Syntheses and Optoelectronic Properties of Planar Compounds 3,7-diaryl-Month 2015 1,5,2,4,6,8-dithiotetrazocine

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- P3HT 300000 Fluorescence Accept an Give an 200000 electron electron from to cathode donor 100000 600 700 80

Planar molecules 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines would be potential acceptor materials of organic solar cell because of their containing SN units. One-pot synthetic procedures of 3,7-diaryl-1, 5,2,4,6,8-dithiotetrazocine compounds are developed to improve their yields up to 2.1-5.9 times as much as those in literatures. The geometries of title compounds were optimized by the density functional theory calculations. Their optoelectronic properties were studied by ultraviolet and cyclic voltammetry spectra and fluorescence quenching experiments. The highest occupied and lowest unoccupied molecular orbital energy level values show that these compounds are suitable to be employed as acceptor materials for developing bulk heterojunction organic solar cells with high open circuit voltages. Emission fluorescence of poly (3-hexylthiophene) at excited state in dichloromethane was quenched by addition of title compound. Therefore, these compounds used as acceptor materials could exhibit good mobility.

J. Heterocyclic Chem., 00, 00 (2015).

INTRODUCTION

Organic solar cell materials have continuously drawn great interest because of their several advantages, such as cheap price, light weight, and easy combination and modification [1,2]. Designs and syntheses of desired organic compounds for developing electron donor and acceptor materials are fatal procedures in fabrication of bulk heterojunction (BHJ) solar cells with high power conversion efficiency (PCE) [3–6]. Generally, the desired organic compounds should exhibit several characters, such as, suitable band gap energy, good solubility, and mobility [7-14]. In the past two decades, C₆₀ or C₇₀ derivatives [15–18] were employed popularly as electron acceptor materials of organic solar cells since Wudl et al. synthesized [6,6]-phenyl C61-butyric acid methyl ester (PCBM) in 1995 [19]. However, the lowest unoccupied molecular orbital (LUMO) energy level is so low that open circuit voltage (V_{oc}) of BHJ organic solar cells fabricated by poly(3-hexylthiophene) (P3HT) and PCBM is small (0.55–0.64 V) [20,21]. Therefore, many non-fullerene small-molecule acceptor compounds were designed and synthesized to improve V_{oc} of BHJ organic solar cells [20-24]. However, PCE values of BHJ organic solar cells fabricated by these organic acceptor compounds and P3HT are low in spite of their high V_{oc} values [22,23]. Because short circuit current (J_{sc}) values of these organic solar cells are low because of low mobility of acceptor materials and unsuitable size of phases aggregated by acceptor molecules [24]. In efficient BHJ solar cells with high J_{sc} values, acceptor compounds should be aggregated into acceptor material phases with suitable sizes [24-26]. Moreover, acceptor materials should exhibit a good mobility [24-26]. In general, planar acceptor compounds aggregated easily into ordered geometries because of π - π interaction among molecules [27,28]. Electrons would transfer easily from one molecule to an adjacent molecule in a J-aggregation [29–35]. Therefore, planar compounds could be potential electron-acceptor materials with good



mobility. A planar electron acceptor with suitable LUMO energy level could be desired for developing BHJ organic solar cells with high V_{oc} and J_{sc} . Many polymers containing SN units are good electron conductor [4]. Acceptor materials aggregated by 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine compounds could exhibit a high electron mobility because of their containing SN units.

Planar molecules, 9,9'-bifluorenylidene (99'BF) derivatives, are good electron acceptors, because geometries of 99'BF derivatives change reversibly when they gain or lose electrons [18]. Moreover, BHJ solar cells fabricated by P3HT:D99'BF (12-(3,6-dimethoxyfluoren-9-ylidene)-12Hdibenzo[b,h]-fluorine) exhibited a high V_{oc} (1.2 V) [18]. The geometries of title compounds change reversibly, similar to that of 99'BF, when they gain or lose electrons. The reversible change when 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine gain and lose electrons are shown in Figure 1.

Based on quantum chemistry calculations, geometries of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine were optimized [36–50]. The calculation results show that these compounds are planar. Therefore, these compounds could be potential acceptor materials.

However, the synthetic methods of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine in literatures were complex [37–42]. Moreover, the yields of these compounds were very low. Therefore, developing an efficiently synthetic procedure would be very important to acquire the practical electron acceptor materials. In this paper, an one-pot procedure that tri(trimethylsilyl)arylamidine reacted with SCl₂ to directly synthesize title compounds is reported to improve the yields from 2.4%–9.0% in literatures [37–42] to 5.1%–29.3%.

RESULTS AND DISCUSSIONS

One-pot synthetic methods. Synthetic routes of compound 1, 2, 3, 4, and 5 were shows in Scheme 1.

Compound 1, 2, and 3 were synthesized respectively by Boeré et al., [37] Gronowitz et al. [41], and Bond et al. [38] The yields of compound 1, 2, and 3 were 5.4% [37], 5.0% [39], and 2.4% [38], respectively, because of air-sensitive intermediate, 4-aryl-1,2,3,5-dithiadiazolium chloride. 4-Aryl-1,2,3,5-dithiadiazolium chloride would decompose when it exposed to air. Therefore, the total yield would be low. For example, Scholz et al. synthesized compound 1 with a total yield 4%–9% [42]. The yield of 4-phenyl-



Figure 1. The structures of title compounds and those with a seized electron.

Scheme 1. Synthetic routes of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine.





1,2,3,5-dithiadiazolium chloride was 10%–15%. Although the yield of the reaction of 4-phenyl-1,2,3,5-dithiadiazolium chloride with oxygen gas was 40%–60%. In the one-pot synthesis, intermediate 4-aryl-1,2,3,5dithiadiazolium chloride was not separated from solution so that the total yields of compound **1**, **2**, and **3** are 28.6%, 29.3%, and 5.1%, respectively. Moreover, pure 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine was acquired conveniently from reactive solution by filtration instead of chromatography in literatures [37–39]. Therefore, the one-pot synthesis is an efficient and convenient procedure.

Molecular orbital energy levels. The maximal absorption wavelength (λ_{max}) and onset wavelength (λ_o) in the UV–vis absorption spectra were summarized in Table 1. Difference of energy levels between the LUMO and highest occupied molecular orbital (HOMO) (*Eg*) was defined in terms of the onset wavelength [46],

$$Eg = hc/\lambda_o \tag{1}$$

where *h* is Plank's constant, 6.626×10^{-34} J·s; c is the speed of light; and λ_o is the onset wavelength.

Table 1

UV–vis absorption wavelengths and energy levels of the 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines.

No.	λ_{max} (nm)	λ_o (nm)	E _{re} (eV)	E _{LUMO} (eV)	E _{HOMO} (eV)	Eg (eV)
1 2 3 4 5	411 448 423 451 455	445 485 447 495 500	-1.40 -1.30 -1.35 -1.20 -1.20	-3.45 -3.55 -3.65 -3.65	-6.25 -6.10 -6.27 -6.15 -6.13	2.80 2.55 2.77 2.50 2.48

The LUMO energy level values of the acceptors were estimated from the reduction potential onset $(E_{LUMO} = -(E_{re} + E_{Fc+/Fc}) = -(E_{re} + 4.85))$, whereas the HOMO energy levels (E_{HOMO}) were calculated from the E_{LUMO} values and the E_g values $(E_{HOMO} = E_{LUMO} - E_g)$. The results were summarized in Table 1.

In Table 1, HOMO energy levels of the 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines (-6.10 to - 6.27 eV) are similar to that of PCBM (-6.1 eV). LUMO energy levels of these compounds (-3.45 to -3.65 eV) are 0.65–0.85 eV higher than that of PCBM (-4.3 eV). HOMO and LUMO energy levels of most of donors were -4.90 eV to -5.5 eV and -2.90 eV to -3.4 eV, respectively [47,48]. Therefore, the organic BHJ solar cell fabricated by 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine and P3HT could exhibit a high open circuit voltage.

HOMO energy level of compound 3 (-6.27 eV) is slightly lower than that of compound 1 (-6.25 eV). Similarly, HOMO energy level of compound 4 (-6.15 eV)and compound 5 (-6.13 eV) are slightly lower than that of compound 2 ($-6.10 \,\text{eV}$). Because bromo is a weak electron-withdrawing group so that HOMO energy levels of bromoaryl compounds are lower than that of corresponding aryl compounds, respectively. Because of the effect of bromo substituent on energy level of compound, LUMO energy levels of compound 4 (-3.65 eV) and 5 (-3.65 eV) are 0.1 eV lower than that of compound 2 (-3.55 eV). LUMO energy level of compound 3 (-3.50 eV) is 0.05 eV lower than that of compound 1 (-3.45 eV). The reduced values (0.05 eV-0.10 eV) of LUMO energy levels of these compounds are larger than those of corresponding HOMO energy levels (0.02 eV–0.05 eV). As a result, the difference between LUMO and HOMO energy levels of bromoaryl compounds would be smaller than those of corresponding aryl compounds, respectively. Therefore, LUMO and HOMO energy levels would be effective tuned by introducing bromo substituent to aryl rings [49].

Part **b** in Figure 2 shows clearly that there is an absorption peak in range from 400 nm to 500 nm because of

 π -conjugated well of 1,5,2,4,6,8-dithiotetrazocine and thienyl rings. Therefore, the compounds would be π -stacked regularly so that electrons would transfer easily from one acceptor to another. The CV spectrum shows that the 3,7-di[2-thienyl]-1,5,2,4,6,8-dithiotetrazocine can accept and lose electrons reversibly. CV and UV spectra of compound 1, 3, 4, and 5 are similar to those of 3,7-di[2-thienyl]-1,5,2,4,6,8-dithiotetrazocine. Therefore, 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine would be potential acceptors for developing BHJ organic solar cells.

Fluorescence quenching experiments. The fluorescence quenching experiments were performed. Percentages of the fluorescence quenching increase with weights of the added acceptors increasing. The fluorescence was almost completely quenched when the weight of the acceptor compound was 3 times as much as that of P3HT. In order to study on variety in the fluorescence quenching when different acceptor was added, the weight of the added acceptor compound was a third as much as that of P3HT.

In Figure 3, the black line was the fluorescent emission spectrum of a solution of P3HT in CH₂Cl₂. The red, green,



Figure 3. Fluorescence quenching experiments of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 2. CV and UV of compound 2.

blue, and slight blue lines were respectively the fluorescent emission spectra of solution of P3HT and acceptor 1, 2, 3, or 5 in CH₂Cl₂. The weight of the title compound was 1/3 weight of P3HT. Figure 3 shows clearly that emission fluorescence of P3HT in excited state was reduced respectively 27%, 37%, 43%, and 83% when compound 1, 2, 3, or 5 was added respectively into a solution of P3HT in CH₂Cl₂. These curves show that an excited electron in P3HT was easily transferred to 1,5,2,4,6,8-dithiotetrazocine derivative so that P3HT recovered from excited state to ground state. As a result, the emission fluorescence of P3HT at excited state was reduced. Therefore, acceptor materials aggregated by these compounds could exhibit high mobility. The geometries of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines. In Scheme 2, dihedral angles of compound 1, 2, 3, 4, and 5 between aryl rings and 1,5,2,4,6,8-dithiotetrazocine ring are 1.90°, 0.00°, 0.56°, 0.00°, and 0.00°, respectively. Dihedral angles of compound 1, 2, 3, 4, and 5 with a seized electron between aryl rings and 1,5,2,4,6,8-dithiotetrazocine ring are 0.08°, 0.04°, 0.03°, 0.00°, and 0.00°, respectively. Therefore, all structures of title compounds and that with a seized electron are planar. Two aryl rings and 1,5,2,4,6,8-dithiotetrazocine ring are coplanar so that whole molecule is π -conjugated well. Therefore, these acceptor compounds would aggregate into J-aggregation through π - π stacking [37,38]; as a result, electrons would transfer easily from a molecule to

Scheme 2. Geometries of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



an adjacent molecule [31-35]. Because hydrogen bond was formed between a hydrogen atom in thienyl (or phenyl) ring and a nitrogen atom in 1,5,2,4,6,8-dithiotetrazocine ring; as a result, thienyl (or phenyl) ring is in 1,5,2,4,6,8dithiotetrazocine ring plane. These hydrogen bonds and interactions result that the π–π stacking 3.7diaryl-1,5,2,4,6,8-dithiotetrazocine was stacked up to J-aggregation, which is useful property for developing BHJ solar cell with high PCE. [9,32-35,50] When a 1,5,2,4,6,8dithiotetrazocine derivative accepted a electron, the structures of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine with a seized electrons would keep planar structure. When seized electrons transferred to cathode, the structures of 3,7diaryl-1,5,2,4,6,8-dithiotetrazocine would be recovered reversibly.

CONCLUSION

A one-pot synthetic method is reported to prepare 3,7diaryl-1,5,2,4,6,8-dithiotetrazocines for developing acceptor materials of organic solar cell. CV and UV-vis spectra were determined for calculating their LUMO and HOMO energy levels. The HOMO and LUMO energy level values show that these compounds are suitable to be employed as acceptor materials for developing organic BHJ solar cells with high open circuit voltages. The results of fluorescence quenching experiments show that the electrons were transferred spontaneously from P3HT to 3,7-diaryl-1,5,2,4,6,8dithiotetrazocine. Results of theoretical calculations show the geometries of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocines and those with seized electrons are planar and change reversibly when they gain or lose electrons. Results of both theoretical calculation and fluorescence quenching suggest that acceptor materials aggregated by 3,7-diaryl-1,5,2,4,6,8dithiotetrazocine would exhibit high mobility. This paper suggests a useful way of developing desired acceptor materials for organic BHJ solar cell.

EXPERIMENTAL

Materials and methods. Melting points were determined on a Yanaco micro melting point apparatus (uncorrected). ¹H NMR were recorded on Bruker AM 300 (Germany), and δ were given in ppm (relative to TMS) and coupling constants (*J*) in Hz. Mass spectra were recorded by a GCMS-QP2010 gas chromatogram mass spectrometer under GC/MS mode. UV–visible spectra were recorded on a Lambda 25 Perkin-Elmer spectrophotometer. IR spectra were recorded on a Brucker Vector 22 spectrophotometer, in which samples were embedded in KBr thin films. Precoated silica gel plates (GF254) were used for analytical TLC. All solvents were purified by standard procedures. All chemicals were purchased from Sigma or Aldrich.

Synthesis of 3.7-diaryl-1.5.2.4.6.8-dithiotetrazocines. 3.7-*Diphenyl-1,5,2,4,6,8-dithiotetrazocine* (1). N,N,N'-Tri (trimethylsilyl)benzamidine was synthesized similar to the literature [40]. Benzonitrile (4.4 g, 42.7 mmol) was added into Et₂O (100 mL). The result solution was added dropwise into another solution of (Me₃Si)₂NLi·OEt₂ (10.8 g, 45.8 mmol) in Et₂O (160 mL). The reaction solution was refluxed for 24 h. The ether was distilled off, and toluene (40 mL) was added. Then, a solution of ClSiMe₃ (4.87 g, 45.8 mmol) in toluene (15 mL) was added into the reaction solution. The reaction mixture was refluxed for 5 h. After cooling to room temperature, deposit LiCl was separated from the light orange solution by filtration. The solvent toluene was removed by distillation. The tri(trimethylsilyl)benzamidine was acquired by vacuum distillation (91–93°C, 3 mmHg) as a white crystal (11.0 g, 73.6%). ¹H NMR (DCCl₃): δ = 7.23 (s, 5H), 0.002 (s, 27 H).

Compound 1 was synthesized by one-pot method. Tri (trimethylsilyl)benzamidine (3.6 g, 9.4 mmol) and SCl₂ (4 mL, 7.2 g, 69.9 mmol) were added into CH₃CN (100 mL). The result solution was heated and stirred at 60°C for 2 h. Excess SCl₂ was removed from the reaction solution. SbPh₃ (3.6 g, 10.3 mmol) in CH₃CN (50 mL) was added dropwise into the reaction solution. At 60°C, air was led in the reaction bottle for 18h. The mixture was filtered to get a pure 3,7-diphenyl-1,5,2,4,6,8-dithiotetrazocine, a yellowgreen plate-like crystal (0.40 g, 1.3 mmol, 28.6%). IR spectrum of the compound is according with literature [37]. ¹H NMR (DCCl₃): $\delta = 8.54$ (d, J = 8.6 Hz, 4H), 7.60–7.42 (m, 6 H). MS (EI): m/z = 298 (M⁺), 135 ([PhCNS₂]⁺); calcd for $C_{14}H_{10}N_4S_2$ [M⁺]: 298.3. Elem. Anal. Calcd. for C₁₄H₁₀N₄S₂ (298.3): C, 56.38; H, 3.37, N, 18.73; S, 21.49. Found: C, 56.35, H, 3.38, N, 18.78; S, 21.53. IR (KBr): v = 1696 (S=N), 1618 (C=N), 1593 and 1489 (C=C) cm⁻

3,7-Di(2-thienyl)-1,5,2,4,6,8-dithiotetrazocine (2). N,N,N'-Tri(trimethylsilyl)-2-thienylamidine was synthesized similar to N,N,N'-tri(trimethylsilyl)benzamidine. 2-Thiophenonitrile was employed to replace benzonitrile. The N,N,N'-tri(trimethylsilyl)-2-thienylamidine was acquired by vacuum distillation (118–120°C, 3 mmHg) as a yellow liquid (60.2%).

Similar to the synthetic method of compound **1**, compound **2** was synthesized by one-pot method. It was acquired as yellow crystal (29.3%). IR spectrum of the compound is according with literature.⁴⁰ ¹H NMR (DCCl₃): δ = 7.92 (d, J = 4.0 Hz, 2H), 7.48 (d, J = 5.0 Hz, 2H), 7.18 (dd, J_a = 4.0 Hz, J_b = 5.0 Hz, 2H). MS (ESI): *m*/*z* = 311 [M = 1]⁺; calcd for C₁₀H₆N₄S₄ [M + 1] ⁺: 311.0. Elem. Anal. Calcd. for C₁₄H₁₀N₄S₂ (310.4): C, 38.74, H, 1.96, N, 18.03; S, 41.32. Found: C, 38.69, H, 1.95, N, 18.05; S, 41.34. IR (KBr): *v* = 1662 (S=N), 1608 (C=N), 1430 (C=C in thiophene) cm⁻¹.

3,7-Di(4-bromophenyl)-1,5,2,4,6,8-dithiotetrazocine (3). N,N, N'-Tri-(trimethylsilyl)-4-bromobenzamidine was synthesized similar to N,N,N'-tri(trimethylsilyl)-benzamidine. 4-Bromobenzonitrile was employed to replace benzonitrile.

The N, N, N'-tri(trimethylsilyl)-4-bromobenzamidine was acquired by vacuum distillation (150–153°C, 3 mmHg) as a light green crystal (68.2%).

Similar to the synthetic method of compound 1, compound 3 was synthesized by one-pot method. It was acquired as a yellow solid (5.1%). IR spectrum of the compound is according with literature.³⁹ ¹H NMR (DCCl₃): δ =8.43 (d, 4H, J=8.8Hz), 7.69(d, 4H, J=8.8Hz). MS (FI)⁺: *m*/*z*=455.9; 457.9; 453.9 (M⁺; Abundance ratio=2:1:1); calcd for C₁₄H₈Br₂N₄S₂ [M⁺]: 455.9, 457.9, 453.9 (Abundance ratio=2:1:1). Elem. Anal. Calcd. for C₁₄H₈Br₂N₄S₂ (456.2): C, 36.86; H, 1.77; N, 12.28; S, 14.06. Found: C, 36.83, H, 1.77, N, 12.24; S, 14.08. IR (KBr): *v*=1658 (S=N), 1583 and 1479 (C=C in benzene ring) cm⁻¹.

3-(4-Bromothiophen-2-yl)-7-(thiophen-2-yl)-1,5,2,4,6,8-dithiotetrazocine (4). 3,7-Di(2-thienyl)-1,5,2,4,6,8dithiotetrazocine (0.2 g, 0.65 mmol) and NBS (0.267 g, 1.5 mmol) was added into 1,2-dichlorobenzene (40 mL), and the solution was heated up to 120°C for 30 h. The solvent was removed, and MeOH (30 mL) was added. The mixture was filtered to get a yellow pure compound (228 mg, 90.1%). ¹H NMR (DCCl₃): $\delta = 7.93$ (d, J=4.0 Hz, 1H), 7.70 (d, J=4.0 Hz, 1H), 7.51 (d, J=4.0 Hz, 1H), 7.18 (dd, J=4.0 Hz, 1H), 7.13 (d, J=4.0 Hz, 1H). MS (FI)⁺: m/z=389.9, 387.9 (M⁺; Abundance ratio = 1:1); calcd for $C_{10}H_5BrN_4S_4$ [M⁺]: 387.9, 389.9 (Abundance ratio=1:1). Elem. Anal. Calcd. for C₁₀H₅BrN₄S₄ (389.3): C, 30.85; H, 1.29; N, 14.39; S, 32.94. Found: C, 30.89; H, 1.30; N, 14.38; S, 32.96. IR (KBr): v = 1675 (S = N), 1605 (C = N), 1530 and 1425 (C=C in thiophene) cm^{-1}

3,7-Di(4-bromothiophen-2-yl)-1,5,2,4,6,8-dithiotetrazocine 3,7-Di(2-thienyl)-1,5,2,4,6,8-dithiotetrazocine (0.2 g, (5). 0.65 mmol) and NBS (0.445 g, 2.5 mmol) were added into 1,2-dichlorobenzene (40 mL). The reaction mixture was heated up to 170°C for 15h. The solvent was removed. Then, MeOH (30 mL) was added. Mixture was stirred for 30 min. The mixture was filtered to get yellow pure compound (259 mg, 85.1%). ¹H NMR (DCCl₃): δ = 7.71 (d, J = 4.0 Hz, 2H), 7.12 (d, J = 4.0 Hz, 2H). MS (FI)⁺: m/z = 467.8, 469.8, 465.8 (M⁺; Abundance ratio = 6:4:3); calcd for $C_{10}H_4Br_2N_4S_4$ [M⁺]: 467.8, 469.8, 465.8 (Abundance ratio=6:4:3). Elem. Anal. Calcd. for C₁₀H₄Br₂N₄S₄ (468.2): C, 25.65; H, 0.86; N, 11.97; S, 27.39. Found: C, 25.63; H, 0.86; N, 11.95; S, 27.41. IR (KBr): v=1701 (S=N), 1598 (C=N), 1530 and 1422 (C=C in thiophene) cm^{-1} .

Cyclic voltammetry experiment. At room temperature, cyclic voltammetry was performed using an electrochemical workstation (CH instruments Inc., CHI, model 750A) and conducted using $0.1 \text{ mol } \text{L}^{-1}$ tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The working, auxiliary, and reference electrodes were a glassy carbon electrode, a Pt wire and Ag/Ag⁺, respectively. The

scan rate was 100 mV s^{-1} . Ferrocene was added to the sample solution at the end of the experiment. The ferrocenium/ferrocene (Fc⁺/Fc) redox couple was used as an internal potential reference ($E_{Fc+/Fc}$ = 4.85 eV). The potential in CH₂Cl₂ was calibrated according to literature [43,44].

Fluorescence quenching experiment. At room temperature, the fluorescence quenching experiments were performed by fluorescence spectrometry [45] (CaryEclipse, Varian Co. USA). P3HT (30 mg) was added into THF (10 mL) for determining fluorescence of the solution. Then 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine (10 mg) was added the above solution for determining fluorescence quenching of the solution.

Computational details. Geometries of 3,7-diaryl-1,5,2,4,6,8-dithiotetrazocine were optimized by the density functional theory (DFT) calculations using Gaussian03 software at the B3LYP/6-31G(d) level [36,51].

Acknowledgments. This work was supported by Jiangsu Specially-Appointed Professor Program (R2012T01), Foundation for special project on the Integration of Industry, Education, and Research of Jiangsu Province (BY2012028), Scientific Research Foundation for Returned Scholars from Ministry of Education of China (2013S010), the Priority Academic Program Development of Jiangsu Higher Education Institutions, and CICAEET.

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