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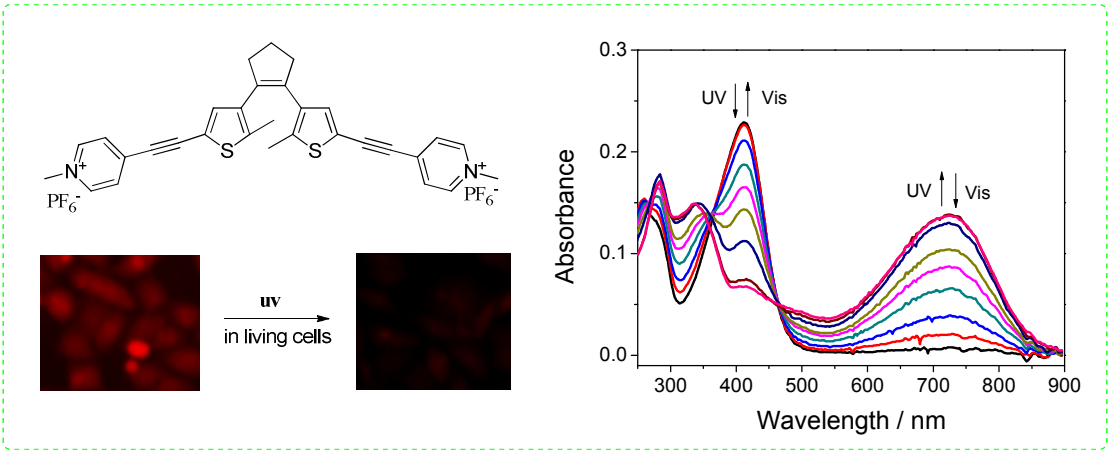
Graphical Abstract



Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Cyanine-based dithienylethenes: synthesis, characterization, photochromism and biological imaging in living cells †

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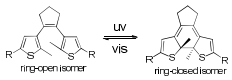
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Photochromic materials have been widely used in the many fields such as electro-optical functional materials and novel bio-materials. In this study, six cyanine-based dithienylethene compounds were successfully developed, and their photoisomerization and emission change properties were fully investigated. The results indicated that the UV/vis absorption of pyridinium-based compounds displayed the near-infrared absorption, while their fluorescence showed the quenching emission as a result of the changes structure from open-ring isomers to closed-ring isomers. Therefore these cyanine-based compounds could be applied not only in photochromic materials, but also they could be used as a fluorescence switch. Accordingly, one of these compounds was successfully used in the biological imaging of living cells. These results suggest that cyanine-based dithienylethenes may be used as photoswitchable bio-materials in the future.

Introduction

Photochromic materials can undergo conformational change between two isomers with changes in the absorption spectra with UV and visible light, and have significant potential applications in many fields such as electro-optical functional materials and novel bio-materials. [1] Recently, there has been increasing interest in photochromic dithienylethene derivatives due to their remarkable fatigue resistance, excellent thermally irreversible properties, high sensitivity and fluorescent switchable character. [2] It is well known that near-infrared light has deeper penetration and weaker energy than visible light, and is more suitable for application in electro-optical functional materials and bio-materials. [3] Therefore, to make the characteristic low-energy absorption band of photoisomerization reach the near-infrared region is significant. In addition to the development of near-infrared photochromic dithienylethenes, two main strategies have been employed to design materials with excellent near-infrared photochromic behavior. On the one hand, increasing the extent of π-conjugation of the dithienylethenes by changing the functional groups on the R (Scheme 1) sites of the dithienylethene backbone or substituting the bridge unit (cyclopentene) by other conjugated moieties has become a popular strategy, however, these compounds usually have poor stability. [4] On the other hand, the functional groups on the R sites have also been substituted by cyanine moieties. It is well known that cyanines such as indoline and pyridinium are regarded as successful candidates for near-infrared absorption when they are introduced into the conjugated system. [5] Herein, we present six examples of cyanine-based dithienylethenes with pyridinium moieties on the R sites, and their photoisomerization properties and emission spectra were fully investigated. The results showed that (1) the UV/vis absorption of pyridinium-based compounds displayed the near-infrared absorption, and (2) their fluorescence showed the quenching emission as a result of the changes structure in the process of photoisomerization. These researches suggested that they could be used as the near-infrared photochromic dyes. At the same time, the property of fluorescence switch made them have a capability of fluorescence imaging in living cells.

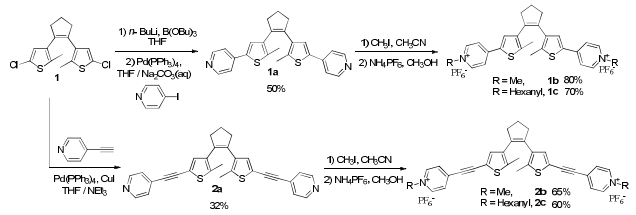


Scheme 1. Ring-Opening and Ring-Closing Photoisomerization of Dithienylethenes.

Result and discussion

1. Design and synthesis

The backbone of dithienylethene was synthesized via the McMurry coupling reaction using previously reported methods.[6] The McMurry coupling reaction is an organic reaction in which two ketone or aldehyde groups are coupled to an alkene using titanium chloride compound ($TiCl_4$) and a reducing agent (Zn). The photochromic cyanine-based dithienylethenes **1a** was prepared using Suzuki coupling reaction. The Suzuki coupling reaction is the organic reaction where the coupling partners are a boronic acid with a halide catalyzed by a palladium (0) complex. **1b** and **1c** were prepared by a previously published method with modifications.[5a, 7] **2a** was synthesized by the Sonogashira coupling reaction. The Sonogashira reaction is a cross-coupling reaction used in organic synthesis to form carbon-carbon bonds. It employs a palladium catalyst to form a carbon-carbon bond between a terminal alkyne and an aryl or vinyl halide. **2b** and **2c** were prepared by an analogous method to **1b** and **1c**. The synthetic route is outlined in Scheme 2. Their identities were confirmed by ^1H, ^{13}C NMR, ESI mass spectrometry, and satisfactory elemental analyses.



Scheme 2. The synthetic routes of six cyanine-based dithienylethenes.

2. Photochromism of Cyanine-Based Dithienylethene.

Considering the influence of solvent on dyes, the UV/vis absorption of **1a-1c** and **2a-2c** in the photostationary state following irradiation with 302 nm UV light was investigated in different solvents. [5a] Compared with the absorption in dimethyl sulfoxide, methanol, acetonitrile and dichloromethane, dithienylethenes **1a-1c** and **2a-2c** displayed different absorption following photoirradiation with UV light (See supporting information Figure S1). Among these compounds, the observed absorption of **1b** was in good agreement with a previous report. [5a] This was assigned to a probable solvent-induced intramolecular charge transfer (CT) absorption band. [8] Compared with the new absorption band in near-infrared region (500-900 nm) [5a] of **2b** in dimethyl sulfoxide, it red-shifted 95 nm in dichloromethane. **1c** and **2c** also showed a similar red-shift in dichloromethane. Accordingly, dichloromethane was selected as the solvent to investigate photoisomerization behavior. Similar photochromic behavior in different solvents was also observed for the other cyanine-based dithienylethenes.

The photoisomerization behaviors of **1a-2c** induced by photoirradiation in CH_2Cl_2 were measured at room temperature. They underwent photoisomerization between ring-open isomer and ring-closed isomer following alternating irradiation with UV light (λ = 302 nm) and visible light (λ > 402 nm). As shown in Figure 1(A), the absorption maximum of compound **1b** was observed at 340 nm ($\varepsilon = 2.06 \times 10^4$ L mol^{-1} cm^{-1}) and 382 nm ($\varepsilon = 2.19 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π-π* transition. [9] This colorless solution turned yellow-green and a new absorption band centered at 726 nm ($\varepsilon = 2.07 \times 10^4$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light. Following irradiation with visible light (λ > 402 nm), the colored ring-closed isomer of **1b** underwent a cycloreversion reaction to the initial colorless ring-open isomer. The cyclization and cycloreversion quantum yields of **1b** were 0.239 and 0.028, respectively. The photochromic switching of **1b** was reversible in CH_2Cl_2 solution (See supporting information in Figure S2). The stability test of **1b** was shown in Figure S7. Similarly, the absorption maximum of compound **2b** in CH_2Cl_2 was observed at 416 nm ($\varepsilon = 1.14 \times 10^4$ L mol^{-1} cm^{-1}) (Figure 1(B)) and this colorless solution turned shadowy green and a new absorption band centered at 736 nm ($\varepsilon = 0.68 \times 10^4$ L mol^{-1} cm^{-1}) appeared when it was irradiated with 302 nm UV light, as a result of a ring-closure reaction to give the ring-closed isomer of **2b**. Following irradiation with visible light (λ > 402 nm), the colored ring-closed isomer of **2b** underwent a cycloreversion reaction to the initial colorless ring-open isomer. The cyclization and cycloreversion quantum yields of **2b** were 0.728 and 0.055, respectively. Additionally, compared with **1b**, **2b** displayed higher cyclization and cycloreversion quantum yields. Moreover, the absorption maximum and the new absorption band [5a] of **2b** showed 34 nm and 10 nm red shifts, possibly due to the larger π-conjugation. Specially, **2b** showed a better thermal stability (See supporting information in Figure S7). The results suggested that these pyridinium-based dithienylethenes may be used as near-infrared photoswitchable materials. Similar photochromic behaviors were also observed in **1c** and **2c** (Figure S3). Furthermore, we found that the pyridinium-based dithienylethenes showed an approximate 180-190 nm red-shift in comparison to the corresponding pyridine-based dithienylethenes **1a** and **2a** (Figure S3)**,** due to the existence of the cyanine moiety. The photochromic parameters of **1a-2c** are summarized in Table 1.

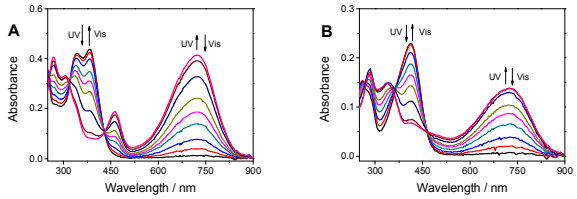


Figure 1. Absorption spectral changes of **1b** (A), **2b** (B) by photoirradiation in CH_2Cl_2 (2.0×10^{-5} mol/L).

Table 1. Absorption characteristics and photochromic quantum yields of cyanine-based dithienylethenes in CH_2Cl_2 (2.0×10^{-5} mol/L)

Compound	λ_{max}^{Abs} / nm [a] ($\varepsilon \times 10^4$)	λ_{max}^{Abs} / nm [b] ($\varepsilon \times 10^4$)	Φ [c]	
	(Open)	(PSS)	$\varphi_{o\text{-}c}$(λ / nm)	$\varphi_{c\text{-}o}$(λ / nm)
1a	282(3.56)	552(1.58)	0.321(552)	0.018(282)
1b	382(2.19)	726(2.07)	0.239(726)	0.028(382)
1c	386(2.47)	726(2.50)	0.194(726)	0.026(386)
2a	338(2.84)	566(1.12)	0.458(566)	0.022(338)
2b	416(1.14)	736(0.68)	0.728(736)	0.055(416)
2c	416(4.82)	736(0.87)	0.570(454)	0.013(237)

a Absorption maxima of open-ring isomers.

b Absorption maxima of closed-ring isomers.

c Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.

3. Fluorescence of Cyanine-Based Dithienylethene.

The fluorescent properties of cyanine-based dithienylethenes were investigated and the fluorescence changes in **1a-2c** induced by photoirradiation in CH_2Cl_2 were measured at room temperature. As shown in Figure 2(A), **1b** exhibited yellow fluorescent emission at 555 nm in CH_2Cl_2. Its fluorescent quantum yield was measured to be 0.0126, using quinoline sulfate (φ_f = 0.55, in 0.1 M aqueous H_2SO_4) as a reference. The emission intensity of dithienylethene **1b** rapidly decreased on irradiation with 302 nm UV light and the structure changed from the open state to the closed state. Dithienylethene **2b** showed emission at 610 nm with a fluorescent quantum yield (0.00091) in Figure 2(B), and a quenching fluorescence was observed with UV irradiation. Moreover, a switch-on fluorescence was found when the closed-ring isomers underwent visible photoirradiation. Similar fluorescent properties were also observed for solutions of **1c** and **2c** (Figure S4). The fluorescent quantum yield of **1c** and **2c** were 0.0078 and 0.00067, respectively.

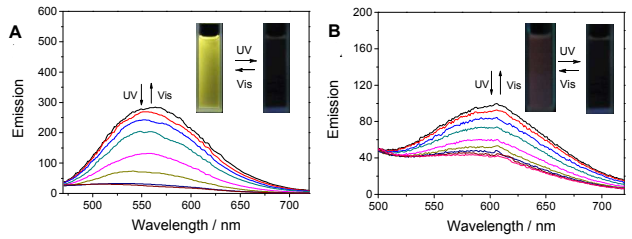


Figure 2. Emission intensity changes and the Fluorescence changes of **1b** (A) and **2b** (B) in CH_2Cl_2 (2.0×10^{-5} mol/L) with UV/vis light irradiation (λ_{ex} = 370 nm).

4. Density functional theory (DFT) calculation of Cyanine-Based Dithienylethene.

The density functional theory (DFT) calculation was subsequently performed to gain a deeper insight into the molecular structures of the open-ring and closed-ring forms. Details of the optimized structures are shown in Figure 3 and Figure S5. For the open forms, the optimized structures of $\mathbf{1b_o}$ and $\mathbf{2b_o}$ showed good symmetry. The dihedral angles between the cyclopentene ring and the two thiophene rings of $\mathbf{2b_o}$ were 46.00(1)º and 51.08(2)º, respectively. The distance between the centers of the two thiophene rings was 4.994(1) Å. Furthermore, the unparallel confirmation of this molecule was useful for the photocyclization reaction. [2a] In addition, the distance between the two reactive carbons was 3.667 Å, which was short enough for the cyclization reaction to take place. Photochromic reactivity usually only appears when the distance between the reactive carbon atoms is less than 4.2 Å in the solid state. [10] The DFT calculation suggested that the LUMO of $\mathbf{1b_c}$ was largely localized on two pyridine units and the energy level gap was 1.61 ev. As shown in Figure 3, for $\mathbf{2b_c}$, the HOMO was largely localized on the photochromic moiety, the LUMO was largely localized on two pyridine ethynylene units, and the energy level gap was 1.33 ev. Furthermore, we found that the pyridinium-based dithienylethenes had a lower energy level compared with the corresponding pyridine-based dithienylethenes, **1a** and **2a** (Figure S5)**,** due to the existence of the cyanine moiety. Moreover, the energy level gaps of their closed isomers were smaller in comparison to the corresponding open isomers. In addition, the HOMO of their open isomers was largely localized on the photochromic moiety, and the LUMO was largely localized on two pyridine units. Unlike the open isomers, the HOMO and LUMO of the closed isomers were both largely localized on the photochromic molecule and two pyridine units. The energy of frontier molecular orbitals in the model complexes of **1a**-**2c** is summarized in Table 2.

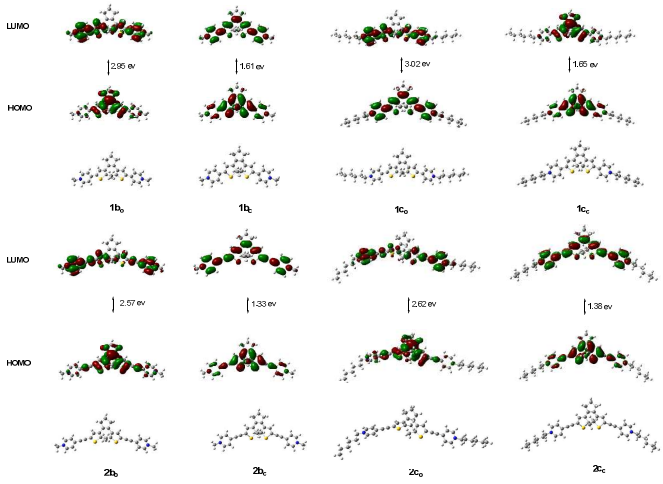


Figure 3. The optimized structures and Plots of HOMO and LUMO for cyanine-based dithienylethenes at B3LYP/6-31G* level, by using Gaussian 09 program.

Table 2. Energy of frontier molecular orbitals in the model complexes of cyanine-based dithienylethenes

Compound	HOMO [ev]	LUMO [ev]	E_g [ev]
$\mathbf{1a_o}$	-5.71	-1.52	4.19
$\mathbf{1a_c}$	-4.86	-2.54	2.33
$\mathbf{1b_o}$	-10.48	-7.53	2.95
$\mathbf{1b_c}$	-9.91	-8.30	1.61
$\mathbf{1c_o}$	-10.31	-7.29	3.02
$\mathbf{1c_c}$	-9.71	-8.07	1.65
$\mathbf{2a_o}$	-5.65	-1.85	3.79
$\mathbf{2a_c}$	-4.83	-2.72	2.08
$\mathbf{2b_o}$	-9.79	-7.22	2.57
$\mathbf{2b_c}$	-9.12	-7.79	1.33
$\mathbf{2c_o}$	-9.64	-7.03	2.62
$\mathbf{2c_c}$	-8.95	-7.58	1.38

5. Cell imaging of Cyanine-Based Dithienylethene.

The properties described above inspired us to investigate photochromism in living cells. Herein, cyanine-based dithienylethene **2b** was used in cells and imaged by fluorescence microscopy. HeLa cells were incubated with **2b** (50 μM) at 5% CO_2 and 37℃ for 4 h. Intensity of fluorescence was observed in HeLa cells when fixed cells were incubated with **2b**. As shown in Figure 4, strong red fluorescence of **2b** in HeLa cells was observed. When selected cells was irradiated with 365 nm light for 6 min, the red fluorescence was gradually bleached, which indicated that the majority of **2b** was transformed from the open isomer to the closed isomer. HeLa cells were not obviously reduced after repeating this process several times. The cytotoxicity of **2b** was checked by a MTT assay (Figure S6). After incubation for 24 h in the presence of 20.0-60.0 μM **2b**, more than 95% cell viability was observed, a low level of toxicity. These results suggest that cyanine-based dithienylethene **2b** may be used as a photoswitchable fluorescent material in living cells.

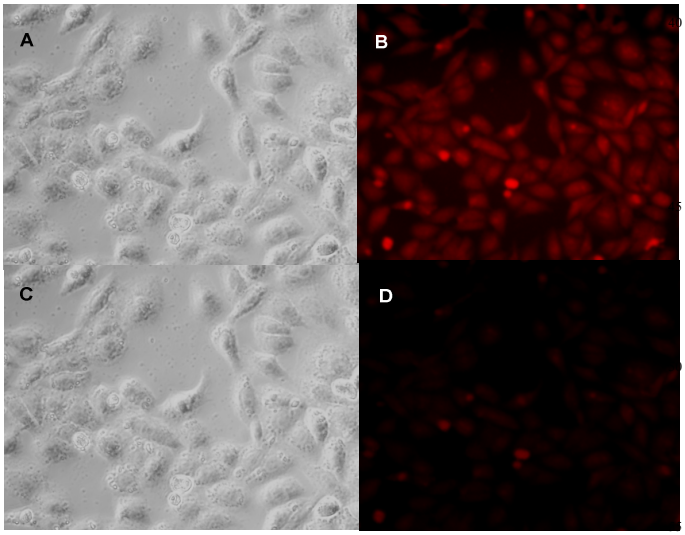


Figure 4. Bright-field images (A), (C) and Fluorescence microscope images (B), (D) of the live HeLa cells with **2b** in red channel (520-620 nm) before and after 365 nm irradiation for 6 min.

Conclusions

In summary, six cyanine-based dithienylethene compounds were successfully developed and their photoisomerization and emission change properties fully investigated. The results indicated that the UV/vis absorption of pyridinium-based compounds displayed the near-infrared absorption, while their fluorescence showed the quenching emission as a result of the changes structure from open-ring isomers to closed-ring isomers. Therefore these cyanine-based compounds could be applied not only in photochromic materials, but also they could be used as a fluorescence switch. Accordingly, one of these compounds was successfully used in the biological imaging of living cells. These results suggest that cyanine-based dithienylethenes may be used as photoswitchable bio-materials in the future.

Experimentals

General

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium-benzophenone. All reagents and starting materials were obtained commercially and used without further purification. Column chromatography was used on silica gel (200-300 mesh). NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz or 600MHz) and their chemical shifts are relative to TMS. Electrospray ionisation (ESI) mass spectra were carried on API 2000. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were taken on a Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). 1,2-Bis(5-formyl-2-methylthien-3-yl)cyclopentene was prepared by literature methods.[6] The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.[11]Targe t compounds **1a-1c** were prepared according to the synthetic route presented in Scheme 2 by modified procedures of reported methods.[5a, 7]

Synthesis of 1a

Compound **1** (1.32 g, 4.0 mmol) was dissolved in 15 mL of anhydrous THF under nitrogen at room temperature. *n*-BuLi (6.40 mL, 2.5M, 8.0 mmol) was slowly added and the mixture stirred for 20 min. Than $B(OBu)_3$ (6.40 mL, 8.0 mmol) was added and stirring was continued at room temperature for 3 h. Then in another flask added 4-Iodopyridine (2.0 g, 10.0 mmol), $Pd(PPh_3)_4$ (0.55 g, 7% mol) and Na_2CO_3(aq) (24 mL, 20% wt) under nitrogen, than the above system was added to the second flask quickly under nitrogen, and stirring was continued for 17 h at 50℃. The reaction mixture was then allowed to reach ambient temperature, filtrate, and extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4), concentrated and the product purified by silica gel column chromatography using (petroleum ether and ethyl acetate, v/v = 2:1) as the eluent to obtain the target compound as a purple solid in a yield of 50 %. ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm = 2.01 (s, 6H, CH_3), 2.09-2.12 (m, 2H, CH_2), 2.85 (t, *J* = 7.8 Hz, 4H, CH_2), 7.22 (s, 2H, thiophene-H), 7.34 (d, *J* = 5.4 Hz, 4H, py-H), 8.52 (d, *J* = 4.8 Hz, 4H, py-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.57, 22.87, 38.36, 119.15, 126.17, 134.67, 136.54, 137.18, 141.16, 150.17. ESI MS m/z = 415.2 [M + H^+]; calculated exact mass = 414.1. Anal.calcd for $C_{25}H_{22}N_2S_2$: C, 72.43; H, 5.35; N, 6.76. Found: C, 72.13; H, 5.20; N, 6.75.

Synthesis of 1b

To a solution of **1a** (0.83 g, 2.0 mmol) in anhydrous CH_3CN (20 mL) was added CH_3I (0.85 g, 6.0 mmol) under argon atmosphere. The mixture was refluxed for 24 h. After removing the solvent, the residue was dissolved in MeOH (5.0 mL), and then saturated NH_4PF_6 (5.0 mL, aq) was added to yield a yellow green precipitate. After filtering, washing with H_2O and drying under a vacuum, the compound **1b** was obtained as the yellow green solid in 80% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 1.95 (s, 6H, CH_3), 2.00-2.04 (m, 2H, CH_2), 2.76 (t, *J* = 7.2 Hz, 4H, CH_2), 4.04 (s, 6H, CH_3), 7.65 (s, 2H, thiophene-H), 7.81 (d, *J* = 6.4 Hz, 4H, py-H), 8.28 (d, *J* = 6.4 Hz, 4H, py-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 14.78, 23.20, 38.61, 47.54, 118.00, 122.07, 133.39, 135.77, 139.42, 145.39, 148.97. ESI MS m/z = 443.3 [M - $2PF_6^-$ - H^+]; calculated exact mass = 734.1. Anal.calcd for $C_{27}H_{28}F_{12}N_2P_2S_2$: C, 44.15; H, 3.84; N, 3.81. Found: C, 44.00; H, 3.55; N, 3.70.

Synthesis of 1c

Compound **1c** was prepared by an analogous method to **1b** and obtained as the yellow green solid in 70% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 0.79 (t, *J* = 6.4 Hz, 6H, CH_3), 1.21 (br, 16H, CH_2), 1.96 (s, 6H, CH_3), 2.01-2.06 (m, 2H, CH_2), 2.78 (t, *J* = 7.2 Hz, 4H, CH_2), 4.26 (t, *J* = 7.6 Hz, 4H, CH_2), 7.68 (s, 2H, thiophene-H), 7.83 (d, *J* = 6.4 Hz, 4H, py-H), 8.33 (d, *J* = 6.4 Hz, 4H, py-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 13.83, 14.88, 22.70, 23.28, 25.85, 31.39, 61.13, 122.49, 133.68, 135.87, 139.59, 144.55, 145.39, 149.34. EI MS m/z = 584.6 [M - $2PF_6^-$];

calculated exact mass = 874.2. Anal.calcd for $C_{37}H_{48}F_{12}N_2P_2S_2$: C, 50.80; H, 5.53; N, 3.20. Found: C, 50.60; H, 5.50; N, 3.18.

Synthesis of 2a

To a solution of **1** (0.99 g, 3.0 mmol) in anhydrous THF (60 mL) and NEt_3 (60 mL) was added $pd(pph_3)_4$ (0.62 g, 0.3 mmol) and CuI (0.10 g, 0.3 mmol) under argon atmosphere. The mixture was stirred at room temperature for 30 min then 4- ethynyl pyridine was added. The mixture was refluxed for 24 h. After removing the solvent, the precipitate was purified on a silica gel column using petroleum ether/ethyl acetate (1:1) as the eluent to obtain the target compound as a purple solid in a yield of 32 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 1.94 (s, 6H, CH_3), 1.96-2.04 (m, 2H, CH_2), 2.79 (t, J = 7.2 Hz, 4H, CH_2), 7.05 (s, 2H, thiophene-H), 7.32 (d, J = 3.6 Hz, 4H, py-H), 8.57 (d, J = 3.6 Hz, 4H, py-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 14.49, 38.27, 87.83, 90.06, 117.79, 125.03, 128.53, 131.26, 134.30, 138.74, 149.69. ESI MS m/z = 463.1 [M + H^+]; calculated exact mass = 462.1. Anal.calcd for $C_{29}H_{22}N_2S_2$: C, 75.29; H, 4.79; N, 6.06. Found: C, 75.10; H, 4.68; N, 6.00.

Synthesis of 2b

Compound **2b** was prepared by an analogous method to **1b** and obtained as the yellow green solid in 65% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 2.03 (s, 6H, CH_3), 2.03-2.08 (m, 2H, CH_2), 2.82 (t, J = 6.4 Hz, 4H, CH_2), 4.22 (s, 6H, CH_3), 7.34 (s, 2H, thiophene-H), 7.88 (d, J = 5.6 Hz, 4H, py-H), 6.85 (d, J = 6.0 Hz, 4H, py-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 14.43, 23.24, 38.61, 48.49, 89.84, 98.27, 116.59, 128.91, 135.69, 138.26, 140.39, 143.64, 145.47. ESI MS m/z = 491.3 [M - 2PF_6^- - H^+]; calculated exact mass = 782.1. Anal.calcd for $C_{31}H_{28}F_{12}N_2P_2S_2$: C, 47.57; H, 3.61; N, 3.58. Found: C, 47.50; H, 3.31; N, 3.49.

Synthesis of 2c

Compound **2c** was prepared by an analogous method similar to that used for to **1b** and was obtained as the yellow green solid in 60% yield. ^{1}H NMR (400 MHz, CD_3CN): δ ppm = 0.90 (t, J = 6.4 Hz, 6H, CH_3), 1.33 (br, 16H, CH_2), 1.95 (s, 6H, CH_3), 1.98-2.03 (m, 2H, CH_2), 2.82 (t, J = 6.8 Hz, 4H, CH_2), 4.43 (t, J = 6.8 Hz, 4H, CH_2), 7.35 (s, 2H, thiophene-H), 7.90 (d, J = 5.6 Hz, 4H, py-H), 8.54 (d, J = 7.2 Hz, 4H, py-H). ^{13}C NMR (100 MHz, CD_3CN): δ ppm = 13.79, 14.46, 22.65, 25.79, 31.33, 38.59, 61.98, 89.95, 98.30, 116.57, 129.20, 135.62, 137.72, 138.29, 140.51, 144.52. ESI MS m/z = 631.7 [M - 2PF_6^- - H^+]; calculated exact mass = 922.2. Anal.calcd for $C_{41}H_{48}F_{12}N_2P_2S_2$: C, 53.36; H, 5.24; N, 3.04. Found: C, 53.30; H, 5.10; N, 3.00.

Acknowledgements

We acknowledge financial support from National Natural Science Foundation of China (21272088, 21472059, 21402057) and the Program for Academic Leader in Wuhan Municipality (201271130441). The work was also supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education, and the Natural Science Foundation of Hubei Province (2013CFB207).

Notes and references

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† Electronic Supplementary Information (ESI) available: [NMR and Mass spectra. See DOI: 10.1039/b000000x/

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