Dyes and Pigments 136 (2017) 161-167

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The photocyclization-dependent ratiometric fluorescent switch: Synthesis, characterization and properties of some terpyridyl-based dithienylethenes



PIGMENTS

Fang Hu^{a, *, 1}, Chuanyin Jiang^{b, 1}, Wenju Liu^b, Jinjian Wang^a, Jun Yin^b, Sheng Hua Liu^{b, **}

^a Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, 315211, China ^b Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan, 430079, China

ARTICLE INFO

Article history: Received 21 July 2016 Received in revised form 18 August 2016 Accepted 21 August 2016 Available online 24 August 2016

Keywords: Dithienylethenes Terpyridyl Triphenylamine Photochromism Fluorescent switch

ABSTRACT

Some terpyridyl-based dithienylethenes were synthesized and their structures were confirmed by NMR spectroscopy, mass spectroscopy and elemental analysis. The photochromic properties and fluorescence behaviors of these compounds have been measured upon irradiation with UV or visible light in solution. UV/vis absorption spectra and fluorescence spectra indicated that the dithienylethenes displayed obvious photochromism and fluorescent switch properties. Specially, when compared with other terpyridyl-based dithienylethenes, the triphenylamine and terpyridyl-based dithienylethene showed the photocyclization-dependent ratiometric fluorescent switch behaviors. Density functional theory indicated that the photocyclization-dependent ratiometric fluorescent changes were due to the donor-acceptor system of the switch.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Photochromism refers to a reversible change in the properties of a molecule in response to light [1,2]. Photochromic compounds, such as spiropyrans, azobenzene, fulgides and diarylethenes have been extensively investigated because of their potential applications in photonic devices such as memory media and optical switching [3–6]. Recently, there has been an increasing interest in photochromic dithienylethene derivatives due to their remarkable fatigue resistance, excellent irreversible thermal properties, high sensitivity and switchable fluorescent character [7–16].

The photochromic dithienylethene fluorescence switches have been the most extensively studied because of their potential applications in biological imaging materials [17-20]. However, with regard to photocyclization, most of their fluorescence intensity was quenched, which was bad for the measuring accuracy in the biological imaging [21-25]. It is well-known that the ratiometric

¹ These two authors made equal contributions.

fluorescent switch would make the measuring accuracy eliminate some influences from micro environment [26-29]. Therefore, developing the dithienylethene-based ratiometric fluorescent switch is significant for applying in bio-imaging. At present, several main strategies have been employed to design the ratiometric fluorescent switch, which include electronic interaction, and intramolecular excimer formation [23,30]. For example, professor He Tian et al. introduced the perylene diimide group acting as a bridge to connect the two dithienylethenes [23]. In the open isomer of dithienylethene, there was a strong electronic interaction between the pervlene diimide group and two dithienvlethene units. and the fluorescence was very weak. In the closed isomer of the switch, the electronic interaction between them was hold back, and the fluorescence was increased. Subsequently, Liu's group reported a triazole-bridged dithienylethene compound with two pyrene units, and found the open-ring isomer showed intramolecular pyrene excimer fluorescence, but the closed-ring isomer showed pyrene monomer fluorescence [30]. However, these compounds usually had poor solubility, and were reported rarely. On the basis of our previous work, herein we present an unprecedented example of the triphenylamine and terpyridyl-based dithienylethere by introducing donor- π -acceptor (D- π -A) dye [31] moieties into the two sides of the dithienylethene backbone. As shown



^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: hufang@nbu.edu.cn (F. Hu), chshliu@mail.ccnu.edu.cn (S.H. Liu).

in Scheme 1B, the triphenylamine and terpyridyl-based dithienylethene (**I-50**) shows the photocyclization-dependent ratiometric fluorescent switch behaviors, affording the ring-closed isomer (**I-5c**). It is worth mentioning that other dithienylethenes (by introducing donor– π (D– π), π –acceptor (π –A), donor– π –donor (D– π –D) [32] and acceptor– π –acceptor (A– π –A) dye moieties into the two sides of the switch) undergo photocyclization reaction with the fluorescent quenching (Scheme 1A).

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodiumbenzophenone (diethyl ether, THF) or calcium hydride (dichloromethane). Methanol was freshly distilled over magnesium-iodine. Triethylamine were freshly distilled over KOH pellets. The Starting materials 1, 2 and 3 were prepared according to the previously reported methods [33]. The photochromic dithienylethenes I-1 [34] and **I-2** [35] were prepared according to literature reports. Elemental analyses (C, H, and N) were performed by the Microanalytical Services, College of Chemistry, CCNU. ¹H and ¹³C NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ¹H and ¹³C NMR chemical shifts are relative to TMS. UV-Vis spectra were obtained on U-3310 UV spectrophotometer. UV light was irradiated using ZF5 UV lamp (302 nm), and visible light irradiation ($\lambda > 420$ nm) was carried out by using a LZG 220 V 500 W tungsten lamp with cutoff filters. The quantum yields were determined by comparing the reaction yields of the diarylethenes against 1, 2-bis (2-methyl-5-phenyl-3-thienyl) cyclopentene.

2.2. Synthesis

2.2.1. Synthesis of the terpyridyl-based dithienylethenes (I-1 to I-5) 2.2.1.1. Synthesis of I-3. Compound 1 (2.64 g, 8.0 mmol) was dissolved in 15 mL of anhydrous THF under nitrogen and cooled to -78 °C. *n*-BuLi (3.20 mL, 2.5 M, 8.0 mmol) was slowly added and the mixture was stirred for 20 min. Then B(OBu)₃ (3.20 mL, 8.0 mmol) was added and stirring was continued at room temperature for 3 h. Then in another flask added compound **3** (2.20 g, 6.8 mmol), Pd(PPh₃)₄ (0.55 g, 7% mol) and Na₂CO₃(aq) (24 mL, 20%



Scheme 1. The structure of other dithienylethenes (A) and the triphenylamine and terpyridyl-based dithienylethene (B).

wt) under nitrogen, then the above system was added to the second flask guickly under nitrogen, and stirring was continued for 17 h at 50 °C. The reaction mixture was then allowed to reach ambient temperature, filtrate, and extracted with dichloromethane. The combined organic layers were dried (Na₂SO₄), concentrated and the product was purified by silica gel column chromatography using (petroleum ether and dichloromethane. v/v = 10:1) as the eluent to give 1.65 g of the product. Yield: 45%. ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, I = 8.5 Hz, Ar-2H), 7.25 (t, I = 7.7 Hz, Ar-4H), 7.10 (d, *I* = 7.8 Hz, Ar-4H), 7.06–6.99 (m, Ar-4H), 6.90 (s, 1H, thiophene-H), 6.62 (s, 1H, thiophene-H), 2.89-2.77 (m, 2H, CH₂), 2.76-2.65 (m, 2H, CH₂), 2.10-2.01 (m, 2H, CH₂), 1.97 (s, 3H, CH₃), 1.88 (s, 3H, CH₃). ^{13}C NMR (100 MHz, CDCl_3): δ 147.49 (s), 146.76 (s), 139.61 (s), 137.33 - 134.95 (m), 133.60 (d, J = 10.2 Hz), 133.18 (s), 129.23 (s), 128.63 (s), 126.42 (d, J = 74.4 Hz), 124.58 (d, J = 61.9 Hz), 123.90 (s), 122.88 (s), 77.32 (s), 77.00 (s), 76.68 (s), 38.37 (d, J = 10.4 Hz), 22.86 (s), 14.28 (d, J = 17.1 Hz). MS: m/z = 537.1346 (M⁺), calculated exact mass: 537.1352. Anal.calcd for C33H28CINS2: C, 73.65; H, 5.24; N, 2.60. Found: C, 73.60; H, 5.20; N, 2.60.

2.2.1.2. Synthesis of **I-4**. The synthesis procedure is similar to **I-3**. The product was purified by silica gel column chromatography using (petroleum ether and dichloromethane, v/v = 10:1) as the eluent to give the product. Yield: 40%. ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 8.6 Hz, 4H, Ar–H), 7.28–7.20 (m, 8H, Ar–H), 7.15–7.07 (m, 8H, Ar–H), 7.02 (dd, *J* = 11.1, 4.4 Hz, 8H, Ar–H), 6.95 (s, 2H, thiophene-H), 2.83 (t, *J* = 7.4 Hz, 4H, CH₂), 2.11–2.04 (m, 2H, CH₂), 1.97 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 147.47 (s), 146.63 (s), 139.35 (s), 136.57 (s), 134.45 (s), 133.62 (s), 128.97 (d, *J* = 43.9 Hz), 128.74–126.74 (m), 126.03 (s), 124.06 (d, *J* = 31.5 Hz), 123.74–123.67 (m), 123.74–123.67 (m), 122.94 (d, *J* = 26.7 Hz), 77.29 (s), 77.23–77.09 (m), 76.82 (d, *J* = 31.9 Hz), 38.46 (s), 22.94 (s), 14.43 (s). MS: *m/z* = 746.10 (M⁺), calculated exact mass: 746.28 (M⁺). Anal.calcd for C₅₁H₄₂N₂S₂: C, 82.00; H, 5.67; N, 3.75. Found: C, 82.01; H, 5.64; N, 3.70.

2.2.1.3. Synthesis of I-1. The synthesis procedure is similar to I-3. The product was purified by silica gel column chromatography using (petroleum ether and acetone, v/v = 20:1) as the eluent to give the product. Yield: 40%. ¹H NMR (400 MHz, CDCl₃): δ 8.75–8.66 (m, 6H, pyridine-H), 7.87 (dd, J = 15.5, 7.9 Hz, 4H, pyridine-H), 7.76 (d, J = 8.4 Hz, 2H, Ar–H), 7.32 (t, J = 19.7 Hz, 2H, Ar-H), 7.09 (s, 1H, thiophene-H), 6.64 (s, 1H, thiophene-H), 2.96-2.79 (m, 2H, CH2), 2.79-2.67 (m, 2H, CH2), 2.13-1.97 (m, 5H, CH₂-CH₃), 1.90 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 156.51 (s), 156.03 (dd, J = 30.5, 12.5 Hz), 149.22 (d, J = 34.5 Hz), 136.83 (s), 135.09 (s), 132.00 (s), 128.79 (s), 127.61 (s), 126.73 (s), 125.88 (d, J = 58.3 Hz), 125.59 (s), 125.53 (s), 125.72–123.41 (m), 121.31 (s), 118.38 (d, J = 10.9 Hz), 77.29 (s), 76.81 (d, J = 32.0 Hz), 76.41–76.11 (m), 38.35 (d, J = 9.6 Hz), 22.84 (s), 14.43 (s), 14.18 (s). MS: $m/z = 601.02 \text{ (M}^+\text{)}$, calculated exact mass: 601.14 (M⁺). Anal.calcd for C₃₆H₂₈ClNS₂: C, 71.80; H, 4.69; N, 6.98. Found: C, 71.77; H, 4.64; N, 6.97.

2.2.1.4. Synthesis of **I-2**. The synthesis procedure is similar to **I-3**. The product was purified by silica gel column chromatography using (petroleum ether and acetone, v/v = 10:1) as the eluent to give the product. Yield: 30%. ¹H NMR (400 MHz, CDCl₃): δ 8.79–8.69 (m, 8H, pyridine-H), 8.64 (d, J = 7.9 Hz, 4H, pyridine-H), 7.92–7.81 (m, 8H, pyridine-H), 7.63 (d, J = 8.3 Hz, 4H, Ar–H), 7.36–7.29 (m, 4H, Ar–H), 7.16 (s, 2H, thiophene-H), 2.89 (t, J = 7.3 Hz, 4H, CH₂), 2.12 (dd, J = 14.6, 7.6 Hz, 2H, CH₂), 2.04 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 155.95 (d, J = 31.2 Hz), 149.39 (s), 149.01 (s), 138.91 (s), 136.79 (t, J = 22.1 Hz), 135.13 (s), 134.59 (s), 127.62 (s), 125.55 (s), 124.43 (s), 123.73 (s), 121.28 (s), 118.33 (s),



Scheme 2. The synthetic routes of terpyridyl-based dithienylethenes.

78.08–76.22 (m), 76.82 (d, J = 32.0 Hz), 76.82 (d, J = 32.0 Hz), 38.48 (s), 31.53 (s), 22.97 (s), 14.31 (d, J = 43.1 Hz). MS: m/z = 874.20 (M⁺), calculated exact mass: 874.29 (M⁺). Anal.calcd for C₅₇H₄₂N₆S₂: C, 78.23; H, 4.84; N, 9.60. Found: C, 78.20; H, 4.85; N, 9.60.

2.2.1.5. Synthesis of **I-5**. The synthesis procedure is similar to **I-3**. The product was purified by silica gel column chromatography using (petroleum ether and acetone, v/v = 20:1) as the eluent to give the product. Yield: 35%. ¹H NMR (400 MHz, CDCl₃): δ 8.90–8.56 (m, 6H, pyridine-H), 7.87 (s, 4H, pyridine-H), 7.62 (d, *J* = 5.1 Hz, 2H, Ar–H), 7.33 (dd, *J* = 34.9, 24.2 Hz, 8H, Ar–H), 7.16–6.92 (m, 10H, Ar–H, thiophene-H), 2.85 (s, 4H, CH₂), 2.09 (s, 2H, CH₂), 2.00 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 156.17 (s), 155.87 (s), 151.67–150.48 (m), 149.26 (d, *J* = 37.3 Hz), 148.02 (s),

147.09 (d, J = 80.0 Hz), 139.51 (s), 138.80 (s), 136.85 (d, J = 7.1 Hz), 136.59 (s), 135.23 (d, J = 19.0 Hz), 134.89 (dd, J = 68.1, 35.5 Hz), 133.67 (s), 128.97 (d, J = 47.2 Hz), 127.62 (s), 127.42–124.36 (m), 124.36–123.48 (m), 122.93 (d, J = 21.7 Hz), 121.31 (s), 118.35 (s), 77.30 (s), 76.99 (s), 76.67 (s), 38.47 (s), 22.97 (s), 14.48 (d, J = 7.4 Hz). MS: m/z = 811.2908 (M + H) ⁺, calculated exact mass: 810.2851(M)⁺. Anal.calcd for C₅₄H₄₂N₄S₂: C, 79.97; H, 5.22; N, 6.91. Found: C, 79.93; H, 5.25; N, 6.90.

3. Results and discussion

3.1. Synthesis

Triphenylamine served as an electron donor, and was widely



Fig. 1. Single crystal structure of triphenylamine-based dithienylethene I-3.



Scheme 3. Photochromism and photograph of the color of compound I-5 in THF (2.0 \times 10-5 mol/L).



Fig. 2. Absorption spectral changes (A) and emission intensity changes ($\lambda_{ex} = 340$ nm) (B) of 1-5 by photoirradiation in THF (2.0 × 10⁻⁵ mol/L).



Fig. 3. Absorption spectral changes of I-1 (A), I-2 (B), I-3 (C) and I-4 (D) by photoirradiation in THF (2.0×10^{-5} mol/L).

Table 1
Absorption characteristics and photochromic quantum yields of the terpyridyl-based dithienylethenes in THF (2.0 \times 10 ⁻⁵ mol/L).

Compound	$\lambda_{\rm max}^{\rm Abs}/{\rm nm^a}~(e imes 10^{-4})$	$\lambda_{\rm max}^{\rm Abs}/{ m nm^b}~(arepsilon imes 10^{-4})$	Φ^{c}	${\it \Phi}^{ m c}$	
	(Open)	(PSS)	$\varphi_{o-c}(\lambda/nm)$	$\varphi_{c-o}(\lambda/nm)$	
I-1	282(6.65)	512(2.15)	0.43(512)	0.006(282)	
I-2	286(7.30)	566(3.15)	0.49(566)	0.011(286)	
I-3	352(3.90)	504(2.75)	0.48 (504)	0.007(352)	
I-4	354(4.90)	552(2.80)	0.48 (552)	0.006 (354)	
I-5	284(6.30)	565(2.55)	0.43(565)	0.005(284)	

^a Absorption maxima of open-ring isomers.
 ^b Absorption maxima of closed-ring isomers.

^c Quantum yields of open-ring (φ_{c-o}) and closed-ring isomers (φ_{o-c}), respectively.



Fig. 4. Emission intensity changes of **I-5** at 407 nm, 496 nm and 530 nm in THF (2.0×10^{-5} mol/L) with UV light irradiation ($\lambda_{ex} = 340$ nm).



Fig. 5. Fluorescence intensity and the fluorescence change of **I-5** before (black line) and after (red line) UV irradiation in THF ($2.0 \times 10^{-5} \text{ mol/L}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

used in memory storage. A terpyridyl unit was chosen as the electron acceptor because of its electron-deficient properties and good rigid plane. Hence, the photochromic dithienylethenes **I-1** to

I-5 bearing triphenylamine and terpyridine functionality were synthesized as shown in Scheme 2. They were prepared by modification of a literature procedure [36–40]. All of the newly synthesized triphenylamine and terpyridyl-based dithienylethenes were characterized by ¹H and ¹³C NMR spectroscopy, EI mass spectroscopy and elemental analysis. The structure of **I-3** was also verified by X-ray crystallography (Fig. 1). The crystal data and structure refinement for **I-3** are summarized in Table S1. A single crystal of **I-3** suitable for X-ray diffraction analysis was grown by slow diffusion of hexane into a solution of this complex in dichloromethane.

3.2. Photochromism of the terpyridyl-based dithienylethenes

The photoisomerization behaviors of I-5 induced by photoirradiation in THF were measured at room temperature. It underwent photoisomerization between the ring-opened isomer and ring-closed isomer upon alternating irradiation with UV light $(\lambda = 302 \text{ nm})$ and visible light $(\lambda > 402 \text{ nm})$ (Scheme 3). As shown in Fig. 2A, the absorption maximum of terpyridyl-based dithienylethene with triphenylamine I-5 was observed at 284 nm $(\varepsilon = 6.30 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$ as a result of a π - π * transition [41]. This colorless solution turned purple and a new absorption band centered at 565 nm ($\varepsilon = 2.55 \times 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) appeared when it was irradiated with 302 nm UV light. Upon irradiation with visible light (λ > 402 nm), the colored ring-closed isomer of **I-5** underwent a cycloreversion reaction to give the initial colorless ring-opened isomer (Scheme 3). The cyclization and cycloreversion quantum vields of I-5 were 0.43 and 0.005, respectively. Similar photoisomerization behaviors were also observed for solutions of I-1, I-2, I-3 and I-4, as shown in Fig. 3. The photochromic parameters of I-1 to I-5 are summarized in Table 1. From this data, it was found that the symmetry of molecular structure had an effect on their absorption wavelength. When compared with the absorption maximum of unilateral derivatives in the visible region, the corresponding bilateral derivatives displayed a red shift of ~50 nm. Fig. S1 and Fig. S2 show that all of them have good fatigue resistance and thermal stability. The response times of I-1 to I-5 are shown in Fig. S3.



Fig. 6. Emission intensity changes of I-1 (A), I-2 (B), I-3 (C) and I-4 (D) in THF (2.0×10^{-5} mol/L) with UV/vis light irradiation ($\lambda_{ex} = 340$ nm).

Table 2

Fluorescence emission characteristics and fluorescent quantum yields of the terpyridyl-based dithienylethenes before and after UV irradiation in THF ($2.0 \times 10^{-5} \text{ mol/L}$).

Compound	$\lambda_{\rm max}^{\rm f}/{\rm nm}^{\rm a}$	λ_{max}^{f}/nm^{b}	φ_{f}
I-1	435	435	0.034
I-2	423	446	0.039
I-3	413	413	0.033
I-4	416	421	0.038
I-5	407, 530	496	0.026

• f Fluorescent quantum yields of open-ring.

^a Emission maxima of open-ring isomers.

^b Emission maxima of closed-ring isomers.

3.3. Fluorescence of the terpyridyl-based dithienylethenes

The change in fluorescence for I-5 induced by photo-irradiation in THF was measured at room temperature (Fig. 2B). It was surprising that the emission intensity at 407 nm and 530 nm of I-5 rapidly decreased and a new emission band at 496 nm slowly appeared with a change in color from yellow to blue upon irradiation with UV light at 302 nm (Figs. 2B, 4 and 5). Irradiation with visible light (λ > 402 nm) resulted in a cycloreversion reaction and restored the original emission spectrum. The photocyclizationdependent ratiometric fluorescent switch behaviors of I-5 were almost different from the conventional photochromic fluorescence switches, most of whose fluorescence intensity was quenched with regard to photocyclization (Scheme 1A) [14–19,42]. But different fluorescent properties were observed for solutions of I-1 to I-4 upon irradiation with UV light at 302 nm (in Fig. 6). As shown in Fig. 6A, I-1 exhibited blue fluorescent emission at 435 nm in THF. The emission intensity of dithienylethene I-1 rapidly decreased upon irradiation with UV light at 302 nm with the structure changing from the open isomer to the closed isomer. Moreover, a switch-on fluorescence could be found when the closed-ring isomers underwent visible light irradiation. Similar fluorescent properties were also observed for solutions of I-2, I-3 and I-4, as

shown in Fig. 6. Their fluorescence changes were in good agreement with conventional photochromic fluorescence switches (Scheme 1A). In comparison to the corresponding unilateral and bilateral derivatives I-1 to I-4, dithienylethene I-5 shows obvious fluorescence color change characteristics induced by photoirradiation. It means the triphenylamine and terpyridyl-based dithienylethene I-5 showed the photocyclization-dependent ratiometric fluorescent switch behaviors (Scheme 1B and Fig. 5). Fluorescence emission characteristics and fluorescent quantum yields of I-1 to I-5 are summarized in Table 2. When compared with the emission maxima of open-ring isomers of I-10 to I-40, two emission maxima were observed in I-50, which was possible due to the donor-acceptor system.

3.4. The density functional theory calculations of the terpyridylbased dithienylethenes

In order to further investigate the photocyclization-dependent ratiometric fluorescent switch behaviors of I-5, density functional theory calculations at the B3LYP/6e31G* level using the Gaussian 09 program were used, as presented in Fig. 7. From the frontier molecular orbitals, we could observe the electron density. For I-50, the electron density chiefly located in the triphenylamine group in HOMO orbitals, and the LUMO of I-50 was distributed over the terpyridyl group possible due to the donor-acceptor system of I-50. The energy level gap was 3.24 eV. However, the HOMO of I-5c was distributed over the photochromic molecule and parts of triphenylamine group, and the LUMO of I-5c was distributed over the photochromic molecule and parts of terpyridyl and triphenylamine groups. The energy level gap was 2.30 eV. Furthermore, the photoisomerization also influenced the molecular donor-acceptor system, which resulted in the photocyclization-dependent ratiometric fluorescent switch behaviors. However, from the frontier molecular orbitals of I-1 to I-4, we observed their electron density was different from the donor-acceptor system of I-5. As shown in Fig. S4, we found that HOMO of terpyridyl-based dithienylethenes



Fig. 7. The optimized structures and plots of HOMO and LUMO of I-50 and I-5c at B3LYP/6-31G* level, by using Gaussian 09 program.

I-10 and **I-20** was distributed over the photochromic molecule, but the LUMO of them was distributed over the terpyridyl unit. Their energy level gap was 3.77 eV and 3.73 eV, respectively. However, both HOMO and LUMO of their closed forms were distributed over the dithienylethene and part of terpyridyl group. For the triphenylamine-based dithienylethenes **I-30** and **I-40**, their HOMO and LUMO were distributed over the triphenylamine group, and HOMO and LUMO of their closed forms were distributed over the dithienylethene and part of triphenylamine unit. Specially, comparing with the corresponding unilateral and bilateral derivatives **I-1** to **I-4**, the energy level gap of **I-5** both in the open form and closed form was the smallest.

4. Conclusions

In summary, we have reported some terpyridyl-based dithienylethenes. Their structures were well characterized by NMR spectroscopy and mass spectrometry. Their photoisomerization and changes in emission properties have been fully investigated. UV/vis absorption spectra and fluorescence spectra indicated that these dithienylethenes displayed obvious photochromism and fluorescent switch properties. Specially, I-5 showed the photocyclization-dependent ratiometric fluorescent switch behaviors. Density functional theory indicated that the photocyclization-dependent ratiometric florescent changes due to the donor-acceptor system of I-5. This work provides an alternative strategy for designing the photocyclization-dependent ratiometric fluorescent switch.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Nos. 21072070, 21272088, 21472059 and 21602122), the Program for Academic Leader in Wuhan Municipality (No. 201271130441), the Natural Science Foundation of Ningbo City (No. 2016A610051), the financially supported by research funds of NBU (No. ZX2015000586) and the K. C. Wong Magna Fund in Ningbo University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.08.047.

References

- [1] Feringa BL. Molecular Switches. Weinheim, Germany: Wiley-VCH; 1990.
- [2] Duerr H, Bouas-Laurent H. Photochromism: Molecules and Systems. Amsterdam: Elsevier; 2003.
- [3] For selected reviews, see Griffiths J. II. Photochemistry of azobenzene and its derivatives. Chem Soc Rev 1972;1:481–93.
- [4] For selected reviews, see Yokoyama Y. Fulgides for memories and switches. Chem Rev 2000;100:1717–39.
- [5] For selected reviews, see Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100:1685–716.
- [6] For selected reviews, see Kllajn R. Spiropyran-based dynamic materials. Chem Soc Rev 2014;43:148–84.
- [7] For selected reviews, see Tian H, Yang S. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97.
- [8] For selected reviews, see Dong H, Zhu H, Meng Q, Gong X, Hu WP. Organic photoresponse materials and devices. Chem Soc Rev 2012;41:1754–808.
- [9] Zou Y, Yi T, Xiao S, Li F, Li C, Gao X, et al. Amphiphilic diarylethene as a photoswitchable probe for imaging living cells. J Am Chem Soc 2008;130:15750–1.
- [10] Yin J, Lin Y, Cao XF, Yu GA, Tu HY, Liu SH. The synthesis and photochromic properties of two *bis*(phosphine) ligands based on dithienylethene backbone and their oxides, sulfurets and selenides. Dyes Pigm 2009;2:152–5.
- [11] Al-Atar U, Fernandes R, Johnsen B, Baillie D, Branda NR. A photocontrolled molecular switch regulates paralysis in a living organism. J Am Chem Soc 2009;131:15966-7.
- [12] Li ZY, Zhang C, Ren YL, Liu SH, Yin J. Amide- and urea-functionalized

dithienylethene: synthesis, photochromism, and binding with halide anions. Org Lett 2011;22:6022-5.

- [13] Pang SC, Hyun H, Lee S, Jang D, Lee MJ, Kang SH, et al. Photoswitchable fluorescent diarylethene in a turn-on mode for live cell imaging. Chem Commun 2012;48:3745–7.
- [14] Liu K, Wen Y, Shi T, Li Y, Li F, Zhao Y, et al. DNA gated photochromism and fluorescent switch in a thiazole orange modified diarylethene. Chem Commun 2014;50:9141–4.
- [15] Li ZY, Hu F, Liu G, Xue W, Chen XQ, Liu SH, Yin J. Photo-responsive [2]catenanes: synthesis and properties. Org Biomol Chem 2014;12:7702–11.
- [16] Hu F, Huang J, Cao MJ, Chen Z, Yang YW, Liu SH, Yin J. Dithienylethene-based rotaxanes: synthesis, characterization and properties. Org Biomol Chem 2014;12:7712–20.
- [17] Kawai T, Sasaki T, Irie M. A photoresponsive laser dye containing photochromic dithienylethene units. Chem Commun 2001:711–2.
- [18] Irie M, Fukaminato T, Sasaki T, Tamai N, Kawai T. Organic chemistry: a digital fluorescent molecular photoswitch. Nature 2002;420:759–60.
- [19] Fukaminato T, Sasaki T, Kawai T, Tamai N, Irie M. Digital photoswitching of fluorescence based on the photochromism of diarylethene derivatives at a single-molecule level. J Am Chem Soc 2004;126:14843–9.
- [20] For selected reviews, see Zhang J, Wang J, Tian H. Taking orders from light: progress in photochromic bio-materials. Mater Horiz 2014;1:169–84.
- [21] Jiang G, Wang S, Yuan W, Jiang L, Song Y, Tian H, et al. Highly fluorescent contrast for rewritable optical storage based on photochromic bisthienylethene-bridged naphthalimide dimer. Chem Mater 2006;18:235–7.
- [22] Ohara H, Morimoto M, Irie M. Photochromism of dithienylethene single crystals having anthracene substituents. Photochem Photobiol Sci 2010;9: 1079–81.
- [23] Tan WJ, Li X, Zhang JJ, Tian H. A photochromic diarylethene dyad based on perylene diimide. Dyes Pigm 2011;89:260–5.
- [24] Fukaminato T, Doi T, Tamaoki N, Okuno K, Ishibashi Y, Miyasaka H, Irie M. Single-molecule fluorescence photoswitching of a diaryletheneperylenebisimide dyad: non-destructive fluorescence readout. J Am Chem Soc 2011;133:4984–90.
- [25] Hu F, Cao M, Ma X, Liu SH, Yin J. Visible-light-dependent photocyclization: design, synthesis, and properties of a cyanine-based dithienylethene. J Org Chem 2015;80:7830–5.
- [26] Nolan EM, Lippard SJ. Tools and tactics for the optical detection of mercuric ion. Chem Rev 2008;108:3443–80.
- [27] Lee MH, Cho BK, Yoon JY, Kim JS. Selectively chemodosimetric detection of Hg(II) in aqueous media. Org Lett 2007;9:4515–8.
- [28] Kumari N, Dey N, Jha S, Bhattacharya S. Ratiometric, reversible, and partsper billion level detection of multiple toxic transition metal ions using a singleprobe in micellar media. ACS Appl Mater Interfaces 2013;5:2438–45.
- [29] Zhang Y, Chen H, Chen D, Wu D, Chen Z, Zhang J, et al. A colorimetric and ratiometric fluorescent probe for mercury (II) inlysosome. Sensors Actuators B 2016;224:907–14.
- [30] Hu F, Hu M, Liu W, Yin J, Yu G, Liu SH. Synthesis and photochromic properties of triazole-bridged dithienylethene compounds with pyrene units. Tetrahedron Lett 2015;56:452–7.
- [31] Mengel AKC, He B, Wenger OS. A triarylamine-triarylborane dyad with a photochromic dithienylethene bridge. J Org Chem 2012;77:6545–52.
- [32] Fukudome M, Kamiyama K, Kawai T, Irie M. Photochromism of a dithienylethene having diphenylamino side groups in the bulk amorphous phase. Chem Lett 2001;01:70-1.
- [33] Piao X, Zou Y, Wu J, Li C, Yi T. Multiresponsive switchable diarylethene and its application in bioimaging. Org Lett 2009;17:3818–21.
- [34] Xu LJ, Xu GT, Chen ZN. Recent advances in lanthanide luminescence with metalorganic chromophores as sensitizers. Coord Chem Rev 2014;273–274:47–62.
 [35] Li J, Wang JY, Chen ZN. Sensitized Eu^{III} luminescence through energy transfer
- [35] Li J, Wang JY, Chen ZN. Sensitized Eu^{***} luminescence through energy transfer from PtM₂ (M = Ag or Au) alkynyl chromophores in PtM₂Eu₂ heteropentanuclear complexes. J Mater Chem C 2013;1:3661–8.
- [36] Li X, Shi L, Zhang L, Wen H, Chen ZN. Syntheses, structures, and sensitized lanthanide luminescence by Pt Ln (Ln) Eu, Nd, Yb) energy transfer for heteronuclear PtLn₂ and Pt₂Ln₄ complexes with a terpyridyl-functionalized alkynyl ligand. Inorg Chem 2007;46:10892–900.
- [37] Zhong YW, Vila N, Henderson JC, Abruña HD. Dithienylcyclopentenes-Containing transition metal bisterpyridine complexes directed toward molecular electronic applications. Inorg Chem 2009;48:991–9.
- [38] Zhong YW, Vila N, Henderson JC, Flores-Torres S, Abruña HD. Dinuclear transition-metal terpyridine complexes with a dithienylcyclo- pentene bridge directed toward molecular electronic applications. Inorg Chem 2007;46: 10470–2.
- [39] Migulin VA, Krayushkin MM, Barachevsky VA, Kobeleva OI, Valova TM, Lyssenko KA. Synthesis and characterization of nonsymmetric cyclopentenebased dithienylethenes. J Org Chem 2012;77:332–40.
- [40] Migulin VA, Krayushkin MM, Barachevsky VA, Kobeleva OI, Novikov VV, Lyssenko KA. Synthesis and studies of symmetric dibenzothienylcyclopentenes. Tetrahedron 2015;71:584–98.
- [41] Li Z, Liao L, Sun W, Xu C, Zhang C, Fang C, Yan C. Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative. J Phys Chem C 2008;112:5190–6.
- [42] Hu F, Jiang L, Cao M, Xu Z, Huang J, Wu D, et al. Cyanine-based dithienylethenes: synthesis, characterization, photochromism and biological imaging in living cells. RSC Adv 2015;5:5982–7.