3** and **8**−**10** at −1.01 to −1.04 V versus SCE is in close resemblance to the potentials of compounds **4**−**6** and is tentatively assigned to the reduction of Bodipy. The second irreversible reduction wave, which occurs at about −1.22 to −1.27 V versus SCE, is only observed in compounds **8**−**10**. In view of the observation of a similar irreversible reduction wave at −1.27 V versus SCE for the spiropyran without Bodipy (compound SP-alkyne), the irreversible reduction wave is tentatively assigned to the reduction of spiropyran.

Photophysical Properties. The electronic absorption spectra of compounds **1**−**7** in dichloromethane show intense absorption bands with molar extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1} at about 280−320 nm and 354−370 nm, which are tentatively ascribed to $\pi \rightarrow \pi^*$ transitions of indole, naphthoxazine, and $S_0 \rightarrow S_2$ transition of Bodipy, similar to those observed in other related systems.[93,94] Compounds **8**−**10**, on the other hand, show intense absorption bands at about 260−270 nm and 360−370 nm in their electronic absorption spectra, which are also tentatively assigned as $\pi \rightarrow \pi^*$ transitions of indole, phthoxazine, and $S_0 \rightarrow S_2$ transition of Bodipy. In addition to the intense absorption at about 360−370 nm, compounds **1**−**6**, **8**−**10** also show another intense band at about 500−520 nm in their electronic absorption spectra. This absorption band, with molar extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1}, is ascribed to $S_0 \rightarrow S_1$ transition of Bodipy, typical of the Bodipy system. The photophysical data of compounds **1**−**10** are summarized in Table 2. Upon addition of

Table 2. Photophysical Data of Compounds 1−10 in Dichloromethane at 298 K

	absorption	emission	
compd	λ_{max} [nm] (ε_{max} [dm^3 mol^{-1} cm^{-1}])	λ_{em} [nm]	φ_{em}[b]
1	319 (14220), 359 (17210), 484 (21990), 511 (79550)	526	0.11
1-TFA		526	−[c]
2	320 (14990), 360 (17820), 485 (22740), 510 (85270)	526	0.13
2-TFA		526	−[c]
3	319 (15980), 359 (15380), 484 (18810), 510 (70610)	526	0.16
3-TFA		526	−[c]
4	370 (12210), 484 (19740), 510 (73720)	526	0.33
4-TFA		526	−[c]
5	371 (12370), 484 (20570), 510 (76990)	526	0.33
5-TFA		526	−[c]
6	370 (10530), 484 (17340), 510 (64320)	526	0.33
6-TFA		526	−[c]
7	318 (10310), 347 (5910)	440	−[c]
7-TFA		−[a]	−[c]
8	266 (23180), 357 (20950), 484 (21290), 511 (79590)	526	0.11
8-TFA		526	−[c]
9	265 (24250), 357 (21450), 484 (22040), 510 (82360)	526	0.14
9-TFA		526	−[c]
10	265 (22150), 357 (19410), 484 (19920), 510 (74320)	526	0.16
10-TFA		526	−[c]

[a]Nonemissive excited at 540 nm. [b]The fluorescence quantum yield, measured at room temperature using Rhodamine 6G in water (ϕ = 0.78) as a standard. [c]The emission quantum yield was not measured.

trifluoroacetic acid (TFA), compounds **1**−**3** exhibited color changes from orange to purple with the growth of a new absorption band at ca. 550 nm and a well-defined isosbestic point at ca. 360 nm. With reference to previous studies on related spirooxazines,[95] the acidochromic behavior is attributed to the cleavage of the spiro carbon−oxygen bond in spirooxazine that leads to the planarization of the two originally orthogonal heterocycles to form the ring-opened structure, giving rise to an increase in the extent of π-conjugation (Scheme 1). Compounds **8**−**10**, on the other hand, also exhibit acidochromism with the growth of an absorption band at about 350−450 nm, but the color of the solution does not show an obvious change.

To gain further insight into the nature of the absorption of the photochromic compounds, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed for the closed form, open form, and protonated open form of **1** and **8**. Selected singlet−singlet transitions for the closed forms and open forms in **1** and **8** are listed in Table S1 and the orbitals involved in the transitions are shown in Figures S1−S6 of the Supporting Information. For **1**, the first singlet−singlet transition of the closed form is attributed to the π−π^* transition of the Bodipy, while it is the π−π^* transition of the merocyanine unit for the protonated open form. The second singlet−singlet transition is the π−π^*(Bodipy) transition. On the other hand, the first singlet−singlet transition for both the closed form and protonated open form of **8** is the π−π^* transition of the Bodipy. The calculation is in line with the growth of a lower-

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energy absorption band upon addition of trifluoroacetic acid in the spirooxazine derivatives, which further supports the assignment from the photophysical study. When compared to the protonated open forms in **1** and **8**, the $\pi-\pi^*$ transition of the merocyanine unit in the open forms is red-shifted.

Upon excitation at λ = 360 nm, compounds **1**−**6** and **8**−**10** exhibited green emission at about 526 nm in dichloromethane at room temperature. This emission band is assigned to Bodipy-centered fluorescence. The relative insensitivity of the UV-vis absorption and emission properties upon variation of the oligoether chain length suggested the lack of an effective communication between Bodipy and SO/SP through the oligoether bridge. Upon excitation at the isosbestic point, the emission intensity is gradually quenched with increasing concentration of TFA from 10 equivalents to 40 equivalents. The emission spectra of compound **1** upon addition of different amounts of TFA are shown in Figure 1. The extent of

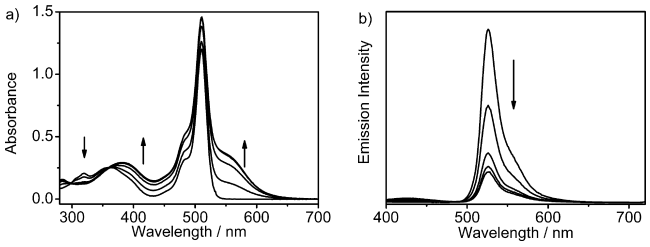

Figure 1. (a) UV−vis absorption spectral changes of **1** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of different amounts of TFA (0, 10, 20, 30, 40 equiv). (b) Emission spectral changes of **1** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of different amounts of TFA (0, 10, 20, 30, 40 equiv).

luminescence quenching of compounds **1**−**3** has been estimated by the ratio $[1 - (I/I_0)]$ of the emission spectra plotted in emission intensity versus wavenumber, where I and I_0 denote the integrated area under the emission spectra in the presence and absence of 40 equiv of TFA and are related to the emission quantum yields. The values for compounds **1**−**3** are 82%, 87%, and 85%, respectively. The mechanism for fluorescence quenching is proposed to be energy transfer from Bodipy to the open form of spirooxazine as there is a significant spectral overlap between the absorption spectrum of the open form of spirooxazine and the emission spectrum of Bodipy (Figure 2). Energy transfer is further supported by the lack of fluorescence quenching for compounds **4**−**6** (Figure 3) and **8**−**10** upon addition of TFA owing to the poor of spectral overlap between the electronic absorption of the open form of spiropyran and the emission of Bodipy (Figure 2). These results support the occurrence of energy transfer from Bodipy to the ring-opened merocyanine for compounds **1**−**3**.

Transient Absorption Properties. In order to provide additional data regarding energy transfer properties of compounds **1**−**3** upon addition of TFA, femtosecond transient absorption spectra have been measured in dichloromethane solution (0.1 M ^{n}Bu$_4$NPF$_6$) with and without the presence of 40 equiv of TFA at room temperature. Compounds **1**−**3** show similar bleaching bands at ca. 511 nm (Figure 4), which is in good agreement with the depletion of the ground state absorption, with time constants ranging from 700 to 1100 ps. Upon addition of 40 equiv of TFA, the bleaching at ca. 460−584 nm in the visible region undergoes a faster decay involving multiple decay components (Figure 5). In addition, a

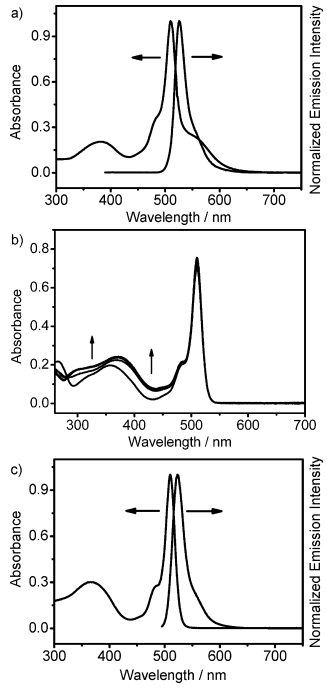

Figure 2. (a) UV−vis absorption and emission spectra of **1** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) in the presence of 40 equiv of TFA. (b) UV−vis absorption spectral changes of **8** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of different amounts of TFA (0, 10, 20, 30, 40 equiv). (c) UV−vis absorption and emission spectra of **8** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) in the presence of 40 equiv of TFA.

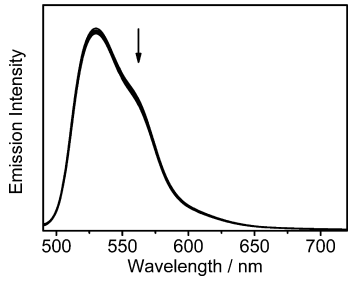

Figure 3. Emission spectral changes of compound **6** (1.6×10^{-5} M) in dichloromethane (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of different amounts of TFA (0, 10, 20, 30, 40 equiv).

moderately intense excited state absorption feature at ca. 585−680 nm is also observed. In view of its close resemblance the absorption features of the control compound **7** upon addition of 40 equiv of TFA and the lack of the absorption feature at 585−680 nm for **1**−**4** without TFA, the negative bands that occurred at 460−584 nm for these compounds could be assigned as derived from the bleaching of the ground state of Bodipy, mixed with the decay of the ring-opened merocyanine. The positive bands at about 585−680 nm could be assigned as the excited state absorption of the ring-opened merocyanine in the presence of TFA.

Compounds **1**−**3** all show three transient absorption decay time constants of 1.4−2.8, 18.6−30.7, and 261.5−435.5 ps upon addition of 40 equiv of TFA. In view of the observation of the similar absorption features for **1**−**3** and **7** with 40 equiv of TFA, the fast decay observed at 511 nm with time constants of about 1.4−2.8 ps was tentatively ascribed to the vibrational

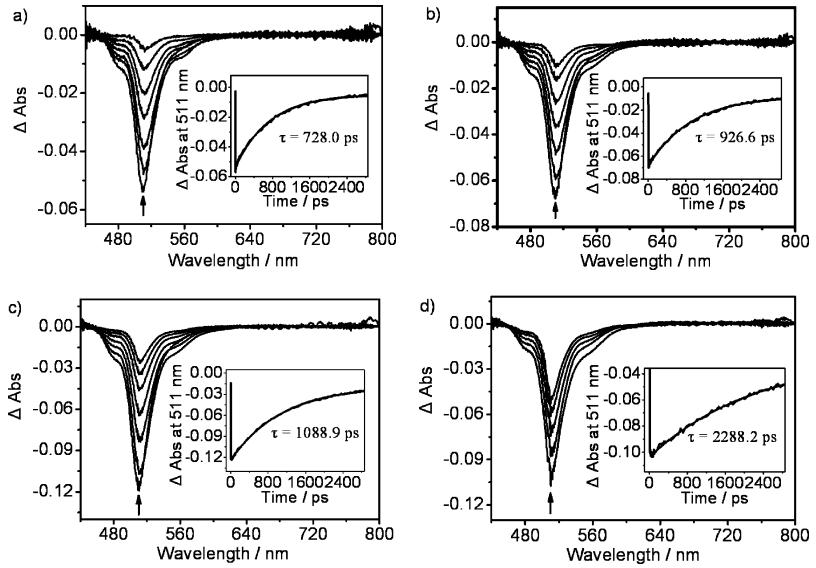

Figure 4. Transient absorption difference spectra of (a) **1**; (b) **2**; (c) **3**; and (d) **4** in dichloromethane (0.1 M $^{n}Bu_4NPF_6$) at 298 K following 400 nm pulsed laser excitation. The insets show the transient absorption decay kinetics at 511 nm.

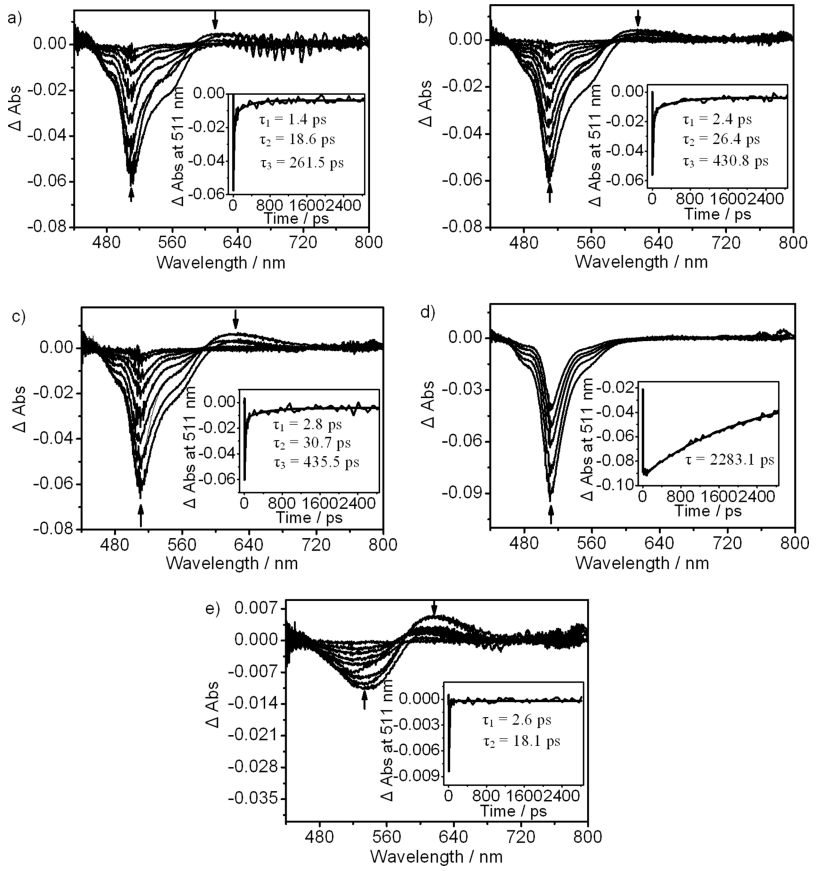

Figure 5. Transient absorption difference spectra of (a) **1**; (b) **2**; (c) **3**; (d) **4**; and (e) **7** in dichloromethane (0.1 M $^{n}Bu_4NPF_6$) upon addition of 40 equiv of TFA at 298 K following 400 nm pulsed laser excitation. The insets show the transient absorption decays at 511 nm.

relaxation and solvent dynamics of the open form of spirooxazine and Bodipy, which is commonly observed in other related systems.[96,97] Similarly, the decay time constants of about 18.6−30.7 ps for **1**−**3** and **7** are tentatively assigned to the relaxation of the open form due to the lack of decay time constants of 18.6−30.7 ps for **1**−**4** without TFA, and their close resemblance to that of the decay kinetics of **7**. In view of the lack of longer decay components in **7**, the slow transient decay at 511 nm with time constants of 261.5−435.5 ps for **1**−**3** in the presence of TFA were tentatively assigned to the decay of Bodipy excited state. The significant reduction of decay time constants in **1**−**3** and the absence of obvious change in time constants in other control compounds clearly support the quenching of the Bodipy excited state by the ring-opened

merocyanine. Thus, the efficiencies of energy transfer η are also determined by $\eta = 1 - (\tau/\tau_0)$, where τ and τ_0 are the time constants of the slower component of compounds **1**−**3** with 40 equivalents of TFA and that without TFA, respectively. The energy transfer efficiencies η for compounds **1**−**3** are found to be 64%, 54%, and 60%, respectively. They do not appear to show a strong dependence on the length of the oligoether linker as evidenced by the emission spectral changes and ultrafast transient absorption spectra. This may arise from the flexibility of the linker which would allow the donor and acceptor units to adopt a folded structure and to come close to each other.

Photochromic Properties. On prolonged excitation at 355 nm, all the compounds containing spirooxazine or spiropyran changed their color in acetonitrile. With reference to previous studies on spirooxazines,[98,99] this is attributed to a photochromic reaction, in which the spiro carbon−oxygen bond is cleaved, leading to the formation of the open form of spirooxazine. However, the open form is thermally unstable and quickly undergoes bleaching reaction to the closed form. The kinetics for the bleaching reaction of the open forms of compounds SO, SP, **1**−**3**, and **8**−**10** after excitation at 355 nm have been investigated in acetonitrile by using UV-vis absorption spectroscopy at various temperatures. By monitoring the absorbance at 620 nm for compounds SO and **1**−**3** and 565 nm for compounds SP and **8**−**10**, the kinetics for the bleaching reactions are investigated and the rate constants of compounds SO, SP, **1**−**3**, and **8**−**10** at various temperatures are summarized in Table 3. The results show that the rate of the bleaching reaction of compounds **8**−**10** is much slower than that of compounds **1**−**3**, consistent with the previous report that $-NO_2$ moiety in spiropyran can stabilize the photomerocyanine.[100] Larger rate constants are obtained at higher temperature for these compounds, which indicates that the bleaching reaction is an activated process, consistent with positive values for the activation enthalpy ($\Delta H^{\ddagger}$). Rate constants of compounds **1**−**3** at the same temperature are similar and are larger than that of SO, which may be due to negative activation entropy ($\Delta S^{\ddagger} = -9.97$ J mol^{-1} K^{-1}) of SO. Negative activation entropy suggests that the disorderness in the activated complex in the transition state in relation to the open form in SO is increased, which is not favorable for the bleaching reaction. On the contrary, the rate constants of compounds **8**−**10** at the same temperature are similar and lower than that of **SP**, which could be observed at 25°C. The relatively lower activation enthalpy and positive activation entropy for compound SP may be the crucial reason that facilitates the bleaching reaction.

Table 3. Summary of Rate Constants *k* for the Bleaching Reaction of Spirooxazine- And Spiropyran-Containing Derivatives at Various Temperatures in Acetonitrile

	k (10^{-2} s^{-1}) in acetonitrile					
compd	278 K	281 K	284 K	287 K	290 K	293 K
1	5.3	7.4	11.2	16.2	23.7	27.4
2[a]	6.3[a]	9.0[a]	13.5[a]	17.6[a]	26.6[a]	38.9[a]
3	6.0	8.5	11.9	16.6	23.1	33.7
SO	3.6	4.8	6.4	9.3	12.6	19.4
	k (10^{-4} s^{-1}) in acetonitrile					
compd	298 K	302 K	306 K	310 K	314 K	318 K
8	5.8	8.3	13.7	22.1	37.9	61.2
9	6.1	9.0	13.8	23.4	38.9	64.2
10	6.4	10.3	16.5	28.3	50.7	75.4
SP-alkyne[b]	1.1[b]	1.5[b]	2.1[b]	3.3[b]	4.9[b]	7.4[b]

[a]From left to right: Rate constants *k* were measured at 279, 282, 285, 288, 291, and 294 K, respectively. [b]From left to right: Rate constants k were measured at 283, 286, 289, 292, 295, and 298 K, respectively.

The thermodynamic activation parameters have been determined by using the Eyring and Arrhenius equations. The Eyring and Arrhenius plots of compounds SO, **3**, and **10** are shown in Figure 6. The thermodynamic activation parameters of compounds SO, SP, **1**−**3**, and **8**−**10** are summarized in Table 4. Activation energies (E_a) of 91−99 kJ mol^{-1} for compounds SP and **8**−**10** are obtained, which are larger than that of 75−84 kJ mol^{-1} for compounds SO and **1**−**3**. Similarly, the activation enthalpies ($\Delta H^{\ddagger}$) of compounds SP and **8**−**10** (89−97 kJ mol^{-1}) are also larger than those of compounds SO and **1**−**3** (72−82 kJ mol^{-1}). Both activation energy (E_a) and activation enthalpy ($\Delta H^{\ddagger}$) indicate that the rate of bleaching reaction of compounds containing spiropyran (SP and **8**−**10**) is less favorable than that of compounds containing spirooxazine (SO and **1**−**3**), consistent with the lower rate constants of compounds SP and **8**−**10** relative to that of compounds SO and **1**−**3** at various temperatures.

The activation enthalpies and entropies for the bleaching reactions in spirooxazine-containing compounds SO and **1**−**3** range from 72 to 82 kJ mol^{-1} and from −9.97 to 23.20 J mol^{-1} K^{-1}, respectively. In contrast, the activation enthalpies and entropies for the reactions in spiropyran-containing compounds

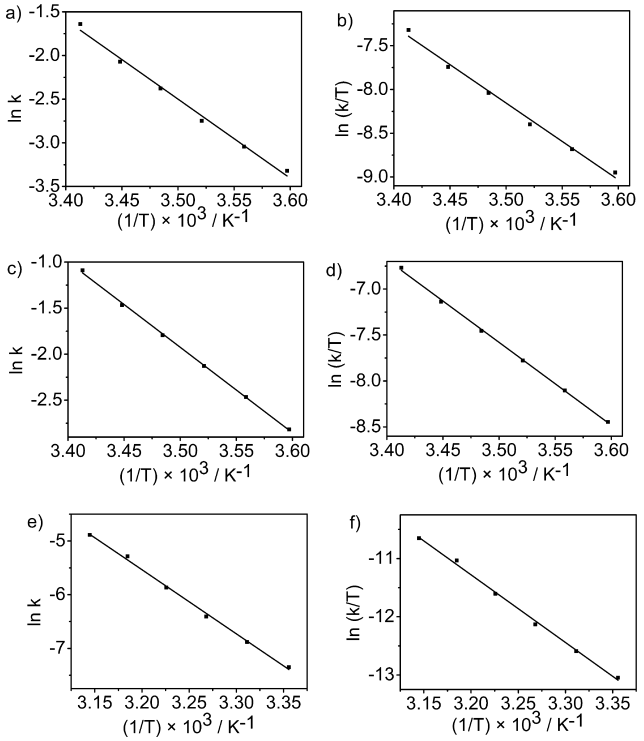

Figure 6. (a) Arrhenius and (b) Eyring plots for the thermal bleaching reaction of SO (1.3×10^{-4} M) in acetonitrile. (c) Arrhenius and (d) Eyring plots for the thermal bleaching reaction of compound **3** (1.4×10^{-4} M) in acetonitrile. (e) Arrhenius and (f) Eyring plots for the thermal bleaching reaction of compound **10** (7.3×10^{-5} M) in acetonitrile.

Table 4. Summary of the Activation Parameters for the Bleaching Reactions of the Spirooxazine- And Spiropyran-Containing Derivatives in Acetonitrile

	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}_{298K}$ (kJ mol^{-1})	E_a (kJ mol^{-1})
1	75.49 ± 3.96	2.99 ± 13.88	74.60 ± 8.10	77.88 ± 3.96
2	81.14 ± 2.12	23.20 ± 7.41	74.23 ± 4.33	83.56 ± 2.12
3	74.80 ± 1.12	1.25 ± 3.94	74.43 ± 2.99	77.17 ± 1.13
SO	72.99 ± 3.19	−9.97 ± 11.14	75.96 ± 6.51	75.33 ± 3.20
8	91.78 ± 3.20	0.38 ± 10.39	91.67 ± 6.30	94.35 ± 3.21
9	91.16 ± 3.48	−1.24 ± 11.31	91.53 ± 6.85	93.72 ± 3.49
10	96.61 ± 2.50	17.79 ± 8.14	91.31 ± 4.98	99.15 ± 2.51
SP-alkyne	89.37 ± 2.85	5.28 ± 9.81	87.80 ± 5.77	91.78 ± 2.86

SP and **8**−**10** range from 89 to 97 kJ mol^{-1} and from −1.24 to 17.79 J mol^{-1} K^{-1}, respectively. The activation entropy ranges from close to zero when $\Delta H^{\ddagger}$ is small to $\Delta S^{\ddagger}$ = 23.20 J mol^{-1} K^{-1} when $\Delta H^{\ddagger}$ is large for the spirooxazine-containing compounds, which is similar for the spiropyran-containing compounds. A careful investigation on the variation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in spirooxazine-containing compounds and spiropyran-containing compounds has been performed. An isokinetic relationship, which means a linear proportionality between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, is observed for compounds **1**−**3** and **8**−**9**, respectively (Figure 7). However, compounds SO and SP

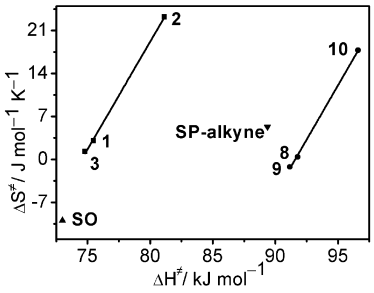

Figure 7. Plots of activation enthalpy against activation entropy for the bleaching reactions of the ring-opened merocyanines of compounds **1**−**3**, SO, SP-alkyne, and **8**−**10**.

are not in line with compounds **1**−**3** and **8**−**10**, respectively. This is indicative of a common bleaching reaction mechanism for compounds **1**−**3** and a common bleaching reaction mechanism for compounds **8**−**10**. From the slope of the plot, an isokinetic temperature of 285 K for compounds **1**−**3** and 283 K for compounds **8**−**10** are obtained.

Upon excitation at 355 nm, compounds **1**−**3** and **8**−**10** exhibit photochromism that show the generation of the open form of spirooxazine and spiropyran. The open form generated for compounds **1**−**3** is thermally unstable and quickly undergo thermal bleaching reaction to the closed form within five minutes at 5 °C or room temperature. Thus, their emission spectral changes upon irradiation have not been performed. In contrast, the ring-opened merocyanines for compounds **8**−**10** undergo thermal bleaching reaction to the closed form relatively slowly, which renders the investigation of the energy transfer reactions for compounds **8**−**10** more amenable to study. On prolonged excitation at 355 nm, compound **10** exhibits photochromism with a small growth in absorbance of the band at 565 nm. The electronic absorption spectra of the ring-opened merocyanine form of compound **10** with different irradiation time are shown in Figure 8. Upon excitation at λ = 360 nm, the emission at about 526 nm is found to be slightly

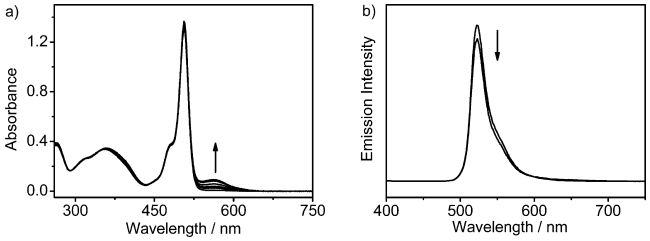

Figure 8. (a) UV−vis absorption spectral changes of compound **10** in acetonitrile upon irradiation at λ = 355 nm at 298 K. (b) Emission spectral changes of compound **10** in acetonitrile upon irradiation at λ = 355 nm at 298 K.

quenched after prolonged excitation at 355 nm due to small conversion to the open form of spiropyran. In view of a good spectral overlap between the emission of Bodipy and the absorption of the ring-opened merocyanine form, the results suggest that energy transfer occurs from Bodipy to ring-opened merocyanine. The emission spectral changes of compound **10** are also shown in Figure 8.

CONCLUSION

In summary, two series of photochromic spirooxazine- and spiropyran-containing Bodipy derivatives have been designed and synthesized, and their electrochemical, photophysical, ultrafast transient absorption, and photochromic properties have been studied. Upon addition of TFA, the emission of Bodipy is significantly quenched and efficient energy transfer occurs from Bodipy to the ring-opened merocyanine in compounds **1**−**3**. On the contrary, no energy transfer occurs from Bodipy to the open form of spiropyran in compounds **8**−**10** because there is no spectral overlap between the emission of Bodipy and the absorption of the ring-opened merocyanine (MC-H form). Upon excitation at 360 nm, the emission of Bodipy is slightly quenched due to small conversion to the open form of spiropyran and energy transfer from Bodipy to the ring-opened merocyanine (MC form) has been proposed in compounds **8**−**10** owing to their good spectral overlap. The rate constants and activation parameters of the bleaching reaction of compounds SO, SP-alkyne, **1**−**3**, and **8**−**9** have been determined in acetonitrile. The results show that the activation parameters have a great effect on the rate constants of the bleaching reactions and compounds **1**−**3** and **8**−**10** have a common bleaching reaction mechanism, respectively.

ASSOCIATED CONTENT

Supporting Information

Selected singlet excited states of **1** and **8**, selected molecular orbitals of **1** and **8**, Cartesian coordinates of the optimized

structures, and their calculated PBE0/CPCM electronic energies (hartrees). This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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