



# Synthesis, photophysical and thin-film self-assembly properties of novel fluorescent molecules with carbon–carbon triple bonds



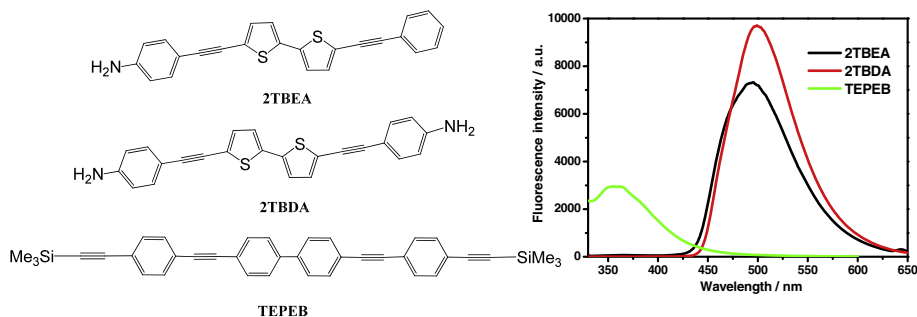
Qingfen Niu, Hongjian Sun, Xiaoyan Li\*

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China

## HIGHLIGHTS

- Three novel fluorescent molecules with carbon–carbon triple bonds **2TBEA**, **2TBDA** and **TEPEB** were designed and synthesized.
- Their optical and electrochemical properties were investigated.
- Thin-film materials.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Three novel fluorescent molecules with carbon–carbon triple bonds **2TBEA**, **2TBDA** and **TEPEB** are successfully designed and synthesized. Their thermal, photophysical, electrochemical, electronic and thin-film self-assembly properties were characterized. Three dyes showed typical photoluminescence (PL) emission behaviors, the PL intensities firstly increased and then decreased with gradually decreasing concentration. The appealing fluorescence properties indicated that three dyes could be used as good fluorescent materials. Additionally, the thin-film self-assembly behaviors of three dyes were also investigated. The microstructures of their optical microscopy (OM) images exhibited high flexibility. Furthermore, SEM and AFM surface morphology of these self-assembly nanostructures revealed that three well-defined long-range order of rod-like and tube-like self-assembly systems exhibited interesting morphology properties. Therefore, three compounds may be of great interest for the development of organic thin-film materials.

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## Introduction

Organic  $\pi$ -conjugated materials have emerged as key players in the development of new generations of organic-based devices such as organic light-emitting diodes (OLEDs), lasers, organic field-effect transistors (OFETs), photovoltaic cells, molecular electronic junctions, and biosensors over the last few decades. Similarly,

$\pi$ -conjugated oligomers [1–5] share a large number of the properties of  $\pi$ -conjugated polymers with certain advantages including their well-defined structure, easier purification, fewer defects and the possibility to introduce functionalities. Applications of organic  $\pi$ -conjugated materials reached the commercialization stage involving the use of organic  $\pi$ -conjugated polymers [6–10] and molecules [11–14] as driving and switching elements in OLEDs. Additionally, another high technological relevance is the incorporation of organic  $\pi$ -conjugated oligomers [15–24] or polymers [25–31] as the semiconducting layer in OFETs. Currently, OLEDs and OFETs

\* Corresponding author. Tel.: +86 (531)88361350; fax: +86 (531)88564464.  
E-mail address: [xli63@sdu.edu.cn](mailto:xli63@sdu.edu.cn) (X. Li).

have been integrated in the fabrication of smart pixels where OLEDs are driven by organic transistors [32–35].

Thanks to the researchers, a wide variety of organic semiconductors based on  $\pi$ -conjugated molecules and linearly fused aromatic compounds have already been exploited [36,37]. However, there is still much going on research into the new organic  $\pi$ -conjugated compounds with high mobility, solubility and environmental stability, to realize their full potential in the electronic and optical devices [38–42]. Recently, thiophene-based materials have attracted increasing attention for their potential applications in the fields of organic semiconductors owing to their light weight, good chemical stability, high carrier mobility and the ease of structural tuning to adjust their electronic, optical, morphological and film-formed properties [43–48]. It has been reported that oligothiophenes end-capped with strong electron donors (such as diphenylamino-fluorenyl moieties) have become highly efficient hole-transporting bis-dipolar emitters for OLEDs [49]. What is more, phenylene-thiophene backbone containing amide moieties can also force self-assembling in the desired way through hydrogen bonding and dipole–dipole interactions [2]. These compounds in the thin-film state can self-assemble into well-defined long one-dimensional structures with high structural order due to the combination of the strong hydrogen bonding and  $\pi$ -stacking interactions. However, the morphology of the  $\pi$ -conjugated polymers or oligomers in cast or spin-coated film is considered to be an important factor to determine the device performances [50].

For the time being, many scientists are paying a good deal of attention to acetylenic-based organic  $\pi$ -conjugated polymers or oligomers for their wide applications in photovoltaic devices [51–61]. Meanwhile, a large number of researchers are interested in an increase of the open circuit voltage, which is defined as the quasi-Fermi level splitting between the donor HOMO and the acceptor LUMO. However, the specific electric parameter is involved in solar cells as the result of the electron-withdrawing nature of the  $C\equiv C$  group leading to an enhanced electron affinity, and consequently to a higher oxidation potential and a lower HOMO level [51–53,62–64]. Thus materials of this type used as donors may provide a new route to the improved photovoltaic device performances. Most recently, a new class of thiophene-based or biphenyl-based semiconductors containing carbon–carbon triple bonds with good self-ordering, photophysical, optical, electrochemical, electronic and film-formed properties have been investigated [65–73]. To date, the total number of the materials containing carbon–carbon triple bonds for high-performance organic devices with enhanced environmental stability is not much. Therefore, the design and synthesis of more modified thiophene–phenylene or biphenylene derivatives containing carbon–carbon triple bonds is promising approach to high-performance organic devices.

Based on the published observations, the incorporation of arylene ethynylene structural motifs into organic  $\pi$ -conjugated systems are expected to make them more interesting and desirable properties and hence are of great interest to us. In order to design and synthesize more new compounds with carbon–carbon triple bonds, and further investigate their structure–property relationships, herein three new compounds 4-((5'-(phenylethynyl)-[2,2'-bithiophen]-5-yl)ethynyl)aniline (**2TBEA**), 4,4'-([2,2'-bithiophene]-5,5'-diylbis(ethyne-2,1-diyl))dianiline (**2TBDA**) and trimethyl((4-((4'-((4-((trimethylsilyl)buta-1,3-diyn-1-yl)phenyl)ethynyl)-[1,1'-biphen-yl]-4-yl)ethynyl)phenyl)ethynyl)silane (**TEPEB**) (Fig. 1) containing carbon–carbon triple bonds were successfully designed and synthesized. The three compounds were fully characterized with respect to thermogravimetric analysis (TGA), UV–vis absorption spectroscopy, photoluminescence (PL) emission spectroscopy, cyclic voltammetry (CV), density functional theory (DFT) calculations, X-ray powder diffraction (XRD). Furthermore, their thin-film self-assembly morphology properties of these compounds were

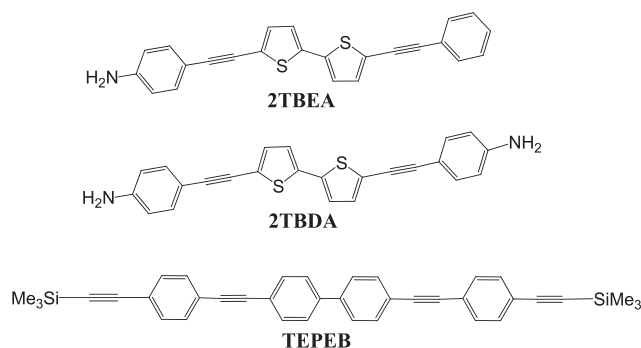


Fig. 1. The structures of dyes **2TBEA**, **2TBDA** and **TEPEB**.

characterized by optical microscope (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The three fluorescent dyes exhibited good photophysical, electrochemical and thin-film self-assembly morphology properties. However, these good properties of three compounds with carbon–carbon triple bonds may be of great interest for the development of photovoltaic materials and organic thin-film materials.

## Experimental

### Materials

2-Bromothiophene and 2,5-dibromothiophene were purchased from the China Medicine Shanghai Chemical Reagent Corp, China. All other chemicals were purchased from Aldrich and Acros and used as received without further purification. N-iodosuccinimide (NIS) [74], 2,2'-bithiophene (2T) [75], 4-((5'-iodo-[2,2'-bithiophen]-5-yl)ethynyl)aniline [76], 4-ethynylaniline and 4-((trimethylsilyl)ethynyl)aniline [77] were prepared according to the published procedures. Catalyst  $Pd(PPh_3)_2Cl_2$  [78] was prepared from  $PdCl_2$  according to the published literature. 4,4'-Diethynyl-1,1'-biphenyl [79] was prepared from 4,4'-diiodo-1,1'-biphenyl according to the published literature. Solvents were purified and dried according to the standard procedures.

### Measurements and characterizations

$^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker AVANCE 300 NMR Spectrometer with  $CDCl_3$  as the solvent with tetramethylsilane (TMS) as an internal reference. LC–MS were obtained from Agilent 6510 Accurate-Mass Q-TOF LC/MS system. Infrared measurements with the KBr pellet technique were performed within the 4000–400  $cm^{-1}$  region on a Bruker ALPHA FT-IR spectrometer. Ultraviolet absorption (UV) spectra of these samples ( $CHCl_3$  solution) were recorded using a Hitachi U-4100 spectrometer. Photoluminescence (PL) measurements were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp. Cyclic voltammetry (CV) measurement was performed on a CHI832 electrochemical instrument with a three-electrode cell in a solution of 0.1 M tetrabutylammonium perchlorate ( $n-Bu_4NClO_4$ ) in anhydrous dichloromethane at room temperature under nitrogen atmosphere with a scan rate of 100 mV/s. The working electrode was glass–carbon electrode, the counter electrode was a platinum wire, and the reference electrode was  $Ag/AgCl$  ( $Ag$  in 0.1 M  $AgNO_3$  solution of MeCN) which was separated by a diaphragm. Ferrocene–ferrocenium ( $Fc/Fc^+$ ) couple was chosen as internal standard. Thermogravimetric analysis (TGA) measurements were obtained by TA Q500 instrument with heating rate of 10  $^{\circ}C/min$  under nitrogen condition from room temperature to 800  $^{\circ}C$  at ambient pressure. OM was performed on a BX-51 polarization optical microscope (Olympus, Japan). The

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