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SYNTHESIS AND CHARATERIZATION OF 1,3,4-OXADIAZOLES CARRYING TRIAZOLOPYRIDINONE AND CARBAZOLE AS THE POTENTIAL BLUISH-GREEN ELECTROLUMINESCENT MATERIALS FOR THE SINGLE LAYER DEVICE

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Abstract – 1,3,4-Oxadiazoles carrying triazolopyridinone and carbazole were synthesized and characterized for the electroluminescent materials in single layer devices. Carbazole and triazolopyridinone were introduced into 2,5-centers of 1,3,4-oxadiazole core to assist the control of fundamental photolytic process due to their electron-donating nature, excellent photo-conductivity, and flexible structure properties. Study from spectrometry and cyclic voltammetry revealed that the 1,3,4-oxadiazole derivatives carrying these two heterocyles are able to be used as the potential bluish-green electroluminescent materials.

INTRODUCTION

Thin-film organic light-emitting diodes (LEDS) based on small molecules are of great interest due to their potential application in the large-screen emissive flat-panel color displays or as white back-lights for liquid crystal displays.[1] To accomplish optimal efficiency and device lifetime, the injection and the transport of holes and electrons must be balanced, such that similar densities of the two carriers are

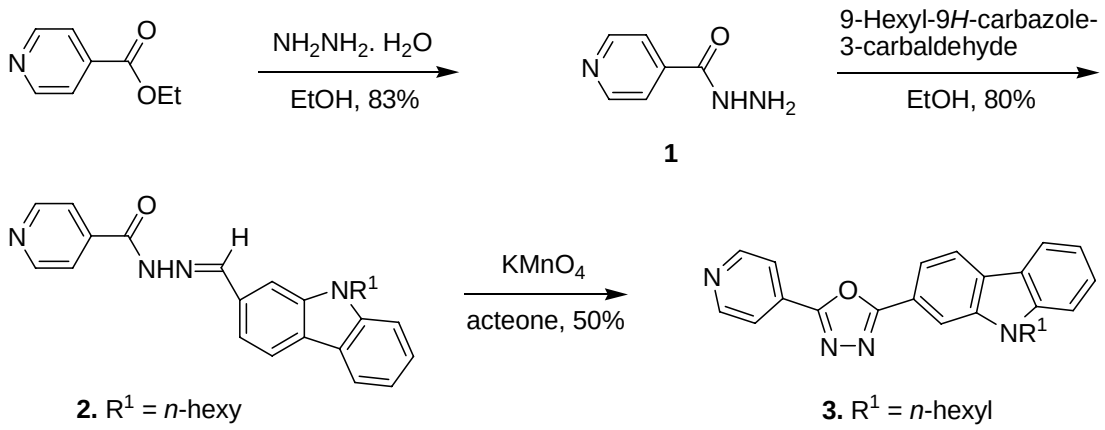
achieved. As a result, the efficient mixture of hole- and electron-transporting materials into a blend,[2,3] or the copolymerization of hole- and electron-transporting groups in the simple single-layer device was investigated to meet the approach. To fulfill such requirement, easily synthesized materials of 1,3,4-oxadiazole carrying triazolopyridinone and carbozole moieties with good film-forming properties and temporal stability are studied in this work.

Carbazole,[4] triazolopyridinone[5,6] and their derivatives can be easily functionalized and are beneficial for raising the glass-transition temperature and thermal stability. In particular, carbazole and its derivatives have been used extensively for the construction of functional materials such as photorefractive materials,[7] photoconductors,[8] nonlinear optical materials,[9] light-emitting materials,[10] and hole-transporting materials,[11] as flexible building blocks due to their inherent electron-donating nature, excellent photo conductivity, and unique nonlinear optical property. Triazolopyridinones own the electron-donating properties and are investigated to improve the photolytic properties.[6] Pyridine, being an electron-deficient heterocycle, was introduced to the main chain of a conjugated system to improve the electron-transporting of 1,3,4-oxadiazole.[12] In this paper, we first report the 1,3,4-oxadiazole-triazolopyridinone-carbozole hybrids as new potential blue and bluish-green electroluminescent materials for single layer devices. From the structural point of view, carbazole, pyridine and triazolopyridinone moieties were introduced to 1,3,4-oxadiazole molecule structure as the chromophores to emphasize the conjugation and expect to tune electroluminescent efficiencies and hole- or electron-transport property.

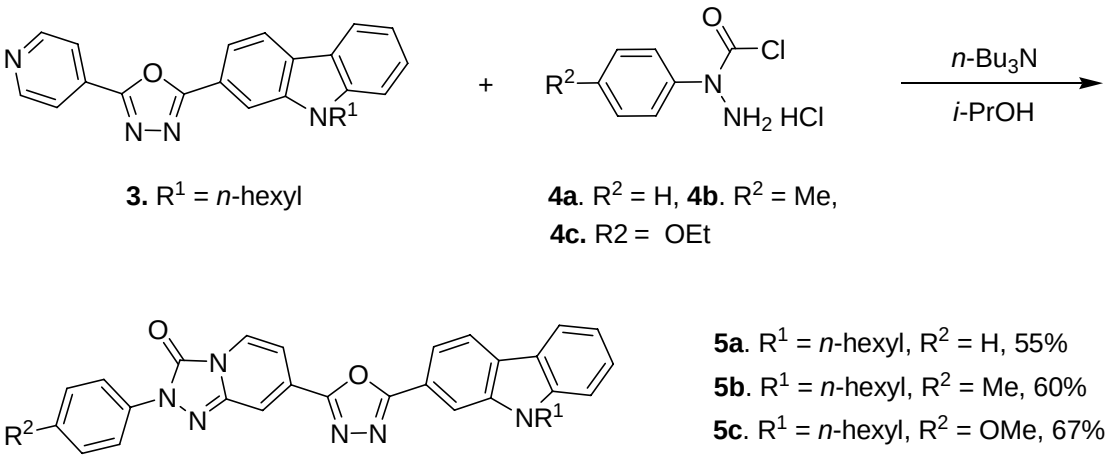
RESULTS AND DISCUSSION

Scheme **1** shows the synthesis of the 1,3,4-oxadiazole-pyridine-carbazole (**3**). Isonicotinohydrazide (**1**) was prepared in 83% yield as a white solid by the reaction of ethyl isonicotinate with hydrazine monohydrhydrate at reflux in EtOH overnight.[13] Isonicotinohydrazide (**1**) was treated with 9-hexyl-9*H*-carbazole-3-carbaldehyde to give the acyl hydrazone (**2**) as a yellow solid in 80 % yield. Upon reflux with $KMnO_4$ in acetone, **2** provided 2-carbazol-2-yl-5-(4-pyridyl)-1,3,4-oxadiazole (**3**) in 58% isolated yield by oxidative cyclization.

We treated the 1,3,4-oxadiazole (**3**) with *N*-aminochloro-*N*-arylamide hydrochlorides (**4a**–**4c**)[14] at 80 °C in *i*-PrOH in the presence of tribulylamine for 2 h,[13] to yield the crude triazolopyridinone derivatives (**5a**–**5c**). The crude products (**5a**–**5c**) were purified by recystallization from CH_2Cl_2 to give the pure products (**5a**–**5c**) as light yellow solid in 55–67 % yields (Scheme 2).



Scheme 1



Scheme 2

The UV-vis spectra of the 1,3,4-oxadiazole derivative (**3**) and their triazolopyridinone derivatives (**5a**–**5c**) measured in CH_2Cl_2 are almost identical, which show four peaks at 242, and ~315 nm in CH_2Cl_2. The main absorption band at 242 nm is contributed from carbazole and 1,3,4-oxadiazole moieties,[15] and the λ_{max} values of pyridine in the range 296–300 nm in CH_2Cl_2. When the pyridine was modified to the triazolopyridinone, it brought about a slightly red shift to 306 nm. The chromophore effects of pyridine and triazolopyridinone are resembled. Figure 1 shows the photoluminescence (PL) spectra of **3** and **5a**–**5c** in $CHCl_3$. The excitation wavelengths for **3** are between 380 and 450 nm and the λ_{max}s of PL is ~ 430 nm and has the intense blue fluorescenc. When the structures (**5a**–**5c**) own the triazolopyridinone moieties, they have obviously red-shift and exhibit the intense bluish-green fluorescence in $CHCl_3$ (λ_{max}s of PL is 478–486 nm, see Figure 1). The solution fluorescence quantum yields (Φ_f) of **5a**–**5c,** all of which fall in the range 0.68–0.71, were determined relative to that of 2-phenyl-5-(4-biphenyl)-1,3,4-oxzdiazole in benzene (Φ_f = 0.80, see Table 1).[16] The PL spectrum of the vacuum evaporatedfilms **5c** on quartz substrates, with a landa maximum at 503 nm, showed a red-shift (~20 nm) with respect to its solution spectrum (Figure 2). Most of the published analogues of **3** and **5** were estimated as a potential bluish

electroluminescent materials. At any rate, we successfully treated the 2-carbozolyl-5-pyridyl-1,3,4-oxadiazole (**3**) with the acid chloride (**4**) to form the triazolopyridinone core by means of the dehydration–cyclization reaction. The triazolopyridinone moiety efficiently conjugate and connect two chromophores (oxadiazole and pyridine) to provide the bluish-green electroluminescent materials.

Table 1. UV-Vis absorption maxima and photoluminescence peak wavelength of the 1,3,4-oxadiazole derivatives (**3** and **5a**–**5c**)

Compound			λ_{max} /nm of UV-Vis	λ_{max} /nm of PL	Φ_f [a]
Substrate	R^1	R^2	CH_2Cl_2	$CHCl_3$	
3	*n*-hexyl	-	314	430	-
5a	*n*-hexyl	H	322	478	0.68
5b	*n*-hexyl	Me	312	479	0.67
5c	*n*-hexyl	OMe	308	486	0.71

[a]Φ_f: Fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene ($\Phi_f = 0.8$).

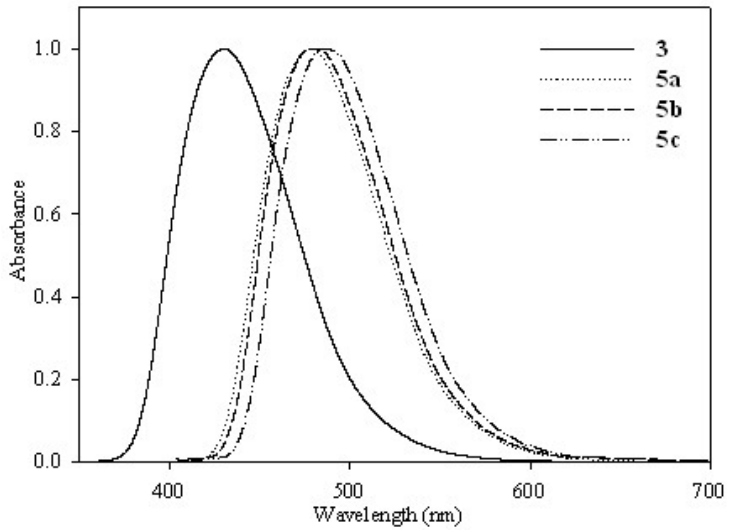


Figure 1. The fluorescence spectra of 3 and **4a**–**4c** in chloroform solution

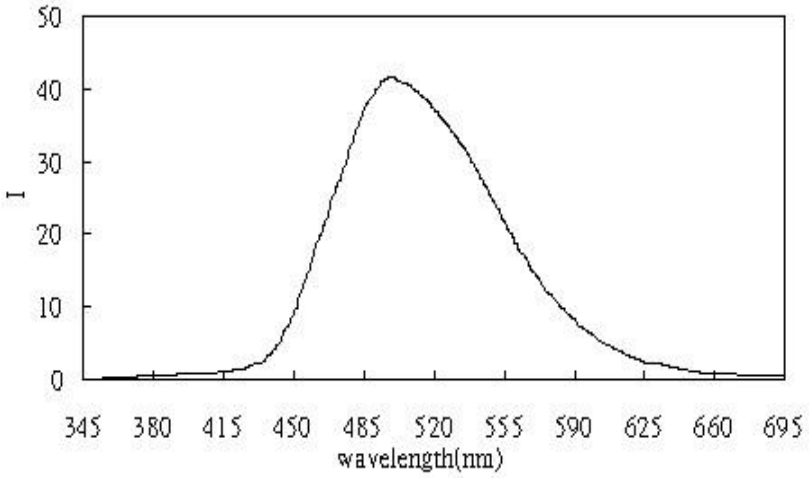


Figure 2. Normalized photoluminescence spectra of **5c** (vacuum evaporated film)

The electrochemical behaviors of **5a**–**5c** were investigated by cyclic voltammetry in solution. The measurements were carried out at a platinum electrode using millimolar solution in using CH_2Cl_2 containing 0.1 M of the supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), in a three electrode cell an potentiostat assembly. The potential was measured against Ag/AgCl as reference electrode and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system.[17] The data were tabulated in Table 2. Upon the anodic sweep, **5a**–**5c** showed irreversible reduction processes. The bandgap energies of 1,3,4-oxadiazole-triazolopyridinone-carbazole derivatives (**5a**–**5c**) were estimated from the onset wavelength (λ_{onset}) of the UV-vis absorption.[18] From the high electron affinities, **5a**–**5c** owned the potential of electron-transporting and highly efficient bluish-green electroluminescent materials.

Table 2. Electrochemical properties of **5a**–**5c**

Compound	*E*onset[a] (v)	*E'*onset[b] (v)	*Ip*[c] = E_{HOMO} (eV)	*Eg*[d,e] = Bandgap energy (eV)	*Ea*[f] = E_{LUMO} (eV)	Φ_f[g]
5a	1.35	1.16	–5.96	3.21	–2.75	0.74
5b	1.44	1.25	–6.05	3.21	–2.84	0.76
5c	1.24	1.05	–5.85	3.21	–2.64	0.69

[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
[d] The bandgap energy estimated based on the value 386 nm
[f] *Ea* = *Ip* + *Eg*
[g] Φ_f: Fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene

We are successful to prepare a series of the 5-triazolopyridinone-2-carbazolyl-1,3,4-oxadiazole derivatives (**5a**–**5c**) by treating the 2-carbazolyl-5-pyridyl-1,3,4-oxadiazole with *N*-aminochloro-*N*-arylamide hydrochloride (**4a**–**4c**). Carbazole, pyridine and triazolopyridinone moieties in **5a**–**5c** obviously play an excellent assistant role in controlling fundamental photolytic process. The 1,3,4-oxadiazole derivatives (**5a**–**5c**) could be as the new potential bluish-green electroluminescent materials.

EXPERIMENTAL

General. Isonicotinohydrazide[5] and *N*-aminochloro-*N*-arylamide hydrochloride[14] were synthesized according to literature procedures. 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.

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). ^{1}H-NMR spectra were obtained on a Bruker (200 MHz) spectrometer by use of $CDCl_3$ as solvent. ^{13}C-NMR spectra were obtained on a a Bruker (50 MHz) spectrometer by use of chloroform-*d* as solvent. ^{13}C chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.0 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, respectively, in anhydrous CH_2Cl_2 and anhydrous 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.[17]

9-Hexyl-9*H*-carbazole.[6] A solution of 9*H*-carbazole (16.7 g, 0.10 mole, 1.0 equiv.), and KOH (8.40 g, 0.15 mole, 1.5 equiv.) were mixed and stirred in H_2O (40 mL) solution at rt for 15 min. Tetrabutylammonium bromide (1.0 g, 10.3 mmol, 0.11 equiv.) was added dropwise into the reaction mixture, then 1-bromohexane (24.8 g, 0.15 mol, 1.5 equiv.) was added dropwise into the reaction mixture and heat-up to 60 °C for 3 h. After the reaction was completed, the reaction mixture was extracted with EtOAc (150 mL × 2). The combined EtOAc solutions were washed with water and saturated aqueous NaCl. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. EtOH (100 mL) was added to the residue and precipitated the desired product. The wet cake was dried in vacuum oven overnight to give the 9-hexyl-9*H*-carbazole as white powder in 80% yield (20.0 g, 80.0 mmol): mp 56–57 °C[6]; ^{1}H NMR (DMSO-*d*6, 200 MHz) δ 0.78 (t, *J* = 7.2 Hz, 3H, CH_3), 1.05–1.30 (m, 6H, CH_2), 1.73 (m, 2H, CH_2), 4.36 (t, *J* = 6.9 Hz, 2H, CH_2), 7.17 (dd, , *J* = 6.8, 8.2 Hz, 2H, ArH), 7.56 (d , *J* = 8.2 Hz, 2H, ArH), 8.09 (dd, *J* = 6.8, 8.2 Hz, 2H, ArH), 8.14 (d , *J* = 8.2 Hz, 2H, ArH).

9-Hexyl-9*H*-carbazole-3-carbaldehyde A solution of cold $POCl_3$ (130 mL) was added dropwise into DMF solution (60 mL) in ice-bath and warmed-up to rt for 1 h. The reaction mixture was stirred at rt for 2 h. 9-Hexyl-9*H*-carbazole (25.1 g, 0.10 mol, 0.10 equiv.) was added into the reaction mixture in ice-bath overnight. After the reaction completed, the reaction mixture was quenched with $NaHCO_3$ aqueous solution (100 mL) and stirred for 1 h. The precipitation was filtered and washed with cold EtOH (50 mL). The wet cake was dried in vacuum oven overnight to give the 9-hexyl-9*H*-carbazole-3-carbaldehyde as white powders in 72% yield (20.1 g, 72.1 mmol): mp 58–59 °C; ^{1}H NMR (DMSO-*d*6, 200 MHz) δ 0.78 (t, *J* = 7.2 Hz, 3H, CH_3), 1.10–1.25 (m, 6H, CH_2), 1.71–1.74 (m, 2H, CH_2), 4.41 (t, *J* = 6.9 Hz, 2H, CH_2), 7.28 (dd, *J* = 6.7, 7.8 Hz, 1H, Ar-H), 7.51 (dd, *J* = 6.7, 8.0 Hz, 1H, ArH), 7.65 (d, *J* = 9.0 Hz, 1H, ArH), 7.72 (d, *J* = 8.0 Hz, 1H, ArH), 7.95 (d, *J* = 7.8 Hz, 1H, ArH), 8.26 (d, *J* = 9.1 Hz, 1H, ArH), 8.73 (s, 1H, Ar-H), 10.06 (s, 1H, CHO).

***N*-[1-Aza-2-(9-hexylcarbazol-3-yl)vinyl]-4-pyridylcarboxamide (2)** A solution of isonicotinohydrazide (6.00 g, 4.37 mmole, 1.1 equiv.) and 9-hexyl-9*H*-carbazole-3-carbaldehyde (1.08 g, 4.30 mmole, 1.0 equiv.) in EtOH (50 mL) was stirred at 40 °C for 6 h. After the reaction completed, the reaction mixture was concentrated under reduced pressure to remove EtOH. The residue was added with cold EtOH (25 mL), filtrated and washed with cold EtOH (15 mL). The wet cake was dried in vacuum oven overnight to give the isonicotinic acid[(9-hexyl-9*H*-carbazol-3-yl)methylene] hydrazide (**2**) as yellow powders in 80%

yield (1.37 g, 3.43 mmol): ^{1}H NMR (DMSO-*d*6, 200 MHz) δ 0.79 (t, *J* = 6.7 Hz, 3H, CH_3), 1.16–1.35 (m, 6H, CH_2), 1.69–1.85 (m, 2H, CH_2), 4.42 (t, *J* = 6.8 Hz, 2H, CH_2), 7.22 (t, *J* = 7.3Hz, 1H, ArH), 7.45 (t, *J* = 7.3 Hz, 1H, ArH), 7.82–7.86 (m, 2H, ArH), 7.82–7.91 (m, 2H, ArH), 8.24 (d, *J* = 7.6 Hz, 1H, ArH), 8.50–8.61 (m, 2H, ArH), 8.78 (d, *J* = 5.7 Hz, 2H, ArH), 11.98 (s, 1H, NH).

(9-Hexyl-carbazol-2-yl)-5-(4-pyridyl)-1,3,4-oxidiazole (3). A solution of the hydrazone **2** (4.00 g, 10.1 mmole, 1.0 equiv.) and $KMnO_4$ (4.00 g) in acetone (45 mL) was stirred at 50 °C for 4 h. After the reaction completed, the reaction mixture was concentrated under reduced pressure to remove acetone. The residue was added with a saturated Na_2SO_3 aqueous solution (30 mL), and extracted with CH_2Cl_2 (30 mL). the reaction mixture was extracted with EtOAc (120 × 2 mL). The combined EtOAc solutions were washed with water and saturated aqueous NaCl. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The wet cake was dried in vacuum oven overnight to give the oxadiazole **3** as yellow powders in 50% yield (10.0 g, 40.0 mmol): mp 142–143 °C; ^{1}H NMR (DMSO-*d*6, 200 MHz) δ 0.79 (t, *J* = 6.6 Hz, 3H, CH_3), 1.16–1.27 (m, 6H, CH_2), 1.74–1.79 (m, 2H, CH_2), 4.45 (t, *J* = 6.9 Hz, 2H, CH_2), 7.29 (t, *J* = 7.4 Hz, 1H, ArH), 7.53 (t, *J* = 7.4 Hz, 1H, ArH), 7.68 (d, *J* = 8.2 Hz, 1H, ArH), 7.83 (d, *J* = 8.7 Hz, 1H, ArH), 8.10 (d, *J* = 4.3 Hz, 2H, ArH), 8.23 (dd, *J* = 1.2, 7.6 Hz, 1H, ArH), 8.34 (d, *J* = 7.6 Hz, 1H, ArH), 8.87 (d, *J* = 4.3 Hz, 2H, ArH), 8.99 (d, *J* = 1.2 Hz, 1H, ArH); FABMS *m/z* (relative intensity) 399 (M+1, 19), 398 (M, 55). Anal. Calcd for $C_{25}H_{26}N_4O$: C, 75.35; H, 6.58; N, 14.06. Found: C, 75.26; H, 6.61; N, 14.14.

Standard Procedure for the synthesis of 5-triazopyridinone-2-carbazolyl-1,3,4-oxadiazole derivatives (5a–5c): A solution of carbazolylpyridyl-1,3,4-oxadiazole (**3**, 1.62 mmole, 1.0 equiv) was stirred with *n*-tributylamine (1 mL) in *i*-PrOH (15 mL). The reaction mixture was heated up to 80 °C and the acid chloride (**4**, 1.78 mmole, 1.1 equiv) was added into the reaction mixture. After the reaction completed, the separating-product was collected by filtration while hot and washed with cold EtOH (10 mL) to give the crude product. The crude product was dried and crystallized from CH_2Cl_2 to give a pure (**4a**–**4c)** as light yellow solid in 55–67% yields.

Compound (4a): mp 252–254 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (t, *J* = 6.8 Hz, 3H, CH_3), 1.18–1.25 (m, 6H , CH_2), 1.88–1.92 (m, 2H , CH_2), 4.36 (t, *J* = 6.9 Hz, 2H , CH_2), 7.33–7.56 (m, 8H), 7.93–8.01 (m, 2H), 8.14–8.23 (m, 4H), 8.88 (d, *J* = 1.2 Hz, 1H); IR (KBr) 1715 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 529 (M+1, 29), 528 (M, 61). Anal. Calcd for $C_{32}H_{28}N_6O_2$: C, 72.71; H, 5.34; N, 15.90. Found: C, 72.65; H, 5.46; N, 15.79.

Compound (4b): mp 259–261 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (t, *J* = 6.8 Hz , 3H , CH_3), 1.18–1.26 (m, 6H, CH_2), 1.88–1.91 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 4.36 (t, *J* = 6.7 Hz, 2H, CH_2),

7.26–7.33 (m, 5H), 7.48–7.55 (m, 4H), 7.92–8.04 (m, 2H), 8.18–8.22 (m, 2H), 8.86 (d , *J* = 1.2 Hz, 1H); IR (KBr) 1714 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 543 (M+1, 19), 542 (M, 31). Anal. Calcd for $C_{33}H_{30}N_6O_2$: C, 73.04; H, 5.57; N, 15.49. Found: C, 73.11; H, 5.60; N, 15.51.

Compound (4c): mp 228–230 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.89 (t, *J* = 6.8 Hz, 3H, CH_3), 1.18–1.28 (m, 6H), 1.89–1.92 (m, 2H), 4.36 (t, J = 6.8 Hz, 2H, CH_2), 7.03 (d, *J* = 8.9 Hz, 2H), 7.26–7.40 (m, 2H), 7.45–7.56 (m, 3H), 7.95–8.06 (m, 4H), 8.17–8.27 (m, 2H), 8.88 (d , *J* = 1.3 Hz, 1H); IR (KBr) 1710 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 559 (M+1, 36), 558 (M, 66). Anal. Calcd for $C_{33}H_{30}N_6O_3$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.87; H, 5.55; N, 15.12.

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