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Oligophenylenevinylenes in Spatially Confined Nanochannels: Monitoring Intermolecular Interactions by UV/Vis and Raman Spectroscopy**

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Perhydrotriphenylene-based channel-forming inclusion compounds (ICs) and thin films made of polyphenylenevinylene (PPV)-type oligomers with terminal alkoxy groups are investigated and compared in a combined experimental and theoretical approach. Interchromophore interactions and host-guest interactions are elucidated by UV/Vis and Raman spectroscopy. The impact of the local environment of the chromophore on the optical and photophysical properties is discussed in light of quantum-chemical calculations. In stark contrast to thin films where preferential side-by-side orientation leads to quenching of photoluminescence (PL) via non-emissive traps, the ICs are found to be attractive materials for opto-electronic applications: they offer high chromophore concentrations, but at the same time behave as quasi-isolated entities of tightly packed, well-oriented objects with high PL quantum yields and the possibility of color tuning.

1. Introduction

Polyphenylenevinylene (PPV) derivatives are attractive materials for optoelectronic applications. A main limitation for

their widespread applications is the rather low efficiency of light emission^[1] due to the unfavorable side-by-side organization of the polymer chains.^[2] This leads to a reduced photoluminescence quantum yield in films, compared to isolated molecules in solution, since the high exciton mobility in tightly packed systems opens alternative non-radiative deactivation pathways from structural and chemical defects. One approach to overcome this problem is to introduce disorder in a systematic way, such as by appropriate side-chain substitution.^[3] Due to the weakness of the van der Waals interactions, however, such molecular materials exhibit distributions of packing structures and spatial arrangements that cannot be fully controlled by the synthetic route and, in general, the intrinsic anisotropy of the emitted light is lost in these systems. Supramolecular approaches, such as by the use of conjugated rotaxanes^[4], have been used successfully to reduce the intermolecular interactions between conjugated chains and therefore improve their luminescence and charge-transport properties. An alternative approach is to include the molecules in all-organic channel-forming host compounds, such as perhydrotriphenylene (PHTP) (see Fig. 1), with

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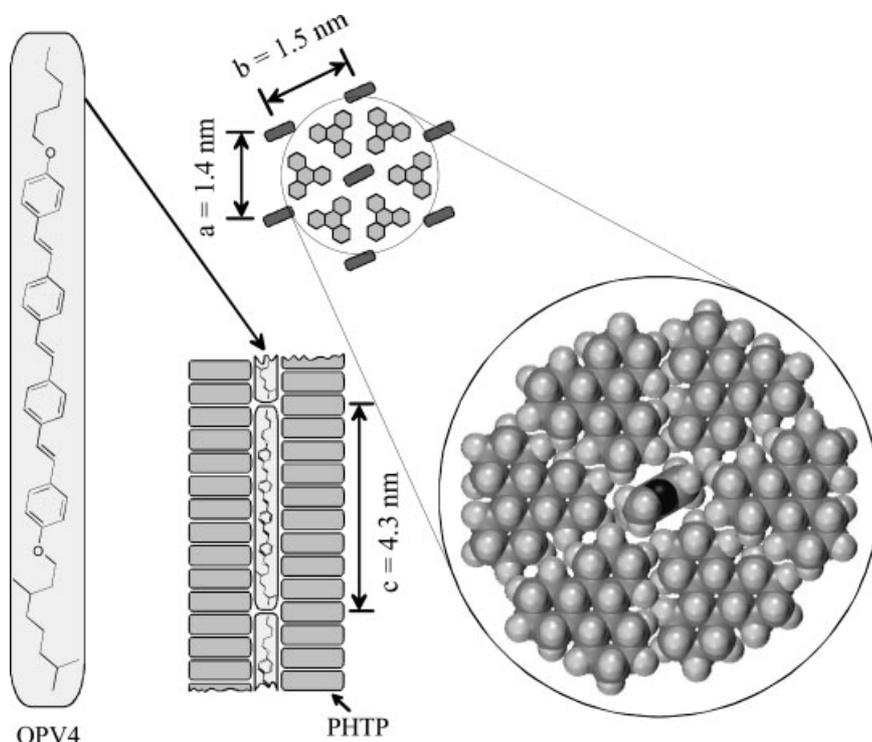


Figure 1. Structure of the OPV4 PHTP inclusion compound (top view and side view along the channels).

channel diameters that do not allow for molecular aggregation.^[5,6] The guest structure, and hence its properties, are dictated by the interactions of the molecules with the surrounding host. The typical interchannel distances of 14–15 Å in such nanostructures prevent unfavorable side-by-side interactions. In this way, highly luminescent^[7,8] and at the same time highly anisotropic materials can be prepared.^[9]

In these systems, the extent of guest-guest^[10] and host-guest interactions as well as their influence on the electronic and vibrational properties of the guest molecule is still an open question. In this contribution, we address these issues in the case of a four-ring model PPV oligomer, OPV4 (Fig. 1), with terminal alkoxy substituents acting as spacers to minimize head-to-tail interactions. Guest-guest and host-guest interactions are investigated by UV/Vis absorption, photoluminescence (PL), and, especially, Raman spectroscopy, which is shown to be a useful tool to probe molecular environments. The description afforded by such spectroscopic investigations is supported by the results of quantum-chemical calculations.

2. Results and Discussion

2.1. Optical and Photophysical Properties

2.1.1. Inclusion Compounds (ICs)

The absorption and photoluminescence spectra of OPV4 ICs at different temperatures are presented in Figure 2a. The room-temperature spectra show a vibronic progression, better

resolved than in solution, which is due to the well-defined and rigid environment within the channels of the PHTP host compound.^[11] The long low-energy tail in the absorption spectra is due to light scattering at the crystal surface of the IC. Upon cooling to 4 K, the photoluminescence of the IC shows spectral narrowing and a red-shift of about 200 cm⁻¹. The red-shift is ascribed to a change in the polarizability of the PHTP matrix due to an increase in the density of the material,^[12] whereas planarization of the conjugated backbone plays only a minor role due to an – in any case – planar S₁ state.^[11,13] The increase in the relative intensity of the 0–0 emission band upon cooling is also observed for highly diluted solutions due to the reduction of inhomogeneous broadening.^[11] In the IC, reduction of self-absorption effects induced by narrowing of the 0–0 absorption and emission bands also contributes to this relative increase in intensity (see inset of Fig. 2a).

The features characteristic of OPV4 ICs are also found for the five-ring OPV5 oligomer, even though the spectral positions are red-shifted by 900 cm⁻¹ due to the extension of the conjugation backbone.

A closer inspection of the low-temperature photoluminescence spectra of OPV4 is presented in Figure 3, in which the IC emission spectrum is compared to that of the unsubstituted oligomer (*p*-distyrylstilbene (DSS)) in dilute solid (frozen) solution and with the results of quantum-chemical calculations. The spectral features observed in solid solution originate from the coupling of totally symmetrical vibrational modes to the electronic transition.^[11] The spectrum of DSS simulated with the Hartree-Fock (HF)/Restricted Configuration Interaction scheme involving Singly excited configurations (RCIS) method is in excellent agreement with the corresponding experimental spectrum (Fig. 3), as long as the vibrational frequencies ν_i are scaled in order to account for the systematic overestimation of ν_i by the HF method. The observed red-shift of the experimental spectrum compared to the calculated one is entirely due to solvent effects, as it was demonstrated for the HF/RCIS method for this class of compounds in ref.^[11] Density functional theory (DFT) is less time-consuming and much more accurate in calculating vibrational properties. (Time-dependent) DFT ((TD-)DFT) is therefore an attractive method for calculating the electronic spectra within a single approach. The spectrum calculated for the substituted OPV4 oligomer (Fig. 3) is identical to that of DSS, demonstrating that the alkoxy substituents do not participate in the geometric changes induced upon electronic excitation. The calculated spectrum is in reasonable agreement with experiment, see Fig. 3; however, it is not as accurate as the Hartree-Fock

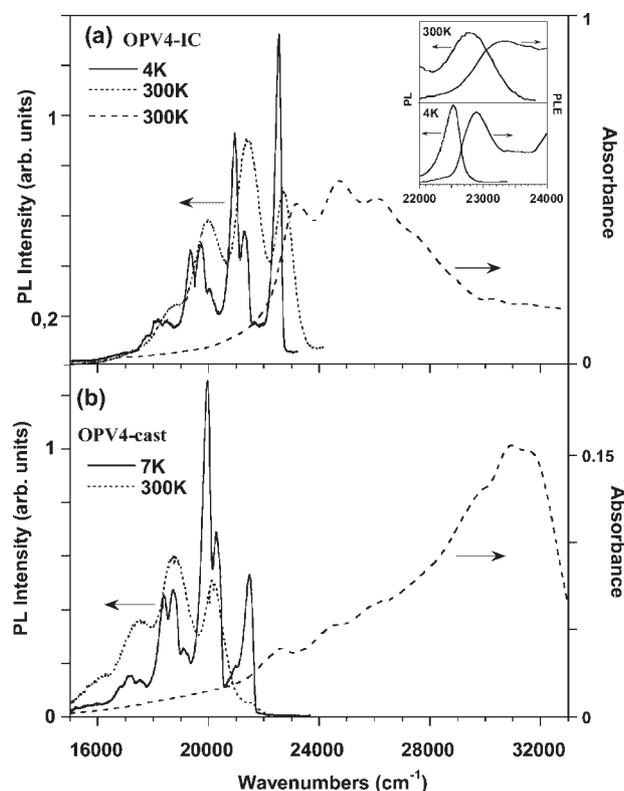


Figure 2. Photoluminescence and absorption spectra of OPV4 inclusion compounds (a) and cast films (b) at room temperature (dotted lines) and low temperature (solid lines). In the inset of (a), the PL and photoluminescence excitation (PLE) profiles of OPV4-IC in the 0–0 spectral region is reported at two different temperatures to evidence the variation in the overlap between the absorption and emission spectra. The PL spectra are scaled to similar intensities for clarity.

calculations since DFT underestimates the reorganization energy and hence the intensity of the higher-lying vibronic transitions.

The spectrum of the OPV4 IC is very similar to the DSS spectrum in solid solution, indicating that no contribution from intermolecular vibronic coupling is apparent in the OPV4 IC spectrum. The reorganization energy $\Delta\nu$ of the spectrum $I(\nu)$, which corresponds to the difference between the vertical (ν_{vert}) and adiabatic transition energy (electronic origin, ν_{00}),^[11]

$$\Delta\nu = \frac{\int I(\nu)\nu d\nu}{\int I(\nu)d\nu} - \nu_{00}, \quad (1)$$

is easily estimated by looking at the features around 1500 cm^{-1} below ν_{00} . They are found to be less intense in the ICs compared to DSS in solution, thus pointing to changes in the electronic coupling with the a_g vibrational modes in this spectral region (*vide infra*). The red-shift of the OPV4 IC spectrum compared to that of DSS in solid solution by 480 cm^{-1} , both recorded at low temperatures (Fig. 3) is reminiscent of the red-shift of 500 cm^{-1} between OPV4 and DSS in hexadecane solutions at room temperature. It is mostly due to the electron-donating positive mesomeric

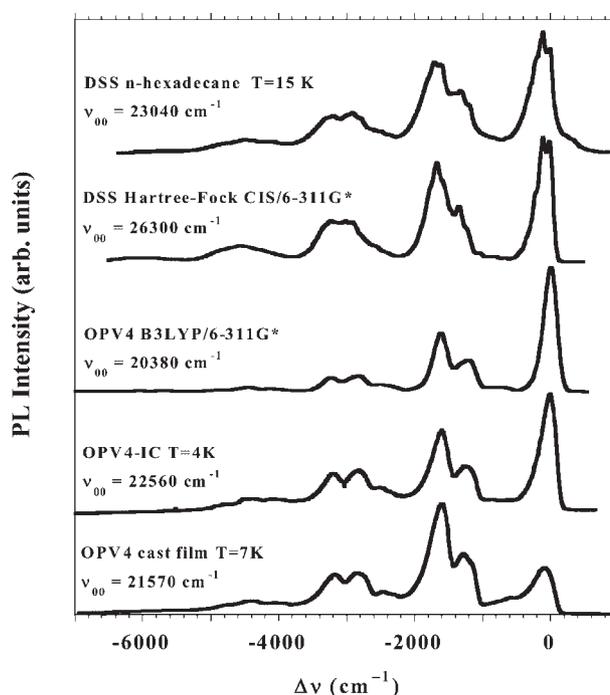


Figure 3. Photoluminescence spectra of the unsubstituted (DSS) and alkoxy-substituted (OPV4) four-ring oligomer. From bottom to top: cast film of OPV4 at 7 K; inclusion compound of OPV4 at 4 K; calculated spectrum of OPV4 at the B3LYP/6-311G* level of theory; calculated spectrum of DSS at the Hartree-Fock CIS/6-311G* level; ^[11] experimental spectrum of DSS in *n*-hexadecane at 15 K. For better comparison, the abscissa scale is normalized to the electronic origin ν_{00} .

(+M) effect of the terminal alkoxy substituents that induce a shift of 590 cm^{-1} estimated at the TD-DFT level of theory. The almost-identical shifts observed for OPV4 in solution and in the IC compared to DSS clearly demonstrate that the OPV4 molecules in the channels of PHTP have to be considered as quasi-isolated entities due to the large interchannel separations of 15 \AA and large intrachannel separation induced by the terminal alkoxy spacers.^[14] This makes inclusion compounds highly attractive, since the solution properties are conserved, although the molar concentration is estimated to be as high as 0.23 mol L^{-1} (this corresponds to a host-guest ratio of 18.2:1). The creation of quasi-isolated entities in the solid state is further confirmed by the photophysical properties: the PL quantum yield of the ICs as well as their decay times are close to the values in solution, see Table 1.

2.1.2. Thin Films

The absorption and photoluminescence spectra of an OPV4 cast film are shown in Figure 2b. The absorption spectrum is highly asymmetric and blue-shifted with respect to the IC spectrum. The shape matches the absorption characteristics of H-aggregates observed for all molecular crystals with a preferential parallel orientation of the $S_0 \rightarrow S_1$ transition

Table 1. Photoluminescence quantum yields Φ_F and lifetimes τ of OPV4 and OPV5 at room temperature, in CH_2Cl_2 solution, in inclusion compounds, and in the solid state.

	Solution		Inclusion compound		Cast films
	Φ_F	τ	Φ_F	τ	
		[ns]		[ns]	
OPV4	0.95	0.94	0.84	0.74	0.13 ^[a] , 0.35
OPV5	insoluble	insoluble	0.74	0.65	0.40 ^[a] , 0.60

[a] KBr pellet.

dipole moments.^[15–17] This strongly suggests that the OPV4 molecules are also oriented in parallel in the films. The relative intensity of the 0–0 line in the emission spectrum of the OPV4 cast film is significantly reduced compared to the IC spectrum (Fig. 2 and 3). This cannot be ascribed to self-absorption effects since the absorption of the cast film is very weak at the low energy side of the spectrum, see Figure 2. According to quantum-chemical calculations performed by Spano^[18] and Meskers^[19] on molecules with preferential parallel orientations, the decrease in the 0–0 band intensity is related to a significant electronic coupling between the molecules, which spreads the excitation among neighboring molecules thus reducing coupling between delocalized electronic states and localized *intramolecular* vibrations. The electronic interactions are also responsible for the large red shift of the emission spectra by 990 cm^{-1} and 1150 cm^{-1} compared to those of the OPV4 and OPV5 ICs, respectively (Fig. 2). Except for the 0–0 features, the vibronic replicas of the cast films are found to be nearly identical to those of the inclusion compounds, see Figure 2 and 3. This indicates that no contribution of vibronic coupling with *intermolecular* vibrational modes is observed in these samples, thus giving strong evidence that the packing is of the ‘herringbone’ type rather than a cofacial arrangement.^[17] Indeed, the herringbone structure is observed in single crystals of the unsubstituted five-ring oligomer.^[20]

In contrast to the inclusion compounds, the PL quantum yields, Φ_F , in cast films are significantly lower and depend on the sample preparation conditions. $\Phi_F = 0.13$ is measured for OPV4 microcrystallites diluted in KBr pellets and $\Phi_F = 0.35$ for cast films deposited from chloroform solutions. A reduction in Φ_F is also observed for the five-ring oligomer, see Table 1. These values are in agreement with those reported in the literature for solid-state samples of the corresponding unsubstituted oligomers.^[21] Time-resolved PL of the cast films exhibits further differences compared to the ICs, showing strongly non-exponential decay curves that can be reasonably fitted by a biexponential decay with one very fast component. The results are consistent with the strong electronic coupling between the molecules in the solid state that promotes a high mobility of the excitations in the aggregated state. Therefore, excitation quenching at non-emissive traps is most likely to occur, thereby reducing the PL efficiency in the aggregates and introducing complex time-decay behavior.

2.2. Raman Spectra

Non-resonant Raman spectra of the OPV4 powder and IC recorded at an excitation wavelength of 1064 nm are shown in Figure 4. In the $1100\text{--}1700\text{ cm}^{-1}$ range, five characteristic vibrational bands are observed around 1180 , 1330 , 1550 , 1590 and 1630 cm^{-1} . The assignment of these bands provided by DFT calculations agrees essentially with those described in the literature for PPV-type materials.^[22,23] The four bands at lower energy can be assigned to a combination of C–C stretching in the phenylene and vinylene groups, with a strong admixture of C–H bending, see Table 2. The last one at 1630 cm^{-1} , predicted to be a doublet for OPV4 by the quantum-chemical calculations, is ascribed exclusively to a stretching of the vinylene group (Table 2). Very similar Raman spectra are obtained for the five-ring OPV5 oligomer for both the powder and IC.

The frequencies of the Raman modes of the IC differ slightly from those of the powder and feature a weak dependence on oligomer size. The main difference between the IC and the powder relates to changes in the intensity of the modes. While the three bands around 1590 cm^{-1} are almost unchanged, the intensity of ν_1 and ν_2 are significantly smaller in the IC, both for OPV4 and OPV5. Therefore, the intensity ratio between $\nu_1 \approx 1180\text{ cm}^{-1}$ and $\nu_4 \approx 1590\text{ cm}^{-1}$, I_1/I_4 , which decreases by more than 50% going from the powder to the IC (Table 3), can be used as a probe of the environment.^[24,25] Changes in the C–H bond lengths and angles are expected to be the most sensitive to environmental restrictions.^[26] Figure 5 depicts the normalized atomic displacements associated with both modes, as calculated at the DFT B3LYP/6-311G* level. The normal-

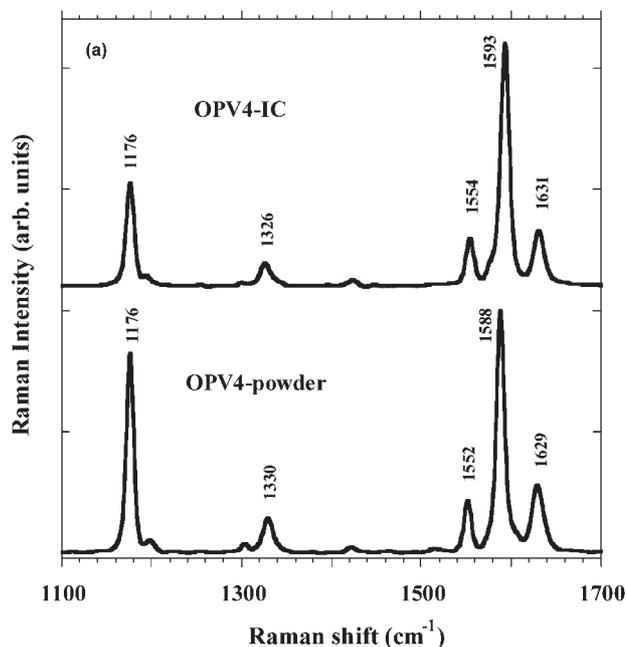


Figure 4. Raman spectra of OPV4 recorded on powder samples (bottom) and inclusion compounds (top). The intensity is normalized to the band at approximately 1590 cm^{-1} .

Table 2. Prominent Raman active modes (ν_i) of OPV4 in the 1100–1700 cm^{-1} range as calculated at the DFT B3LYP/6-311G* level of theory. Relative amplitudes q_i/q_4 are calculated according to Eq. (2). Experimental frequencies of OPV4 IC are given for comparison.

Mode	Frequency		Description: main contributions	Force constants [$\text{mdyn} \cdot \text{\AA}^{-1}$]	q_i/q_4
	[cm^{-1}]				
	exp.	calc.			
ν_1	1176	1193	phenylene & vinylene C–C stretching/bending; C–H-bending	1.852	1.7
ν_2	1326	1366	phenylene & vinylene C=C stretching; C–H-bending	1.532	2.0
ν_3	1554	1581	phenylene & vinylene C=C and C–C stretching/bending; C–H-bending	7.687	1
ν_4	1593	1626	phenylene & vinylene C=C and C–C stretching; C–H-bending	7.135	1
ν_{5a}	1631	1685	vinylene C=C and C–C stretching	8.185	1
ν_{5a}		1688	vinylene C=C and C–C stretching	8.239	1

ized vibrational patterns are very similar for the two modes and do not explain at a first glance the very unequal sensitivity of ν_1 and ν_4 . The main difference between the two modes is the magnitude of the force constant, with $k_1 = 1.852 \text{ mdyn} \text{ \AA}^{-1}$, and $k_4 = 7.135 \text{ mdyn} \text{ \AA}^{-1}$, respectively. The relative amplitude, expressed in normal coordinates,

$$\frac{q_i}{q_4} = \sqrt{\frac{\nu_i \cdot k_4}{\nu_4 \cdot k_i}} \quad (2)$$

gives a direct measure for the demanded cavity size of the vibrations. For ν_1 , the calculated amplitude ratio is $q_1/q_4 = 1.7$, see Table 2. Therefore, ν_1 will be much more sensitive than ν_4 (ratio of 1) to the very tight environment of the channel walls in the PHTP host system of the IC, where both host and guest molecules are in van der Waals contact. On the contrary, the proposed herringbone arrangement in the powder samples offers a less restricted space for the ν_1 mode, since the distance between the hydrogens and the adjacent molecule in the direction of the molecule's short axis (in the direction of the nuclear displacement of the hydrogens) is always $>3 \text{ \AA}$, that is to say, much larger than the van der Waals distance. The confinement is expected to be even less pronounced in solution, though this cannot be directly probed due to the fact that OPV4 is insoluble in CS_2 . Accordingly, a short unsubstituted oligomer, *trans*-stilbene (TS), which shows very similar Raman features compared to the longer oligomers,^[22] was used to evaluate the intensity of the Raman bands in solution. The I_1/I_4 intensity ratio of TS decreases in the series: solution $>$ powder $>$ IC (see Table 3), thus supporting the fact that the ν_1 mode is sensitive to

geometry restrictions imposed by the molecular environment.

The impact of the restricted environment of PHTP, as elucidated by the Raman results on large amplitude modes is consistent with the low-temperature PL data, as described in Section 2.1. Indeed the smaller Raman activity of the ν_1 and ν_2 vibrational modes leads to smaller reorganization energies. Complementary results on the restrictions of out-of-plane modes were obtained from absorption data (see Sec. 2.1), where the pronounced vibronic structure proves a much

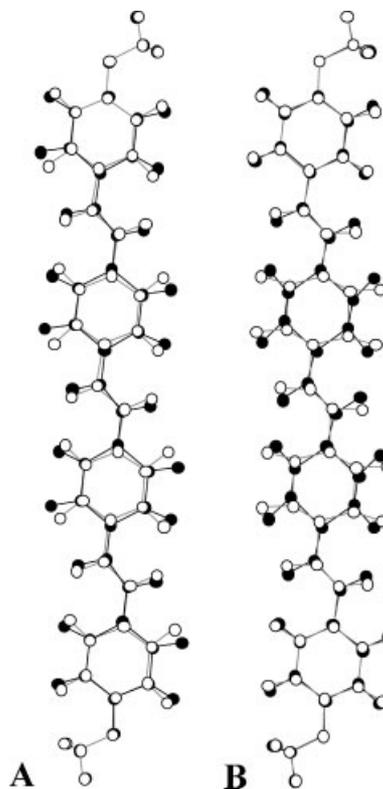


Figure 5. Vibrational displacements associated with the a_g modes at (A) $\nu_1 = 1193 \text{ cm}^{-1}$ and (B) $\nu_4 = 1626 \text{ cm}^{-1}$ for OPV4, as calculated at the DFT level. The two substructures, represented with solid and open symbols, give the relative displacements of the atoms in the $+/-$ directions. The sum of the squared displacements of all atoms equals unity.

Table 3. The intensity ratio of I_1/I_4 from Raman spectra of OPV5, OPV4 and *trans*-stilbene (TS) in powder samples and inclusion compounds.

Ratio	OPV5		OPV4		TS		
	Powder	IC	Powder	IC	Solution: CS_2	Powder	IC
I_1/I_4	0.66	0.36	0.83	0.43	0.7	0.54	0.36

steeper potential for low-frequency torsional modes as compared to solution.^[12,27] The rigidity of the channel walls is moreover confirmed by experimental studies which probe rotational restrictions (²H NMR,^[27] and polarized photoluminescence spectroscopy^[9]), and by theoretical calculations (molecular mechanics^[9] and quantum-chemical studies^[28]).

3. Conclusions

The UV/Vis and Raman spectra of PPV-like π -conjugated molecules with terminal alkoxy spacers in channel-forming inclusion compounds (ICs) and in thin films were investigated by a joint experimental and theoretical approach. Specific interchromophoric and host-guest interactions and their impact on the optical properties were successfully elucidated. The optical properties of the thin films and ICs are highly anisotropic. In the films, well-known H-aggregation leads to low-emissive materials. The ICs are very attractive for optoelectronic applications since they contain a large density of molecules that act as quasi-isolated entities with high PL quantum yield and a large anisotropy at the microscopic scale. Raman spectroscopy was shown to be a useful tool to probe the spatial confinement in the nanochannels formed in the ICs from the attenuation of Raman bands for large amplitude modes with nuclear displacements in direction of the channel walls.

4. Experimental

Synthesis: The four-ring terminally-substituted oligophenylenevinylene, OPV4, (Fig. 1) was synthesized as follows: a solution of 4'-hexyloxystilbene-4-carbaldehyde (154 mg, 0.5 mmol) and diethyl 4'-(3,7-dimethyloctyloxy)stilbene-4-methylphosphonate (244 mg, 0.5 mmol) in 12 mL of anhydrous tetrahydrofuran (THF) was degassed and cooled to 0°C. Under nitrogen, a solution of KOtBu (68 mg, 0.6 mmol) in 2 mL of anhydrous THF was added to the stirred mixture. The solution immediately turned greenish and stirring was continued for 45 min. Acetic acid (2 N, 1 mL) was added followed by drop-wise addition of methanol. The precipitated product was filtered using a Büchner funnel, dried in vacuum and recrystallized from 1,2-dichlorobenzene. The solid was filtered and washed thoroughly with toluene followed by ethanol.

Yield: 112 mg (34%); mp 318°C; IR (KBr): ν = 3005, 2940, 2910, 2850, 1595, 1505, 1458, 1414, 1380, 1297, 1268, 1245, 1232, 1171, 965, 953, 831 cm^{-1} ; MS (FD) 640 (100), [M⁺], 320 (56) [M²⁺]; Anal. calcd for C₄₆H₅₆O₂: C 86.25, H 8.75; found: C 85.88, H 8.51.

The synthesis of symmetrically 4,4'-bi(3,7-dimethyloctyloxy)-substituted five-ring OPV5 oligomer will be reported elsewhere. *Trans*-stilbene (TS) was obtained from Aldrich. Perhydrotriphenylene (PHTP) was synthesized as reported in the literature. [29] Inclusion compounds (ICs) of the molecules in PHTP (see Fig. 1) were prepared by melting and successively cooling a mixture of guest molecules and PHTP in a Mettler 820 DSC apparatus under nitrogen atmosphere at a cooling rate of 0.1 K min⁻¹ [15]. Cast films were obtained from chloroform solutions deposited on quartz substrates.

Photoluminescence CW measurements were obtained with a SPEX 270M monochromator equipped with a N₂ cooled charge-coupled device CCD, by exciting with a monochromated Xe lamp. PL quantum yields, Φ_F , were measured in CH₂Cl₂ diluted solution by using coumarin 314 and quinine sulfate as references. Solid state Φ_F

were obtained with a home-made integrating sphere, according to the procedure reported in ref. [30], by exciting with a monochromated Xe lamp. Samples possessing different absorbances (powders and KBr pellets) were measured and the Φ_F obtained with an error of about 10%. Low-temperature measurements were performed with a He continuous-flow Oxford cryostat, in backscattering geometry. Time-resolved PL measurements were performed using the second harmonic of a Coherent Mira Ti:sapphire laser as excitation source and a Hamamatsu Streak camera with a time resolution better than 2 ps to detect the luminescence. Non-resonant Raman spectra of solutions, ICs and crystalline powder samples were measured on a Bruker IF66 + FRA 106 Fourier transform infrared spectrometer using the 1064 nm excitation line. The Raman spectra of the PHTP ICs were corrected by subtracting the spectrum of pure PHTP.

Computational Methods: Quantum-chemical calculations of the equilibrium geometries and vibrational frequencies in the electronic ground state and in the first excited state (S₀ and S₁, respectively), and of the adiabatic and vertical transition energies were performed at different levels of theory: (i) *ab initio* Hartree-Fock (HF), coupled for excited-state characterization to a Restricted Configuration Interaction scheme involving Singly excited configurations (RCIS), with the GAUSSIAN 98 program package [31], and (ii) (time-dependent) density functional theory (TD)-DFT calculations with the TURBOMOLE V5-7 package [32] using Becke's three-parameter B3LYP exchange-correlation functional. [33] The standard 6-311G* basis set was used, [34] assuming a planar geometry for the molecular backbone and substituting the long alkoxy chains with methoxy groups. The Huang-Rhys (HR) factors were calculated with the DUSHIN program. [35] The Franck-Condon (FC) factors were calculated as previously described, [11] including the complete set of totally symmetrical (a_g) vibrational modes. Since the HF method overestimates the vibrational frequencies by 5–10%, the B3LYP-calculated frequencies were used in the HF simulations of the spectra. Although the calculated hybrid HF/DFT spectra yield a better agreement with experiment than those obtained by a pure DFT approach, the latter is justified by the fact that: (i) it can be used for large systems at a low computational cost; (ii) it successfully reproduces substituent effects [13]; and (iii) the calculated vibrational frequencies and intensities are in reasonable agreement with experiment.

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