## **Supplementary Information**

# Effects of Conjugation Length and Resonance Enhancement on Two-Photon Absorption in Phenylene-Vinylene Oligomers

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- 1. Discussion on the origin of background signals observed in the two-photon experiments.
- 2. Preparation and characterization of the phenylene-vinylene (PV) oligomers.
- 3. Excitation-wavelength-dependence of the PV3 and PV4 emission spectra.

#### 1. Origin of background signals observed in the two-photon experiments.

We previously reported that, for two-photon experiments performed in toluene in which either singlet oxygen phosphorescence or a photoacoustic signal was used as a probe, background signals derived from light absorption by the solvent can complicate the analysis of data.<sup>1</sup> We also demonstrated that one can compensate for these background signals by recording a complementary wavelength-dependent data set from the neat solvent and then subtracting the latter from the data containing the desired information.

For the data recorded in the present study in which the PV fluorescence was used as a probe, we likewise observed background signals that must be considered in the analysis of the data. We ascertained that the background signals in the present study are not a consequence of two-photon excitation. Rather, these signals scale linearly with an increase in the incident laser power and can also be observed upon *cw* irradiation. Moreover, we ascertained that a significant fraction of this background signal is due to inefficient rejection of our excitation light by the filters used to spectrally isolate the fluorescence. Other experiments indicate that this background signal also has a component that derives from Raman scattering by the solvent (*e.g.*, background signal that is solvent-dependent).

At irradiation wavelengths over the range 730-1000 nm, the signal intensity from the neat solvent was always below 40% of the total signal observed from a system containing the PV, most often <15%. No signal was observed from the neat solvent when irradiating over the range 540 - 730 nm.

### 2. Preparation and characterization of the phenylene-vinylene (PV) oligomers.

**2.1. General Comments.** Starting materials and reagents were purchased from commercial suppliers and were used without further purification. Unless otherwise stated, solvents were all reagent grade and used without further purification. THF was freshly distilled from

sodium/benzophenone ketyl radical. All reactions were performed under an inert argon atmosphere. Chromatographic separations using the dry column vacuum chromatography (DCVC) technique were performed on silica gel 60 (SiO<sub>2</sub>, particle size 0.015-0.040 mm) using gradient elution (stationary phase/mobile phase). Melting points are uncorrected.

Chemical shifts for the <sup>1</sup>H-NMR spectra are reported with the solvent as the reference  $(\text{CDCl}_3: \delta - 7.26 \text{ ppm}, \text{DMSO } \delta - 2.52 \text{ ppm})$  and were recorded at 250.1 MHz. Data are reported as follows: chemical shift, multiplicity, integration and coupling constants (Hz). The spectrum for PV2 was also recorded on a 500 MHz spectrometer. (As an aside, the <sup>1</sup>H-NMR spectra appended to this document were all recorded about one year after the original spectra were recorded at the time the molecules were synthesized, and thus provide an additional check of the molecules as they were actually used in the optical experiments.) Chemical shifts for the <sup>13</sup>C-NMR spectra are reported with the solvent as the reference (CDCl<sub>3</sub>:  $\delta$  - 77.0 ppm) and were recorded at 62.9 MHz. Unless otherwise stated the spectra were recorded at 300 K.

#### 2.2. Details on the Synthesis and Characterization of PV0-PV4.



Chart 1. Structures of the molecules synthesized in the present study.

PV3

PV4

n=3

n=4

4-(*N*,*N*-Diphenylamino)-benzaldehyde (PV0) was synthesized using a published procedure.<sup>2</sup> Thereafter, PV1-PV4 were synthesized using the general procedure shown in

Scheme 1. The extension reagent shown in step 1 of Scheme 1 containing a phosphonate ester and an acetal-protected aldehyde (*i.e.*, [4-(5,5-dimethyl-[1,3]dioxan-2-yl)-benzyl]-phosphonic acid diethyl ester) was likewise prepared using a published procedure.<sup>3</sup>



Scheme 1. General procedure for the synthesis of PV1-PV4. This cycle was started using PV0 as the first reactant (*i.e.*, n = 0 in the Scheme).

#### 4-[2-(4-Diphenylamino-phenyl)-vinyl]-benzaldehyde (PV1):

To a solution of 4-(*N*,*N*-Diphenylamino)-benzaldehyde (2.07 g, 7.57 mmol) and [4-(5,5dimethyl-[1,3]dioxan-2-yl)-benzyl]-phosphonic acid diethyl ester (4.08 g, 11.9 mmol) in THF (100 ml) was added KO<sup>t</sup>Bu (2.02 g, 18.0 mmol) and the reaction mixture was refluxed for 1 h. The mixture was quenched with 3 M HCl (100 ml) and refluxed overnight. The quenched reaction mixture was washed with brine (2 x 100 ml) and dried with MgSO<sub>4</sub>. Celite was added and the solvent removed *in vacuo*. The remaining solid was loaded on a column and purified by DCVC (n-heptane/1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) leaving 1.59 g of the title compound as a yellow powder; mp 141-143 °C; <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 K): 9.98 (s, 1H), 7.86 (d, 2H, *J*=8 Hz), 7.62 (d, 2H, *J*=8 Hz), 7.41 (d, 2H, *J*=9 Hz), 7.33-7.22 (m, 4H), 7.20-6.97 (m, 10H) ; <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 300 K): 191.4, 148.3, 147.4, 143.9, 135.1, 131.8, 130.4, 130.2, 129.4, 127.8, 126.6, 125.4, 124.9, 123.4, 123.0; Anal. Calcd. for C<sub>27</sub>H<sub>21</sub>NO: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.10; H, 5.70; N, 3.60.

#### 4-(2-{4-[2-(4-Diphenylamino-phenyl)-vinyl]-phenyl}-vinyl)-benzaldehyde (PV2):

Prepared as PV1 according to scheme 1. Yield: 1.08 g (70 %), light orange powder; mp 231-233 °C; <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 300 K): 10.00 (s, 1H), 7.88 (d, 2H, *J*=8 Hz), 7.66 (d, 2H, *J*=8 Hz), 7.52 (s, 4H), 7.40 (d, 2H, *J*=9 Hz), 7.34-6.92 (m, 16H); <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 300 K): 191.5, 147.6, 147.5, 143.5, 138.0, 135.5, 135.3, 131.8, 131.2, 130.2, 129.3, 128.7, 127.4, 127.3, 126.9, 126.8, 126.7, 126.3, 124.6, 123.4, 123.1; Anal. Calcd. for C<sub>35</sub>H<sub>27</sub>NO: C, 88.02; H, 5.70; N, 2.93. Found: C, 88.14; H, 5.39; N, 2.81.

In the 250 MHz <sup>1</sup>H-NMR spectrum, the singlet observed at 7.52 ppm with an integral of 4H is due to the four hydrogens on the middle aromatic ring that yield a resonance at the same frequency. However, when the spectrum for this compound was recorded using a 500 MHz instrument, one observed that this "singlet", as expected, was actually two closely-spaced doublets (see attached spectrum).

# 4-{2-[4-(2-{4-[2-(4-Diphenylamino-phenyl)-vinyl]-phenyl}-vinyl}benzaldehyde (PV3):

Prepared as PV1 according to Scheme 1. Yield: 0.60 g (99 % mass yield), orange solid; mp >300 °C; <sup>1</sup>H-NMR(DMSO, 400 K): 10.01 (s, 1H), 7.89 (d, 2H, *J*=8 Hz), 7.78 (d, 2H, *J*=8 Hz), 7.66-7.01 (m, 26H), 6.98 (d, 2H, *J*=9 Hz). MS (MALDI-TOF): m/z calculated for C<sub>43</sub>H<sub>33</sub>NO = 579.26; found = 579.19.

As in the <sup>1</sup>H-NMR spectrum of PV2, two slightly broadened singlets, each of which has an integral corresponding to 4H, can be assigned to the hydrogens on the two middle aromatic rings.

Note also that PV3 and PV4 (below) are sufficiently insoluble that <sup>1</sup>H-NMR spectra could be obtained only upon heating the sample to 400 K. It was simply not realistic to record the <sup>13</sup>C-NMR spectra for these compounds because the prolonged use of such a high temperature would damage the spectrometer.

4-[2-(4-{2-[4-(2-{4-[2-(4-Diphenylamino-phenyl)-vinyl]-phenyl}-vinyl}-phenyl]-vinyl}-phenyl]-vinyl]-benzaldehyde (PV4):

Prepared as PV1 according to Scheme 1. Recrystalized from DMSO. Yield: 0.60 g (99 % mass yield), orange solid; mp >300 °C; <sup>1</sup>H-NMR(1,2-dichlorbenzol, 400 K): 10.22 (s, 1H), 8.01 (d, 2H, J=7 Hz), 7.82 (d, 2H, J=15 Hz), 7.63 (d, 2H, J=8 Hz), 7.78-6.99 (m, 12H), 7.59-7.15 (m, 20H). MS (MALDI-TOF): m/z calculated for C<sub>51</sub>H<sub>39</sub>NO = 681.30; found = 681.41.

#### General Comments on Compound Purity:

For each PV oligomer, we observed only a single resonance in the <sup>1</sup>H-NMR spectrum that can be assigned to the aldehyde hydrogen (Figure 1 and appended spectra). In samples of the longer homologues (*i.e.*, PV2-PV4), a most probable impurity would be one or more of the shorter homologues and this would presumably give rise to additional aldehyde resonances. Such additional resonances were not observed. Another possible impurity would be the elongation reagent with a phosphonate ester attached. However, this latter compound would give rise to distinct resonances in the aliphatic region of the <sup>1</sup>H-NMR spectrum, and these were likewise not observed. On the basis of these NMR measurements, we assess the purity of these compounds as being no worse than 95%.

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**Figure 1.** <sup>1</sup>H-NMR spectra for PV0-PV4. Enlarged versions of the individual spectra are also appended to this document.

When working with PV3 and, particularly, PV4, our efforts were hampered by the fact that these compounds are essentially insoluble. This has ramifications in obtaining some spectral information (*e.g.*, molar absorption coefficient for PV4 in toluene, see Table 1 in the text) and in both purifying and further characterizing these compounds. Thus, for example, HPLC is precluded; given our conservative NMR-based estimate that, at most, these samples could consist of 5% impurities, we would need to dissolve an appreciable amount of material just to see an impurity. Low solubility also precluded obtaining a high-resolution electrospray MS. However, we were able to obtain MALDI-TOF MS (spectra are appended), which when combined with the NMR data are sufficient for the characterization of these compounds.

#### 3. Excitation-wavelength-dependence of the PV3 and PV4 emission spectra.

Unlike data recorded from PV0-PV2, the emission spectra of PV3 and PV4 depend slightly on the excitation wavelength. As shown in Figures 2-3, these spectral changes are more pronounced for PV4.



Figure 2. Emission spectra of PV3 and PV4 in THF recorded as a function of the excitation wavelength. The red box superimposed on the PV4 data represents the spectral bandwidth (FWHM) of the filter used to isolate this emission in our two-photon experiments.



**Figure 3.** Emission spectra of PV3 and PV4 in toluene recorded as a function of the excitation wavelength.

As mentioned in the article text, the data in Figures 2-3 could reflect a number of phenomena including the possibility that these samples may contain small amounts of the shorter oligomer homologues.

#### **References:**

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