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Synthesis and optical properties of novel anthracene-based stilbene derivatives containing an 1,3,4-oxadiazole unit

Xinwei Li, Daohang He*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

A series of anthracene-based stilbene derivatives containing an 1,3,4-oxadiazole unit were efficiently synthesized by a four-pots reaction sequence. All of the target compounds were characterized using, FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and elemental analysis. For the samples, the UV–visible absorption coefficient, maximum wavelength, fluorescence excitation wavelength, fluorescence emission wavelength and fluorescence quantum yield, were measured in dilute tetrahydrofuran solution. Cyclic voltammetry studies revealed that the molecules have low-lying LUMO and HOMO energy levels suggesting these compounds may possess good electron-transporting or hole-blocking properties.

1. Introduction

Over the past decades, the development of organic light-emitting diode (OLED) materials has attracted much attention, owing to their potential application in flat panel displays and solid-state light sources. Stilbene derivatives are well known not only for their considerable biological and medical activities [1–3], but also for their fluorescence in the visible light range, large Stokes shifts and high quantum yields [4–6]. Moreover, stilbene derivatives have been extensively investigated for various potential applications including optical brighteners, PPV-type electroluminescent copolymer and organic electroluminescent (EL) materials [7–13]. Fluorescent heterocyclic compounds are of interest in many areas such as emitters for electroluminescence devices, molecular probes for biochemical research, in traditional textile and polymer fields, fluorescent whitening agents and photoconducting materials [14–18]. 1,3,4-Oxadiazoles are an important class of heterocyclic compounds with broad spectrum of biological activities, compounds and have been developed as materials for EL devices since these compounds possess high electron-accepting properties and display strong fluorescence with a high quantum yield [19–22]. Fluorescent characteristics rely largely on molecular structure and molecular assembly. There is presently great interest to increase the structural or spatial dimensions of π-conjugated molecules in order to tune and acquire more favorable physical properties [23]. Anthracene derivatives have a rigid structure, wide energy gaps and high fluorescent quantum efficiency [24]. A great deal of anthracene-based electroluminescent materials have been developed [25,26].

Based on these ideas, we recently synthesized a series of novel anthracene-based stilbene derivatives containing a 1,3,4-oxadiazole unit. It is envisioned that the introduction of the 1,3,4-oxadiazole unit and anthracene core into the stilbene skeleton can improve their photo-electric properties, by extending conjugated styryl units. As expected, the emission color of these compounds can be easily tuned from blue to green by increasing conjugation length. Particularly, all of the compounds exhibited desirable HOMO levels (−5.51 to −6.06 eV), which have promising potential for application in OLEDs.

2. Experimental

2.1. Chemicals and instruments

All chemicals and reagents were commercially available and used without further purification. All solvents were carefully dried and freshly distilled according to common laboratory techniques.

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[*] Corresponding author. Tel./fax: +86 20 87110234.
E-mail address: daohanghe@yahoo.com.cn (D. He).

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Melting points were recorded on Electrothermal digital RY-1 melting point apparatus and were uncorrected. FT-IR spectra were measured as KBr pellets on a Bruker Vector 33 in the region of 4000–400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-400 MHz NMR spectrometer using TMS as an internal standard. Mass spectra were obtained with a HPLC/MS LCQDECA spectrometer (APCI). Elemental analyses were performed on a Vario EL Ш CHN elemental analyzer. UV–vis absorption spectra were recorded on a Hitachi UV-3010 spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature. The purity of the compounds was confirmed by TLC on silica gel 'G'-coated glass plates. The cyclic voltammograms reported here were recorded with a CHI830B electrochemical workstation at a constant scan rate of 50 mV s^{-1}. The measurements were performed in 1 mmol L^{-1} dichloromethane solutions of the samples with tetrabutylammonium hexafluorophosphate solution (0.1 mol L^{-1} in dichloromethane) as supporting electrolyte at room temperature. The cyclic voltammetric system was constructed using a three-electrode undivided electrochemical cell consisted of a Pt working electrode, a Pt-wire counter electrode, and a Ag/$AgNO_3$ reference electrode (0.1 mol L^{-1} in CH_2Cl_2) under protection of nitrogen, and each measurement was calibrated with an internal standard, ferrocene/ferrocenium redox system [27,28]. The fluorescence quantum yields $\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$ where A is the absorbance at the excitation wavelength, F the area under the fluorescence curve and n the refraction index. Subscripts s and x refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol ($\Phi = 0.89$) was taken as the standard [29].

2.2. Synthesis

2.2.1. Synthesis of 2-(anthracen-9-yl)-5-(p-tolyl)-1,3,4-oxadiazole 1

4-Methylbenzohydrazide (15 g, 0.1 mol) and anthracene-9-carbaldehyde (21 g, 0.1 mol) were dissolved in ethanol (500 mL). The mixture was heated under reflux for 1 h until the disappearance of the starting material by TLC to give a clear yellow solution. Chloramine-T (27 g, 0.3 mol) was poured into the mixture and stirred for 4 h at 76 °C. The excess ethanol was evaporated under reduced pressure, and then the mixture was washed with water and filtered. The residue was recrystallized from acetone giving 27.3 g of compound **1** as yellow crystals, yield 75.4%; m.p. 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H, anthracen-H), 8.08 (d, $J = 8.2$ Hz, 2H, C_6H_4 2,6-H), 8.10–8.05 (m, 4H, anthracen-H), 7.58–7.50 (m, 4H, anthracen-H), 7.35 (d, $J = 8.0$ Hz, 1H, C_6H_4 3,5-H), 2.45 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$):δ 165.97, 162.82, 142.55, 131.46, 131.41, 131.04, 129.91, 128.77, 127.70, 127.10, 125.71, 125.13, 121.16, 117.40, 21.71; APCI MS: *m*/*z*, 337(M + 1, 100), 338(M + 2, 24).

2.2.2. Synthesis of 2-(anthracen-9-yl)-5-(4-(bromomethyl)phenyl)-1,3,4-oxadiazole 2

To a stirred solution of **1** (8.8 g, 26 mmol) in carbon tetrachloride (300 mL) was added N-Bromosuccinimide (NBS) (5.5 g, 31 mmol), the reaction was heated under reflux for 8 h and then the excess cooled solvent. The resulting mixture was filtered, washed with ethanol. The residue was recrystallized from THF/ethanol giving 8.34 g of compound **2** as solid, yield 77.5%; m.p. 185–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H, anthracen-H), 8.19 (d, $J = 8.4$ Hz, 2H, C_6H_4 2,6-H), 8.15–8.08 (m, 2H, anthracen-H), 8.06–7.98 (m, 2H, anthracen-H), 7.56 (d, $J = 8.4$ Hz, 2H, C_6H_4 3,5-H), 7.57–7.55 (m, 4H, anthracen-H), 4.55 (s, 2H, CH_2); APCI MS: *m*/*z*, 415(M + 2, 100), 418(M + 3, 25).

2.2.3. Synthesis of 4-(5-(anthracen-9-yl)-1,3,4-oxadiazol-2-yl) benzylphosphonate 3

A mixture of compound **2** (8.15 g, 20 mmol) and triethyl phosphite (4.8 mL, 28.1 mmol) was heated under reflux for 5 h. The excess triethyl phosphate was evaporated under reduced pressure, and then filtered by addition of hexane. The residue was recrystallized from THF/hexane giving 8.96 g compound 3 as yellow solid, yield 95.1%; m.p. 138-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (s, 1H, anthracen-H), 8.16 (d, $J = 8.0$ Hz, 2H, C_6H_4 2,6-H), 8.12–8.09 (m, 2H, anthracen-H), 8.07–8.02 (m, 2H, anthracen-H), 7.59–7.53 (m, 4H, anthracen-H), 7.50 (dd, $J = 8.3$ Hz, 2.2 Hz, 2H, C_6H_4 3,5-H), 4.10–4.03 (m, 4H, OCH_2), 3.25 (d, $J = 22.1$ Hz, 2H, CH_2), 1.28 (t, $J = 7.1$ Hz, 6H, CH_3); APCI MS: *m*/*z*, 473(M + 1, 100), 474(M + 2, 30).

2.2.4. Typical procedure for the synthesis of compounds ***4a–h***

To a stirred solution of the aromatic aldehyde (1.7 mmol) and the intermediate **3** (0.9 g, 1.7 mmol) in anhydrous N,N-dimethylformamide (15 mL) under nitrogen atmosphere was added dropwise a solution of *t*-BuOK (2 g, 3%) in ethanol. The reaction proceeded at room temperature overnight. Then the resulting mixture was filtered and washed with ethanol. The residue was recrystallized from ethanol/DMSO.

*2.2.4.1. 2-(anthracen-9-yl)-5-(4-styrylphenyl)-1,3,4-oxadiazole (**4a**).* Yield 83.5%; m.p. 203–204 °C; FT-IR (KBr, cm^{-1}): 3053, 3028, 1626, 1606, 1569, 1545, 1497, 1447, 1420, 1362, 1200, 1184, 1085, 1005, 961, 891, 754, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H, anthracen-H), 8.19 (d, $J = 8.2$ Hz, 2H, C_6H_4–H), 8.14–7.99 (m, 4H, anthracen-H), 7.69 (d, $J = 8.3$ Hz, 2H, C_6H_4–H), 7.60–7.52 (m, 6H, anthracen-H C_6H_5 2,6-H), 7.39 (t, $J = 7.5$ Hz, 2H, C_6H_5 3,5-H), 7.30 (t, $J = 7.5$ Hz, 1H, C_6H_5 4-H), 7.26 (d, $J = 16.4$ Hz, 2H, CH=CH), 7.16 (d, $J = 16.3$ Hz, 2H, CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.72, 163.00, 140.97, 136.72, 131.48, 131.17, 131.06, 128.83, 128.79, 128.32, 127.76, 127.49, 127.42, 127.14, 126.82, 125.74, 125.12, 122.61; APCI MS: *m*/*z*, 425(M + 1, 100), 426(M + 2, 35); Anal. Calcd. for $C_{30}H_{20}N_2O$(424.5): C, 84.88; H, 4.75; N, 6.60; Found: C, 83.76; H, 4.90; N, 6.63.

*2.2.4.2. 2-(anthracen-9-yl)-5-(4-(2-(naphthalen-1-yl)vinyl)phenyl)-1,3,4-oxadiazole (**4b**).* Yield 86.1%; m.p. 241–242 °C; FT-IR (KBr, cm^{-1}): 3053, 1626, 1605, 1572, 1544, 1494, 1445, 1420, 1362, 1201, 1183, 1086, 1006, 962, 889, 758, 770, 743, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.25 (d, $J = 4.8$ Hz, 1H, naphthalene-H), 8.23 (d, $J = 8.3$ Hz, 2H, C_6H_4 2,6-H), 8.14–8.06 (m, 4H, anthracen-H), 8.05 (d, $J = 16.1$ Hz, 1H, CH=CH), 7.90 (d, $J = 7.7$ Hz, 1H, naphthalene-H), 7.85 (d, $J = 8.2$ Hz, 1H, naphthalene-H), 7.80 (d, $J = 6.0$ Hz, 1H, naphthalene-H), 7.79 (d, $J = 8.1$ Hz, 2H, C_6H_4 3,5-H), 7.62–7.54 (m, 4H, anthracen-H), 7.57–7.49 (m, 3H, naphthalene-H), 7.22 (d, $J = 16.0$ Hz, 1H, CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 163.04, 141.19, 134.35, 133.77, 131.49, 131.38, 131.06, 130.42, 128.80, 128.74, 128.70, 128.22, 127.77, 127.56, 127.32, 126.36, 126.01, 125.75, 125.69, 125.13, 123.92, 123.60, 122.77, 117.29; APCI MS: *m*/*z*, 475(M + 1, 100), 476(M + 2, 40); Anal. Calcd. for $C_{34}H_{22}N_2O$ (474.5): C, 86.05; H, 4.67; N, 5.90; Found: C, 85.78; H, 4.38; N, 6.23.

*2.2.4.3. 2-(anthracen-9-yl)-5-(4-(2-(anthracen-9-yl)vinyl)phenyl)-1,3,4-oxadiazole (**4c**).* Yield 87.8%; m.p. >300 °C; FT-IR (KBr, cm^{-1}): 3048, 3026, 1626, 1608, 1573, 1545, 1493, 1447, 1421, 1365, 1202, 1183, 1089, 1008, 960, 890, 849, 784, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.44 (s, 1H, anthracen-H), 8.38–8.33 (m, 2H, anthracen-H), 8.28 (d, $J = 8.3$ Hz, 2H, C_6H_4 2,6-H), 8.16–8.07 (m, 4H, anthracen-H), 8.10 (d, $J = 16.3$ Hz, 1H, CH=CH) 8.06–7.99 (m, 2H, anthracen-H), 7.85 (d, $J = 8.3$ Hz, 2H, C_6H_4 3,5-H), 7.82–7.63 (m, 4H, anthracen-H), 7.53–7.43 (m, 4H, anthracen-H), 7.04 (d,

$J = 16.6$ Hz, 1H, CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.70, 163.12, 140.82, 136.16, 131.95, 131.54, 131.51, 131.08, 129.72, 128.82, 127.80, 127.64, 127.60, 127.27, 127.02, 125.80, 125.76, 125.29, 125.13, 123.07, 117.27; APCI MS: *m*/*z*, 525(M + 1, 100), 526(M + 2, 40); Anal. Calcd. for $C_{38}H_{24}N_2O$ (524.2): C, 87.00; H, 4.61; N, 5.34; Found: C, 87.17; H, 4.77; N, 5.63.

*2.2.4.4. 2-(anthracen-9-yl)-5-(4-(4-fluorostyryl)phenyl)-1,3,4-oxadiazole (**4d**).* Yield 82.5%; m.p. 240–241 °C; FT-IR (KBr, cm^{-1}):3050, 3027, 1626, 1598, 1578, 1541, 1509, 1446, 1421, 1364, 1234, 1215, 964, 837, 732; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H, anthracen-H), 8.19 (d, $J = 8.2$ Hz, 2H, C_6H_4 2,6-H), 8.14–8.01 (m, 4H, anthracen-H), 7.67 (d, $J = 8.2$ Hz, 2H, C_6H_4 3,5-H), 7.60–7.47 (m, 6H, anthracen-H C_6H_4 2,6-H), 7.22 (d, $J = 16.3$ Hz, 2H, CH=CH), 7.08 (t, $J = 8.4$ Hz 2H, C_6H_4 3,5-H), 7.07 (d, $J = 16.1$ Hz, 2H, CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.68, 163.01, 140.80, 132.92, 131.49, 131.06, 129.91, 128.79, 128.41, 128.33, 127.76, 127.52, 127.22, 127.07, 125.74, 125.11, 122.66, 117.28, 115.94, 115.72; APCI MS: *m*/*z*, 443(M + 1, 100), 444(M + 2, 35); Anal. Calcd. for $C_{30}H_{19}FN_2O$(442.5):C, 81.43; H, 4.33; N, 6.33; Found: C, 81.72; H, 4.95; N, 6.80.

*2.2.4.5. 2-(anthracen-9-yl)-5-(4-(4-chlorostyryl)phenyl)-1,3,4-oxadiazole (**4e**).* Yield 93.3%; m.p. 277–278 °C; FT-IR (KBr, cm^{-1}): 3053, 3026, 1626, 1605, 1567, 1544, 1495, 1445, 1421, 1362, 1202, 1185, 1087, 1007, 959, 891, 841, 726; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.19 (d, $J = 8.2$ Hz, 2H, C_6H_4 2,6-H), 8.14–8.01 (m, 4H, anthracen-H), 7.68 (d, $J = 8.2$ Hz, 2H, C_6H_4-3,5-H), 7.61–7.52 (m, 4H, anthracen-H), 7.48 (d, $J = 8.4$ Hz, 2H, C_6H_4 2,6-H), 7.36 (d, $J = 8.4$ Hz, 2H, C_6H_4 3,5-H), 7.20 (d, $J = 16.3$ Hz, 1H, CH=CH), 7.13 (d, $J = 16.3$ Hz, 1H, CH=CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.65, 163.04, 140.60, 135.24, 133.95, 131.51, 131.47, 131.06, 129.79, 129.02, 128.80, 128.01, 127.96, 127.77, 127.53, 127.18, 125.75, 125.10, 122.84; APCI MS: *m*/*z*, 459(M + 1, 100), 461(M + 3, 45); Anal. Calcd. for $C_{30}H_{19}ClN_2O$(458.1):C, 78.51; H, 4.17; N, 6.10; Found: C, 78.67; H, 4.74; N, 6.60.

*2.2.4.6. 2-(anthracen-9-yl)-5-(4-(4-bromostyryl)phenyl)-1,3,4-oxadiazole (**4f**).* Yield 90.5%; m.p. 281–282 °C; FT-IR (KBr, cm^{-1}): 3053, 3025, 1626, 1605, 1569, 1545, 1495, 1445, 1421, 1361, 1201, 1185, 1086, 1073, 1007, 959, 891, 840, 727; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H, anthracen-H), 8.19 (d, $J = 8.2$ Hz, 2H, C_6H_4 2,6-H), 8.13–8.04 (m, 4H, anthracen-H), 7.68 (d, $J = 8.2$ Hz, 2H, C_6H_4 3,5-H), 7.60–7.53 (m, 4H, anthracen-H), 7.51 (d, $J = 8.4$ Hz, 2H, C_6H_4 2,6-H), 7.42 (d, $J = 8.4$ Hz, 2H, C_6H_4 3,5-H), 7.19 (d, $J = 16.5$ Hz, 1H, CH=CH), 7.14 (d, $J = 16.5$ Hz, 1H, CH=CH); APCI MS: *m*/*z*, 503(M+, 85), 504(M + 2, 100), 506(M + 3, 25); Anal. Calcd. for $C_{30}H_{19}BrN_2O$(503.4):C, 71.58; H, 3.80; N, 5.56; Found: C, 72.02; H, 3.92; N, 6.06.

*2.2.4.7. 2-(anthracen-9-yl)-5-(4-(2-methoxystyryl)phenyl)-1,3,4-oxadiazole (**4g**).* Yield 83.6%; m.p. 216–217 °C; FT-IR (KBr, cm^{-1}): 3049, 3006, 2933, 2831, 1627, 1604, 1573, 1543, 1496, 1463, 1421, 1362, 1334, 1247, 1201, 1183, 1085, 1007, 962, 890, 745, 725; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H, anthracen-H), 8.17 (d, $J = 8.4$ Hz, 2H, C_6H_4 2,6-H), 8.13–8.05 (m, 4H, anthracen-H), 7.70 (d, $J = 8.4$ Hz, 2H, C_6H_4 3,5-H), 7.64 (d, $J = 16.6$ Hz, 1H, CH=CH), 7.63 (d, $J = 7.5$ Hz, 1H, C_6H_4 6-H), 7.59–7.53 (m, 4H, anthracen-H), 7.29 (t, $J = 8.5$ Hz, 1H, C_6H_4 4-H), 7.18 (d, $J = 16.5$ Hz, 1H, CH=CH), 6.99 (t, $J = 7.5$ Hz, 1H, C_6H_4 5-H), 6.93 (d, $J = 8.2$ Hz, 1H, C_6H_4 3-H), 3.92 (s, 1H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.80, 162.92, 157.18, 141.68, 131.47,

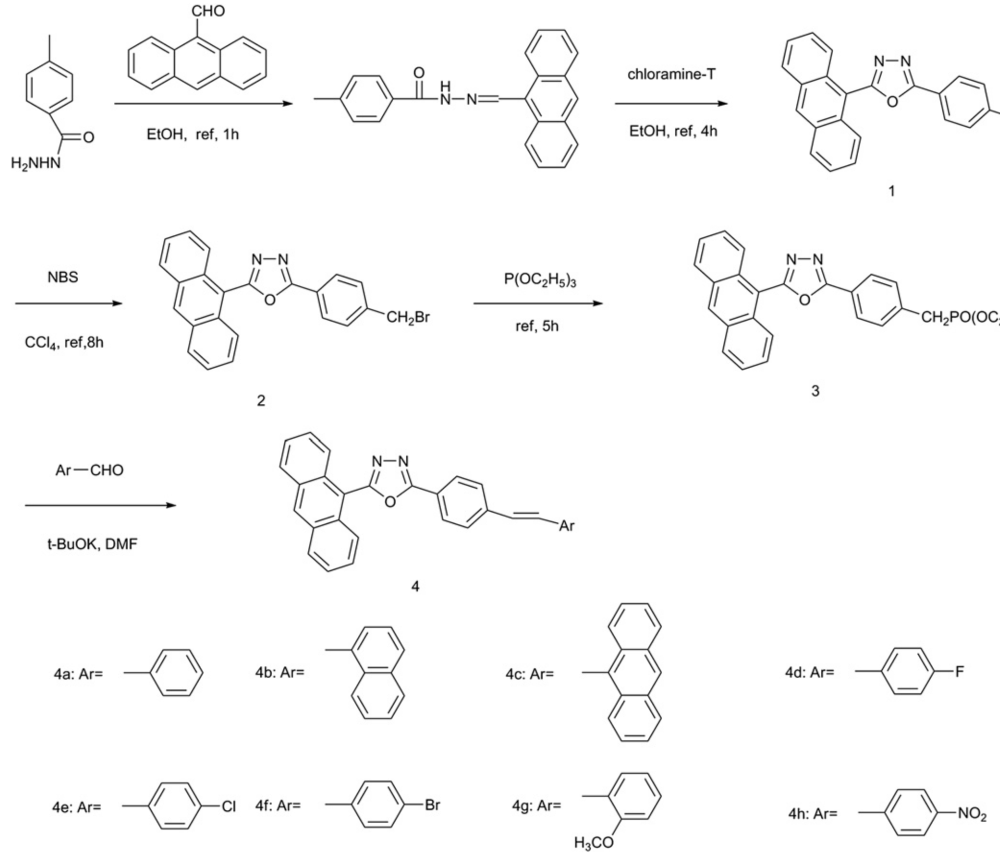

Fig. 1. The synthetic route of new target compounds.

Table 1
UV–vis, fluorescent and electrochemical parameters of target compounds.

Compound	λ_{max}(nm)[a]	$\times 10E^{-4}\varepsilon_{max}$(L mol^{-1} cm^{-1})[a]	λ_{ex}(nm)[a]	λ_{em}(nm)[a]	Stokes shifts(nm)[b]	Φ_x[c]	E_g(eV)[d]	E_{ox}(V)[e]	E_{red}(V)[e]	$E_{HOMO/LUMO}$(eV)[f]
4a	334	5.00	337	488	151	0.78	2.54	1.14	−1.39	−5.94/−3.40
4b	351	4.03	368	488	120	0.66	2.37	1.01	−1.35	−5.81/−3.44
4c	388	3.12	396	496	100	0.43	2.05	0.70	−1.34	−5.50/−3.45
4d	335	4.69	337	488	151	0.78	2.61	1.16	−1.44	−5.96/−3.35
4e	337	4.99	339	487	148	0.77	2.67	1.26	−1.41	−6.06/−3.39
4f	338	6.03	341	488	147	0.74	2.55	1.13	−1.42	−5.93/−3.38
4g	349	6.03	353	489	136	0.77	2.60	1.17	−1.42	−5.97/−3.37
4h	368	5.40	339	488	149	0.09	–[g]	–	–	–

[a] Solution in 10^{-5} mol L^{-1} THF.
[b] Stokes shifts = $\lambda_{em}-\lambda_{ex}$.
[c] The fluorescence quantum yields were measured in THF using Rhodamine B in ethanol ($\Phi = 0.89$) as the standard.
[d] $E_g = (E_{ox}-E_{red})$.
[e] E_{ox} and E_{red} are measured vs. ferrocene/ferrocenium.
[f] $E_{HOMO} = (-4.8-E_{ox})$, $E_{LUMO} = (-4.8-E_{red})$.
[g] Not determined.

131.44, 131.05, 129.40, 128.77, 127.78, 127.41, 127.15, 126.70, 126.06, 125.78, 125.73, 125.14, 122.28, 120.82, 117.35, 111.01, 55.54; APCI MS: *m*/*z*, 455(M + 1, 100), 456(M + 2, 38); Anal. Calcd. for $C_{31}H_{22}N_2O_2$ (454.5):C, 81.92; H, 4.88; N, 6.16; Found: C, 81.77; H, 5.09; N, 6.55.

2.2.4.8. *2-(anthracen-9-yl)-5-(4-(4-nitrostyryl)phenyl)-1,3,4-oxadiazole (**4h**).*

Yield 89.6%; m.p. 287–288 °C; FT-IR (KBr, cm^{-1}): 3050, 3030, 1627, 1592, 1567, 1542, 1512, 1497, 1444, 1422, 1341, 1264, 1201, 1180, 1110, 1086, 1007, 960, 889, 852, 752, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H, anthracen-H), 8.25 (d, *J* = 8.6 Hz, 2H, C_6H_4 3,5-H), 8.23 (d, *J* = 8.2 Hz, 2H, C_6H_4 2,6-H), 8.15–8.03 (m, 4H, anthracen-H), 7.73 (d, *J* = 8.2 Hz, 2H, C_6H_4 2,6-H), 7.68 (d, *J* = 8.6 Hz, 2H, C_6H_4 3,5-H), 7.61–7.53 (m, 4H, anthracen-H), 7.33 (d, *J* = 16.5 Hz, 1H, CH=CH), 7.28 (d, *J* = 16.2 Hz, 1H, CH=CH); APCI MS: *m*/*z*, 470(M + 1, 100), 471(M + 2, 45); Anal. Calcd. for $C_{30}H_{19}N_3O_3$(469.5):C, 76.75; H, 4.08; N, 8.95; Found: C, 76.91; H, 4.60; N, 9.14.

3. Results and discussion

3.1. *The synthesis and characterization*

The synthetic pathway and the structures of the target compounds are shown in Fig. 1. A series of novel anthracene-based stilbene derivatives containing an 1,3,4-oxadiazole unit were synthesized in good yield by the oxidative cyclization of hydrazones derived from aromatic aldehydes and 4-methylbenzohydrazide by chloramine-T, bromination of N-Bromosuccinimide (NBS), esterification, and Wittig–Horner reaction. The key stage in the synthesis of these target compounds is the preparation of intermediate **1**, in which chloramine-T was used as oxidative cyclization agent under mild reaction conditions. The chemical structures of the target compounds are confirmed by FT-IR,^{1}H NMR, ^{13}C NMR, MS and elemental analysis, which were shown detailed in experiment section. 1,3,4-Oxadiazole is the electron-accepting five-membered hetero-aromatic unit containing two imine –C=N– groups. Because of the electron-withdrawing ability of the imine –C=N– group, the ^{13}C NMR data of target compounds show the chemical shifts of two C atoms of the imine –C=N– group around 165.0 and 163.0 ppm. According to the chemical shifts and coupling constant (16.0–16.7 Hz) of doublet of CH=CH in the ^{1}H NMR spectra of target compounds, it was indicated that two protons had different chemical environments owing to the effect of different substituents belonging to the trans-structure, which could confirm the existence of stilbene. The melting points data of target compounds indicate that most of them have high melting points of >200 °C.

3.2. *Optical properties*

The optical properties for all new target compounds are summarized in Table 1. The UV–vis absorption spectra and fluorescence spectra of the compounds are shown in Figs. 2 and 3 (in 10^{-5} mol L^{-1} tetrahydrofuran solution). It can be observed that the eight compounds **4a**–**h** have quite similar UV–vis absorption characteristics. The maximum absorption peaks (λ_{abs}), which can be attributed to the charge-transfer (CT) type π–π* electronic transitions, situate in 334–388 nm in solution. The CT absorption band of the compounds strongly depends on the conjugation length. As can be seen in Fig. 2, the largest red-shift of the CT band was observed at 388 nm for compound **4c**, which possesses the longest conjugation length, relative to that of the other compounds. Whereas, compound **4a**, having a shorter conjugation length (compared to **4b**) exhibits a blue shifted absorption maximized at 334 nm. The introduction of two anthracene groups extends the conjugation length of the molecular structure. The longer wavelength absorption band of **4c** can be attributed to the π-π* transition in the 1,3,4-oxadiazole, stilbene and anthracene. Compared with the maximum absorption peak of compound **4a** (334 nm), compound **4g** (349 nm) had a greater shift toward higher wavelengths in accord with the stronger electron donating methoxy

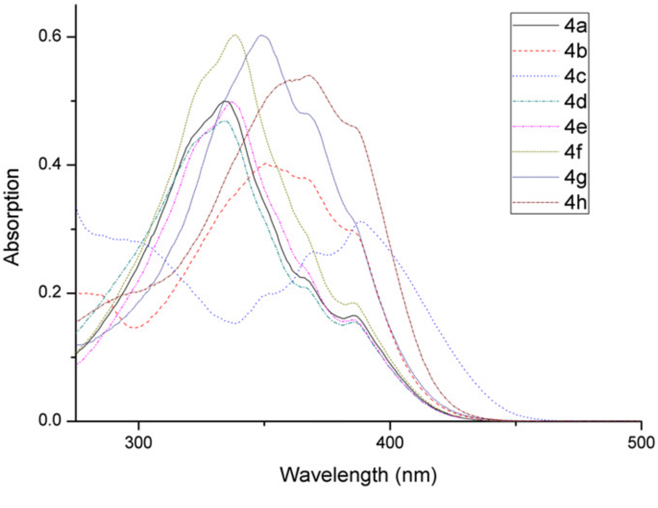

Fig. 2. The absorption spectra of target compounds (1 × 10^{-5} mol L^{-1} in THF).

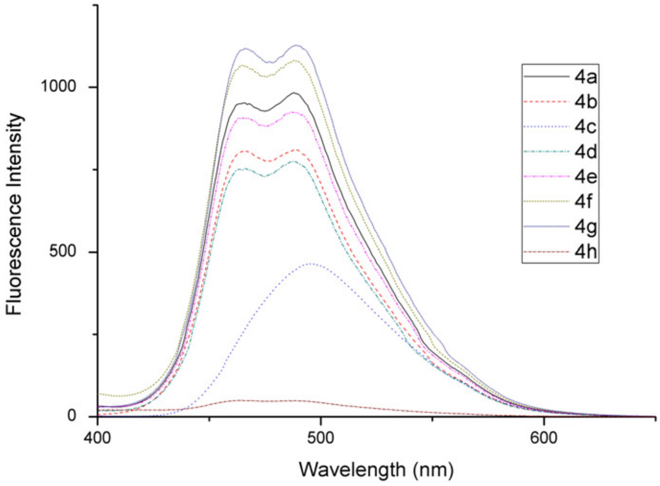

Fig. 3. The emission spectra of target compounds (1×10^{-5} mol L^{-1} in THF).

group. Compounds **4d**, **4e** and **4f** had the similar maximum absorption peaks, indicating that the halogen substituents have a limited effect on their electronic energy levels. As can be seen in Table 1 and Fig. 3, these compounds were highly fluorescent and exhibit strong blue-green fluorescence. The efficient π-conjugation in molecule is known to be responsible for charge-transfer nature of the emissive excited state. The reason is attributed to the anthracene, which would make the electron-pair in the highest occupied molecular orbit possess a lower energy; the electron-pair could be excited easily to transit into a higher orbit. The relatively high fluorescence quantum yield (0.43–0.78) and large Stokes shift (100–151 nm) of the new compounds **4a**–**4g** can be explained in the same way. Upon UV photoexcitation, compound **4h** exhibits quite weak fluorescence in solution owing to the existence of the electron-withdrawing nitro-substituent, which would make the electron-pair on the phenyl ring absorb higher energy to shift π^* orbit from π orbit, and the maximum emission peak (λ_{em}) locates at 488 nm. Concerning the fluorescence quantum yields of compounds **4a**–**4c**, it can be found that the Φ_x values for **4a**–**4c** decrease with the increase of conjugation. It may be attributed to the difference in the steric hindrance imposed by the 1,3,4-oxadiazole, anthracene skeleton, π-bridges, linkages and dihedral angles between two units that seem to affect the planarity of the molecules.

3.3. *Electrochemical properties*

To obtain information on the charge injection capabilities, the electrochemical behavior of the target compounds was investigated by cyclic voltammetry in 1 mmol L^{-1} dichloromethane solution. The oxidation and reduction potentials, energy levels, and the band gaps of new target compounds are summarized in Table 1. All the compounds exhibit quasireversible reduction waves upon the cathodic sweeps, with reduction potentials of-1.34 ~ −1.44 V vs $Ag/AgNO_3$, while the oxidation processes exhibit irreversible waves when swept anodically, the potentials of oxidation for the compounds are located at 0.70–1.26 V vs $Ag/AgNO_3$. The HOMO and LUMO energy levels of the target compounds were estimated from anodic and cathodic onset of cyclic voltammetry data to be from −6.06 to −5.50 eV, and from −3.45 to −3.35 eV, respectively. Their electrochemical band gaps (E_g), calculated from cyclic voltammetry data (E_{ox}–E_{red}), are 2.05–2.67 eV.

4. Conclusion

The approach reported here for the anthracene-based stilbene derivatives containing an 1,3,4-oxadiazole unit could be an efficient method, especially for industry, as the reaction conditions are mild, the yield is good and the product is easily purified. It can be concluded that the absorption and fluorescence characteristic of the new target compounds show a significant dependence on their molecular structure. These compounds exhibit high fluorescence quantum yield (Φ_x), bright green emission with a large Stokes shift. These observations indicate that the high π-conjugated molecule structure enhances the light absorption and the fluorescence emission ability of the target compound**s** due to the contribution of anthracene. These compounds could possess a medium strong fluorescence-emitting ability with Φ_x values in the region of 0.34–0.78. Electrochemical measurements indicate that the target compounds have good electron affinities of 2.05–2.67 eV, implying that they may have good electron injection capabilities.

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