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Synthesis of efficient blue and red light emitting phenanthroline derivatives containing both hole and electron transporting properties

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Abstract—Two phenanthroline derivatives containing a hole transporting triphenylamine and an electron transporting 1,3,4-oxadiazole unit have been prepared with high yield. UV–vis absorption and fluorescence measurement indicated they are high efficient light-emitting materials. The compounds are 6-(5-(4-*N*,*N*′-diphenylaminophenyl)-1,3,4-oxadiazol-2-yl) quinoxalino[2,3-*f*] phenanthroline (**9**, $\lambda_{max} = 635$ nm, 40% quantum yield), and 1-ethyl-2-(4-(5-(4-*N*,*N*′-diphenylaminophenyl)-1,3,4-oxadiazol-2-yl)phenyl)imidazo[4,5-*f*]phenanthroline (**14**, $\lambda_{max} = 461$ nm, 78% quantum yield). Preliminary study on electroluminescence for the two fluorescent dyes prepared from vacuum evaporation resulted in blue and red light emitting organic light emitting diodes (OLED).

Classical chelates based on 2,2′-bipyridyl and 1,10-phenanthroline have undergone an explosive development are in parallel with the rapid development of coordination chemistry in past decade. The construction of highly sophisticated molecular architecture incorporating various transition metals relies on the availability of multifunctional ligands.[1–4] In the course of developing such ligands, it is vital to have the disposal of facile synthetic methods, which lead to the synthesis of novel chelates bearing various functional groups with high yield. Oxadiazoles, triphenylamine and their derivatives are known electron and hole transporting materials and are typically used for the construction of heterojunction multi-layers OLED. The derivatives of phenanthroline, which have excellent hole blocking and electron transporting properties, are likely to have interesting value in the construction of such molecular device too.[5] Multifunctional molecules containing all the three components—triphenylamine, oxadiazole and phenanthroline fused together had not been described in the literatures. In this report, new synthetic procedures for the preparation of two such multifunctional 1,10-phenanthrolines derivatives with different fluorescent characteristics with good yield are described.

Our approach towards the preparation of multifunctional phenanthroline derivatives relies on two types of C=N bond formation. One can take advantage of the easily access 1,10-phenanthroline-5,6-dione as the starting material.[5] 1,10-Phenanthroline was treated with H_2SO_4, HNO_3 and KBr to afford 1,10-phenanthroline-5,6-dione **6** with 80% yield. Reaction of **6** with equimolar of 3,4-diaminobenzoic acid under HAC catalyst in absolute ethanol afforded compound **7** with 90% yield. Compounds **2**–**4** were synthesized according to methods described in literature.[6] Phenanthroline derivative **9** was prepared from acid chloride compound **8** and **4** with high yield (60%).[7,8] A summary of the synthetic procedures is shown in the following schematic diagram (see Scheme 1).

In order to correlate the photoluminescent properties with the effective conjugation length. Another multifunctional phenanthroline compound with similar structure was synthesized. The procedures are shown in Scheme 2. Compounds **11**, **12** were prepared by

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Keywords: Phenanthroline derivatives; Fluorescence dyes; Hole and electron transporting.

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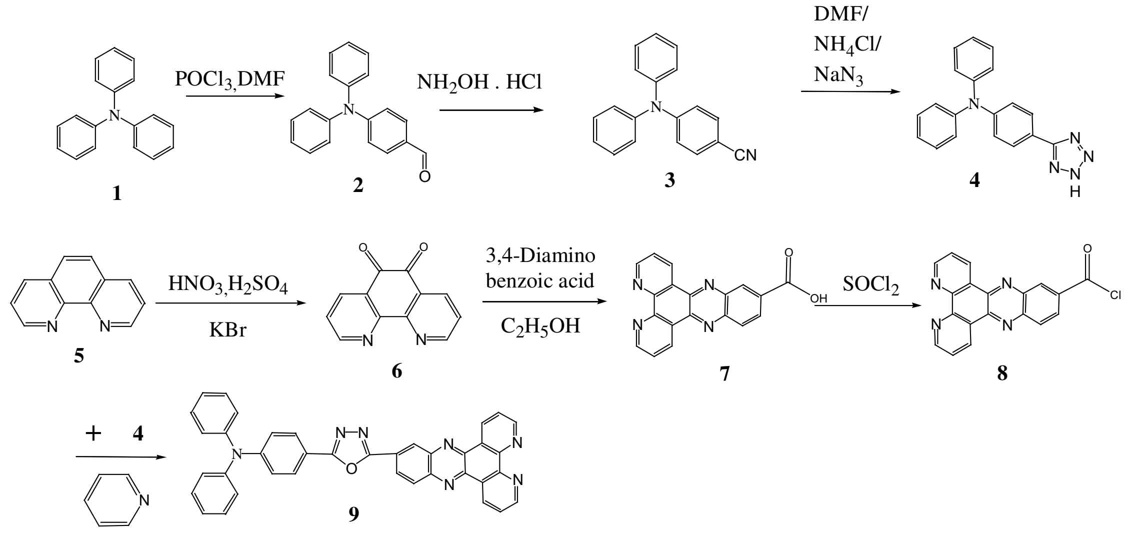
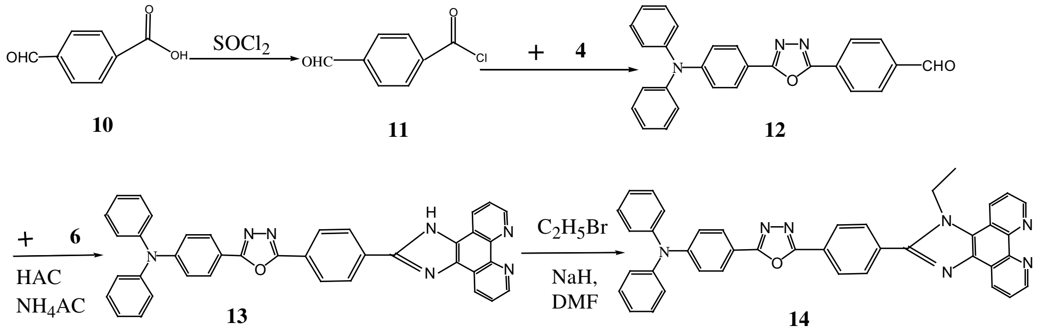


Scheme 1. Synthetic routines for compound **9**.



Scheme 2. Synthetic routines for compound **14**.

procedures similar to **8**, **9**. Reaction of **6** and **12** in the presence of pure acetic acid and ammonium acetate afford compound **13** (80% yield).[9,10] Compound **13** was then allowed to react with bromoethane under the presence of NaH to obtain phenanthroline derivative **14** with over 50% yield.[11] Both the final products **9** and **14** are soluble in $CHCl_3$, THF and acetone.

All compounds were characterized by ^1H NMR (JEOL 270 FT NMR) and MS (FAB).[7,9–11] The absorption and photoluminescent (PL) spectra of compounds **9** and **14** in THF are presented in Figure 1. The absorption spectrum of **9** extended into the visible region shown typical CT band around 416 nm and broad $\pi \rightarrow \pi^*$ transition band around 347 nm is a result of extended conjugation of the phenanthroline moiety. Emission of compound **9** is red at 635 nm ($\lambda_{ex} = 416$ nm, quantum yield = 40%), whereas the absorption and emission maximum of **14** were 372, and 461 nm (blue), respectively, ($\lambda_{ex} = 362$ nm, quantum yield = 78%).[12] The significant differences in the emission characteristics of **9** and **14** are results of electron delocalization are being allowed in between the six-member pyrazine ring and phenyl-groups in **9** whereas the five-member imidazole ring and phenyl-groups in **14** are connected through a single bond with little π-conjugation. As the conjugation length of **9** is longer than that of **14**, considerable bathochromic and hyperchromic shifts were observed.[13]

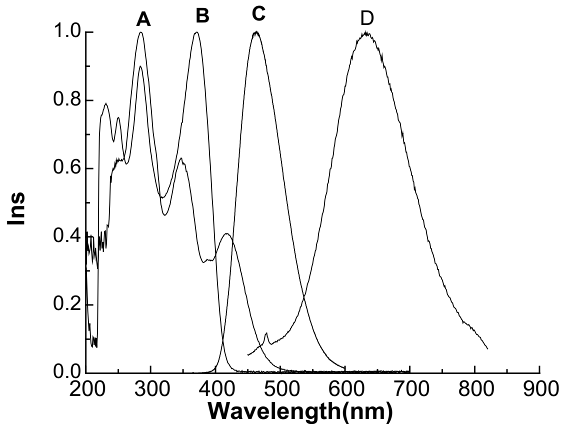


Figure 1. UV–vis absorption and fluorescence spectra of compound **9** and **14** in THF (A, D represent UV–vis, PL spectra of **9**, respectively; B, C represent UV–vis, PL spectra of **14**, respectively).

In conclusion, this report has described two synthetic routes for the preparation of novel multifunctional 1,10-phenanthroline derivatives. The two compounds have different light-emitting characteristics but are both functional charge transporting materials. We are currently exploring the photo and electroluminescent properties of these two compounds in OLEDs fabricated from traditional vacuum deposition method. Further studies for the two compounds to be used as metal coordination ligand for multifunctional molecular materials are under investigation.

Acknowledgements

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7. General procedures for the synthesis of Compounds **8** and **9**. To dipyrido(3,2-a,2′,3′-c)phenazine-8-carboxylic acid (3.28 g, 10 mmol) was added thionyl chloride (60 mL) and the mixture was refluxed for 24 h. The solution was concentrated to 10 mL under reduced pressure and then benzene (40 mL) was added. The benzene was removed also under reduced pressure later. To the residue 200 mL dry pyridine was added and then stirred until dissolved. The triphenylaminetetrazole (3.13 g, 10 mmol) in 100 mL dry pyridine was added dropwise into the mixture, and refluxed for three days. The crude product was concentrated under reduced pressure leaving a red residue. The desired product was obtained by sol–gel column chromatography using chloroform/hex (9:1) as the eluent. 6-(5-(4-*N*,*N*′-Diphenylaminophenyl)-1,3,4-oxadiazol-2-yl) quinoxalino[2,3-*f*] phenanthroline (**9**): Yellow needle; mp 300 °C (DSC); ^{1}H NMR (270 MHz) δ (ppm) (CDCl$_3$) 9.64 (d, *J* = 8.1 Hz, 2H), 9.30 (s, 2H), 9.00 (s, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 8.02–8.07 (m, 2H), 7.80–7.85 (m, 2H), 7.30–7.39 (t, *J* = 8.1 Hz, 4H), 7.12–7.19 (m, 8H); MS (FAB): 594 (M$^+$+1). Anal. Calcd for $C_{38}H_{23}N_7O$ C: 76.88%, H: 3.90%, N: 16.52%. Found C: 76.40%, H: 3.90%, N: 16.21%.
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9. 2-(4-*N*,*N*′-Diphenylaminephenyl)-5-(4-formalphenyl)-1,3,4-oxadiazole (**12**). ^{1}H NMR (270 MHz) δ (ppm) (CDCl$_3$) 10.1 (s, 1H), 8.30 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 2.7 Hz, 2H), 8.02–7.92 (m, 2H), 7.36–7.30 (m, 4H), 7.19–7.09 (m, 8H). MS (FAB): 418 (M$^+$+1).
10. 2-(4-(5-(4-*N*,*N*′-Diphenylaminophenyl)-1,3,4-oxadiazol-2-yl)phenyl)imidazo[4,5-*f*] phenanthroline (**13**). ^{1}H NMR (270 MHz) δ (ppm) (DMSO-d_6) 9.05 (dd, *J* = 2.7, 5.4 Hz, 2H), 8.99 (d, *J* = 8.1 Hz, 2H), 8.54 (d, *J* = 8.1 Hz, 2H), 8.32 (d, *J* = 8.1 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.89 (s, 2H), 7.40 (t, *J* = 8.1 Hz, 4H), 7.21–7.15 (m, 6H), 7.03 (d, *J* = 8.1 Hz, 2H), 14.05 (N–H). MS (FAB): 608 (M$^+$+1).
11. 1-Ethyl-2-(4-(5-(4-*N*,*N*′-diphenylaminophenyl)-1,3,4-oxadiazol-2-yl)phenyl)imidazo[4,5-*f*] phenanthroline (**14**). ^{1}H NMR (270 MHz) δ (ppm) (CDCl$_3$) 9.18 (dd, *J* = 2.7, 5.4 Hz, 2H), 9.09 (dd, *J* = 2.7, 5.4 Hz, 1H), 8.6 (d, *J* = 8.1 Hz, 1H), 8.3 (d, *J* = 5.4 Hz, 2H), 8.01–7.93 (m, 4H), 7.75 (dd, *J* = 5.4, 2.7 Hz, 2H), 7.37–7.31 (m,4H), 7.20–7.11 (m, 8H), 4.73 (dd, *J* = 5.4, 2.7 Hz, 2H), 1.67 (t, *J* = 8.1 Hz, 5.4 Hz, 3H). MS (FAB): 636 (M$^+$+1). Anal. Calcd for $C_{41}H_{29}N_7O\cdot H_2O$, C: 75.33%, H: 4.78%, N: 15.00%. Found C: 74.87%, H: 4.96%, N: 14.78%.
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