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Synthesis, Photonic Characteristics, and Mesomorphism of an Oligo Biphenylene Vinylene π-Electron System

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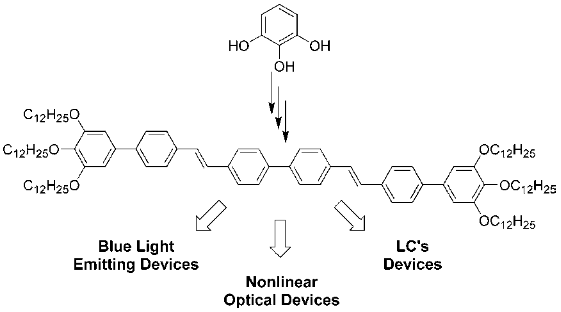
ABSTRACT



The synthesis and photonic and liquid-crystalline properties of a novel oligo biphenylene vinylene (OBV) chromophore with an extended π-electron system are reported; the compound exhibits high fluorescence, a large two-photon absorption cross-section, and two- and three-dimensional liquid-crystalline mesophases.

Conjugated organic materials have attracted considerable attention in recent years due to numerous potential applications in various fields such as light-emitting diodes,[1] photovoltaic cells,[2] optical power limiting,[3] three-dimensional microfabrication,[4] and two-photon laser scanning fluorescence imaging.[5] To date, many types of organic materials have been designed and fabricated for this purpose, most of which have a linear molecular shape, such as oligo(phenylenevinylene) (OPV),[6] oligo(*p*-phenylene) (OPP),[7] oligo(phenyleneethynylene) (OPE),[8] and oligo(thiophene) (OT).[9] Their particular electronic properties led us to the design of a conjugated organic oligo biphenylene vinylene (OBV) molecule based on biphenylene motifs linked together

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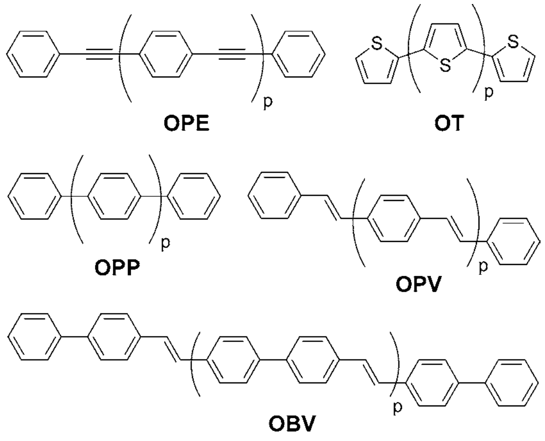
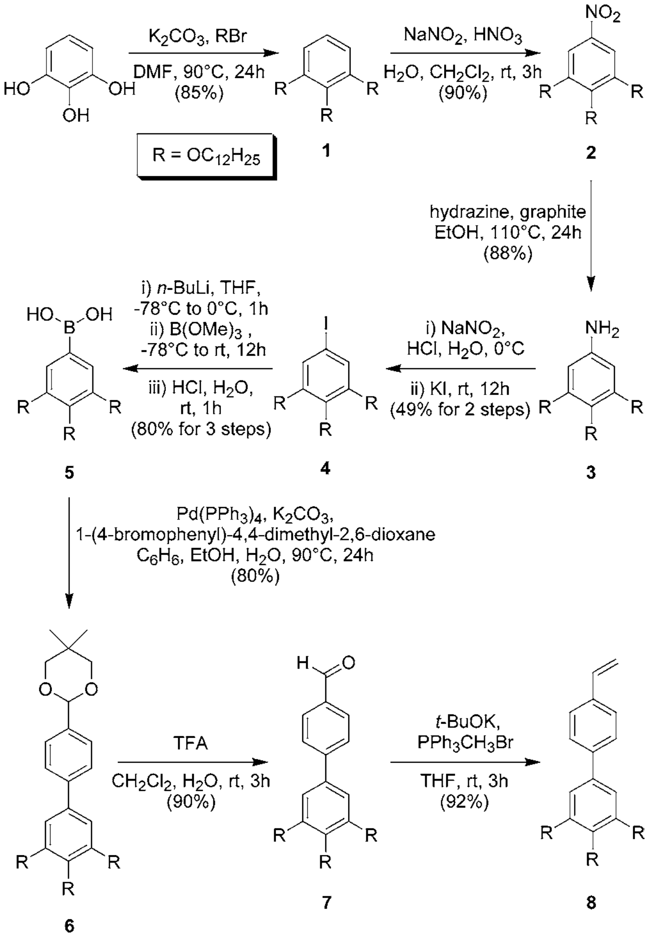
through double bonds. Such a novel molecular structure may lead to promising applications for light-emitting and nonlinear optical devices.



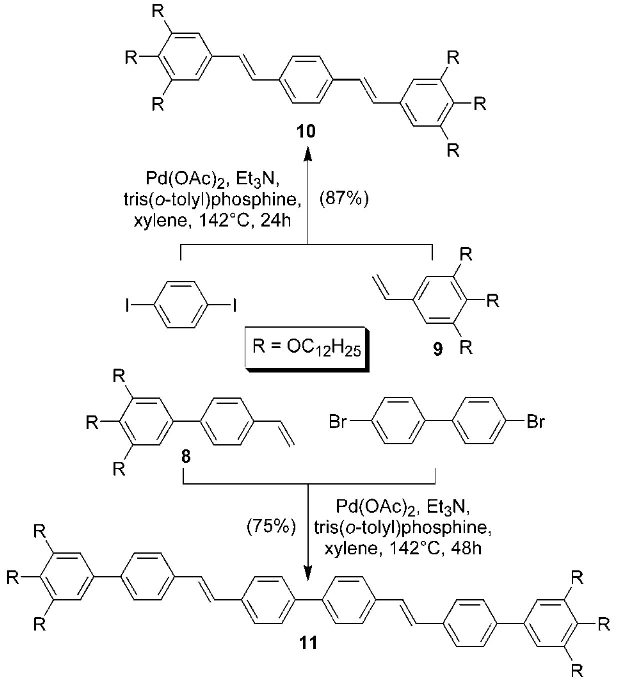
In this paper, we report on the synthesis of two hexacatenar molecules (mesogens with a long rigid core bearing three aliphatic chains at both extremities),[10] the OBV-3 **11** and the OPV analogue **10**, their one- and two-photon properties, and their thermal behavior.

The synthetic approach for both OPV and OBV motifs relies upon a symmetrical bis Heck reaction. Such a cross-coupling is known to be efficient to form C−C connections between two sp^2 carbons and highly stereoselective (mainly the (*E*)-stereoisomer is obtained) contrary to other methods used for the preparation of stilbenyl compounds.

Scheme 1. Synthesis of the Building Block **8**



Scheme 2. Preparation of the OPV **10** and OBV **11**



Since the direct halogenation of **1**, obtained from pyrogallol, did not lead to the expected compound **4**, another synthetic strategy for functionalization of pyrogallol derivative **1** in position 5 was envisaged. It started by the nitration of **1** with sodium nitrite and nitric acid in a biphasic medium H_2O/CH_2Cl_2 (Scheme 1). Subsequent reduction of **2** using the graphite−hydrazine system led to the corresponding aniline derivative **3**, which was then successfully converted into the iodo derivative 3,4,5-tridodecyloxyiodobenzene **4** by a Sandmeyer reaction. Despite moderate yields (50%), gram-scale materials could nevertheless be prepared. The boronic acid **5** was prepared according to the classical “one-pot” synthesis. To avoid spontaneous dehydration, leading to trimerization,[11] the acid was used immediately. To facilitate the purification of the resulting biphenyl product **7**, and thus to increase the reaction yield, in our hands it appeared judicious, prior to the Suzuki coupling reaction, to modify the polarity of the aldehyde adduct by converting the aldehyde function in acetal. Coupling **5** and 1-(4-bromophenyl)-4,4-dimethyl-2,6-dioxane in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in a $C_6H_6/EtOH/H_2O$ (2/1/1) mixture at 90 °C led to intermediate **6** in high yield (90%). After purification, **6** is hydrolyzed by treatment with TFA in the

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CH_2Cl_2/H_2O mixture to generate the corresponding aldehyde **7**. Despite the strong acidity of the reaction mixture, no secondary product formation was observed. The key precursor 3,4,5-tridodecyloxy-*p*-phenylstyrene **8** was formed by reaction of **7** in THF with phosphorus ylide formed in situ by addition of *t*-BuOK on commercially available methyltriphenylphosphonium bromide.

Both the OBV-3 (**11**) and OPV-3 (**10**) compounds were prepared from Heck coupling between **8** and 4,4′-dibromobiphenyl and between **9**[12] and 1,4-diiodobenzene, respectively (Scheme 2).

The UV absorption/emission properties of these compounds were investigated, and the typical one-photon absorption and fluorescence spectra of **10** and **11** are shown in Figure 1.

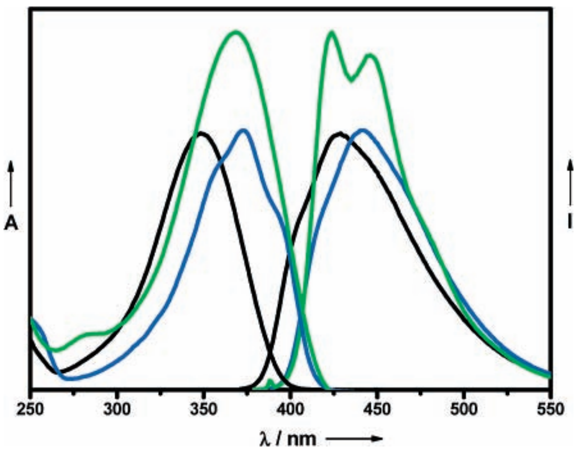

Figure 1. Linear absorption (*A*) and fluorescence (*I*) spectra of commercially available **stilbene-420** (black) reference in water, **10** (blue), and **11** (green) in CH_2Cl_2 ($c = 10^{-5}$ mol L^{-1}).

Both hexacatenars **10** and **11** are highly fluorescent in solution and in the solid state. The absorption maximum of **11** ($\lambda_{max} = 369$ nm) is slightly blue-shifted (4 nm) with respect to that of **10** ($\lambda_{max} = 373$ nm) (Table 1). The absorption and emission bands of **11** are broadened and intense. It is also interesting to note that **11** has an inherently higher solution fluorescence quantum yield than **10** and emits with a clear deep blue light. Given this, such systems may be regarded as potentially promising candidates for blue-emitting layers in electroluminescent devices.

Table 1. Photophysical Data of **10** and **11** in CH_2Cl_2

photophysical data	**stilbene-420**	**10**	**11**
λ_{abs} [nm][a]	348	373	369
log ϵ	4.80	4.81	4.95
λ_{ex} [nm][a]	361	379	396
λ_{em} [nm][b]	429	442	424 (444)
$fwhm_{abs}$ (width)[nm][c]	61.2 (55.5)	63.4 (60.5)	71.0 (63.0)
$fwhm_{em}$ (width)[nm][c]	83.8 (79.0)	68.8 (74.0)	68.2 (60.0)
Φ_f[d]	0.64	0.77	0.93
Stokes shift [nm]	81	69	55 (75)
β [cm/GW][e]	0.3	2.0	4.8
σ_2TPA [10^{-20} cm^4 GW^{-1}]	5.0	33.4	80.0
σ_2'TPA [GM][f]	124	832	1992

[a] Only the largest absorption maxima are listed. [b] Wavelength of emission maximum when excited at the absorption maximum. [c] Full widths at half maximum. [d] Quantum efficiencies using fluorescein in 0.1 N NaOH as a standard.[16] [e] $\beta = \sigma_2 N_A d \times 10^{-3}$ where N_A is the Avogadro constant and d the concentration of the TPA compound in the solution.[17] [f] σ_2' [GM] $\approx 24.9\sigma_2$ [10^{-20} cm^4 GW^{-1}]. 1GM (Goppert−Mayer) = 10^{-50} cm^4 s photon^{-1} molecule^{-1}.

It has been observed by various groups recently that symmetrical linear conjugated molecules bearing donor groups at each end, so-called "push-push", can display high nonlinear absorption behavior characterized by large two-photon absorption (TPA) cross-section σ_2 values.[13] In particular, **stilbene-420** has been shown to present good optical limiting properties in concentrated solutions due to multiphoton absorption.[14] We have investigated the TPA properties of the OBV and OPV derivatives using 150 fs pulses delivered by a Ti:sapphire amplified laser operating at a wavelength of 790 nm with a repetition rate of 5 kHz. The typical measured nonlinear transmission curves obtained for the **stilbene-420** reference, **10**, and **11** are shown in Figure 2.

With basic theoretical considerations and taking into account the spatial (transverse) Gaussian distribution and a Gaussian temporal shape for the pulse, the TPA coefficient β and the corresponding σ_2 can be obtained from the curves of Figure 2.[15] The nonlinear photophysical data of **10** and **11** are summarized in Table 1 and compared to **stilbene-420**. It appears clearly that the new OBV derivative **11** leads to an improved σ_2 in comparison with the OPV analogue **10**. This result supports our molecular engineering strategy for finding new and very efficient TPA chromophores.

Due to their structures and with respect to criteria compatible for LC-phase formation, the thermal behavior of compounds **10** and **11** was investigated using thermal optical polarized microscopy, DSC, and X-ray diffraction.

Due to the longer size of the biphenylene building units, the molecular anisotropy necessary for mesophase induction is more readily attainable with OBV compound **11** than with OPV compound **10**. And indeed, only the polycatenar triblock molecule **11** exhibits mesophases over wide temperature ranges, whereas **10** melts directly into the isotropic

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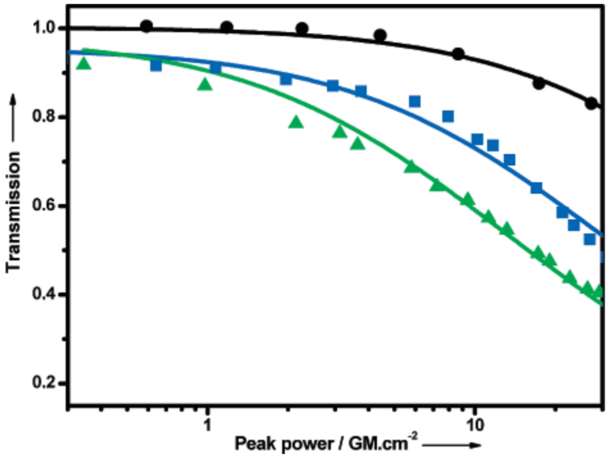

Figure 2. Nonlinear transmission of **stilbene-420** (black circle) reference in water, **10** (blue square), and **11** (green triangle) in CH_2Cl_2 ($c = 10^{-2}$ mol L^{-1}). The continuous lines are the best fit to a TPA law (see Supporting Information).

liquid at 59 °C. The transition temperatures and the corresponding enthalpy changes determined from DSC scans are recorded in Table 2.

Table 2. Thermal Behavior of **11**

11	transition temperatures (°C) [ΔH (kJ mol^{-1})]
heating	Cr 64.4 [2.4], M_{tet} 143.2 [0.8], Col_h 155.6 [0.1]
cooling	I 157.1 [0.1], Col_h 148.5 [0.8], M_{tet} 31.0 G

Cr, crystalline phase; G, glassy state; I, isotropic liquid; Col_h, hexagonal columnar phase; M_{tet}, three-dimensional body-centered tetragonal phase.

The liquid-crystalline behavior was probed by the observation under polarized optical microscopy of unusual textures showing birefringent and fluid domains, coalescing into a uniform monodomain on increasing the temperature, and by small-angle X-ray diffraction studies. A typical texture exhibited by **11** is shown in Figure 3. On slow cooling from the isotropic liquid, a homeotropic texture is developed for the columnar hexagonal phase. On further cooling, the formation of beautiful fernlike domains growing from the latter along two or three preferential directions was observed. These domains then merged into an unusual hexagonal shape mosaic texture with perfectly defined edges. On cooling, this phase is frozen into a glassy state. X-ray diffraction analysis confirmed the presence of two mesophases: at high temperature, a columnar phase with a two-dimensional hexagonal lattice, the Col_h phase ($a = 46.4$ Å), and at lower temperature, another mesophase, M_{tet}, characterized by a three-dimensional body-centered tetragonal space group ($a = 59.3$ Å, $c = 83.8$ Å). The presence of the large 4-fold symmetry defects observed all over the M_{tet} texture (Figure 3) is indeed compatible with a three-dimensional tetragonal symmetry.[18] For the Col_h phase, the classical model is proposed, involving the piling of clusters made of a few molecules.[10,19] In contrast, the supramolecular organization of the M_{tet} phase is more complicated and may resemble the micellar model proposed in rod-coil systems.[20] It would then consist of the formation of clusters containing a few molecules, these aggregates being localized at the nodes of a three-dimensional tetragonal lattice (one in the center and one on the corner).

Figure 3. Representative optical textures of the three-dimensional body-centered tetragonal mesophase of **11** at 147 °C obtained by cooling from the Col_h mesophase.

In summary, a new conjugated organic material based on biphenylene vinylene motifs has been synthesized. In contrast to the OPV-3 analogue, the OBV-3 hexacatenar **11** exhibited a columnar hexagonal phase and an unusual three-dimensional phase with a body-centered tetragonal symmetry. The good one- and two-photon optical properties of **11** strongly suggest that such materials can be considered as attractive components for the elaboration of photoactive materials.

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

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