Heteroatom Chemistry
Volume 17, Number 2, 2006

New Synthesis of Highly Potential Efficient Bluish-Green Electroluminescent Materials Based on 1,3,4-Oxadiazole–Triazolopyridinone–Carbazole Derivatives for Single-Layer Devices

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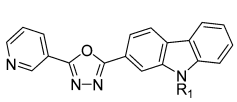
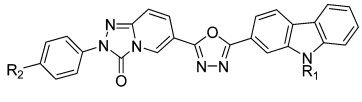
Received 11 April 2005; revised 4 September 2005

ABSTRACT: *New potential bluish-green electroluminescent materials of 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives were synthesized and characterized for single-layer devices. Carbazole, pyridine, and triazolopyridinone were completely introduced into 1,3,4-oxadiazole skeletal to play assistant roles in controlling fundamental photolytic process due to the electron-donating nature, excellent photoconductivity, and flexible structure properties. Following the spectroscopic studies and the measurements of cyclic voltammogram, 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives were highly efficient bluish-green electroluminescent materials.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:160–165, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20201



R_1 = *n*-hexyl



R_1 = *n*-hexyl, R_2 = H, Me, OEt

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 backlights for liquid crystal displays [1]. To accomplish optimal efficiency and device lifetime, the injection and transport of holes and electrons must be balanced, such that similar densities of the two carriers are achieved. Two approaches can be employed to balance carrier injection and transport, both incorporating hole- and electron-transporting materials into a LED [2]. One approach is to fabricate a multilayer device with discrete hole-transporting and/or electron-transporting layers [1,3]. A second approach is to mix hole- and electron-transporting materials into a blend [4,5], or to copolymerize

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Contract grant sponsor: National Science Council of Republic of China.
Contract grant number: NSC-850-6368.

hole- and electron-transporting groups together [6,7] and prepare simple single-layer devices where the active layer performs hole transport, electron transport, and light emission. To fulfill such requirement, easily synthesized materials of 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives with good film-forming properties and temporal stability are desirable in this work.

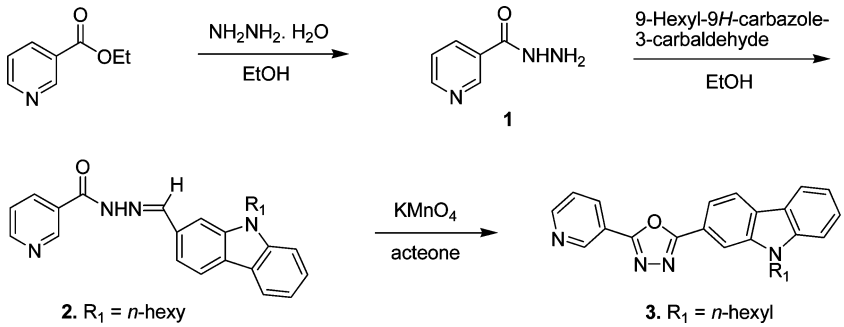
Carbazole [8], triazolopyridinone [9,10], and their derivatives can be easily functionalized; these moieties are beneficial for raising the glass transition temperature and thermal stability. Carbazole and its derivatives have applied extensive in functional materials as flexible building blocks for construction due to their inherent electron-donating nature, excellent photoconductivity, and unique nonlinear optical property, such as photorefractive materials [11], photoconductors [12], nonlinear optical materials [13], light-emitting materials [14], and hole-transporting materials [15]. Some of the molecules related to triazolopyridinone have been studied in the medical chemistry [9]. Triazolopyridinone analogues are characterized by the same fragment A, with two distinct basic nitrogen atoms: one aromatic and the other aliphatic position. Triazolopyridinones own the electron-donating properties and are investigated to improve the photolytic properties [10]. Pyridine [16] is an electron-deficient heterocycle, and it has been established that the introduction of pyridine units into the main chain of conjugated system to improve the electron-transporting properties. In this paper, we first report the 1,3,4-oxadiazole–triazolopyridinone–carbazole 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

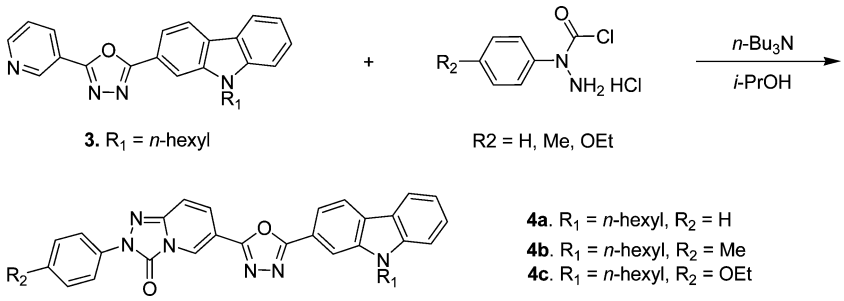
Scheme 1 shows the synthetic route for the generation of 1,3,4-oxadiazole–pyridine–carbazole compound (**3**). Nicotinohydrazide was prepared by the reaction of ethyl nicotinate on hydrazine monohydrhydrate at reflux in the EtOH solution for overnight [17]. After the reaction was completed, the corresponding compound nicotinohydrazide was provided as a white solid in 80% yield. Nicotinohydrazide was applied to 9-hexyl-9*H*-carbazole-3-carbaldehyde to give the corresponding nicotinic acid[(9-hexyl-9*H*-carbazol-3-yl)methylene] hydrazide **2** as yellow solid in 78% yields. Nicotinic acid[(9-hexyl-9*H*-carbazol-3-yl)methylene] hydrazide **2** was performed the dehydration–cyclization reaction at reflux with the strong oxidant reagent $KMnO_4$ in acetone solution to provide 1,3,4-oxadiazole–pyridine–carbazole compound (**3**) in 70% isolated yield.

α-Chloroformylarylhydrazine hydrochloride was synthesized according to our previous publish procedure [18]. We treated 1,3,4-oxadiazole–pyridine–carbazole compound (**3**) with α-chloroformylarylhydrazine hydrochloride with various substituents, including H, CH_3, and OEt groups at 80°C in *i*-PrOH solution for 2 h [17]. The solid product was formed and the hot-filtration was performed to isolate the crude 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives **4a–4c**. The residues (**4a–4c**) were purified by recystallization from CH_2Cl_2 to give the pure corresponding products (**4a–4c**) as light yellow solid in 60–68% yields (see Scheme 2).

The UV–Vis spectra of 1,3,4-oxadiazole–pyridine–carbazole derivatives **3** and 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives **4a–4c** were measured in CH_2Cl_2 and $CHCl_3$ solutions. Absorption spectra of **3** and **4a–4c** are almost identical, which show four peaks at 242, 274, 304, and 330 nm in CH_2Cl_2. The main peak absorption



SCHEME 1



SCHEME 2

peak at 242 nm is contributed from carbazole and 1,3,4-oxadiazole moieties [20]. The λ_{max} values of pyridine is in the range 296–300 nm in CH_2Cl_2. When the pyridine was modified with α-chloroformylarylhydrazine hydrochloride to form the triazolopyridinone heterocycles, the absorption have a slightly red-shift to 306 nm (see Fig. 1). The chromophore effect of pyridine and triazolopyridinone are resemblance. Figure 2 shows the photoluminescence (PL) spectra of **3** and **4a–4c**. The excitation wavelengths for **3** are between 380 and 450 nm in CH_2Cl_2 solution, respectively, and the λ_{max}s of PL is ~409 nm and has the intense blue fluorescence in CH_2Cl_2 or $CHCl_3$. When the structures (**4a–4c**) own the triazolopyridinone moieties, the compounds have obviously redshift and exhibit the intense bluish-green fluorescence in CH_2Cl_2 or $CHCl_3$ solution (λ_{max} of PL is 385–545 nm). The solution fluorescence quantum yields (Φ_f) of **4a–4c**, all of which fall in the range 0.69–0.76, were determined relative to that of 2-phenyl-5-(4-biphenyl)-1,3,4-oxzdiazole in benzene ($\Phi_f = 0.80$, see Table 1) [21]. The PL spectrum **4a** of the vacuum-evaporated films on quartz substrates, with a maximum at 498 nm, shows a red-shift (~25 nm) with respect to the solution spectrum as shown in Fig. 3. Most of the published 1,3,4-oxadiazole–pyridine–carbazole analogues were estimated as a potential bluish electroluminescent material. Whatever, we successfully treated 1,3,4-oxadiazole–pyridine–

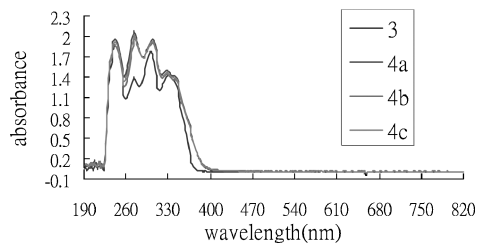


FIGURE 1 The UV–Vis absorption of **3** and **4a–4c** in dichloromethane solution.

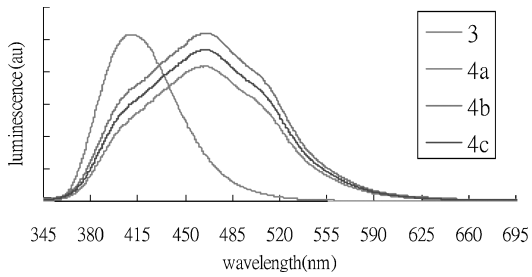


FIGURE 2 The fluorescence spectra of **3** and **4a–4c** in dichloromethane solution.

carbazole **3** with α-chloroformylarylhydrazine hydrochloride by means of the dehydration–cyclization reaction to form the triazolopyridinone core. The triazolopyridinone moiety efficiently conjugates and connects two chromophores (oxadiazole and pyridine) to provide the bluish-green electroluminescent materials.

The electrochemical behavior of **4a–4c** was 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 in potentiostat assembly. The

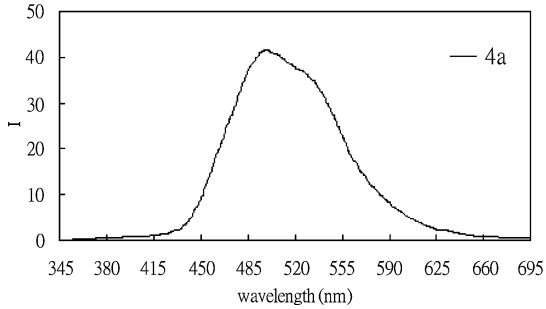


FIGURE 3 Normalized photoluminescence spectra of **4a** (vacuum-evaporated film).

TABLE 1 Electrochemical Properties of **4a–4c**

Compound	E_{onset}[a] *(V)*	E'_{onset}[b] *(V)*	I_p[c] $= E_{HOMO}$ *(eV)*	E_g[d,e] $=$ *Bandgap energy (eV)*	E_a[f] $= E_{LUMO}$ *(eV)*	Φ_f[g]
4a	1.35	1.16	−5.96	3.21	−2.75	0.74
4b	1.44	1.25	−6.05	3.21	−2.84	0.76
4c	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]$I_p = -(E'_{onset} + 4.8)$.
[d]E_g: the bandgap energy estimated from the onset wavelength of UV–Vis absorption.
[e]The bandgap energy estimated based on the value 386 nm.
[f]$E_a = I_p + E_g$.
[g]Φ_f: fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene.

potential was measured against Ag/AgCl as reference electrode, and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system [19]. The data were tabulated in Table 1. Upon the anodic sweep, **4a–4c** showed irreversible reduction processes. The bandgap energies of 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives **4a–4c** were estimated from the onset wavelength (λ_{onset}) of the UV–Vis absorption [22]. From the high electron affinities, **4a–4c** owned the potential of electron-transporting and highly efficient bluish-green electroluminescent materials.

CONCLUSION

We are successful to prepare a sires of new potential bluish-green electroluminescent materials based on 1,3,4-oxadiazole–triazolopyridinone–carbazole derivatives by using 1,3,4-oxadiazole–pyridine compound with α-chloroformylarylhydrazine hydrochloride. Triazolopyridinone moiety obviously plays an excellent assistant role in controlling fundamental photolytic process.

EXPERIMENTAL [17–19]

9-Hexyl-9H-carbazole

A solution of 9*H*-carbazole (16.7 g, 0.10 mole, 1.0 equiv.) and potassium hydroxide (8.40 g, 0.15 mole, 1.5 equiv.) was mixed and stirred in H_2O (40.0 mL) solution at room temperature for 15 min. Tetrabutylammonium bromide (1.0 g, 10.3 mmol, 0.11 equiv.) was added dropwise into the reaction mixture as catalyst. And then 1-bromohexane (24.8 g, 0.15 mol, 1.5 equiv.) was added dropwise into the reaction mixture and heated up to 60°C for 3 h. After the reaction was completed, the reaction mixture was extracted with EtOAc (150 × 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. Ethanol (100 mL) was added to the residue and precipitated the desired product. The wet cake was dried in vacuum oven for 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; ^{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, Ar-H), 7.56 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.09 (dd, $J = 6.8$, 8.2 Hz, 2H, Ar-H), 8.14 (d, $J = 8.2$ Hz, 2H, Ar-H).

9-Hexyl-9H-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 room temperature for 1 h. The reaction mixture was stirred at room temperature 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 for overnight. After the reaction was 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 for overnight to give the 9-hexyl-9*H*-carbazole-3-carbaldehyde as white powder 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, Ar-H), 7.65 (d, $J = 9.0$ Hz, 1H, Ar-H), 7.72 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.95 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.26 (d, $J = 9.1$ Hz, 1H, Ar-H), 8.73 (s, 1H, Ar-H), 10.06 (s, 1H, CHO).

Nicotinic Acid[(9-hexyl-9H-carbazol-3-yl)methylene] Hydrazide **2**

A solution of nicotinohydrazide (5.00 g, 3.64 mmol, 1.1 equiv.) and 9-hexyl-9*H*-carbazole-3-carbaldehyde (0.90 g, 3.58 mmol, 1.0 equiv.) in EtOH (50 mL) was stirred at 40°C for 6 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove EtOH. The residue was added with cold EtOH (20 mL), filtrated and washed with cold EtOH (10 mL). The wet cake was dried in vacuum oven for overnight to give the nicotinic acid[(9-hexyl-9*H*-carbazol-3-yl)methylene] hydrazide as yellow powder in 78% yield (1.11 g, 2.79 mmol): ^{1}H NMR (DMSO-d_6, 200 MHz): δ 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 1.10–1.23 (m, 6H, CH_2), 1.75 (m, 2H, CH_2), 4.42 (t, $J = 6.9$ Hz, 2H, CH_2), 7.22 (t, $J = 3.4$ Hz, 1H, Ar-H), 7.47 (t, $J = 3.4$ Hz, 1H, Ar-H), 7.75–7.88 (m, 3H, Ar-H), 7.96 (t, $J = 4.7$ Hz, 1H, Ar-H), 8.30 (d, $J = 4.7$ Hz, 1H, Ar-H), 8.47–8.61 (m, 3H, Ar-H), 8.85 (s, 1H, Ar-H), 9.16 (s, 1H), 12.10 (b, 1H, NH).

9-Hexyl-2-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-9H-carbazole **3**

A solution of nicotinic acid [(9-hexyl-9*H*-carbazol-3-yl)methylene]hydrazide (5.00 g, 12.60 mmol, 1.0 equiv.) and $KMnO_4$ (5.00 g) in acetone (50 mL) was stirred at 50°C for 4 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure to remove acetone. The residue was added with a saturated $NaSO_3$ aqueous solution (30 mL) and extracted with CH_2Cl_2 (30 mL). The reaction mixture was extracted with EtOAc (150×2 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 for overnight to give the 9-hexyl-9*H*-carbazole as white powder in 80% yield (20.0 g, 80.0 mmol). The wet cake was dried in vacuum oven for overnight to give the 9-hexyl-2-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl)-9*H*-carbazole as yellow powder in 70% yield (3.49 g, 8.82 mmol): mp 223–225°C; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 1.10–1.23 (m, 6H, CH_2), 1.75 (m, 2H, CH_2), 4.44 (t, $J = 6.9$ Hz, 2H, CH_2), 7.32 (t, $J = 4.8$ Hz, 1H, Ar-H), 7.60 (t, $J = 4.8$ Hz, 1H, Ar-H), 7.65–7.79 (m, 2H, Ar-H), 7.86 (d, $J = 4.2$ Hz, 1H, Ar-H), 8.24 (d, $J = 4.5$ Hz, 1H, Ar-H), 8.36 (d, $J = 4.5$ Hz, 1H, Ar-H), 8.54 (d, $J = 4.2$ Hz, 1H, Ar-H), 8.80 (d, $J = 3.5$ Hz, 1H, Ar-H), 8.98 (s, 1H), 9.32 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 14.21, 22.38, 26.46, 28.85, 31.31, 42.90, 110.30, 110.60, 113.86, 120.19, 120.59, 122.10, 122.28, 122.81, 124.69, 126.27, 127.12, 134.47, 141.05, 142.26, 147.69, 152.69, 162.67, 162.91.

Standard Procedure for 6-(5-(9-Hextyl-9H-carbazol-3-yl)-1,3,4-oxadiazol-2-yl)-2-phenyl-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one Derivatives **4a–4c**

A solution of 9-hexyl-2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]-9*H*-carbazole **3** was stirred in *i*-PrOH (15.0 mL) and *n*-tributylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride was added into the reaction mixture. After the reaction was completed, the hot-filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give a pure **4a–4c** as light yellow solid in 60–68% yields.

6-(5-(9-Hexyl-9H-carbazol-2-yl)-1,3,4-oxadiazol-2-yl)-2-phenyl-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one **4a**

A solution of 9-hexyl-2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]-9*H*-carbazole **3** (0.53 g, 1.34 mmol, 1.0 equiv.) was stirred in *i*-PrOH (15 mL) and triethylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride (0.29 g, 1.47 mmol, 1.1 equiv.) was added into the reaction mixture. After the reaction was completed, the hot-filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give a pure **4a** as light yellow solid in 60% yield (425 mg, 0.804 mmol): mp 278–280°C; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 1.20–1.30 (m, 6H, CH_2), 1.79 (m, 2H, CH_2), 4.46 (t, $J = 6.9$ Hz, 2H, CH_2), 7.28–7.36 (m, 3H), 7.57–7.67 (m, 4H), 7.84 (t, $J =$ 4.5 Hz, 2H), 8.08 (d, $J = 4.0$ Hz, 2H), 8.25 (d, $J = 3.1$ Hz, 1H), 8.25 (d, $J = 3.1$ Hz, 1H), 8.35 (d, $J = 3.5$ Hz, 1H), 8.77 (s, 1H), 9.04 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 14.21, 22.38, 26.46, 28.85, 31.31, 42.90, 110.30, 110.60, 113.86, 120.19, 120.59, 121.22, 122.10, 122.28, 122.81, 123.55, 124.69, 125.65, 126.27, 127.12, 134.47, 141.05, 142.26, 149.52, 152.69, 158.69, 162.21, 168.67, 169.91; IR (KBr) 1602 (m, C=N), 1725 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 528 (M, 25), 529 (M + 1, 30), 250 (100), 77 (36). Anal. Calcd for $C_{32}H_{28}ClN_6O_2$: C, 72.71; H, 5.34; N, 15.90. Found: C, 72.76; H, 5.36; N, 15.90.

6-(5-(9-Hexyl-9H-carbazol-2-yl)-1,3,4-oxadiazol-2-yl)-2-p-tolyl-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-one **4b**

A solution of 9-hexyl-2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]-9*H*-carbazole **3** (0.51 g, 1.32 mmol, 1.0 equiv.) was stirred in *i*-PrOH (15 mL) and triethylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride (0.29 g, 1.46 mmol, 1.1 equiv.) was added into the reaction mixture. After the reaction was completed, the hot-filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give a pure **4b** as light yellow solid in 65% yield (473 mg, 0.872 mmol): mp 265–267°C; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 1.20–1.30 (m, 6H, CH_2), 1.79 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 4.46 (t, $J = 6.9$ Hz, 2H, CH_2), 7.29–7.34 (m, 2H), 7.52 (t, $J = 5.0$ Hz, 1H), 7.76 (d, $J = 4.5$ Hz, 2H), 7.84–7.96 (m, 4H), 8.28 (d, $J = 3.1$ Hz, 1H), 8.42 (d, $J = 3.2$ Hz, 1H), 8.74 (s, 1H), 9.03 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 14.21, 21.38, 22.89, 26.45, 28.88, 31.21, 42.89, 110.30, 113.86, 120.39, 121.62, 122.30, 122.58, 122.71, 123.25, 124.29, 125.55, 126.77, 127.22, 134.27, 141.15, 142.56, 147.69, 149.42, 152.59, 158.39, 162.91, 168.57, 169.71; IR (KBr) 1602 (m, C=N), 1722 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 542 (M, 15), 543 (M + 1, 14), 318 (100), 91 (50). Anal. Calcd for $C_{33}H_{30}ClN_6O_2$: C, 73.04; H, 5.57; N, 15.49. Found: C, 73.04; H, 5.57; N, 15.55.

2-(4-Ethoxyphenyl)-6-(5-(9-hexyl-9H-carbazol-2-yl)-1,3,4-oxadiazol-2-yl)-[1,2,4]triazolo[4,3-a]-pyridin-3(2H)-one **4c**

A solution of 9-hexyl-2-[5-(pyridin-3-yl)-1,3,4-oxadiazol-2-yl]-9*H*-carbazole **3** (0.55 g, 1.36 mmol, 1.0 equiv.) was stirred in *i*-PrOH (15 mL) and triethylamine (1.0 mL) solution. The reaction mixture was heated up to 80°C. α-Chloroformylarylhydrazine hydrochloride (0.34 g, 1.49 mmol, 1.1 equiv.) was added into the reaction mixture. After the reaction was completed, the hot-filtration was performed and washed with cold ethanol (10 mL) to isolate the solid crude product. The crude product was dried and crystallized from CH_2Cl_2 to give a pure **4c** as light yellow solid in 68% yield (530 mg, 0.925 mmol): mp 294–296°C; ^{1}H NMR (DMSO-d_6, 200 MHz): δ 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 1.22–1.34 (m, 9H), 4.02 (q, $J = 5.0$ Hz, 2H, CH_2), 1.79 (m, 2H, CH_2), 4.46 (t, $J = 6.9$ Hz, 2H, CH_2), 4.46 (t, $J = 6.9$ Hz, 2H, CH_2), 7.28–7.33 (m, 2H), 7.67–7.55 (m, 4H), 7.89 (d, $J = 3.7$ Hz, 2H), 8.1 (d, $J = 3.5$ Hz, 2H), 8.20 (d, $J = 3.6$ Hz, 1H), 8.35 (d, $J = 4.0$ Hz, 1H), 8.78 (s, 1H), 9.05 (s, 1H); ^{13}C NMR (DMSO-d_6, 50 MHz): δ 14.21, 14.30, 22.38, 26.46, 28.85, 31.31, 42.90, 64.26, 110.10, 110.40, 113.88, 120.29, 120.99, 121.52, 122.08, 122.18, 122.41, 123.15, 124.89, 125.55, 126.77, 1274.18, 134.27, 141.26, 146.69, 149.62, 152.99, 158.49, 162.61, 168.27, 168.91; IR (KBr) 1602 (m, C=N), 1720 (m, C=O) cm^{-1}; FABMS *m/z* (relative intensity) 572 (M, 40), 573 (M + 1, 30), 541 (100), 121 (60). Anal. Calcd for $C_{34}H_{32}ClN_6O_3$: C, 71.31; H, 5.63; N, 14.48. Found: C, 71.35; H, 5.60; N, 14.68.

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