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Quinoxalines Incorporating Triarylamine: Dipolar Electroluminescent Materials with Tunable Emission Characteristics

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Dipolar compounds (abbreviated as **QuPy**) featuring quinoxaline acceptors and diarylamine or triarylamine donors were prepared via palladium-catalyzed C-N or C-C bond formation in good yields. They possess high thermal stability with a high decomposition temperature ($T_d > 400$ °C) and exhibit no crystalline character. The emission colors of the materials vary from green to orange red and are dependent on the nature of the electron-withdrawing segments and solvents. Two types of double-layer organic light-emitting diodes (OLEDs) were constructed using these dipolar compounds as hole-transporting/emitting layers and TPBI or Alq₃ as an electron-transporting layer: (I) ITO/**QuPy**/Alq₃/Mg:Ag and (II) ITO/**QuPy**/TPBI/Mg:Ag (TPBI = 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene; Alq₃ = 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene). The recombination zone in most of those devices were confined in the quinoxaline layers. The green to orange colors in these devices correspond well with the film PL of the material used. The relation between the energy levels of the compounds and the performance of the light-emitting diode are discussed.

Keywords: Quinoxaline; Triarylamine; Electroluminescent materials; Dipolar compounds.

INTRODUCTION

In the past decade, electroluminescent (EL) devices based on small organic molecules or polymers attracted considerable interest^{1,2} after the reports by Kodak's team¹ and Cambridge's group.¹ Dipolar compounds have potential application in optoelectronics due to their charge transfer character which may lead to prominent optical non-linearity³ or red-shifted emission.⁴ Organic light emitting diodes⁵ (OLEDs) require non-crystalline film capable of carrying both holes and electrons. In recent years, a wide array of dipolar compounds have been synthesized for electroluminescent applications. Prominent among them are those with oxadiazole/amine,^{6,7} pyridine/quinolineamine,⁸ thiophene or pyrrole/benzothiadiazole⁹ and carbazole/cyanovinylene¹⁰ combinations. Better balance of hole and electron transporting to confine the excitons in the emitting layer may be achieved via the use of these dipolar com-

pounds.

We have been interested in molecules that incorporate multiple functions for applications in OLEDs. Earlier we reported dipolar systems: (i) carbazole based pyrene amines^{11,13} (ii) acenaphthopyrazine derivatives¹⁷ and (iii) cyanocarbazole derivatives,¹⁸ and demonstrated their promising hole-transporting and emitting properties. In a continuation of our efforts¹¹⁻¹⁸ on the preparation of materials with both light-emitting and charge transporting properties for OLEDs, we report herein the synthesis of quinoxaline- and pyridopyrazine-based conjugated materials end-capped with donor fragments (triarylamine or diarylamine). A thiophene moiety is introduced in the conjugation chain in order to enhance the dipolar character. The presence of the thiophene moiety also facilitates the synthesis of the target molecules. We have evaluated the function of these materials in double layer OLEDs by using them as the hole-transporting and emitting layer. A quinoxaline segment has been

used as a building block in hole-blocking or electrontransporting polymers and small molecules.^{19,20} However, only recently have triarylamine-quinoxaline dyads and related derivatives been systematically explored as electroluminescent materials.²¹

RESULTS AND DISCUSSION

Synthesis and optical properties

Scheme I illuminates synthetic procedures of these dipolar compounds (abbreviated as **QuPy**). Compounds **3-6** containing quinoxaline or pyridopyrazine and diarylamine segments were prepared via palladium catalyzed C-N bond cross coupling reactions which were developed by Hartwig²² et al. Compounds **7-9** were synthesized by Stille's cross-coupling reactions²³ with the formation of C-C bonds. Two different diaryl(tributylthienyl)amines mentioned in our previous report²⁴ were allowed to react with the corresponding dibromo quinoxaline derivatives (**1**

and **2**) in dimethyl formamide to form the desired products in good yields. The dipolar materials are yellow or orange red in color and soluble in most solvents. In the electronic spectra of **3-6** (Fig. 1, Chart 1), the bands arising from the π - π^* and charge-transfer (CT) transitions were observed.

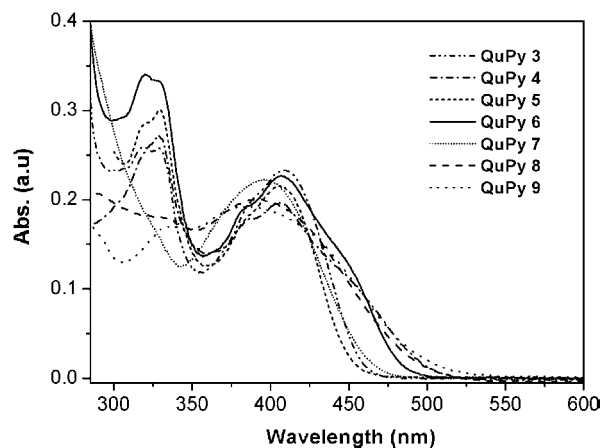
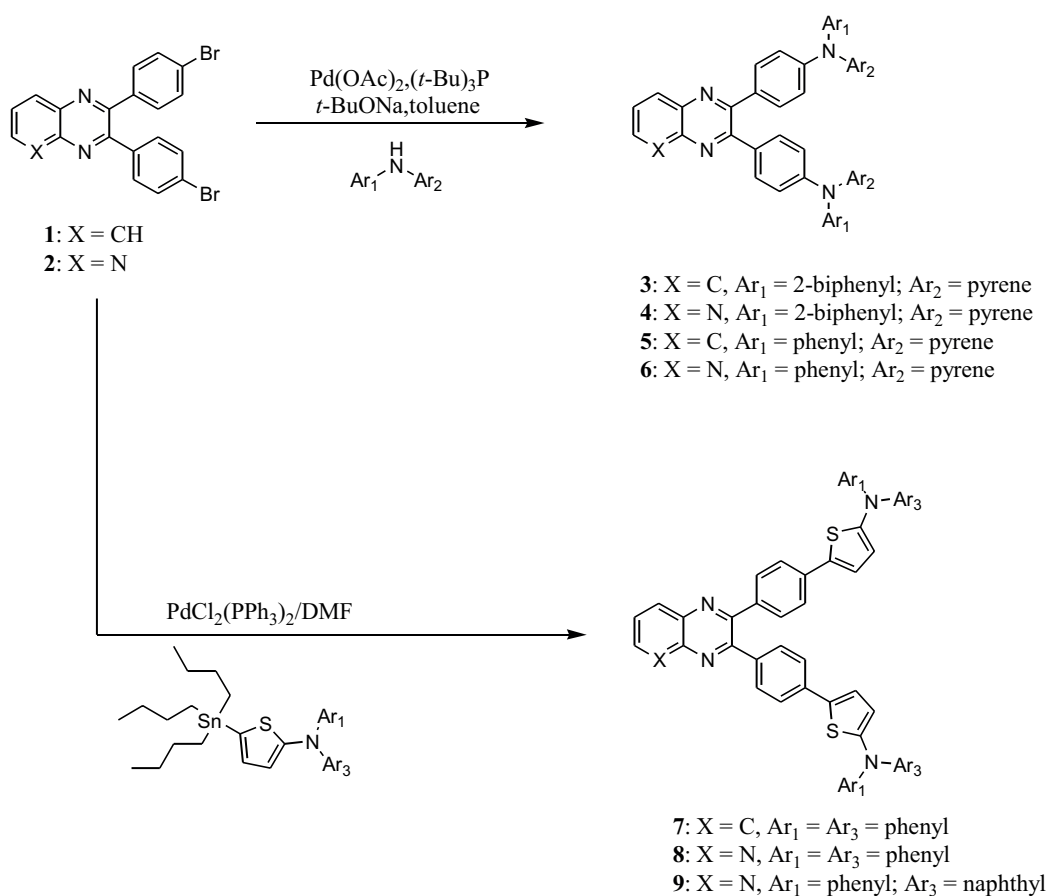


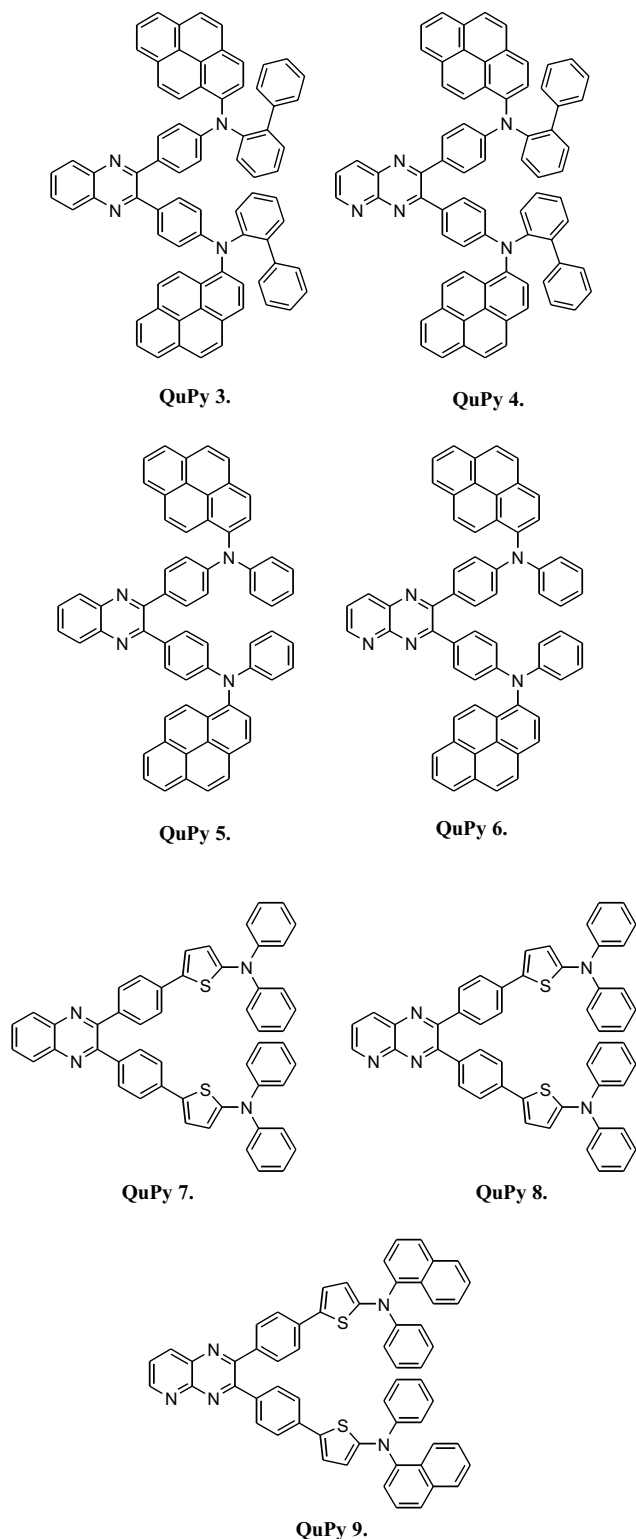
Fig. 1. The absorption spectra of the **QuPys** in dichloromethane solution.

Scheme I Synthesis of QuPys 3-9



The lower energy bands, without notable solvatochromism, are assigned as mainly of CT transition. In **7-9** (Chart 1), an

Chart 1



additional high-energy transition with weaker intensity is also realized. This is attributed to the $n\text{-}\pi^*$ transition arising from the terminal diphenylamine moieties. No discrete charge transfer bands are found in these compounds and we assume that they are buried in the $\pi\text{-}\pi^*$ transition. In less polar solvents such as toluene, all the compounds emit green light of moderate intensity. The emission band shifts to longer wavelength on increasing the acceptor strength, i.e., replacement of the quinoxaline moiety by the pyridopyrazine segment (**3** vs. **4**; **5** vs. **6**, and **7** vs. **8**; Fig. 2). On increasing the solvent polarity the emission band also shifts bathochromatically. However, the emission intensity diminishes significantly.

Thermal properties

The glass forming capability and thermal stability of these materials were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The pertinent data are listed in Table 1. All the compounds are thermally stable up to 400 °C in nitrogen atmosphere. The decomposition temperature increases progressively on incorporating the chromophores such as pyrene. Thus, **QuPy 3** to **6** exhibit the highest T_d among all. No crystallization and melting behaviors were detected for **QuPy 3**, **4**, **8**, and **9** during repetitive heating/cooling cycles. However, only **QuPy 4** exhibited glass transition endotherm behavior in DSC plots. On the contrary, **QuPy 5** and **6** displayed melting isotherms during the first heating cycle, but rapid cooling of the melt led to the formation of glass which persisted in the subsequent heating cycles (Fig. 3). Fast cooling of the melt also suppresses the formation of crystals for **QuPy 7**, but no glass transition can be identified. The glass transition temperatures of the compounds appear to be rather high among commonly used hole-transport materials, such as 1,4-bis(1-naphthylphenylamino)biphenyl ($\alpha\text{-NPD}$, $T_g = 100$ °C), and 1,4-bis(phenyl-m-tolylamino)biphenyl (TPD, $T_g = 60$ °C),²⁵ and many starburst arylamines.²

Electrochemical properties

The dipolar transport ability of a material can be confirmed by its propensity to stabilize both cation and anions. Electrochemical measurements can be used as a rough judgment of the dipolar radical formation character. We have studied these molecules by cyclic voltammetric instrument in acetonitrile and the redox potentials are reported in Table 1. All the molecules undergo a single-step

Table 1. Physical data of the compounds **QuPy 3-QuPy 9**

| Parameter | | Compound | | | | | | |
|--|--------------------------|-------------------|--------------------|-------------------|--------------------|------------------------|-----------------------|------------------------|
| | | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| λ_{abs} , nm | toluene | 327,410 | 327,408 | 330,406 | 328,408 | 396 | 291,389 | 266,334,386 |
| | CH_2Cl_2 | 325,404 | 328,408 | 274,323,401 | 275,322,404 | 292,391 | 290,390 | 268,333,385 |
| λ_{em} , nm (Φ_{f} , %) ^a | toluene | 492(52) | 535(27) | 500(34) | 527(33) | 523(21) | 570(18) | 570(11) |
| | CH_2Cl_2 | 571(7) | 622(NA) | 590(3) | 625(NA) | 629(NA) | 672(NA) | 679(NA) |
| | film | 517 | 577 | 520 | 575 | 542 | 614 | 605 |
| T_{m} , T_{c} , T_{g} | | NA, NA, NA | NA, NA, 181 | 324, NA, 140 | 304, NA, 176 | 260, NA, NA | NA, NA, NA | NA, NA, NA |
| T_{d} ($^{\circ}\text{C}$) | | /520 | /540 | /478 | /496 | /418 | /423 | /400 |
| E (ΔE_{p}) ^b , mV | | 510(42), -1963 | 500(103), -1848 | 513(80), -1954 | 484(101), -1745 | 332(105), -2088(90) | 358(62), -1833(89) | 357(92), -1855(107) |
| HOMO, ^c eV | | 5.31 | 5.27 | 5.31 | 5.26 | 5.14 | 5.15 | 5.15 |
| LUMO, ^c eV | | 2.58 | 2.79 | 2.56 | 2.78 | 2.53 | 2.59 | 2.67 |
| Band gap, ^c eV | | 2.73 | 2.48 | 2.75 | 2.48 | 2.61 | 2.56 | 2.48 |

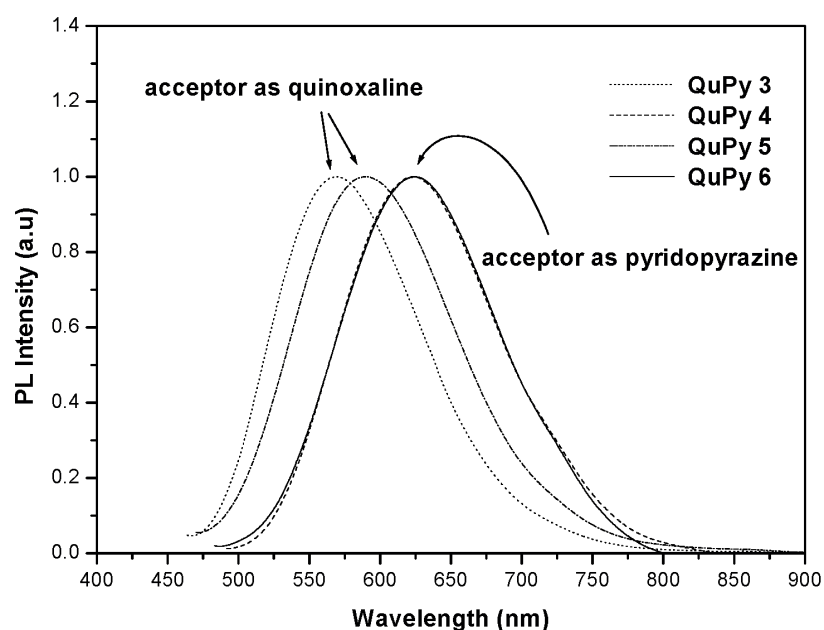
^a Quantum yield was measured relative to coumarin 6 (63% in CH_3CN). Corrections due to the change in solvent refractive indices were applied.

^b Measured in CH_3CN . All the potentials are reported relative to ferrocene, which was used as the internal standard in each experiment. Ferrocene oxidation potential was located at +332 mV relative to the Ag/AgNO_3 nonaqueous reference electrode. The concentration of the compound was 1×10^{-3} M.

^c HOMO energy was calculated with reference to ferrocene (4.8 eV). Solvent to vacuum correction was not applied. Band gap was derived from the observed optical edge and LUMO energy was derived from the relation, band gap = HOMO - LUMO.

two-electron reversible oxidation attributable to the diphenylamine core. **QuPy 7, 8, and 9** exhibited an obvious one-electron reversible reduction arising from the quinoxaline or pyridopyrazine segment. The typical cyclic voltammograms are shown in Fig. 4 for **QuPy 3-5**. Only quasi-reversible cathodic reduction waves could be observed in

QuPy 3-6. The cathodic wave attributable to the reduction of the azine (pyridopyrazine or quinoxaline) segment progresses anodically on increasing the acceptor strength (**4** > **3, 6** > **5**, and **8** > **7**). A counter effect due to the electron-withdrawing azine and electron-donating triarylamine is also noticed on the oxidation and reduction potentials, re-

Fig. 2. The emission spectra of the **QuPy 3-6** in dichloromethane.

spectively. In addition the extension of the conjugation chain by incorporation of one thiophene ring in the dipolar molecules such as **QuPy 7**, **8**, and **9** leads to a lower oxidation potential.

The energy of the HOMO of these materials, calculated with reference to ferrocene (4.8 eV), ranges from 5.14 to 5.31 eV. The optical edge was utilized to derive the bandgap. This together with the HOMO energy were used to calculate the LUMO energy. As expected, the pyridopyrazine derivatives possess lower LUMO energies and smaller band gaps when compared to the simple quinoxaline derivatives. They (2.53–2.79 eV) are slightly higher

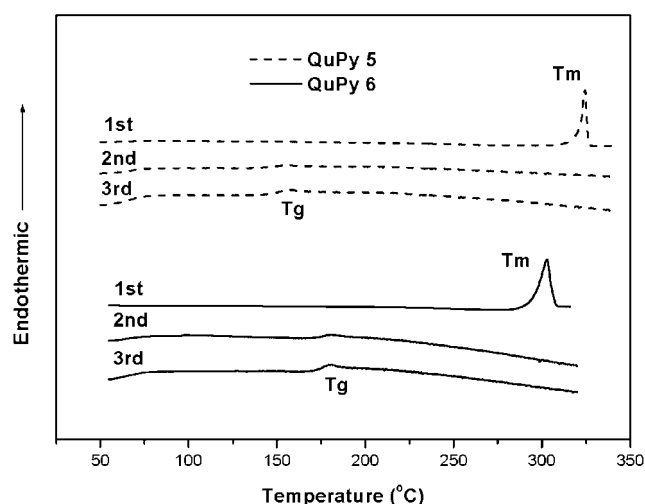


Fig. 3. Differential scanning calorimetry plot of **QuPys 5** and **6**.

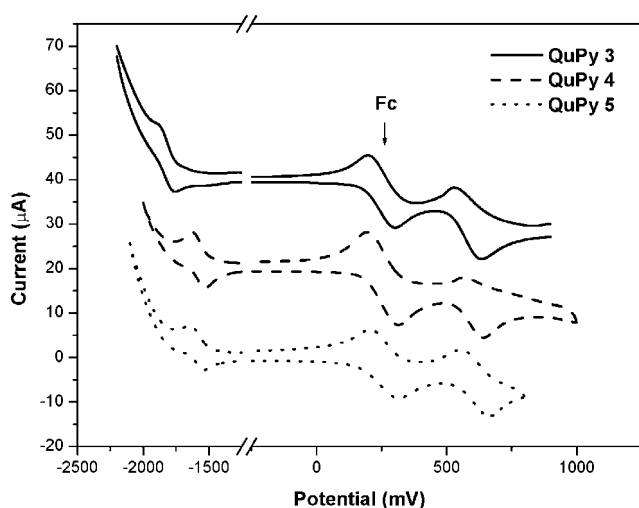


Fig. 4. Cyclic voltammogram of **QuPys 3–5** measured in dichloromethane solution.

than those observed for quinoxaline monomers^{20d} and quinoxaline heterocycle hybrid polymers,^{20d} and this is attributed to the presence of electron-donating triarylamine in the quinoxalines which raises the LUMO level. Molecules that can stabilize both cation and anion radicals are suggested to be beneficial for OLED devices.²⁶

Electroluminescent properties

Electron-transporting materials TPBI and Alq₃ were synthesized according to literature procedures²⁷ and were sublimed twice prior to use. Prepatterned ITO substrates with an effective individual device area of 3.14 mm² were cleaned as described in a previous report.¹⁴ Double-layer EL devices using quinoxaline derivatives as the HTL and TPBI or Alq₃ as the ETL were fabricated. All devices were prepared by vacuum deposition of 400 Å of the HTL, followed by 400 Å of TPBI or Alq₃. The *I*-*V* curve was measured on a Keithley 2400 source meter in an ambient environment. The light intensity was measured with a Newport 1835 optical meter. An alloy of magnesium and silver (10:1, 500 Å) was deposited as the cathode, which was capped with 1000 Å of silver.

In view of the low-lying LUMO of **QuPy 3–9** (Fig. 5), we attempted to use them as the electron-transporting/emitting layer. However, both the double-layer device (ITO/NPB (40 nm)/**QuPy** (40 nm)/Mg:Ag) (NPB: 4,4-bis-*N*-(1-naphthyl)-*N*-phenylamino)-biphenyl) and single-layer device (ITO/**QuPy** (80 nm)/Mg:Ag) exhibited only very low efficiencies with maximum brightness less than 500 cd/m², indicating poor electron-transporting ability of these compounds. Therefore, two types of double-layer devices using **QuPys** as both hole-transporting and emitting materials, and TPBI or Alq₃ as the electron-transporting materials, were fabricated: (I) ITO/**QuPy** (40 nm)/Alq₃ (40 nm)/Mg:Ag; (II) ITO/**QuPy** (40 nm)/TPBI (40 nm)/Mg:Ag. The performance parameters of all the devices are collected

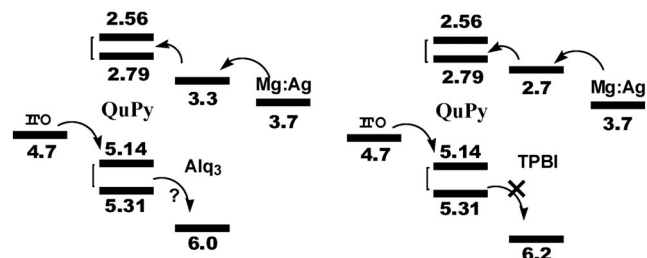


Fig. 5. Energy alignments of the **QuPys** with Alq₃ and TPBI.

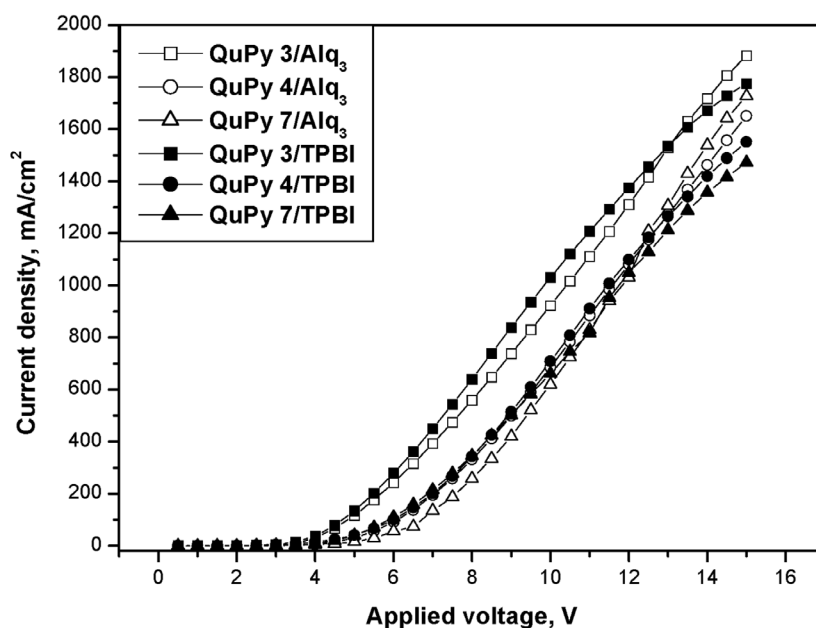
Table 2. Electroluminescent data of the devices fabricated from **QuPy 3-QuPy 9**^a

| | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| V_{on} , V | 3.0; 3.0 | 3.0; 3.0 | 3.0; 4.5 | 4.5; 3.5 | 3.5; 3.0 | 4.5; 5.0 | 3.0; 3.5 |
| L_{max} , cd/m^2 | 25370 (11); | 24956 (13); | 14552 (10); | 3036 (13); | 13960 (13); | 974 (13); | 7075 (13); |
| (V at L_{max} , V) | 30334 (12.5) | 29344 (14) | 8219 (12.5) | 22297 (13.5) | 21032 (15) | 692 (13) | 6120 (15) |
| λ_{em} , nm | 516; 512 | 574; 578 | 510; 508 | 574; 576 | 544; 542 | 590; 606 | 602; 606 |
| CIE (x,y) | 0.27, 0.57; 0.25, 0.57 | 0.46, 0.51; 0.49, 0.50 | 0.26, 0.54; 0.23, 0.55 | 0.47, 0.50; 0.49, 0.50 | 0.38, 0.57; 0.38, 0.58 | 0.46, 0.49; 0.55, 0.43 | 0.50, 0.47; 0.56, 0.42 |
| fwhm, nm | 82; 76 | 118; 108 | 84; 74 | 124; 106 | 94; 86 | 150; 110 | 134; 108 |
| $\eta_{\text{ext,max}}$, % | 1.1; 1.2 | 1.1; 1.1 | 0.72; 0.35 | 0.58; 0.84 | 0.49; 1.0 | 0.06; 0.09 | 0.38; 0.60 |
| $\eta_{\text{p,max}}$, lm/W | 2.8; 2.7 | 1.9; 1.8 | 1.2; 0.35 | 0.11; 1.1 | 1.0; 1.6 | 0.05; 0.07 | 0.57; 0.77 |
| $\eta_{\text{c,max}}$, cd/A | 3.5; 3.7 | 3.0; 3.2 | 2.2; 1.1 | 0.28; 2.4 | 1.7; 2.1 | 0.13; 0.17 | 0.83; 1.0 |
| L , cd/m^2 (*) | 3445; 3632 | 2988; 3165 | 2004; 470 | 230; 2189 | 1640; 1842 | 132; 174 | 809; 782 |
| η_{ext} , % (*) | 1.07; 1.16 | 1.1; 1.1 | 0.65; 0.12 | 0.08; 0.77 | 0.48; 0.53 | 0.05; 0.09 | 0.37; 0.42 |
| η_{p} , lm/W (*) | 2.2; 2.4 | 1.5; 1.7 | 1.2; 0.20 | 0.11; 1.1 | 0.77; 1.0 | 0.05; 0.06 | 0.39; 0.36 |
| η_{c} , cd/A (*) | 3.4; 3.6 | 3.0; 3.2 | 2.0; 0.46 | 0.23; 2.2 | 1.6; 1.8 | 0.13; 0.17 | 0.81; 0.78 |

^a The measured values are given in order of the devices I and II. L_{max} , maximum luminance; L , luminance; V_{on} , turn-on voltage; V , voltage; $\eta_{\text{ext,max}}$, maximum external quantum efficiency; $\eta_{\text{p,max}}$, maximum power efficiency; $\eta_{\text{c,max}}$, maximum current efficiency; η_{ext} , external quantum efficiency; η_{p} , power efficiency; η_{c} , current efficiency; fwhm, full width at half maximum. *, at a current density of 100 mA/cm^2 . V_{on} was obtained from the x-intercept of $\log(\text{luminance})$ vs applied voltage plot.

in Table 2. The current-voltage (I-V) and luminance-voltage (L-V) characteristics are shown in Fig. 6 and Fig. 7. Fig. 8 shows the EL spectra of the devices I and II. Light is emitted from the **QuPys** in the device I. A small contribution of emission from Alq_3 was evident in the device I of all compounds: the fwhms were slightly wider than those of the device II. Since the difference of the HOMO energy between

QuPy and Alq_3 (HOMO = 6.00 eV) is less than that between **QuPy** and TPBI (HOMO = 6.2 eV), more leakage of holes into the Alq_3 layer in the devices II is expected. Bright green to orange red emission was realized for all the devices. The solid film photoluminescence spectra are almost superimposable with the electroluminescence spectra of device II, indicating that the excitons are effectively confined

Fig. 6. Current density vs applied voltage characteristics of the devices I and II for selected **QuPys**.

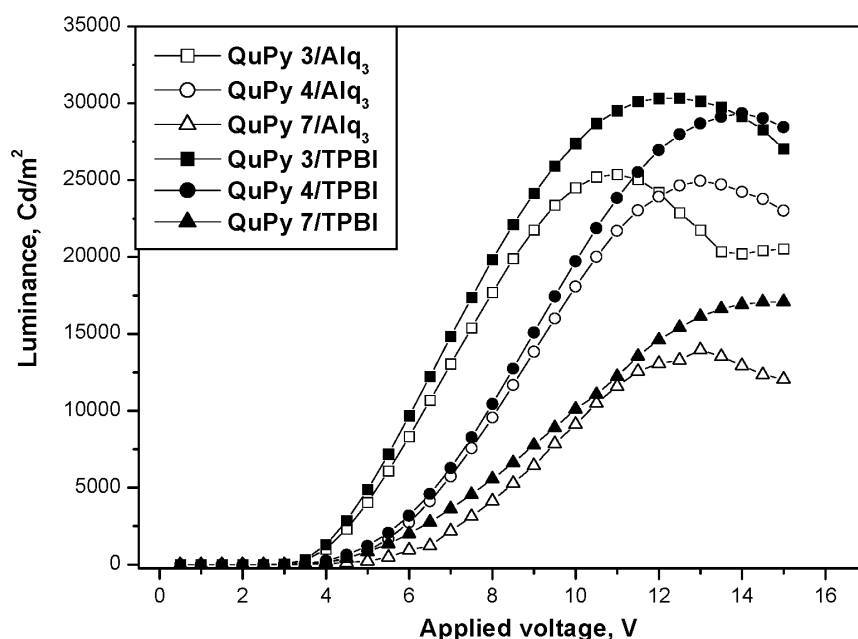


Fig. 7. Luminance vs applied voltage characteristics of the devices I and II for selected QuPys.

in our dipolar compounds. Because the HOMOs of the molecules lie very close to the work function of indium-titanium oxide (ITO), the hole injection should be facile and the low drive voltages (defined as the voltage required to achieve a brightness of 1 cd/m^2) for the devices seem to attest this. The devices II of compounds **3** and **4** exhibited maximum luminance of 30334 lm/w at 12.5 V and 29344 lm/w at 14 V , respectively. Incorporation of thienyl entity in the conjugation chain is beneficial in increasing the emission wavelength.²⁴ Indeed, QuPy **8** and **9** emit in the

longer wavelength region (orange-red) than does **4**. However, the performance of the devices fabricated from **8** and **9** is inferior to that of **4**.

SUMMARY

Quinoxaline/pyridopyrazine-triarylamine conjugates with varied conjugation were prepared by Hartwig or Stille coupling reactions and employed as electroluminescent materials. The emission colors of these materials were tunable from green to orange red by changing the nature of the amine and quinoxaline units. The quinoxaline fragment in the triarylamine compartment leads to the efficient confinement of the excitons in the HTL layer. Our future studies will be asymmetric congeners aiming at better balance of electron and hole mobilities.

EXPERIMENTAL

All column chromatography was using silica gel (230-400 mesh, Macherey-Nagel GmbH & Co.) as the stationary phase. The ^1H NMR spectra were recorded on a Bruker AC300 or AMX400. Electronic absorption spectra were measured using a Cary 50 spectrophotometer. Emis-

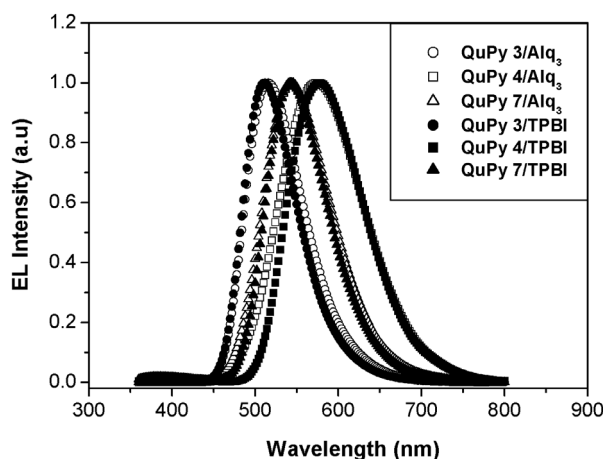


Fig. 8. EL spectra of the devices I and II for selected QuPys.

sion spectra were recorded by a Hitachi F-4500 spectrometer. Emission quantum yields were measured with reference to coumarin 6 in CH₃CN²⁸. Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. DSC measurements were carried out using a Perkin-Elmer 7 series thermal analyzer at a heating rate of 10 °C/min. TGA measurements were performed on a Perkin-Elmer TGA7 thermal analyzer. Mass spectra (FAB) were recorded on a JMS-700 mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

General Procedure for the Syntheses of the Donor-Acceptor QuPy (3-6)

A two-necked round-bottomed flask was charged with Pd(OAc)₂ (1 mmol % per halogen atom), NaO^tBu (1.2 equiv per halogen atom), dibromoquinoxaline derivative **1** and **2** (X = CH or N, 1.0 mmol) and the corresponding secondary amine (2.1 mmol). Dry toluene was added, and the reaction was stirred under nitrogen for 10 min. Tri-*tert*-butylphosphine (2 mmol %) in dry toluene was added through a syringe (the stock solution contained 1.0 mmol of the phosphine in 1 mL of dry toluene). The reaction mixture was heated at 80 °C till TLC indicated total consumption of amine. The reaction was quenched with water (30 mL) and the organic layer taken into 100 mL of diethyl ether, washed with a brine solution, and dried over MgSO₄. Evaporation of the solvent under vacuum resulted in a yellow to orange color solid that was adsorbed in silica gel and purified by column chromatography using dichloromethane/*n*-hexane as the eluant.

2,3-Bis[4-(*N*-2-biphenylpyrenylamino)phenyl]quinoxaline (**3**)

Yellow solid, Yield: 86%. ¹H NMR (CDCl₃): δ 6.51 (t, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 8.0 Hz, 4H), 7.01-7.03 (m, 4H), 7.25-7.28 (m, 16H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.64-7.68 (m, 4H), 7.87-7.90 (m, 4H), 7.95-7.99 (m, 6H), 8.05-8.09 (m, 2H). FAB MS: *m/e* 1017.2 (M⁺). Anal. Calcd for C₇₆H₄₈N₄: C, 89.74; H, 4.76; N, 5.51. Found: C, 89.23; H, 5.10; N, 5.27.

2,3-Bis[4-(*N*-2-biphenylpyrenylamino)phenyl]pyrido[2,3-*b*]pyrazine (**4**)

Yellow solid. Yield: 84%. ¹H NMR (DMSO-*d*₆): δ 6.59-6.64 (m, 4H), 6.68-6.74 (m, 6H), 7.15-7.18 (m, 8H), 7.26-7.36 (m, 8H), 7.53-7.67 (m, 6H), 7.75 (dd, *J* = 8.34

and 1.77 Hz, 1H, pyridyl), 7.84-7.89 (m, 2H), 7.93-7.98 (m, 2H), 8.07-8.08 (m, 4H), 8.17-8.22 (m, 4H), 8.42 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.8 Hz, 1H, pyridyl), 9.04 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.8 Hz, 1H, pyridyl). FAB MS: *m/e* 1018.2 (M⁺). Anal. Calcd for C₇₅H₄₇N₅: C, 88.47; H, 4.65; N, 6.88. Found: C, 88.28; H, 4.95; N, 6.69.

2,3-Bis[4-(*N*-phenylpyrenylamino)phenyl]quinoxaline (**5**)

Yellow solid, Yield: 78%. ¹H NMR (CDCl₃): δ 6.99-7.04 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.67-7.71 (m, 4H), 7.81 (d, *J* = 8.0 Hz, 2H, quinoxaline), 7.90-7.94 (m, 4H), 8.02 (d, *J* = 8.0 Hz, 2H, quinoxaline), 8.03-8.06 (m, 4H), 8.09-8.15 (m, 6H). FAB MS: *m/e* 865.2 (M⁺). Anal. Calcd for C₆₄H₄₀N₄: C, 88.86; H, 4.66; N, 6.48. Found: C, 88.26; H, 4.89; N, 6.31.

2,3-Bis[4-(*N*-phenylpyrenylamino)phenyl]pyrido[2,3-*b*]pyrazine (**6**)

Yellow-red solid. Yield: 80%. ¹H NMR (CDCl₃): δ 6.92-6.97 (m, 4H), 7.01-7.05 (m, 2H), 7.12-7.24 (m, 5H), 7.40 (d, *J* = 7.3 Hz, 2H, C₆H₄), 7.52 (d, *J* = 8.4 Hz, 2H), 7.65 (m, 2H, C₆H₄), 7.70 (d, *J* = 8.3 Hz, 1H, pyridyl), 7.77-7.82 (m, 2H), 7.88-7.92 (m, 5H), 7.98 (d, *J* = 9.5 Hz, 2H), 8.04-8.05 (m, 5H), 8.10-8.13 (m, 5H), 8.46 (d, *J* = 8.34 Hz, 1H, pyridyl), 9.05 (br, 1H, pyridyl). FAB MS: *m/e* 886 (M⁺). Anal. Calcd for C₆₃H₃₉N₅: C, 87.37; H, 4.54; N, 8.09. Found: C, 87.07; H, 5.01; N, 7.69.

General Procedure for the Synthesis of the Donor-Acceptor QuPy (7-9)

To a flask containing a mixture of diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine (2.2 mmol), dibromoquinoxaline derivative (X = CH or N, 1.0 mmol), and PdCl₂(PPh₃)₂ (0.10 mmol) was added DMF (5 mL). The solution mixture was heated at 80 °C for 24 h, then cooled, and MeOH was added. The solid formed was collected by filtration. Further purification through a column chromatograph using CH₂Cl₂/*n*-hexane as eluent gave products as a yellow powder.

2,3-Bis[4-(2-*N,N*-diphenylamino-5-thiophenyl)phenyl]quinoxaline (**7**)

Yellow solid, Yield: 81%. ¹H NMR (CDCl₃): δ 6.71 (d, *J* = 4.0 Hz, 2H, C₄H₂S), 7.09 (t, *J* = 8.0 Hz, 4H, C₆H₅), 7.16-7.18 (m, 8H), 7.32-7.36 (m, 8H), 7.38 (d, *J* = 4.0 Hz,

2H, C₄H₂S), 7.60-7.62 (m, 8H), 7.85-7.87 (m, 2H, quinoxaline), 8.12-8.15 (m, 2H, quinoxaline). FAB MS: *m/e* 781.1 (M⁺). Anal. Calcd for C₅₂H₃₆N₄S₂: C, 79.97; H, 4.65; N, 7.17. Found: C, 80.05; H, 4.86; N, 7.11.

2,3-Bis[4-(2-*N,N*-phenylamino)-5-thiophenyl]pyrido[2,3-*b*]pyrazine (8)

Yellow solid, Yield: 80%. ¹H NMR (CDCl₃): δ 6.63-6.65 (m, 2H), 7.02-7.06 (m, 4H), 7.15-7.18 (m, 10H), 7.24-7.28 (m, 8H), 7.45-7.50 (m, 4H), 7.53-7.56 (m, 2H), 7.62-7.64 (m, 2H), 7.67 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.8 Hz, 1H, pyridyl), 8.47 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.8 Hz, 1H, pyridyl), 9.12-9.13 (m, 1H, pyridyl). FAB MS: *m/e* 782.0 (M⁺). Anal. Calcd for C₅₁H₃₅N₅S₂: C, 77.33; H, 4.51; N, 8.96. Found: C, 77.70; H, 4.40; N, 8.74.

2,3-Bis[4-(2-*N,N*-phenylnaphthalenylamino)-5-thiophenyl]pyrido[2,3-*b*]pyrazine (9)

Yellow solid, Yield: 83%. ¹H NMR (CDCl₃): δ 6.57-6.59 (m, 2H), 6.90-6.94 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 4H, C₆H₄), 7.09 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.5 Hz, 2H), 7.17-7.21 (m, 4H), 7.39-7.52 (m, 14H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.66 (m, 1H, pyridyl), 7.81 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.48 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.8 Hz, 1H, pyridyl), 9.11 (m, 1H, pyridyl). FAB MS: *m/e* 881.9 (M⁺). Anal. Calcd for C₅₉H₃₉N₅S₂: C, 80.33; H, 4.46; N, 7.94. Found: C, 80.51; H, 4.50; N, 7.84.

ACKNOWLEDGMENT

We thank Academia Sinica, National Chiao Tung University, and the National Science Council for financial support.

Received April 25, 2005.

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