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Cruciform p–n diblock conjugated oligomers for electroluminescent applications†

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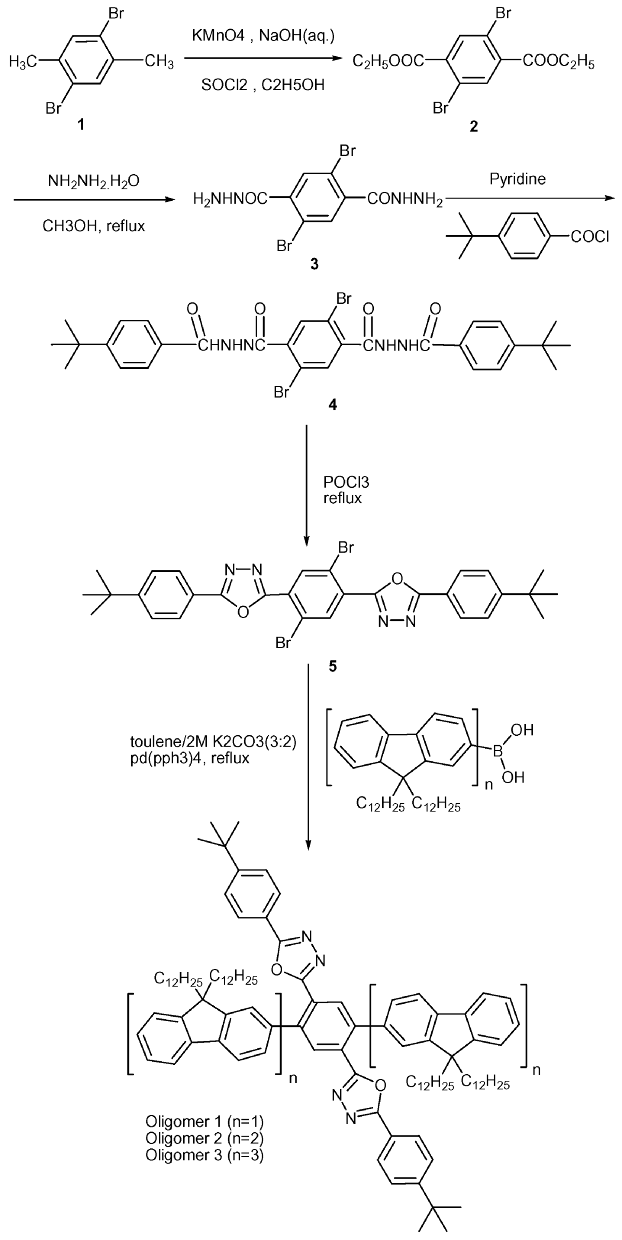
The optoelectronic properties of the cruciform p–n diblock oligomers 1–3 can be independently tuned by the oligofluorene and oxadiazole branches to increase the charge mobility.

π-Conjugated organic molecules have attracted much interest because of their applications in organic light-emittig diodes (OLEDs), organic field-effect transistors (OFETs), photovoltaics, and nonlinear optics, *etc.*[1,2] Most of these applications would benefit from a full understanding of charge transport properties, which depend on the chemical and electronic structures of the π-conjugated systems. So far, the most intensely studied molecules are linear conjugated π-systems, in which the molecule is composed of a p-dopable block (*e.g.* an oligothiophene unit) and an n-dopable block (*e.g.* an aromatic oxadiazole moiety).[3] However, the n-dopable block inserted into the p-type polymer mainchain will partially act as a hole-blocking unit due to its high electron deficiency. *Vice versa*, the hole-transporting unit will lower the electron mobility. Therefore, it is difficult to further improve the charge injecting and transporting properties.[4]

Compared to linear conjugated molecules, the energy levels of the HOMO and LUMO of most cruciform π-systems are spatially separated and the independent properties of each branch mostly maintained.[5,6] These unique properties are crucial for molecular electronic applications, *e.g.*, adding donor and/or acceptor substituents to cross-shaped chromophores at suitable positions can lead to independent electronic shifts in the LUMO and HOMO.[6] However, alternative modes of π-electron delocalization, in particular cross conjugation, are much less frequently encountered, and the nature of cross-conjugated π-delocalization is thus far less understood.[7] In 2003, first functionalized cruciform π-system was developed by Nuckolls *et al.* to test the electronic properties of the film.[8] More recently, Bunz and co-workers reported a series of cruciform π-systems dealing with hybrid phenylene-ethynylene/phenylene-vinylene oligomers.[5,6,9]

Herein we report a new series of functionalized cruciform p–n diblock oligomers (see Scheme 1) for electroluminescent applications. In the cruciforms, the oligofluorene branch, which is π-excessive, acts as a hole-transporting channel, while the di(1,3,4-oxadiazole) phenylene branch, which is π-deficient, acts as an electron-transporting channel. Variation of the length of oligofluorenes affords the possibility of tuning



Scheme 1 Synthetic routes of the oligomers.

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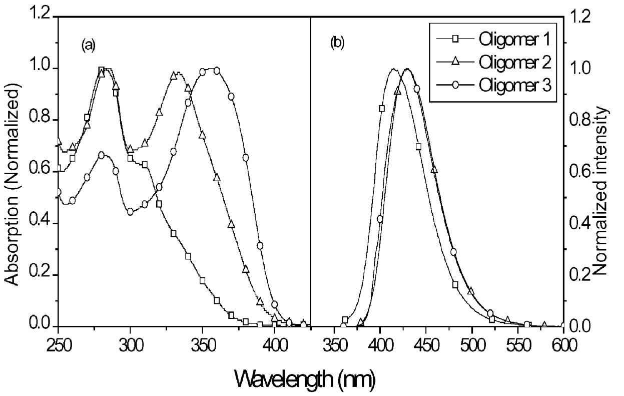


Fig. 1 Absorption and emission spectra of the oligomers in dilute cyclohexane solution.

redox behavior (related to the energy levels of the HOMO and LUMO of the oligomers) and the emissive color of the resultant oligomers.[10]

It is noticed that the oligomers exhibit two absorption peaks in solution, corresponding to the oxadiazole branch and the oligofluorene branch, respectively (Fig. 1a). The identical absorption maximum of the oxadiazole segment of the oligomers (*ca.* 280 nm) suggests that the electronic interactions between the oxadiazole branch and the oligofluorene branch are quite limited, which may be due to the twist of the two branches.[11] The longer wavelength peak in the region of 310–355 nm is attributed to the electron transition of π–π^* along the conjugated backbone of the oligofluorene. The other predominant feature of the absorption spectra of the oligomers is a steadily increasing molar absorption as the number of fluorene monomer units is increased and the maximum absorption peaks shift to the long wavelength region, appearing at 310 nm for oligomer **1**, 333 nm for oligomer **2** and 355 nm for oligomer **3**. A strong solvatochromism was also observed on the absorption spectra. In dilute chloroform, only one absorption peak was observed and the maximum absorption of the oligomers shifted to longer wavelength. Compared to the absorption, the oligomers only show an emission maximum appearing at 415 nm for oligomer **1**, and at 429 nm for oligomers **2** and **3**, respectively. This indicates the existence of efficient energy transfer from the oxadiazole segment to the oligofluorene branch.[6,11] The physical properties of the oligomers are presented in Table 1. It is noted that all of the cruciforms are highly efficiently fluorescent (0.55 < Φ < 0.75) in cyclohexane, while the emission quantum yields are lower in chloroform. The thermal stability of the oliogmers has substantially improved through the introduction of oxadiazoles. The decomposition temperatures of 5% weight loss in nitrogen were determined to be above 400 °C according to TGA experiments.

Table 2 Electrochemical properties of the oligomers

Oligomer	$E_{red/onset}$[a]/V	$E_{ox/onset}$[b]/V	E_{HOMO} [c]/eV	E_{LUMO} [c]/eV	Energy gap/eV
1	−2.06	1.09	5.79	2.64	3.15
2	−2.03	0.90	5.60	2.67	2.93
3	−2.08	0.84	5.54	2.62	2.92

[a] Reduction potentials measured by cyclic voltammetry in THF (1×10^{-3} mol L^{-1}). [b] Oxidation potentials measured by cyclic voltammetry in CH_2Cl_2 (1×10^{-3} mol L^{-1}). [c] Estimated from the onset oxidation and reduction potential (*vs.* Ag/Ag^+) plus 4.7.

Detailed data for the cyclic voltammograms are listed in Table 2. Most of the oligomers possess two anodic and cathodic peaks, which can be attributed to two different blocks of the oligomers. When scanning cathodically, the oligomers show reversible reduction peaks around −2.0 V, which may be due to the same oxadiazole segment in these oligomers. However, the reduction potential of the oligomers show little dependence on the increase of fluorene number in the oligofluorene branch. This implies that the reduction properties of the oligomers are dominated by the oxadiazole branch. On sweeping anodically, unlike their reduction peaks, the oxidation potentials of the oligomers are sensitive to the variation in the fluorene number in the oligofluorene branch. The onset potential for oxidation is reduced from 1.09 to 0.84 V, with increasing fluorene number in the fluorene branch from oligomer **1** to **3**. It is demonstrated that the HOMO level of the oligomers can be effectively adjusted by changing the fluorene number in the oligofluorene branch.[10] It is difficult to confirm whether the two crossed π-systems are electronically coupled or only topologically cross-conjugated. But it is acceptable to say that attachement of the oxadiazole branch significantly modulates the electronic properties of the oligofluorene.

In order to thoroughly understand the optical (*i.e.*, band gap, solvatochromicity) and the redox properties of the oligomers, quantum chemical calculations were performed. The geometries of all the molecules were optimized using the Gaussian 03 program[12] at the B3LYP/3-21G* level, and the alkyl at the C9 position of the fluorene group was substituted by an H atom due to its minor influence on the electrical and optical properties. The HOMO is localized on the oligofluorene branch of the cruciform, while the LUMO is localized on the oxadiazole part (Fig. 2). HO and LU orbitals overlap only in the central benzene ring. This result is also consistent with

Table 1 Physical properties of cruciform p–n diblock oligomers

Oligomer	M_w	T_d/°C	$\lambda_{abs,sol}$[a]/nm	$\lambda_{abs,film}$[a]/nm	$\lambda_{PL,sol}$[c]/nm	$\lambda_{PL,film}$[c]/nm	Band gap[b]/eV	FWHM[d]/nm (FWHM/eV)	$\Phi_{f,sol}$[e]
1	1480.3	418.2	310 (280)	316	415	429	3.26	70 (17.76)	0.55
2	2482.0	408.4	333 (280)	342	429	441	3.07	57 (21.81)	0.75
3	3483.6	404.1	355 (280)	356	429	446	3.05	67 (18.55)	0.70

[a] Absorption maxima in solution (cyclohexane, 1×10^{-6} mol L^{-1}) and in films on quartz substrates. [b] Optical band gap derived from the onset of UV-Vis absorption spectra of oligomer solutions. [c] Emission maxima in solution (cyclohexane, 1×10^{-6} mol L^{-1}) and in films on quartz substrates; the excitation wavelength corresponds to the absorption maximum. [d] Full width at half-maximum of the film PL spectra. [e] 9,10-Diphenylanthrecene standard (Φ_{PL} = 0.95 in cyclohexane).

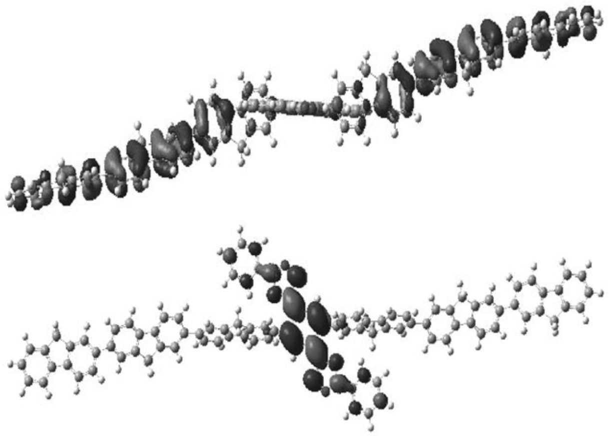


Fig. 2 HOMO and LUMO electron densities of oligomer **3** (alkyl groups omitted). Top: HOMO of oligomer **3**. Bottom: LUMO of oligomer **3**. The HOMO is almost completely localized on the oligofluorenes branch of the cruciform, while the LUMO is almost fully localized on the oxadiazole substructure.

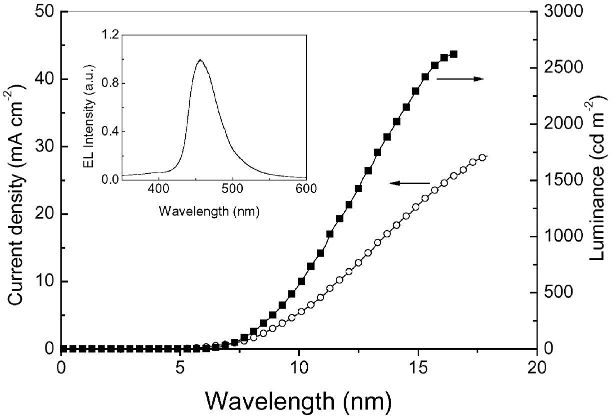
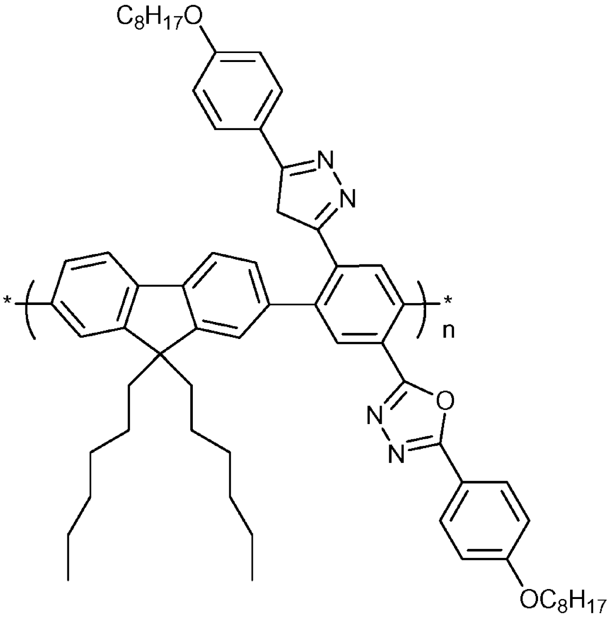


Fig. 3 Current–voltage and luminescence–voltage characteristics of the ITO/PEDOT:PSS/oligomer **3**/Ca/Al device. Inset is the EL spectrum of the OLED device from **3**.

the electrochemical analysis. The excited states of the oligomers must show charge separation, which explains the sensitivity of their emission wavelength towards the polarity of the solvent. An increasingly polar solvent stabilizes the excited state and leads to a bathochromically shifted emission.[6]

To evalutate our cross-shaped materials, a device of oligomer **3** has been fabricated with the configuration ITO/ PEDOT:PSS/oligomer **3**/Ca/Al and its electroluminescence (EL) behavior was compared with a device of fluorene-based conjugated polymers containing oxadiazole pendants (ITO/PEDOT:PSS/Polymer/Ca/Al) (The chemical formula of the polymer is depicted in Scheme 2).[13] The EL data of the OLED devices are listed in Fig. 3 and Table 3. The maximum luminance of the oligomer **3** device is 2622 cd m^{-2} at 16.5 V and its luminance efficiency is 1.6 cd A^{-1}, which is much higher than that of the polymer. The lower turn-on voltage and higher maximum brightness are due to better charge injection and transport and efficient charge recombination,[13] which may be due to the two independent channels in the cruciform. The oligofluorene branch acts as a hole transporting channel, while the di(1,3,4-oxadiazole)phenylene branch acts as an electron-transport channel. The conventional fluorene-based conjugated polymers containing oxadiazole pendants such as polymer behave considerably more like poly(fluorene-alt-phenyl). However, if the oxadiazole groups and oligofluorenes laterally attach to the benzene ring, the electronic properties of the resulting oligomer **3** are different from both oligofluorenes and oxadiazoles. The independent properties of both branches are mostly maintained.[6] This result suggests that the cross-shaped p–n diblock structure can more efficiently increase charge mobility.



Scheme 2 Chemical formula of the polymer

In summary, these results together show that the optoelectronic properties of the cruciform oligomers **1–3** can be independently tuned by the oligofluorene and oxadiazole branches. The cross-shaped p–n diblock structure can more efficiently increase the charge mobility. These monomers can be used in the synthesis of diverse sets of cross-conjugated fluorene–oxadiazole derivatives with fine-tuned optical/electronic properties. Further studies of these materials are continuing to discern to what extent cross-conjugation exists as an electronic coupling of the oxadiazole backbone to the oligofluorene arm beyond the topological aspect.

Experimental

Materials

Chemicals were reagent grades and purchased from Aldrich, Acros, and Lancaster Chemical Co. Toluene and tetrahydrofuran (THF) were distilled to keep them anhydrous before use.

Table 3 EL data of the OLED devices

Sample	$\lambda_{\max,\mathrm{EL}}$/nm	$V_{\mathrm{on}}{}^{a}$ /V	$V_{\mathrm{on}}{}^{b}$/V	$L_{\max}$/cd m^{-2}
3	456	5.5	6.5	2622
Polymer	452	7.5	7.5	126

[a] V_{on} is the turn-on voltage for the current. [b] V_{on} is the turn-on voltage for light.

Instruments

The NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. Molecular masses were determined by laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MASS). UV-Vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. The concentration of the oligomer solution was adjusted to $\sim$0.001 mmol L^{-1}. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 °C min^{-1} under N_2. Elemental microanalyses were carried out on a Vario EL III CHNOS Elementar analyzer. Cyclic voltammetry (CV) was performed at a scanning rate of 200 mV s^{-1} on an AUTOLAB.PGSTAT30 potentiostat/galvanostat system (Ecochemie, Netherlands), which was equipped with a three-electrode cell. Pt wires were used as the counter electrode and the working electrode, and Ag/Ag^+ was used as a reference electrode. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) was used as a supporting electrolyte. The reduction and oxidation behavior of the oligomers were measured in solutions of THF and CH_2Cl_2 (1×10^{-3} mol L^{-1}), respectively. According to de Leeuw *et al.*, the ionization potential (E_{HOMO}) and electron affinity (E_{LUMO}) are approximately equal to the onset oxidation potential and the onset reduction potential (*vs.* Ag/Ag^+) plus 4.7 eV, respectively.[14]

Fluorescence quantum yields (Φ_f) of the oligomers in cyclohexane solution were measured by using 9,10-diphenylanthracene as standard: quantum yield is 0.95 in cyclohexane.[15] Values are calculated according to eqn (1), where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the fluorescence quantum yield of the standard, I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbance of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

$$\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2 \qquad (1)$$

General syntheses

The general synthetic routes of the desired oligomers are outlined in Scheme 1. Oligofluorene derivatives were synthesized according to the literature.[15–17] Firstly, 2,5-dibromo-*p*-xylene (**1**) was oxidized with potassium permanganate under alkali conditions to afford 2,5-dibromoterephthalic acid. This is the key step for the synthesis of the oxadiazole monomer (20% yield). Then, the acid group was further esterified to give 2,5-dibromoterephthalic acid diethyl ester (**2**).[18] After the ester groups had been converted to benzoyl hydrazide (**3**), they were reacted with aryl chloride to form compound **4**. Finally, oxadiazole monomer (**5**) was produced by the dehydrative cyclization of hydrazides in $POCl_3$. The resulting oligomers were synthsized by palladium-catalyzed Suzuki cross-coupling reactions.

Acknowledgements

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