

Organic light emitting diodes based on end-substituted oligo(phenylenevinylene)s

Tao, Y.; Donat-Bouillud, A.; D'Iorio, M.; Lam, J.; Gorjanc, T. C.; Py, C.; Wong, M. S.; Li, Z. H.

Published in:
Thin Solid Films

DOI:
[10.1016/S0040-6090\(99\)01019-6](https://doi.org/10.1016/S0040-6090(99)01019-6)

Published: 01/03/2000

Document Version:
Peer reviewed version

[Link to publication](#)

Citation for published version (APA):

Tao, Y., Donat-Bouillud, A., D'Iorio, M., Lam, J., Gorjanc, T. C., Py, C., Wong, M. S., & Li, Z. H. (2000). Organic light emitting diodes based on end-substituted oligo(phenylenevinylene)s. *Thin Solid Films*, 363(1), 298-301. [https://doi.org/10.1016/S0040-6090\(99\)01019-6](https://doi.org/10.1016/S0040-6090(99)01019-6)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent publication URLs

Organic light emitting diodes based on end-substituted oligo(phenylenevinylene)s

Ye Tao, Anne Donat-Bouillud, M D'Iorio, Jennifer Lam[†], Timothy C. Gorjanc[†], and Christophe Py

Institute for Microstructural Sciences, National Research Council of Canada,

M-50 Montreal Road, Ottawa, Ontario, Canada, K1A 0R6

Man Shing Wong, Zhong Hui Li

Department of Chemistry, Hong Kong Baptist University,

Kowloon Tong, Kowloon, Hong Kong

Abstract

We report our investigation of the electroluminescent properties of multilayer organic light emitting devices using a series of three-phenyl-ring oligo(phenylenevinylene)s with poly(alkyleneoxy) electron-donors and hexylsulfonyl electron-acceptors as emitting materials. The emission color varies from blue to green depending on the substituted end-groups in the molecules. The insertion of hole blocking and electron injecting layers significantly improves the electroluminescent efficiency and extended the operational life time. The maximum electroluminescence efficiency reached is 1.9 cd/A for the blue diodes, and 2.3 cd/A for the blue-green diodes.

Introduction:

Poly(phenylenevinylene) (PPV) and its derivatives has been the material of choice for polymer light emitting diodes¹ (PLEDs). Many researchers are working on the modification of PPV's electronic and mechanical properties by introducing substituents in the molecular structure. For example, substitution on the phenyl ring of PPV with two alkoxy groups can reduce the PPV energy gap by nearly half an electron volt², while providing greater solubility and better film-forming properties. Over the past few years, various soluble PPV derivatives and copolymers have been synthesized in an attempt to tune the electronic and emissive properties and to enhance the solubility and processibility of these materials^{3,4}.

Understanding how the different functional groups in PPV affect its physical properties is a critical step towards rational modification of the material. However, a broad molecular weight distribution, and the presence of blocks with different conjugation length in the polymeric material can complicate the investigation. Therefore, oligomers of PPV are of particular great interest. Their well-defined chemical structure together with their improved solubility and processibility allow access to detailed interpretation of experimental measurements while providing insight into the physical properties of the related polymers. It is well known that in oligo(phenylenevinylene)s (OPVs), the shorter conjugated segment improves the fluorescence yields and the electroluminescence efficiency, and that the wavelength for absorption and emission decreases with decreasing conjugated length. This is especially useful in the search for blue light emitting materials. For these reasons, different types of OPVs have been synthesized and their absorption, luminance and electronic properties⁵⁻⁷ have been investigated. In addition, many oligomer materials can be thermally sublimed under vacuum, allowing for the preparation of multilayer OLED structures and devices in an ultra clean and well controlled environment thus overcoming the uncertainties involved in wet processes.

Recently, Wong et al⁸ have synthesized a series of highly soluble three-phenyl-ring (distyrylbenzenes) bearing poly(alkyleneoxy) electron-donor(s) and/or hexylsulfonyl electron-acceptor(s) as end-groups. Unlike the lateral substitution, substituents attached at the ends of a molecule do not generally disrupt the co-planarity of the π -conjugated system. The effects of end-substitution on absorption spectroscopic properties, third-order nonlinear optical properties and thermal behavior have been discussed by Wong et al⁸. In this work, we investigate the effect of end-substitution on the electroluminescent properties of these three-phenyl-ring oligo(phenylenevinylene)s (OPV(1)s), and explore the possible application of these OPVs in OLEDs as emitting materials.

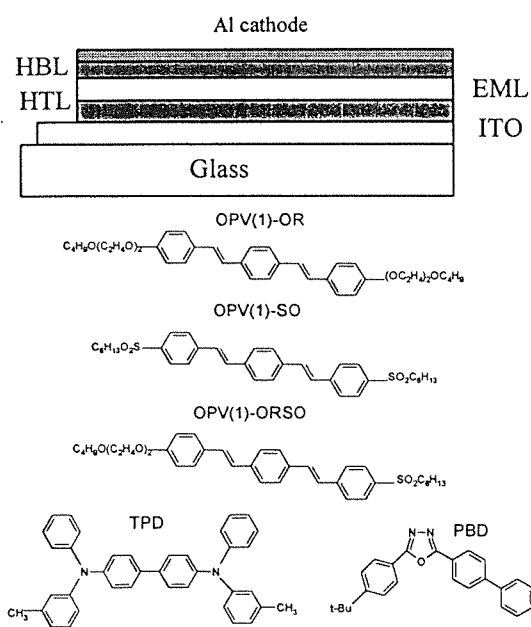


Figure 1 A typical device structure used in this work and the molecular structure of OPV(1)-OR, OPV(1)-SO, OPV(1)-ORSO, TPD and PBD. D and A represent donor and acceptor respectively.

Experimental details

Figure 1 shows the molecular structure of the OPV(1)s, N,N' -diphenyl- N,N' -bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine (TPD) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) along with a typical device structure used in this study. In these oligomers, the backbones are kept the same, but the end groups are substituted systematically. The difference in electronic properties of the substituents attached to the conjugated backbone will shift the highest occupied molecular orbital or HOMO level, the lowest unoccupied molecular orbital or LUMO level and the energy gap of the

OPV(1)s, leading to different absorption and emission behavior. The PM3 semi-empirical quantum mechanical calculations show that the ground state optimized molecular geometry of the three OPV(1)s possesses a good co-planarity of the π -conjugated system. The selection of long chain substituents in our materials is meant to enhance solubility during synthesis and purification as well as to prevent crystallization.

The organic light emitting diodes were prepared on commercial ITO coated glass substrates (Applied Films Corp.) with sheet resistance of $12 \Omega/\square$, and an ITO thickness of ~ 120 nm. Before lithographic patterning, the ITO substrates were cleaned using cleanroom soap, acetone, and isopropanol. The anodes were formed by etching the patterned ITO substrates in a solution of HCl:HNO₃:H₂O (25:2:25). The patterned ITO substrates were treated in a UV ozone oven for ten minutes before loading into the vacuum chamber. The device structures consisted of 50 nm TPD as a hole transport layer (HTL), 50 nm OPV(1) as an emissive layer (EML), 20 nm PBD or 2 nm LiF as the hole blocking layer (HBL), and thermally evaporated aluminum and silver layer as a cathode. The thermal evaporation was carried out in an Edwards Auto 306 coater equipped with a cryo-pump, using either tungsten or molybdenum boats. All depositions were performed at high vacuum (2×10^{-7} torr). A typical growth rate of 2 \AA/s was used and the substrates were all held at room temperature. The active device area is $1.0 \times 5.0 \text{ mm}^2$. The devices were operated and characterized in air. The EL spectra and luminance were measured by using a Photo Research®-650 SpectraColorimeter, and the current-voltage (I-V) characteristics were measured with a Keithley 236 source measure unit.

Results and Discussion

The results of UV-vis absorption, photoluminescence, and cyclic voltammeter measurements of the OPV(1)s used in this work are summarized in Table 1. The symmetrically substituted OPV(1)–

Table 1 The optical and electrical properties of the OPV(1)s

	(0-0 phonon) abs. peak (eV) (in CHCl ₃)	abs. max. (eV) (in CHCl ₃)	(0-0 phonon) PL (eV) (in CHCl ₃)	PL max. (eV) (in CHCl ₃)	PL max. (eV) (thin film)	abs.edge (eV) (in CHCl ₃)	IP (eV)
OPV(1)	3.18	3.38	3.04	2.88	2.57	3.07	5.47
-OR OPV(1)	3.18	3.38	3.04	2.88	2.49	3.07	n/a
-SO OPV(1)	n/a	3.26	n/a	2.60	2.41	2.70	5.52
-ORSO							

OR (acceptor groups at two ends) and OPV(1)-SO (donor groups at two ends), show no difference in their UV absorption properties. The 0-0 phonon absorption peaks at 390 nm (3.18 eV) and the absorption maxima at 367 nm (3.38 eV) are red shifted by ~ 0.11 eV as compared to the unsubstituted OPV(1)⁵. Such a red shift is consistent with the fact that the donating and withdrawing substituents at the para- position of distyrylbenzene enhance the π -electron delocalization along the entire unsaturated system. The asymmetrically substituted OPV(1)-ORSO shows a significant shift towards longer wavelengths, and its vibronic features are not clearly visible. The OPV(1)-ORSO is an asymmetrically (donor-acceptor) substituted conjugated system, and the excitation is generally dominated by the intra-molecular charge-transfer excitation which gives a strong and intense absorption in the UV-vis spectrum. It is usually featureless and rather symmetrical. Its red-shift can be explained by the interaction between the donor (OR) and the acceptor (SO) groups at the extremities of the molecules, a so-called push-pull effect, which effectively enhances π -electron delocalization asymmetrically.

The PL spectra of OPV(1)-OR and OPV(1)-SO are also very similar. The 0-0 phonon emission peaks are at 408 nm (3.04 eV) while the PL maxima are at 431 nm (2.88 eV). The PL emission of OPV(1)-ORSO exhibits a larger red-shift with the PL maximum at 478 nm (2.60 eV). The PL spectra of OPV(1)-OR and OPV(1)-SO thin films show a larger red-shift compared to their spectra in solution, which is usually the case for solution and solid state spectra. The PL emission maxima

of OPV(1)-OR, OPV(1)-SO and OPV(1)-ORSO are at 483 nm (2.57 eV), 489 nm (2.49 eV), and 514 nm (2.41 eV) respectively.

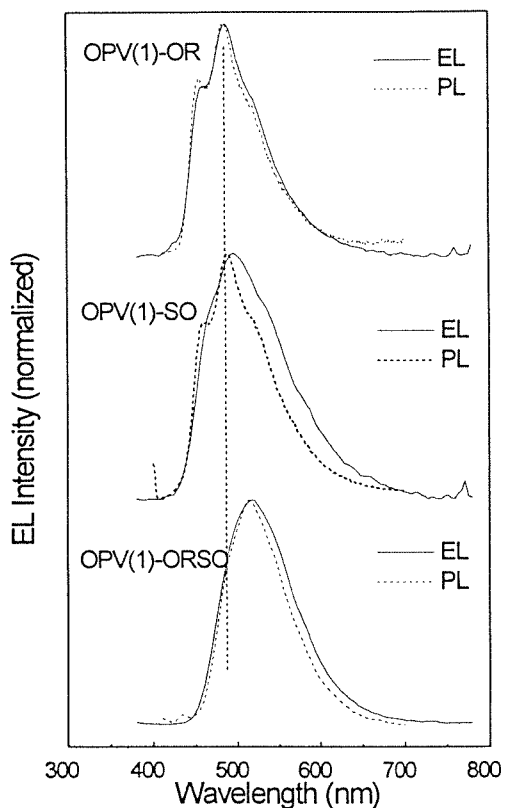


Figure 2 The EL spectra measured in OLEDs using OPV(1) as emitting materials. The dashed spectra are the corresponding PL spectra from the same material.

but it is broadened in the high-wavelength tail. The reason for this broadening is not clear, but one possible explanation is a molecular packing effect, which leads to a red shift. The EL maxima of OPV(1)-SO and OPV(1)-ORSO are at 496 nm (2.50 eV), with a FWHM of 100 nm and 520 nm (2.38 eV), with a FWHM of 100 nm respectively. The EL spectrum of OPV(1)-ORSO is very similar to the PL spectrum, indicating the emission is from the OPV(1)-ORSO. The shapes of the EL emission spectra of OPV(1)s based OLEDs are independent of the applied voltages in the measured range (5-25 V). This result excludes the possibility of exciplex formation at the

The EL emission spectra were measured in OLEDs using OPV(1)s as emitting materials in the structure described in Figure 1. All devices showed rectifying behavior in their current-voltage characteristics. The turn-on voltages for these devices vary between 5 and 10 V, and the luminance is $\sim 8 \text{ cd/m}^2$ at 12 volts. The EL spectra are shown in Figure 2 in comparison with the corresponding PL spectra. The EL spectrum of OPV(1)-OR is nearly identical to its thin film PL spectrum, indicating that the EL emission originates from the OPV(1)-OR. Its maximum is at 486 nm (2.55 eV), and the full width at half maximum (FWHM) is 90 nm. The EL spectrum of OPV(1)-SO is identical to the thin film PL spectrum at low wavelength,

HTL/EML or EML/HBL interface regions, since the intensity of exciplex emission is usually voltage dependent.

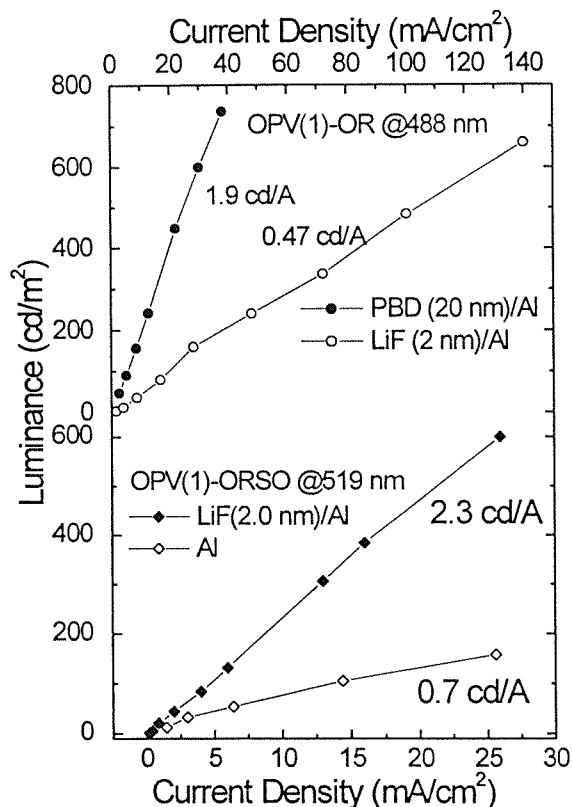


Figure 3 Electroluminescence efficiency of OPV(1)-OR based devices, and OPV(1)-ORSO based devices.

increase the efficiency and device life time. In the OPV(1)-OR based devices, the insertion of a LiF layer (2 nm) increased the EL efficiency from 0.2 cd/A to 0.47 cd/A, and the insertion of a PBD layer (20 nm) further increased the efficiency to 1.9 cd/A (Figure 3). For the OPV(1)-ORSO based devices, the insertion of a 2 nm LiF layer increased the EL efficiency from 0.7 cd/A to 2.3 cd/A (Figure 3). A thin PBD layer in OLEDs is generally recognized as a hole-blocking layer, while LiF can enhance electron injection if applied at the cathode side. We believe that, like most organic semiconductors, OPV(1)-OR and OPV(1)-ORSO conduct holes much better than electrons, and that the hole injection barrier is much lower than the electron injection barrier, as is usually the case in

We found that the OLEDs made from OPV(1)-OR and OPV(1)-ORSO were much more stable than the one made from OPV(1)-SO with the TPD/OPV(1) configuration. This might be related to the possible formation of aggregates in the OPV(1)-SO layer. The performance of OPV(1)s based OLEDs depends heavily on the multilayer structures used. Devices with double layer structure (ITO/TPD/OPV(1)s/ Al/Ag) had very short life time (< 30min.), and the EL efficiency was very poor. The application of a PBD or LiF layer between the OPV(1)s and aluminum cathode is necessary in order to

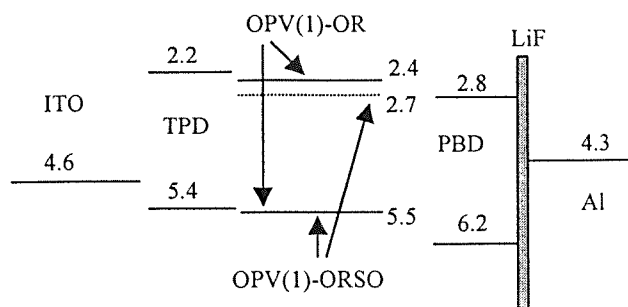


Figure 4 Ideal energy-levels for OPV(1)-OR and OPV(1)-ORSO devices with PBD or LiF as hole blocking layers. All levels are referenced to vacuum.

blue and blue-green OLEDs, especially when aluminum is used as cathode material (Figure 4). In these devices, the majority of charge carriers are holes. By directly reaching the cathode, they make up a large portion of the electric current passing through the device but without contributing to the EL. The insertion of a

LiF layer between the OPV(1)-OR layer (or OPV(1)-ORSO) and the Al cathode effectively enhances the electron injection⁹ while preventing holes from reaching the cathode. In the case of OPV(1)-OR, the insertion of a PBD layer is more effective than the LiF layer, as the PBD layer is thicker than the LiF. The device efficiency of OPV(1)s based OLEDs is appropriate for applications. However, the life time of OPV(1)-OR and OPV(1)-ORSO devices is so far very limited. Depending on the addition of a silver layer on top of the aluminum cathode, the device life time in air varies between 30 to 100 min. when driven at an initial brightness of 50 cd/m² at constant current. We believe that the device lifetime can be greatly improved if proper physical encapsulation is used.

In conclusion, we have demonstrated that end-substitution can fine tune the electronic and emission properties of oligo(phenylenevinylene)s. The end-substituted OPV(1)s can be effectively used as emitting materials in organic light emitting devices. While no efforts were made to optimize the device structure with respect to the layer thickness, blue electroluminescence with a brightness of 700 cd/m² at an efficiency of 1.9 cd/A, and blue-green electroluminescence with a brightness of 600 cd/m² at an efficiency of 2.3 cd/A were observed. The key steps to increase the electroluminescence efficiency and extend the lifetime of these devices are to enhance the electron

injection efficiency, reduce the hole concentration, and encapsulate the device in vacuum or inert atmosphere.

Acknowledgements

We would like to thank Dan Roth of National Research Council of Canada for his technical support. The work of M. S. W. was partly supported by the FRG (FRG/98-99/II-09) from HKBU. The support of a NSERC operating grant is gratefully acknowledged (J.L. and T.C.G.).

[†] Permanent address: Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

References

- 1 J. Burroughs, D. D. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990).
- 2 P. L. Burn, A. Kraft, D. R. Baigent, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, A. B. Holmes, and R. W. Jackson, *J. Am. Chem. Soc.* **115**, 10117 (1993).
- 3 R. M. Gurge, A. Sarker, P. M. Lahti, B. Hu, and F. E. Karasz, *Macromolecules* **29**, 4287 (1996).
- 4 R. M. Gurge, A. M. Sarker, P. M. Lahti, B. Hu, and F. E. Karasz, *Macromolecules* **30**, 8286 (1997).
- 5 S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama, G. Katzer, and W. Fabian, *J. Chem. Soc. Perkin Trans. 2*, 861 (1991).
- 6 N. N. Barashkov, D. J. Guerrero, H. J. Olivos, and J. P. Ferraris, *Synth. Met.* **75**, 153 (1995).
- 7 A. Schmidt, M. L. Anderson, D. Dunphy, T. Wehrmeister, K. Muellen, and N. R. Armstrong, *Adv. Mater.* **7**, 722 (1995).
- 8 M. S. Wong, M. Samoc, A. Samoc, B. Luther-davies, and M. G. Humphrey, *J. Mater. Chem* **8**, 2005 (1998).
- 9 L. S. Hung, C. W. Tang, and M. G. Mason, *Applied Physics Letters* **70**, 152 (1997).