

# Supplemental information

## Tailored electronic structure and optical properties of conjugated systems through aggregates and dipole-dipole interactions

Young Il Park, Cheng-Yu Kuo, Yong-Shin Park, Jennifer S. Martinez, Olena Postupna, Andriy Zhugayevych, Seungho Kim, Jongwook Park, Sergei Tretiak, Hsing-Lin Wang

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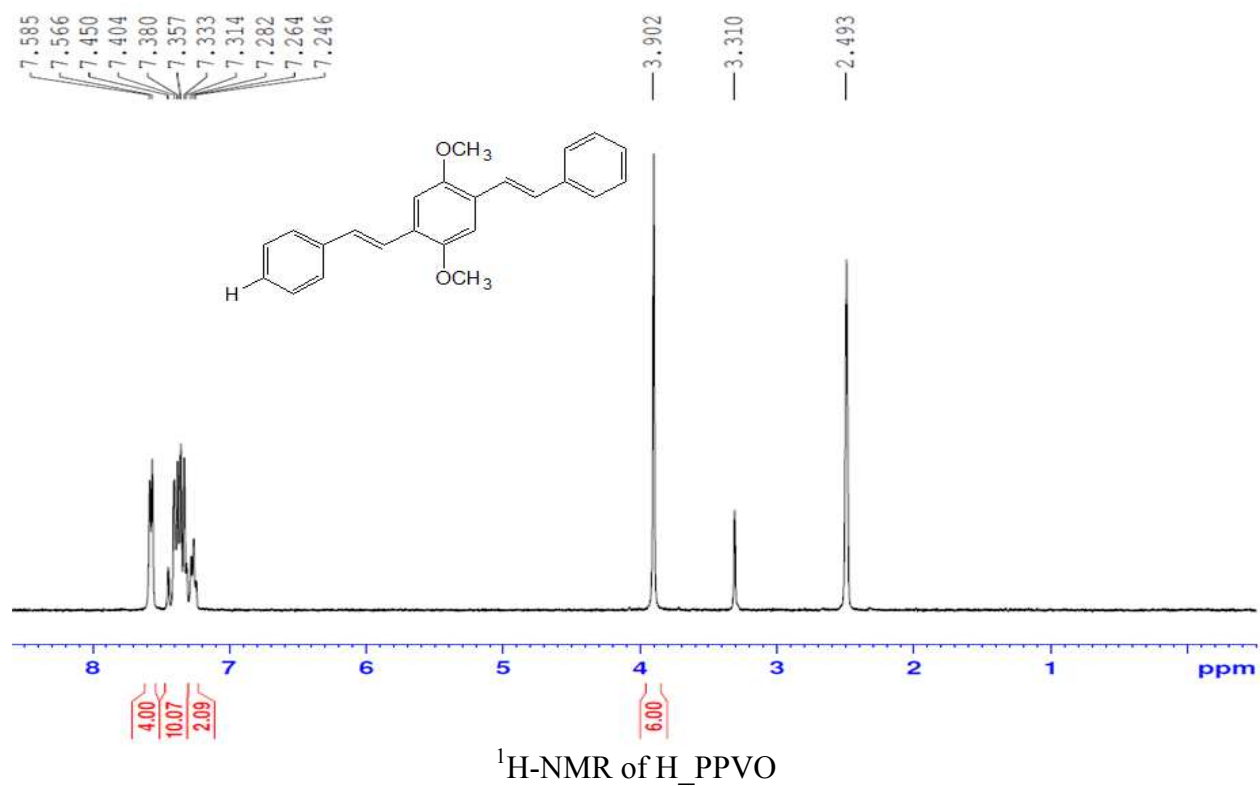
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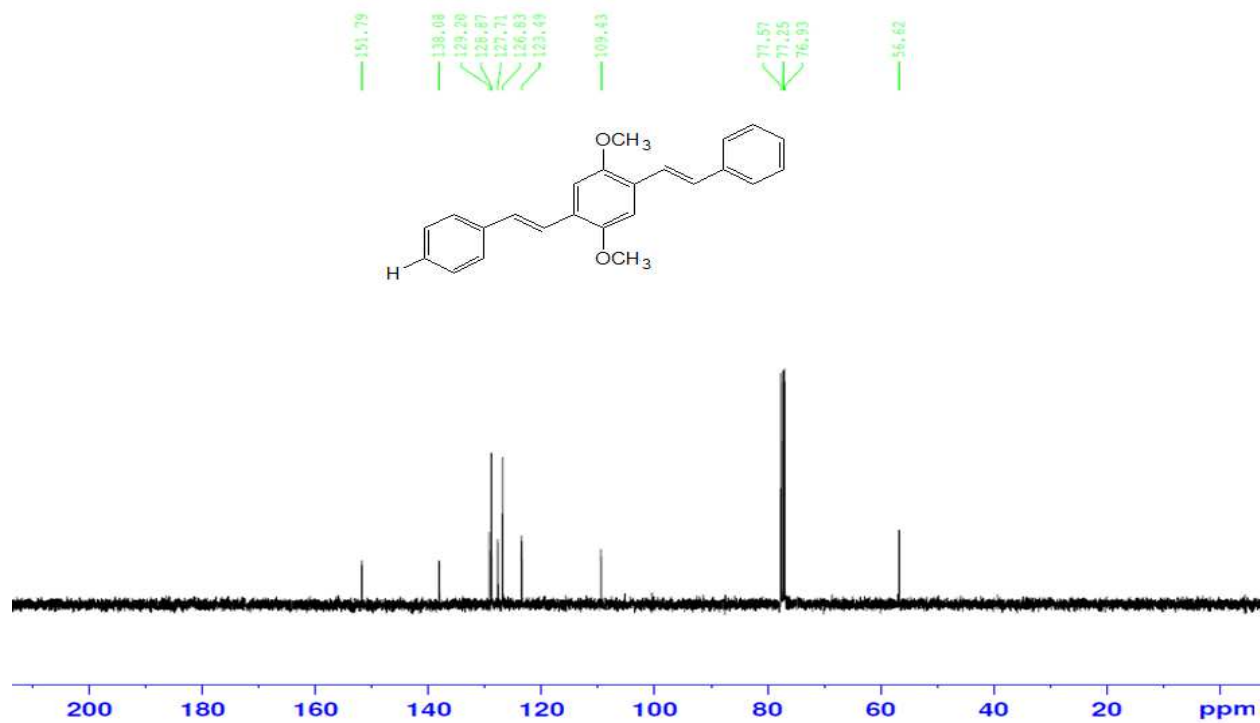
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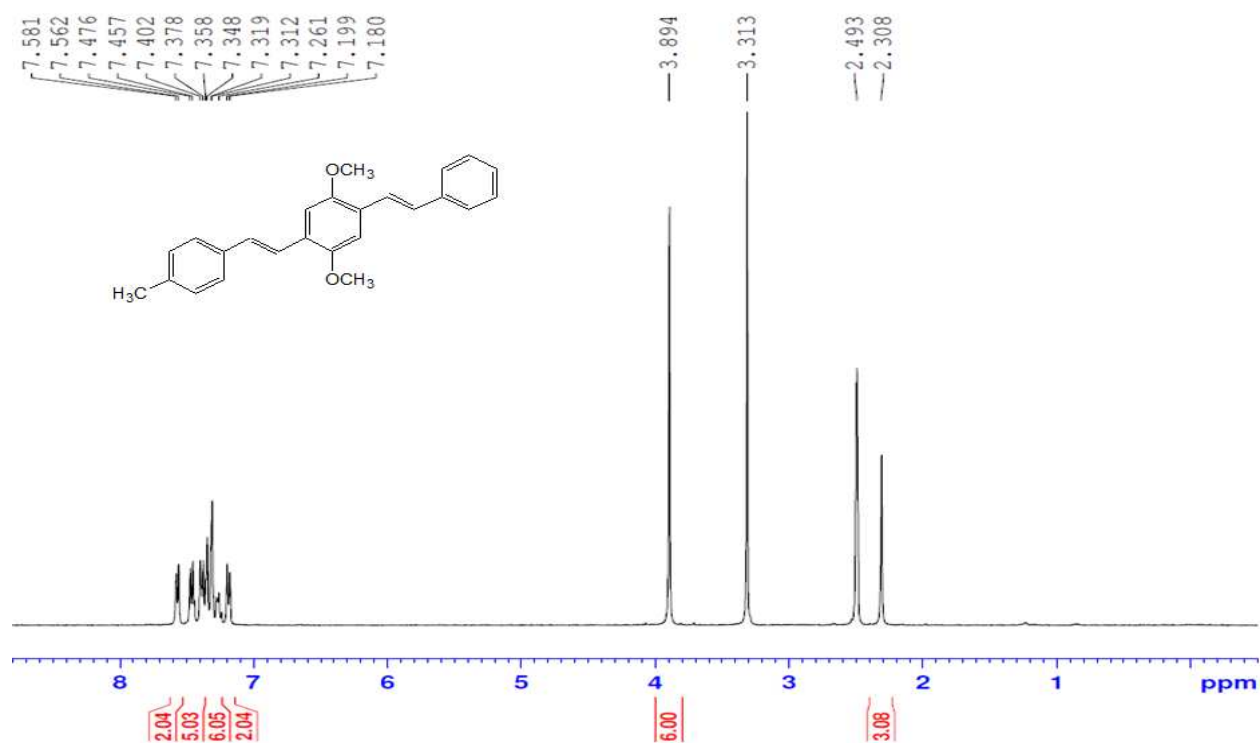
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# 1. $^1\text{H}$ and $^{13}\text{C}$ NMR data of PPVO derivatives

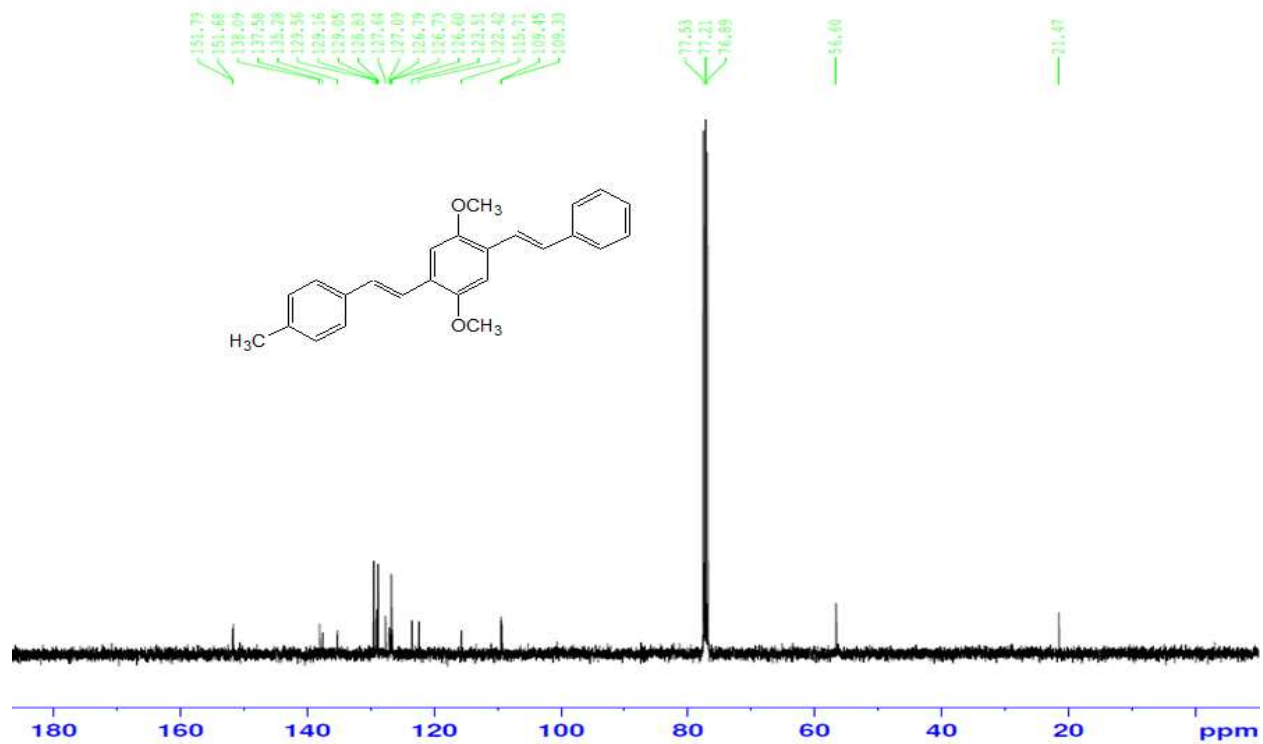




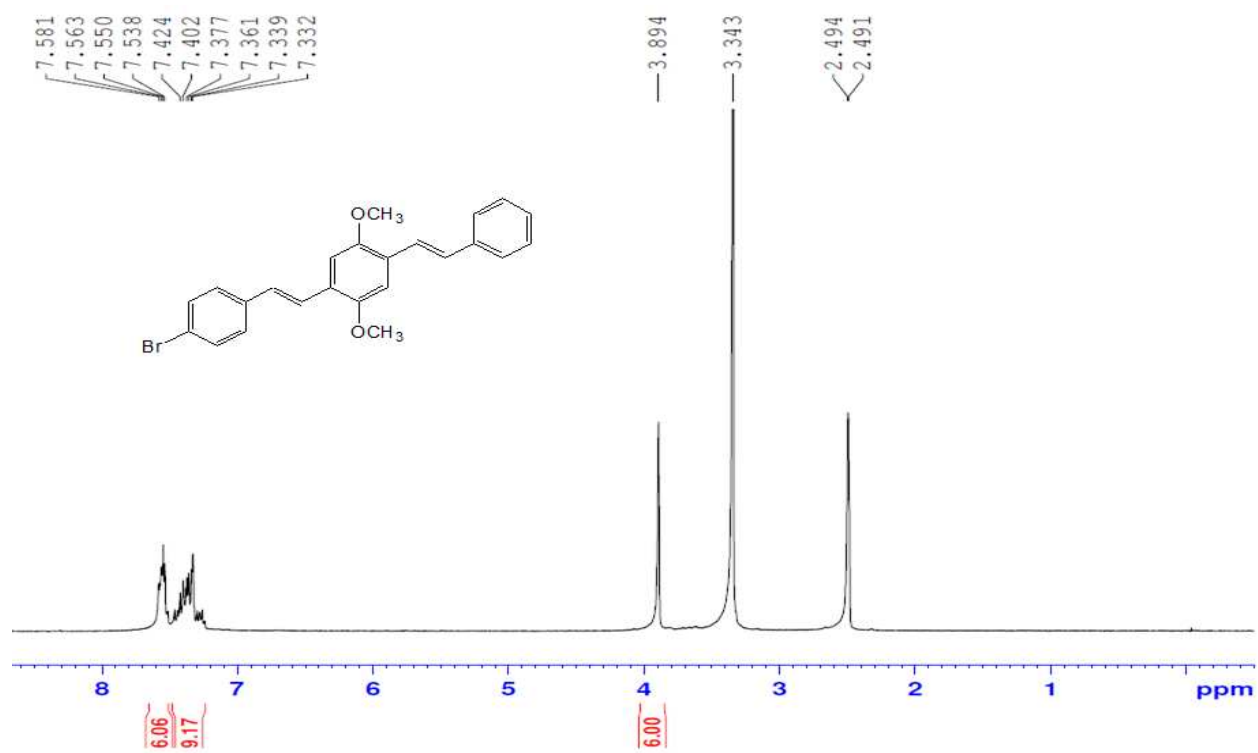
$^{13}\text{C-NMR}$  of H\_PPVO



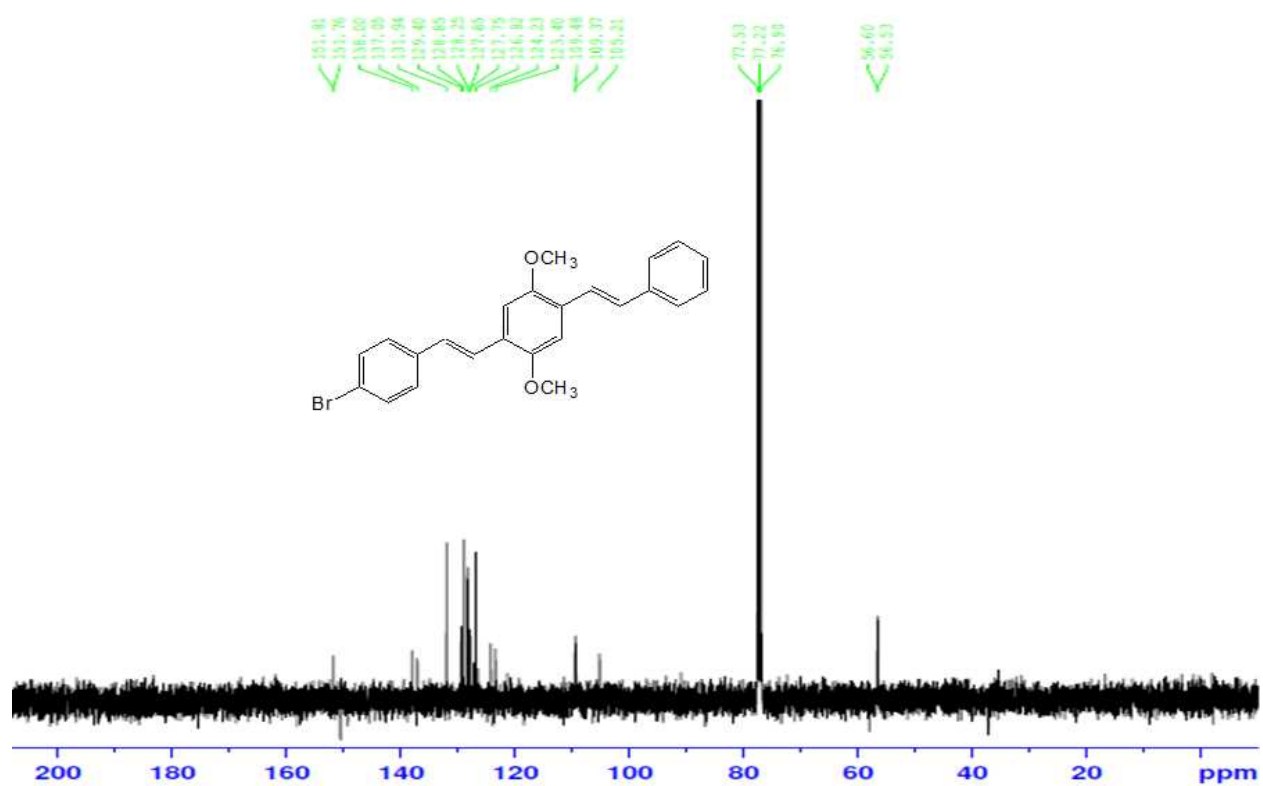
$^1\text{H-NMR}$  of CH<sub>3</sub>\_PPVO



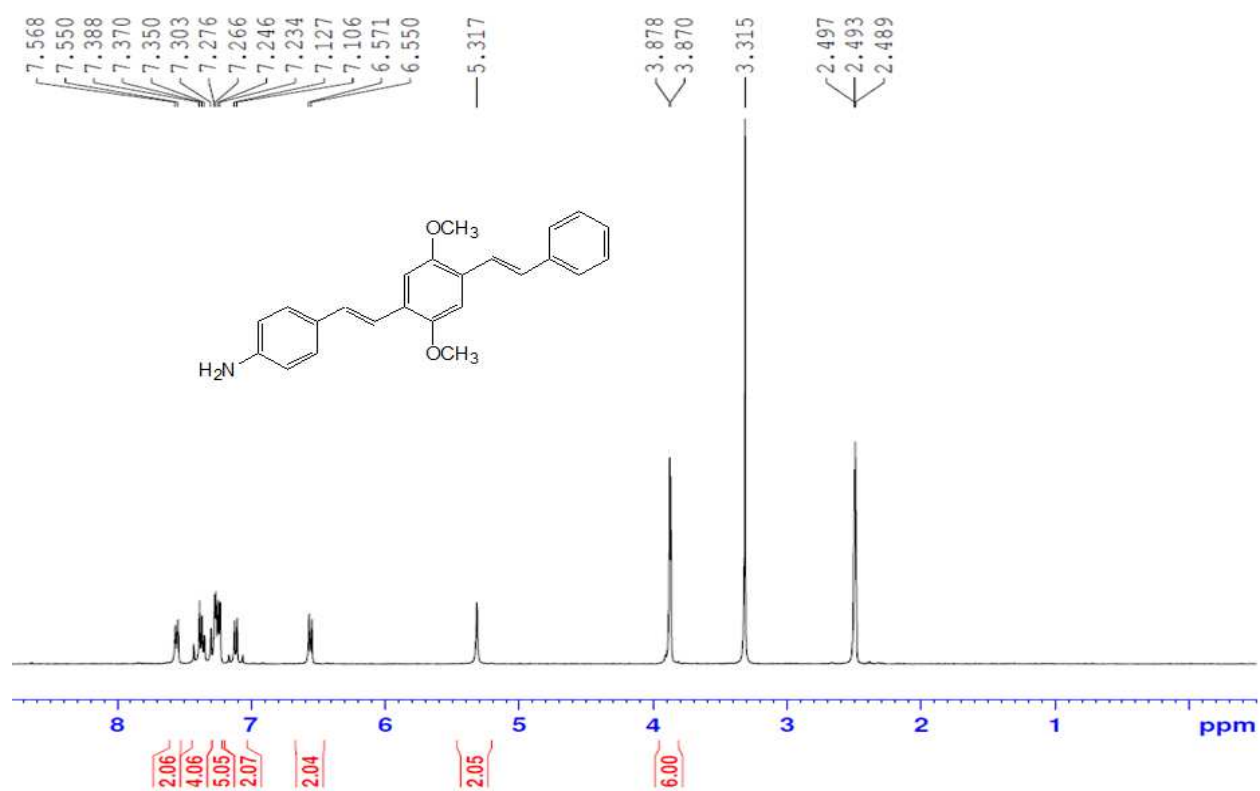
<sup>13</sup>C-NMR of CH<sub>3</sub>\_PPVO



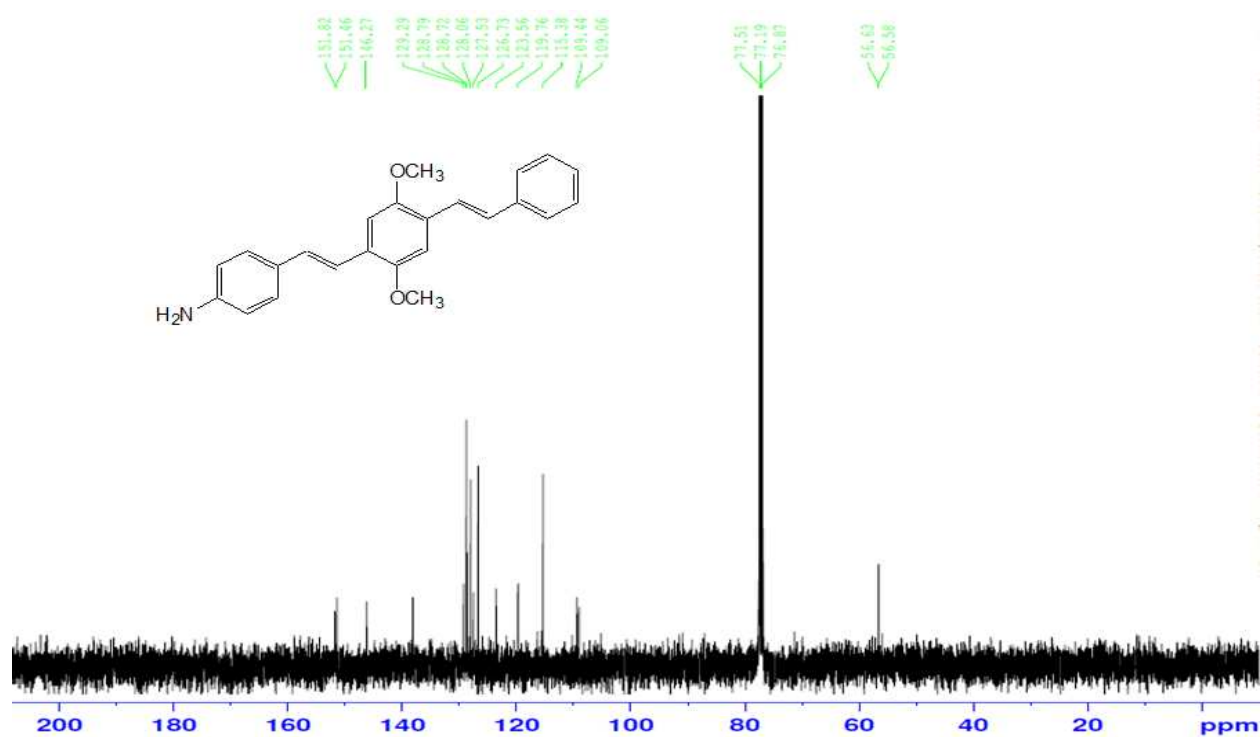
<sup>1</sup>H-NMR of Br\_PPVO



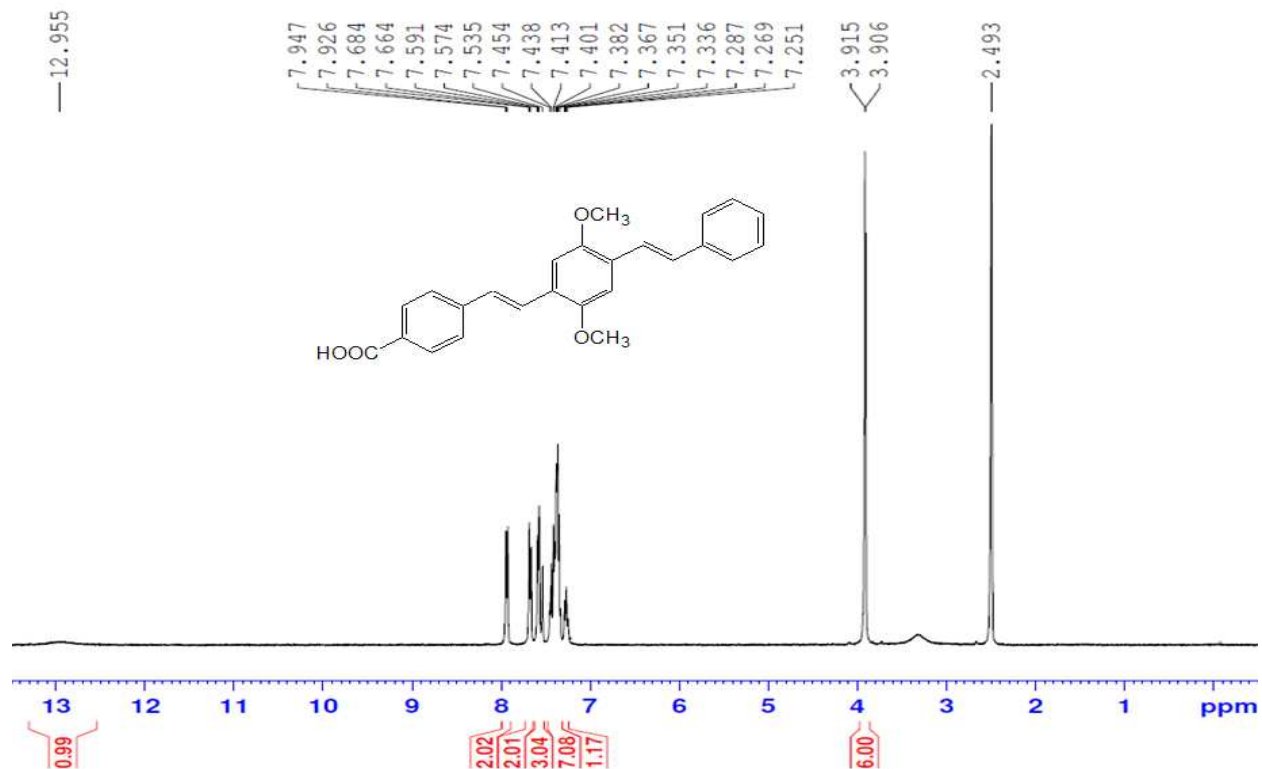
$^{13}\text{C}$ -NMR of Br\_PPVO



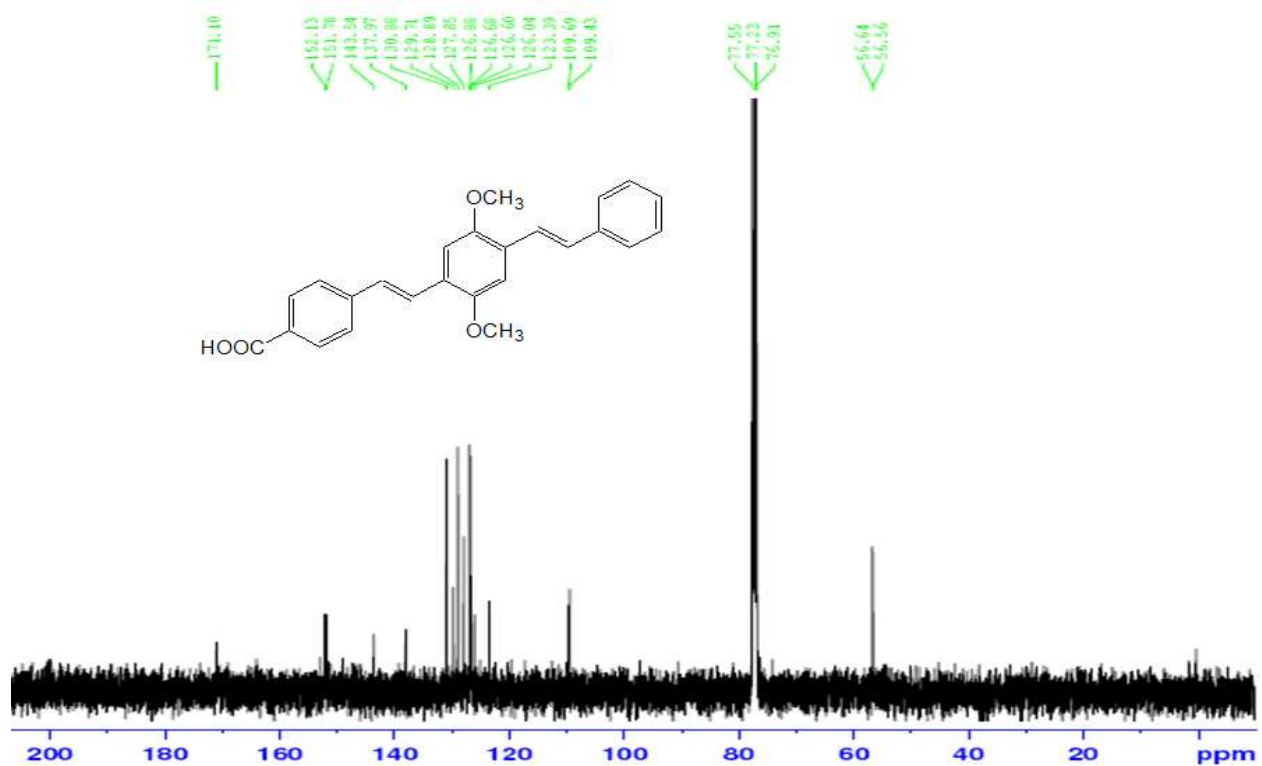
<sup>1</sup>H-NMR of NH<sub>2</sub>\_PPVO



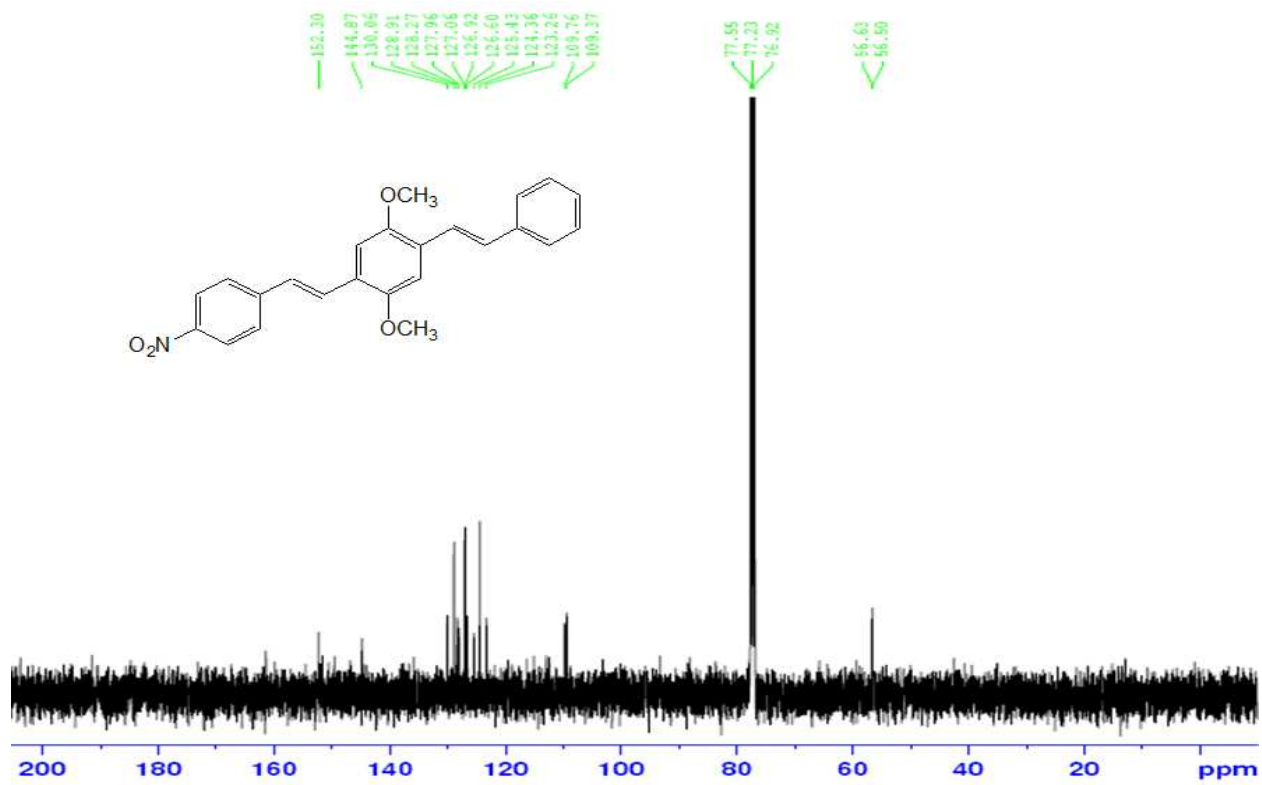
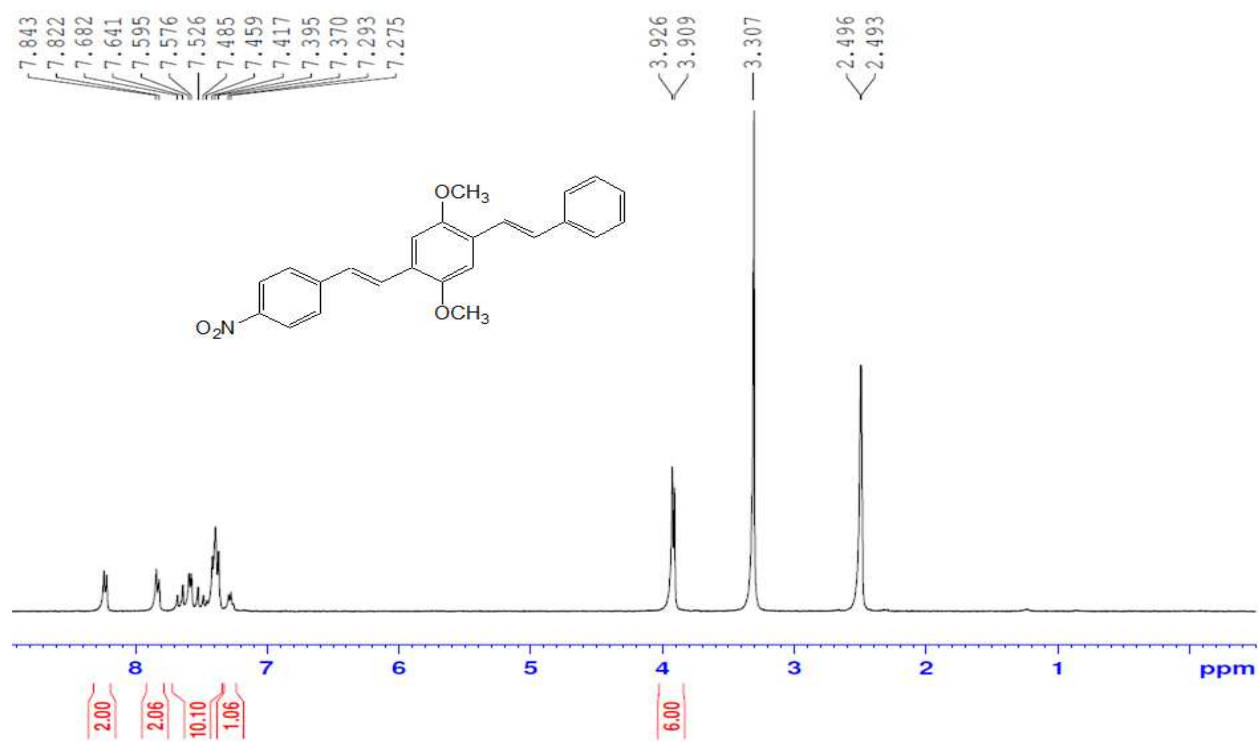
<sup>13</sup>C-NMR of NH<sub>2</sub>\_PPVO



<sup>1</sup>H-NMR of COOH\_PPVO



<sup>13</sup>C-NMR of COOH\_PPVO





## 2. Conformational analysis

Molecular dynamics (MD) simulations with TINKER [J. W. Ponder, TINKER 6.0, <http://dasher.wustl.edu/tinker/>] using the MM3 force field [N. L. Allinger et al, J. Comput. Chem. 11, 868 (1990)] were carried out to discover alternative conformations. For most of the molecules at room temperature within 100 ps of the simulation time, a 360-degree rotation of the benzene rings and the interconnecting vinyl groups is observed. A few conformations with energies spread over 0.1 eV, were obtained by optimizing the MD snapshots. A conformation with an inverted vinyl group (Fig. 5S) was studied by ab-initio methods. The calculated absorption spectrum differs insignificantly (less than 10 nm) from that of the ground state conformation. Consequently, only the lowest energy conformation is used for further investigation.

		H_PPVO	CH <sub>3</sub> _PPVO	Br_PPVO	NH <sub>2</sub> _PPVO	COOH_PPVO	NO <sub>2</sub> _PPVO
Solution (Toluene)	UV	392	393	395	401	402	425
	PL	440	440	467	461	461	522
Stock Shift In solution		48	47	72	60	59	97
Solution (CHCl <sub>3</sub> )	UV	389	389	392	397	400	426
	PL	446	446	454	482	482	627
Stock Shift In solution		57	57	62	85	82	201
Film	UV	406	401	391	412	413	445
	PL	494	480	496	516	514	596
Stock Shift in film		88	79	105	104	101	151
PL (Film – Solution(Toluene))		54	40	29	55	53	74
Film	HOMO	5.39	5.36	5.18	4.98	5.20	5.51
	LUMO	2.66	2.62	2.78	2.37	2.57	3.20
Q. Y.		0.89	0.90	0.89	0.29	0.79	0.01

Table S1. List of  $\lambda_{max}$ , for UV-Vis absorption, photoluminescence, Stokes shift and quantum yield of all six PPVOs. These results reveal a strong correlation between the molecular dipole and optical properties. Such correlations are interpreted as due to strong molecular solvent interactions and the formation of various aggregates as manifested by the light scattering

Media	abbr	$\epsilon_{static}$	$\epsilon_{optical}$
Toluene	tol	2.37	2.24
Chloroform	clf	4.71	2.09
Chlorobenzene	clb	5.70	2.32
Tetrahydrofuran	thf	7.43	1.97
Acetonitrile	an	35.69	1.81
Dimethyl sulfoxide	dms	46.83	2.01

Table S2: List of all the media used in the theoretical calculations, their abbreviations and values of static and optical dielectric constants.

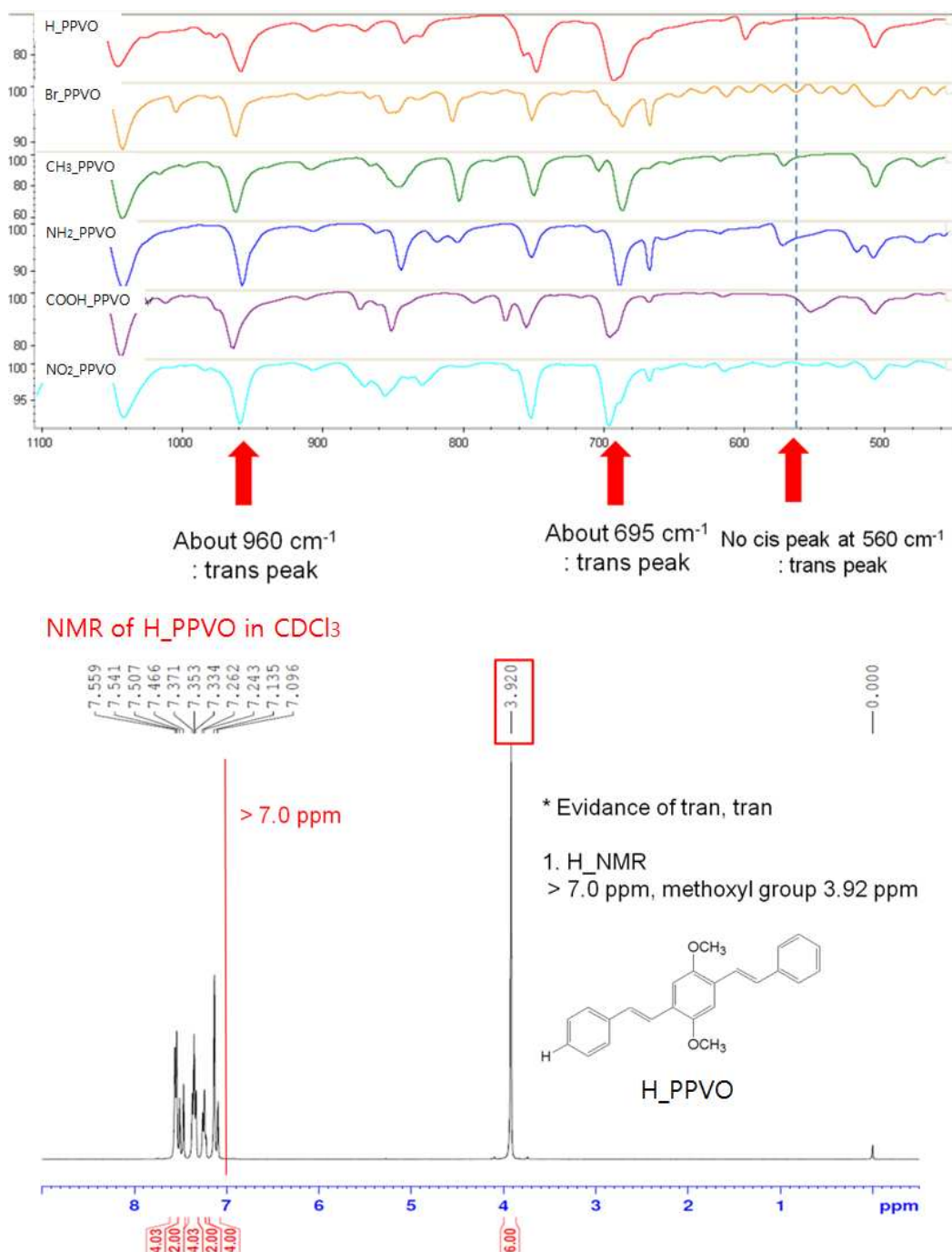


Figure S1. (Top) FT-IR spectra of all six PPVOs. Two peaks at  $960\text{ cm}^{-1}$  and  $695\text{ cm}^{-1}$  reveal only *trans-trans* conformation in all six PPVOs. Lacking the peak at  $\sim 560\text{ cm}^{-1}$  suggest that no *cis-trans*, and *cis-cis* conformations. (Bottom) NMR spectrum of H-PPVO shows that all aromatic protons have a chemical shift above  $7.0\text{ ppm}$  further validates the fact that only *trans-trans* conformation in the H PPVO. In fact, the chemical shifts of all six PPVOs have aromatic proton greater than  $7.0\text{ ppm}$  (see experimental section).

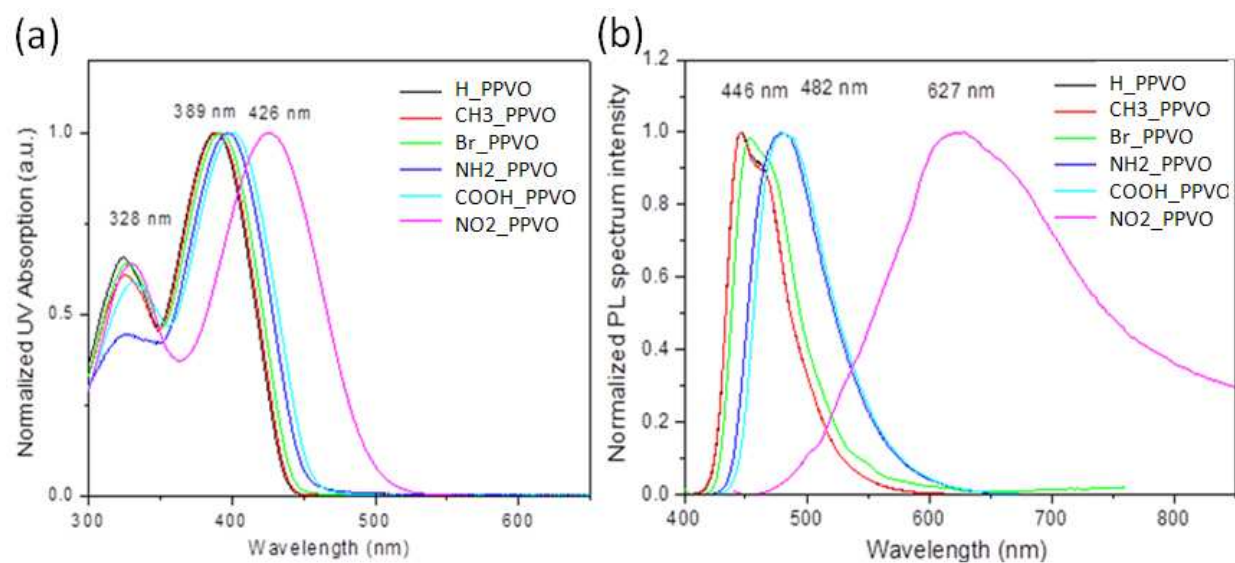
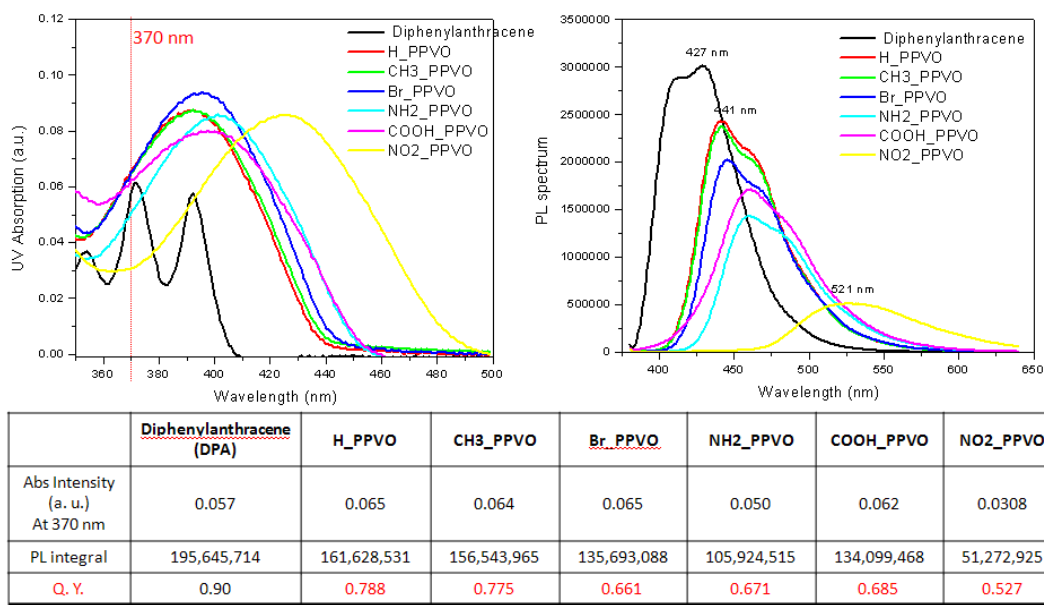


Figure S2. UV-Vis spectra (a) and photoluminescence spectra (b) of six PPVOs in chloroform solution. Both spectra show end group-dependent optical properties that are attributed to the molecular dipole and formation of aggregates states in PPVO solutions.



$$Q.Y_{F(A)} = Q.Y_{F(ref)} \times (PL_A / UV_A) \times (UV_{ref} / PL_{ref}) \times (\eta_A / \eta_{ref})^2$$

( $\eta$  : refractive index,  $\eta$  of Ethanol : 1.3614,  $\eta$  of Toluene : 1.4969)

Solvent : Ethanol (DPA), Toluene (PPVO derivatives)

Figure S3, Determination of quantum yields of six PPVOs in toluene solution. PL spectra were recorded by excitation wavelength of 370 nm, which is different from Figure 1 in which excitation wavelength is the wavelength of max of absorbance spectra.

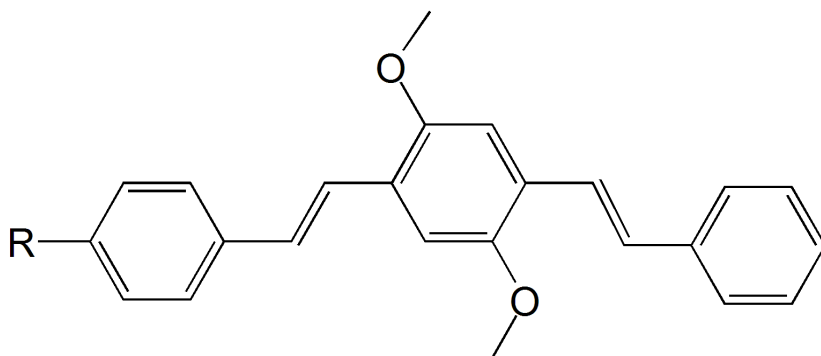


Figure S4. Alternative conformation accessible at 300K.

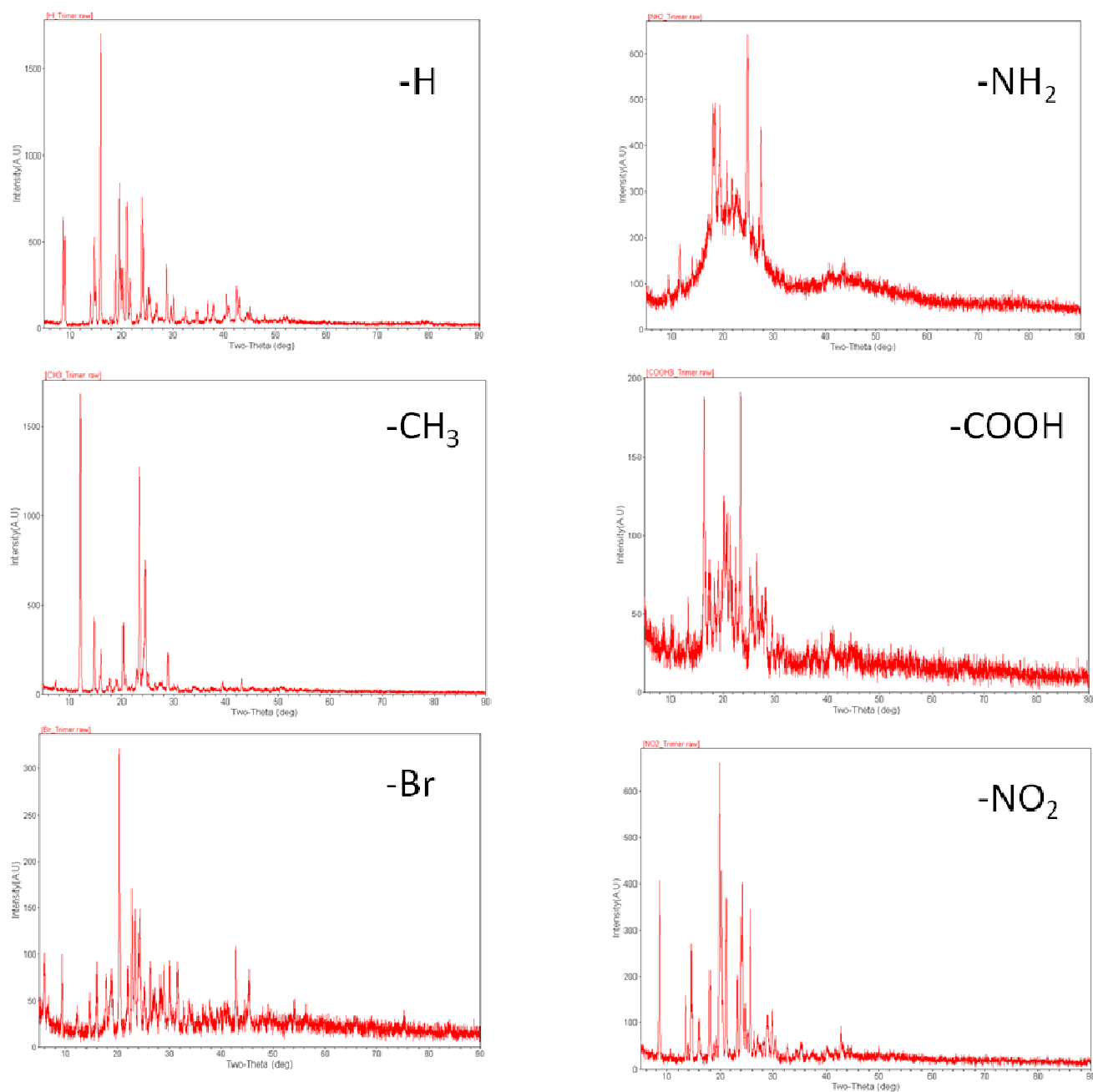


Figure S5. XRD spectra of six oligomer samples. Of all oligomer samples, we find high crystalline nature of the H-, Br- and NO<sub>2</sub>- oligomer.

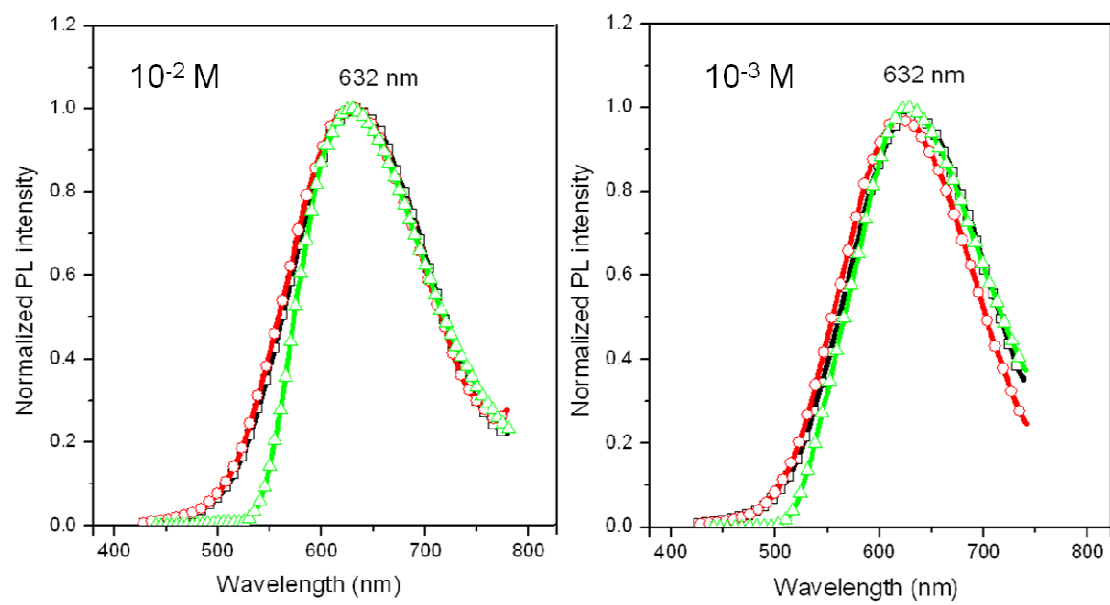


Figure S6. PL spectra of front face geometry using laser beam focus on the front of the cuvette, ( $\blacksquare$ ) and 90° angle relative to the excitation beam ( $\bullet$ ). PL spectrum of  $\text{NO}_2\text{-OPPV}$  in  $\text{CHCl}_3$  solution ( $\blacktriangle$ ) under normal PL setting.