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Tunable Optical Properties of Chromophores Derived from Oligo(*p*-phenylene vinylene)

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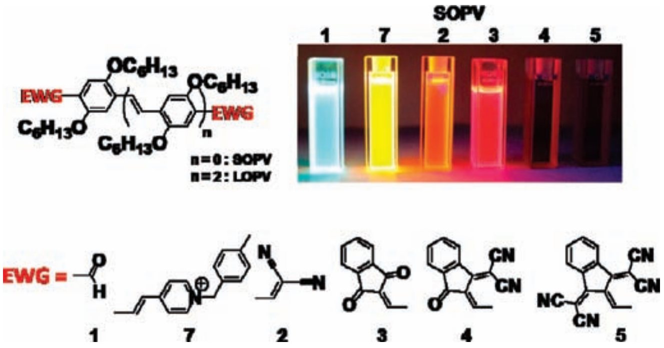
ABSTRACT



A series of 11 symmetric push−pull chromophores consisting of electron-accepting groups connected through a central π-conjugated system derived from oligo(*p*-phenylene vinylene) (OPV) were designed and synthesized. Electronic and spectroscopic properties were investigated by UV−visible absorption, fluorescence spectroscopy, and cyclic voltammetry. By finely tuning the electron-withdrawing ability of the acceptors as well as the length of the π-conjugated spacer, a wide range of dyes exhibiting strong absorption and emission were obtained.

During the last decades, organic-based optoelectronic materials displaying strong absorption and emission properties have received great scientific attention. In these fields, linear π-oligomers[1] and notably *p*-phenylene vinylene (PPV) derivatives are of particular interest as their high luminescence quantum yields make them excellent candidates for efficient Organic Light-Emitting Diodes (OLEDs).[2] The main characteristics of OPVs are broad absorption bands, high luminescence quantum yields in solution and in the solid state,[3] and large Stokes shifts. Moreover, addition of electron-donating groups such as alkoxy groups onto the phenylene

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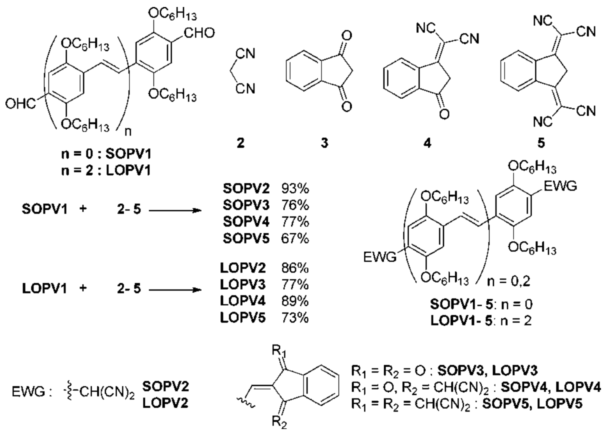
units enables us to tune the absorption and emission positions as well as the film formation ability.[4] When OPVs are substituted with such electron-donating groups, they can act as donors in push−pull systems if connected to electron acceptors. In this configuration, only a few oligomers have been reported, namely with C_{60},[5] nitro,[6] hexylsulfonyl,[7] dicyano,[8] pyridine,[9] and formyl[10] groups as acceptors. Herein, we report the preparation and properties of 11 new chromophores, **SOPV2−5,7** and **LOPV2−7**, constructed with two different central π-conjugated cores in conjugation with six different acceptors. Depending on the nature of the electron-withdrawing substituents, the newly synthesized OPVs exhibit either an efficient luminescence or a strong absorption.

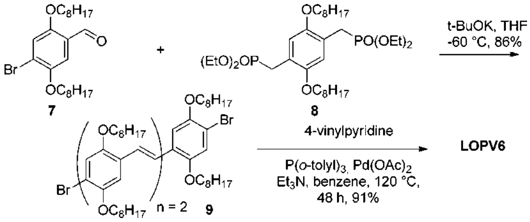
Chromophores **SOPV2−7** and **LOPV2−5,7** were prepared according to two different strategies. The first one, used for the synthesis of **SOPV2−5** and **LOPV2−5**, consisted of a Knoevenagel condensation between commercially available aldehydes **SOPV1** or **LOPV1** and the corresponding acceptors **2−5** (Scheme 1). Knoevenagel reactions furnished all dyes with yields ranging from 67 to 93%. The same procedure was used for all condensations, except for **SOPV5** and **LOPV5** for which highly sterically hindered acceptor **5** was used (see Supporting Information).

Scheme 1. Routes to Oligomers **SOPV2−5** and **LOPV2−5**



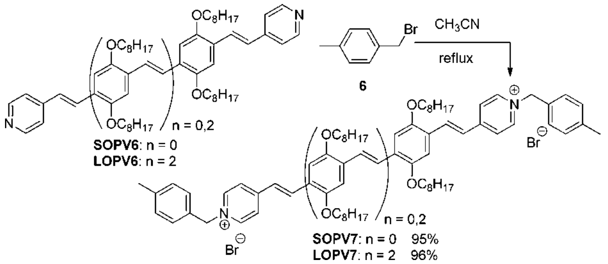
SOPV6 was prepared according to a synthesis reported in the literature,[9] and extended **LOPV6** was obtained in two steps following the procedure shown in Scheme 2. In the first step, **9** was synthesized using a Horner−Wadsworth−Emmons olefination, starting from **7**[9] and **8**,[11] and isolated in 86% yield. Then, the synthesis of **LOPV6** relied upon a symmetrical Heck cross-coupling reaction. Coupling of **9** with 4-vinylpyridine in the presence of $Pd(OAc)_2$, Et_3N, and $P(o\text{-tolyl})_3$ in a benzene/water (1/1) mixture at 120 °C provided oligomer **LOPV6** in 91% yield.

Scheme 2. Synthesis of Extended Oligomer **LOPV6**



Oligomers **SOPV7** and **LOPV7** were synthesized by alkylation of dipyridines **SOPV6** and **LOPV6** with 4-methylbenzyl bromide **6** (Scheme 3). **6** was used in this study indeed to strengthen the accepting ability of the accepting fragments of the oligomers but also as a model capable to mimic 4-mercaptobenzyl bromide that will be subsequently used to functionalize **SOPV6** and **LOPV6** for Self-Assembled Monolayer (SAM) applications.

Scheme 3. Routes to Oligomers **SOPV7** and **LOPV7**



Optical properties of **SOPV1−7** and **LOPV1−7** were investigated by means of UV−visible and fluorescence spectroscopies in solution and in the solid state. All spectroscopic results with fluorescence quantum yields are summarized in Table 1. All dyes showed a strong intramolecular charge transfer (ICT) absorption band in the visible region with maximum position ranging from 398 nm for **SOPV6** to 542 nm for **SOPV5** in CH_2Cl_2. Long OPVs, which possess a stronger electron-releasing group, exhibit

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Table 1. Electrochemical and Photophysical Data of **9** and Oligomers **SOPV1−7** and **LOPV1−7**

compd	λ_{abs} [nm][b]	log ε	λ_{em} [nm][c]	$Ø_F$[d]	τ (ns)[e]	Stokes shift [nm]	ΔE (eV)[f]	λ_{abs} [nm][g]	λ_{em} [nm][h]	$E°_{red}$ (1) [V][i]	$E°_{red}$ (2) [V][i]	ΔE_{red} (1) [V][i]	ΔE_{red} (2) [V][i]
SOPV1[a]	403	2.47	467	0.40	$<10^{-3}$	64	3.07	n.m.	n.m.	n.o.	n.o.	n.o.	n.o.
LOPV1[a]	449	4.73	521	1	1.77	72	2.76	444	556	−1.85	n.o.	0.21	n.o.
9	410	4.72	467	0.36	$<10^{-3}$	57	3.02	416	507	n.o.	n.o.	n.o.	n.o.
SOPV2	477	2.90	564	1.67	9.72	87	2.60	472	567	−1.02	−1.31	0.21	0.21
SOPV3	512	4.30	622	1.34	5.40	110	2.42	530	696	−0.97	−1.56	0.17	0.12
SOPV4	548	4.37	n.o.	n.d.	n.d.	n.d.	2.26	n.m.	n.m.	−0.85	−1.41	0.23	0.24
SOPV5	542	4.31	n.o.	n.d.	n.d.	n.d.	2.28	555	n.o.	−0.61	−1.70	0.60	0.33
SOPV6	398	4.50	470	1.22	$<10^{-3}$	72	3.11	430	484	-0.99^{irr}	n.o.	n.d.	n.o.
SOPV7	490	4.52	616	0.25	1.23	126	2.53	n.m.	n.m.	−1.10	n.o.	0.26	n.o.
LOPV2	518	4.90	624	0.25	1.89	106	2.39	n.m.	n.m.	−1.49	n.o.	0.17	n.o.
LOPV3	550	4.95	662	0.09	1.22	112	2.25	n.m.	n.m.	−1.40	n.o.	0.09	n.o.
LOPV4	611	4.85	765	<0.01	n.d.	154	2.03	n.m.	n.m.	-1.27^{irr}	n.o.	0.42	n.o.
LOPV5	640	4.73	n.o.	n.d.	n.d.	n.d.	1.93	n.m.	n.m.	−0.96	n.o.	0.20	n.o.
LOPV6	452	4.94	570	0.07	1.27	118	2.74	n.o.	n.m.	-1.24^{irr}	n.o.	0.40	n.o.
LOPV7	535	4.22	n.o.	n.d.	n.d.	n.d.	2.32	n.m.	n.m.	−1.30	n.o.	0.20	n.o.

[a] Compounds **SOPV1** and **LOPV1** were purchased from Aldrich and used as supplied commercially. n.d.: not determined. n.m.: not measured. n.o.: not observed. [b] Absorption maximum in CH_2Cl_2. [c] Emission maximum in CH_2Cl_2. [d] Fluorescence quantum yield in CH_2Cl_2. Compound **LOPV1** was used as a standard (λ_{ex} = 495 nm). $Ø_F$(**LOPV1**) = 0.48 in toluene,[15] $Ø_F$(**LOPV1**) = 0.52 measured in CH_2Cl_2. [e] Fluorescence lifetime. [f] Optical band gap determined in CH_2Cl_2. [g] Solid state absorption maximum. [h] Solid state emission maximum. [i] CV in DMF on gold electrode vs Ag/AgCl, with Bu_4NPF_6 (0.1 M) as supporting electrolyte. Scan rate: 100 mV/s. $E°_{red}$ is the reduction standard potential, while ΔE_{red} *is the peak to peak potential difference for each redox signal.*

red-shifted ICT bands with maxima ranging from 452 nm for **LOPV6** to 640 nm for **LOPV5** in the same solvent (Figure 1). As expected for each series, a bathochromic shift of the charge transfer band is observed when the electron-withdrawing power of the acceptor increases. Replacement of aldehydes in **SOPV1** and **LOPV1** by the strong electron acceptor **5** leads to bathochromic shifts as large as 139 nm for short OPVs and 191 nm for the long ones. Compared to results obtained in the literature by substitution of methyl groups by cyano groups (shift of 60 nm)[8b] or nitro groups (shift of 50 nm)[6] in OPVs similar to **LOPV1**, dyes reported in this letter exhibit much larger shifts. In addition, by using the electron acceptor power as a tool to modulate the position of the ICT band, progressive substitution of the aldehyde functions in **SOPV1** and **LOPV1** by a series of acceptors leads to dyes able to partially cover the visible region (from 398 nm for **SOPV6** to 640 nm for **LOPV5**).

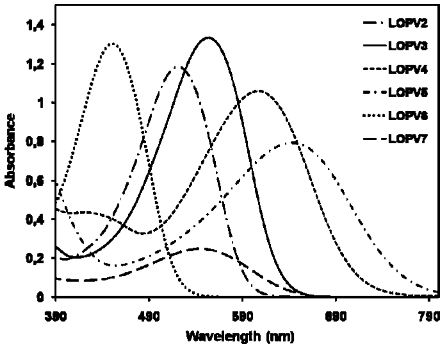

Figure 1. Absorption spectra of **LOPV2−7** recorded in CH_2Cl_2.

The solvatochromic behavior was investigated for all dyes. The largest shift of the position of the ICT absorption band was observed for **SOPV4** with $\Delta\lambda$ = 73 nm. A pronounced solvatochromism was observed for all dyes, except for **SOPV6** ($\Delta\lambda$ = 10 nm) and **LOPV7** ($\Delta\lambda$ = 16 nm), either containing pyridines or pyridiniums as electron acceptors. Examination of the solvatochromism revealed a good correlation with the solvent parameters π^* determined by Kamlet and Taft.[11] A negative solvatochromism was observed for all dyes except for **SOPV6** and **SOPV7**. Surprisingly, the unexpected behavior evidenced for **SOPV6** and **SOPV7** was not observed with the corresponding extended **LOPV6** and **LOPV7**.

Fluorescence spectra of dyes were recorded in solvents of varying polarity at 495 nm. Similar results were obtained with degassed and nondegassed solutions. All investigated dyes exhibited intense fluorescence at room temperature with maxima ranging from 470 nm for **SOPV6** to 765 nm for **LOPV4** in CH_2Cl_2, except for three dyes (**SOPV4,5** and **LOPV5**) for which no emission was detected. Fluorescence properties of **SOPV1−3,6,7** and **LOPV1−4,6,7** are similar to that reported for analogue systems. A significant decrease of the photoluminescence quantum yields is observed at room temperature when the conjugation length is increased.[5,12] As already mentioned above for absorption measurements, an increase of the accepting ability of the acceptor substituents induces a large red shift of the maximum fluorescence wavelength as illustrated with **LOPV3** (λ_{em} = 662 nm) and **LOPV4** (λ_{em} = 765 nm) in CH_2Cl_2. Similarly, when the power of the donor fragment increases, significant bathochromic shifts are observed as

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illustrated with **SOPV6** and **LOPV6** ($\Delta\lambda_{em} = 100$ nm in CH_2Cl_2).

The effect of the solvent polarity on the position of the maximum fluorescence wavelength was also investigated (see Supporting Information). An increase of the polarity induced a red shift of the maxima for all dyes and resulted in larger Stokes shifts, except for **LOPV6** and **LOPV7**. An increase of the Stokes shift with the polarity of the solvent is indicative of significant charge redistribution upon excitation.[13] Among all the dyes studied in this letter, **LOPV6** is the chromophore presenting the largest Stokes shifts, ranging from 118 nm in CH_2Cl_2 to 183 nm in dioxane. Solid state photoluminescence investigations revealed a red shift of the emission maxima compared to the ones obtained in solution, therefore illustrating intermolecular interactions such as π-stacking.[14]

Electrochemical behavior of all dyes was investigated by cyclic voltammetry (CV) in DMF on a gold electrode. The resulting redox potentials are gathered in Table 1. As expected, the reduction potentials shift positively with the increasing withdrawing power of the terminal substituents (e.g., from **2** to **5**). However, it can be emphasized that short and long OPV derivatives have very different electrochemical features (see Figure 2): SOPVs show two distinct and well separated redox waves, while LOPVs display only one wave at a significantly more negative potential. The SOPV behavior looks like the one of quinone derivatives, i.e., typical of two identical redox moieties in close intramolecular interactions; thus, addition of the second electron is made notably more difficult than the first by the electrostatic repulsion, resulting in a negative shift. The difference between the two successive reduction potentials is slightly lower than in the case of a phenyl linker (e.g., 0.58 V for TCNQ vs 0.29 V[15] for **SOPV2**) and much less than for similar compounds with an EDOT linker.[16] Conversely, in LOPV derivatives, this interaction becomes much smaller because the bridge does not favor electronic communication, probably because of the donor effect of the *O*-alkyl side chains and distortion from planarity. Thus, only one redox wave can be seen on the voltammograms, as in noninteracting symmetrical systems, occurring unsurprisingly at a more positive value than for similar OPVs without terminal accepting groups.[17] Nevertheless, the noticeable more negative potential for this reduction compared to analogous SOPVs is wondering, as well as the relative peak currents that do not scale with a two-electron reduction for LOPVs. We assumed that possible interactions with the electrode surface could be the reason for this behavior. Actually, albeit not dependent on the electrode material, the shape of the cyclovoltammogram is altered upon decreasing the concentration. In that case, the reduction peak splits into two close but distinguished signals (see Supporting Information), confirming that the two redox moieties in LOPVs are actually reduced at nearly the same potential. For most of these systems, the reversibility is moderate in the conditions of investigations, and electrochemical kinetics are rather sluggish as illustrated by the high value of peak-to-peak potential differences.

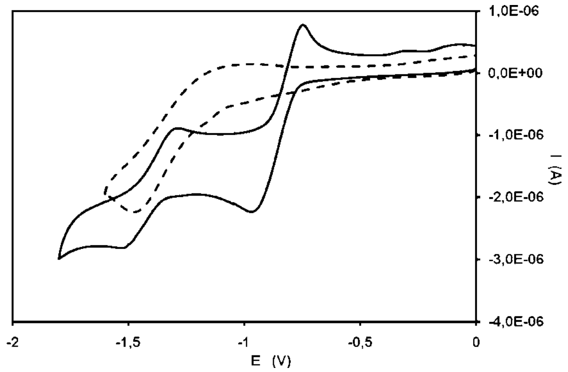

Figure 2. Reduction waves of **LOPV4** (dashed line) and **SOPV4** (solid line).

To summarize, a series of 11 new chromophores covering the visible region have been designed and synthesized in high yields. The absorption and emission properties of these chromophores were efficiently controlled by tuning both the acceptor power of the acceptor substituents in the oligomers and the length of the conjugated electron-releasing core. Strong solvatochromism was also evidenced for both absorption and emission. Finally, specificities of their electrochemical behavior were investigated.

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Supporting Information Available: Experimental procedures and spectroscopic characterizations for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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