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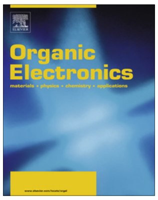

# The locally twisted thiophene bridged phenanthroimidazole derivatives as dual-functional emitters for efficient non-doped electroluminescent devices

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ABSTRACT

A series of locally twisted dual-functional materials namely **PIPT**, **PITT** and **PIFT** have been designed and synthesized by introducing different polyaromatic hydrocarbon groups to a phenanthroimidazole backbone through a thiophene bridge. In these molecules, the thiophene bridge and phenanthroimidazole platform are nearly coplanar and this endows these materials with relatively shallow HOMO levels (−5.35 to −5.21 eV). On the other hand, the bulky polyaromatic hydrocarbon units introduce non-planar twisty structures which reduce molecular aggregations. These three materials show color-tunable emission (emission peak from 468 to 532 nm in film) and high thermal stability ($T_g > 160$ °C). Simple trilayer devices using these three phenanthroimidazole derivatives as non-doped emitting layers exhibit low turn-on voltages (2.3–2.7 V) and high maximum efficiencies of 3.74, 6.15 and 6.89 cd/A for **PIPT**, **PITT** and **PIFT**, respectively. Above all, owing to their shallow HOMO levels for enabling efficient hole-injection, even simpler bilayer devices employing these materials as hole-transporting emitters show low turn-on voltages (2.6–2.8 V) and high efficiencies of 5.77 cd/A for **PIPT**, 6.03 cd/A for **PITT** and 6.04 cd/A for **PIFT**, respectively. These comparable performances with those of the trilayer configurations show the efficient hole-injection/transport ability of these three newly developed emitters.

## 1. Introduction

Since the pioneering work on multilayered organic light-emitting devices (OLEDs) by Tang and Van Slyke [1], research on OLEDs have been intensively pursued for their applications in full-color display and solid-state lighting [2,3]. The past decades have witnessed significant advance of OLEDs through developing novel efficient electroluminescent (EL) materials and device structures [4–10], resulting in wide commercial applications. However, cost reduction in OLED manufacturing remains an important challenge.

In addition to the capital investment, the manufacturing cost of OLED mainly includes the costs for materials and device fabrication. A high performance OLED normally requires a sophisticated device configuration containing several organic layers with different functions including light-emission, carrier injection, transportation, blocking,

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etc. [11,12]. While this allows individual optimization of each material for its specific function, the device complexity and thus fabrication cost will be inevitably increased. Hence, simplifying the device configurations by using multifunctional materials is an attractive approach for cost saving [13–17].

Thiophene is an electron-rich moiety widely incorporated in various organic semiconductors for applications in organic photovoltaic cells (OPVs) [18–22], organic field-effect transistors (OFETs), etc. [23–25]. Thiophene-embedded conjugated systems normally exhibit high electrical conductivity as a result of their planar structure and strong intermolecular interactions (S…S and S…$\pi$) induced by the high polarizability of their sulfur atoms. However, these intermolecular interactions often cause fluorescence quenching [26]. For this reason, thiophene derivatives typically do not give efficient fluorescence [27–30]. Hence, the key for developing efficient thiophene-based emitters is to reduce the intermolecular interactions in their solid states.

Phenanthroimidazole is a thermally stable and highly emissive heterocyclic aromatic compound and a number of phenanthroimidazole derivatives have been developed as bipolar and high efficiency emitters for OLEDs [31–34]. In our previous works, Zhang et al. showed that introduction of a thiophene ring on the C2-position of phenanthroimidazole can effectively decrease the ionization potentials ($I_p$) of the compounds to enable efficient hole-injection from the hole-transporting layer (HTL) [28]. However, the added thiophene group also increases intermolecular interaction and reduced EL performance. Most recently, we reported three highly efficient bipolar blue phenanthroimidazole derivatives, TTP-TPI, DPT-TPI and DPF-TPI by incorporating polyaromatic hydrocarbon groups to the phenanthroimidazole backbone through a phenyl bridge [31]. It was shown that introduction of the bulky polyaromatic groups can effectively reduce intermolecular interactions and enhance EL performance. However, the $I_p$ of these materials are far from the work functions of the ITO electrode and thus do not allow these materials to directly accepting holes from the anode efficiently for simplifying the device configurations.

In this work, we designed and synthesized a series of new materials, **PIPT**, **PITT** and **PIFT**, by combining phenanthroimidazole and different bulky polyaromatic hydrocarbon groups through a thiophene ring. It is anticipated that the electron-rich thiophene bridge would endow these materials with high-lying HOMO levels and thus reduce the hole-injection barrier into these materials. At the same time, intermolecular interactions of these compounds are expected to be effectively reduced by the highly twisted substituents on the 1-imidazole position as well as the end-capping polyaromatic hydrocarbon groups. We also expect that these three materials possess good thermal and morphological stabilities as a result of the bulky polyaromatic hydrocarbon groups. Thermal, photophysical, and electroluminescent properties of the compounds were comprehensively investigated. These three new phenanthroimidazole derivatives have been demonstrated to be efficient host emitter with good hole-transporting properties.

## 2. Experimental section

Starting materials 5-ethynylthiophene-2-carbaldehyde [35], 1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one [36], and 7,9-diphenyl-8*H*-cyclopenta-[*a*]acenaphthylen-8-one [37] were synthesized according to the literature procedures. All other chemicals and solvents were used as received from commercial suppliers without further purification.

### 2.1. Syntheses

5-(3′,6′-Diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)thiophene-2-carbaldehyde (**1**). 5-Ethynylthiophene-2-carbaldehyde (0.36 g, 2.64 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (0.92 g, 2.40 mmol) were dissolved in o-xylene (70 mL) under an argon atmosphere, and the resultant mixture was heated for 24 h at 150 °C. After the mixture was cooled to room temperature, ethanol (100 mL) was added. The precipitate was filtered, washed with ethanol (150 mL), and dried in vacuum. Following column chromatography (petroleum ether: $CH_2Cl_2$ = 1:1) on silica gel, **1** was obtained as a white solid. Yield: 0.81 g (68.6%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.92–9.68 (m, 1H), 8.43 (dd, $J$ = 8.2, 1.5 Hz, 2H), 7.85–7.63 (m, 2H), 7.56 (d, $J$ = 8.5 Hz, 1H), 7.53–7.47 (m, 4H), 7.47–7.37 (m, 5H), 7.37–7.26 (m, 4H), 7.22 (dd, $J$ = 8.0, 1.5 Hz, 2H), 7.15–6.98 (m, 2H), 6.61 (d, $J$ = 3.9 Hz, 1H). MS (ESI$^+$): *m*/*z* 493.0 (MH$^+$). Calcd for $C_{35}H_{24}OS$: 492.63.

5-(1,4-Diphenyltriphenylen-2-yl)thiophene-2-carbaldehyde (**2**) and 5-(7,10-diphenylfluoranthen-8-yl)thiophene-2-carbaldehyde (**3**) were synthesized with the similar procedure as for **1** except that different ketones were used as starting materials as shown in Scheme 1.

(**2**) Yield: 0.76 g (65.4%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.92–9.68 (m, 1H), 8.43 (dd, $J$ = 8.2, 1.5 Hz, 2H), 7.85–7.63 (m, 2H), 7.56 (d, $J$ = 8.5 Hz, 1H), 7.53–7.47 (m, 3H), 7.47–7.37 (m, 5H), 7.37–7.26 (m, 3H), 7.22 (dd, $J$ = 8.0, 1.5 Hz, 2H), 7.15–6.98 (m, 2H), 6.61 (d, $J$ = 3.9 Hz, 1H). MS (ESI$^+$): *m*/*z* 491.4 (MH$^+$). Calcd for $C_{35}H_{22}OS$: 490.61.

(**3**) Yield: 0.90 g (62.8%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.76 (s, 1H), 7.76 (dd, $J$ = 11.0, 8.2 Hz, 2H), 7.72–7.66 (m, 2H), 7.62–7.48 (m, 8H), 7.48–7.42 (m, 2H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.34–7.27 (m, 2H), 6.87 (d, $J$ = 3.9 Hz, 1H), 6.57 (d, $J$ = 7.2 Hz, 1H). MS (ESI$^+$): *m*/*z* 465.5 (MH$^+$). Calcd for $C_{33}H_{20}OS$: 464.58.

1-(4-(*Tert*-butyl)phenyl)-2-(5-(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)thiophen-2-yl)-1*H*-phenanthro[9,10-*d*]imidazole (**PIPT**). 9,10-Phenanthrenequinone (0.31 g, 1.50 mmol), 5-(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)thiophene-2-carbaldehyde (**1**) (0.74 g, 1.50 mmol), 4-*tert*-butylbenzenamine (0.27 g, 1.80 mmol), and ammonium acetate (1.16 g, 15.0 mmol) were added into glacial acetic acid (30 mL) and the mixture was refluxed for 24 h under an argon atmosphere. After cooling to room temperature, a dark yellow mixture was obtained and poured into a methanol solution under stirring. The separated solid was filtered off, washed with methanol, and dried to give a yellow solid. The solid was purified by column chromatography (petroleum ether: $CH_2Cl_2$ = 2:1) on silica gel, PIPT