Supporting Information

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Avoiding the Center-Symmetry Trap: Programmed Assembly of Dipolar Precursors into Porous, Crystalline Molecular Thin Films

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Experimental section

Synthesis of asymmetric Cu(BPDC)(Me₂-BPY) SURMOF

The Cu(BPDC)(Me₂-BPY) SURMOF was synthesized in a fluidic cell by layer-by-layer method on a self-assembled monolayer (SAM) functionalized Au substrate. The Au substrate (100-nm Au/2-nm Ti evaporated on Si wafers) was first functionalized with an 11-mercaptopoundecanol (MUD) terminated SAM. Subsequently, the substrate was rinsed with absolute ethanol and dried under an N₂ stream. The freshly prepared substrate was then
placed in a fluidic cell. Using automatized channel pumps, a 1 mM copper acetate ethanol solution (retention time = 15 min) and a 0.1 mM BPDC+ 0.1mM Me₂-BPY ethanol solution (retention time = 25 min) at 75 °C were injected alternately. Between each injection step, the substrates were rinsed with ethanol for 25 s of flow time to remove unreacted metal/linker or by-products from the surface. The thickness of the samples was controlled by the number of deposition cycles (30, 50 and 70 cycles).

![Diagram of pillared-layer SURMOF design](image)

**Figure S1**: A schematic illustration of non-centrosymmetric pillared-layer SURMOF design using an asymmetric pillar.

**Synthesis of symmetric Cu(BPDC)(BPY) SURMOF**

For Cu(BPDC)(BPY) SURMOF synthesis, an identical method was used, except replacing the Me₂-BPY with the BPY pillar.

For XPS measurements, to realize the built-in electric field, in the last cycle of SURMOF preparation instead of 0.1 mM BPDC+ 0.1mM Me₂-BPY/BPY solution, a 0.1 mM tetrabromoterephthalic acid (Br₄-BDC)+ 0.1mM Me₂-BPY/BPY solution was used.

**X-ray diffraction (XRD)**
The XRD measurements for out-of-plane (co-planar orientation) were carried out using a Bruker D8-Advance diffractometer equipped with a position-sensitive detector Lynxeye in geometry, variable divergence slit and 2.3° Soller-slit was used on the secondary side. The Cu-anode which utilize the Cu Kα₁,₂-radiation (λ= 0.154018 nm) was used as a source.

**Infrared Reflection Absorption Spectra (IRRAS)**

The infrared spectra were recorded with a Fourier-Transform Infrared Reflection Absorption (FT-IRRA) Spectrometer Bruker Vertex 80 with liquid nitrogen-cooled mercury–cadmium–telluride mid-band detector. The spectra were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal. A perdeuterated 1-hexadecanethiol self-assembled monolayer on a gold substrate was used as a background reference sample.

**X-ray photoelectron spectroscopy (XPS)**

The XPS measurements were carried out under an ultra-high vacuum with a base pressure of 1×10⁻⁹ mbar. Core-level spectra were recorded under normal emission with a Scienta R4000 hemispherical electron analyzer using Al-Kα radiation (1486.6 eV). Firstly, for every sample the survey XP spectrum was measured and no unexpected contaminations were observed in these spectra. Then, the detailed C1s, O1s, N1s, Cu2p, and combined Au4f+Cu3p+Br3d XP spectra were recorded. The detailed C1s, O1s, N1s, Cu2p XP spectra look rather similar both for symmetric (Cu(BPDC)(BPY)) and asymmetric (Cu(BPDC)(Me₂-BPY)) SURMOFs demonstrating a good quality of the samples. No reasonable differences in these detailed XP spectra were observed in dependency on the layer thickness. The combined Au4f+Cu3p+Br3d XP spectrum was used for the determination of the built-in electric field effect. For a precise determination of the Br3d/Au4f-lines position and necessary correction the CasaXPS software was used. Since there is an overlapping between Au4f₇/₂ and Cu3p peaks Au4f₅/₂ peak has been chosen for the correction procedure. All spectra were fitted with Voigt profile (10% of Lorentz contribution) using linear background for Au4f₅/₂ peak and Shirley background for Br3d peak. The line correction was adjusted to Au4f₅/₂ peak at 87.8 eV.

For these experiments a few series of samples with the same layer thickness (at least two samples in the series) were prepared. Then every sample was divided into 2-3 pieces and
every piece was investigated separately. The deviations of binding energy values were less than 0.1 eV and they are presented in the Inset to Figure S4 as the error bars.

**SHG-Experiments**
For the SHG measurements a diode-pumped picosecond Nd:YAG laser (Ekspla) with a repetitions rate of 50 Hz, a pulse duration of 28 ps ± 10%, pulse energy around 30 mJ, and a beam diameter of approximately 5 mm were used. The central wavelength of 1064 nm resulted in an SHG signal of 532 nm. The measurements were taken in reflection mode under an angle of 60° to the surface normal. The SHG signal was focused onto a monochromator and detected by a photo-multiplier tube. P-polarization was used for the incident as well as for the detected light. The SURMOFs were prepared on substrates of sapphire (CrysTec, single crystal, (0001) surface, both sides polished).

**Scanning electron microscope (SEM)**
The SEM measurements were carried out using a Field Emission Gun (FEI) Philips XL SERIES 30 ESEM-FEG (FEI Co., Eindhoven, NL). To avoid charging and increasing sample conductivity, all samples were coated with a ~5 nm thick platinum film before recording the SEM micrographs. High-vacuum conditions (base pressure of 5·10⁻⁶ mbar) were applied for all specimens, the acceleration voltage was set to 20 keV.

**DFT Simulations**

**Theoretical approach**

For our studies the FHI-aims code¹⁻⁴ was applied and when studying thin films, which are intrinsically periodic only in two dimensions, we relied on the repeated slab approach. Periodic replicas of the slab were decoupled in the z-direction (i) quantum-mechanically by a vacuum region with a width of at least 20 Å and (ii) electrostatically via a self-consistently determined dipole layer included within the vacuum gap.⁵,⁶

For the calculations we employed the Perdew-Burke-Ernzerhof (PBE)⁷,⁸ and the hybrid Heyd-Scuseria-Ernzerhof (HSE06)⁹ exchange-correlation functionals (the latter using a screening parameter of omega=0.11 Bohr⁻¹)¹⁰. To account for long-range van der Waals interactions the recently developed non-local version of the many-body dispersion (NL-MBD) correction was employed, which extends the MBD approach to hybrid metal-organic
systems. As far as the basis set is concerned the FHI-aims default tight settings were used for the PBE simulations, while for the HSE06 calculations the 5g basis functions were disregarded on C and O atoms. Convergence criteria for the self-consistency cycle were set to the default values (changes in the charge density: $10^{-5}$, changes in the total energy: $10^{-6}$ eV, changes in forces: $10^{-4}$ eV·Å$^{-1}$). To determine the occupation of the Kohn-Sham eigenstates we used a Gaussian broadening function with a width of $\sigma=0.01$ eV. As the studied systems contain Cu atoms, the atomic ZORA approximation was used to account for relativistic effects. When calculating systems in a spin-triplet configuration, the two spins are set to be collinear and the calculation is initialized with one more electron in the spin-up than in the spin-down channel on each of the two Cu-atoms in the paddlewheel.

Geometry optimizations were performed employing the Broyden-Fletcher-Shanno-Goldfarb optimization algorithm enhanced by the trust radius method, with a tolerance threshold of $10^{-2}$ eV·Å$^{-1}$. For the cluster calculations, geometries were optimized using both, the PBE as well as the HSE06 functional. Considering the size of the studied unit cells (e.g. 156 atoms for the monolayer system) and the resulting enormous computational costs of hybrid functional calculations on periodic systems, we refrained from optimizing periodic structures with the HSE06 functional. In such instances HSE06 calculations were performed only based on the PBE geometries (HSE06@PBE).

For the periodic PBE calculations a $3\times3\times3$ \textGamma-centered k-point grid was used for the bulk, while a $3\times3\times1$ grid was employed for thin films. This grid is considered well converged, bearing in mind the large size of the unit cell ($15.25 \times 15.25 \times 14.00 \text{ Å}$) and the fact that the electronic bands in all considered systems are flat. Moreover, testing a $4\times4\times4$ grid increased the band gap of the bulk triplet configuration (for details see below) by only $3\times10^{-4}$ eV. For the HSE06 calculation, the k-point grid was further reduced to $2\times2\times2$ and $2\times2\times1$ to keep the computational effort at an acceptable level. This is, again, justified by the flat bands and by the observation that for the polar monolayer system (the largest system we attempted to calculate with a $3\times3\times1$ grid) the difference in the gap and in the vacuum-level shift between the $2\times2\times1$ and the $3\times3\times1$ grids was only 3 meV and $2\times10^{-7}$ eV, respectively. Shifts in the vacuum level were derived from the energetic difference between the vacuum levels below and above the slab reported in the FHI-aims. The plot of the electrostatic energy was produced using VESTA 3.4.4 and 3D geometries were plotted with OVITO 3.3.0.

**Studied systems and geometries**
Overall, three types of structures were studied (see Figure S2): (i) Clusters consisting of (saturated) Cu-paddlewheels with attached 2,6-dimethyl-4,4’-bipyridine (Me₂-BPY) apical linkers to calculate binding energies between nodes and linkers and to test methodological aspects, (ii) the bulk structure of the Cu(BPDC)(BPY) SURMOF to optimize the unit-cell geometry of the system and also to assess certain methodological issues, and (iii) saturated mono- and multi-layers of the Cu(BPDC)(Me₂-BPY) SURMOF to understand, how polar apical linkers affect the electronic properties of a SURMOF thin film.

As far as the clusters are concerned, we started geometry optimizations from differently distorted starting geometries at the PBE, HSE06 levels enforcing either a closed-shell singlet or an open shell triplet spin state. In addition to the two cluster structures shown in Figure S2a, also the isolated Me₂-BPY molecule and the rest of the cluster were calculated separately.
Figure S2: Examples for the structures modeled in the current manuscript. (a) saturated Cu-paddlewheel clusters bonded to a 2,6-dimethyl-4,4'-bipyridine molecule in the dipole down (left) and dipole up (right) configurations; (b) side and top-views of the bulk MOF built using apolar 4,4'-bipyridine linkers. (c) Monolayer (left) and trilayer structures of 2,6-dimethyl-4,4'-bipyridine linked thin films with the top and bottom Cu-paddlewheels saturated by pyridine units. The black rectangles/squares indicate the unit cells for calculations employing periodic boundary conditions.
The geometry optimizations of the bulk structure could be performed only for the apolar 4,4'-bipyridine linkers, as polar unit cells in conjunction with 3D periodic boundary conditions would cause spurious electric fields.\textsuperscript{15} When optimizing the monolayer structure, the lateral dimensions of the unit cell in the directions of the 4,4'-biphenyldicarboxylic linkers were kept fixed at the bulk values (15.22 Å), while the vertical size of the unit cell was increased to 51.00 Å to ensure a large enough vacuum gap between periodic replicas of the slab (see section above). The atomic positions within the unit cells were fully optimized for both polar Me\textsubscript{2}-BPY and apolar BPY apical linkers. Multilayer structures were constructed from replicating the central elements of the monolayer without further geometry optimizations.

**Describing the spin-state of the Cu-paddlewheels and methodological tests**

In the ground state, the spins of the Cu atoms in the paddlewheels are antiferromagnetically coupled, forming an open-shell singlet. The corresponding open-shell triplet state is, however very close in energy with the difference being below 2 kJ/mol.\textsuperscript{16,17} As the proper treatment of the open-shell singlet configuration would typically require the use of multireference methods, which are out of the question for systems as complex as the present one, Cu paddlewheels in MOFs are typically simulated as triplets.\textsuperscript{18–20} This is also done here for the clusters and the bulk system, which contain only a single paddlewheel (per unit cell). The situation becomes significantly more complex for the layered structures from Figure S2c, which contain \(\geq 2\) paddlewheels, where we did not succeed in converging higher multiplicities. Therefore, the only feasible strategy for simulating the layered structures from Figure S2c to describe them as closed-shell singlets. To justify that approach, we performed extensive tests on the cluster structures described above, comparing binding energies, their asymmetries, the dipole moments of the clusters and the obtained band gaps. In particular structures calculated with the PBE and HSE06 functionals, HSE06 single point calculations based on PBE geometries, and clusters modeled in their singlet and triplet spin states were considered, where we calculated each of the possible permutations (testing also the impact of dropping the 5g functions in the basis set). These tests led to the following conclusions:

- There is a distinct difference in the binding energies and their asymmetries between the closed-shell singlet and open-shell triplet calculations. I.e., for reliably obtaining binding energies, calculations in the triplet state are crucial. The absolute binding energies are larger in the HSE06 calculations by \(\sim 100\) meV (consistent with the tendency of hybrid functionals to bond more strongly), but the asymmetry of the binding energy is only
weakly affected (67 meV for PBE vs. 58 meV for HSE06). Thus, the binding energies and their asymmetries reported in the main manuscript are the ones obtained for the triplet state calculated with the HSE06 functional. They are also reported in Table S1.

- As expected, band gaps were larger for the HSE06 calculations (bearing in mind the excessive many-electron self-interaction error of PBE). This is particularly pronounced for the triplet state. It becomes most relevant, when calculating shifts in the electrostatic energy for thin layers, as such shifts result in a decrease of the global band gap. Thus, for such calculations the HSE06 needs to be used to avoid a spurious gap closure. Notably, the above-mentioned differences between PBE and HSE06 calculations relate to the functional used in the electronic structure calculations; the functionals used in the optimizations have hardly any impact.

- None of the methodological aspects has an impact on the calculated dipole moments of either the molecule or the up- and down-clusters (beyond a few percent). This is particularly true for singlet vs. triplet calculations.

- As a consequence, shifts of the electrostatic energies in the polar layers could be performed for closed-shell singlets employing the PBE geometries. Due to the above-mentioned problem of a premature gap closure, HSE06 calculations of the electronic structure could be performed for the monolayer and trilayer systems (see Figure S2), while at the PBE level only the monolayer could be calculated. The corresponding results are shown in Table S1.

**Main results of the simulations**

**Table S1:** Calculated binding energies (BE) and dipole moments (µ) for the dipole-up and dipole-down configurations shown in Figure S2a. Additionally, the binding energy difference (ΔBE) between the two conformations as well as the dipole moment (µ mol) of the Me2-BPY molecule are listed. The binding energy is calculated as the difference between the complete cluster and its geometry-optimized constituents (saturated node = cluster with Me2-BPY removed, and Me2-BPY). Solvent effects were not considered in the calculations. Additionally, the shift in electrostatic energy (vacuum levels, ΔVL) between the bottom and top sides of the layers for Cu(BPDC)(Me2BPY) SURMOF mono- and tri-layers (shown in Figure S2c) calculated with the PBE and HSE06 functionals are shown.

| cluster  | BE / meV | µ / Debye | polar layers | ΔVL^PBE | ΔVL^HSE06 |
|----------|----------|-----------|--------------|---------|-----------|
| up       | 758.8    | 1.04      | monolayer    | -0.26   | -0.27     |
| down     | 700.4    | 4.14      | trilayer     | ---     | -0.82     |
DFT calculations of the first hyperpolarizabilities

To qualitatively predict the SHG efficiency of studied SURMOF thin films we chose simplified molecular models. Since all SHG properties of presented SURMOF originate from Me$_2$BPy pillar linkers having dipole moment orientation either up or down parallel to the z-axis, we reduced our unit cell only to them. All contributions arising from Cu paddlewheels as well as BPDC linkers connecting Cu metallic centers are neglected. Molecular models used here are presented in Figure S6. Corresponding volume of the unit cell was kept as it is: 3.3014·10$^{-27}$ m$^3$.

First hyperpolarizability calculations of the simplified bipyridine linker models were performed with PBE0 exchange-correlation functional$^{21}$ and def2-TZVP basis set$^{22}$ for all atoms as a closed-shell singlet electronic configuration. SHG calculations are based on the evaluation of the quadratic response functions as it is implemented$^{23}$ in DALTON2020 DFT code$^{24}$ for the 1064 nm. The values obtained from those calculations are reported in Tables S2 and S3.

| $\sigma_{ik}$ | xxx | xxy | xxz | xyy | xyz | xzz | yxx | yxy | yxz |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| up           | -0.028 | 0.078 | 4.427 | 0.010 | -65.281 | -0.039 | 0.087 | 0.000 | -67.130 |
| down         | 0.028 | -0.078 | -4.427 | -0.010 | 65.281 | 0.039 | -0.087 | 0.000 | 67.130 |

| $\sigma_{ik}$ | yyy | yyz | yzz | zxx | zxy | zxz | zyy | zyz | zzz |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| up           | -0.072 | 41.764 | -0.074 | 3.418 | -59.775 | -0.038 | 31.553 | -0.068 | 19.086 |
| down         | 0.072 | -41.764 | 0.074 | -3.418 | 59.775 | 0.038 | -31.553 | 0.068 | -19.086 |

Theoretical prediction of the macroscopic second-order susceptibilities of Cu(BPDC)(Me$_2$BPY) SURMOF crystalline thin films

Calculation of the macroscopic non-linear susceptibility from the molecular properties of the crystalline materials has been rigorously derived elsewhere$^{25-27}$ and will not be repeated here. In short, macroscopic second-order susceptibility $\chi^{(2)}_{ijk}$ in the global (laboratory) coordinate system defined by $IJK$ indexes in SI units is defined by:

$$\chi^{(2)}_{ijk}(-2\omega; \omega, \omega) = \frac{1}{\varepsilon_0 V} f_I(2\omega)f_J(\omega)f_K(\omega) \times \sum \sum \cos \theta_I^{(s)} \cos \theta_J^{(s)} \cos \theta_K^{(s)} \beta^{(s)}_{ijk}(-2\omega; \omega, \omega)$$
where \( V \) is the volume of the periodic unit cell of crystalline material, \( f_{i,j,k}^{(s)}(\omega) \) are local-field factors and \( \varepsilon_0 \) is vacuum permittivity. Double summation goes over \( N \) molecules in the one unit cell indexed here by \( s \) and \( ijk \) axes of the local (molecular) coordinate system. Cosines describe rotation from the molecular frame to the laboratory frame for each molecule in the unit cell. The smart choice off molecular coordinate system which coincides with the global coordinate system, i.e. positive \( z \)-direction is normal to the plane defined by BPDC linkers connecting Cu metallic centers, renders all cosine terms to give value equal to 1. The \( \beta_{i,j,k}^{(s)} \) terms are molecular first (quadratic) hyperpolarizabilities calculated using the DFT method for the given frequency (wavelength).

The local-field factors:

\[
 f_l(\omega) = \frac{(n_{ii}(\omega))^2 + 2}{3}
\]

are determined using the refractive indexes \( n_{ii} \) of the material in \( x \), \( y \), and \( z \)-direction. Refractive indexes for the 1064 and 532 nm are qualitatively estimated based on the work from Redel et al.\(^2\) where they determined refractive indexes for the Cu-BDC SURMOF-2 thin film for the length of the BPDC linker 1.5 nm. The values used are 1.2 for all three directions at the 1064 nm and 1.24 for the 532 nm.

The applied approach is not exact due to the precision of the DFT method itself and since it neglects inter-molecular interactions within the unit cell and/or interactions between neighboring unit cells of the crystalline thin-film material. Here, the most important asymmetric \( \text{Me}_2\text{-BPY} \) pillar linkers are sufficiently spaced (>1.5 nm) which minimizes dipole-dipole interactions between them justifying the application of the above-presented theory.

**Table S3**: macroscopic second-order susceptibility for the Cu(BPDC)(\( \text{Me}_2\text{-BPY} \)) with dipole oriented up and down and supercell consisting of 1000 unit cells with ratio 517/483 of up/down oriented dipoles.

| \( \chi_{ij,k}^{(2)}(\text{pm/V}) \) | \( xxz \) | \( xyz \) | \( yxz \) | \( yyz \) | \( zxx \) | \( zxy \) | \( zyy \) | \( zzz \) |
|---|---|---|---|---|---|---|---|---|
| up | 0.008 | -0.111 | -0.114 | 0.074 | 0.006 | -0.102 | 0.054 | 0.032 |
|                | \(d_{15}\) | \(d_{14}\) | \(d_{25}\) | \(d_{24}\) | \(d_{31}\) | \(d_{36}\) | \(d_{32}\) | \(d_{33}\) |
|----------------|------------|------------|------------|------------|------------|------------|------------|------------|
| **down**       | -0.008     | 0.111      | 0.114      | -0.074     | -0.006     | 0.102      | -0.054     | -0.032     |
| **supercell 517/483** | 0.0       | -0.004     | -0.004     | 0.002      | 0.0        | -0.003     | 0.002      | 0.001      |
| **\(d_{ij}^{(2)} (\text{pm/V})\)** | \(d_{15}\) | \(d_{14}\) | \(d_{25}\) | \(d_{24}\) | \(d_{31}\) | \(d_{36}\) | \(d_{32}\) | \(d_{33}\) |
| **up**         | 0.004      | -0.056     | -0.057     | 0.036      | 0.003      | -0.051     | 0.027      | 0.016      |
| **down**       | -0.004     | 0.056      | 0.057      | -0.036     | -0.003     | 0.051      | -0.027     | -0.016     |
| **supercell 517/483** | 0.0       | -0.002     | -0.002     | 0.001      | 0.0        | -0.002     | 0.001      | 0.001      |
Supplementary experimental results

Figure S3: IRRAS of the Cu(BPDC)(Me$_2$-BPY) and Cu(BPDC)(BPY) SURMOFs.

Figure S4. XPS data recorded for symmetric (Cu(BPDC)(BPY), black curve, 70 nm) and several asymmetric (Cu(BPDC)(Me$_2$-BPY)) SURMOFs of different thicknesses. All the SURMOFs are coated with a Br$_4$-BDC containing layer on top. The inset: dependence of the binding energy of Br3d peak on the thickness for symmetric (black symbols) and asymmetric (red symbols) MOFs.
Figure S5. SEM image (left: cross-section; right: top view) of the asymmetric (Cu(BPDC)(Me$_2$-BPY)) SURMOF prepared with a repetition of 70 cycles. Considering the scale bar, the thickness of the SURMOF layer has amounted to 150±50 nm.

Supplementary theoretical results

Figure S6: Molecular “unit cell” models used for first hyperpolarizability calculations. Asymmetric and symmetric pillar linkers extracted from optimized layered SURMOF are oriented along the z-axis.
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