Supporting Information for

Spectral multitude and spectral dynamics reflect changing conjugation length in single molecules of oligophenylenevinylenes

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1. Synthesis of oligophenylenevinylenes

oligo(*p*-phenylene vinylene) precursor (OPV-OH) was synthesized by palladium-catalyzed Heck condensation(1) of 1,4-divinylbenzene with 1,4-dibromo-2,5-bis(2-hydroxyethoxy)benzene prepared from 1,4-dihydroxybenzene via bromination and a subsequent nucleophilic substitution reaction with 2-chloroethanol. OPV-OH was esterified with 2-bromopropionyl bromide to obtain a macroinitiator (OPV-MI). Then, atom transfer radical polymerization of styrene was carried out in anisole / NMP (50:50) at 90^{o}C for 1 h under nitrogen atmosphere using OPV-MI as an initiator.(2) N, N, N' ,N" , N" -Pentamethyldiethylenetriamine and copper (I) bromide were used as a ligand and a catalyst, respectively. The reaction mixture was then precipitated in methanol, filtered, followed by subsequent Soxhlet extraction (methanol, THF) to recover yellow powder from the THF fraction (yield; 10%, M_n = 4300, M_w /M_n = 1.5).

1) Spiliopoulos I. K.; Mikroyannidis J. A. *J. Polym. Sci.: Part A: Polym. Chem.* **2002**, *40*, 2591-2600
2) Shen J; Tsuchiya K.; Ogino K. *J. Polym. Sci. : Part A: Polym. Chem.* **2008**, *46*, 1003-1013

2. Molecular dynamics simulations of ground state conformation

Molecular dynamics were carried out using Discovery Studio 2.5.5 with CHARMm force field. The calculations were run in 1fs steps for 1.5 ns. Solvent permittivity is set for the value corresponding to toluene. Example of the ground state conformation of PS-OPV is shown in Figure S1.

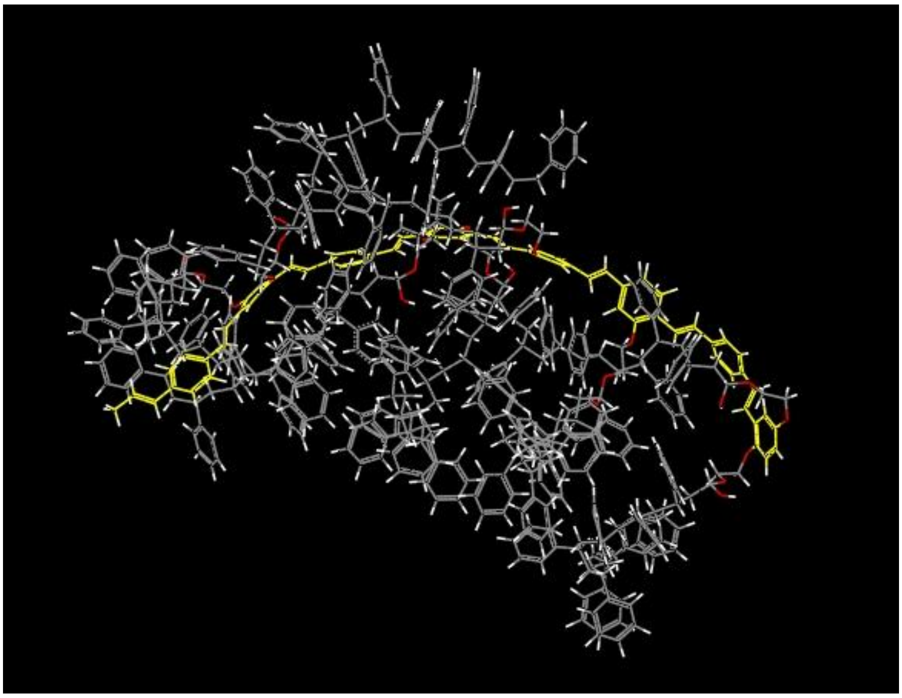

Figure S1. Ground state conformation of PS-OPV.

3. Spectral dynamics of R-OPV and PS-OPV

The Figure S2 shows examples of spectral jumps of PS-OPV in PMA and of R-OPV in PS. In both experiments, the excitation laser is 441.6 nm. The accumulation time per spectrum is 0.5 s in the PMA matrix and 1 s in the PS matrix.

The Figure S3 presents histograms of the distributions of persistence times for both OPVs in the PMA matrix.

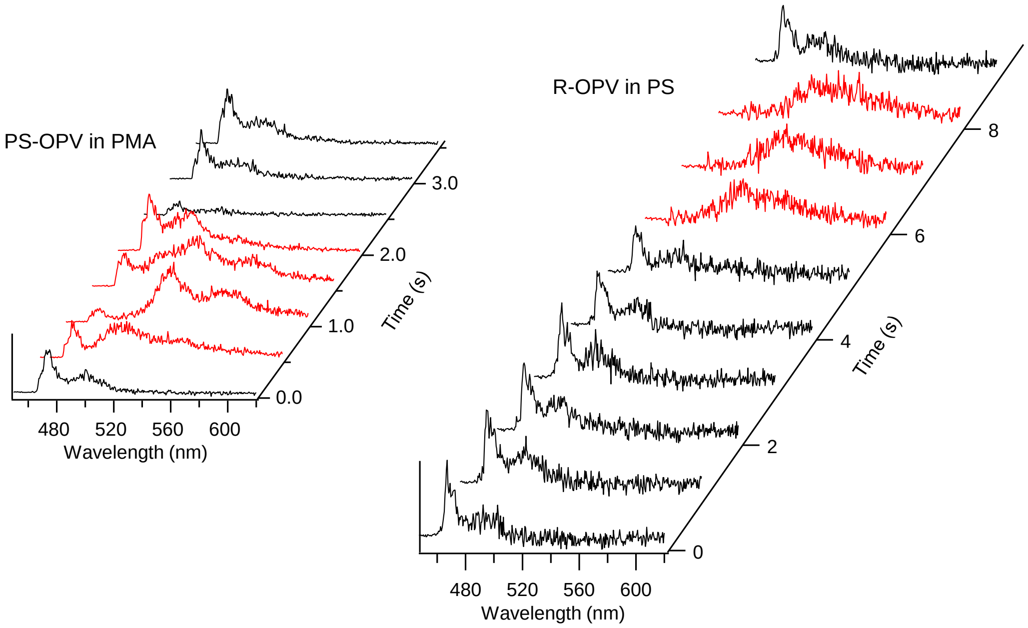

Figure S2. Spectral jumps of PS-OPV and R-OPV in different matrices.

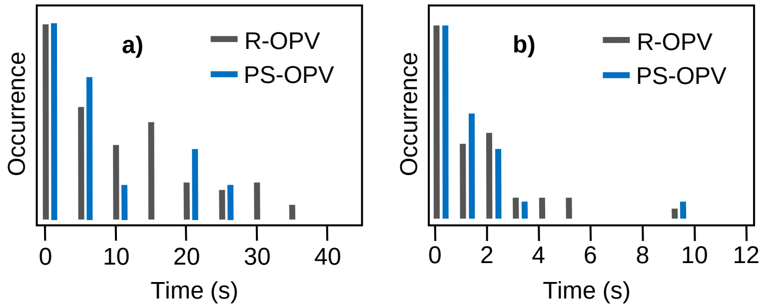

Figure S3. Persistence times before spectral jumps of R-OPV and PS-OPV in PMA. a) type III to type I change; b) type I to type III change.

4. Simulations of the torsional energy barrier

The simulations were carried out using the Gaussian09 program. DFT was performed with the B3LYP/6-31G+(d) basis set. The model compound is shown in Figure S4b. Initially, the conformation including the side chains was optimized in the ground state. After that the central phenylene ring was rotated in 10^o - 15^o increments of the angle θ and at each point the total energy was calculated. This process was repeated for different initial conformations of the side chains, and for different values of the tilt angle ϕ of the first phenylene ring with respect to the common plane (Figure S4a). Examples of two such calculations for $\phi = 0^o$ and $\phi = 90^o$ are shown in Figure S4c, d.

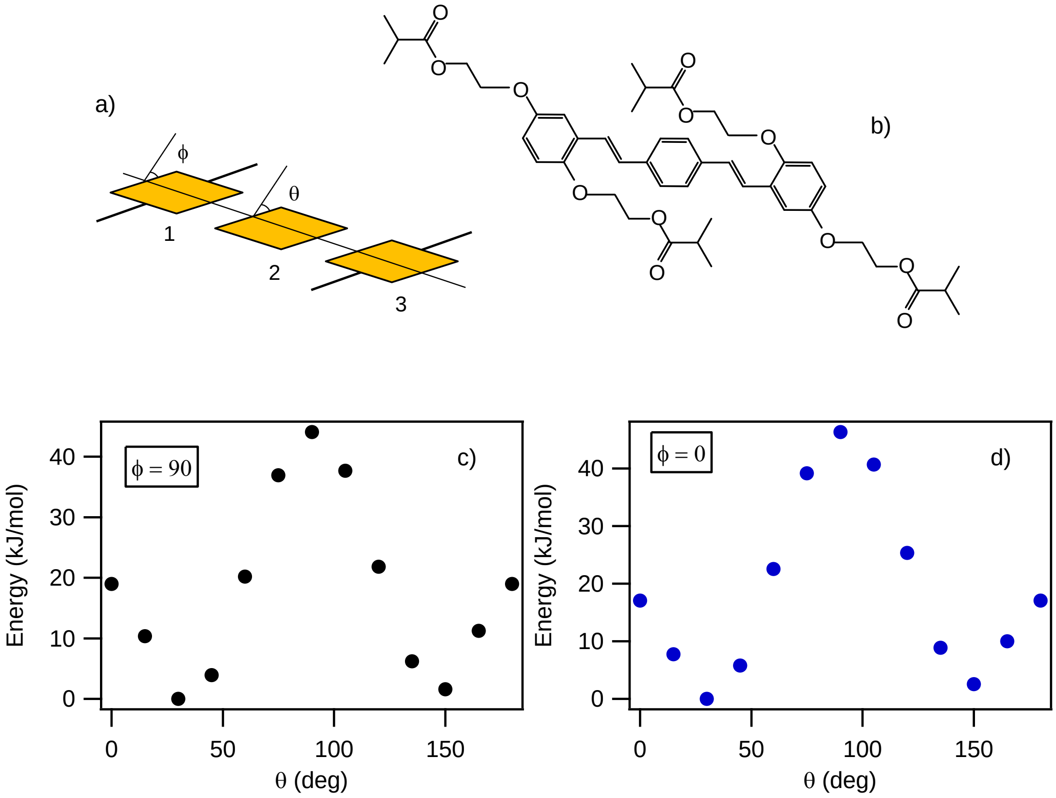

Figure S4. Calculation of the torsional energy barrier.