



New PPV oligomers containing 8-substituted quinoline for light-emitting diodes

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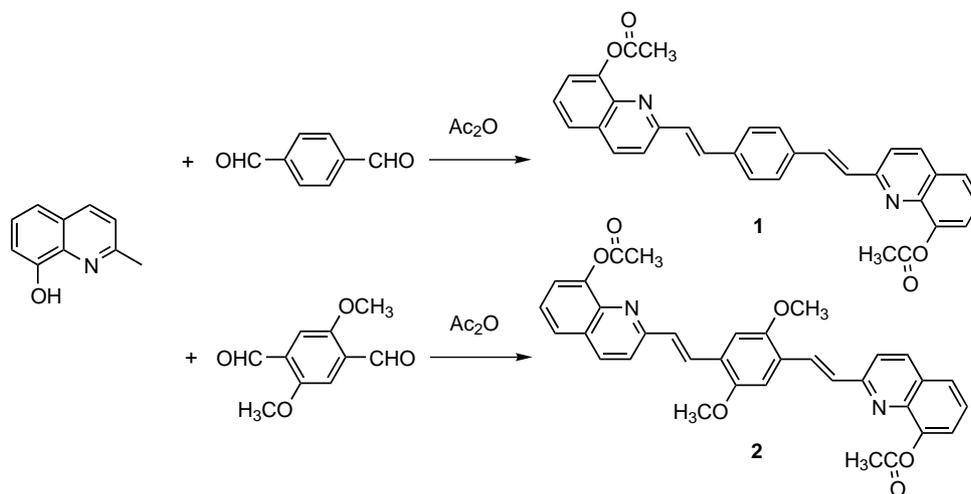
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Abstract—Two new poly(phenylenevinylene) (PPV) oligomers, 2,2'-(1,4-phenylenedivinylene)bis-8-acetoxy quinolines were synthesized via a Knoevenagel condensation reaction. The single-crystal X-ray diffraction study shows that there are intermolecular $\pi\cdots\pi$ interactions in the solid state of 2,2'-(1,4-phenylenedivinylene)bis-8-acetoxyquinoline. Electroluminescent properties using these compounds as emitters have been investigated. © 2002 Elsevier Science Ltd. All rights reserved.

One of the most exciting developments in molecular electronics is the utilization of organic materials for opto-electronic applications, particularly light-emitting diode devices (LEDs).¹ The strong coupling between geometry and electronic structure is the source of the fascinating physics of these π -conjugated molecules and polymers.² A key issue in designing light-emitting materials is the adjustment of their emission wavelength.^{1c} Recently, the 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.³

It is well-known that well-defined π -conjugated oligomers play a crucial role in determining the relationships between molecular structures and bulk polymer properties and have been the subject of increasing attention in the last years, because (i) their precise chemical structure and conjugated length gives rise to defined functional properties and (ii) they are able to produce high purity films by vacuum deposition.⁴



Scheme 1.

Keywords: PPV oligomers; 8-substituted quinoline; light-emitting diodes.

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For the molecular design aspect, it is necessary to design well-defined conjugated molecules presenting excellent opto-electronic properties. This provides the opportunity for a fine-tuning of the system properties. The aim of the present work is to develop new poly(phenylenevinylene) (PPV) oligomers containing an 8-substituted quinoline for organic light-emitting diodes.

Here we present the one-pot synthesis of a new family of PPV oligomers: 2,2'-(1,4-arylenevinylene)bis-8-acetoxy quinolines (**1** and **2**). The reason for using 8-quinolinol as the building block is that both tris(8-hydroxyquinolinolato) aluminum (Alq_3)⁵ and polyquinoline⁶ are excellent electroluminescent and electron-transporting materials. In addition, pyridine-based conjugated polymers can also be used in LEDs made from environmentally stable metal electrodes because of the high electron affinity of the pyridine ring.⁷ To the best of our knowledge, reports about PPV oligomers containing 8-quinolinol are rare. Herein the synthesis, structure and light-emitting properties of the title compounds are described.

The synthesis of target compounds **1** and **2** is shown in Scheme 1. The one-step coupling reactions of 8-hydroxyquinoline and 1,4-benzenedicarbaldehyde and 2,5-dimethoxy-1,4-benzenedialdehyde in acetic anhydride at 125°C lead to the formation of condensation products **1** and **2**, in which the hydroxy groups have also been acetylated.⁸ Compounds **1** and **2** were obtained as yellowish powders and fully characterized by ¹H NMR spectroscopy and elemental analysis. For example, compound **2** exhibits two doublets at 7.39 and 8.12 ppm with a three-bond coupling constant $^3J_{\text{H,H}} = 16.0$ Hz arising from *trans* carbon–carbon double bonds in its ¹H NMR spectrum, indicating the presence of *trans*-configuration in the vinylene units. It is concluded that the Knoevenagel condensation reaction between 8-hydroxyquinoline and 2,5-dimethoxy-1,4-benzenedialdehyde gives compound **2**, as expected.

To investigate the intermolecular interaction of the title compounds, their crystal growths were carried out under ambient conditions.⁹ Fig. 1 shows the crystal structure and cell packing diagram of 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, along with the two acetoxy groups. The C(12)–C(13)–C(14) angle (128.7(3)°) is larger than that of C(10)–C(12)–C(13) (123.5(3)°). It can also be seen from Fig. 1 (bottom) that the shortest intermolecular $\pi\cdots\pi$ interaction distance between two quinolyl rings is 3.436 Å, indicating that there is an extensive stacking between molecules of **1** by $\pi\cdots\pi$ interactions in the crystal lattice. Munakata et al. confirmed that strong intermolecular interactions as well as intermolecular aromatic stacking could assist charge-transfer pathways.¹⁰ The intermolecular $\pi\cdots\pi$ interactions suggest that compound **1** can possess charge transport properties, which are essential for electroluminescent materials.

Although compound **1** contains two acetoxy groups at the 8-positions of the quinolyl rings, it exhibits intense fluorescence both in solution (438 nm) and in solid state (531 nm and a shoulder peak at 500 nm), which may be attributed to its orderly stacking caused by strong intermolecular $\pi\cdots\pi$ interactions.

To explore its electroluminescent (EL) properties, the double-layer EL device [ITO/NPB(50 nm)/**1** (50 nm)/Mg:Ag(10:1)] was fabricated by vapor deposition of the organic molecules onto ITO-coated glass substrate at a deposition rate of 3–5 Å s⁻¹ at 5×10⁻⁶ Torr. In this case, NPB (*N,N'*-di-[naphthalenyl]-*N,N'*-diphenyl)-(1,1'-biphenyl)-4,4'-diamine) was chosen as the hole transporting material, and compound **1** was used as the emitting-layer and electron-transporting layer. Compound **1** was expected to have certain electron transporting abilities due to the presence of the quinoline unit, as both tris(8-hydroxyquinolinolato) aluminum (Alq_3) and polyquinoline have been shown to be good electron-transporting materials.

All the measurements were carried out at room temperature in air. It was found that the EL spectrum shown in Fig. 2 is nearly identical to its photoluminescent (PL) spectrum, indicating that the EL emission originates from compound **1**. It exhibits a fine vibronic structure characteristic of PPV with a maximum peak at 535 nm and a shoulder peak at 503 nm. Fig. 3 shows typical voltage–luminance (V–L) and current–voltage (I–V) curves. The device emits a green light under a forward bias. The turn-on voltage is about 6 V, and the maximum luminance can reach up to ~788 cd m⁻² at 18 V. The maximum luminous efficiency is estimated to be 0.13 lm W⁻¹.

In summary, two new PPV oligomers containing 8-substituted quinoline have been synthesized and characterized. It was found that there are strong intermolecular $\pi\cdots\pi$ interactions and orderly stacking in the solid state

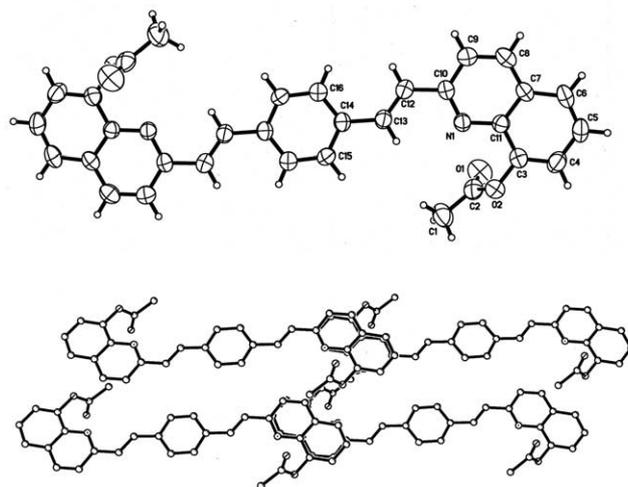


Figure 1. Top: the molecular structure of **1** with labeling scheme and 50% thermal ellipsoids. Bottom: unit cell packing diagram of **1**.

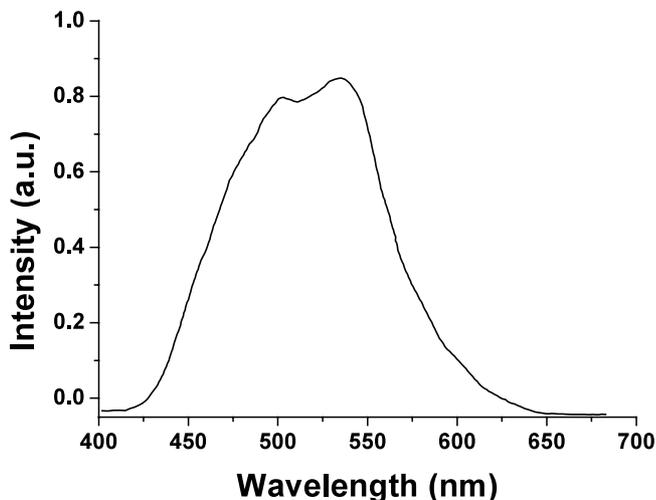


Figure 2. The EL spectrum for a device with structure of ITO/NPB /1/ Mg:Ag (10:1).

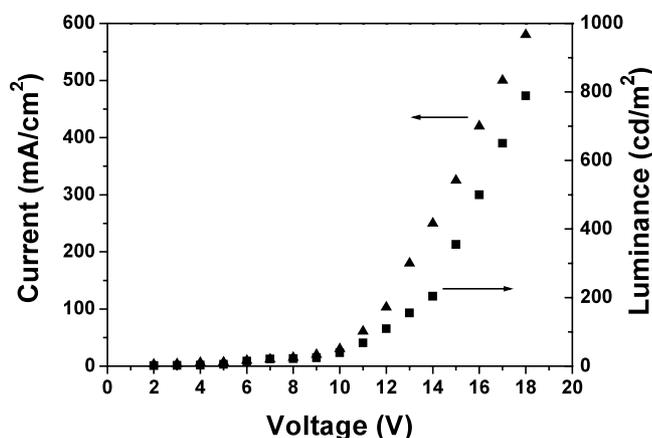


Figure 3. The voltage-current (V-I) and voltage-luminance (V-L) characteristics of a device with structure of ITO/NPB /1/ Mg:Ag (10:1).

of 2,2'-(1,4-phenylenedivinylene)bis-8-acetoxy quinoline, which is responsible for its PL and EL properties. A double-layer device investigation, using this compound as both emitting layer and electron-transporting layer, demonstrated that these new PPV-oligomers containing 8-substituted quinoline will be promising candidates in organic electroluminescent devices. Further research on their transporting properties, tuning of emission wavelength and optimum conditions for the device fabrication is in progress in our laboratory.

Acknowledgements

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- 2,2'-(1,4-Phenylenedivinylene)bis-8-acetoxy quinoline (**1**): A mixture of 8-hydroxyquinoline (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 onto ice water (100 mL) and stirred overnight. The brown solid obtained was filtered off, washed thoroughly with water, and dried to afford compound **1**. A purified sample (3.7 g, 82%) was obtained as a yellow solid by recrystallization from DMF. Mp 252–254°C. ¹H NMR (CDCl₃), δ [ppm] 2.59 (s, 6H, CH₃COO); 7.40 (d, 2H, *J*=16.4 Hz, *trans*-olefinic); 7.43–7.51 (m, 4H, aromatic); 7.66–7.72 (m, 10H, 8H quinolinol ring except 4-position as well as 2H olefinic); 8.16 (d, 2H, 4-position at quinolinol ring). Anal. Calcd for C₂₂H₁₈N₂O₄: C, 76.80; H, 4.80; N, 5.60. Found: C, 76.93; H, 5.01; N, 5.54.
- 2,2'-(2,5-Dimethoxy-1,4-phenylenedivinylene)bis-8-acetoxy quinoline (**2**): This compound was prepared by the same procedure: yield 53%; mp 240–242°C. ¹H NMR (CDCl₃) δ [ppm] 2.60 (s, 6H, CH₃COO); 3.99 (s, 6H, CH₃O); 7.29 (s, 2H, Ar-H); 7.39 (d, 2H, *J*=16.0 Hz, olefinic); 7.43–7.50 (m, 4H, 6, 7-position at quinoline ring); 7.70 (d, 2H, *J*=6.8 Hz, 5-position at quinoline ring); 7.77 (d, 2H, *J*=8.8 Hz, 3-position at quinoline ring); 8.12 (d, 2H, *J*=16.0 Hz, olefinic); 8.15 (d, 2H, *J*=8.4 Hz, 4-position at quinoline ring). Anal. Calcd for C₂₆H₂₂N₂O₆: C, 76.12; H, 5.22; N, 5.22. Found: C, 76.83; H, 5.01; N, 5.38.
- Crystal data for compound **1**: C₂₂H₁₈N₂O₄, *M*=500.53, monoclinic, space group *P*2₁/*c*, *a*=6.0900(12), *b*=14.867(3), *c*=13.880(3), β=94.09(3), *V*=1253.5(4) Å³, *Z*=2, *D*_c=1.326 g cm⁻³, μ=0.88 cm⁻¹, 3183 reflections measured, no. of unique reflections=2178 (*R*_{int}=0.0178), no. of parameters=173, *R*₁=0.0409 and ω*R*₂=0.0694 with *I*>2σ(*I*). The diffraction data was collected on a Siemens P4 single-crystal diffractometer over a 2θ range of 2.01–25.01° with graphite-monochromated Mo Kα radiation. The structure was solved with the direct method of SHELXS 86¹¹ and refined with full-matrix least-squares techniques using the SHELXL 93 program.¹² Non-hydrogen atoms were refined anisotropically. The crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication num-

ber CCDC 170715. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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