

Supplementary Information

Regulating the stability of 2D crystal structures using an oxidation state dependent molecular conformation

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1. Experimental details
 - (a) X-ray crystallography
 - (b) Thin film fluorescence measurements.
 - (c) Scanning tunneling microscopy.
2. Molecular orbital calculations.
3. Solid state fluorescence spectra.

1. Experimental

(a) X-ray Crystallography. Crystals of TDtBHPP suitable for crystallography were grown by slow evaporation of a solution of the porphyrins in a 1:1 mixture of dichloromethane and *n*-hexane. A rhombic block was selected and mounted on a glass fiber using paraffin oil which was then placed in the diffractometer coldstream at 200 K. Data were collected on a Bruker SMART APEX diffractometer using graphite-monochromated MoK α radiation. Refinement was by direct methods using SHELXL-97. TDtBHPP: C₇₆H₉₄N₄O₄·3C₆H₁₄, M = 1386.07 g/mol, crystal size 0.3 x 0.3 x 0.2 mm³, colour: purple-red, rhombic block, space group *P*-1, *a* = 10.643(2), *b* = 14.476(3), *c* = 15.377(3) Å, α = 97.08(3)°, β = 102.40(3)°, γ = 110.63(3)°, *U* = 2113.5(7) Å³, *Z* = 1, ρ_{calcd} = 1.089 mg/m³, 17899 reflections measured, 7878 were unique (Rint. 0.0469); Refinement against *F*² to *w*R²: 0.1343, R1 = 0.0642 (3903 reflections with *I* > 2 σ (*I*)), 606 parameters, 0 restraints. The porphyrin molecule lies on an inversion centre. Additionally, one hexane solvate is inversion disordered and only its position can be determined.

(b) Thin Film Fluorescence Measurements. Fluorescence measurements were performed in air on samples evaporated onto glass substrates and using the total internal reflection geometry. Porphyrin and oxidized porphyrin were excited using the 441.6-nm line of a He-Cd laser and the 514.5-nm line of an Ar ion laser, respectively. Laser light was focused onto the glass substrate from the backside using an objective lens with a numerical aperture of 1.45. Light emitted from the sample was collected by the same objective lens, and analyzed using a spectrograph equipped with a liquid-nitrogen-cooled

CCD camera. The spectra are corrected for the energy-dependent sensitivity of the photodetection system.

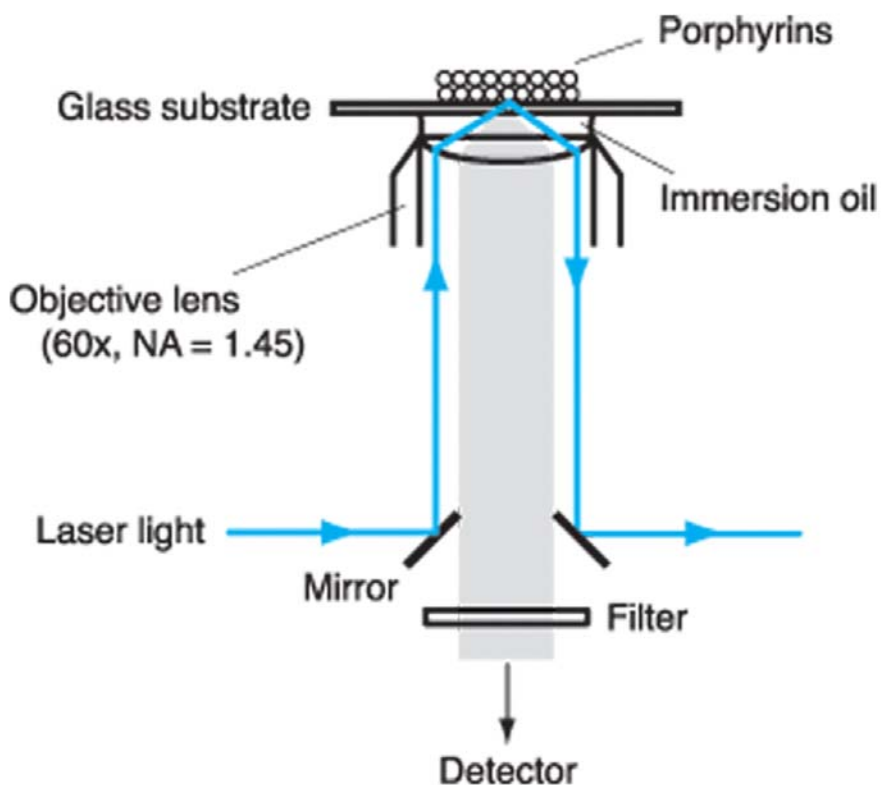


Fig. S1. Instrumental geometry used for the solid state fluorescence measurements.

(c) Scanning Tunneling Microscopy

The atomically clean single crystals of Cu(111) used as substrates were prepared by Ar^+ sputtering and annealing (700K) cycles. Sub-monolayer coverage of the substrate was assured by sublimation for 10 mins at 320°C from a Knudsen cell to the metal substrate over an intervening distance of 30 cm in ultra-high vacuum (1×10^{-8} Pa). STM was performed in ultrahigh vacuum.

2. Molecular Orbital Calculations

Molecular orbital structures and energies and electrostatic surfaces of the molecules studied were calculated using *Gaussian 03* Revision B.04^{S1} and figures generated using Gaussview.

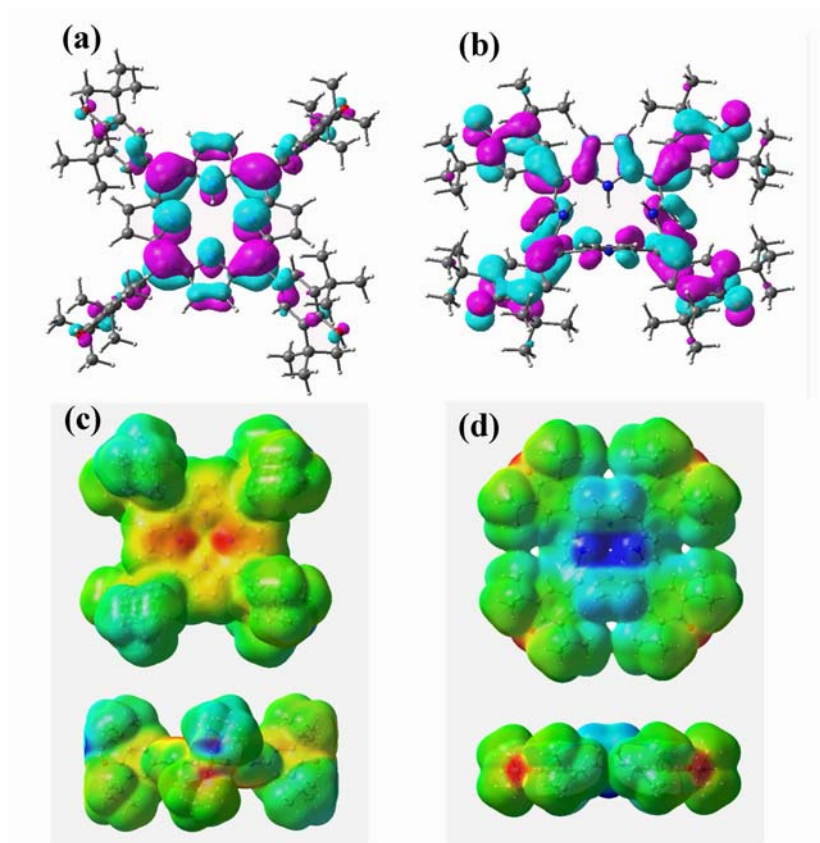


Fig. S2. Structures of the highest occupied molecular orbitals (HOMO) of (a) TDtBHPP; (b) Ox(TDtBHPP) calculated at the B3LYP/3-21G(*) level of density functional theory (DFT). Panels (c) and (d) show the electrostatic surfaces of TDtBHPP and Ox(TDtBHPP), respectively, in plan and side-on elevations. The electrostatic surfaces match closely the morphology of the molecules observed by STM for TDtBHPP, having a large dihedral angle between porphyrin and phenyl substituents, and for Ox(TDtBHPP), where the substituents approach coplanarity.

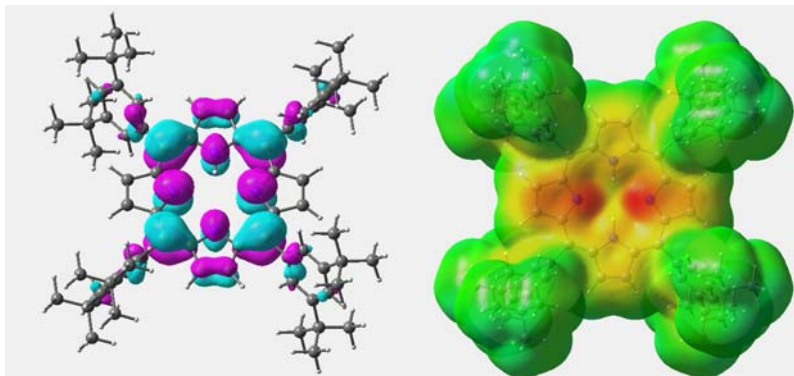


Fig. S3. L.H.S. Molecular orbital (HOMO) and R.H.S electrostatic potential surface of 5,10,15,20-tetrakis(3,5-di-t-butylphenyl)porphyrin, the non-phenolic analogue of TDtBHPP.

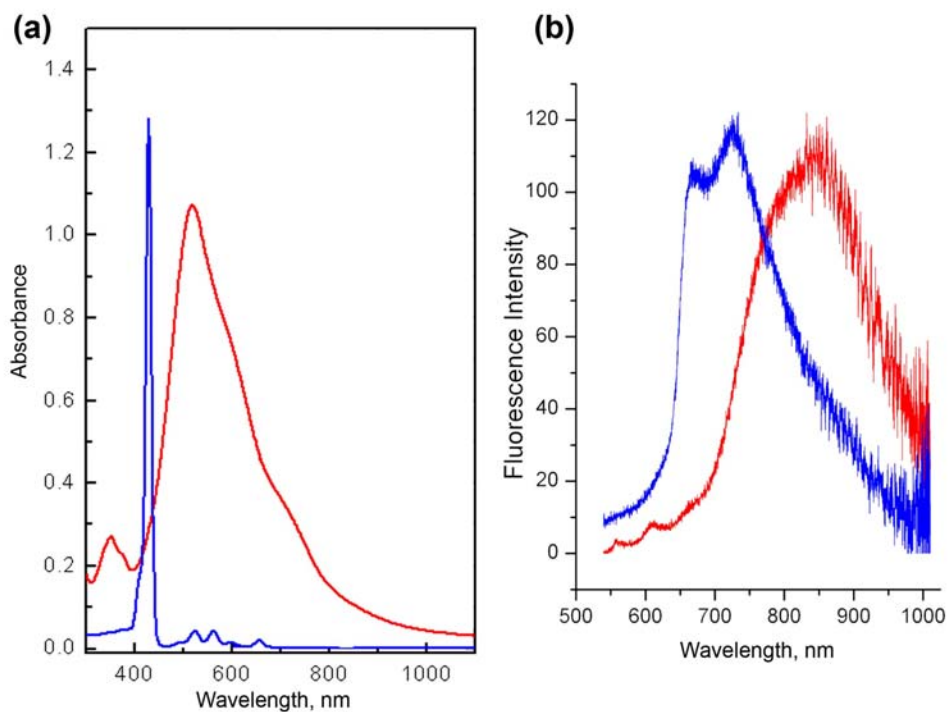


Fig. S4. (a) Electronic spectroscopy of TDtBHPP) and Ox(TDtBHPP). UV/Vis and fluorescence emission of TDtBHPP (blue) and Ox(TDtBHPP) (red) measured from 1,2-dichlorobenzene solutions. (b) Fluorescence spectra of multilayer films (2 monolayers approx.) of the compounds after deposition by sublimation onto a glass substrate. TDtBHPP (blue); Ox(TDtBHPP) (red).

References

- S1. *Gaussian 98* (Revision A.9), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.