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Synthesis of novel electro-transporting emitting compounds

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Abstract

A new type of naphthalimide derivatives (**NI-OXZ**) containing oxadiazole moiety has been synthesized and successfully developed as organic electro-transporting electro-luminescent (EL) materials. The high electron affinity of oxadiazole moiety in the dyad molecules can increase the electron-injection properties and keep the carrier balance. The relative high T_g value for such naphthalimide–oxadiazole dyads are particularly desirable for enhancing the stability and lifetime of opto-electronic devices. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Naphthalimide derivatives; Synthesis; Electro-transporting emitters

1. Introduction

Fluorescent dyes are currently of great interest in various application fields such as emitters for copy-preventing, solar energy collecting materials, and fluorescent film for agriculture purposes and functional materials. Much progress has been made in organic thin film electro-luminescence (EL) after it was reported by Tang and Vanslyke [1]. Although 8-hydroxyquinoline aluminum (Alq_3) is still considered to be important due to its thermal stability, good thin film forming and efficient electron-transporting capability [2,3], it is very necessary to design and develop novel high efficient EL materials that reduce the device current-density and improve the lifetime of the EL device. As a part of our continuing interest in this area [4,5], we are now describing a new route to synthesize novel electro-transporting emitters for high performance electro-luminescent devices. In this work, we have incorporated high electron-affinity oxadiazole into the naphthalimide chromophore and synthesized novel naphthalimide-oxadiazole (**NI-OXZ**) dyads shown in Scheme 1. Such dyads containing electron-transporting moiety could improve the balance of charge injection and control the location of the recombination region. In this way, it might be possible to avoid the complication of doping in the emitter layer and to find an appropriate device structure to minimize the carrier recombination efficiency.

2. Results and discussion

The synthetic route of **NI-OXZ** is depicted in Scheme 1. The key intermediate 4-carboxyl-1,8-naphthalic anhydride **4** was synthesized by Friedel–Crafts acetylation and oxidation. The reaction of acenaphthene **1** with acetic anhydride in the presence of catalyst anhydrous aluminum chloride gave 4-acetyl acenaphthane **2** in the yield of 69%.

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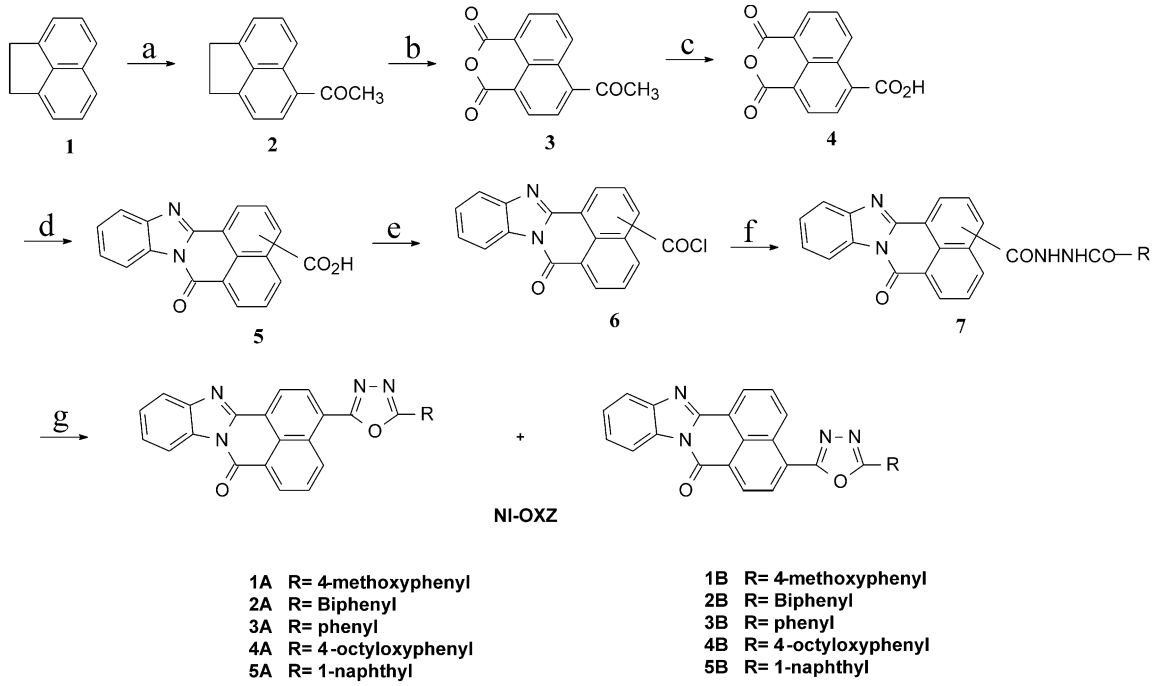
However, the one-step oxidation of **2** with sodium dichromate to obtain 4-carboxy-1,8-naphthalic anhydride **4** according to the method cited in reference [6] was not successful. The presence of the single proton resonance at 2.1 ppm confirmed that the acetyl group of **2** did not transform to the carboxyl group and the obtained product is 4-acetyl-1,8-naphthalic anhydride **3**. Fortunately, the acetyl group of **3** can be easily transformed to 4-carboxyl-1,8-naphthalic anhydride via the Hoffman degradation with sodium hypochlorite. It proceeded smoothly to give **4** in the yield of 90%, which was well characterized by ^{1}H-NMR. The characteristic singlet for the CH_3CO group at 2.1 ppm was not observed.

The target luminescent materials (**NI-OXZ**) were readily prepared via several steps. For instance, 4-carboxyl-1,8-naphthalic anhydride proceeded in acetic acid for 5 h with 1,2-diaminobenzene to furnish golden solid 7-oxo-7*H*-benzo[*de*]benzo[4,5]-imidazo[2,1-*a*]isoquinoline-3-carboxylic acid **5** in almost 100% yield. Next, the carboxylic acid group of **5** was converted into the acetyl chloride **6** by reflux in neat thionyl chloride. Compound **6** was not purified and reacted directly with phenyl hydrazide, and lost a molecule of water to afford an inseparable isomeric mixture, i.e. **NI-OXZ2$_A$** and **NI-OXZ2$_B$**. The product showed single spot on TLC (R_f = 0.27). However, the ^{1}H-NMR (500 MHz) was able to assign the differences. Table 1



Scheme 1. Reaction conditions: (a) $(CH_3CO)_2O$, $AlCl_3$, CH_2ClCH_2Cl, 0–5 °C, 3 h; (b) $Na_2Cr_2O_7$, CH_3CO_2H, 90–100 °C, 2 h; (c) NaClO, NaOH, 65–75 °C, 1 h; (d) 1,2-diaminobenzene, CH_3CO_2H, 105 °C, 5 h; (e) $SOCl_2$, reflux, 3 h; (f) the hydrazide, pyridine, dry THF, reflux, 5 h; (g) $POCl_3$, reflux, 5 h.

Table 1
Theoretical calculations of the chemical shift values of the protons in the isomeric mixture of NI-OXZ2$_A$ and NI-OXZ2$_B$

Calculated δ variables	H_1	H_2	H_3	H_4	H_5	H_6	$H_7(H_{7'})$	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}
NI-OXZ2$_A$	7.863	7.611	7.701	7.395	8.201	7.815	8.013	8.939	8.840	8.796	7.289	7.220	7.434	7.235
NI-OXZ2$_B$	7.863	7.611	7.701	7.395	7.860	8.741	8.121	7.585	8.744	8.796	7.289	7.220	7.434	7.235

lists the theoretical calculations of the chemical shift values of the protons in the isomeric mixture of NI-OXZ2$_A$ and NI-OXZ2$_B$. The chemical shift position for benzene is δ 7.27. The introduction of oxadiazole group (with high electron-affinity) into the naphthalimide leads to deshielding of the protons and thus to higher δ values. Such electronic effect has a marked influence on the ortho protons (H_8 of the NI-OXZ2$_A$ and H_6 of the NI-OXZ2$_B$), while it has much less on others. Therefore, the diastereoisomerism gives rise to different chemical shifts of the protons ortho to the oxadiazole group. As shown in Fig. 1, the proton resonance peaks a and b are corresponding to H_8 (**NI-OXZ2$_A$**) and H_6 (**NI-OXZ2$_B$**). The integration peaks a and b are just equal to that of one hydrogen. From the integration ratio, the ratio of isomeric mixture (**NI-OXZ2$_A$/ NI-OXZ2$_B$**) is about 1.37:1.

We also observed the same phenomena in other target compounds. Table 2 shows the proportions between A and B configurations of the target compounds according to the integration ratios of peak a and b, respectively. Further studies showed that the ratio of the isomers formed is strongly dependent on the reaction temperature. Fortunately, we did not observe the difference in the absorption and photo-luminance (PL) of the isomeric mixture. As a case of **NI-OXZ1$_A$** and **NI-OXZ1$_B$** depicted in Fig. 2, the visible absorption peak and PL peak are 410.4 and 512.4 nm, respectively.

The absorption and emission data of the dyads in chloroform are listed in Table 3. Comparing with 4-dimethylamino-*N*-ethyl-1,8-naphthalimide (its absorption peak at 415.6 nm in chloroform), the peak at about 413–418 nm corresponds to the absorption of the naphthalimide moiety. All of the NI-OXZ dyes display strong greenish-yellow fluorescence. Considering the emission of *N*-ethyl-4-dimethylamino-1,8-naphthalimide ($\lambda^{ex}_{max} = 415.6$ nm, $\lambda^{fl}_{max} = 503$ nm in $CHCl_3$), the fluorescence

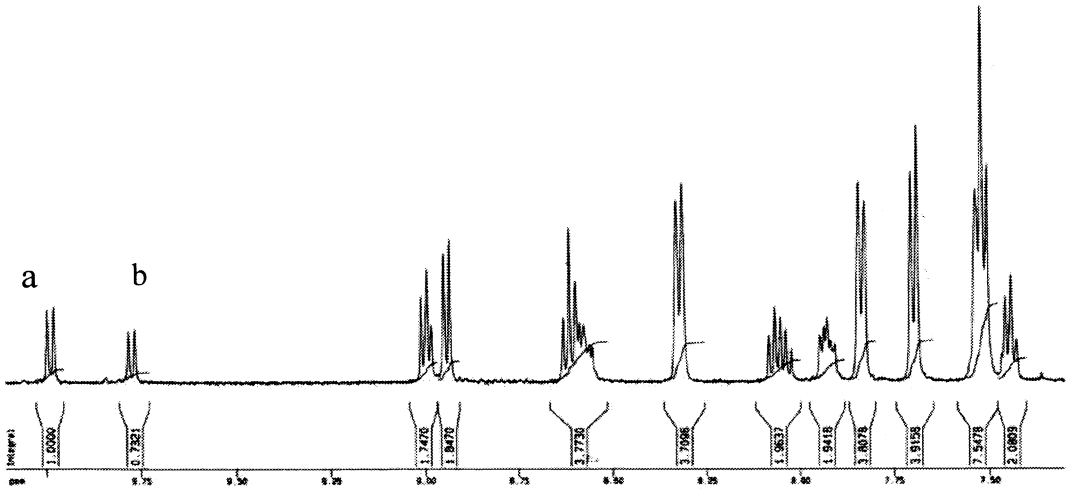


Fig. 1. ^{1}H-NMR of the isomeric mixture of NI-OXZ2$_A$ and NI-OXZ2$_B$ (section).

Table 2
Proportions between A and B configurations of the target isomeric mixtures according to the integration ratio of the ^{1}H-NMR peak a and b

	NI-OXZ1	NI-OXZ2	NI-OXZ3	NI-OXZ4	NI-OXZ5
Integration of peak a	1.0000	1.0000	1.0000	0.9696	1.0000
Integration of peak b	3.348	0.7321	0.3403	0.1651	0.9830
Proportion (A:B)	0.30:1	1.37:1	2.94:1	5.87:1	1.02:1

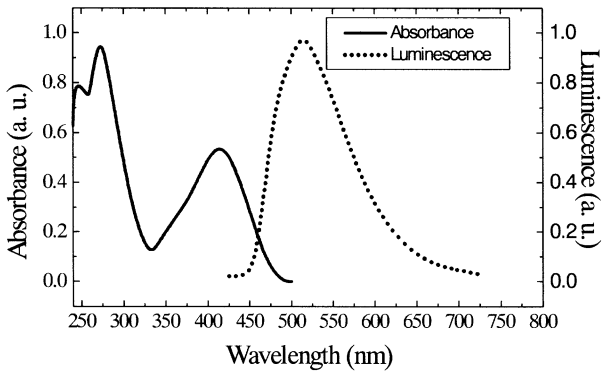


Fig. 2. The absorption and photoluminescent spectra of the isomeric mixture of NI-OXZ1$_A$ and NI-OXZ1$_B$.

Table 3
The absorption (λ^{ab}_{max}/nm) and fluorescence (λ^{fl}_{max}/nm) spectra data of the dyads in $CHCl_3$ (2×10^{-5} M)

Compounds	NI-OXZ1	NI-OXZ2	NI-OXZ3	NI-OXZ4	NI-OXZ5
λ^{ab}_{max}	276.4	289.5	305.5	276.5	298
	(4.56)	(4.44)	(4.11)	(4.41)	(4.27)
(log ε)	414.6	418	416	415.5	413
	(4.34)	(4.42)	(4.23)	(4.29)	4.25
λ^{fl}_{max}	512	507	505	507	504

peak (500–512 nm) of the dyes here is originated from the naphthalimide moiety regardless of different excitation wavelengths. Although oxadiazole was a fluorescent chromophore (peak at around 440 nm in chloroform), the characteristic PL emission of oxadiazole moiety in NI-OXZ dyes was not detected. This shows that in such naphthalimide dyad derivatives the emission of oxadiazole moiety is quenched completely, which means that there exists an effective singlet–singlet energy transfer from oxadiazole to naphthalimide due to the overlap between the absorption of naphthalimide moiety and the emission of oxadiazole moiety [7,8].

The opto-electronic equipment has to be designed to accept temperature excursions as high as 80 °C. This is a problem since the glass transition temperature or recrystallization temperature of many organic materials are in this range [9]. Materials having high glass transition temperatures are particularly desirable for enhancing the stability and lifetime of the devices. In fact, no distinct glass transition state was observed when compound NI-OXZ1$_A$ and NI-OXZ1$_B$ were taken on the second heat (shown in Fig. 3). Thermal analysis results therefore indicated that these target compounds have high T_g and good thermal stability, which is very essential for fabricating stable organic EL devices. The carrier-transporting mobility, photoluminescence and electroluminescence have been studied. Further work to determine the carrier-transporting mobility and the EL properties of these compounds is in progress.

3. Experimental

Absorption spectra were recorded on a Shimatzu UV-260 and Varian Cary 500 spectrometer and fluorescence spectra were determined with a Hitachi-850 fluorescent spectrometer. ^{1}H-NMR spectra were recorded on a Brucker AM 500 spectrometer with tetramethylsilane (TMS) as

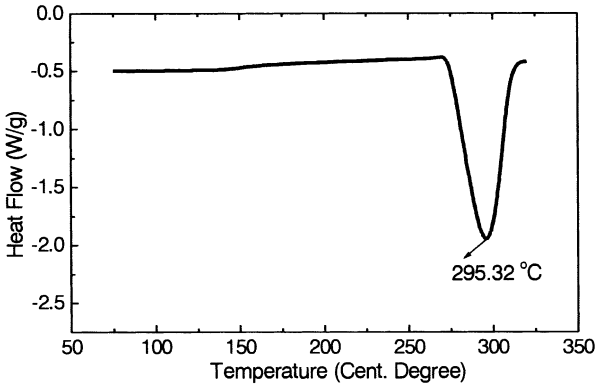


Fig. 3. Differential scanning calorimeter traces of the isomeric mixture of NI-OXZ1$_A$ and NI-OXZ1$_B$.

internal reference. Mass spectra were carried out on a HP 5989 mass spectrometer. Glass transition temperatures (T_g) were measured using a differential scanning calorimeter TA DSC 2910 Instrument at a scan rate of 10 °C/min. All solvents were distilled prior to use. Reactions were monitored by thin-layer chromatography. The structural data of these compounds were summarized in Table 4.

3.1. The synthesis of 3-[5-diphenyl-[1,3,4]oxadiazol-2-yl]-benzo[de]benzo[4,5]imidazo[2,1-a] isoquinolion-7-one (NI-OXZ2$_A$) and 4-[5-diphenyl-[1,3,4]oxadiazol-2-yl]-benzo [de]benzo[4,5]imidazo[2,1-a]isoquinolion-7-one (NI-OXZ2$_B$)

*3.1.1. 4-Acetyl acenaphthene (**2**)*

To a solution of acenaphthene (30 g, 195 mmol) in 1,2-dichloroethane (150 ml) at 0–5 °C was added acetic anhydride/ aluminum chloride (124 ml) dropwise in 1 h. The mixture turned brown. After being stirred for an additional 1 h, the mixture was controlled at 6–8 °C for 2 h. The mixture was poured into concentrated HCl (50 ml) and ice (250 g) and stirred until the ice melted. The resultant mixture was extracted twice with chloroform (25 ml) and the combined organic extracts were washed twice with water (50 ml). The organic layer was then decolorized with activated carbon and the filtrate was cooled. The precipitate was filtered, dried under vacuum and recrystallized in methanol to give **2** (26.2 g) as a yellow solid in 69% yield, m.p. 63–65 °C.

*3.1.2. 4-Acetyl-1,8-naphthalic anhydride (**3**)*

Into a three necked round-bottomed flask were added **2** (8 g, 41 mmol) and glacial acetic acid (150 ml). After stirring for 0.5 h until 4-acetyl acenaphthene was dissolved, sodium dichromate (60 g, 200 mmol) was added. The suspension was stirred vigorously at 90–100 °C for 2 h and then cooled for 0.5 h. The mixture turned from brown to dark green. The resulting mixture was poured into ice/water (200 ml), filtered and washed with water. The collected light green solid was treated with sodium hydroxide (1 g, 25 mmol) in a 3% aqueous solution (60 ml) of potassium carbonate. The resulting mixture was stirred and heated at 80–90 °C for 0.5 h, then filtered. After cooling, the filtrate was acidified with concentrated hydrochloric acid to pH 3–4 and the precipitated product was filtered, washed well with water, dried to give **3** (2.0 g) as a pale white solid in 20.4% yield, m.p. 204–206 °C.

*3.1.3. 4-Carboxyl-1, 8-naphthalic anhydride (**4**)*

To an aqueous solution of sodium hypochlorite (50 ml, active chlorine $\geqslant$5.2%, free alkali 7.8–8.0%) at 45–55 °C was added **3** (2.0 g, 8.3 mmol) in a 3% aqueous solution (80 ml) of sodium hydroxide. The reaction mixture was stirred at 65–75 °C for 1 h. After cooling for 10 min, the mixture was treated with sodium bisulfite (0.4 g, 3.8 mmol) and was stirred vigorously until the sodium bisulfite was dissolved. The mixture was filtered and the filtrate was acidified with hydro-

Table 4
Summary of spectroscopic data for the dyes prepared in this study

Dye	^{1}H-NMR (500 MHz) and MS
NI-OXZ1	^{1}H-NMR ($CDCl_3$): 3.93 (s, 3H, $-OCH_3$), 7.08 (d×d, $J=7.0$ Hz, $J=1.9$ Hz, 2H), 7.54 (m, 2H), 7.89 (m, 1H), 8.00 (m, 1H), 8.17 (m, 2H), 8.54 (m, 2H), 8.90 (m, 1H), 8.96 (d×d, $J=6.3$ Hz, $J=1.0$ Hz, 1H), 9.74 (d×d, $J=7.7$ Hz, $J=1.0$ Hz, 0.77H), 9.95 (d×d, $J=7.6$ Hz, $J=1.0$ Hz, 0.23H) MS (EI 70 eV) *m/e*: 444 (100%) [M^+], 445 (22.20%) [$M^+ + 1$], 135 (26.11%)
NI-OXZ2	^{1}H-NMR ($CDCl_3$): 7.44 (t, $J=7.3$ Hz, 1H), 7.52 (t, $J=7.6$ Hz, 4H), 7.70 (d, $J=7.7$ Hz, 2H), 7.84 (d, $J=8.0$ Hz, 2H), 7.93 (m, 1H), 8.05 (m, 1H), 8.32 (d, $J=7.9$ Hz, 2H), 8.58 (m, 2H), 8.94 (d, $J=7.5$ Hz, 1H), 9.00 (m, 1H), 9.77 (d, $J=8.6$ Hz, 0.42H), 9.99 (d, $J=8.6$ Hz, 0.58H) MS (EI 70 eV) *m/e*: 490 (100%) [M^+], 491 (35.67%) [$M^+ + 1$], 181 (31.36%), 433 (11.45%)
NI-OXZ3	^{1}H-NMR ($CDCl_3$): 7.54 (m, 2H), 7.59 (m, 3H), 7.98 (m, 1H), 8.06 (t×d, $J=7.3$ Hz, $J=1.2$ Hz, 1H), 8.24 (d×d, $J=6.1$ Hz, $J=1.7$ Hz, 2H), 8.58 (m, 2H), 8.94 (m, 1H), 9.18 (m, 1H), 9.78 (d, $J=8.6$ Hz, 0.25H), 9.99 (d×d, $J=8.6$ Hz, $J=0.8$ Hz, 0.75H) MS (EI 70 eV) *m/e*: 414 (79.556%) [M^+], 105 (100%), 77 (45.118%), 297 (16.635%), 269 (16.617%), 63 (14.521%)
NI-OXZ4	^{1}H-NMR($CDCl_3$): 0.91 (t, 3H, $-CH_2C\mathbf{H}_3$), 1.42 (m, 10H, $-(C\mathbf{H}_2)_5CH_3$), 1.84 (m, 2H, $-OCH_2C\mathbf{H}_2(CH_2)_5CH_3$), 4.02 (t, $J=6.2$ Hz, 2H,$-OC\mathbf{H}_2(CH_2)_6CH_3$), 7.02 (d, $J=8.3$ Hz, 2H), 7.44 (m, 2H), 7.84 (m, 1H), 7.96 (t, $J=7.8$ Hz, 1H), 8.08 (d, $J=8.4$ Hz, 2H), 8.38–8.46 (m, 2H), 8.77 (m, 2H), 9.66 (d, $J=8.5$ Hz, 0.15H), 9.86 (d, $J=8.5$ Hz, 0.85H) MS (EI 70 eV) *m/e*: 542 (54.40%) [M^+], 543 (20.54%) [$M^+ + 1$], 304 (100%), 306 (34.08%), 305 (33.09%), 270 (24.55%), 430 (23.63%), 338 (16.62%)
NI-OXZ5	^{1}H-NMR($CDCl_3$): 7.54 (m, 2H), 7.66 (m, 2H), 7.77 (m, 1H), 7.97 (m, 2H), 8.08 (q, $J=8.5$ Hz, 1H), 8.13 (d×d, $J=8.0$ Hz, $J=2.9$ Hz, 1H), 8.41 (q, $J=7.6$ Hz, 1H), 8.59 (m, 1H), 8.66 (q, $J=6.2$ Hz, $J=6.3$ Hz, 1H), 8.96 (m, 1H), 9.09 (d, $J=7.4$ Hz, 1H), 9.38 (q, $J=8.3$ Hz, $J=8.4$ Hz, 1H), 9.85 (d, $J=8.5$Hz, 0.50H), 10.06 (d, $J=8.5$ Hz, 0.50H) MS (EI 70 eV) *m/e*: 464 (100.00%) [M^+], 465 (34.72%) [$M^+ + 1$], 155 (30.08%), 407 (19.48%), 297 (18.50%), 269 (16.86%), 127 (13.45%), 408 (13.13%)

chloric acid to pH 2–3. The precipitated product was filtered and washed well with water to pH 7, dried to give **4** (1.8 g) in 90% yield. m.p. 274–277 °C.

*3.1.4. Synthesis of isomers (**5**). 7-oxo-7H-benzo[de] benzo[4,5] imidazo[2,1-a]isoquinoline-3-carboxylic acid and 7-Oxo-7H-benzo[de]benzo[4,5] imidazo-[2,1-a]isoquinoline-4-carboxylic acid*

The reaction was performed under the protection of argon atmosphere. Into a three necked flask were added **4** (0.5 g, 2.1 mmol), 2- diaminobenzene (0.7 g, 6.4 mmol) and glacial acetic acid (25 ml). The reaction mixture was heated at 104–105 °C for 5 h, diluted by the addition of cold water (50 ml) and glacial acetic acid (25 ml). The resulting mixture was stirred at 60 °C for 1 h, cooled to 50 °C and filtered. The filter cake was washed well with water to pH 7, dried to give **5** (0.64 g) as a golden yellow solid in 99% yield. m.p. >270 °C. ^{1}H-NMR(DMSO): 7.50 (m, 2H), 7.86 (m, 1H), 7.94–8.02 (m, 1H), 8.40 (m, 2H), 8.69 (d, $J=7.2$ Hz, 1H), 8.74 (d, $J=7.6$ Hz, 1H), 9.02 (d, $J=8.6$ Hz, 0.31H), 9.29 (d, $J=8.6$ Hz, 0.69H). MS (EI 70 eV) *m/e*: 314(15.51%)[M^+], 315 (4.42%)[$M^+ + 1$], 17 (26.75%), 18 (100.00%).

*3.1.5. Synthesis of isomers (**6**). 7-Oxo-7H-benzo-[de]benzo[4,5]imidazo[2,1-a]isoquinoline-3-carbonyl chloride and 7-oxo-7H-benzo[de]benzo-[4,5]imidazo[2,1-a]isoquinoline-4-carbonyl chloride*

Into a three necked round-bottomed flask were added **5** (0.7 g, 2.23 mmol) and dry dichloro sulfoxide (30 ml). The reaction mixture was refluxed 74 °C for 3 h till **5** was dissolved in dry thionyl chloride. The solution turned orange. The resulting mixture was evaporated at reduced pressure to dryness to give **6** as an orange residue (in a sealed flask) which was used in the next step without further purification.

3.1.6. 4-Acetyl biphenyl

To a solution of biphenyl (72 g, 470 mmol) in carbon disulfide (500 ml) was added dry aluminum chloride (72 g, 539 mmol). After 10 min of stirring at 40 °C, acetyl chloride (60 ml) was added dropwise to the mixture in 25 min. The resulting reaction mixture was heated to reflux (46–47 °C) and stirred for 3–4 h. The mixture turned from violet to dark green. After cooling to room temperature for 10 min, the mixture was poured into ice/H_2O (600 ml). The resulting mixture was filtered and washed with H_2O to pH 7 and give 4-acetyl biphenyl 71.5 g as a yellowish solid in 78% yield. m.p.123–124 °C.

3.1.7. Biphenyl-4-carboxylic acid

To a stirring solution of sodium hydroxide (70 g, 1750 mmol) in H_2O (300 ml) at –5 °C was added bromine (30 ml) dropwise. The solution was stirred below 5 °C and it turned light green. After 4-acetyl biphenyl (35 g, 180 mmol) was added and heated at 60–70 °C for 4 h, the mixture became milk-white. Sodium sulfite was added until discoloration of starch iodide paper did not take place. The mixture was filtered to give a milk-white filter cake which was dissolved in a 10% aqueous solution (400 ml) of sodium hydroxide at 80 °C. The resulting mixture was filtered hot and the filtrate was neutralized with 1:1 HCl to give biphenyl-4-carboxylic acid 8.0 g as a milk-white solid in 22.8% yield. m.p. 225–227 °C.

3.1.8. Biphenyl-4-carboxylic acid ethyl ester

Into a three necked round-bottomed flask were added biphenyl-4-carboxylic acid (8.0 g, 40 mmol), benzene (120 ml), absolute ethyl alcohol (8 ml) and concentrated sulfuric acid (0.5 ml). The reaction mixture was refluxed for about 24 h, monitored by the thin layer chromatography (TLC). The mixture was filtered and the filtrate was evaporated at reduced pressure to give deep red oil. The oil was poured into H_2O (200 ml) and treated with sodium carbonate anhydrous to pH 8–9. The mixture was extracted with chloroform (3×50 ml). The combined organic extracts were washed with saturated sodium chloride and H_2O to pH 7, dried with magnesium sulfate (anhydrous). The mixture was evaporated to give biphenyl-4-carboxylic acid ethyl ester 9.0 g as orange oil in 99% yield.

3.1.9. Biphenyl-4-carboxylic acid hydrazide

To biphenyl-4-carboxylic acid ethyl ester (9.0 g, 39.8 mmol) stirred in 60 ml of absolute ethyl alcohol at 60 °C was added hydrazine hydrate (26 ml) dropwise under argon atmosphere. After being stirred for 3 h, the reaction mixture was cooled over a night. The precipitated product was filtered and washed with H_2O, dried to give biphenyl-4-carboxylic acid hydrazide (4.6 g) as a yellowish solid in 54% yield. m.p. 196–198 °C.

*3.1.10. Synthesis of isomers (**7**). Diphenyl-N′-(7-oxo-7H-benzo[de]benzo[4,5]imidazo[2,1-a] isoquinoline-3-carbonyl)-hydrazide and Diphenyl-N′-(7-oxo-7H-benzo[de]benzo[4,5]imidazo[2,1-a] isoquinoline-4-carbonyl)-hydrazide*

To a suspension of **6** (0.77 g, 2.23 mmol) in dry tetrahydrofuran (60 ml) were added biphenyl-4-carboxylic acid hydrazide (0.7 g, 3.3 mmol) and pyridine (1 ml). The reaction mixture was refluxed at 66 °C for 5 h and then evaporated until 60% tetrahydrofuran was removed. The orange mixture was poured into ice/water (100 ml) and the precipitated product was filtered and washed well with water, dried. The collected solid product was treated with ethanol (50 ml) at 70 °C for 0.5 h and filtered to give **7** (0.85 g) as an orange solid in 76% yield. m.p. > 270 °C.

*3.1.11. Synthesis of isomers (**NI-OXZ2**). 3-[5-Diphenyl-[1,3,4]oxadiazol-2-yl]-benzo[de]benzo-[4,5]imidazo[2,1-a]isoquinolion-7-one (**NI-OXZ2$_A$**) and 4-[5-diphenyl-[1,3,4]oxadiazol-2-yl]-benzo[de]-benzo[4,5]imidazo[2,1-a]isoquinolion-7-one (**NI-OXZ2$_B$**)*

A mixture of **7** (0.85 g, 1.67 mmol) and dry phosphorus oxychloride (60 ml) was refluxed at 105 °C for 5 h and the solution turned brown. The resulting mixture was evaporated at reduced pressure until 70% phosphorus oxychloride was removed. After cooling to room temperature, the mixture was poured into ice/water (150 ml) and the precipitate was filtered and washed well with water. The crude product was recrystallized to give **NI-OXZ2** (0.45 g) as a yellowish solid in 56% yield. m.p. > 270 °C.

4. Conclusions

A new type of naphthalimide derivatives (NI-OXZ) containing oxadiazole moiety has been synthesized through acylation, oxidation, condensation and dehydration according to the molecular designing principle. The UV-vis absorption, fluorescence spectra and the glass transition temperature were tested. There exists an effective singlet-singlet energy transfer from oxadiazole to naphthalimide in such dyad systems due to the overlap between the absorption of naphthalimide moiety and the emission of oxadiazole moiety. Such dyads containing electron-transporting moiety could improve the balance of charge injection and control the location of the recombination region. In this way, it might be possible to avoid the complication of doping in the emitter layer and to find an appropriate device structure to minimize the carrier recombination efficiency for the application of OLED.

Acknowledgements

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