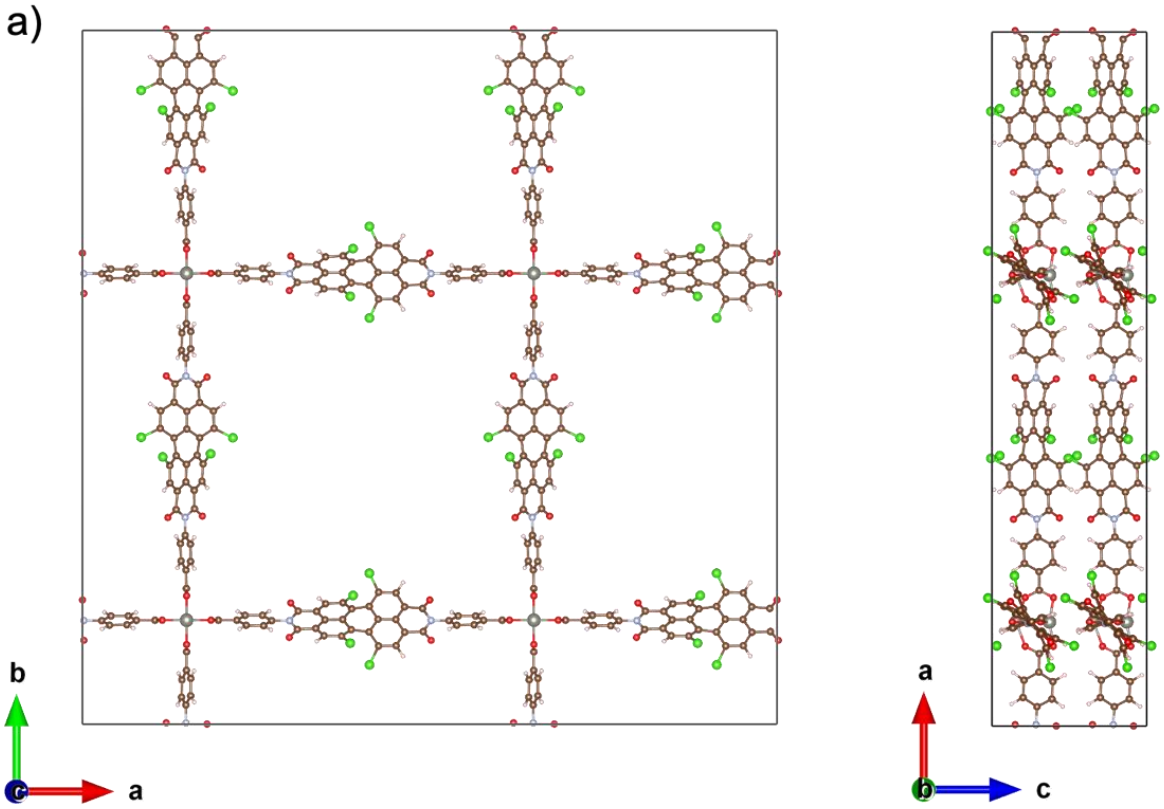
Electronic Supplementary Material (ESI) for Dalton Transactions.

Insight on the generation of near infra-red (NIR) absorbing species in electrochromic Surface-anchored Metal-Organic Frameworks

Antoine Mazel[1], Matteo Fornasarig[2], Josianne Owona[2,3], Lionel Truflandier[2], Frédéric Castet[2], Aline Rougier[1]

[1]Univ. Bordeaux, CNRS, Bx INP, ICMCB, UMR 5026, F-33600 Pessac, France
[2]Univ. Bordeaux, CNRS, Bx INP, ISM, UMR 5255, F-33405 Cedex Talence, France
[3]Donostia International Physics Center (DIPC), Manuel Lardizabal Ibilbidea 4, 20018 Donostia, Euskadi, Spain

Supporting information



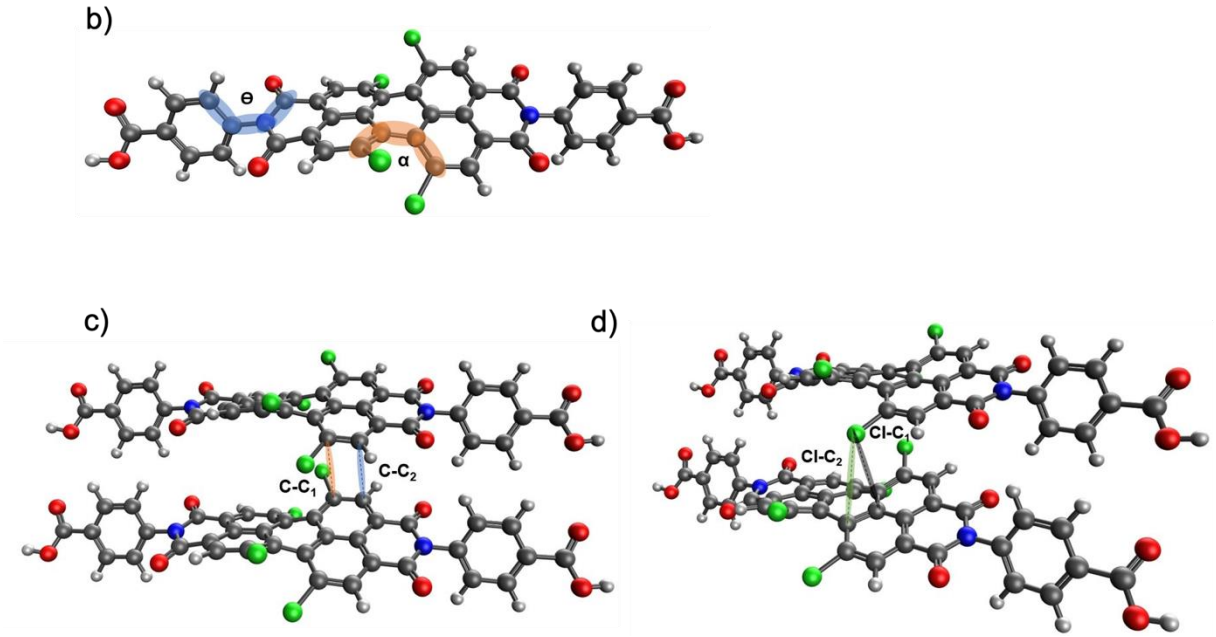


Figure S1: a) Calculated crystal unit cell; b) Structure of a PDI organic ligand extracted from the optimized crystal unit cell, with definition of the dihedral angles α (yellow) and Θ (blue); c) and d) Shortest C-C and C-Cl distances between neighbouring PDI units.

Table S1: Calculated unit cell parameters *a*, *b* and *c* (Å), dihedral angles (α and Θ, degrees), and shortest interlayer C-C and C-Cl distances (Å) – see Figure S1 for angles and distances definition.

a	b	c	α	Θ	C-C_1	C-C_2	Cl-C_1	Cl-C_2
56.10	56.11	12.47	31.2-30.7	55.0-64.0	3.46	3.34	3.50	3.85

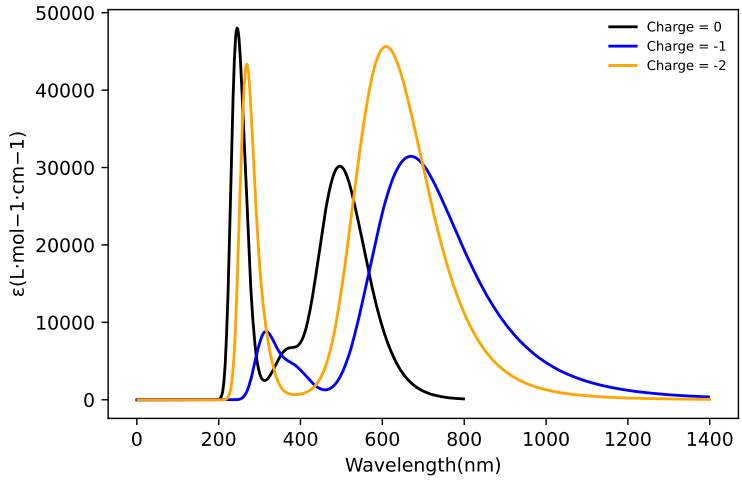


Figure S2: Absorption spectra of the neutral and reduced states of a PDI ligand extracted from the optimized crystal structure, as calculated at the CAM-B3LYP/6-311+G(d) level.

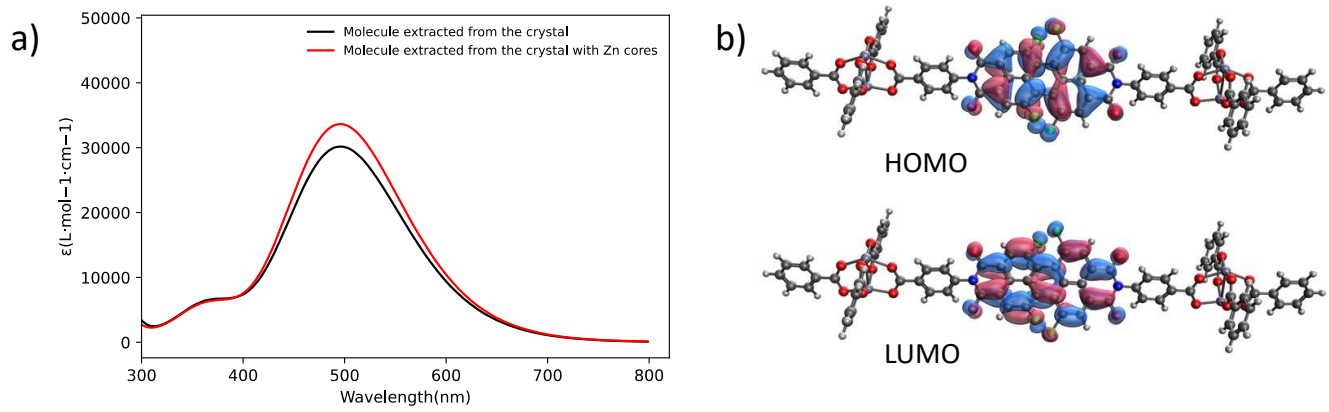


Figure S3: a) Absorption spectra of a PDI ligand extracted from the optimized crystal structure (black), and of the same ligand connected on both sides to a metallic node, as calculated at the CAM-B3LYP/6-311+G(d) level. The lowest-energy band is due to an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest occupied one (LUMO), represented in b).

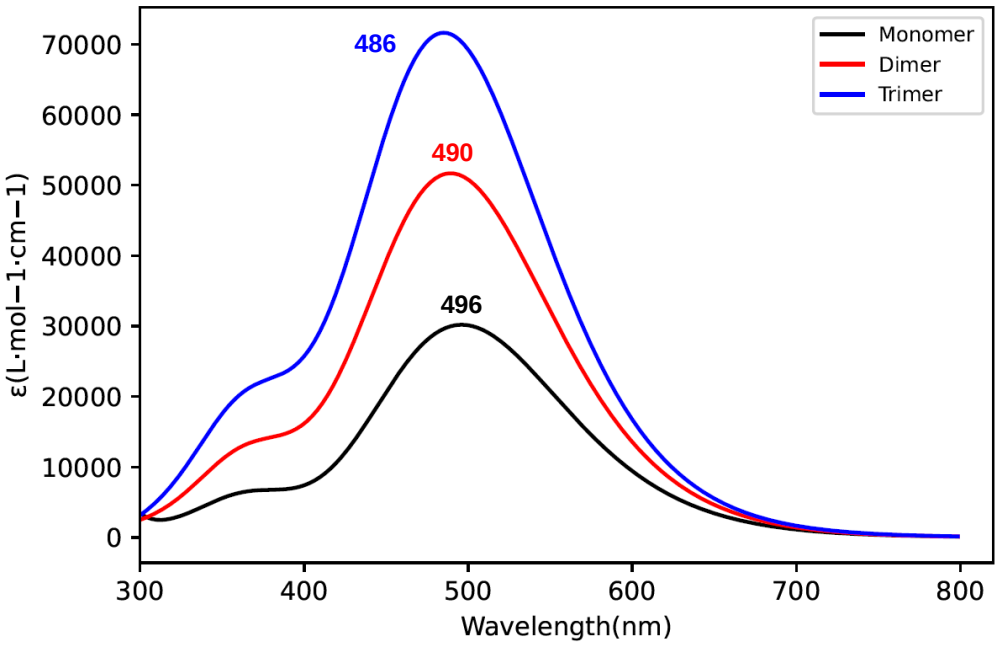


Figure S4: Absorption spectra of a PDI monomer (black), dimer (red) and trimer (blue) extracted from the optimized crystal structure, calculated at the CAM-B3LYP/6-311G(d) level.