Synthesis, characterization, photoluminescent and electroluminescent properties of new conjugated 2,2'-(arylenevinylene)bis-8-substituted quinolines

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A series of new PPV oligomers containing 8-substituted quinoline, 2,2'-(arylenevinylene)bis-8-quinoline derivatives, were designed and synthesized via a Knoevenagel condensation reaction of quinaldine, 8-hydroxy- or 8-methoxy-quinoline with aromatic dialdehydes. These PPV oligomers were characterized by 1H and 13C NMR, X-ray diffraction, elemental analysis, UV-visible and fluorescence spectroscopies. The X-ray diffraction investigation showed that there are intramolecular π−π interactions in the solid state in 1 and 3. The optical and photoluminescent properties study demonstrated that the emission color of the resulting materials varies from blue to yellow and is dependent on the substituents (π-donor and π-acceptor groups) on both sides of the conjugated molecules and the aromatic core in the middle of the conjugated backbones. The electroluminescent devices using compounds 1–4 as the emitters and electron-transporting layers were fabricated with the structure ITO/NPB/emitter/LiF/Al. The best device performance with the maximum brightness of 5530 cd m−2 and the luminous efficiency of 2.4 cd A−1 is achieved by using compound 4, with intramolecular charge transfer character, as the emitter; these values represent a more than 5-fold improvement in brightness and efficiency compared to compound 3 without methoxy groups on the phenyl rings.

Introduction

The development of well-defined π-conjugated oligomers has been the subject of intensive research for optoelectronic applications, particularly organic light-emitting devices (LEDs),1–4 because (i) their precise chemical structure and conjugated length give rise to defined functional properties, (ii) they are able to give high purity films by vacuum deposition,5,6 (iii) they can serve as model systems for understanding the relationships between bulk material properties and molecular structures in the parent polymers.7 Recently, interest in the modification of the conjugated backbones by either changing the central cores in the conjugated molecules or changing the electron-donating and/or electron-withdrawing groups to investigate the structural influence on the LED properties was underlined.8

The aim of the present work is to develop new poly-(phenylenevinylene) (PPV) oligomers containing 8-substituted quinoline for organic light-emitting diodes. The reason for using 8-substituted quinoline as the building block is that both tris(8-hydroxyquinolinate)aluminum (Alq3)9 and polyquinolines10 are excellent electroluminescent and electron-transporting materials. In addition, pyridine based conjugated polymers can be used in LEDs made from environmentally stable metal electrodes because of the high electron affinity of the pyridine ring.11 Therefore, the new class of PPV oligomers containing 8-substituted quinolines is expected to offer the combined properties of PPV and quinolines for organic LED application.

In our previous communication, we reported the synthesis and preliminary light-emitting property of two PPV oligomers containing 8-substituted quinolines.12 Here, we present the synthesis, structure characterization, electrochemical, photoluminescent and electroluminescent properties of the 2,2'- (arylenevinylene) bis-8-substituted quinolines (compounds 1–6) (see Scheme 1 for structures).

Experimental

General

1H NMR spectra were recorded on a Varian Spectrometer operating at 400 MHz. Chloroform (CDCl3) and dimethylsulfoxide (DMSO-d6) were used as solvents, and tetramethylsilane (TMS) as internal standard. C, H, N, elemental analyses were conducted with Bio-Rad Co’s elemental analytical instrument. UV-vis spectra for compounds 1–6 were obtained from their solutions in chloroform using a Varian Cray 50 spectrometer. A 1 cm quartz cell was used. A typical concentration of 1.5 × 10−5 mol L−1 was used for the measurements. Photoluminescent spectra were obtained from the same solutions, using a Perkin Elmer LS50B luminescence spectrometer.

Materials

Standard methods have been used to synthesize 8-methoxy-quinaldehyde13 and 2,5-dimethoxy-1,4-benzenedicarbaldehyde,14 1,4-Benzenedicarbaldehyde, 2,5-thiophenedicarboxaldehyde, isophthalaldehyde, methyl iodide, quinaldine and 8-hydroxy-quinaldehyde (from Aldrich) as well as triethylamine, acetic anhydride (from Beijing Chemical Company) were used without further purification. All reactions were carried out under nitrogen.

Synthesis of 2,2'-((1,4-phenylenevinylene)bisquinoline (1). A mixture of quinaldine (2.68 g, 20 mmol), 1,4-benzenedicarb aldehyde (1.34 g, 10 mmol) and acetic anhydride (10 mL) was stirred and heated at 125 °C for 40 h under N2. It was subsequently poured into ice water (100 mL) and stirred overnight. The brown-green solid obtained was filtered off, washed thoroughly with water, and dried to afford compound 1. A purified sample (3.26 g, 85%) was obtained as a green solid by recrystallization from a mixture of ethanol and chloroform.
M.p. 244–246°C. ¹H NMR (CDCl₃), δ [ppm] 7.49 (d, 2H, J = 16.0 Hz, trans-olefinic), 7.56 (d, 2H, J = 8.0 Hz, Ar-H), 7.71–7.75 (m, 8H, Ar-H), 7.83 (d, 2H, J = 8.0 Hz, Ar-H), 8.13 (d, 2H, J = 8.4 Hz, 3-position at quinoline), 8.18 (d, 2H, J = 8.4 Hz, 4-position at quinoline). ¹³C NMR (CDCl₃), δ [ppm] 119.42, 126.22, 127.39, 127.50, 127.72, 129.25, 129.35, 129.78, 133.81, 136.36, 136.89, 148.33, 155.87.

Elemental analysis for C₂₈H₂₀N₂, calcd: C, 87.50; H, 5.21; N, 7.29. Found: C, 87.72; H, 5.39; N, 7.52%.

Synthesis of 2,2'-[1,4-phenylenedivinylene]bis-8-methoxyquino-
line (2). A mixture of 8-methoxyquinoline (3.46 g, 20 mmol), 1,4-benzenedicarbaldehyde (1.34 g, 10 mmol), and acetic anhydride (10 mL) was stirred and heated at 125°C for 40 h under N₂. It was subsequently poured into ice water (100 mL) and stirred 2 h. After extraction with dichloromethane (3 × 30 mL), the organic layer was washed with water and dried over anhydrous Na₂SO₄. The solvent was then evaporated. The resulting residue was purified by chromatography (petroleum ether:ethyl acetate = 2:1 as eluent) to give 2.7 g of product (yield 74%). M.p. 256–258°C; ¹H NMR (CDCl₃) δ [ppm] 4.13 (s, 6H, OCH₃), 7.06 (d, 2H, J = 7.6 Hz, 5-position at quinoline), 7.41 (m, 4H, 6,7-position at quinoline), 7.56 (d, 2H, J = 16.4 Hz, olefinic), 7.64 (d, 2H, J = 16.4 Hz, olefinic), 7.66 (s, 4H, Ar-H), 7.77 (d, 2H, J = 8.8 Hz, 3-position at quinoline), 8.12 (d, 2H, J = 8.8 Hz, 4-position at quinoline). ¹³C NMR (CDCl₃), δ [ppm] 56.52, 108.36, 119.77, 119.84, 126.81, 127.71, 128.81, 130.92, 133.84, 136.36, 137.23, 140.49, 155.47, 155.58. Elemental analysis for C₃₀H₂₄N₂O₂, calcd: C, 81.08; H, 5.41; N, 6.31. Found: C, 81.67; H, 5.61; N, 6.60%.

Scheme 1  The synthetic routes to compounds 1–6.
Synthesis of 2,2-(1,4-phenylenedivinylene)bis-8-acyetoxyquinoline (3). A mixture of 8-hydroxyquinaline (3.18 g, 20 mmol), 1,4-benzenedicarbaldehyde (1.34 g, 10 mmol) and acetic anhydride (10 mL) was stirred and heated at 125 °C for 40 h under N2. It was subsequently poured into ice water (100 mL) and stirred overnight. The brown solid obtained was filtered off, washed thoroughly with water, and dried to afford compound 3. A purified sample (3.7 g, 82%) was obtained as a yellow solid by recrystallization from DMF. M.p. 252–254 °C.

\[ \text{1H NMR (CDCl}_3\text{), } \delta \text{ [ppm]} 2.59 \text{ (s, 6H, CH}_2\text{COO)}; 7.40 \text{ (d, 2H, } J = 16.4 \text{ Hz, trans-olefinic); 7.43–7.51 \text{ (m, 4H, Ar-H); 7.66–7.72 \text{ (m, 10H, 8H quinolinol ring except 4-position as well as 2H olefinic); 8.16 \text{ (d, 2H, 4-position at quinolinol ring)}.} \]

\[ \text{13C NMR (CDCl}_3\text{), } \delta \text{ [ppm]} 21.51; 118.11; 120.06; 122.11; 125.99; 126.47; 127.89; 134.51; 136.74; 137.27; 141.46; 147.84. \]

Synthesis of 2,2-(5,5-dimethyl-1,4-phenylenedivinylene)bis-8-acyetoxyquinoline (4). A mixture of 8-hydroxyquinaline (3.18 g, 20 mmol), 2,5-dimethyl-1,4-benzenedicarbaldehyde (1.94 g, 10 mmol), and acetic anhydride (10 mL) was stirred and heated at 125 °C for 40 h under N2. It was subsequently poured into ice water (100 mL) and stirred for 2 h. After extraction with dicholomethane (3 mL), the organic layer was washed with water and dried over anhydrous Na2SO4. The solvent was then evaporated. The resulting residue was purified by chromatography (petroleum ether: ethyl acetate 2:1 as eluent) to give 2.7 g of product (yield 53%). M.p. 240–242 °C. \[ \text{1H NMR (CDCl}_3\text{), } \delta \text{ [ppm]} 2.60 \text{ (s, 6H, CH}_2\text{COO); 7.42 \text{ (d, 2H, } J = 16.4 \text{ Hz, olefinic); 7.50 \text{ (m, 3H, Ar-H); 7.59 \text{ (d, 2H, } J = 7.6 \text{ Hz, quinoline ring), 7.69–7.75 \text{ (m, 6H, quinoline ring); 7.85 \text{ (s, 1H, Ar-H); 8.17 \text{ (d, 2H, } J = 8.8 \text{ Hz, 4-position at quinoline).}}} \]

\[ \text{13C NMR (CDCl}_3\text{), } \delta \text{ [ppm]} 21.51, 118.11, 120.06, 122.11, 125.99, 126.47, 127.89, 129.70, 129.94, 134.25, 137.33, 138.42, 147.78, 151.42, 153.79, 156.12, 170.33. \]

Elemental analysis for C32H24N2O4, calcd: C, 77.68; H, 5.40; N, 5.60. Found: C, 77.93; H, 5.01; N, 5.54%.

**X-Ray crystallography**

Crystals of compounds 1 and 3 were obtained from solutions of CHCl3/petroleum ether and were mounted on glass fibers. The data for 1 were collected on a R-AXIS Rapid IP diffractometer, operating at −50 °C, and the data for 3 were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation. The data for compounds 1 and 3 were collected over the range of 1.79–27.48° and 2.01–25.01°, respectively. No significant decay was observed for all samples during the data collection. The structure was solved with the direct method of SHELXS-86 and refined with full-matrix least-squares techniques using the SHELXL-93 program. All non-hydrogen atoms were refined anisotropically. The crystal of 1 belongs to the triclinic space group P1, and the crystal of 3 belongs to the monoclinic space group P2_1/c.

The crystallographic data for compounds 1 and 3 are given in Table 1. Selected bond lengths and angles are given in Table 2. CCDC numbers 195035 (compound 1) and 170715 (compound 3). See http://www.rsc.org/suppdata/jm/b2/b210408c/ for crystallographic files in cif or other electronic format.

**Cyclic voltammery**

Cyclic voltammograms were recorded with a computer controlled EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV s⁻¹. Measurements were performed in a conventional three-electrode cell. The working electrode was glassy carbon (diameter 0.8 mm), the counter electrode was a platinum mesh and the reference electrode was Ag/AgCl with a salt bridge containing 0.1 M tetrabutylammonium perchlorate (TBAP) in dichloromethane as the supporting electrolyte. All the experiments were carried out at room temperature and oxygen was removed from all solutions by bubbling nitrogen.

**Fabrication and characterization of the light-emitting devices**

The EL devices using I–4 as the emitting layer were fabricated on an indium tin oxide (ITO) substrate. The ITO glass was routinely cleaned by ultrasonic treatment in detergent solutions, followed by being rinsed with acetone, boiled in water. The glass was dried in a vacuum oven between each cleaning step. The electroluminescent device was fabricated by...
C–H…N hydrogen bonds between the quinoline nitrogen and quinoline hydrogen in compound 1. Imtermolecular distance 3.42 Å between two adjacent molecules. Intermolecular interactions suggest that compounds 1 and 3 are connected by the extensive array of π–π stacking and hydrogen-bonding interactions.

**Table 2** Selected bond lengths [Å] and angles [deg] for 1 and 3

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<td>C(14)–C(15)</td>
<td>1.397(3)</td>
<td>C(13)–C(14)–C(15)</td>
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**Results and discussion**

**Syntheses and structures**

All the symmetrically disubstituted chromophores were obtained by Knoevenagel condensation reactions. It is well known that the methyl group at the 2-position of the quinoline ring can be activated by the N atom, then can condense with an aldehyde catalyzed by acid or base.17,18 In this paper, an acid catalyst was selected. Quinaldine (2 mol) reacted with 1 mol of the appropriate aldehyde, leading to the formation of condensation product 1. The synthesis of compound 2 was conducted in two stages. First 8-hydroxyquinaldine was reacted with methyl iodide. After separation and purification, the resulting 8-methoxyquinaldine was reacted with 1,4-benzenedicarbaldehyde, affording 2. For compounds 3–6, the hydroxy groups were acetylated. The chemical structures of compounds 1–6 were characterized by IR, 1H NMR spectroscopy and elemental analysis.

To investigate the intermolecular interactions of the title compounds, their crystal growths were carried out under ambient conditions. Fig. 1 shows the crystal structure and cell packing diagram of compound 1 and Fig 2 shows the intermolecular hydrogen-bonding interactions in compound 1. As we can see from Fig. 1 (top), the crystal structure of 1 has an inversion center. Two quinolyl rings in 1 are completely coplanar with the benzene ring, but are on opposite sides of the divinylenebenzylene backbone. Intermolecular π–π stacking and hydrogen-bonding interactions are the most remarkable structural features of compound 1. A view of the packing of 1 [Fig.1 (bottom)] shows face to face π–π interactions with the shortest intermolecular π–π interaction distance 3.42 Å between two adjacent molecules. Intermolecular C–H…N hydrogen bonds between the quinoline nitrogen and quinoline hydrogen in compound 1 are observed (Fig. 2). The contact between C7–H hydrogen and the quinoline nitrogen atom (N1) of the neighbouring molecule is 2.489 Å. This is clearly within the sum of the van der Waals radii for hydrogen (1.2 Å) and nitrogen (1.55 Å).19 The C21–H…N angle is 163°. These results indicate that the molecules are connected by the extensive array of π–π stacking and hydrogen-bonding interactions.

The crystal structure and cell packing diagram of compound 3 are shown in Fig. 3. Two quinolyl rings in 3 are also coplanar with the benzene ring, on opposite sides of the divinylenebenzylene backbone along with the two acetoxy groups. It can also be seen from Fig. 3 (bottom) that there is extensive stacking between molecules of 3 by π–π interactions in the crystal lattice with the shortest intermolecular π–π interaction distance between two quinolyl rings 3.436 Å.

Munakata et al. confirmed that strong intermolecular interactions as well as intermolecular aromatic stacking could assist charge-transfer pathways.20 The intermolecular π–π interactions suggest that compounds 1 and 3 may possess charge transport abilities, which are essential properties for electroluminescent materials.  

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** Top: one of the independent molecular structure of 1 with labeling schemes and 50% thermal ellipsoids. Bottom: molecular packing diagram of 1 showing the intermolecular π–π interactions.
Electrochemical properties

In order to gain information on the charge injection, electrochemical measurements of 1–4 were performed. Typical cyclic voltammetry (CV) curves of compounds 3 and 4 are shown in Fig. 4. The values of onset redox potentials and the HOMO, LUMO energy levels for compounds 1–4 are summarized in Table 3. The energy levels were calculated using the ferrocence (FOC) value of 2.4.8 eV as the standard and the formal potential of FOC was measured to be 0.12 V against Ag/Ag\textsuperscript{+}. Under a positive scan, irreversible anodic waves was observed for these compounds and the onset potential values located at 1.16–1.39 V, which were higher than that of the model compound, 1,4-bis(4-tert-butylstyril)benzene (1.04 V). Under a negative scan, they showed reductive waves and the onset reduction potentials were between −1.35 and −1.57 V. However, no reduction is observed for model compound 1,4-bis(4-tert-butylstyril)benzene. Obviously this means that introduction of 8-substituted quinoline moieties provides a site of reduction at the unbonded electrons on the nitrogen atom because it is relatively electron deficient. As the reduction process in an electrochemical cell is related to the electron capture ability (or electron injection ability), it was concluded that incorporation of quinoline units onto the OPV backbone enhances the electron affinity significantly, which is beneficial for the construction of highly efficient electroluminescent devices. From the HOMO and LUMO energy levels we can see the low LUMO values (−3.11 to −3.33 eV) will greatly facilitate the electron injection from the cathode of the OLEDs, indicating that an air stable metal such as Al can be chosen as a cathode.

UV-visible absorption

Absorption spectra for compounds 1–3 in CHCl\textsubscript{3} solution are shown in Fig. 5. They exhibited a single structureless and broad absorption peak at 378 nm, which could be assigned to the absorption of the \(\pi-\pi^*\) transition of the conjugated segment. The absorption spectra of 3–6 are shown in Fig. 6, which describes the impact of the variation of aromatic core on the absorption. With \(m\)-phenylene as an aromatic core in the conjugated backbone, compound 5 possessed a blue-shifted absorption peak at 346 nm, as compared to 378 nm for 3. It is clear that the incorporation of the \(m\)-phenylene linkage provides a means of tuning the absorption properties.

### Table 3 Redox properties for compounds 1–4

<table>
<thead>
<tr>
<th>Compd.</th>
<th>(E^{\text{ox}}/V)</th>
<th>(E^{\text{red}}/V)</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
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</table>

Onset potentials vs. Ag/Ag\textsuperscript{+}. \(E_{\text{FOC}} = 0.12 \text{ V vs. Ag/Ag}^+\).
The methoxy and acetoxy substituted compounds PL spectra of compounds core is responsible for the blue light emission. Fig. 7 shows respectively. These suggest that the bisquinolylvinylenebenzene gives a maximum emission peak centered at 446 nm. Because 3 of the kink of meta-phenylene, compound 5 emits blue light with a maximum emission at 429 nm. With the incorporation of the thiophene unit. It should be noted that a large length. The replacement of the phenyl ring by a thienyl ring molecule and then yields a reduction in the effective conjugated p electron delocalization of the conjugated originates from compound identical to its PL spectrum in the film state with the maximum light was observed. It was found that the EL spectrum is nearly from the center core to the end groups, which is responsible for the large red-shift. Another is merely from the electron-donating effect of the methoxy group, similar to the red-shift of MEH-PPV (\(\lambda_{PL} = 590\) nm) relative to PPV (\(\lambda_{PL} = 520\)nm).

Electroluminescence of compounds 1–4
To investigate their electroluminescent properties, organic LEDs based on compounds 1–4 as the emitting layer and NPB (N,N-di(4-naphthyl)benzene)-N,N-diphenyl(1,1'-biphenyl)-4,4'-diamine) as the hole transport layer were constructed because they exhibit intense emissions in both solution and powder states under UV excitation (365 nm). We were unable to examine the electroluminescent properties of compounds 5 and 6 due to their relatively weak emissions in the solid state.

In our experiment, we found that compound 1 was difficult to deposit due to its low volatility. This may be associated with its severe rigidity. After introducing substituent groups at the 8-positions of quinoline rings, compounds 2–4 were easily evaporated during vacuum deposition. It seems that the end substituents were beneficial to reduce the molecular rigidity by free rotation of single bonds. As a result the EL performance of compound 1 was not studied here. Here the detailed device properties of compounds 3 and 4 were presented.

Fig. (top) shows the photoluminescent (PL) spectrum of compound 3 in film state and the electroluminescent (EL) spectrum of structure ITO/NPB (50 nm)/NPB (50 nm)/NPB (50 nm)/LiF (1 nm)/Al (200 nm). From the device of compound 3 a bright green light was observed. It was found that the EL spectrum is nearly identical to its PL spectrum in the film state with the maximum emission peak at 518 nm, indicating that the EL emission originates from compound 3. The current–voltage–luminance (I–V–L) characteristics of double-layer devices using 3 as an emitter are shown in Fig. (bottom). From it one can see that the turn-on voltage was as low as 5 V and the maximum brightness was over 1000 cd m\(^{-2}\) at about 18 V. The maximum current efficiency and power efficiency of the device are estimated to be 0.43 cd A\(^{-1}\) and 0.13 lm W\(^{-1}\), respectively.

The PL spectrum of compound 4 in film state and the corresponding EL spectrum are shown in Fig. (top). Compared with the green light emitting device of compound 3, this device gave a brighter yellow emission with a maximum emission at 506 nm. Compared to 3, its emission was red-shifted by about 42 nm. This unusual large red shift of compound 4 relative to compound 3 was also observed in its UV-vis absorption. Two possibilities may be considered for the red-shift phenomenon. One is associated with the push–pull effect. It is well known that methoxy is an electron-donor (D) group and the quinolyl ring is an electron-acceptor (A) group. The resulting compound 4 looks like D–π–A structural character and may be involved in the intramolecular charge transfer from the center core to the end groups, which is responsible for the large red-shift. Another is merely from the electron-donating effect of the methoxy group, similar to the red-shift of MEH-PPV (\(\lambda_{PL} = 590\) nm) relative to PPV (\(\lambda_{PL} = 520\) nm).

Photoluminescence
The PL spectra of compounds 1–3 in chloroform solutions, recorded with an excitation wavelength \(\lambda_{ex} = 365\) nm, are listed in Fig. 5. The parent compound 1, 2,2’-(1,4-phenylenevinylene)bis-8quinoline, displays an emission peaked at 435 nm. The methoxy and acetoxy substituted compounds 2 and 3 give maximum emission wavelengths at 443 nm and 439 nm, respectively. These suggest that the bisquinolylvinylenebenzene core is responsible for the blue light emission. Fig. 7 shows the PL spectra of compounds 3–6 in CHCl\(_3\) solutions. Compound 3 gives a maximum emission peak centered at 446 nm. Because of the kink of meta-phenylene, compound 5 emits blue light with a maximum emission at 429 nm. With the incorporation of the thiophene unit, compound 6 shifts the emission to green (emission peak at 510 nm). Compound 4 shows a green emission with maximum peak located at 481 nm and a shoulder

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wavelength of 551 nm. From Fig. 9 (bottom) we can see that the turn-on voltage of this device for compound 4 was only 3 V. The maximum brightness can reach up to 5530 cd m\(^{-2}\) at 16 V. The maximum current efficiency of 2.4 cd A\(^{-1}\) was obtained at an operating voltage of 7.6 V with a luminance of 500 cd m\(^{-2}\), about a 5-fold improvement in brightness and luminous efficiency compared to compound 3 without methoxy groups on the phenyl ring. We believe that the dramatic improvement of the device performance from bisquinoline-containing PPV oligomer 3 to 4 is associated with the difference in chemical structures. This means that when two methoxy groups are introduced into the phenyl ring in the middle of the π-conjugated backbone, the resultant intramolecular charge transfer plays an important role in enhancing the device performance. High EL behavior has been demonstrated in similar molecular systems characteristic of intramolecular charge transfer.\(^{28-30}\)

Conclusions

We have developed six new PPV oligomers containing quinoline heterocycles by the simple one-pot Knoevenagel condensation reaction. The resulting PPV oligomers cover the emission region from 435 nm to 510 nm, depending on the substituents (electron-donating and electron-withdrawing groups) on both sides of the conjugated molecules and the aromatic core in the middle of the conjugated backbones. Four of them, compounds 1–4, have been demonstrated to be promising green/yellow emitters and electron transport materials in organic electroluminecent devices. More important, compound 4 which possesses intramolecular charge transfer character exhibits a significant improvement in double-layer LED performance, with a maximum brightness of 5530 cd m\(^{-2}\) and a luminous efficiency of 2.4 cd A\(^{-1}\). Further investigation such as device structure optimization is in progress.

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