



Synthesis and characterization of cross-conjugated cruciforms with varied functional groups

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ABSTRACT

A series of novel oligo(*p*-phenylenes) (OPPs) derivatives with bisdiene side-chains are synthesized and fully characterized. These cruciforms are soluble in common organic solvents and show good thermal stability. Absorption and emission spectra are recorded to study the effect of different electron-withdrawing and electron-donating groups on photophysical properties. Powder XRD shows crystalline structures for all the cruciforms. Single crystal XRD studies show tight-packing along the planar bisdiene axis but significant twisting along phenylene units, which correlate the role of functionalization along the bisdiene axis in tuning the band gaps of the cruciforms.

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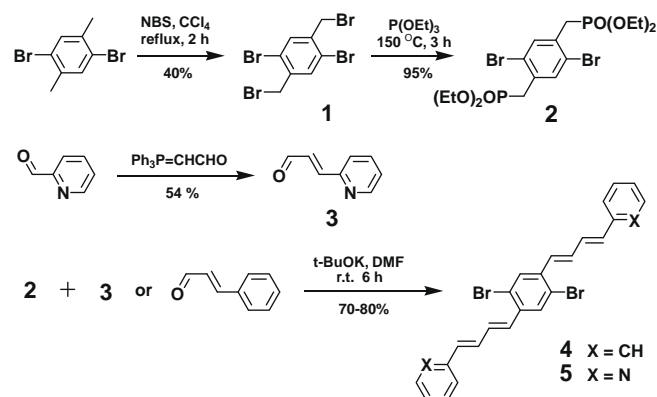
Conjugated organic molecules have gained significant interest due to the possibility of developing functional materials by introducing different functional groups.¹ Besides linear conjugation, research efforts are being focused on exploring extended cross-conjugation and omni-conjugation, which offer interesting photophysical, electrochemical, and self-assembly properties.² However, conjugated polymers often suffer from the inevitable defects incorporated during synthesis, which interrupt the effective conjugation length. Furthermore, due to strong aggregation, it can be difficult to elicit accurate information regarding the role of individual conjugated side-chains as their effect can be masked by the whole polymeric system. Hence, we are interested in designing structurally well-defined and soluble cross-conjugated molecules. It is interesting to study the effects of various functional groups, introduced on different segments, on the overall photophysical properties of the molecule. Herein, the design, synthesis, and characterization of a series of cruciforms with different electron-donating and electron-withdrawing groups on both segments are reported.

In order to design two cross-conjugated segments, polyaromatic derivatives as one chain and bisdienes as another chain were chosen along with the incorporation of alkyl chains to improve solubility. The bisdiene segments were synthesized via Wittig–Horner reactions between *trans*-cinnamaldehyde or 3-(2-pyridyl)acrolein (Scheme 1).³

The Pd(0)-catalyzed Suzuki coupling between **4** or **5** and the corresponding boronic acids **6–10** (Table 1) in DMF/H₂O (3:2) solvent mixture afforded cruciforms **01–010** in low yields (Scheme 2,

Table 1). We found that protonation of the pyridyl group by an equal amount of TFA made **5** soluble in DMF, so a weaker base, NaHCO₃ (aq 2 M), was used then for the synthesis of **01–05**, to minimize deprotonation and to obtain the target compounds **06–010** in reasonable yields. THF/H₂O (3:2) as the solvent system gave similar yields but toluene/H₂O (3:2) failed to afford the products.

All the cruciforms were readily soluble in common organic solvents such as toluene, CH₂Cl₂, CHCl₃, THF, and DMF but not in hexane, MeOH, or EtOH. The bisdienes all existed in the *trans* conformation as observed by NMR and single crystal XRD. All the products were thermally stable up to 310 °C (TG in Table 2). The results indicated that the electron-withdrawing nitro and pyridine groups tended to influence the stability.



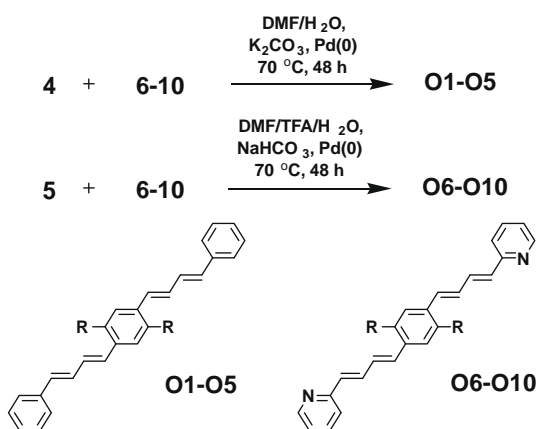
Scheme 1. Synthesis of phenyl and pyridyl-substituted bisdiene segments.

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Table 1
Cross-conjugated cruciforms **O1–O10**

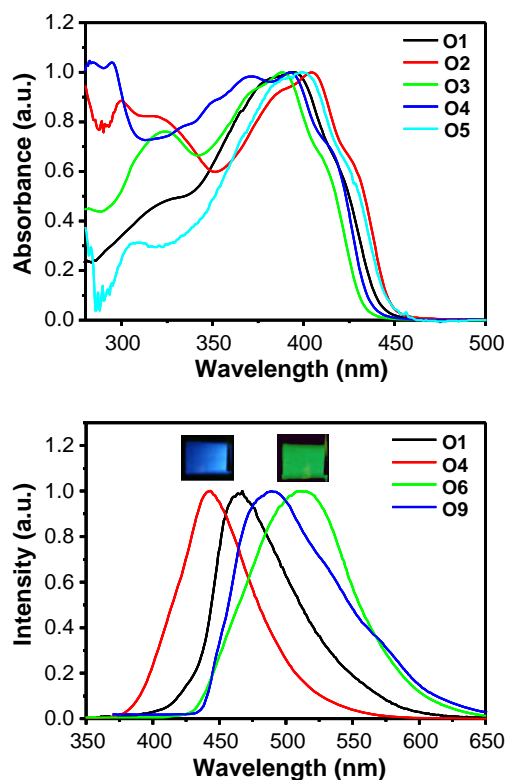
Entry	R	Cruciform, yield (%)
6		O1 (39), O6 (30)
7		O2 (60), O7 (48)
8		O3 (50), O8 (42)
9		O4 (38), O9 (35)
10		O5 (43), O10 (27)

**Scheme 2.****Table 2**

UV–vis (λ_{abs}), emission (λ_{em}), band gap (BG), quantum yield (QY), and decomposition temperature (TG) of **O1–O10**

Cruciform	O1	O2	O3	O4	O5
λ_{abs} (nm)	394	405	388	392	399
λ_{em} (nm)	467	469	447	442	454
BG (eV)	3.14	3.06	3.19	3.16	3.10
QY (%)	3.9	7.7	9.4	7.3	4.8
TG ($^\circ\text{C}$)	270	280	289	310	239
Cruciform	O6	O7	O8	O9	O10
λ_{abs} (nm)	415	426	412	414	425
λ_{em} (nm)	510	509	501	488	498
BG (eV)	2.98	2.91	3.00	2.99	2.91
QY (%)	3.6	8.1	10.3	6.6	5.0
TG ($^\circ\text{C}$)	243	282	288	253	229

UV–vis and fluorescence spectra were recorded for all the cruciforms (Fig. 1) and the results are summarized in Table 2. Strong absorptions were observed in the range 388–405 nm for **O1–O5** and 412–426 nm for **O6–O10**. This indicates that the electron-withdrawing pyridyl group reduced the band gap by lowering the LUMO level.⁴ However, the effect of different functional groups

**Figure 1.** Normalized absorption (top) and emission spectra (bottom) of the cruciforms in THF (10^{-5} M). Insets are photos of the fluorescence.

(nitro, pyridine, etc.) on the absorption maxima was limited. The fluorescence spectra showed emission maxima within the range 442–469 nm for **O1–O5**, while the peak maxima of **O6–O10** were in the range 488–510 nm. The latter series with the pyridine moiety on the bisdiene chain showed ca. 40–50 nm red shifts in the emission maxima. We can only attribute this to the influence of the electron-withdrawing pyridyl group. Also, **O1–O5** showed blue emissions while the remainder gave near-green emissions (Fig. 1).

These results indicated that different functional groups on the 2D-conjugated backbone of the cruciforms have moderate effects on the overall photophysical properties. Cruciform **O7** showed relatively higher emission maxima, probably due to extended conjugation, less steric hindrance as well as the electron-donating effects of the alkoxy groups. Products **O3**, **O4**, **O8**, and **O9** with bulky alkyl chains should influence the planarity of the molecular structure and overall conjugation with a blue shift in emission maxima. Since the two sets of cruciforms only differ in the structure of the bisdiene segment, it would be anticipated that the influence of this segment on the photophysical properties would be more significant compared to the oligoarene segment. Quantum yields (QY) were found to be low for all the products in solution, and which made emissions very weak in the solid state (therefore data were not accurate and not recorded). These were attributed to strong intermolecular interactions and energy loss during resonance energy transfer from an excited donor to a fluorescent acceptor, providing large Stokes' shifts, as is evident in Table 2.

Powder XRD analysis revealed that all the cruciforms were highly crystalline in the solid state (Fig. 2). Products **O1–O5** had similar spectra to those of **O6–O10** (see Supplementary data) with no pretreatment of the samples. It was surprising that **O3** and **O8** bearing a bishexylfluorene group showed ordered packing. Cruciforms **O4** and **O9** bearing a hexylcarbazole group were less-organized in the powder state and the XRD peaks were not well resolved, probably due to the spatial flexibility of the hexyl group.

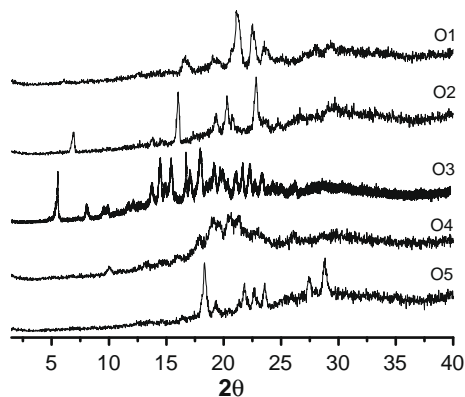


Figure 2. Powder XRD spectra of **O1**–**O5**.

Cruciforms **O2**, **O3**, **O7**, and **O8** showed a sharp peak at a low angle (6–7°), which was assigned to the intermolecular distance separated by the long alkyl chain.

Understanding the molecular structure of the cruciforms is imperative for investigating the structure–property relationships. The single crystal X-ray diffraction study of **O5** showed that it adopted a cruciform shape and the *trans*-bisdiene bond showed complete planarity relative to the central phenyl ring. This result was different from a report^{2h} where the styryl groups showed a departure from planarity with a twisting of approximately 15°.

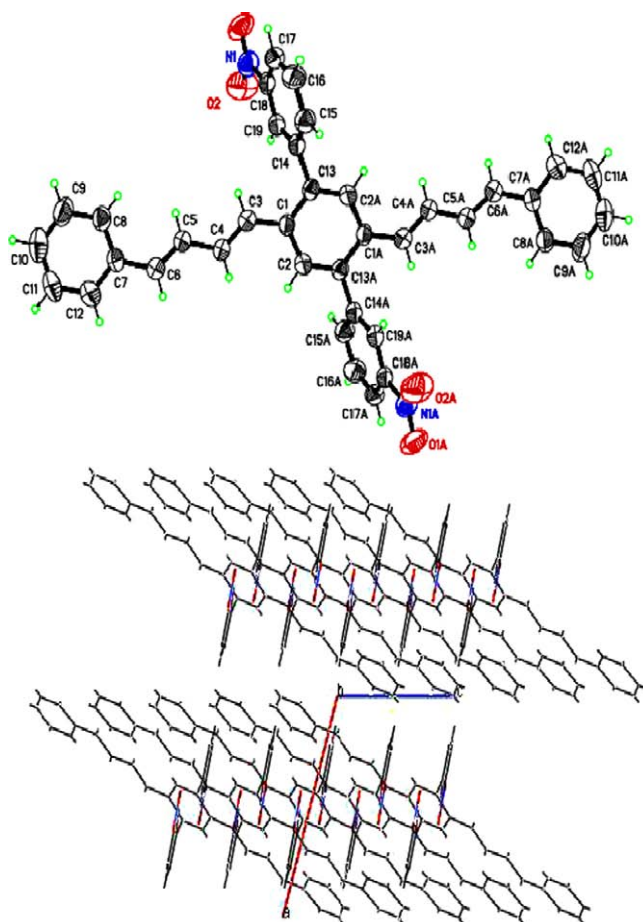


Figure 3. Molecular structure and packing of **O5**. CCDC deposition number: 731098.

The oligoarene unit was highly twisted due to the steric hindrance between the *ortho* protons of neighboring rings (67° relative to the central phenyl ring for **O5**, Fig. 3). The strong twisting along the oligoarene segment also affected the effective conjugation and led to the large structure change from the ground state to the first excited state upon excitation and therefore the large Stokes' shifts. Nevertheless, these cross-conjugated cruciforms were shown to have lower band gaps compared to linear oligoarenes and alkoxy-substituted oligo(*p*-phenylene vinylene)s.⁵

Packing inside the crystal lattice of **O5** showed that molecular planes were parallel to each other with similar segments being face-to-face. The 3-nitrophenyl segments were highly twisted, but parallel to each other. An interplanar distance of 3.7 Å indicates that the intermolecular π – π interaction could be the main driving force for ordered packing; it is also one of the factors resulting in the low QY. From powder XRD and single crystal studies, it appears that such 2D-conjugated cruciforms might aggregate and organize in the lattice.

Differential scanning calorimetry (DSC) studies showed that cruciforms **O2** and **O3** had obvious glass transition behavior and the mesophases were also identified by polarized optical microscopy (POM). A nematic phase for **O2** (Schlieren texture) and smectic-A phase for **O3** were observed (Fig. 4).⁶ The rigid mesogenic units not only force the molecules to take on an extended confor-

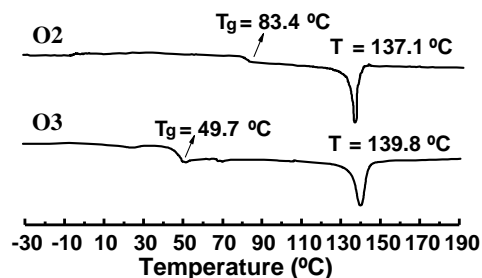


Figure 4. POMs of the textures on cooling of **O2** (top) and **O3** (middle) at a cooling rate of 0.5 °C/min and the DSC spectra (bottom).

mation but also organize them close to each other to form a rigid core through strong π – π interactions. The microseparation between the rigid core and the flexible alkyl chains is the main driving force for the molecules to pack in a more ordered pattern.⁷ Cruciform **O3** had a much more ordered structure, probably because the steric crowding of the bisalkyl chain on the fluorene unit restricted it to a more rigid molecular layout.

In conclusion, a series of cross-conjugated cruciforms have been obtained. The photophysical and solid state properties were investigated by UV–vis, fluorescence, XRD, and POM and correlated with their molecular structures.

Acknowledgments

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Supplementary data

Experimental details, characterization data, and a detailed report of the single crystal of **O5**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.119.

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