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Synthesis and Characterization of Thieno[3,4-*b*]pyrazine Materials for Solution-processible Organic Red Light-emitting Diodes

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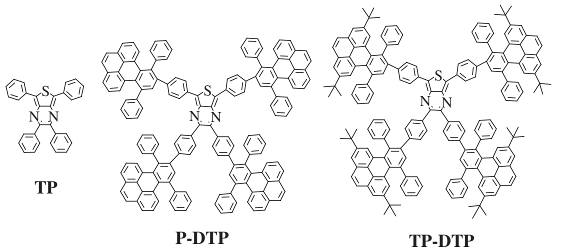
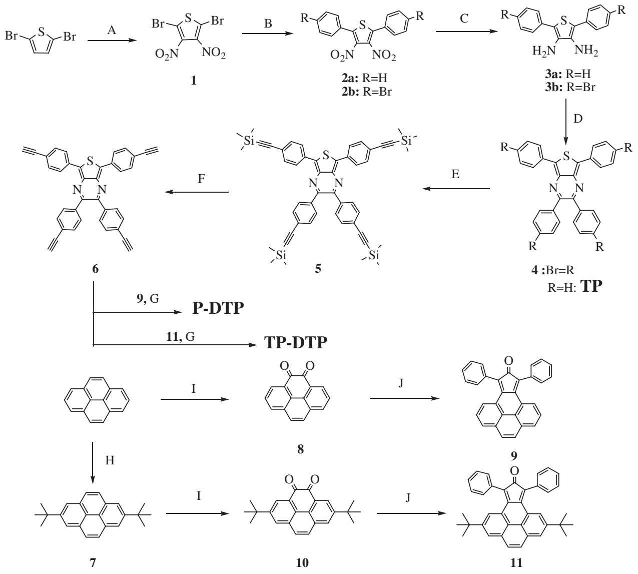
Two novel thieno[3,4-*b*]pyrazine-cored molecules, **P-DTP** and **TP-DTP**, are synthesized and are characterized by extra large Stokes shifts of over 300 nm. The bulky polyaromatic arms enable these molecules to be solution processible and provide site-isolation on the planar emissive core. They exhibit saturated red electroluminescence in nondoped organic light-emitting diodes fabricated by spin coating.

Organic light-emitting devices (OLEDs) have been drawing broad attention due to applications in flat-panel displays and solid-state lightning. Among the three primary color light-emitting materials, red still lags behind.[1–3] It is strongly desired that highly efficient red emitters with good merits such as a large Stokes shift are developed for OLED application, since severe self-absorption due to spectral overlap between the absorption and emission will definitely be unfavorable to light output.[4] Thieno[3,4-*b*]pyrazine derivatives are a series of red fluorophores with large Stokes shifts of over 250 nm and have been used as emitters to fabricate red OLEDs by vacuum evaporation.[3] However, there has been no record of thieno[3,4-*b*]pyrazine derivatives that are suitable for solution processing to fabricate OLEDs. It is well established that solution processing is the most favorable fabrication technique of OLEDs for practical applications.[5,6] Large molecules having bulky arms have been employed for solution-processible OLEDs due to inherent topological features, in which the emissive core is surrounded by a branched shell to prevent self-aggregation and concentration-quenching in solid state.[7–9] Furthermore, these molecules have merit in that they possess repeatable monodispersity and high purity, both of which are essential for ideal device performance.

In this paper, we report the synthesis and light-emitting properties of a group of thieno[3,4-*b*]pyrazine-cored molecules, **P-DTP** and **TP-DTP** (Scheme 1). The polyaromatic arms were introduced into the 2,3,5,7-positions of thieno[3,4-*b*]pyrazine core in order to protect the core via site-isolation, to provide significant molecular weight and viscosity so that the target molecules are suitable for solution processing, and to generate morphologically stable molecules due to the excellent stability of this group. For comparison, a parent compound, **TP**, was synthesized and studied under identical conditions. The synthetic procedures are shown in Scheme 2. The thieno[3,4-*b*]pyrazine emissive core was easily formed by cyclizative condensation of 2,5-diaryl-3,4-diaminothiophene and 1,2-diarylethane-1,2-dione in the presence of *p*-toluenesulfonic acid. The four terminal ethynyl groups were grafted at the periphery of the key intermediate **6** to serve as the reaction sites to introduce the polyaromatic arms. The polyaromatic arms were constructed through Diels–Alder cycloaddition of cyclopentadienone **9** or **11** to the terminal ethynyl groups in **6**. **P-DTP** and **TP-DTP** are well soluble in common organic solvents so that they were easily purified to excellent purity for OLED application.



Scheme 1. Chemical structures of the compounds in the present study.



Scheme 2. Synthetic routes for **TP**, **P-DTP**, and **TP-DTP**. Conditions and reagents; A) H_2SO_4, HNO_3; B) phenylboronic acid or 4-bromophenylboronic acid, $[Pd(PPh_3)_4]$, K_2CO_3; C) Sn, concd HCl; D) *p*-toluenesulfonic acid, 1,2-diphenylethane-1,2-dione or 1,2-bis(4-bromophenyl)ethane-1,2-dione; E) NEt_3, $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, trimethylsilylethyne; F) NH_4F, *n*-Bu_4NF; G) *o*-xylene, **9** or **11**; H) $AlCl_3$, *t*-butyl chloride; I) $NaIO_4$, $RuCl_3 \cdot 3H_2O$; J) KOH, diphenylacetone.

These compounds exhibit two major electronic absorption bands: π–π^* transition at 310–350 nm and charge-transfer (CT) transition at 480–520 nm.[3,6] (Figure 1 and Table 1). They transmit red fluorescence with peaks at 625 and 629 nm in

Table 1. Photophysical data and electroluminescent performance of **TP**, **P-DTP**, and **TP-DPT**

	λ_{abs}/nm	λ_{em}/nm	ϕ/%[a]	Stockes shift/nm	OLEDs performances				
	Toluene/ CH_2Cl_2	Toluene/ CH_2Cl_2	Toluene/ CH_2Cl_2	Toluene/ CH_2Cl_2	V_{on} /V	L_{max}/cd m^{-2} [at the voltage/V]	η_{max}/cd A^{-1} [at mA cm^{-2}]	λ_{max} /nm	CIE(*x*, *y*)
TP	323, 488/320, 482	597/605	60.5/28.4	274/285	—	—	—	—	—
P-DTP	314, 525/311, 523	619/625	55.7/28.7	305/314	5	486 (9.5)	0.32 (11.8)	648	0.66, 0.33
TP-DTP	315, 524/314, 516	620/629	52.5/21.2	305/315	5	473 (10)	0.30 (21.7)	642	0.65, 0.33

[a] Related to rhodamine B as the standard ($\phi = 0.97$ in ethanol).

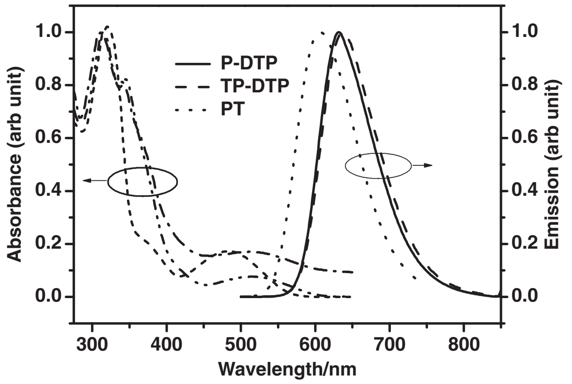


Figure 1. UV–vis absorption and PL spectra of **TP**, **P-DTP**, and **TP-DTP** in CH_2Cl_2 solution (10^{-5} mol L^{-1}, $\lambda_{exc} = 480$ nm).

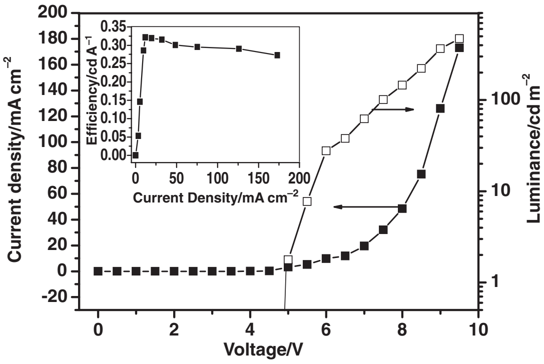


Figure 2. The *L–V–J* characteristics for **P-DTP**-based OLED; insert: Plot of luminance efficiency versus current density for **P-DTP**-based OLED.

dilute CH_2Cl_2 solution upon photoexcitation, with a red shift of over 20 nm relative to the reference **TP**. Furthermore, the full width at half maximum (FWHM) in the PL spectra is 60 and 93 nm for these molecules and **TP**, respectively. The spectra narrowing observed in **P-DTP** and **TP-DTP** should be attributed to the fact that the intermolecular interaction between the planar emissive cores is dramatically eliminated due to the site-isolation of the bulky polyaromatic groups. It is evident that both the red shift and the spectral narrowing due to the introduction of the polyaromatic groups are definitely favorable to a pure and saturated red fluorescence for these larger molecules. For **P-DTP** and **TP-DTP**, the emission spectra of the film is slightly red-shifted compared to that of the solutions (Figure S2 in Supporting Information; SI[11]), which implies a weak intermolecular interaction in the solid state. These red dyes exhibit a high ϕ_F ranging from 55% to 60% in toluene solutions. However, the ϕ_F in CH_2Cl_2 is only a half of that in toluene. This is probably because of the dipolar quenching that could occur in polar solvents.[3] It would be reasonable to presume that **P-DTP** is more efficiently luminescent than **TP-DTP**, if we take into account the effect of the *tert*-butyl groups to increase the molecular vibration and nonirradiative transition chance. The Stokes shifts are calculated as large as 310–320 nm. Such a large Stokes shift is especially valuable for light-emitting materials used in nondoped OLEDs since the absence of self-absorption will definitely facilitate efficient light output from the device.

The redox behavior was investigated by cyclic voltammetry (see SI[11]). **TP** exhibits two reversible reduction waves, and no oxidation was observed. Multiple oxidation waves were additionally detected for **P-DTP** and **TP-DTP**. It would be reasonable to assign the reduction to the thieno[3,4-*b*]pyrazine core and the oxidation to the polyaromatic arms. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were determined to be ca. −5.39 and −3.61 eV for **P-DTP**, −5.35 and −3.51 eV for **TP-DTP**, respectively.

In order to evaluate the electroluminescent (EL) properties, all these compounds were used as the emitting layer to fabricate nondoped OLEDs. The OLEDs have a configuration of ITO/PEDOT:PSS (40 nm)/EML (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm) (see SI[11] for details). Based on the excellent solubility of **P-DTP** and **TP-DTP** in common organic solvents, high-quality neat films without pinholes can be obtained by spin coating their solutions in chlorobenzene to form the EML (emitting layer). As an exception, the **TP** film is deposited by vacuum evaporation since a film of significant thickness could not be obtained via solution due to the low molecular weight and limited solution viscosity.

Both **P-DTP** and **TP-DTP** based OLEDs transmit saturated red EL with peaks at 648 and 642 nm and CIE coordinates of (0.66, 0.33) and (0.65, 0.33) for **P-DTP** and **TP-DTP**, respectively. These coordinates are close to (0.64, 0.33), which are the coordinates of the standard red color of the National Television System Committee (NTSC). Moreover, the EL spectra and CIE coordinates remain nearly unchanged with increasing driving voltage, which offers better device operation compared to red OLEDs with dopants in which the color changes with voltage.[10] The luminance–voltage–current density (*L–V–J*) characteristics for **P-DTP** as an example are displayed in Figure 2. The **P-DTP** device reaches a maximum brightness of 486 cd m^{-2} and a maximum luminance efficiency of 0.32 at 11.8 mA cm^{-1}. A comparable performance was obtained for **TP-DTP**, as shown in Table 1. In contrast, no significant brightness was obtained for the **TP** device. This may be because the small molecular **TP** is not suitable for a nondoped device due to severe emission quenching, further implying the significant contribution of these bulky polyaromatic groups in **P-DTP** and **TP-DTP** to tune their emission performance.

In summary, the newly synthesized thieno[3,4-*b*]pyrazine molecules **P-DTP** and **TP-DTP** are characterized by remarkably large Stokes shifts of over 300 nm. The solution-processed OLEDs using these thieno[3,4-*b*]pyrazine derivatives as nondoped emitting layer exhibited pure and saturated red electroluminescence. This report provides a practical strategy to decorate the highly efficient but planar luminophores to be suitable for application in solution processible and nondoped OLEDs.

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