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Synthesis, characteristics and luminescence properties of oligo(phenylenevinylene) dimers with a biphenyl linkage center†

Feng He,[a] Gang Cheng,[b] Haiquan Zhang,[a] Yan Zheng,[a] Zengqi Xie,[a] Bing Yang,[a] Yuguang Ma,*[a] Shiyong Liu[b] and Jiacong Shen[a]

[a] *Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130023, P.R. China. E-mail: ygma@jlu.edu.cn; Fax: +86-431-8980729; Tel: +86-431-8498981*

[b] *National Laboratory of Integrated Optoelectronics, Jilin University, Changchun, P.R. China*

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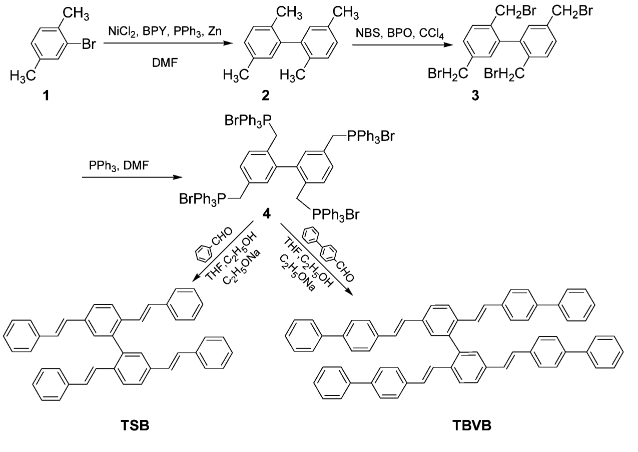
Building a new structual oligo(phenylenevinylene) by linking trimeric phenylenvinylene (TPV) through the phenyl–phenyl bond of a central phenylene ring was reported. The resultant TPV dimers exhibit weak intermolecular interactions and intense blue photoluminescence in the solid state as well as high phase transition temperatures up to 250 °C. Organic light-emitting devices (OLEDs) based on these materials display blue emission with low turn-on voltage (about 3 V), maximum luminance approaching 2000 cd m^{-2} and efficiency up to 1.6 cd A^{-1}.

π-Conjugated organic polymers have attracted considerable attention owing to their interesting properties as materials for charge transport, for non linear optics, for electronics and optoelectronics.[1] Particularly, they are attractive emissive materials for light emitting diodes (LEDs)[2] because they are easily processed and their optical properties can be easily tuned by chemical engineering. Oligomers as model compounds for the corresponding polymers and as active materials themselves have induced great interest. Since their conjugation length is defined and adjustable, the color of the emission is expected to be easily controlled. Typically, trimeric phenylenvinylene (TPV) and its derivatives are widely investigated,[3] which results in an increased understanding of the important conjugated polymer poly(phenylenvinylene) (PPV); while TPV is also a bright pure blue emitter. However, unfortunately, the excellent luminescent properties of TPV [*ca.* photoluminescence (PL) efficiency over 90%] are only obtained in dilute solution, but in the solid state TPV emits very weakly. This solid state fluorescence quenching behavior has been associated with the formation of intermolecular aggregates, especially the side-by-side arrangements known as H-aggregates.[4] This means that the stacking of TPV molecules plays a determining role in the physical properties of these materials. Much work has been done to prevent the aggregation of TPV, which aimed at achieving high-efficient emission in solid state and films.[5] This involves the introduction of a chemical substitutent in TPV,[6] tetrahedral linkage of four TPVs known as tetrakis(4-*tert*-butylstyrylstilbenyl)methane ($C(^tBuSSB)_4$)[7] and covalent assemblies of four TPVs arising from a calix[4]arene core.[8] $C(^tBuSSB)_4$ molecules have been used in the fabrication of devices,[9] however, the device performances were not as good as expected from the high PL efficiency in the solid state (42%), probably due to low carrier mobility induced by a central sp^3-hybridized carbon atom. In this communication we report the versatile synthesis of a new class of dimeric TPVs in which two TPVs are linked through the phenyl–phenyl bond of a central phenylene ring to form a crossing dimeric structure with ~70° twist between the plane of the two TPVs. The optical and electro-optical properties associated with such dimeric structures are also reported.

The syntheses of 2,5,2′,5′-tetrastyrylbiphenyl (**TSB**) and 2,5,2′,5′-tetrakis(4′-biphenylenevinyl)biphenyl (**TBVB**) are shown in Scheme 1. The key precursor 2,5,2′,5′-tetrakismethylbiphenyl (**2**) was obtained *via* a Yamamoto coupling reaction of 2-bromo-1,4-dimethylbenzene. The 2,5,2′,5′-tetrakisbromomethylbiphenyl (**3**) was then obtained by NBS bromination of **2** as crystals. Single crystal data of **3** showed a 71.8° torsion angle between the two conjoint phenyl rings.† The tetra(halomethyl) compound **3** was converted into the tetra(phosphonate) **4** in hot DMF. Reactions of monomer **4** with phenyl formaldehyde or with biphenyl formaldehyde under Wittig conditions in the presence of excess $NaOC_2H_5$ in degassed C_2H_5OH at room temperature gave the oligomers 2,5,2′,5′-tetrastyrylbiphenyl (**TSB**) and 2,5,2′,5′-tetra(4′-biphenylenevinyl)biphenyl (**TBVB**) (yield ~85%), respectively (for details of characterization see ESI).† The oligomers were purified by recrystallization from chloroform–methanol, yielding bright yellow solids displaying high luminescence. X-Ray analysis of oligomers in the powder state showed a broad amorphous band ranging from 5° to 60°, while some sharp crystalline peaks appended to broad amorphous band were also observed. Both oligomers especially **TBVB** showed distinct decreasing in the crystalline characteristics as compared with TPV, which was fully crystalline in the powder state, indicating a depressed intermolecular interaction in the new oligomers. Significantly, few crystalline peaks were observed for the film samples prepared from vacuum deposition of both oligomers, indicating a fully-disordered (glass state) molecular arrangement in sublimated films. The thermal properties of the oligomers were investigated by differential scanning calorimetry (DSC) under a continuous nitrogen purge. There was an endothermic step-transition at *ca.* 220 °C for **TSB** and two closed endothermic step-transitions at 258 °C and 264 °C for **TBVB**; no other phase transitions occurred at temperatures below 220 °C.† Obviously, the first phase transition temperature of both oligomers were high enough for further practical applications.



Scheme 1 Synthesis of oligomers.

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† Electronic Supplementary Information (ESI) available: general experimental procedure, synthesis and characteristization of monomers and oligomers, and OLEDs fabrications. See http://www.rsc.org/suppdata/cc/b3/b306694k/

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The absorption and emission spectra of the two oligomers both in dilute chloroform solution and in sublimated films are shown in Fig. 1 and detailed data are tabulated in Table 1. Optical absorption spectra in chloroform solution for **TSB** and **TBVB** show a λ_{max} at 360 and 376 nm, respectively. The red-shift of **TBVB** to **TSB** reflects the extended conjugation along the TPV due to terminal phenyl rings, whereas **TSB** reveals a slight shift from TPV about 356 nm, indicating that crossing linking of two TPVs *via* the central phenyl–phenyl bond has less effect on the conjugation degree along the TPV. Both oligomers are blue light-emitting materials with high PL efficiencies of 60 and 66% in solution with the longest wavelength emission peaks at λ_{em} = 422 nm (2.94 eV) and λ_{em} = 451 nm (2.75 eV). Although the PL spectrum of the solid film of the oligomers shows a 20–30 nm bathochromic shift to that of their solutions, **TSB** and **TBVB** exhibit bright blue light emission with high solid-state PL efficiencies of 11 and 34%, respectively, which is significantly higher than the efficiency (< 10%) of TPV in solid state.[5]

The multilayer organic light-emitting devices (OLEDs) with the structure of ITO (indium tin oxide)/NPB(40–50 nm)/**TSB** or **TBVB**(30–40 nm)/Alq$_3$(20–30 nm)/LiF/Al were fabricated by thermal deposition in a vacuum chamber, where NPB (*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine) acted as hole transporting layer, and Alq$_3$ as an electron transporting layer. Both oligomers exhibit blue light emission. The EL spectrum of **TSB** devices with a peak at 488 nm is 50 nm red-shifted compared to the PL spectrum, likely due to overlap between the emission spectra of **TSB** and Alq$_3$. **TSB** devices exhibit turn-on voltage at 3 V with maximum luminance efficiency of 1.46 cd A^{-1} (0.57 lm W^{-1}) and luminance of 690 cd m^{-2}, respectively. Substantially better performances (such as efficiency, luminance and pure blue light-emitting) are noted for devices made with **TBVB**. Fig. 2 shows the current density (*I*)–voltage (*V*)–luminance characteristics of the device and the insert is its *L*–*V* (luminance efficiency *vs.* voltage) characteristics. The EL emission peak was measured at λ_{em} = 440 and 460 nm (15 V) with CIE coordinates of x = 0.1726 and y = 0.1689 in the pure blue spectral region.† The luminance efficiency is up to 1.62 cd A^{-1} (1.02 lm W^{-1}) with a maximum luminance of 2150 cd m^{-2} and a turn-on voltage of 3 V for the device with a 30 nm thick active layer (Fig. 2). It is higher than that of the reported oligomer PPV devices (less than 0.1 cd A^{-1}),[9] and is almost comparable with classical blue materials in efficiency (1–4 lm W^{-1}) *ca.* a 4,4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl (DPVBi) based device.[10]

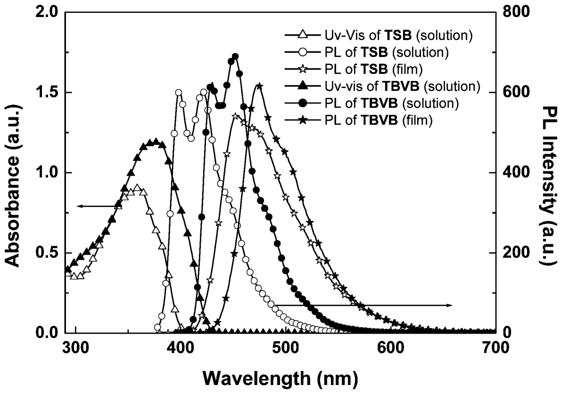

Fig. 1 UV/Vis and PL spectra of the two oligomers in solution (CHCl$_3$) and film at RT, excited at 380 and 395 nm, respectively (2.0 × 10^{-4} M).

Table 1 Syntheses and optical properties of oligomers

Oligomer	Yield (%)	$\lambda_{max,Abs}$/nm (ε/ dm^3 mol^{-1} cm^{-1})	$\lambda_{max, PL}{}^a$/nm ($\phi_{PL}{}^b$)	$\lambda_{max,PL}{}^c$/nm ($\phi_{PL}{}^d$)
TSB	84	360 (109900)	399,422 (0.66)	453 (0.11)
TBVB	86	376 (83300)	430,451 (0.60)	473 (0.34)

[a] Emission spectra were recorded in dilute CHCl$_3$ solutions. [b] in dilute CHCl$_3$, using quinine sulphate in 1 M sulphuric acid as standard. [c] in film, excited at 380 and 395 nm, respectively. [d] in film, calculated by relative method, using polyfluorene film(ϕ_{PL} = 0.26) as standard.†

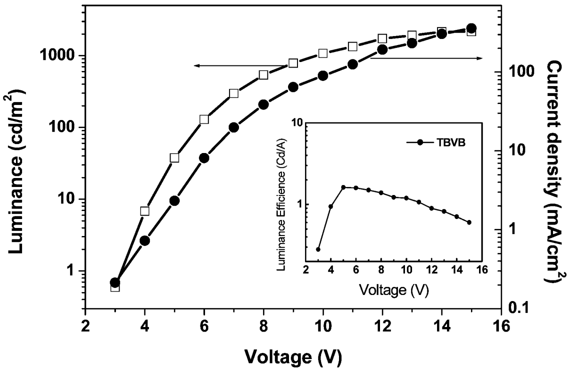

Fig. 2 Current density (*I*)–voltage (*V*) and luminance (*L*)–voltage (*V*) characteristics of OLED of **TBVB**. Insert is *L*–*V* (luminance efficiency *vs.* voltage) characteristics.

In summary, novel dimeric TPV derivatives **TSB** and **TBVB** containing a biphenyl center have been developed. The obtained oligomers exhibit high PL efficiencies both in solution and in solid films, and good thermal stability. Improved EL performance of devices using the new oligomers such as **TBVB** as the active layer in comparison with the excellent blue emitter (*ca.* DPVBi) has also been demonstrated, making this material a promising candidate for further optimisation.

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