Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Conformational control over π-conjugated electron pairing in 1D organic polymers

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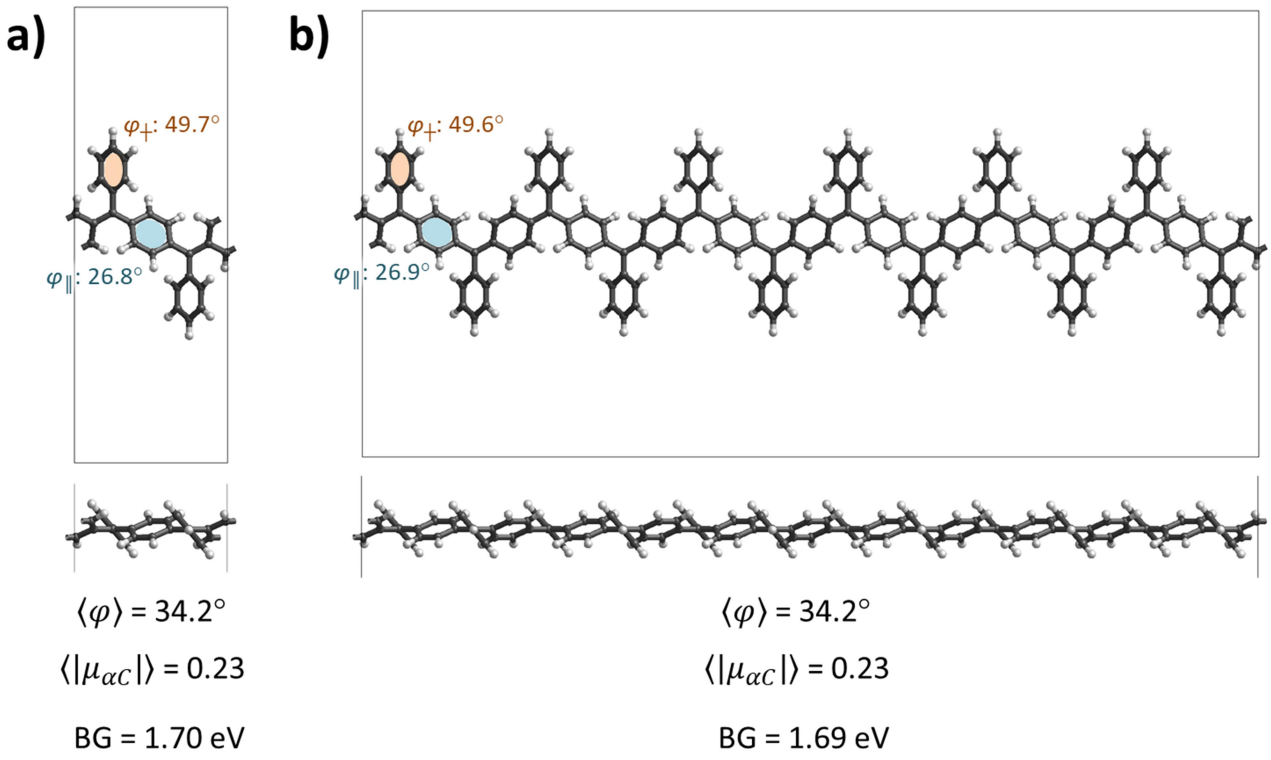

Fig. S1. Comparison of structural and electronic properties for the p-TPM polymer (most flexible considered polymer) obtained upon using **a)** the smallest periodic unit cell utilized throughout our study and **b)** the associated x6 supercell. Both systems where optimized using the settings specified in the Methods section in the main text, except for the smaller k-mesh for the x6 supercell due to its larger size (3 1 1 instead 18 1 1). Some resulting characteristic twist angles for perpendicular ($\varphi_\perp$, orange) and parallel aryl rings ($\varphi_\parallel$, blue) to the polymeric direction are provided. Key quantities such as the overall mean dihedral angle ($\langle\varphi\rangle$), the average of the absolute αC spin population ($\langle|\mu_{\alpha C}|\rangle$) and the electronic band gap (BG) are also provided for both cases at the bottom. As it may be seen, no apparent new distortions appear for the larger system, leading to almost identical structural and electronic properties for both periodic representations.

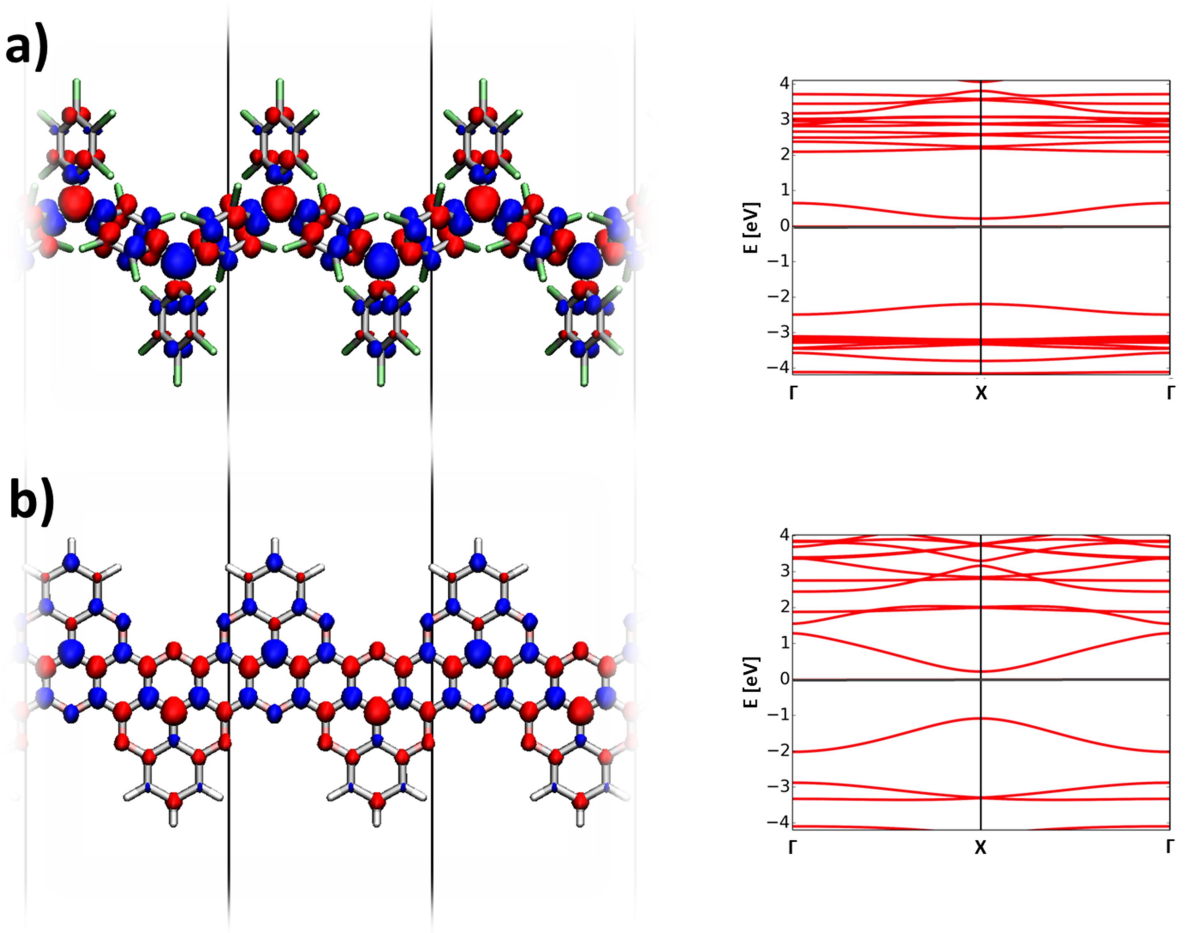

Fig. S2. (left) Spin density isosurface (spin up: blue, spin down: red; iso-surface value: 0.003 e/bohr^3) and (right) associated band structure in the open-shell multi-radical solution for **a)** the p-PTM and **b)** p-oxTAM polymers. Vertical lines indicate the periodic unit cell along the polymer direction. In the band structures the Fermi energy is marked with a black horizontal line.

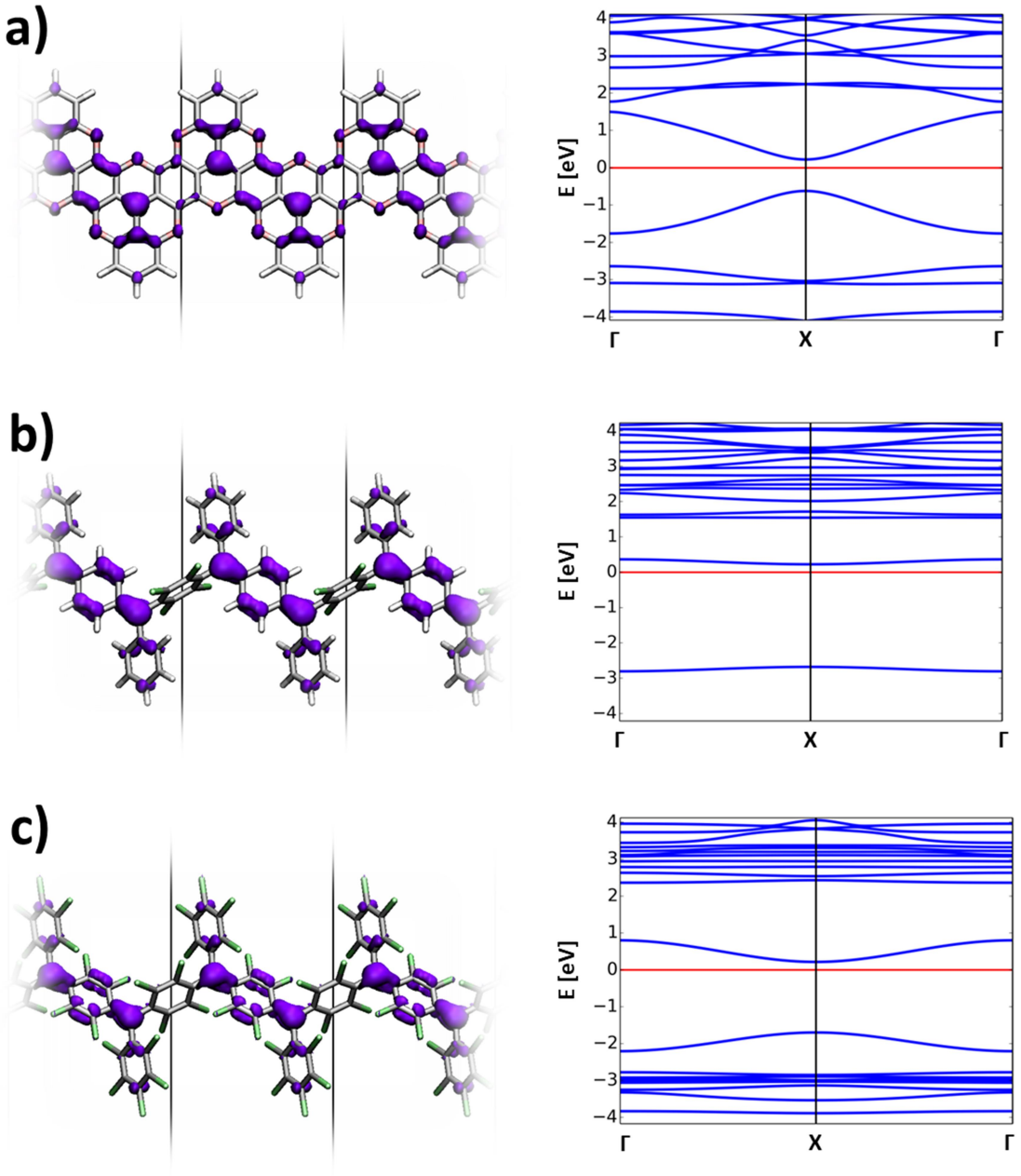

Fig. S3. (left) Highest occupied crystal orbital density (purple; iso-surface value: 0.002 e/bohr^3) and (right) associated band structure in the closed-shell quinoidal solution for **a)** p-oxTAM, **b)** p-BCM and **c)** p-PTM. Vertical lines indicate the periodic unit cell along the polymer direction. In the band structures the Fermi energy is marked with a red horizontal line.

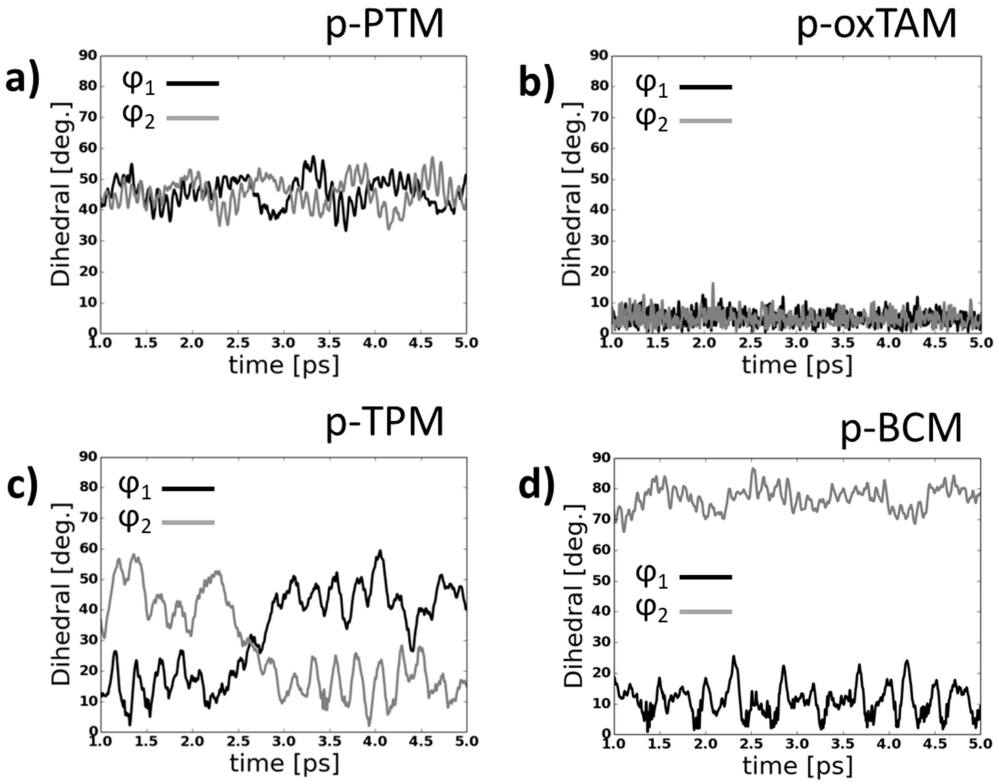

Fig. S4. Variation of the dihedral angles of aryl rings 1 and 2 (φ_1, φ_2 in the main text) during 4 ps of a molecular dynamics at 300 K for **a)** p-PTM, **b)** p-oxTAM, **c)** p-TPM and **d)** p-BCM polymers.

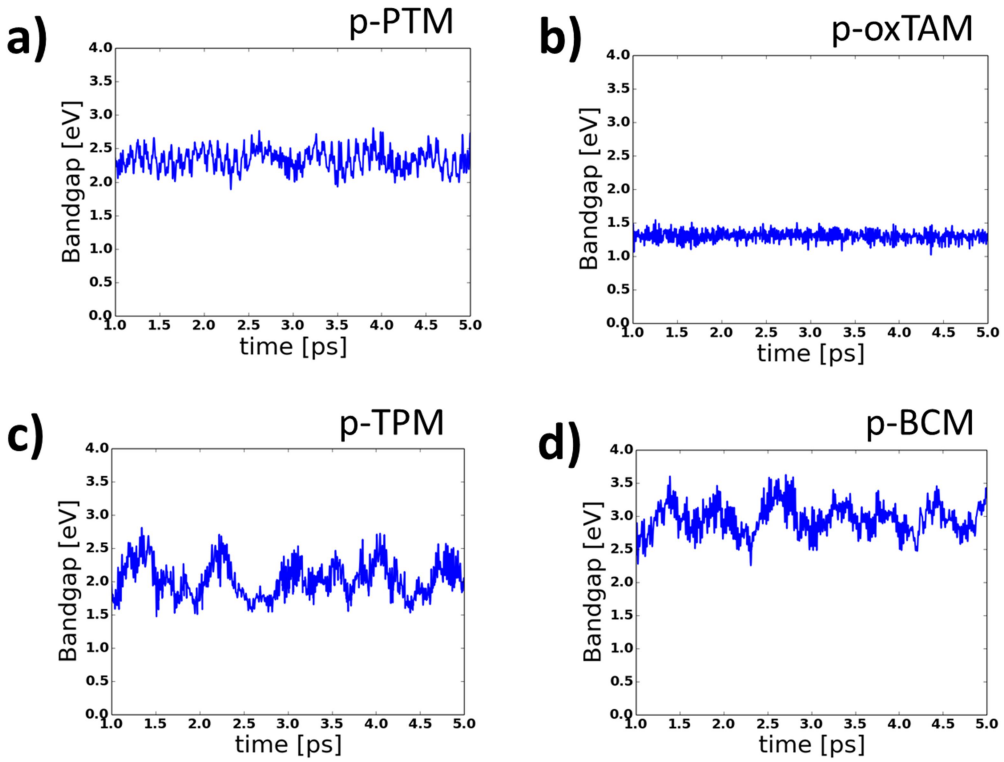

Fig. S5. Variation of the electronic bandgap during 4 ps of a molecular dynamics at 300 K for **a)** p-PTM, **b)** p-oxTAM, **c)** p-TPM and **d)** p-BCM polymers.

Optimized geometries shown in Fig. 2 of the main text (FHI-AIMS format)

Optimized geometry for the p-oxTAM 1D polymer

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lattice_vector     0.00000000     0.00000000    50.00000000
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atom      2.38187188    21.61943158    24.92129605 H
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atom      3.56521465    14.28519596    25.00693796 C
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Optimized geometry for the p-TPM 1D polymer

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atom 8.30800010 11.56233295 26.38211974 C
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atom 7.53384435 12.27116594 25.45708086 C
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atom 6.16408519 12.08487120 23.81624297 H
atom 6.98137060 16.20080006 24.41202457 H
atom 6.28476008 14.42928401 25.43704877 C
atom 6.13393354 15.73270309 24.89477091 C
atom 5.19604654 12.85037516 26.43039097 H
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Optimized geometry for the p-PTM 1D polymer

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Optimized geometry for the p-BCM 1D polymer

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