



Synthesis of Novel Donor-Acceptor Type Molecule Based on Phenothiazine Unit for Organic Light-Emitting Materials

ZEBIAO TANG, XIAOXIA SUN*, HUAYIN SHEN and HEWEI YAN

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, P.R. China

*Corresponding author: Fax: +86 791 83826894; Tel: +86 791 83805183; E-mail: sunxiaoxia77@126.com

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A novel conjugated organic molecule based on central phenothiazine unit as an electronic donor and aldehyde group termini as an electronic acceptor has been designed and constructed. Optical spectra show that, the absorption and fluorescence spectra of M2 are large red-shifted relative to M1 in both states, however, from solution to the solid state, the absorption maxima and emission maxima of M1 and M2 are in the opposite trends (blue-shift). The fluorescence spectra exhibit that the emission maxima of M1 and M2 which range from 485 nm to 588 nm belong to green light region. As expected, the target compounds should be a promising green light-emitting material for applications in organic light-emitting diodes (OLEDs).

Keywords: Phenothiazine unit, Donor-acceptor, Molecule, Light-emitting materials.

INTRODUCTION

Conjugated organic molecules with donor-acceptor (D-A) architectures have attracted a variety of attention during the past decade, due to their great potential applications in electronics and optoelectronics including organic light-emitting diodes (OLEDs), photovoltaic cells and electrochromic cells^{1,2}. Because of their great advantage on physical properties easily being tuned over a wide range by appropriate chemical modification to the structures of donors or acceptors, recently, donor-acceptor (D-A) materials have received a significant amount of interest by researchers, used as light-emitting materials for organic light-emitting diodes^{3,4}. These materials should be donor-acceptor molecules that combine high fluorescence quantum yields with low ionization potential or high electron affinity. It means that, exploring new synthesis and investigation of conjugated D-A molecules are essential to improve the electronic and optoelectronic properties of these materials and turn improvement of the performance of the devices⁵. Thus, a judicious choice of the D-A units could allow the simultaneous control of the HOMO/LUMO levels and the emission colour of the D-A molecule⁶. So far, considerable carbazole, triarylamine and their derivatives have been extensively studied as electron-donating emissive materials in OLEDs⁷. Although carbazole and triarylamine investigated as donor emissive materials have been explored in OLEDs, phenothiazine and its derivatives are stronger and even potentially better electron donors, resulting from their 0.7 eV lower

ionization potentials and more stable radical cations⁸. In the context of improving the properties of light-emitting materials, it affords us a motivation to design new donors and acceptors to construct D-A molecules for organic light-emitting diodes.

In this paper, we design and synthesize a novel conjugated organic molecule based on phenothiazine unit as a donor and aldehyde groups as an acceptor to investigate electronic and optical properties of light-emitting materials for OLEDs. The optical properties were characterized by means of UV-visible and fluorescence spectroscopy in solution and in the solid state, which exhibit that the target compounds **M1** and **M2** should be promising candidates for organic light-emitting diodes.

EXPERIMENTAL

Diethyl ether and tetrahydrofuran (THF) were dried over sodium benzophenone and distilled under argon atmosphere before use. CHCl₃ and DMF were dried over CaH₂ and then distilled under nitrogen atmosphere and deoxygenated by purging with nitrogen for 0.5 h before use in monomer synthesis. Films were easily formed by spin coating from PMMA-THF solution (1 mg mL⁻¹, quartz substrate). Other chemicals were purchased from Acros and used without further purifications.

General procedure

Synthesis of 10-octyl-3,7-di(thiophen-2-yl)-10H-phenothiazine M1: A mixture of 3,7-dibromo-10-octyl-10H-phenothiazine (10 g, 21.3 mmol), tributyl(thiophen-2-

yl)stannane (23.9, 63.9 mmol) and Pd(PPh₃)₂Cl₂ (1.20 g, 1.70 mmol) in dry THF (200 mL) was stirred for 24 h at 80 °C under nitrogen atmosphere. After cooling the mixture to the room temperature, the solvent was removed and the product was purified using column chromatography on a silica gel with petroleum ether. The product was obtained as yellow powders. Yield: 6.73 g, (66 %). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.32 (d, *J* = 6.0 Hz, 4H), 7.14-7.20 (m, 4H), 6.99 (t, *J* = 4.2 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 2H), 1.79-1.72 (m, 2H), 1.40-1.21 (m, 10H), 0.91-0.80 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 143.46, 127.98, 125.03, 124.70, 124.13, 122.30, 115.43, 47.64, 31.76, 29.23, 26.93, 22.63, 14.09 (ppm).

Synthesis of 5,5'-(10-octyl-10*H*-phenothiazine-3,7-diyl)bis(thiophene-2-carbaldehyde) **M2:** Phosphorus oxychloride (20 mL) was carefully added through a dropping funnel to a solution of 10-octyl-3,7-di(thiophen-2-yl)-10*H*-phenothiazine (3.43 g, 7.21 mmol) and DMF (20 mL) in 1,2-dichloroethane (150 mL), keeping the mixture react below 5 °C. After the complete addition of POCl₃, the reaction solution was heated to reflux for 12 h. Then the mixture was poured into a cooled saturated sodium bicarbonate solution, neutralized with sodium bicarbonate solution, extracted with dichloromethane and washed with brine. The organic layer separated and dried over anhydrous magnesium sulfite. The crude product was purified using column chromatography with petroleum ether/dichloromethane (10:1, v/v) as the eluent. The product was obtained as red crystals. Yield: 3.21 g (84 %). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.75 (s, 2H), 7.32 (t, *J* = 2.9 Hz, 2H), 7.31-7.34 (m, 2H), 7.26 (d, *J* = 2.0 Hz, 2H), 7.18 (d, *J* = 3.8 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 3.74 (t, *J* = 7.0 Hz, 2H), 1.70 (t, *J* = 6.9 Hz, 2H), 1.34-1.16 (m, 10H), 0.78 (t, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 182.06, 152.61, 144.67, 141.25, 137.10, 127.27, 125.29, 124.17, 122.73, 115.13, 47.37, 30.83, 28.78, 26.24, 22.13, 13.61 (ppm).

¹H NMR and ¹³C NMR spectra were collected on a Bruker AM-400WB spectrometer in chloroform-*d* as solvent and tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained by using a Bruker Daltonics Autoflex II TOF system. FT-IR spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer with samples in KBr pellets.

RESULTS AND DISCUSSION

Synthetic design: In previous report, the compound **M1** has been synthesized in 66 % yields *via* the still coupling reaction over three steps with a milder and efficient route as illustrated in Fig. 1. At this paper, we construct the target compound **M2** *via* the Vilsmeier-Haack reaction from readily available starting materials (Fig. 1). In the first step, the reaction of 10*H*-phenothiazine and 1-bromooctane in DMSO was under a mild condition to give **1** in 92 % yields. Then bromine was added to 10-octyl-10*H*-phenothiazine and acetic acid in CHCl₃ to give **2** in 96 % yields. Next, the reaction of 3,7-dibromo-10-octyl-10*H*-phenothiazine with 3.0 equiv. of tributyl(thiophen-2-yl) stannane and Pd(PPh₃)₂Cl₂ as a catalyst affords **M1** in 66 % yield. At last, DMF and POCl₃ were used to give **M2** in a yield of 84 %.

The target compound **M2**, 5,5'-(10-octyl-10*H*-phenothiazine-3,7-diyl) *bis*(thiophene-2-carbaldehyde) was successfully synthesized over three steps from readily available starting materials in a high yield, which was so freely soluble in most common organic solvents that it should be a new organic molecule for donor-acceptor type materials. In view of its relatively good electronic and optical properties, we believe such materials should be promising candidates for light-emitting diodes, field-effect transistors or photocells.

Optical properties: The electronic spectra of compounds **M1** and **M2** were recorded in THF solutions and as PMMA thin films on quartz substrates as shown in Table-1. Fig. 2 shows the UV-visible absorption spectra and fluorescence emission spectra of **M1** and **M2** measured in THF solutions and PMMA thin films. Films were easily formed by spin coating from PMMA-THF solutions (1 mg mL⁻¹, quartz substrate). The absorption spectra (Fig. 2a) of **M1** and **M2** exhibit two absorption bands in solution and in the solid state. Obviously, the absorption bands range from 292 to 354 nm, attributing to the localized π-π* transition. In both states, it just brings a small shift of the absorbance bands. From the solution to the solid state (Fig. 2a), the first absorption band of both **M1** and **M2** exhibit a red shift because of segments of thiophene resulting in stronger interactions between molecules in the solid state, while the second absorption band of them reveal a small blue shift. Compared to **M1** in both states, **M2** exhibits a large

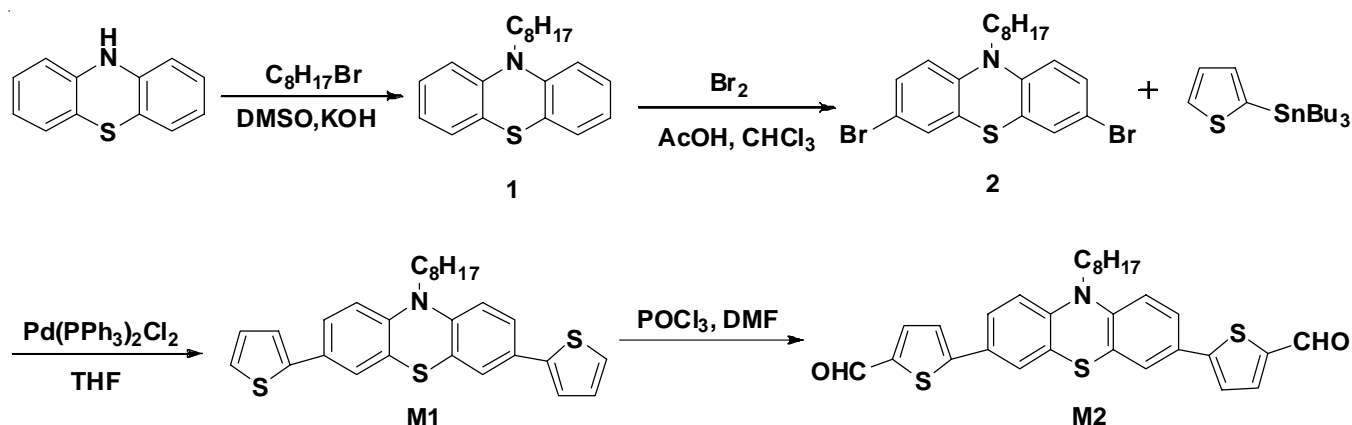


Fig. 1. Synthesis of acceptor **M2**

TABLE-1
 OPTICAL DATA FOR COMPOUNDS **M1** AND **M2**

Compounds	Solution				Film ^d			
	Stokes λ_{onset}^a (nm)				Stokes λ_{onset}^a (nm)			
	λ_{abs}^a (nm)	λ_{lum}^b (nm)	Shift (nm)	E_g^c (eV)	λ_{abs}^e (nm)	λ_{lum}^b (nm)	Shift (nm)	E_g^c (eV)
M1	292,354	496	142	434 (2.86)	294,344	485,608	141	429 (2.89)
M2	324,419	588	169	504 (2.46)	328,412	550,671	138	499 (2.48)

^aMeasured in a dilute THF solution (1×10^{-5} M). ^bExcited at the absorbance maxima. ^cEstimated from the onset of absorbance ($E_g = 1240/\lambda_{\text{onset}}$)

^dFilm were drop cast from PMMA-THF solution (1 mg mL^{-1} , quartz substrate). ^eReported values are the absorbance maxima

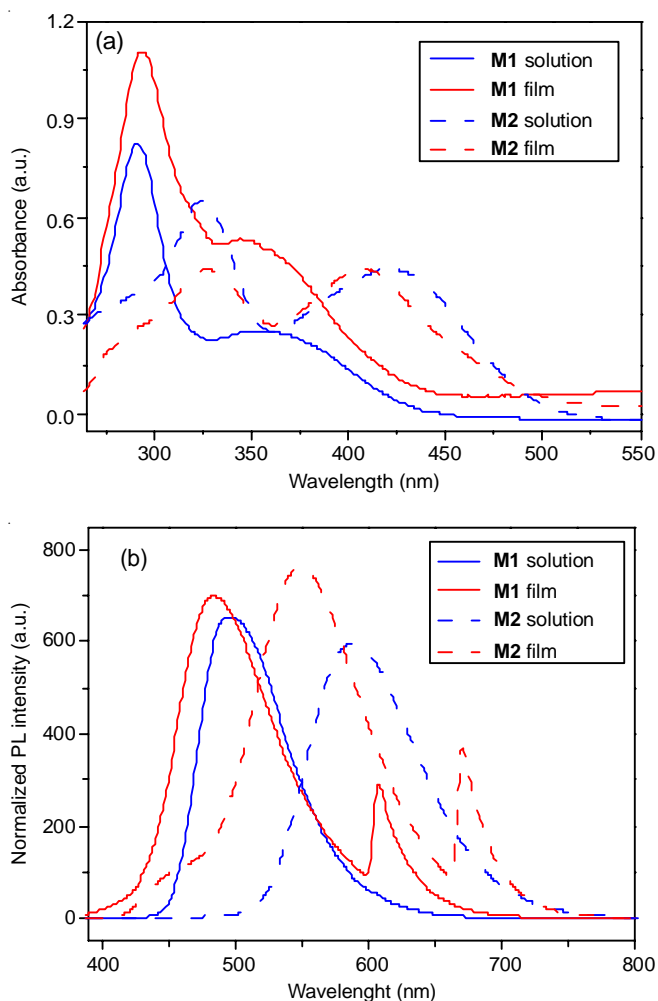


Fig. 2. (a) Absorption and (b) fluorescence spectra of **M1** and **M2** in THF solutions (10^{-5} M) and in PMMA-films

bathochromic shift (32 nm 68 nm) of the absorbance maximum resulting from aldehyde groups taking part in the conjugation as an electron-withdrawing unit. Optical band gaps (Table-1) in solution and in the solid state were approximated by extrapolation of the low-energy side of the absorption spectra to the baseline⁹. In our expectations, the energy band gaps of compounds decrease in the order, **M1** > **M2**, but it reveals a opposite trend from the solution to the solid state.

The fluorescence spectra of **M1** and **M2** have been investigated in dilute THF solutions and in the solid states, as shown in Fig. 2b. In solution, the fluorescence spectra of **M2** exhibit emission maxima at 588 nm, which brings a relatively large bathochromic shift, compared with the emission maxima of **M1**. The phenomenon of bathochromic shifts of the emission

maxima in solution is identical to the optical absorption. Furthermore, in the solid state, **M1** and **M2** exhibit the emission maxima at 485 and 550 nm, with a shoulder at 608 and 671 nm, respectively. Obviously, the emission maxima of **M2** are large red-shifted relative to **M1**, consistent with the absorbance spectra. It is easily obtained that the Stokes shifts of the compounds are relatively large, ranging from 141 to 142 nm in solution and from 138 to 169 nm in the solid state. However, the Stokes shifts of both **M1** and **M2** in solution are larger than that in the solid state. The reason could be that the dipole moment of compounds in solution is larger than that in the solid state and the emitting state of the former would be more stabilized by the ICT¹⁰. From the solution to the solid state, the fluorescence spectra of the compounds are blue-shifted. The fluorescence spectra exhibit that the emission maxima of **M1** and **M2** which range from 485 to 588 nm belong to green light region. Thus, the target compounds are expected to be a promising green light-emitting material for applications in organic light-emitting diodes (OLEDs).

Conclusion

In conclusion, we have successfully designed and constructed a novel conjugated organic molecule based on central phenothiazine unit as an electronic donor and aldehyde groups termini as an electronic acceptor. The target compound **M2** 5,5'-(10-octyl-10*H*-phenothiazine-3,7-diyl) bis(thiophene-2-carbaldehyde) was easily synthesized *via* the Vilsmeier-Haack reaction in high yields with a much milder and more efficient route. Optical properties were characterized by means of UV-visible and fluorescence spectroscopy in solution and in the solid state. It shows that the absorption and fluorescence spectra of **M2** are large red-shifted relative to **M1** in both states, resulting from aldehyde groups taking part in the conjugation as an electron-withdrawing unit. However, from solution to the solid state, the absorption maxima and emission maxima of **M1** and **M2** are small blue-shifted. The fluorescence spectra exhibit that the emission maxima of **M1** and **M2** which range from 485 to 588 nm belong to green light region. In our expectations, compounds **M1** and **M2** should be a promising pure green light-emitting material for applications in organic light-emitting diodes (OLEDs). Moreover, studies on further experiments on electroluminescent properties and film morphology¹¹ are ongoing in our group, which will be reported in due course.

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