Supplementary Information: Electronic and optical properties of archetypical porphyrin crystals and thin films

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S1 CRYSTAL STRUCTURE

The experimental H2TPP crystal data [1] is obtained from Cambridge crystallographic data center [2] [3]. The ionic positions and unit cell are optimized in VASP [4] using the semi-empirical Van der Waals (VdW) correction methods [5]: DFT-D2 [6], DFT-D3 (with [7] and without Becke-Jonson damping function [8], denoted as DFT-D3(BJ) and DFT-D3(ZD) respectively) by Grimme *et al.*; Tkatchenko-Scheffler method DFT-TS [9]; and many-body dispersion energy method (MBD@rSC) [10, 11]. We employ PBE exchange correlation with dispersion correction and PAW [12] potentials of the VASP 5.4 distribution. A $3 \times 3 \times 3$ Γ -centered Monkhorst-Pack K-point grid, an energy cutoff of 650 eV and augmentation cutoff of 1200 eV provide converged results.

In order to minimize potential errors due to Pulay stresses, the relaxation of the crystal structure is performed in consecutive ions-only and ions + supercell shape and volume optimization steps, repeating the iterations until convergence on forces and stress is achieved. The results for H2TPP are given in Tables S1, S2 and S3 together with the experimental X-ray data for comparison purposes. Similar results are obtained for MgTPP which are not stated here due to the lack of corresponding experimental data. Files containing coordinates and lattice parameters as obtained within DFT-D3(ZD) are available as ESI.

In the present DFT calculation zero point vibrations are lacking in the DFT optimization procedure as well as any anharmonic vibrational effects. Besides short-comings of the DFT-VdW methods, this may explain discrepancies in comparison to the experimental data. In our case, DFT-D3(ZD) and MBD@rSC yield very similar results and have the lowest variance with the room temperature experiment. The other tested methods tend to overbind more, and result in a much smaller cell volume.

The porphyrin in the crystal phase is distorted and assumes a saddle shape. The key intramolecular bond distances, and intermolecular distance (Figure S1) are reported in Tables S2 and S3. The hydrogen bond discrepancies between experiment and DFT ($\sim 11\%$) are well known and discussed in the literature and will not be discussed further here. The other calculated intra molecular bond distance are slightly larger ($\sim 4\%$) than in experiment and only slightly depend on the VdW scheme employed in the calculations.

The dihedral angle between the macrocycle plane and the phenyl rings is calculated to be larger in gasphase by almost 10 degrees. The DFT-D2 method, which overbinds, reports the smallest dihedral angles both in gas-phase (by 2 degrees), and in crystal (by 5 degrees). DFT-D3 and MBd@rSC report similar values in the crystal.

We report the binding energy (the energy difference between the molecule in the gas phase and in the crystal) in Table S4 and the cleavage energy (the energy required to cleave the crystal along a layer) in Figure 2. The binding energy indicates that the material is a VdW bound crystal. Again, the DFT-D3 and MBd@rSC methods give very similar binding energies. The cleavage energy is calculated by introducing a fracture in the bulk and then gradually increasing the separation between the two cleaved parts and measuring the variation of the total energy. Calculating the cleavage energy of graphite using exactly the same procedure, yields a value very close to the experimental result [13], taking into account various external factors that can effect the outcome in the experimental setup [13]. The calculated cleavage energies of MgTPP and H2TPP are almost equal, with MgTPP being slightly larger. The values correspond to two thirds of the cleavage energy of graphite [13].

In addition to the experimentally observed crystal packing, we investigate three additional possible scenarios for thick MgTPP films following the strong and weak interaction idea from Perepogu *et al.* [14]: 1) The simple stack where porphyrin molecules are directly on top of each other. 2) Rotated stack, where porphyrin layers are 90° rotated with respect to each other 3) Herringbone where each porphyrin is coordinated with the phenyl rings of another porphyrin perpendicular to it. Each structure was optimized using the described approach along with DFT-D3. The binding energies of the models are reported in Table S5. The most stable structure is

Table S1. Calculated and experimental lattice parameters for the H2TPP crystal. All the structures belong to the space group P-1.

	a (Å)	b (Å)	c (Å)	α	β	γ	Volume $(Å^3)$
Experimental[1]	12.395	10.464	6.433	101.21°	99.33°	95.74°	800.13
DFT-D2	11.965	9.924	6.277	99.90°	100.14°	93.19°	719.98
DFT-D3 (ZD)	12.158	10.349	6.324	100.53°	99.63°	94.32°	766.63
DFT-D3 (BJ)	12.106	10.213	6.297	100.08°	99.75°	93.88°	751.60
DFT-TS	12.025	10.243	6.245	99.87°	100.12°	93.51°	742.71
MBd@rSC	12.119	10.276	6.299	100.28°	99.55°	94.28°	756.76

Table S2. Structural parameters of the H2TPP molecule in the crystal (cf. Fig. S1).

	Exp	D2	D3 (ZD)	D3(BJ)	TS	MBd@rSC
C-C (phenyl) (Å)	1.383	1.394	1.397	1.407	1.407	1.394
C-C (pyr) (Å)	1.338	1.357	1.358	1.359	1.356	1.357
C-H (phenyl) (Å)	0.951	1.088	1.090	1.090	1.090	1.092
C-H (pyr) (Å)	0.950	1.083	1.084	1.084	1.082	1.084
N-H (Å)	0.964	1.021	1.022	1.022	1.022	1.022
N-C (Å)	1.374	1.372	1.375	1.375	1.369	1.370
$lpha_{ m ph}$	59.74°	53.56°	55.33°	54.59°	55.11°	55.26°
d1 (Å)	6.925	6.977	6.990	6.984	7.007	6.974
d2 (Å)	8.564	8.582	8.585	8.581	8.596	8.573
А	3.616	3.308	3.504	3.445	3.316	3.487



Figure S1. Guide to the structural parameters reported in Table S2 and Table S3. The parameter A represents the distance between the pyrrolic nitrogen and the pyrrolic carbon of the next layer in the H2TPP crystal.

the analog to the H2TPP crystal followed by the simple stack.

In the crystal, dispersive bands are observed already at PBE level of theory. The resulting HOMO-LUMO gap, however, is too small and does not reproduce the band-gap renormalization described in the main text. Qualitatively, the presence of these dispersive bands can be discerned from the gas phase molecule as an asymmetrical broadening of the frontier orbitals in DOS. The amount of broadening depends on the structural parameters and coordinates, and thus the VdW correction employed. The impact of different VdW corrections used for the variable cell relaxation on the broadening effect is summarized in Table S6 and Figure S2. Except for the DFT-TS structure, values for the HOMO broadening vary in a narrow range between 110 and 127 meV and for the LUMO between 203 and 254 meV.

In Figures S3 and S4 a quantitative comparison is made between the decomposed charge density of the Gouterman molecular orbitals of the isolated molecule and the band-decomposed charge density of the corresponding band states:

$$\Delta \rho_i(\vec{r}) = |\psi_i^{\rm g}(\vec{r})|^2 - \int_{\rm BZ} |\psi_{i,\vec{k}}^{\rm s}(\vec{r})|^2 dk^3 \qquad (1)$$

where $\psi_i^{\rm g}(\vec{r})$ and $\psi_{i,\vec{k}}^{\rm s}(\vec{r})$ are the wavefunctions of the *i*-th molecular orbital of the isolated molecule and the corresponding band of the crystal respectively, \vec{k} denotes the k-point and the integration is over the Brillouin zone.

Apparently crystallization has only a minor effect on the Gouterman orbitals HOMO and LUMO, with slightly larger deviations on the other two orbitals: In HOMO-1, the electron density is slightly more pronounced over N-H; in LUMO+1, the electron density at the phenyl rings is slightly larger.

	DFT-D2	DFT-D3(ZD)	DFT-D3(BJ)	DFT-TS	MBd@rSC
C-C (phenyl) (Å)	1.405	1.397	1.404	1.404	1.396
C-C (pyr) (Å)	1.458	1.458	1.360	1.359	1.359
C-H (phenyl) (Å)	1.091	1.091	1.091	1.091	1.090
C-H (pyr) (Å)	1.085	1.085	1.085	1.085	1.085
N-H (Å)	1.021	1.021	1.021	1.021	1.021
N-C $(Å)$	1.376	1.378	1.377	1.376	1.370
$lpha_{ m ph}$	60.75°	65.21°	63.69°	68.71°	63.19°
d1 (Å)	6.932	6.938	6.948	6.921	6.926
d2 (Å)	8.635	8.649	8.641	8.654	8.633

Table S3. Structural parameters of the H2TPP molecule in the gas-phase (cf. Fig. S1)



Figure S2. Comparison between the DOS and the band structure of crystals as obtained using DFT-D3 and MBd@rSC.

The same effect is seen at different approximation levels.

and MgTPP [17–20] (see Figure 3).

S2 QUASIPARTICLE ENERGY LEVELS

We employ a sc- GW_0 scheme [4, 15, 16] to obtain quasiparticle levels. The choice of the exchange correlation functional for the initial DFT orbitals, the GW flavor, parameters and convergence are calibrated against NIST data for the gas phase H2TPP A consistent NIST level accuracy for various aromatic molecules and porphyrins is achieved when LDA exchange-correlation and PAW potentials in conjunction with sc-GW₀ is used on the optimized structures obtained in the manner described in previous section. We use an energy cutoff of 800 eV and an augmentation cutoff of 1214 eV. $3\times3\times3$ Γ -centered Monkhorst-Pack K-point grid is used for the crystal. The convergence was achieved by padding additional virtual Kohn-Sham bands en-



Figure S3. Comparison between molecular orbital charge densities of the isolated molecule and the band decomposed charge densities in the H2TPP crystal of the corresponding bands using their difference given by Eq. (1). (a),(b) isosurface plots of the charge density of the isolated molecule of HOMO-1 and HOMO (left) and the corresponding charge density difference $\Delta \rho_i(\vec{r})$ (right). Units are electron/Å³. In the right panels red (green) means charge density in the crystal (isolated molecule) is more dominant in a particular region.

Table S4. The calculated binding energy $E_{\rm b}$ per molecule of the H2TPP crystal for different emperical dispersion correction schemes.

	$E_{\rm b}~({\rm eV})$
PBE	0.192
DFT-D2	2.490
DFT-D3 (ZD)	2.591
DFT-D3 (BJ)	2.529
DFT-TS	3.197
MBd@rSC	2.580

Table S5. The calculated binding energy $E_{\rm b}$ per molecule of different MgTPP supramolecular bulk structures (DFT-D3).

	$E_{\rm b}~({\rm eV})$
Herringbone stack	0.3
Rotated stack	1.7
Simple stack	2.07
P-1 triclinic crystal	2.62

gas phase and 135 eV above the HOMO level for the crystal phase. sc-GW₀ iterations exhibit a convergent oscillatory behavior, different at each quasipar-

compassing 84 eV above the HOMO level for the



Figure S4. Comparison between molecular orbital charge densities of the isolated molecule and the band decomposed charge densities in the H2TPP crystal of the corresponding bands using their difference given by Eq. (1). (a),(b) isosurface plots of the charge density of the isolated molecule of LUMO and LUMO+1 (left) and the corresponding charge density difference $\Delta \rho_i(\vec{r})$ (right). For details see Fig. S3.

Table S6. Band gap $E_{\rm gap}$ and broadening of HOMO and LUMO bands $\Delta_{\rm HOMO}$ and $\Delta_{\rm LUMO}$ in eV for P-1 triclinic structure for H2TPP provided by experiment [1] and the different crystal structures obtained with the indicated VdW schemes and a variable cell relaxation.

$\operatorname{Structure}$	$E_{\rm gap}$	$\Delta_{\rm HOMO}$	$\Delta_{\rm LUMO}$
$\mathbf{Experimental}$	1.569	0.115	0.203
DFT-D2	1.493	0.127	0.250
DFT-D3 (ZD)	1.493	0.119	0.240
DFT-D3 (BJ)	1.534	0.110	0.204
DFT-TS	1.461	0.151	0.119
MBd@rSC	1.487	0.124	0.254

ticle level (lower levels usually converging faster). A 10^{-3} eV level accuracy from HOMO-5 to LUMO+5

is attained after roughly $18 \text{ sc-} \text{GW}_0$ iterations.

Periodic boundary conditions are used in VASP, hence, the energy values obtained from the calculation need a common energy reference. We use the vacuum level for this purpose, in order to be directly comparable with the experiment. It is straightforward to identify the vacuum level in the supercell used for gas phase calculations using the plane average of the potential. However, this strategy is not applicable to the crystal. Instead, we use the following procedure: First we calculate the vacuum level using a slab model with ample vacuum. Then compare the similar potential regions of the crystal and the slab model (probe points) to identify the relative shift between these two calculations, inspired by Alkauskas *et al.* [21]. This is relatively easy due to the layered nature of the material. An example of the procedure is presented in Figure S5. The small shift of the Fermi level can be attributed to surface polarization effects.



Figure S5. Alignment of the energy levels in the bulk to the vacuum level. The crystals considered in this work are layered, thus it is relatively easy to identify similar potential regions between a slab model and crystal bulk (probe points). Then the bulk potential probe point can be referenced to the slab model probe point, and thus the vacuum level.

S3 WANNIER FUNCTIONS

The maximally localized Wannier functions (ML-WFs) method of Marzari and Vanderbilt [22] provides unique Wannier functions by minimizing the spread. We employ these MLWFs for the extrapolation of the quasi particle band structure at the sc-GW level from quasiparticle levels obtained on a dense k-point grid in order to bypass unfeasible direct calculation using solely the sc-GW scheme as described in Refs. [23, 24]. The consistency of this approach is thoroughly verified at the PBE level, and full agreement with directly calculated band structure is obtained.

The quasiparticle energy levels of H2TPP and MgTPP in gas phase are well studied [25]. The macrocycle of the porphyrins (porphine skeleton where phenyl rings attach) is characterized by a 18 electron π - π ring, and two double bonds. The bonding scheme is actually a competition between alternating single and double bonds which promote σ - π bonds to the macrocycle nitrogen, versus the 18 electron π - π ring. In the ground state, the former promotes a C_{2v} symmetry, while the latter promotes a D_{2h} symmetry. Alteration of this bonding scheme leads to a vast number of chemically diverse conformers [26]. This information was used as the basis

for constructing the initial guess for the wannierization procedure.

We calculate 130 bands in wannier90 [27], and read 204 out of 3000 from sc-GW₀ calculation. A disentanglement procedure for the quasiparticle states in an energy range above 6.7 eV is performed with a convergence criteria of 10^{-10} on Ω . After the disentanglement procedure, 10000 iterations are proceeded to obtain a spread convergence on the order of 10^{-11} . Guiding centers are used to prevent local minima. As an initial guess, we set a mixture of random and p_z style orbitals on carbon and nitrogen atoms, and s style orbitals on Hydrogen.

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