The solid-state organization of ‘self-doped’ PPV oligomers

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1. X-band CW-EPR spectra

Figure S1. X-band CW-EPR spectrum recorded at T=20K of (a) electrochemically oxidized (1a), (b) chemically oxidized (1a) (5s exposure time to I2) and (c) chemically oxidized (1a) (30s exposure time to I2). The EPR spectra are normalized to a mw frequency of 9.44 GHz for comparison.
2. DFT model of oxidized (1a)

Figure S2. Structure of oxidized (1a)
Cartesian coordinates of model used as input for EPR computations (in Å)

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3. DFT models of mono-oxidized dimers of two (1d) molecules and comparison with the mono-oxidized (1d) monomer

**General:** the geometry of one single oxidized oligomer (1d) was first optimized as described in the methods section of the paper. This structure was then used to build the model of the dimers by placing two identical oligomers at a fixed distance from each other. A single positive charge was taken for the whole dimer. It is clear that this procedure should only be considered as a proof of principle that the hole can spread out over two oligomer units provided they are close enough, but does not agree with the real structure of the dimer. Current state-of-the-art DFT does not allow a correct geometry optimization of dimer molecules in π-π contact.

a) Model of two (1d) molecules separated by 4.06 Å, dimer mono-oxidized with the phenyl rings are positioned directly above each other.

![Figure S3. Structure of oxidized dimer.](image)

**Cartesian coordinates of atoms in dimer (in Å)**

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Figure S4. Spin density distribution. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.001 and 0.001, respectively.

There is a clear distribution of the spin density over the two oligomers. In the below table, the computed principal $g$ values and the proton hyperfine values of the two protons of one vinylene unit are given (the same values are found for all 4 vinylene units).

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b) Model of two (1d) molecules separated by 10.5 Å, dimer mono-oxidized with the phenyl rings are positioned directly above each other.

Figure S5. Structure of oxidized dimer.

Cartesian coordinates of atoms in dimer (in Å)

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Figure S6. Spin density distribution. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.001 and 0.001, respectively.

There is no significant distribution of the spin density over the two oligomers as is also obvious from the below table with the $^1$H hyperfine values of the two protons of the vinylene units on oligomer 1 and oligomer 2 (the same values are found for both vinylene sites of each oligomer)

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c) Polaron on (1d)

As a comparison, the EPR values of a single (1d) polaron were computed.

![Figure S3. Structure of oxidized (1d).](image)

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Figure S8. Spin density distribution. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.001 and 0.001, respectively.

Principle $g$ values and proton couplings on the two protons of the vinylene unit (the same values are found for both vinylene units)

The obtained values are similar to the ones found for the dimer at 10.5 Å

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5. W-band CW-EPR spectra of oxidized (1b) and (1c)

**Figure S9.** Experimental (black, solid line) and simulation (red, dashed line) W-band CW-EPR spectra of (top) I$_2$ oxidized (1b), and (bottom) I$_2$ oxidized (1c). The simulated spectra are the sum of a broad featureless line with $g \approx 2.0025$ and line width 70MHz and the species with parameters given in Table 1. The spectra are rescaled to 94 GHz. The spectra were taken at 20K.
6. X-band HYSCORE spectra of oxidized (1b) and (1c)

Figure S10. $^1$H matched HYSCORE spectra of (A) electrochemically oxidized (1b), (B) I$_2$ oxidized (1b), (C) electrochemically oxidized (1c), and (D) I$_2$ oxidized (1c).