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Synthesis and Spectroscopic Properties of Finite Ph_2N-Containing Oligo(arylenevinylene) Derivatives That Emit Blue to Red Fluorescence

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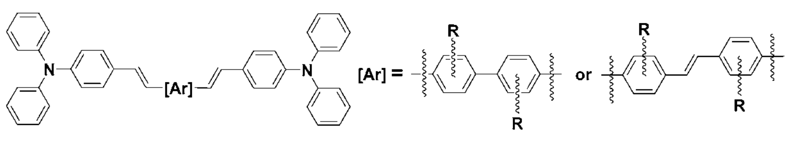
ABSTRACT



A series of oligo(phenylenevinylene) (OPV) derivatives with finite conjugation units were prepared in short steps from few building blocks. The central and terminal aryl groups of these OPV dyes contain cyano and Ph_2N substituents, respectively, which affect color of fluorescence. The wavelength ranges from 472 nm (blue) to 614 nm (red) depending on the position of the cyano group.

The synthesis of new oligo(phenylenevinylene) OPV derivatives has attracted considerable attention[1] because of their widespread application in light-emitting diodes,[2] chemical sensors,[3] nonlinear optics,[4] and organic magnetic materials.[5] The energy gaps between the HOMO and LUMO orbitals of OPV are crucial for the application of these materials.[1−5] Although an increase in the number of repeating segments of phenylenevinylene oligomers may decrease the energy gap, this approach becomes less effective after a finite length of oligomers is achieved. A systematic study by Yu[6] shows that no further red shift is observed for the oligomer (eq 2, Scheme 1) after it reaches 10 aryl groups and nine double bonds, at which point it shows fluorescent emission at 536 nm. The saturation in the emission wavelength arises from the limited electron delocalization of a longer oligomer.

The use of OPV dyes for organic light emitting-diodes (OLED) should enable blue, green, and red fluorescent emission to achieve a full-color display.[7] Common OPV molecules show fluorescent emission at less than 550 nm even with extensive conjugation. In this study, we report the synthesis of functionalized OPV dyes (eq 3) with finite

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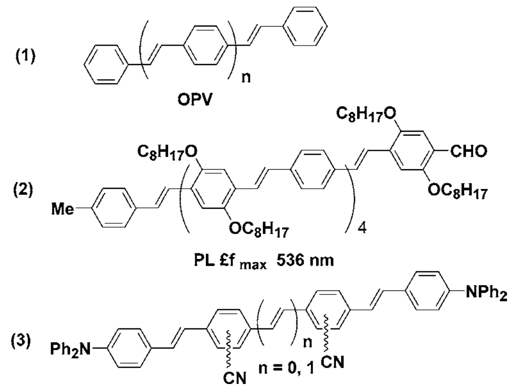
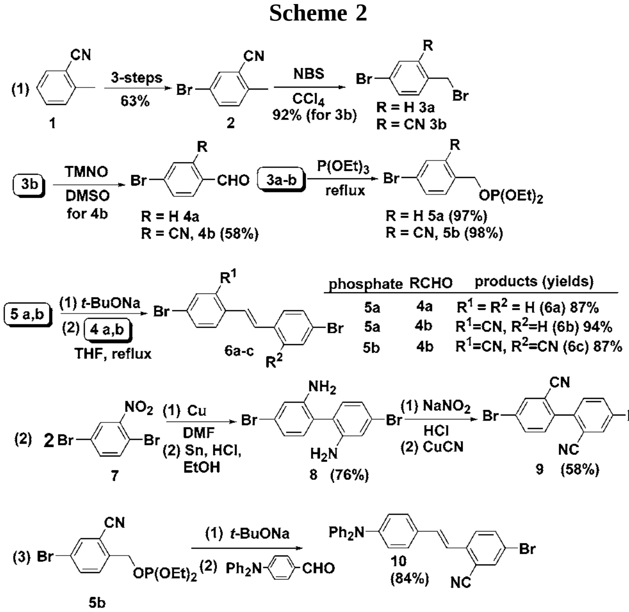
Scheme 1



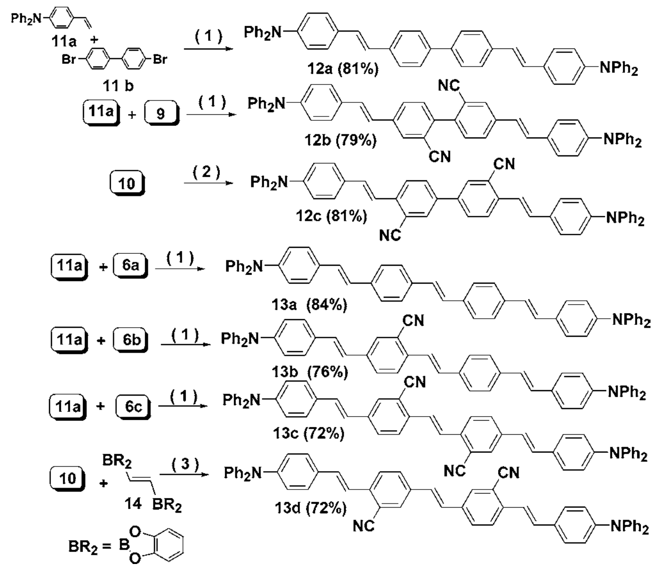
skeletons that can emit full range of visible light. Each terminal phenyl group of these molecules is linked to a diphenylamine group that can enhance fluorescence decay.[8] The central phenyl group is attached with a cyano group to strengthen the efficiency of the electron delocalization within conjugation skeletons.[9] This design was aimed at producing an efficient red OPV dye. Molecules with these finite conjugation skeletons are suitable for sublimation to prepare OLED thin film.

Schemes 2 and 3 show the synthetic protocols for the seven target molecules **12a**–**c** and **13a**–**d**. This approach minimizes the synthetic procedures. Our first goal was to synthesize central aryl cores **6a**–**c** and **10** via the Horner–Wadsworth–Emmons reaction, which gave trans double bonds exclusively (>96%) according to ^{1}H NMR analysis.[10] The synthesis of these four *trans*-stilbene derivatives involves the repeated use of phosphates **5a** and **5b**. The benzyl bromide **3b** not only provided the key phosphates **5b** but also the aldehyde **4b**. Compounds **3a** and **4a** were obtained from commercial sources. The whole synthetic sequence apparently relies on the availability of compound **3b**, which was obtained in four steps from 2-cyanotoluene **1** (see the Supporting Information). Another central aryl core **9** was easily prepared in two steps from the dibromide **7**.

Scheme 2



Scheme 3[a]



[a] Conditions: (1) $Pd(OAc)_2$ (3 mol %), Ph_4PBr (20 mol %), NaOAc (5.0 equiv), DMF, 100 °C, 16 h; (2) $Ni(COD)_2$ (1.1 equiv), DMF, 40 °C, 12 h; (3) $Pd(OAc)_2$ (10 mol %), $Ba(OH)_2$ (1.8 equiv), THF, H_2O.

Scheme 3 shows the synthesis of target oligomers via metal-catalyzed coupling reaction. The synthesis of oligomer **12a** via a double Heck reaction between commercially available **11a** and **11b** is not straightforward. Conventional conditions (5 mol % $Pd(OAc)_2$, Et_3N, toluene, 10 mol % PPh_3, 100 °C) gave the desired product **12a** in only 25% yield after column chromatography. The use of $^tBu_3P$(10 mol %) gave **12a** in 51% yield. The best results were obtained with the phase-transfer reagent Ph_4PBr, which gave **12a** in 81% yield.[11] This coupling reaction gave *trans*-stilbene in purities exceeding 96%. This condition worked well for a series of oligomers including **12b** (79%), **13a** (84%), **13b** (76%), and **13c** (72%). Oligomer **12c** was obtained efficiently by a Ni(COD)-promoted coupling reaction. The availability

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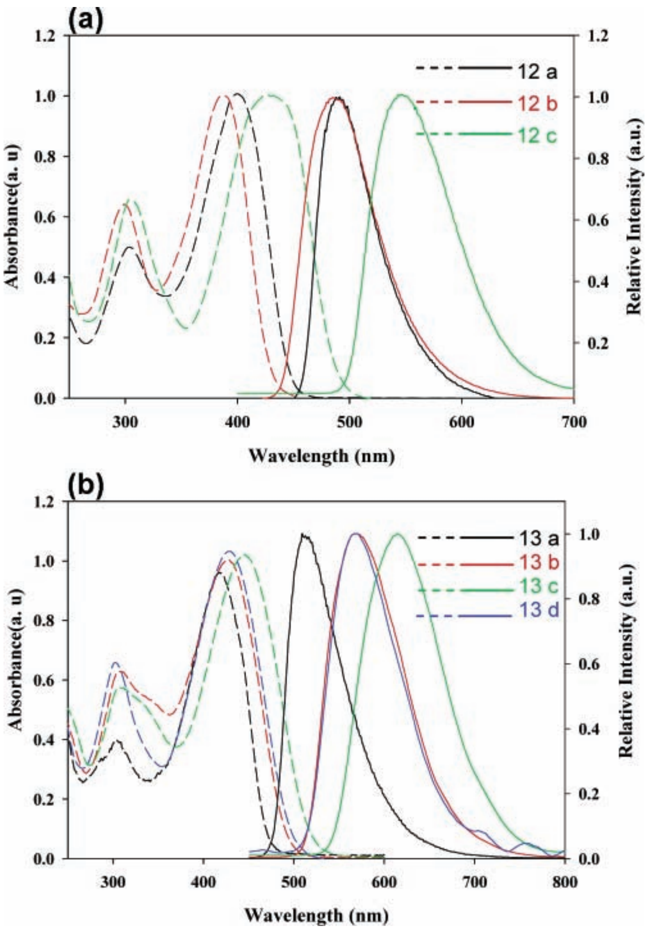

Figure 1. Comparison of **12a−c** (a) and **13a−d** (b) UV and PL spectra in solution (∼5×10^{-5} M in CH_2Cl_2).

of 1,2-vinyl diborate **14**[12] effected a double-Suzuki coupling of aryl bromide **10**, giving **13d** in 72% yield. These seven oligomers were characterized by NMR, Mass and elemental analysis. HLPC analysis of these samples showed that the purity exceeded 95%.

Parts a and b of Figure 1 show UV and PL spectra of OPV dyes **12a−c** and **13a−d** with their spectral data and quantum efficiency[13] given in Table 1. The cyano groups of **12b**, **13b**, and **13c** lie in conjugation with the remote Ph_2N group whereas those of **12c** and **13d** will conjugate with the proximate Ph_2N group. Accordingly, the former is expected to show a greater bathochromic effect than the latter relative to their parent OPVs **12a** and **13a**. Notably, the UV and PL spectra of **12b** are changed very little where the corresponding spectra of **12c** show a significant red-shift. An additional double bond in compound **13a** resulted in a red-shift of PL-emission by 30 nm compared to that of OPV **12a**. The introduction of a cyano group to the central phenyl in **13a** produced a more pronounced change in the absorption and

Table 1. Physical Properties of Oligo(arylenevinylene) Derivatives

compd	λ_{uv} (max)[a]	λ_{PL} (max)	Φ_f[b]	oxid $E_{1/2}$[c] (mV)	redn $E_{1/2}$[d] (mV)
12a	398	480	0.86	839, 1039	
12b	386	472	0.96	938	
12c	428	541	0.37	965	−1677, −1743
13a	386	510	0.84	830, 1220	
13b	433	560	0.61	862, 1001	-1565, −1790
13c	447	614	0.41	911, 1018	-1399, −1611, −1799
13d	429	577	0.32	875	-1502, −1643, −1823

[a] Measured in CH_2Cl_2; fluorescence was recorded by irradiation at the absorption maximum. [b] Measured in CH_2Cl_2 with fluorescein in 0.1 M NaOH ($\Phi_f = 0.95$) as a standard. [c] In CH_2Cl_2 (0.1 M $^nBu_4NPF_6$ as a supporting electrolyte). [d] In THF (0.1 M $^nBu_4NClO_4$ as a supporting electrolyte).

emission wavelengths. The observed trend for λ_{UV} (max) and λ_{PL} (max) for this series of compounds is consistent with our expectation: **13c** > **13b** ≅ **13d** > **13a**. For **12b**, the dihedral angle between the two central phenyl groups is ca. 56.2°, whereas the corresponding angle in **12a** is 39.7°.[14] For compound **12b**, the preference for a high nonplanarity accounts for a poor electron delocalization across these two central groups. The data in Table 1 indicate that a wide range of emission wavelengths (475−615 nm) can be achieved from these finite OPV backbones with the introduction of a cyano position at a suitable position.

Table 1 shows electrochemical data from cyclic voltammetry with Bu_4NPF_6 (0.10 M in CH_2Cl_2) and Bu_4NClO_4 (0.10 M in THF) as supporting electrolytes in anodic oxidation and cathodic reduction respectively.[15] Compounds **12a−c** and **13a−d** show quasi-reversible or two quasi-reversible anodic redox couples which are closely overlapped. This process corresponds to removal of electrons from diphenylamino group. The occurrence of a cathodic redox process depends on the presence of a cyano group which can decrease the LUMO energy level. No reduction behavior was observed for unfunctionalized OPV species **12a** and **13a**, consistent with our expectations. Two or three reversible cathodic redox couples were observed for **12c**, **13b−13c**, which corresponds to sequential reductions at the cyanophenyl groups. Figure 2 shows the CV curves for compounds **12a** and **13c**. One exception case is the dicyano OPV **12b** which does not show a cathodic redox couple. This may be attributed to the nonplanarity of the two central phenyl groups (vide infra), which results in a high energy level for LUMO orbital.

The OLED device was prepared from OPV **12b** because of its high quantum yields. The device structure is ITO/CuPc-(15 nm)/NPB(40 nm)/**12b**(2%) in DNA (30 nm)/Alq_3(30 nm)

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(14) Calculation of dihedral angles between two phenyl planes is performed on the ground-state structure using MOPAC-AM1 computations.

(15) Carbon electrode was used as a working electrode and a platinum wire as a counter electrode, all potentials were recorded versus Ag/AgCl (sat'd) as a reference electrode. Ferrocenium/ferrocene redox couple in $CH_2Cl_2/^nBu_4NPF_6$ occurs at $E_o' = + 0.57$ V vs Ag/AgCl (satd), in THF/$^nBu_4NClO_4$ occurs at $E_o' = + 0.55$ V vs Ag/AgCl (satd).

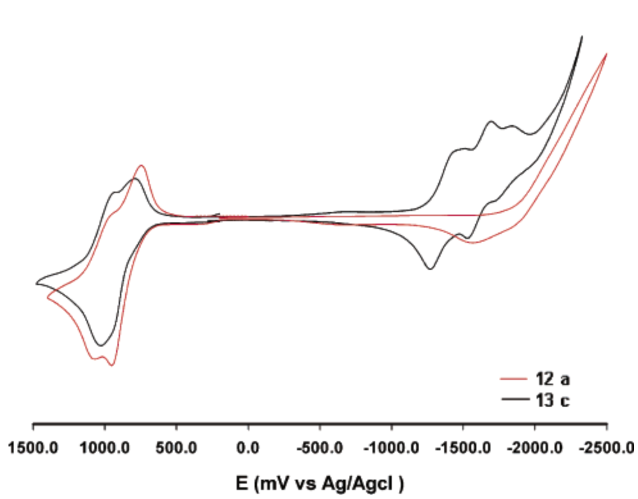

Figure 2. Cyclic voltammogram of oligo(arylenevinylene) **12a** and **13c**.

/Mg−Ag (10:1)(50 nm)/Ag(100 nm) which CuPc (copper phthalocyanine) and NPB (4,4′-bis(*N*-naphthyl)-*N*-phenylamino)biphenyl) were used as hole injector and hole transport layers, respectively, and DNA (9,10-di(2-naphthyl)anthracene) functioned as a host material layer. Such a device gave a blue EL emission at 460 nm very close to the PL spectra of **12b** (472 nm). The turn on voltage at 3.5 V and low working voltages (540 cd/m^2 at 6.0 V and 3120 cd/m^2 at 7.4 V with CIE coordinates of $x = 0.15$; $y = 0.18$) and the maximum brightness 11190 cd/m^2 at 10.5 V indicated the suitability of these functionalized OPV for OLED devices.

In summary, we prepared a series of Ph_2N-containing OPV dyes based on a concise synthetic approach involving few building blocks. These OPV molecules were functionalized with cyano groups to show a wide range of PL emission wavelengths (472−615 nm). The relation of the cyano positions to the photochemical properties of these OPV has been studied by UV, PL and electrochemistry. The suitability of these oligomers for OLED device is reflected by a EL device of OPV **12b** which shows a blue emission with good EL efficiency.

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Supporting Information Available: Synthetic procedures, spectral data, and electrochemical data of oligomers; EL-devices of oligomer **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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