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NEW EFFICIENT BLUE-GREENISH ELECTROLUMINESCENT MATERIALS OF 1,3,4-OXADIAZOLE-BASED PYRAZOLE DERIVATIVES

En-Ming Chang,[b] Chi-Jen Lin,[b] Fung Fuh Wong,*[,a] and Mou-Yung Yeh*[,b,c]

[a]Sustainable Environment Research Center, National Cheng Kung University, No. 500, Sec. 3, An-ming Rd., Tainan City, Taiwan 709, R.O.C.

[b]Department of Chemistry, National Cheng Kung University, No. 1, Ta Hsueh Rd., Tainan, Taiwan 70101, R.O.C.

[c]Nan Jeon Institute of Technology, No.178, Chaocin Rd., Yanshuei Township, Tainan County 737, Taiwan R. O. C.

*Corresponding Author. Tel.: +886 6 384 0136 ext. 212; Fax.: +886 6 384 0960.
E-mail address: wongungfuh@yahoo.com.tw (F. F. Wong).

Abstract – Novel blue-greenish electroluminescent materials of 1,3,4-oxadiazole-based pyrazole derivatives as electronic-transporting molecules have been synthesized and characterized. Those compounds are convenient successful inducted a pyrazole chromophore and multiple 1,3,4-oxadiazole moieties by 1,3-dipolar-cyclization and dehydration-cyclization to promote the conjugation range and exhibit high thermal stability and good physical properties. The chromophore of pyrazole plays assistant role in controlling fundamental electroluminescent process. Spectroscopic studies, the measurements of cyclic voltammogram, thermal characterization and electroluminescent properties have revealed that 1,3,4-oxadiazole-based pyrazole derivatives are efficient blue-greenish electroluminescent materials.

INTRODUCTION

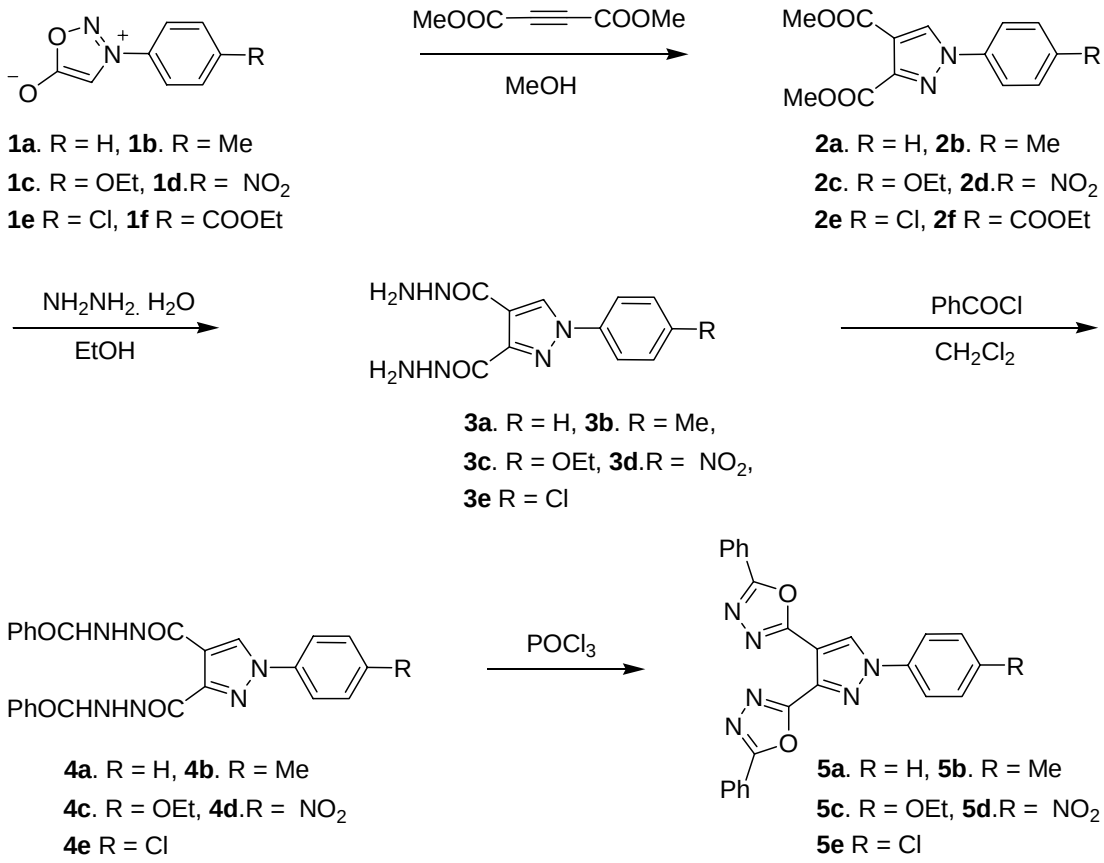
Organic materials have been expected to applicable for practical electroluminescent (EL) devices because of their high florescence efficiency and semiconducting properties. One of the most fascinating advantages of organic materials is possibility of a wide selection of emission colors, particularly in the blue region, in EL displays through the molecular design of organic materials.[1] In this work, we explored a series of new blue emission materials.

1,3,4-Oxadiazole derivatives have been widely exploited as electron-transporting, hole-blocking (ETHB) materials in electroluminescent (EL) devices due to their electron-deficient nature, their high thermal stability and high photoluminescence quantum yield (PLQL).[1] 1,3,4-Oxadiazole-based on heterocyclic compounds were also enthusiastic investigated, for example, 1,3,4-oxadiazole–pyridine hybrids[2], 1,3,4-oxadiazole–pyrimidine hybrids[2], 1,3,4-oxadiazole–carbazole[3] and 1,3,4-oxadiazole–spirobifluorene.[4] The heterocyclic moieties on the molecular structure can provide the improve electron injection, transport properties and confer rigidity. A series of dipyrazolopyridine dyes containing two pyrazole moieties in the main structure were reported by Tao et al. which provide an excellent thermal and morphological stability with high glass transition temperature (*T*g). Highly bright blue or bluish-green emission was observed in these materials.[5]

Due to pyrazole is an electron-rich heterocycle, we established to introduce pyrazole units into the conjugated main chain with 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) having two or three 1,3,4-oxadiazole moieties to improve the electron-transporting properties by using convenient synthesis strategy in 55–70% total isolated yields. Three moieties of 1,3,4-oxadiazole–pyrazole (**5f**) and 1,3,4-Oxadiazole-based pyrazole derivatives (**5a**–**5e**) with different substituted groups in *N*-phenylpyrazole, including -Me, -OEt, -NO_2 and -Cl were investigated in absorption, fluorescence, electrochemical behavior, and thermal properties. The high HOMO values in the range –4.99 to –5.09 were obtained. We have fabricated double-layer organic light-emitting diodes using ITO as the anode, 1,3,4-oxadiazole-based pyrazole derivatives (**5f**) as the emitting material, 4,4'-bis[*N*-(1-naphthyl-1-)-*N*-phenylamino]biphenyl (NPB) as the hole-transporting material and Al as the cathode. The electroluminescent properties indicated (**5f**) is a kind of highly efficient blue-greenish electroluminescent material.

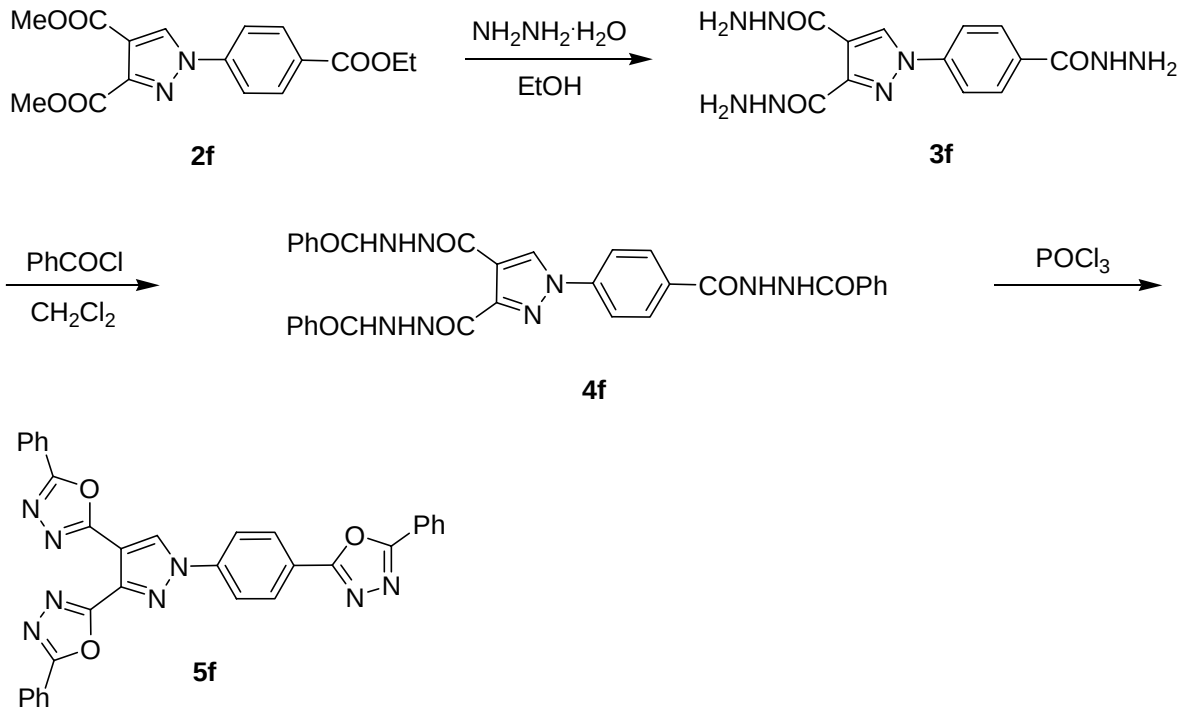
RESULTS AND DISCUSSION

Synthesis: Scheme 1 shows the synthetic route for the generation of five 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5e**). Sydnone compounds (**1a**–**1f**) were prepared by following the literature procedure which was developed by our laboratory.[6] Sydnone compounds (**1a**–**1f**) with various substituents in *N*1-phenyl, including *para*-H, -CH_3, -OEt, -NO_2, -Cl, and -COOEt groups were applied to dimethyl acetylenedicaboxylate (DMAD) to give the corresponding dimethyl 1-aryl-1*H*-pyrazole-3,4-dicarboxylate (**2a**–**2f**) as white solid in almost quantitative yields (93–98%).[8] This 1,3-dipolar cyclization has proved to be an efficient and economical way to generate the pyrazole derivatives.



Scheme 1

Treating 1-aryl-1*H*-pyrazole-3,4-dicarboxylate (**2a**–**2e**) with hydrazine hydrate at reflux afforded the corresponding dihydrazide product (**3a**–**3e**) in good yield (84–95%) according to published reports.[9] By employing the same condition in compound (**2f**), trihydrazide product (**3f**) was provided in 87% yield (see Scheme 2). Di- or trihydrazide compounds (**3a**–**3f**) reacted with benzoyl chloride in CH_2Cl_2 solution at room temperature for 2–3 h to give the corresponding bis(trihydrazide) products (**4a**–**4e**) in 75–85% yield and tri(trihydrazide) (**4f**) in 80% yield.[10] These compounds (**4a**–**4e**) and (**4f**) were performed the dehydration-cyclized to form the 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) in 90–96% excellent yields[11] in the presence of $POCl_3$.



Scheme 2

Optical properties: The UV-vis spectra of 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) were measured in CH_2Cl_2 solution. The λ_{max} values of **5a**–**5d** are in the range 270–290 nm and a gradual red shift is observed (310 nm) in **5d** due to the strong withdrawing nitro group in *para*-position of *N*1-aryl-group. In the case of **5f**, absorption band centers at around 316 nm with increasing the number of oxadiazole moieties (see Figure 1). Figure 2 shows the photoluminescence (PL) spectra of all these new compounds (**5a**–**5f**). To compounds (**5a**–**5b**) and (**5e**), their photoluminescence spectra are located in the range 365–375 nm in CH_2Cl_2 solution, respectively, and the λ_{max}s of PL is ~ 370 nm. The compounds (**5c** and **5d**) owning electron-donating groups (OEt and NO_2) have about 10 nm red-shifted with respect to **5a**. When we synthesized the three oxadiazole moieties on the pyrazole core (**5f**), we found the photoluminescence property did not improve (see Figure 2.).

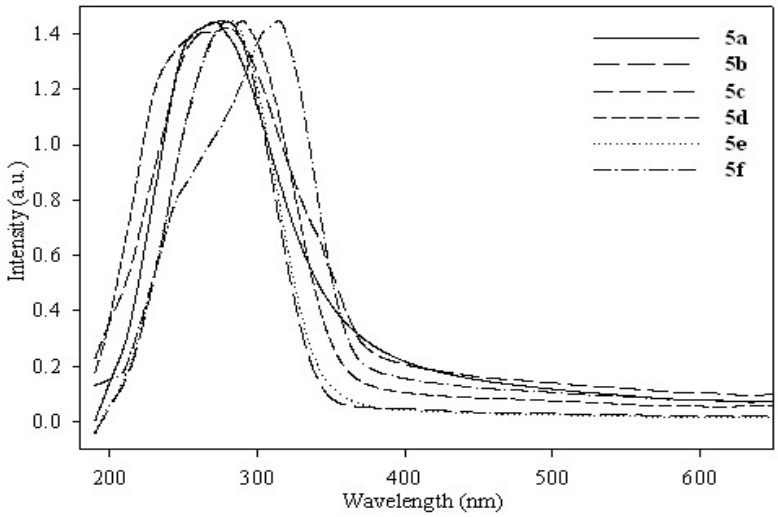


Figure 1. The UV-vis Absorption of **5a**–**5f** in Dichloromethane Solution.

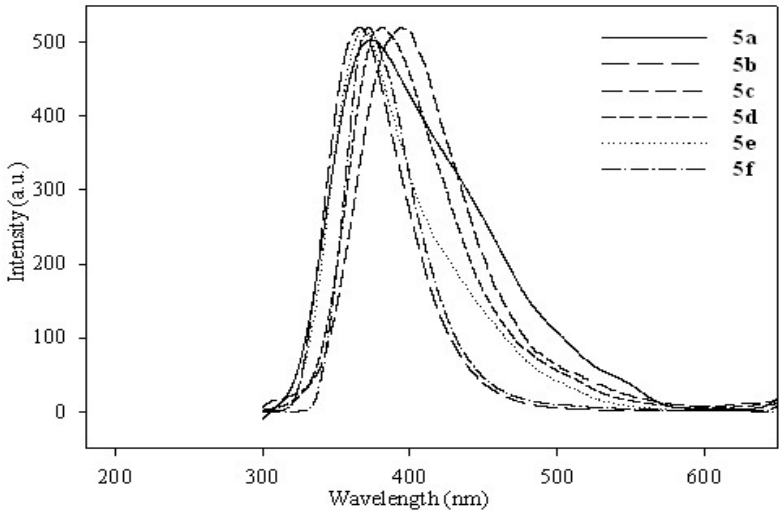


Figure 2. The Fluorescences Spectra of **5a**–**5f** in Dichloromethane Solution.

Cyclic Voltammetry Measresurements: The electrochemical properties of all 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) were investigated by cyclic voltammetry, as shown in Figure 3, and the resulting data were summarized in Table 1. Upon the anodic sweep, **5a**–**5f** showes reversible oxidation processes. Compounds (**5a**, **5c** and **5f**) were used as example and shown in Fig. 3. The bandgap energies of 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) are estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption.[12] Compounds (**5a**–**5f**) have the high LUMO values from –2.58 to –2.94 eV and the high electron affinities.

Table 1. Electrochemical properties of 1,3,4-Oxadiazole-based Pyrazole Derivatives (**5a**–**5f**).

Compound	*E*onset[a] (V)	*E'*onset[b] (V)	*Ip*[c,f] = E_{HOMO} (eV)	*Eg*[d,f] = Bandgap energy (eV)	*Ea*[e,j] = E_{LUMO} (eV)
5a	1.31	1.29	–6.09	3.31	–2.78
5b	1.54	1.52	–6.32	3.54	–2.78
5c	1.34	1.32	–6.12	3.18	–2.94
5d	1.32	1.30	–6.10	3.34	–2.76
5e	1.34	1.32	–6.12	3.54	–2.58
5f	1.34	1.32	–6.12	3.39	–2.73

[a] Measured vs. ferrocene/ferrocenium.
[b] *E'*onset = *E*onset – 0.19 eV (Measured vs. Ag/AgCl)
[c] *Ip* = - (*E'*onset + 4.8)
[d] *Eg*: the bandgap energy estimated from the onset wavelength of UV-vis absorption and the equation Y = –0.033 * X + 11.141 (X = λ_{onset},
[e] *Ea = Ip + Eg*
[f] *1 eV = 96.5 kJ/mol*

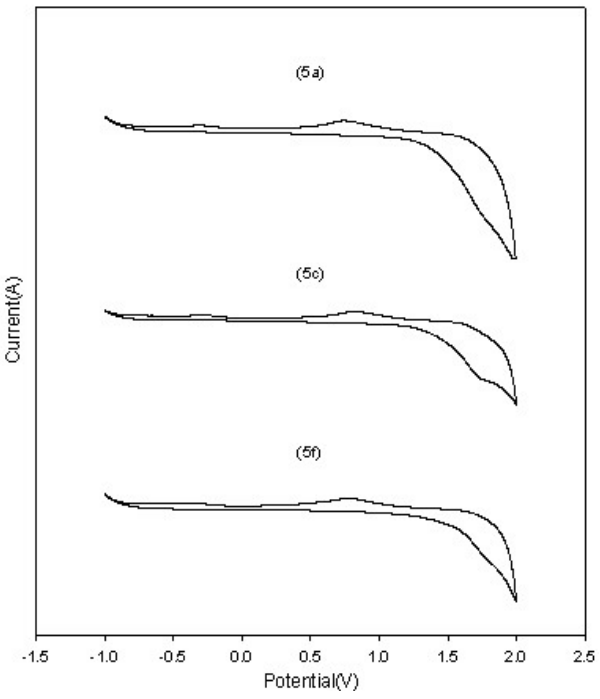


Figure 3. The Cyclic Voltammetry of **5a**, **5c** and **5f** in Dichloromethane Solution.

Thermal properties: The thermal properties of the materials were examined using DSC. The glass transition temperature (*T*g), melting temperature (*T*m) and enthalpies of melting (Δ*H*) are summarized in Table 2 and the DSC curves are shown in Figure 4 as the example. All of 1,3,4-oxadiazole-based pyrazole derivatives (**5a**–**5f**) exhibit a distinct glass transition temperature (*T*g) in the range 71–161 °C, but do undergo recystallization or melting. The compounds (**5a**, **5e** and **5f**) are prone to crystallization and exhibit a clear endothermic melt peak on the first and also on second heating at 187, 215 and 233 °C, respectively. Compounds (**5c** and **5d**) melt only on the first heating at 248 °C and 264 °C, respectively, and form metastable glasses upon cooling from the melt. The *T*g of compounds (**5**c and **5f**) was 161 °C and 153 °C, respectively. As a result, we sought compounds (**5c** and **5d**) as amorphous molecular materials, which readily form amorphous glasses. Their glassy state were greatly affected by the electron-donating groups (OEt, and NO_2). To compound (**5e**) with *N*1-4-chlorophenyl moiety showes a clear endothermic peak on the second heating at 155 °C. We assume that the compounds (**5a**, **5c** and **5d**) are suitable material for vapor deposition to obtain amorphous films[12] and compounds (**5c** and **5d**) with high *T*g own the higher thermal stability.

Table 2. DSC Data of 1,3,4-Oxadiazole-based Pyrazole Derivatives (**5a**–**5f)** (heating and cooling rate: 15 °C).

Compound	*T*g	*T*m (°C)		Δ*H*
	(°C)	1st heating	2nd heating	(J/g)
5a	71	171	-	28.4
5b	73	188	187	43.5
5c	161	248	-	36.8
5d	153	264	-	41.3
5e	85	211	215	40.7
5f	102	236	233	37.1

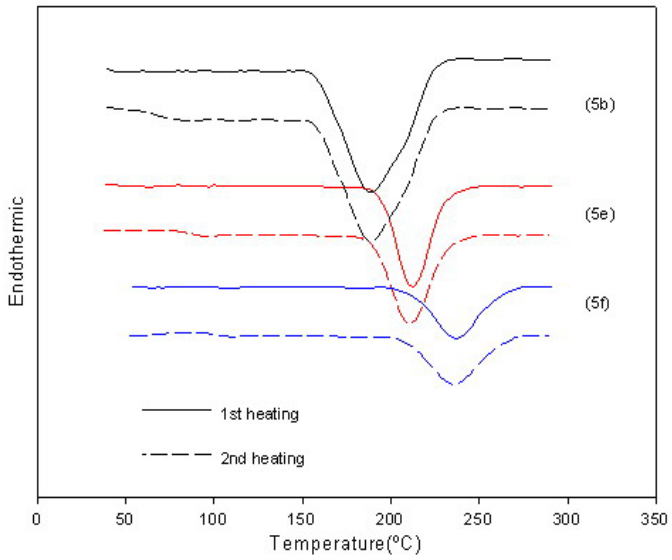


Figure 4. DSC Thermograms of 1,3,4-Oxadiazole-based Pyrazole Derivatives (**5b**, **5e** and **5f**).

Electroluminescent properties: A double-layer OLED devices with a structure of ITO/NPB (30 nm)/ 1,3,4-oxadiazole-pyrazole derivatives (**5f**, 50 nm)/Al (150 nm) were constructed by successive vapor deposition of the materials under vacuum onto the ITO-coated glass substrate.[12] The device was tested in air under ordinary laboratory conditions and was found to emit blue-greenish emission at 8.3 V onset voltage (see Figure 5). In comparison with the PL spectrum of **5f** in solution, the EL spectrum showed some deviation. The EL spectrum of **5f** as vacuum evaporated films on ITO/NPB (30 nm) substrates, shows a red-shift (~90 nm) from 371 nm (the solution spectrum) to 463 nm, which indicates that the exciplex is responsible for the EL emission (see Figure 6). An exciplex formed in the interface was commonly observed when the excited state of electronic-transporting species (i.e., **5f**) participates in charge transfer interaction with hole-transporting species (NPB) in the ground state. As a result, the exciplex gives a broad structureless band at the red side of emission. Figure 5 shows the *I-V* characteristic for the device that used NPB as the hole-transporting material at 100 mA/cm^2 current density. The external luminescent efficiency of **5f** is 1.4%.

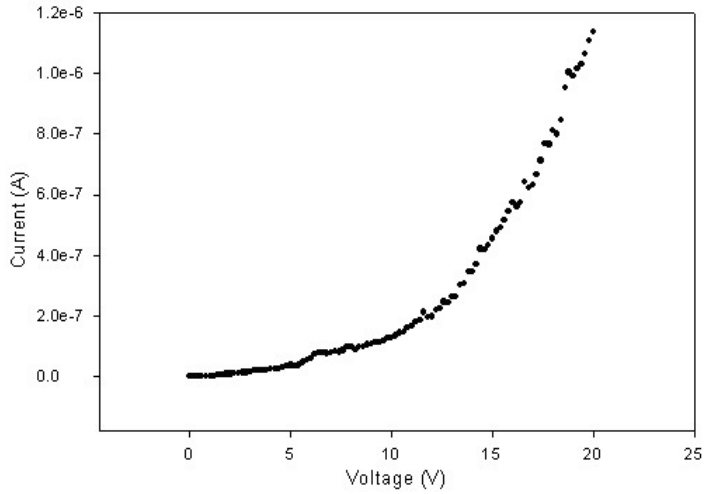


Figure 5. I–V Curves of ITO/NPB/ **5f**/Al.

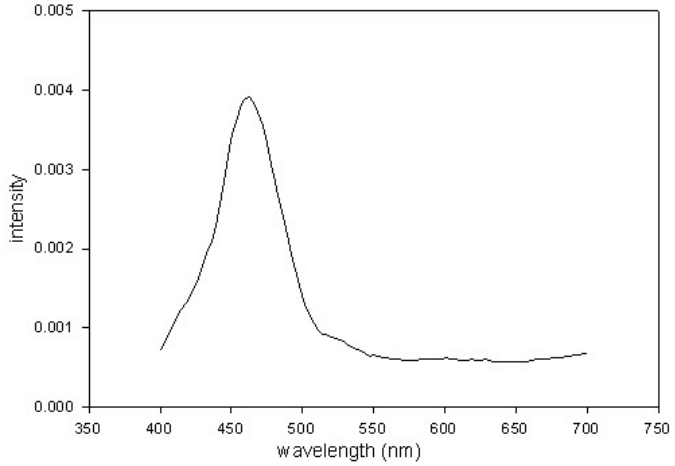


Figure 6. EL Spectrum of ITO/NPB/ **5f**/Al.

We are successful to prepare the series of novel blue electroluminescent materials with bis(oxadiazole) or tri(oxadiazole) moieties and pyrazole as the central unit. The synthetic strategy seems to be general for developing new electronic-transporting molecules. Compounds (**5c** and **5d**) with high *T*g own the higher thermal stability and the device based on 1,3,4-oxadiazole–pyrazole compounds (**5f**) emits blue-greenish light.

EXPERIMENTAL

Sydnones were synthesized according to literature procedures.[6] All chemicals were reagent grade and used as purchased. All reactions were carried out under nitrogen atmosphere and monitored by TLC analysis. Flash column chromatography was carried out on silica gel (230-400 mesh). Commercially available reagents were used without further purification unless otherwise noted. Ethyl acetate, dimethyl sulfoxide, diisopropyl ether, hexanes, glacial acetic acid, methanol, and *p*-xylene were purchased from Mallinckrodt Chemical Co. Dry tetrahydrofuran (reagent grade) and palladium 10 wt. % on carbon were

purchased from Aldrich. Benzoyl chloride, dimethyl acetylenedicaboxylate, hydrazine hydrate, and phosphorus oxychloride were purchased from Acoros Chemical Co.

Analytical thin-layer chromatography (TLC) performed on precoated plates (silica gel 60 F-254) was purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV-visible spectra were measured with a HP 8452A diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a Perkin-Elemer fluorescence spectrophotometer (LS 55). Proton NMR spectra were obtained on a Bruker (300 MHz) spectrometer by use of DMSO-*d6* as solvent. Carbon-13 NMR spectra were obtained on a a Bruker (100 MHz) spectrometer by used of chloroform-*d* as solvent. Carbon-13 chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz). Elemental analyses were carried out on a Heraeus CHN–O RAPID element analyzer.

Cyclic voltammetry Measurements: Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on a PGSTAT 20 electrochemical analyzer. The oxidation and reduction measurements were carried out, in anhydrous CH_2Cl_2 and THF containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The potentials were measured against an Ag/Ag^+ (0.01 M AgCl) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.[7]

Standard Procedure of 1-Phenyl-1*H*-pyrazole Derivatives (2a–2f):[8] A solution of sydnone (**1a**–**1f**, 0.031 mol, 1.0 mol. amt.) and dimethyl acetylenedicaboxylate (5.2g, 0.037 mol, 1.2 mol. amt.) was dissolved and heated in *p*-xylene solution at reflux for overnight. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and precipitated by EtOH (15 mL). The resulting soulution was cooled at –5°C for 4 h. The wet cake was filtered and washed with cold EtOH (10 mL). The wet cake was then dried in vacuum oven for overnight to give the desired product (**2a**–**2f**) in 93–98% yields.

Dimethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (2a): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.77 (s , 3H , OCH_3), 3.87 (s, 3H, OCH_3), 7.40–7.51 (m, 3H, Ar-H), 7.88–7.95 (m , 2H, Ar-H) , 9.16 (s, 1H, pyrazole-H).

Dimethyl 1-*p*-tolyl-1*H*-pyrazole-3,4-dicarboxylate (2b): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.36 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.85 (s , 3H, OCH_3), 7.33 (d, 2H , J = 8.40 Hz, Ar-H), 7.79 (d, 2H, J = 8.40 Hz, Ar-H), 9.09 (s, 1H, pyrazole-H).

Dimethyl 1-(4-ethoxyphenyl)-1*H*-pyrazole-3,4-dicarboxylate (2c): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.31 (t, 3H, J = 7.03 Hz, CH_3), 3.79 (s, 3H, OCH_3), 3.87 (s ,3H, OCH_3), 4.31 (q, 2H, J = 7.03 Hz, CH_2), 8.00–8.13 (m, 4H, Ar-H), 9.25 (s, 1H, pyrazole-H).

Dimethyl 1-(4-chlorophenyl)-1*H*-pyrazole-3,4-dicarboxylate (2d): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.79 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 7.61 (d, 2H, J = 6.93 Hz, Ar-H), 7.96 (d, 2H, J = 6.93 Hz, Ar-H), 9.19 (s, 1H, pyrazole-H).

Dimethyl 1-(4-nitrophenyl)-1*H*-pyrazole-3,4-dicarboxylate (2e): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.82 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 8.23 (d, 2H, J = 7.32 Hz, Ar-H), 8.39 (d, 2H, J = 7.32 Hz, Ar-H), 9.38 (s, 1H, pyrazole-H).

Dimethyl 1-(4-(ethoxycarbonyl)phenyl)-1*H*-pyrazole-3,4-dicarboxylate (2f): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.32 (t, 3H, J = 7.03 Hz, CH_3), 3.79 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.05 (q, 2H, J = 7.03 Hz, CH_2), 7.04 (d, 2H, J = 6.93 Hz, Ar-H), 7.79 (d, 2H, J = 6.93 Hz, Ar-H), 9.01 (s, 1H, pyrazole-H).

Standard Procedure of 1-Phenyl-1*H*-pyrazole-3,4-dicarbohydrazide Derivatives (3a–3f):[9] A solution of 1-phenyl-1*H*-pyrazole derivatives (**2a**–**2f**, 1.0 mol. amt.) and hydrazine hydrate (excess amount, 4.0 mol. amt.) was heated in EtOH solution at reflux for overnight. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and precipitated by EtOAc (15 mL). The resulting solution was cooled at –5°C for 4 h. The wet cake was filtered and washed with cold EtOH (10 mL). The wet cake was, dried in vacuum oven for overnight to give the desired product (**3a**–**3f**) in 84–95% yields.

1-Phenyl-1*H*-pyrazole-3,4-dicarbohydrazide (3a): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 4.57 (s, 2H, NH_2), 4.72 (s, 2H, NH_2), 7.42 (d, 1H, J = 7.12 Hz, Ar-H), 7.54 (t, 2H, J = 7.32 Hz, Ar-H), 8.07 (d, 2H, J = 7.90 Hz, Ar-H), 9.07 (s, 1H, Pyrazole-H), 10.35 (s, 1H, NH), 11.15 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75) MHz) δ 119.27, 119.60, 128.14, 129.99, 133.17, 138.89, 141.94, 160.51, 161.43; IR (KBr) 3395 (br, NH), 1643 (m, C=O) cm^{-1}.

1-*p*-Tolyl-1*H*-pyrazole-3,4-dicarbohydrazide (3b): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.35 (s, 3H, CH_3), 4.55 (s, 2H, NH_2), 4.71 (s, 2H, NH_2), 7.33 (d, 2H, J = 8.54 Hz, Ar-H), 7.93 (d, 2H, J = 8.54 Hz, Ar-H),

8.99 (s, 1H, Pyrazole-H), 10.31 (s, 1H, NH), 11.18 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 20.88, 119.06, 119.49, 130.34, 132.91, 136.67, 141.71, 160.56, 161.44; IR (KBr) 3400 (br, NH), 1646 (m, C=O) cm^{-1}.

1-(4-Ethoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (3c): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.34 (t, 3H, J = 6.86 Hz, CH_3), 4.08 (q, 2H, J = 6.86 Hz, CH_2), 4.55 (s, 2H, NH_2), 4.71 (s, 2H, NH_2), 7.06 (d,2H, J = 8.81 Hz, ArH), 7.96 (d, 2H, J = 8.81 Hz, Ar-H), 8.95 (s, 1H, Pyrazole-H), 10.32 (s, 1H, NH), 11.18 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 14.98, 63.87, 115.38, 118.94, 121.49, 132.29, 132.81, 141.44, 158.33, 160.64, 161.55; IR (KBr) 3395 (br, NH), 1640 (m, C=O) cm^{-1}.

1-(4-Chlorophenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (3d): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 4.57 (s, 2H, NH_2), 4.72 (s, 2H, NH_2), 7.61 (d, 2H, J = 8.52 Hz, Ar-H), 8.11 (d, 2H, J = 8.52 Hz, Ar-H), 9.09 (s, 1H, Pyrazole-H), 10.34 (s, 1H, NH), 11.19 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 119.51, 121.30, 129.90, 132.40, 132.45, 133.45, 137.73, 142.05, 160.35, 161.30; IR (KBr) 3390 (br, NH), 1644 (m, C=O) cm^{-1}.

1-(4-Nitrophenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (3e): ^{1}H NMR (DMSO-d_6, 300 MHz) δ 4.60 (s, 2H, NH_2), 4.76 (s, 2H, NH_2), 8.39 (m, 4H, ArH), 9.28 (s, 1H, Pyrazole-H), 10.48 (s, 1H, NH), 11.20 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 119.24, 119.61, 128.98, 133.15, 138.89, 141.94, 160.48, 161.41; IR (KBr) 3401 (br, NH), 1646 (m, C=O), 1579 (m, NO_2), 1344 (m) cm^{-1}.

1-(4-(Ethoxycarbonyl)phenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (3f): ^{1}H NMR (DMSO-d_6, 300 MHz) : δ 4.64 (m, 6H, NH_2), 7.97 (d, 2H, J = 5.62 Hz, Ar-H), 8.16 (d, 2H, J = 5.62 Hz, Ar-H), 9.13 (s, 1H, Pyrazole-H), 9.88 (s, 1H, NH), 10.37 (s, 1H, NH), 11.21 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) 14.97, 63.88, 115.41, 121.17, 132.29, 132.78, 141.44, 158.33, 160.50, 161.50; IR (KBr) 3400 (br, NH), 1648 (m, C=O) cm^{-1}.

Standard Procedure of 1*H*-Pyrazolecarbohydrazide Derivatives (4a–4f):[10] A solution of 1-phenyl-1*H*-pyrazole-3,4-dicarbohydrazide (**3a**–**3f**, 2.0 g, 1.0 mol. amt.) and pyridine (0.1 mol. amt.) was stirred in CH_2Cl_2 solution at rt for 10 min. Benzoyl chloride (2.7 g, 2.5 mol. amt.) was added to the reaction mixture and stirred at rt for 8 h. After the reaction was completed, the reaction mixture was filtered and washed with cool water (10 mL). The wet cake was dried in vacuum oven for overnight to give the desired product (**4a**–**4f**) in 75–85% yields.

1-Phenyl-*N*3',*N*4'-dibenzoyl-1*H*-pyrazole-3,4-dicarbohydrazide (4a): mp 222–224 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.40–7.60 (m, 9H, Ar-H), 7.90–8.18 (m, 6H, Ar-H), 9.29 (s, 1H, Pyrazole-H), 10.75 (s, 1H, NH), 10.79 (s, 1H, NH), 11.32 (s, 1H, NH), 11.92 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 14.97, 63.88, 115.41, 121.17, 132.29, 132.78, 141.44, 158.33, 160.50, 161.50;IR

(KBr) 1595 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 470 (M+2, 17), 469 (M+1, 82), 468(M, 26), 307 (100).

***N*3',*N*4'-Dibenzoyl-1-*p*-tolyl-1*H*-pyrazole-3,4-dicarbohydrazide (4b)**: mp 252–254 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.37 (s, 3H, CH_3), 7.39 (d, 2H, *J* = 8.34 Hz, Ar-H), 7.47–7.63 (m, 6H, Ar-H), 7.88–7.95 (m, 4H, Ar-H), 8.05 (d, 2H, *J* = 8.34 Hz, Ar-H), 9.22 (s, 1H, Pyrazole-H), 10.71 (s, 1H, NH), 10.72 (s, 1H, NH), 11.14 (s, 1H, NH), 11.90 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 21.86, 120.01, 120.64, 127.41, 128.83, 129.81, 129.91, 131.37, 131.21, 133.39, 133.60, 133.68, 135.32, 137.45, 139.12, 141.65, 160.95, 163.40, 166.53, 167.02; IR (KBr) 1600 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 485 (M+3, 5), 484 (M+2, 32), 483 (M+1, 100), 482 (M, 24).

1-(4-Ethoxyphenyl)-*N*3',*N*4'-dibenzoyl-1*H*-pyrazole-3,4-dicarbohydrazide (4c): mp 250–252 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.34 (t, *J* = 6.81 Hz, 3H, CH_3), 4.09 (q, *J* = 6.81 Hz, 2H, CH_2), 7.10 (d, 2H, *J* = 8.37 Hz, Ar-H), 7.47–7.63 (m, 6H, Ar-H), 7.89–7.98 (m, 4H, Ar-H), 8.07 (d, 2H, *J* = 8.37 Hz, 2H, Ar-H), 9.16 (s, 1H, Pyrazole-H), 10.71 (s, 1H, NH), 10.73 (s, 1H, NH), 11.12 (s, 1H, NH), 11.91 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 14.84, 63.95, 115.45, 118.05, 121.85, 127.93, 128.89, 131.05, 131.14, 132.01, 132.46, 132.75, 134.45, 1366.28, 142.55, 159.75, 161.42, 163.59, 164.02, 166.51, 167.45; IR (KBr) 1602 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 514 (M+2, 23), 513 (M+1, 82), 512 (M, 15), 307 (100).

1-(4-Chlorophenyl)-*N*3',*N*4'-dibenzoyl-1*H*-pyrazole-3,4-dicarbohydrazide (4d): mp 303–305 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.46–7.61 (m, 6H, Ar-H), 7.89–7.96 (m, 4H, Ar-H), 8.11 (d, 2H, *J* = 8.34 Hz , Ar-H), 8.21 (d, 2H, *J* = 8.76 Hz, Ar-H), 9.31 (s, 1H, Pyrazole-H), 10.74 (s, 1H, NH), 10.77 (s, 1H, NH), 11.19 (s, 1H, NH), 11.90 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 117.06, 119.05, 121.21, 127.57, 128.62, 129.64, 131.93, 132.36, 132.53, 134.06, 134.56, 137.11, 137.22, 140.79, 141.59,160.39, 161.95, 165.24, 165.73; IR (KBr) 1599 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 505 (M+3 , 45), 504 (M+2 , 34), 503 (M+1 , 100), 502(M , 29).

1-(4-Nitrophenyl)-*N*3',*N*4'-dibenzoyl-1*H*-pyrazole-3,4-dicarbohydrazide(4e): mp 325–327 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.46–7.62 (m, 4H, Ar-H), 7.87–7.98 (m, 2H, Ar-H), 8.35–8.50 (m, 8H, Ar-H), 9.52 (s, 1H, Pyrazole-H), 10.76 (s, 1H, NH), 10.79 (s, 1H, NH), 11.30 (s, 1H, NH), 11.88 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 118.08, 120.15, 122.50, 127.98, 128.77, 129.80, 132.93, 133.74, 133.93, 135.08, 135.75, 137.54, 137.95, 142.84, 143.04, 161.47, 162.75, 166.27, 167.13; IR (KBr) 1595 (m, C=O), 1575 (m, NO_2), 1340 (m) cm^{-1}; FABMS *m/z* (relative intensity) 515 (M+2, 6), 514 (M+1, 18), 513 (M, 4), 307 (100).

1-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenyl)-*N*3',*N*4'-dibenzoyl-1*H*-pyrazole-3,4-dicarbohydrazide (4f): mp 365–367 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.48–7.61 (m, 3H, Ar-H), 7.91–7.98 (m, 6H, Ar-H), 8.14 (t, 6H, *J* = 8.10 Hz, Ar-H), 8.26 (d, 2H, *J* = 5.07 Hz, Ar-H), 8.37 (d, 2H, *J*

= 5.07 Hz, Ar-H), 9.43 (s, 1H, Pyrazole-H), 10.62 (s, 1H, NH), 10.73 (s, 1H, NH), 10.79 (s, 1H, NH), 10.82 (s, 1H, NH), 11.20 (s, 1H, NH), 11.94 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 109.15, 120.13, 122.78, 123.13, 123.58, 123.92, 127.00, 127.67, 128.31, 128.51, 129.11, 130.11, 131.78, 132.15, 136.54, 140.04, 157.45, 158.03, 163.24, 163.54, 164.04, 164.26; IR (KBr) 1596 (m, C=N) cm^{-1}; FABMS *m/z* (relative intensity) 633 (M+3, 8), 632 (M+2, 26), 631 (M+1, 64), 630 (M, 18), 307 (100).

Standard Procedure of Preparation of 1*H*-Pyrazol-1,3,4-oxadiazole Derivatives (5a–5f):[11] A solution of 1*H*-pyrazole-carbohydrazide derivatives (**4a**–**4f,** 4.2 mmol, 1.0 mol. amt.) in $POCl_3$ (10 mL) was stirred at 90 °C for overnight. After the reaction was completed, the reaction mixture was added with cold water (10 mL) and neutralized with $NaHCO_3$ aqueous solution (10 mL) to precipitate the corresponding products. The crude product was filtrated and washed with cold water (5 mL). The wet cake was crystallized from EtOH and dried in vacuum oven for overnight to give the desired product (**5a**–**5f**) in 90–96% yields.

2-Phenyl-5-(1-phenyl-4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1*H*-pyrazol-3-yl)-1,3,4-oxadiazole (5a): mp 162–164 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.48–7.66 (m, 10H, Ar-H), 7.94–8.16 (m, 5H, Ar-H), 9.64 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 108.39, 120.91, 123.37, 123.52, 127.04, 127.27, 129.40, 129.86, 129.93, 130.31, 132.58, 132.63, 135.94, 138.71, 158.30, 158.56, 164.43, 164.94; IR (KBr) 1234 (m, C–O), 1603 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 434 (M+2 , 9), 433 (M+1, 33), 432 (M, 4), 196 (100). Anal. Calcd for $C_{25}H_{16}ClN_6O_2$: C, 69.44; H, 3.73; N, 19.43%. Found: C, 69.42; H, 3.71; N, 19.43%.

2-Phenyl-5-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1-*p*-tolyl-1*H*-pyrazol-3-yl)-1,3,4-oxadiazole (5b): mp 192–193 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.37 (s, 3H, CH_3), 7.40 (d, 2H, J = 8.02 Hz, Ar-H), 7.57–7.66 (m, 6H, Ar-H), 7.94 (d, 2H, J = 8.02 Hz, Ar-H), 8.04–8.09 (m, 4H, Ar-H), 9.56 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 21.85, 109.07, 120.68, 124.27, 124.43, 127.91, 128.14, 130.71, 130.78, 131.48, 133.09, 133.46, 133.66, 136.49, 137.34, 139.37, 159.20, 159.48, 165.25, 165.76; IR (KBr) 1235 (m, C–O), 1601 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 448 (M+2, 8), 447 (M+1, 25), 446 (M, 5), 105 (100). Anal. Calcd for $C_{26}H_{18}N_6O_2$: C, 69.95; H, 4.06; N, 18.62%. Found: C, 69.89; H, 4.07; N, 18.59%.

2-(1-(4-Ethoxyphenyl)-4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1*H*-pyrazol-3-yl)-5-phenyl-1,3,4-oxadiazole (5c): mp 179–181 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.40 (t, 3H, J = 6.87 Hz, CH_3), 4.04 (q, 2H, J = 6.87 Hz, CH_2), 6.98 (d, 2H, J = 8.93 Hz, Ar-H), 7.38–7.50 (m, 6H, Ar-H), 7.70 (d, 2H, J = 8.93 Hz, Ar-H), 8.05 (d, 2H, J = 7.05 Hz, Ar-H), 8.12 (d, 2H, J = 7.11 Hz, Ar-H), 8.64 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 14.99, 63.97, 115.51, 118.97, 121.45, 127.93, 128.99,

132.05, 132.14, 132.29, 132.46, 132.71, 132.80, 134.28, 140.55, 158.69, 160.11, 161.00, 162.54, 165.61, 166.08; IR (KBr) 1233 (m, C–O), 1604 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 478 (M+2, 61), 477 (M+1, 100), 476 (M, 30). Anal. Calcd for $C_{27}H_{20}N_6O_3$: C, 68.06; H, 4.23; N, 17.64%. Found: C, 68.03; H, 4.20; N, 17.61%.

2-(1-(4-Chlorophenyl)-4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1*H*-pyrazol-3-yl)-5-phenyl-1,3,4-oxadiazole (5d): mp 223–225 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.26–7.86 (m, 8H, Ar-H), 8.14 (d, 2H, *J* = 6.92 Hz, Ar-H), 8.19 (d, 2H, *J* = 6.92 Hz, Ar-H), 8.80 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 108.99, 121.09, 123.37, 123.46, 127.03, 127.28, 129.08, 129.50, 129.98, 130.05, 131.86, 132.08, 134.46, 136.36, 137.05, 158.01, 158.34, 164.98, 165.26; IR (KBr) 1234 (m, C–O), 1607 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 469 (M+2, 44), 468 (M+1, 35), 467 (M, 100). Anal. Calcd for $C_{25}H_{15}ClN_6O_2$: C, 64.31; H, 3.24; N, 18.00%. Found: C, 64.29; H, 3.22; N, 17.98%.

2-(1-(4-Nitrophenyl)-4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1*H*-pyrazol-3-yl)-5-phenyl-1,3,4-oxadiazole (5e): mp 244–246 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.59–7.66 (m, 6H, Ar-H), 8.06–8.12 (m, 4H, Ar-H), 8.38 (d, 2H, *J* = 7.44 Hz, Ar-H), 8.48 (d, 2H, *J* = 7.44 Hz, Ar-H), 9.86 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 117.98, 120.02, 122.50, 127.78, 128.56, 129.80, 130.56, 131.32, 132.54, 133.78, 134.15, 135.02, 135.45, 140.05, 141.71, 160.32, 161.55, 164.76, 165.33; IR (KBr) 1600 (m, C=O), 1575 (m, NO_2), 1340 (m), 1233 (m, C–O) cm^{-1}; FABMS *m/z* (relative intensity) 479 (M+2, 20), 478 (M+1, 71), 477 (M, 33), 203 (100). Anal. Calcd for $C_{26}H_{17}N_7O_3$: C, 65.58; H, 3.60; N, 20.62%. Found: C, 65.54; H, 3.57; N, 20.60%.

2-Phenyl-5-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)-1-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-1*H*-pyrazol-3-yl)-1,3,4-oxadiazole(5f): mp 282–284 °C (EtOH/H_2O); ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.38–7.58 (m, 10H, Ar-H), 7.94–8.27 (m, 8H, Ar-H), 8.35 (d, 2H, *J* = 8.40 Hz, Ar-H), 8.94 (s, 1H, Pyrazole-H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 109.38, 120.13, 123.33, 123.43, 123.58, 123.92, 127.00, 127.67, 128.31, 128.51, 129.11, 130.07, 131.98, 132.14, 136.78, 140.54, 157.90, 158.26, 163.42, 164.94, 165.06, 165.36; IR (KBr) 1604 (m, C=O), 1235 (m, C–O) cm^{-1}; FABMS *m/z* (relative intensity) 578 (M+2, 22), 577 (M+1, 86), 576 (M, 21), 105 (100). Anal. Calcd for $C_{34}H_{22}N_8O_2$: C, 71.07; H, 3.86; N, 19.50%. Found: C, 71.04; H, 3.82; N, 19.47%.

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REFERENCES

1 (a) G. Hughes and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 95. (b) C. Adachi, T. Tsutsui, and S.

Saito, *Appl*. *Phys*. *Chem.*, 1990, **56**, 799.

2 C. Wang, G.-Y. Jung, A. S. Batsanov, M. R. Bryce, and M. C. Petty, *J*. *Mater*. *Chem.*, 2002, **12**, 173.

3 (a) M. Guan, Z. Q. Bian, F. Y. Zhou, Z. J. Li, Z. J. Li, and C. H. Haung, *Chem*. *Commun*., 2003, 2708. (b) Q. Zhang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jing, and F. Wang, *J*. *Mater*. *Chem*., 2004, **14**, 895.

4 Y. Chien, K. Wong, P. Chou, and Y. Cheng, *Chem*. *Commun*., 2002, 2874.

5 Y. T. Tao, C. H. Chuen, C. W. Ko, and J. W. Peng, *Chem*. *Mater*., 2002, **14**, 4256.

6 M.-Y. Yeh, H.-J. Tien, L.-Y. Huang, and M.-H. Chen, *J*. *Chin*. *Chem*. *Soc*., 1983, **30**, 29.

7 M. Thelakkat and H.-W. Schmidt, *Adv*. *Mater*., 1998, **10**, 219.

8 F. Dumitrascu, C. I. Mitan, D. Dumitrescu, C. Drãghici, and M. T. Cãproiu, *Arkivoc*, 2002, **ii**, 80.

9 (a) H. Mayer and F. Staffen, *Monatsh*. *Chem*., 1913, **34**, 525. (b) H. Shinohara, Y. Ichimiya, T. Yoshimura, and M. Okawara, *Kobunshi Kagaku*, 1958, **15**, 839 (*Chem*. *Abstr*., 1960, **54**, 22636i).

10 A.-S. S. Hamad Elgazwy, M. Y. Zaki, N. N. Eid, and A. I. Hashem, *Heterocycl*. *Chem*., 2003, **14**, 570.

11 C. Wang, G.-Y. Jung, Y. Hua, C. Pearson, M. R. Bryce, M. C. Petty, A. S. Batsanov, A. R. Goeta, and J. A. Howard, *Chem*. *Mater*., 2001, **13**, 1167.

12 F.-I. Wu, C.-F. Shu, C.-H. Chien, and Y.-T. Tao, *Synth*. *Met*., 2005, **148**, 133.