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Synthesis, structure–properties of planar, end-substituted, light-emitting oligophenylenevinylenes

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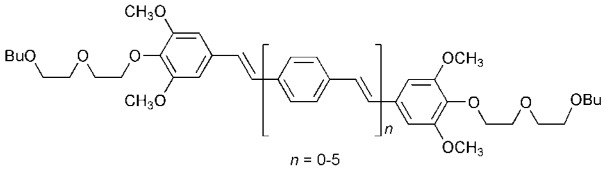
A novel homologous series of highly soluble, multiple alkoxy end-substituted oligophenylenevinylenes (OPV) containing up to six phenyl rings were synthesized. In contrast to the lateral substituted OPVs, our theoretical and experimental evidences have shown that the electron donating groups incorporated at the ends of an oligomer do not affect co-planarity of the π-conjugated system. They can also promote a faster convergence of the HOMO–LUMO energy gap relative to those of unsubstituted OPVs suggesting a shorter effective conjugation length in this series. These end-substituted OPVs containing more than three phenyl-rings exhibit very high fluorescence quantum yields (more than 74%). Multi-layer LEDs using these end-substituted OPVs as emissive layers were fabricated and investigated. We have found that there is a bathochromic shift of the PL and EL maxima with an increase of chain length in this series. All these oligomer-based multi-layer LEDs show very low turn-on-voltage. In addition, the higher homologues of these oligomers suffered from severe interchain interaction leading to a dramatic decrease in the external quantum efficiency; however, this can be alleviated by doping the oligomer into the host matrix.

Investigation of well-defined π-conjugated oligomers is of considerable interest since it can provide an insight into the structural and electronic properties of the related polymeric materials.[1,2] In addition, the ease of obtaining oligomers of high purity and fabricating oligomers into a thin-film offers advantages for using functionalized oligomer as an active component for device applications such as light emitting diodes,[3,4] light modulators[5] and field-effect transistors.[6,7] It is well known that an effective (optimal) conjugation length in π-conjugated polymers exists that is responsible for the ultimate optical and electronic properties of a polymer.[8] However, the subtle modification of the monomeric unit can often lead to a dramatic change in the physical properties of a polymer such as an energy gap or a fluorescent efficiency. As a result, knowledge of the structure–property relationship will certainly be important and useful for the exploration and development of "better" molecular based materials. The promise of efficient light emitting properties of polyphenylenevinylene (PPV) and its derivatives[9] has increasingly drawn attention on its oligomer, oligo-phenylenevinylenes (OPV) which has become one of the widely investigated π-conjugated oligomers over the last few years.[1,10] Because of the planarity and rigidity of the phenylenevinylene unit which are responsible for its unique functional properties, the higher homologues of OPVs are highly insoluble.[11] This often limits further investigations and potential applications. One of the common approaches to enhance the solubility and processability of π-conjugated oligomers and polymers is to introduce substituents (*i.e.* alkyl or alkoxy groups) on the lateral sides of the π-conjugated main chain. However, this often leads to a distortion of the co-planarity of the π-conjugated backbone[12] due to the steric hindrance as well as a change in inter-chain packing mode (or interaction) and hence affecting favourable physical properties such as spectral shift, quantum efficiency of fluorescence[13] and turn-on voltage in light emitting diodes (LED).[14] As a result, it may be of interest to conserve the integrity of the co-planarity of the phenylenevinylene π-conjugated backbone but only a few OPV derivatives have been developed towards this direction.

Wong *et al.*[15] have recently shown that solublizing substituents such as polyalkyleneoxy and alkylsulfonyl groups incorporated at the ends of the π-conjugated skeleton of distyrylstilbene can improve solubility without disrupting the co-planarity of the π-conjugation backbone. Our attempt to prepare longer 4,4′-disubstituted OPVs was again hampered by their insolubility. Although side-substituted OPVs containing up to 11 phenyl-rings were recently synthesized, their π-conjugation backbones are again twisted out of co-planarity.[10] On the other hand, substituents incorporated at the end of the conjugated position of the main chain *i.e.* 4,4′-positions can shift the HOMO and/or LUMO level by electronic effects and thus alter the HOMO–LUMO energy gap of an oligomer. This provides a means to tune the energy gap leading to a change in optical and electronic properties of an oligomer.[16] To further enhance the solubilities of higher homologous OPVs, a multiple end-substitution approach could be used. We herein report the synthesis and optical properties of a novel homologous series of highly soluble, symmetrically multi-alkoxy substituted OPVs containing up to six phenyl rings which were shown to have co-planar π-conjugation backbones. The ground and excited state molecular properties



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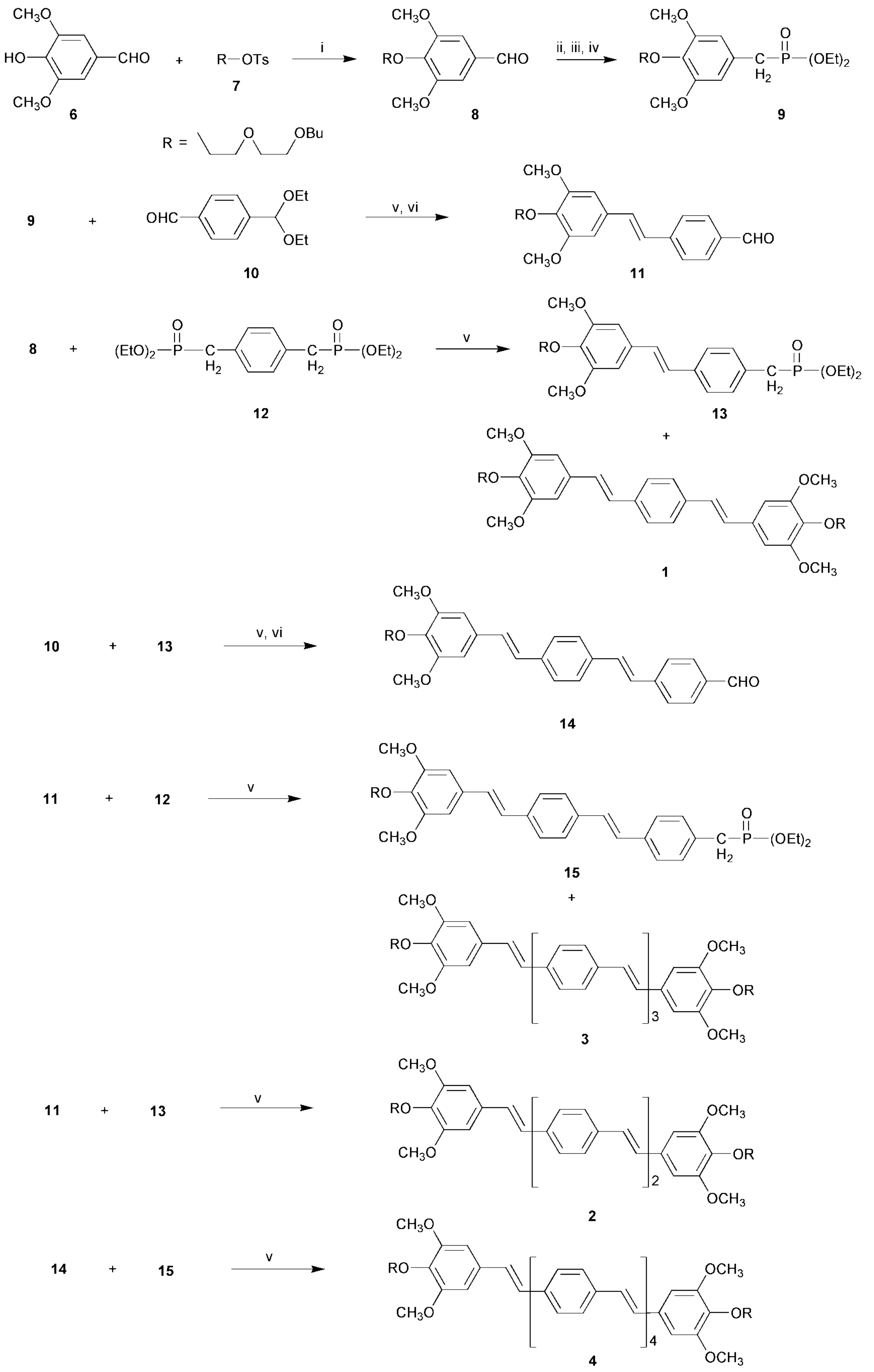

Scheme 1 *Reagents and conditions*: i, Na_2CO, KI, DMF, 60–70 °C; ii, LAH, THF, 0 °C, then HCl; iii, $SOCl_2$, Py, 0 °C; iv, $P(OEt)_3$, 150 °C; v, NaH, DME, room temp.; vi, HCl, acetone.

of the end-substituted OPVs were investigated by PM3 semi-empirical quantum mechanical calculations to understand and correlate the structure–optical properties of the oligomers. In addition, multi-layer LEDs using these end-substituted OPVs as emissive layers were fabricated by vacuum deposition technique and their photoluminescent and electroluminescent properties were investigated.

Results and discussion

The stereoselective Wadsworth–Emmons reaction was used as a key step to synthesize the all *trans* carbon–carbon double bonds of an OPV. The general synthetic sequences are outlined in Scheme 1. In general, the odd-phenyl-ring oligomers (*e.g.* five-phenyl-ring oligomer, **3**) were prepared by the double Wadsworth–Emmons reactions of bis-phosphonate **12** and the corresponding aldehyde (i.e. **11**). The even-phenyl-ring oligomers were synthesized by a convergent $n+n$ approach (*i.e.* $3+3$ for six-phenyl-ring oligomer, **4**). The starting precursors were prepared as follows. The tri-alkoxy substituted benzaldehyde **8** was synthesized by the Williamson ether reaction of 3,5-dimethoxy-4-hydroxybenzaldehyde **6** and 2-(2-butoxyethoxy)-ethyl tosylate 7 in the presence of Na_2CO_3. Phosphonate **9** was prepared according to the following reaction sequence: firstly reduction of **8** by $LiAlH_4$, subsequent transformation of the alcohol into the corresponding benzyl chloride by means of $SOCl_2$ and finally reaction with neat $P(OEt)_3$. The Wadsworth-Emmons reaction of phosphonate **9** and terephthalaldehyde mono(diethyl acetal) **10**, followed by an acid work up, afforded the corresponding styrylbenzaldehyde **11**. Dropwise addition of tri-alkoxy substituted benzaldehyde **8** over excess of bis-phosphonate **12** and NaH in high dilution afforded mono-phosphonate **13** in good yields (62%) relative to three-phenyl-ring oligomer **1** (20%) which is significantly improved over the previous procedure.[15] In a similar fashion, the higher homologous precursors, such as three-phenyl-ring aldehyde **14** was prepared by the Wadsworth–Emmons reaction of mono-phosphonate **13** and aldehyde **10** while three-phenyl-ring phosphonate **15** was prepared from the reaction of **11** and **12**. The seven-phenyl-ring oligomer, **5**, was also synthesized accordingly; however, its solubility is rather poor.

The ground state molecular geometries of 4,4′-dimethoxy- and 3,3′,4,4′,5,5′-hexamethoxy-substituted OPVs were optimized by PM3 semi-empirical methods. The results indicate that the (multiple) end substitution does not disrupt the coplanarity of the π-conjugated backbone of oligomers in the PM3-optimized geometry. It was also found from the calculations that the frontier molecular orbitals of 4,4′-dimethoxy-substituted OPVs are destabilized by the methoxy donating groups as compared to those of the unsubstituted counterparts. However, the unsymmetric destabilization results in the overall decrease in the HOMO–LUMO energy gap (Fig. 1a) in which the HOMO level destabilizes more than the LUMO level. A similar destabilization trend has been theoretically shown in the PPV pentamer side-substituted with methoxy groups.[17] In addition, the destabilization effect diminishes with an increase in the conjugation length. It is important to note that the methoxy donating groups reduce the energy gaps of 4,4′-dimethoxy-substituted OPVs approaching a limit of convergence faster than those of unsubstituted OPVs (Fig. 1a) which suggests a shorter effective conjugation length for the energy gap in this series.

In the electronic absorption spectra, the homologous series of end-substituted oligomers consistently shows vibronic fine structure indicating planarity and restricted rotation of the π-conjugated backbone of OPVs (Fig. 2a). There is a sequential increase in the absorption maxima of the end-substituted OPVs with a concomitant increase in extinction coefficient (ε) as the conjugation length increases (Table 1). The red shifts are towards longer wavelengths relative to those of the corresponding unsubstituted[18] and non-conjugated *meta-tert*-butyl-substituted OPVs[11] before levelling off (Fig. 1a). However, when compared with those of the corresponding OPVs side-substituted with propoxy groups, the red shifts are smaller.[10]

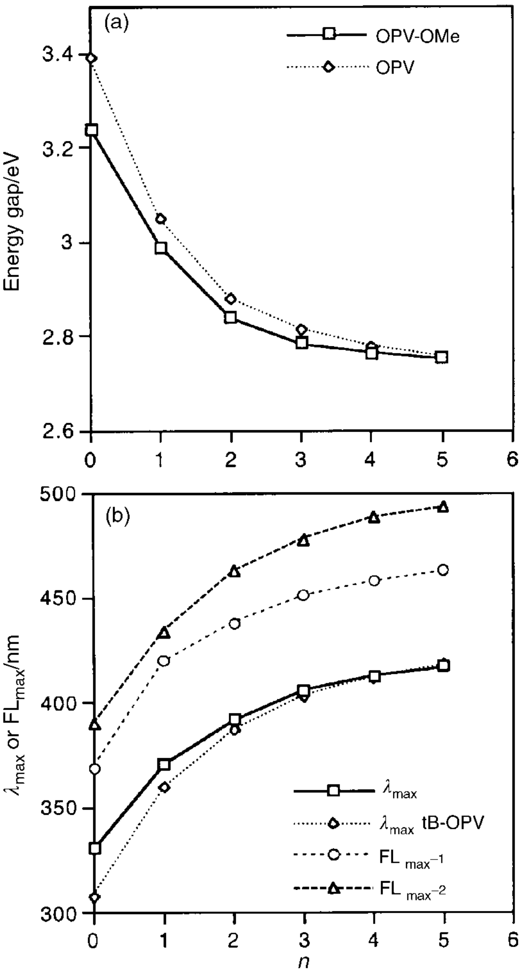

Fig. 1 **a** Plots of PM3 calculated HOMO–LUMO energy gap of unsubstituted OPVs (**OPV**) and 4,4′-dimethoxy substituted OPVs (**OPV(*n*)-OMe**) with correction of solvent interaction against number of phenylenevinylene units (*n*). **b** Plots of absorption and emission maxima of tri-alkoxy substituted OPVs, $n=0$–5, and absorption maxima of *tert*-butyl substituted OPVs (**tB-OPV**) (from ref 11) against number of phenylenevinylene units (*n*).

The solvatochromic effect for this series is rather small ($\delta\lambda_{max}=9$ nm from hexane to DMSO for **1**). Consistent with the theoretical findings shown above, the alkoxy donating groups incorporated at the ends of the main chain promote a faster convergence of the absorption maxima (or energy gap). In contrast, the propoxy groups incorporated on the lateral sides of the π-conjugated main chain slow down the convergence of the absorption maxima.[10] The faster convergence of absorption maxima induced by end-substituted donating groups has also recently been observed in oligothienylenevinylenes.[19]

As found from the fluorescence spectra of the end-substituted OPVs the emission bands are apparently composed of two major emissions. (Fig. 2b) Similar to the absorption behaviour, the emission bands sequentially shift to longer wavelengths with an extension of the conjugation length (Table 1); however, the emission cut-offs remain relatively constant throughout the series. Although the two emission peaks undergo a red shift to a different extent, the corresponding peak maxima also exhibit a tendency of saturation as the conjugation length increases (Fig. 1b). Importantly, there is a dramatic increase in the fluorescence quantum yield moving from two-phenyl-ring oligomer to three-phenyl-ring oligomer **1** (Table 1); however, further addition of the phenylenevinylene unit does not lead to further substantial improvements. On the whole, these end-substituted OPVs

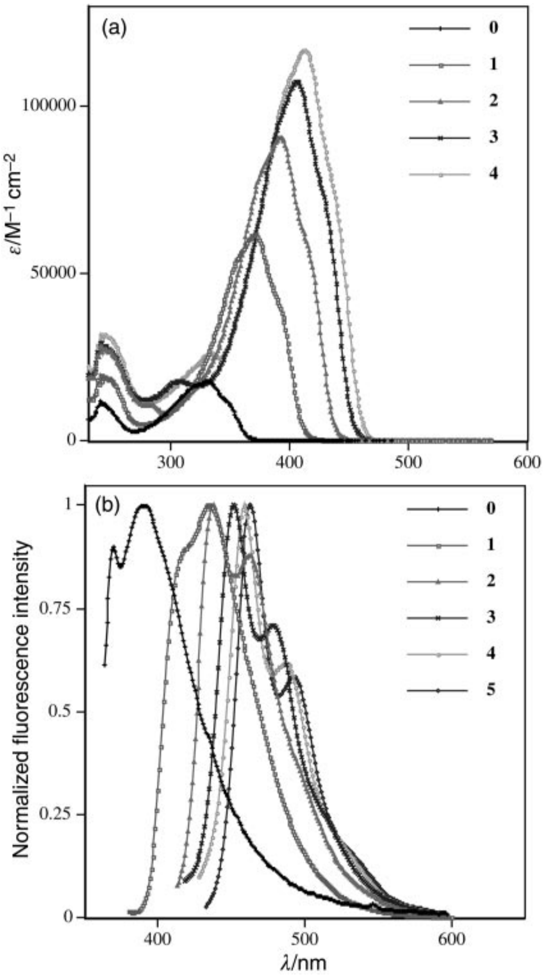

Fig. 2 **a** Absorption spectra of tri-alkoxy substituted OPVs, $n=0$–4, measured in $CHCl_3$. **b** Emission spectra of tri-alkoxy substituted OPVs, $n=0$–5, measured in $CHCl_3$.

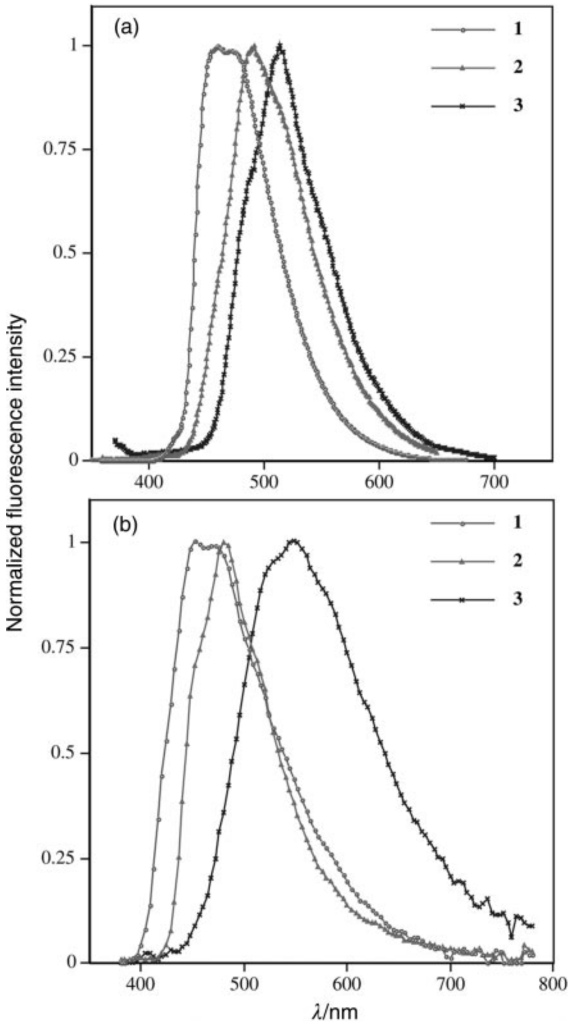

Fig. 3 **a** Photoluminescence spectra of tri-alkoxy substituted OPVs, $n=1$–3. **b** Electroluminescence spectra of tri-alkoxy substituted OPVs, $n=1$–3.

containing more than three phenyl-rings exhibit very high fluorescence quantum yields (more than 74%) suggesting that they may be potential candidates for light emitting applications. Such a high fluorescence quantum yield in this series is likely due to the co-planarity of the π-conjugated system.

The thermal gravimetric analysis indicated that this series of oligomers shows good thermal stability with decomposition temperature in the range of 250–370 °C (Table 1). This suggests that thin-films of these oligomers can be prepared by vacuum evaporation. To avoid the uncertainties involved in wet processes, a vacuum deposition technique which can provide an ultra clean and well controlled environment was employed for the preparation of multi-layer LEDs. Multi-layer LEDs using this series of oligomers as an emissive layer with a structure of (ITO/TPD (40 nm)/OPV (40 nm)/PBD (15 nm)/LiF (1 nm)/Al (150 nm)) were fabricated. The photoluminescence (PL) and electroluminescence (EL) spectra were shown in Fig. 3. In general, the spectral features of the EL are very similar to those of the solid-state PL of the corresponding oligomer suggesting that both emissions arise from the same oligomers. In addition, the EL spectral characteristics of all these devices are voltage independent which excludes the formation of the exciplex at the interfaces. However, EL spectra exhibit various extents of peak broadening and shift relative to those of PL spectra as the chain length increases. The peak broadening may be due to a broad range of energy sites (emissive states) acting as traps and

Table 1 Summaries of physical measurements of tri-alkoxy-substituted OPVs, $n=0$–5 and results of PM3 semi-empirical calculations of 4,4′-dimethoxy substituted OPVs, **OPV(*n*)-OMe**

n	λ_{max}[a]/nm (ε_{max}/10^{-4} M^{-1} cm^{-1})	Emission band maxima[a]/nm	Fluorescence quantum yield[b]	Decomposition temperature [c]/°C	External quantum efficiency [d]/cd A^{-1}	Calcd HOMO[e]/eV	Calcd LUMO[e]/eV	Calcd energy gap/eV	Corrected calcd energy gap[f]/eV
0	331 (1.8)	369, 390	0.11	335		−8.25	−3.109	5.141	3.241
1	371 (6.2)	420, 434	0.78	317	0.31	−8.135	−3.246	4.889	2.989
2	392 (9.2)	438, 463	0.81	369	0.52	−8.092	−3.279	4.737	2.837
3	406 (10.7)	451, 478	0.78	250	0.15	−8.067	−3.384	4.683	2.783
4	413 (11.7)	458, 488	0.74	259		−8.061	−3.398	4.663	2.763
5	417	463, 493				−8.051	−3.4	4.651	2.751

[a]Measured in $CHCl_3$. [b]Determined by dilution method. [c]Determined by TGA. [d]Calculated from the measured luminance divided by the current density passing through the device. [e]Calculated by PM3 semi-empirical quantum mechanical calculations. [f]Corrected for solvent interaction by −1.9 eV (from ref. 22).

recombination centres for injected carriers[20] but the cause of the spectral shift is not known yet.

The methoxy substituents attached onto the non-conjugated *ortho*-positions of the end-capped phenyl rings have a pronounced effect on the solid-state luminescence properties. In addition to the difference in spectral features, the emission maxima of both EL and PL are significantly blue-shifted (~20 nm) in the three-phenyl-ring oligomer, **1**, when compared to that of the corresponding unsubstituted counterparts.[21] Our initial measurement showed that this LED emits blue light at 456 nm with 120 cd m^{-12} at a bias voltage of 7 V which shows potential for further development of blue LEDs.

There is a bathochromic shift of both PL and EL maxima with an extension of the chain length as the energy gap is lowered which is also consistent with the fluorescence behaviour in solution. In addition, all the devices showed clear rectifying behaviour in their current-voltage characteristics. The turn-on voltages of these oligomer-based multi-layer LEDs are all around 4–5 volts.

Based on the initial multilayer device structure mentioned above, the external quantum efficiencies derived from the measured luminance divided by the current density passing through the device were calculated and tabulated in Table 1. The external quantum efficiencies are expected to be enhanced with an increase of chain length; however, there is a dramatic decrease in the external quantum efficiency with a device based on **3** which is likely due to the severe interchain interaction in this longer homologue which is known to be detrimental to the device efficiency. One of the remedies to avoid aggregation is by means of doping an emissive dye into the host material. The external quantum efficiency of an OLED using co-evaporated *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine and **1** (TPD·**1**) as an emissive layer improved to 0.82 cd A^{-1} as compared to 0.31 cd A^{-1} using a single **1** emissive layer. The external efficiency could be increased to 1.3 cd A^{-1} using a composite emissive layer of **1** and LiF. Besides the aggregation improvement, this enhancement may be also due to the improvement of the charge transport properties in the composite layer. We have also observed fragmentation of higher homologues *i.e.* **4** during thermal evaporation and the LED obtained exhibit significant blue shift in the EL and PL and higher turn–on voltage which is likely due to the contribution of its fragments.

In summary, a novel homologous series of highly soluble, multiple alkoxy end-substituted oligophenylenevinylenes containing up to six phenyl rings were synthesized. We have shown that the multiple solubilizing groups substituted at the end of oligophenylenevinylenes can enhance solubility of higher homologues of oligomers but do not disrupt the co-planarity of the π-conjugation backbone. In addition, we have theoretically and experimentally shown that the electron donating groups substituted at the end of OPVs can lead to a faster approach to a limit of convergence and hence promote a shorter effective conjugation length relative to those of the unsubstituted and lateral substituted OPVs. The emission spectra also exhibit a similar tendency of saturation as the conjugation length increases. End-substituted OPVs containing more than three phenyl rings exhibit very high fluorescence quantum yields. Multi-layer LEDs using these end-substituted OPVs as emissive layers were fabricated by vacuum evaporation technique and were investigated. We have found that there is a bathochromic shift of the PL and EL maxima with an increase of chain length in the series. All these oligomer-based multi-layer LEDs show very low turn-on-voltage. Furthermore, there is an increase in the external quantum efficiency with an increase in chain length; however, the higher homologues of these oligomers suffered from severe interchain interaction leading to a dramatic decrease in the external quantum efficiency. Nevertheless, the interchain interaction can be alleviated by doping the oligomer into the host matrix.

Experimental

TPD represents *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine. PBD represents 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole. All the new compounds were fully characterized with standard spectroscopic techniques. All the physical measurements were performed in $CHCl_3$. ^{1}H NMR spectra were recorded using a JEOL JHM-EX270 FT NMR spectrometer and are referenced to the residual $CHCl_3$ 7.24 ppm. Electronic absorption (UV–vis) and fluorescence spectra were recorded using a Varian Cary 100 Scan Spectrophotometer and a PTI Luminescence Spectrophotometer respectively. The corrected energy gaps reported in the Table 1 were calculated by an addition of −1.9 eV for solvent interaction.[22] The fluorescence quantum yields in chloroform using 9,10-diphenylanthracene as a standard were determined by dilution method as described by Parker *et al.*[23] The quantum yields reported here are the average of two independent measurements. Thermal stabilities were determined by using Thermal Gravimetric Analyzer (DTA), Shimadzu TGA-40 with a heating rate of 10 °C min^{-1}. The semi-empirical calculations using the PM3 parameterization were carried out by MOPAC 6 in the Alchemy 2000 software package. The experimental details of the LEDs fabrication can be found in ref. 16 and 21. The general synthetic procedure for the Wadsworth–Emmons reaction can be found in ref. 15.

Improved procedure for the preparation of diethyl 4-[2-(2-butoxyethoxy)ethoxy]-3,5-dimethoxystyrylbenzylphosphonate 13

To a stirred solution of bisphosphonate **12** (6.92 g, 18.3 mmol) and 1.2 equivalent of NaH (0.88 g, 22 mmol) in 500 mL anhydrous DME at 0 °C was added dropwise a solution of trialkoxy-substituted benzaldehyde **8** (2 g, 6.1 mmol) over 1 h. After stirring for 0.5 h at 0 °C, the reaction mixture was slowly warmed up to rt. After stirring for 2 h at rt, the solution mixture was quenched with water. The crude product was either collected by suction filtration or extracted twice with CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was then purified by silica gel chromatography using the gradient elution technique with CH_2Cl_2–ethyl acetate as eluents affording 2.1 g (62%) of **13** and 0.88 g (20%) of **1**.

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.56 Hz, 2H), 7.26 (dd, *J* = 8.19 Hz, *J* = 2.16 Hz, 2H), 6.98 (s, 2H), 6.70 (s, 2H), 4.12 (t, *J* = 5.22 Hz, 2H), 3.99 (m, 4H), 3.82 (s, 12H), 3.84 (t, *J* = 4.98 Hz, 2H), 3.70 (m, 2H), 3.58 (m, 4H), 3.49 (t, *J* = 6.72 Hz, 2H), 3.14 (d, *J* = 21.87 Hz, 1H), 1.55 (m, 2H), 1.32 (m, 2H), 1.23 (t, *J* = 6.89 Hz, 6H), 0.89 (t, *J* = 7.29 Hz, 3H).

1,4-Bis-4-{[2-(2-butoxyethoxy)ethoxy]-3,5,-dimethoxy}styrylbenzene 1:. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42 (s, 4H), 6.99 (d, *J* = 16.2 Hz, 2H), 6.91 (d, *J* = 16.2 Hz, 2H), 6.66 (s, 4H), 4.10 (t, *J* = 4.86 Hz, 4H), 3.82 (s, 12H), 3.77 (t, *J* = 5.00 Hz, 4H), 3.64 (m, 4H), 3.54 (m, 4H), 3.40 (t, *J* = 6.75 Hz, 4H), 1.50 (m, 4H), 1.28 (m, 4H), 0.84 (t, *J* = 7.16 Hz, 6H). MS (FAB) *m*/*z* 722.6 (M^+). HRMS(FAB) $C_{42}H_{58}O_{10}Na$: calc. 745.3928 found 745.3918. Found: C, 69.78; H, 8.09. $C_{42}H_{58}O_{10}$ requires C, 69.72; H, 8.17%. Mp = 66 °C.

1,2-Bis(4-{4-[2-(2-butoxyethoxy)ethoxy]-3,5-dimethoxystyryl}phenyl)ethene 2. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (s, 8H), 7.05 (s, 2H), 6.99 (d, *J* = 16.2 Hz, 2H), 6.91 (d, *J* = 16.2 Hz, 2H), 6.66 (s, 4H), 4.10 (t, *J* = 5.25 Hz, 4H), 3.83 (s, 12H), 3.75 (t, *J* = 5.13 Hz, 4H), 3.64 (m, 4H), 3.53 (m, 4H), 3.40 (t, *J* = 6.675 Hz, 4H), 1.51 (m, 4H), 1.29 (m, 4H), 0.84 (t, *J* = 7.43 Hz, 6H). MS (FAB) *m*/*z* 824.6 (M^+). HRMS(FAB) $C_{50}H_{64}O_{10}$: calc. 824.4499 found 824.4513. Mp = 110 °C.

1,4-Bis(4-{4-[2-(2-butoxyethoxy)ethoxy]-3,5-dimethoxystyryl}styryl)benzene 3. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.44 (s, 12H), 7.06 (s, 4H), 7.00 (d, $J=16.2$ Hz, 2H), 6.92 (d, $J=16.47$ Hz, 2H), 6.67 (s, 4H), 4.10 (t, $J=5.13$ Hz, 4H), 3.83 (s, 12H), 3.75 (t, $J=5.13$ Hz, 4H), 3.65 (m, 4H), 3.53 (m, 4H), 3.40 (t, $J=6.62$ Hz, 4H), 1.51 (m, 4H), 1.28 (m, 4H), 0.84 (t, $J=7.29$ Hz, 6H). MS (FAB) *m*/*z* 926.7 (M^+). HRMS(FAB) $C_{58}H_{70}O_{10}$: calc. 926.4969 found 926.4989. Found: C, 74.86; H, 7.58. $C_{58}H_{70}O_{10}$ requires C, 75.13; H, 7.61%. Mp = 210 °C.

1,2-Bis[4-(4-{4-[2-(2-butoxyethoxy)ethoxy]-3,5-dimethoxystyryl}styryl)phenyl]ethene 4. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.51 (s, 8H), 7.45 (s, 8H), 7.10 (s, 6H), 7.05 (d, $J=16.2$ Hz, 2H), 6.98 (d, $J=16.47$ Hz, 2H), 6.72 (s, 4H), 4.16 (t, $J=5.27$ Hz, 4H), 3.89 (s, 12H), 3.83 (t, $J=5.40$ Hz, 4H), 3.72 (m, 4H), 3.61 (m, 4H), 3.46 (t, $J=6.62$ Hz, 4H), 1.53 (m, 4H), 1.34 (m, 4H), 0.90 (t, $J=7.16$ Hz, 6H). MS (FAB) *m*/*z* 1028.9 (M^+). Found: C, 76.68; H, 7.56. $C_{66}H_{76}O_{10}$ requires C, 77.01; H, 7.44%. Mp = 269 °C.

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References

1 K. Müllen and G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, 1998.

2 R. E. Martin and F. Diederich, *Angew. Chem. Int. Ed.*, 1999, **38**, 1350.

3 N. N. Barashkov, D. J. Guerrero, H. J. Olivos and J. P. Ferrais, *Synth. Met.*, 1995, **75**, 153.

4 J. Salbeck, N. Yu, J. Bauer, F. Weissörtel and H. Bestgen, *Synth. Met.*, 1997, **91**, 209.

5 D. Fichou, J.-M. Nunzi, F. Charra and N. Pfeffer, *Adv. Mater.*, 1994, **6**, 64.

6 H. E. Katz, *J. Mater. Chem.*, 1997, **7**, 369.

7 G. Horowitz, *Adv. Mater.*, 1998, **10**, 365.

8 H. Meier, U. Utalmach and H. Kolshorn, *Acta Polym.*, 1997, **48**, 379.

9 A. Kraft, A. C. Grimsadle and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.

10 U. Stalmach, H. Kolshom, I. Brehm and H. Meier, *Liebigs Ann.*, 1996, 1449.

11 J. Heinze, J. Mortensen, K. Muellen and R. Schenk, *J. Chem. Soc., Chem. Commun.*, 1987, 701.

12 R. E. Gill, A. Meetsma, P. F. van Hutten and G. Hadziioannou, *Chem. Mater.*, 1996, **8**, 1341.

13 M. G. Harrison and R. H. Friend in *Optical Applications*, ed. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998.

14 P. F. van Hutten, J. Wildeman, A. Meetsma and G. Hadziioannou, *J. Am. Chem. Soc.*, 1999, **121**, 5910.

15 M. S. Wong, M. Samoc, A. Samoc, B. Luther-Davies and M. G. Humphrey, *J. Mater. Chem.*, 1998, **8**, 2005.

16 Y. Tao, A. Donat-Bouillud, M. D'Iorio, J. Lam, T. C. Gorjanc, C. Py and M. S. Wong, *Synth. Met.*, 2000, **111–112**, 417.

17 J. Cornil, D. A. dos Santos, D. Beljonne and J. L. Brédas, *J. Phys. Chem.*, 1995, **99**, 5604.

18 H. Meier, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1399.

19 I. Jestin, P. Frére, E. Levillain and J. Roncali, *Adv. Mater.*, 1999, **11**, 134.

20 M. Fahlman, W. R. Salaneck, S. C. Moratti, A. B. Holmes and J. L. Brédas, *Chem. Eur. J.*, 1997, **3**, 286.

21 Y. Tao, A. Donat-Bouillud, M. D'Iorio, J. Lam, T. C. Gorjanc, C. Py, M. S. Wong and Z. H. Li, *Thin Solid Films*, 2000, **363**, 298.

22 U. Mitschke, E. M. Osteritz, T. Debaerdemaeher, M. Sokolowski and P. Baeuerle, *Chem. Eur. J.*, 1998, **4**, 2211.

23 C. A. Parker and W. T. Rees, *Analyst (London)*, 1960, **85**, 587.