Supporting Information

Quantum engineering of mixed-valence 1D conjugated polymers

Lesly Katherine Sánchez De La Cruz [1], Jordi Ribas-Arino[1], Stefan T. Bromley[1,2] and Isaac Alcón[1,*]

[1]*Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028 Barcelona, Spain*

[2]*Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain*

* Corresponding author: ialcon@ub.edu

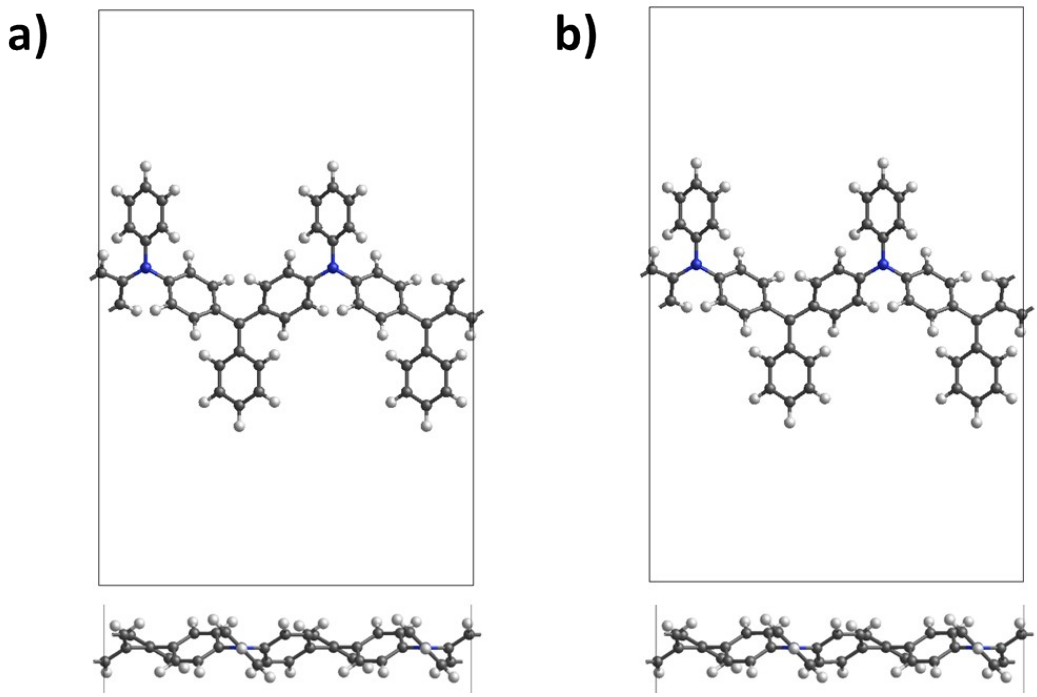

Figure S1. Optimized atomic structure of the NCNC-1DCP in a) the AFM configuration and b) the FM configuration. C, N and H atoms are depicted in grey, blue and white, respectively.

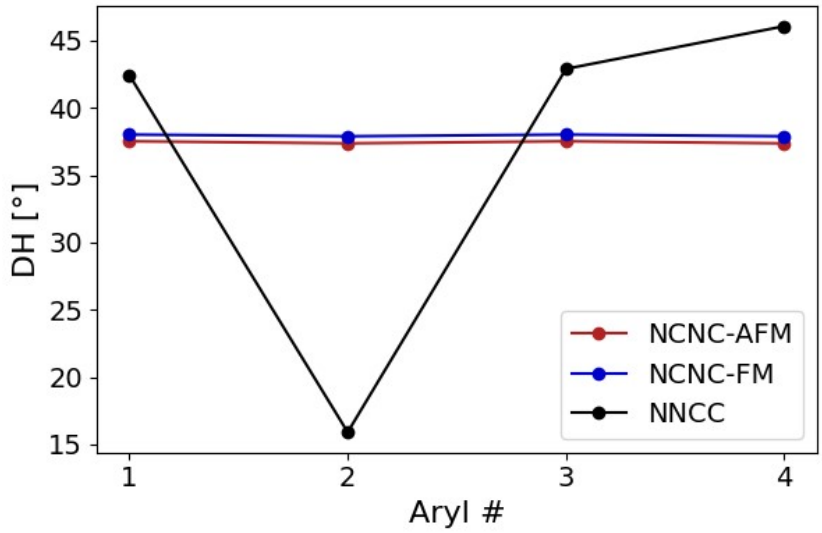

Figure S2. Dihedral angle for the four in-chain aryl rings for the NCNC-1DCP in the AFM (FM) configuration, displayed with red (blue) points, and the NNCC-1DCP (black points). Dihedral angles are calculated with respect to the sp^2 plane of the two αC centres to which each aryl ring is bonded.

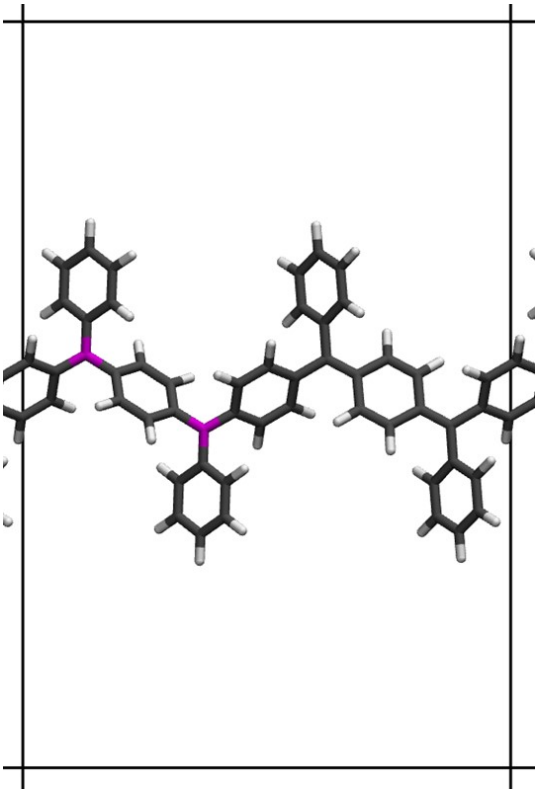

Figure S3. Spatially-resolved spin density for the NNCC-1DCP (iso-value: 0.005 e $bohr^{-3}$) showing no visible signs of spin-polarization and, thus, the closed-shell nature of the system.

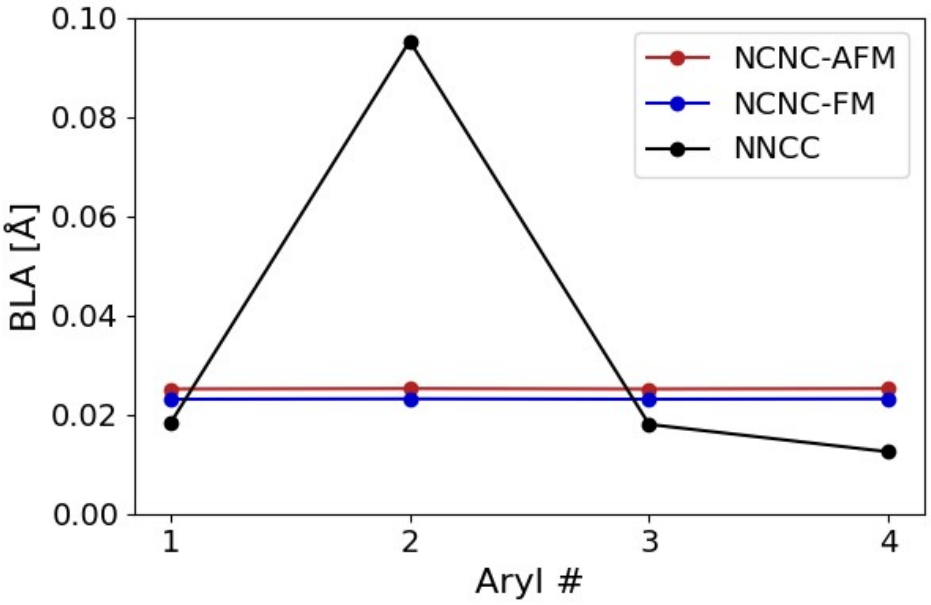

Figure S4. Bond-length alternation (BLA) for the four in-chain aryl rings for the NCNC-1DCP in the AFM (FM) configuration, displayed with red (blue) points, and the NNCC-1DCP (black points). BLA is calculated as done in prior studies focused on TAM 2DCPs.[1]

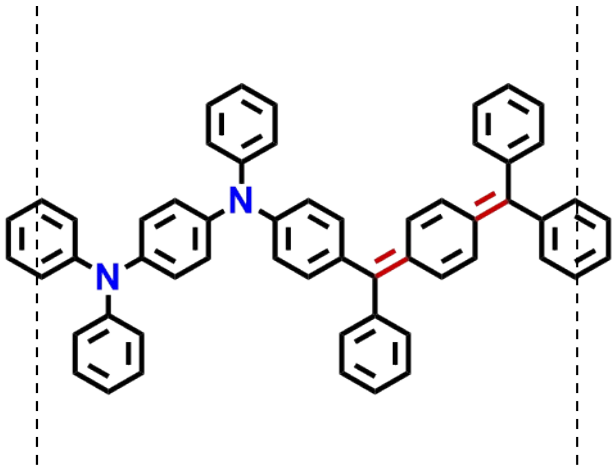

Figure S5. Lewis representation of the Kekulé electron-paired configuration that can only be drawn in the semi-alternant mv-1DCP (i.e. the NNCC-1DCP). The C-C double bonds between phenyl ring #4 and adjacent αC atoms, being the main driving force for the planarization of that ring, are highlighted in red.

Table S1. Average dihedral angle ($\langle\varphi\rangle$) and standard deviation (σ_{DH}) for each in-chain aryl ring during the AIMD run at 300 K (see Methods for details) for the NCNC-1DCP and the NNCC-1DCP. Dihedral angles are calculated for each snapshot as the twist angle between the aryl ring's plane and the sp^2 plane of adjacent αC centers.

$\langle\varphi\rangle$ / σ_{DH}	*Phenyl ring 1*	*Phenyl ring 2*	*Phenyl ring 3*	*Phenyl ring 4*
NCNC-1DCP	38.8° / 8.9°	38.6° / 9.1°	38.0° / 8.8°	38.2° / 8.6°
NNCC-1DCP	42.7° / 9.4°	48.2° / 10.0°	43.2° / 9.2°	15.5° / 4.9°

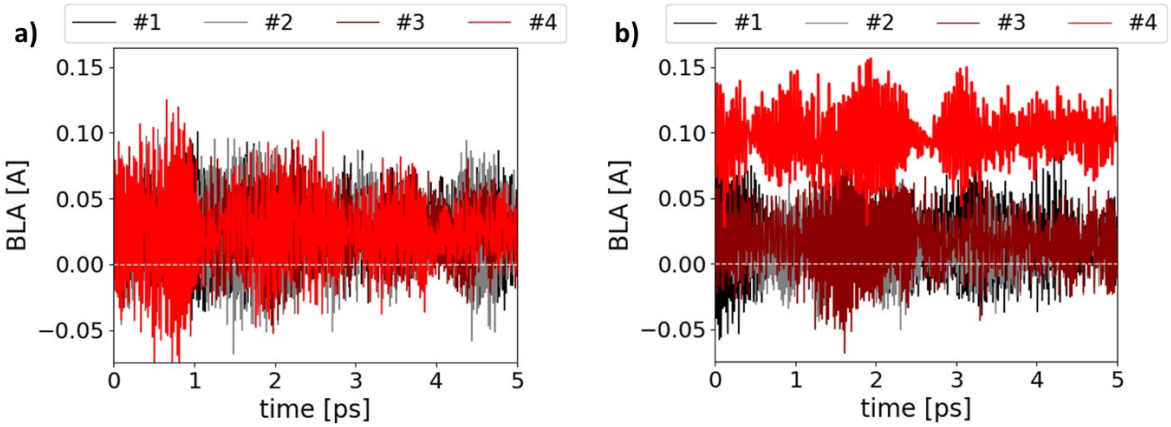

Figure S6. BLA for the four in-chain aryl rings for a) the NCNC-1DCP and b) the NNCC-1DCP during a 5 ps AIMD run at 300 K (see Methods in the main text for details). BLA is calculated as done in prior studies.[1]

Bibliography

1 I. Alcón, R. Santiago, J. Ribas-Arino, M. Deumal, I. de P. R. Moreira and S. T. Bromley, Controlling pairing of π-conjugated electrons in 2D covalent organic radical frameworks via in-plane strain, *Nature Communications*, 2021, **12**, 1705.