Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

SUPPLEMENTARY INFORMATION

Correlations of MM-generated Offsets and a Predictive Capability for New COFs

As shown in **Figure S2**, the strongest correlation between lateral offsets and readily available physico-chemical information was found by plotting the interlayer binding energy against the atomic density; this produced a coefficient of determination (r^2) of 0.94. The layer binding energy was calculated as an average over all energies at the bottom of the potential energy surface to represent a complete sampling of preferentially stacked 2D COF layers. Statistical errors in this value were determined to be insignificant and were omitted from the figure. **Figure S2** shows that the binding energy is essentially linearly dependent with respect to the atomic density. Since the minimum energy configurations were, in almost all instances, nearly eclipsed with minimized electrostatic interaction energies, the projected atomic overlap is a good metric for the total potential energy.

Although a strong correlation exists between binding energy and atomic density, the lateral offset is not well correlated with atomic density. As shown in **Figure S3**, plotting the preferred lateral offset against the atomic density gives a poor r^2 value of 0.55, largely because of the large offset of **BRX-B**. In general, larger atom counts produce larger offsets, but **Figure S3** shows that the relationship differs from class to class. While a positive linear relationship may exist for **DHC**, **HHB**, or **BRX**, the preferred offsets of **HHTP** and **Pc** are roughly independent of atomic density. We also compared the offset with the boron and oxygen atom density. The density was computed by normalizing all boron and oxygen atoms in the unit cell with the cell area. As shown in **Figure S4**, the r^2 value of 0.80 is reasonably good. However, comparing the results in **Figure S4** and **Figure 9**, the boron and oxygen density is a worse predictor of offset than the B-O *dipole* density.

Simulated Powder X-Ray Diffraction Patterns

For each COF previously reported in literature [1-6], we constructed a supercell of 50 stacked layers with each layer stacked in a random direction with the prescribed offset and layer spacing calculated from molecular mechanics. The structure is unoptimized and periodic. Scanning was performed using the freeware Mercury program [7] between 0° and 35° with a full width at half maximum of 0.1° and step size of 0.02°. The intensities of the simulated patterns were truncated to 25% of the height of the (100) peak. Experimental patterns were adapted from literature [1-6] with their intensities also truncated to 25% of the height of the (100) peak. As shown in **Figure S5**, the simulated and experimental diffraction patterns are reasonably matched between 0° and 20°. The discrepancy between simulation and experimental diffraction patterns between 25° and 30° can be attributed to the slightly larger layer spacing calculated from molecular mechanics, given the sensitivity of the (001) peak on the layer spacing. The simulated random stacking modes, which are represented largely by the position of the (100) peak, match the experimental patterns.

FIGURES

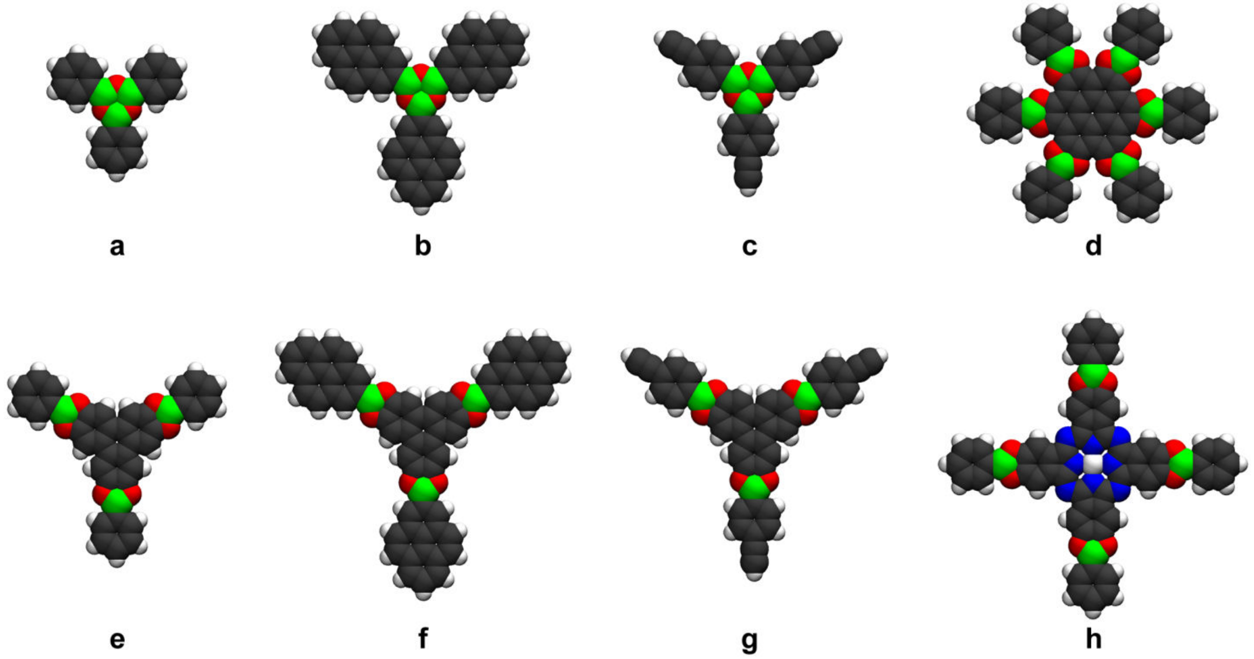


Figure S1. Layer fragments used in DFT calculations to model the intermolecular interactions between layers. **a**. **BRX-Ph**. **b**. **BRX-Py**. **c**. **BRX-DPB**. **d**. **DHC-Ph**. **e**. **HHTP-Ph**. **f**. **HHTP-Py**. **g**. **HHTP-DPB**. **h**. **Pc-Ph**.

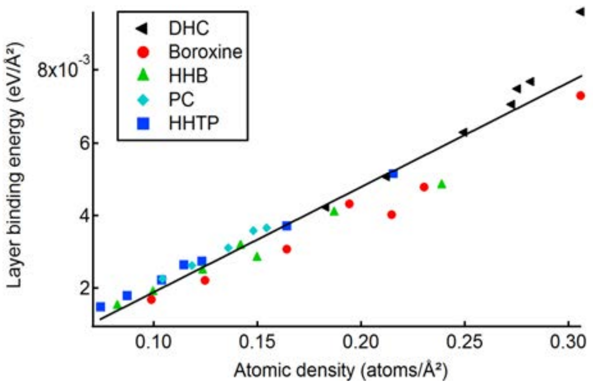


Figure S2. Layer binding energy plotted against COF atomic density.

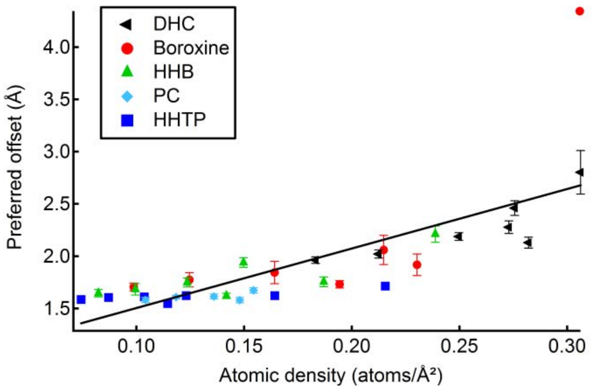


Figure S3. Preferred lateral offset plotted against the atomic density of COF layers.

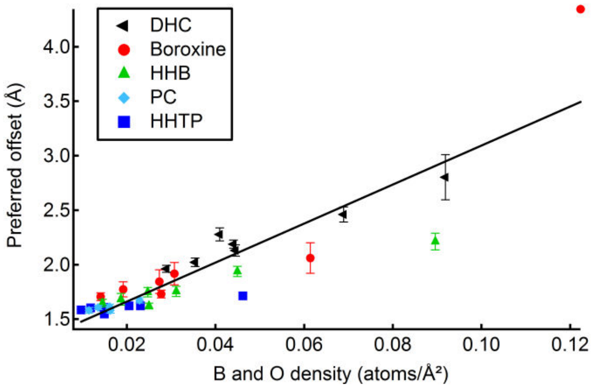


Figure S4. Preferred lateral offset plotted against the boron and oxygen density.

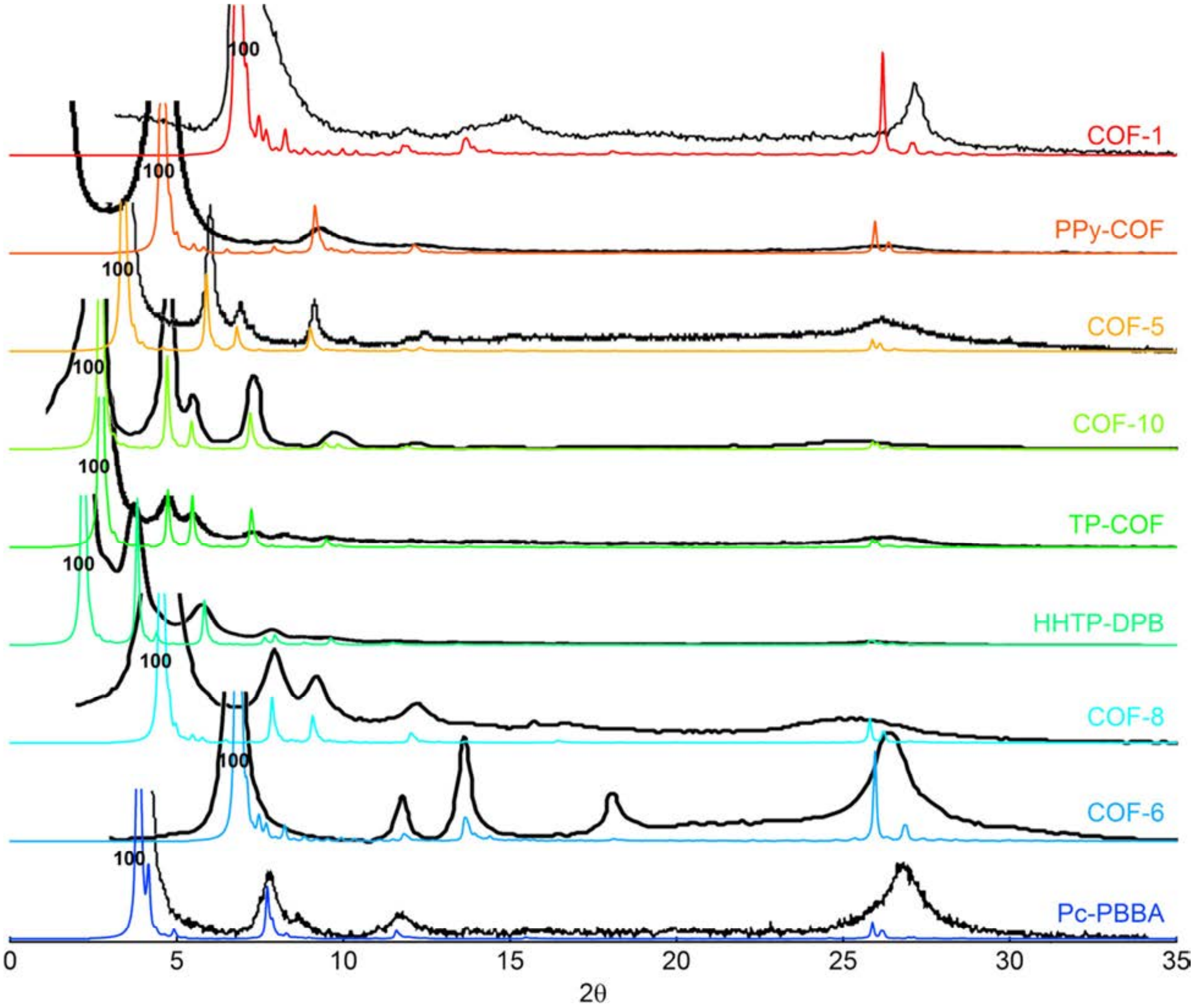


Figure S5. Simulated powder x-ray diffraction patterns of covalent organic frameworks (color) with 50 stacked layers. The (100) peak in each pattern is uniformly truncated to resolve smaller but significant peaks. The experimental patterns are overlaid in black.

COF-1 and COF-5 patterns from A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166. Reprinted with permission from AAAS.

COF-6, COF-8, and COF-10 patterns reprinted (adapted) with permission from A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt and O. M. Yaghi, *J. Am. Chem. Soc.*, 2007, **129**, 12914. Copyright 2007 American Chemical Society.

Pc-PBBA pattern reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry
E. L. Spitler and W. R. Dichtel, *Nature Chem.*, 2010, **2**, 672., Copyright 2010.

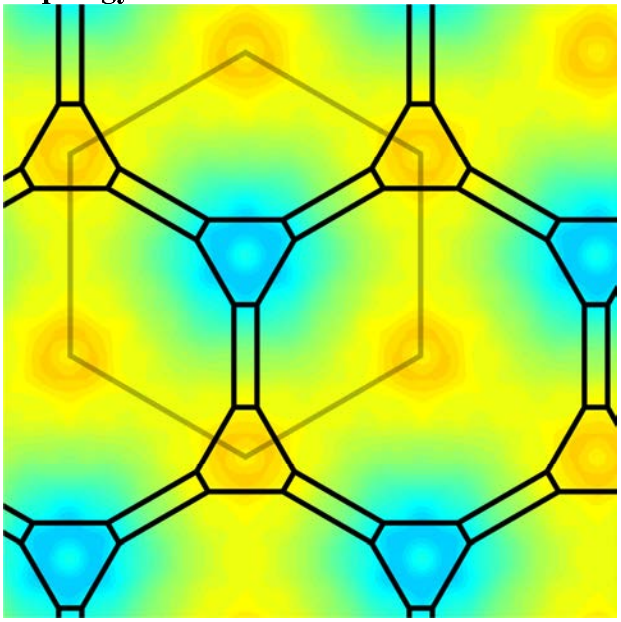
HHTP-DPB pattern reprinted (adapted) with permission from E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, **133**, 19416. Copyright 2011 American Chemical Society.

PPy-COF and TP-COF patterns from [S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5439.] and [S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2008, **47**, 8826.]. Reprinted with permission from Wiley.

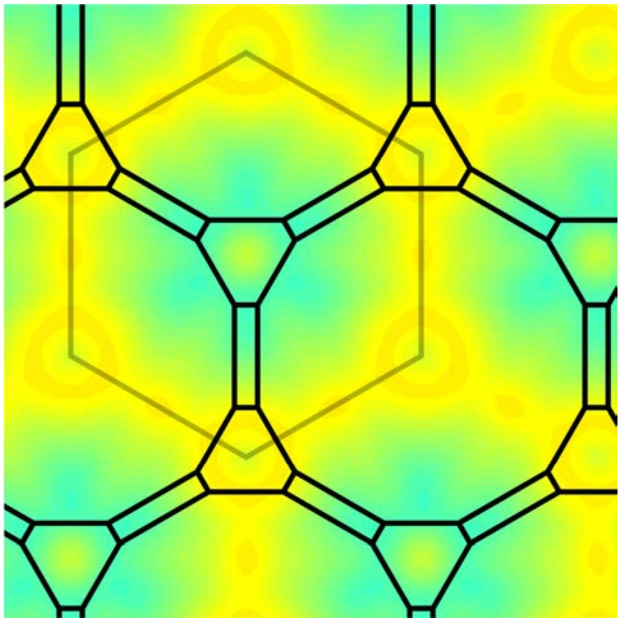
Potential Energy Surfaces with Superimposed Topologies

The two-dimensional unit cells of each covalent organic framework is shown in gray, and the translation of the mobile layer in the two-layer system in relation to the center of the unit cell produces the potential energies shown in the figure. The energy scale is identical to the one in Figure 5 in the main text.

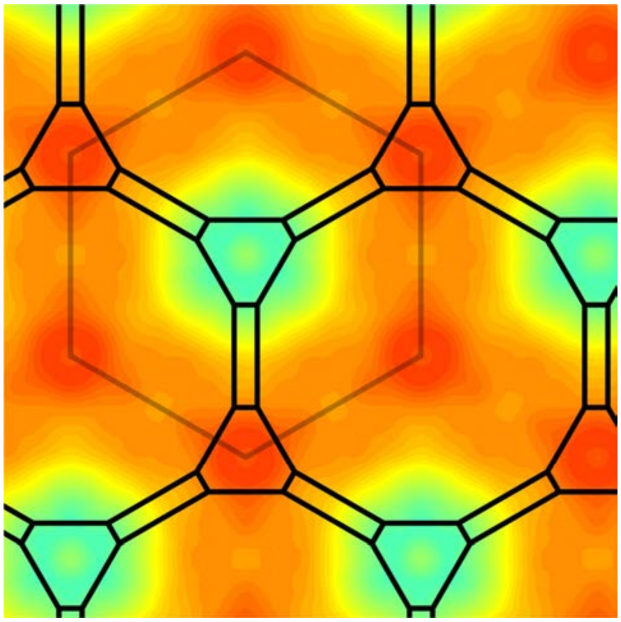
Topology A



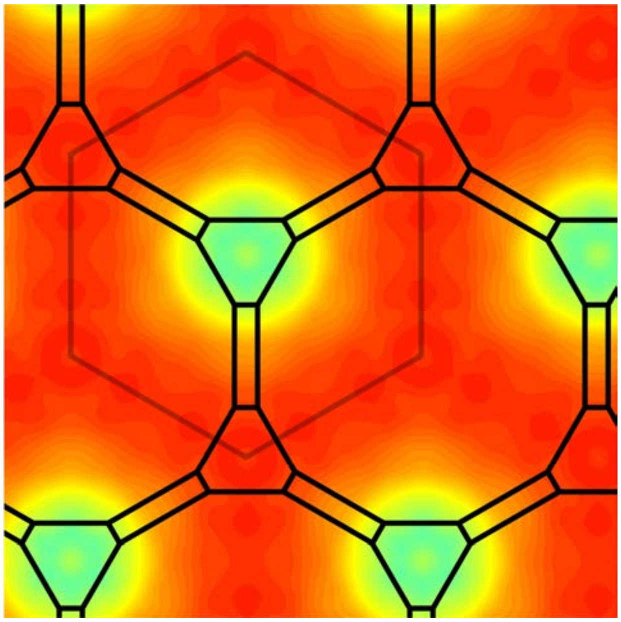
Boroxine-Pyrene



Boroxine-Phenylene



Boroxine-Biphenyl



Boroxine-Diphenylacetylene

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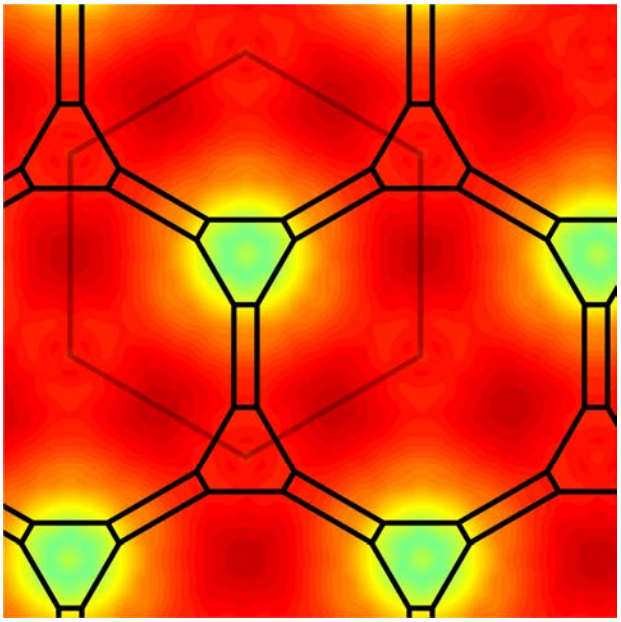
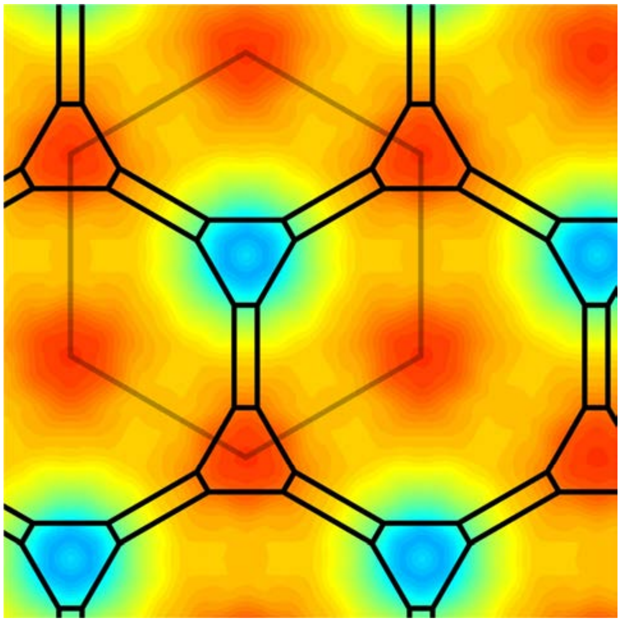
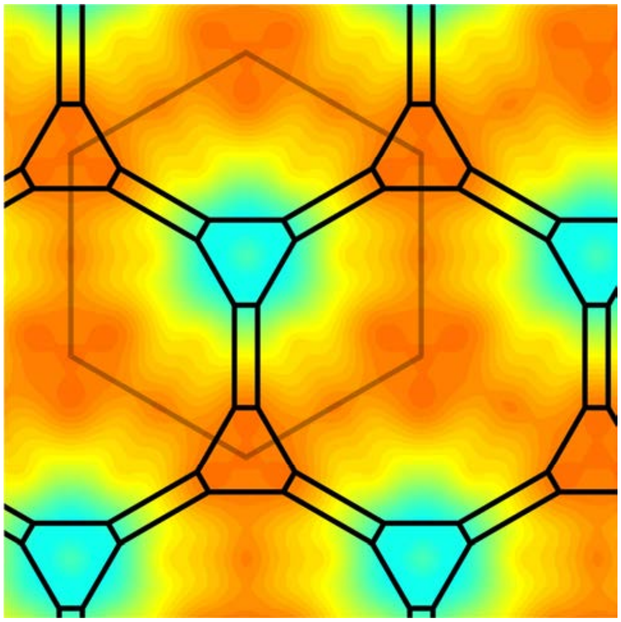


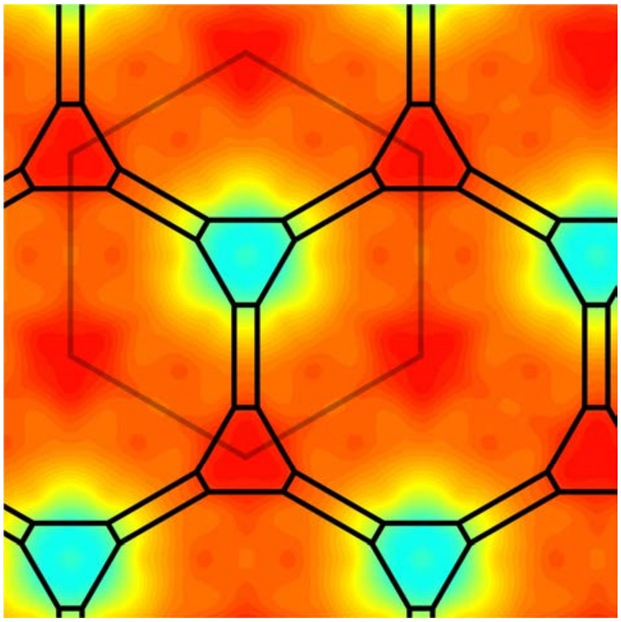
Boroxine-Diphenylbutadiyne



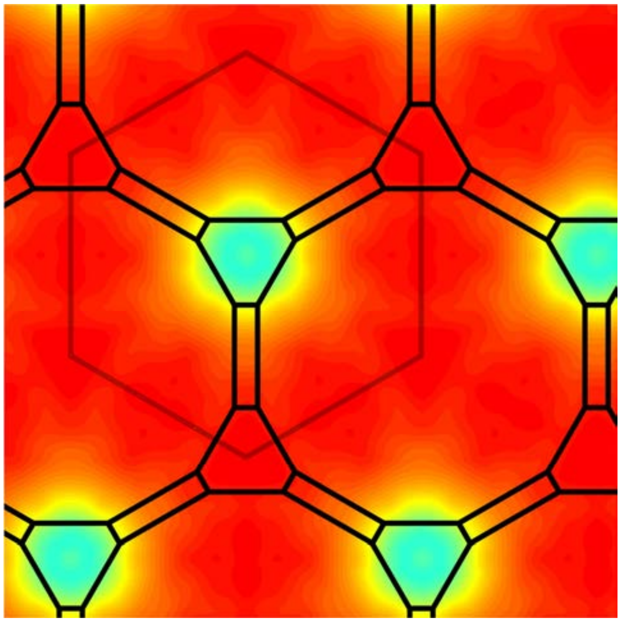
Hexahydroxybenzene-Pyrene



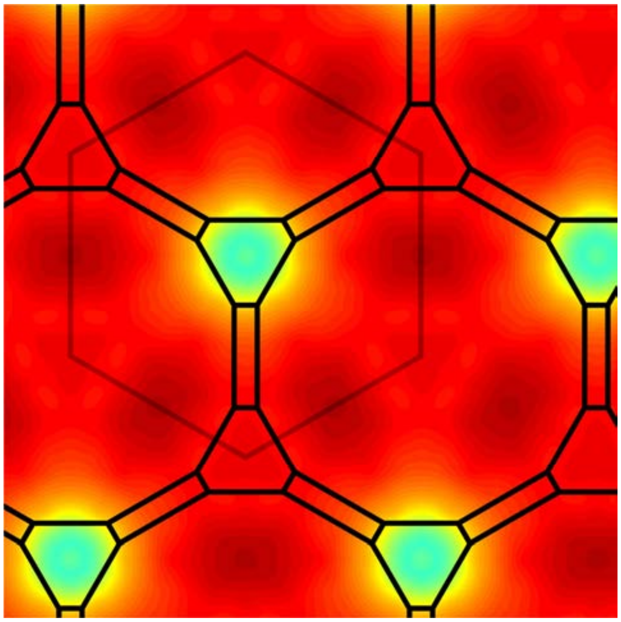
Hexahydroxybenzene-Phenylene



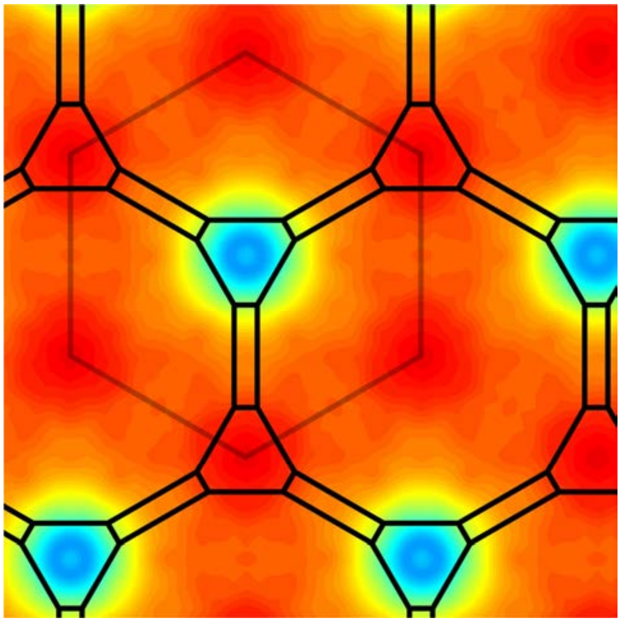
Hexahydroxybenzene-Biphenyl



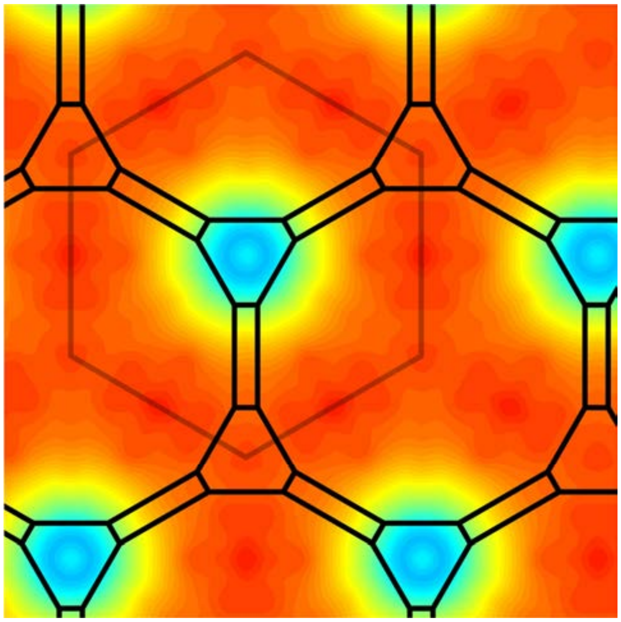
Hexahydroxybenzene-Diphenylacetylene



Hexahydroxybenzene-Diphenylbutadiyne



Hexahydroxytriphenylene-Pyrene



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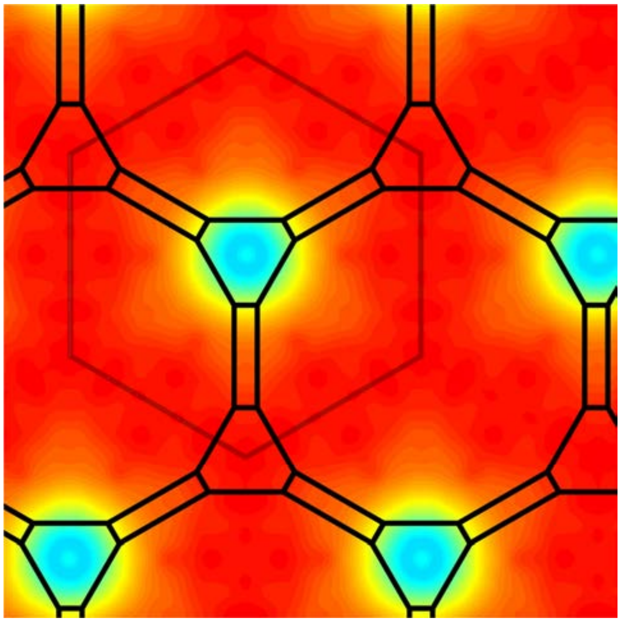

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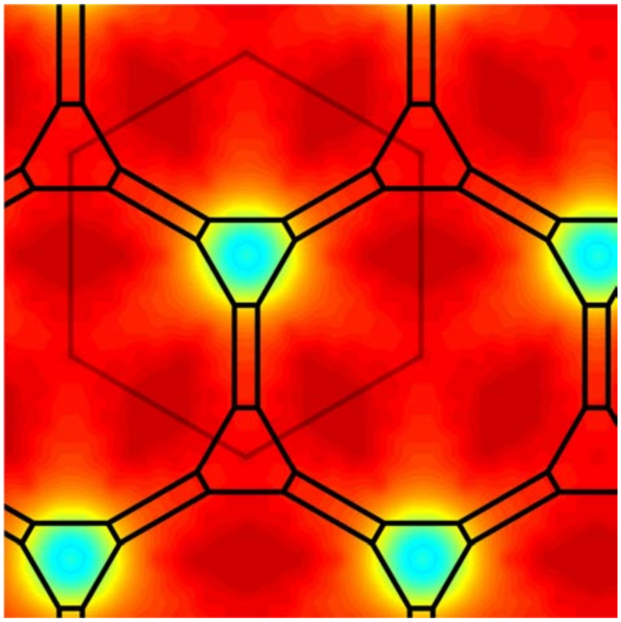
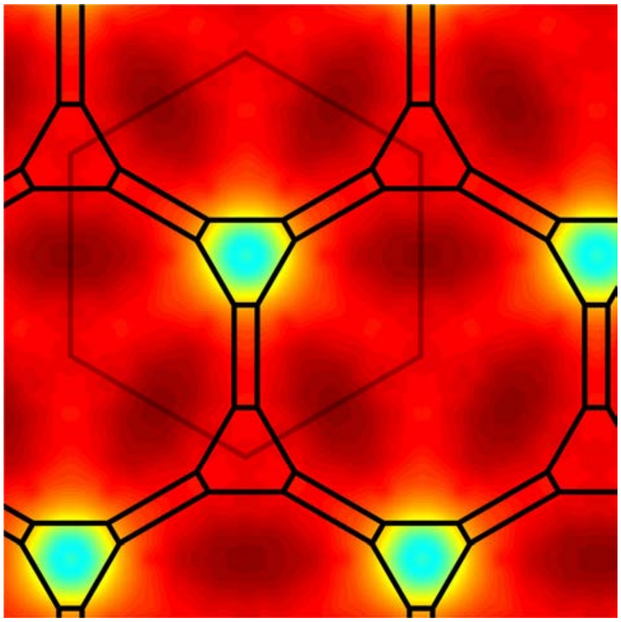
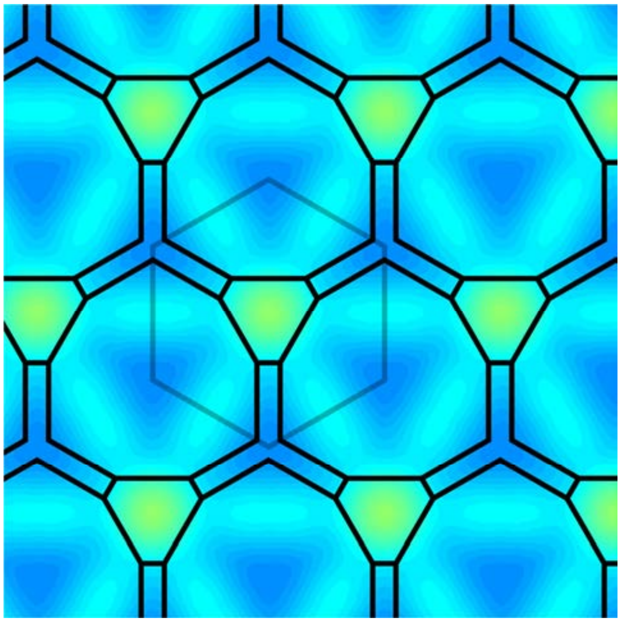


Hexahydroxytriphenylene-Diphenylacetylene

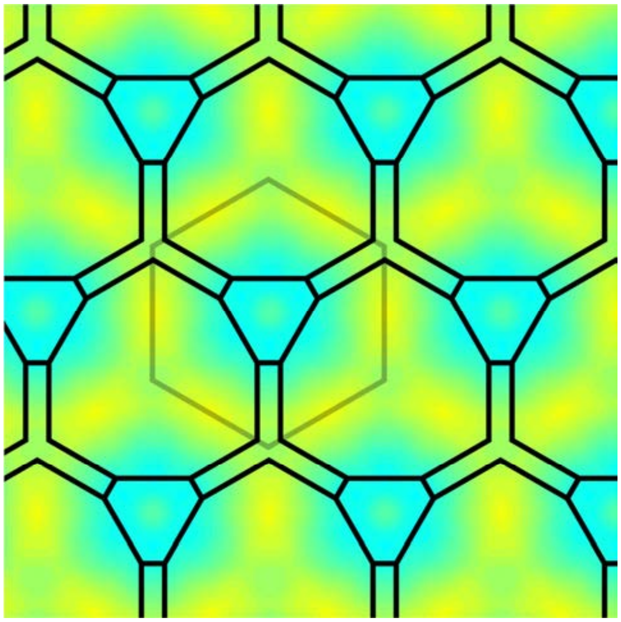


Hexahydroxytriphenylene-Diphenylbutadiyne

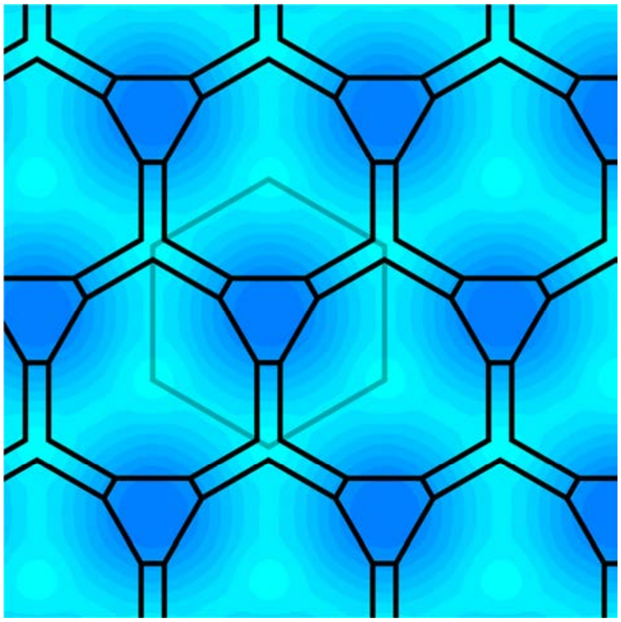
Topology B



Boroxine-1,3,5-Benzene



Boroxine-1,3,5-Triphenylbenzene



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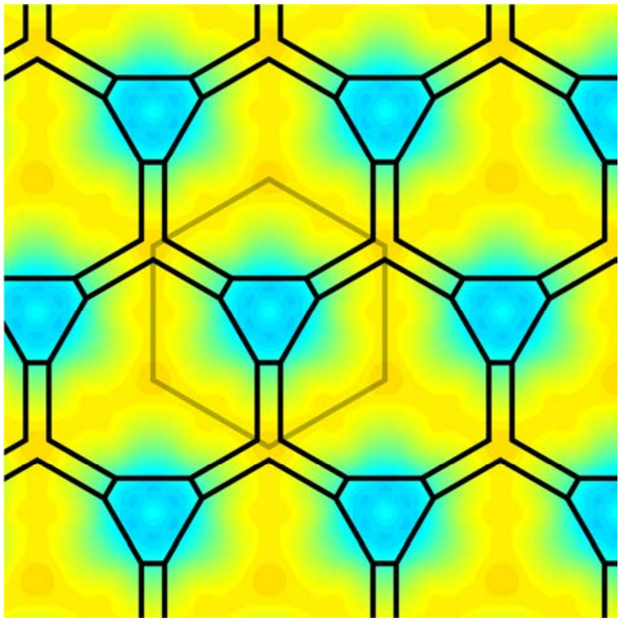

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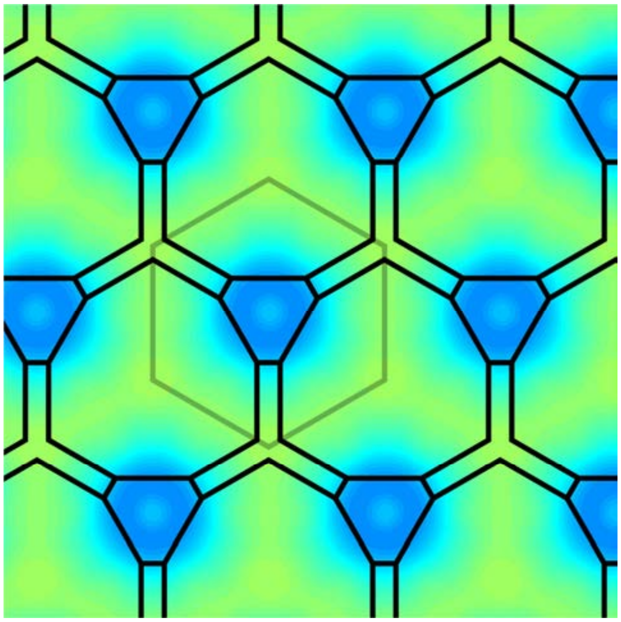

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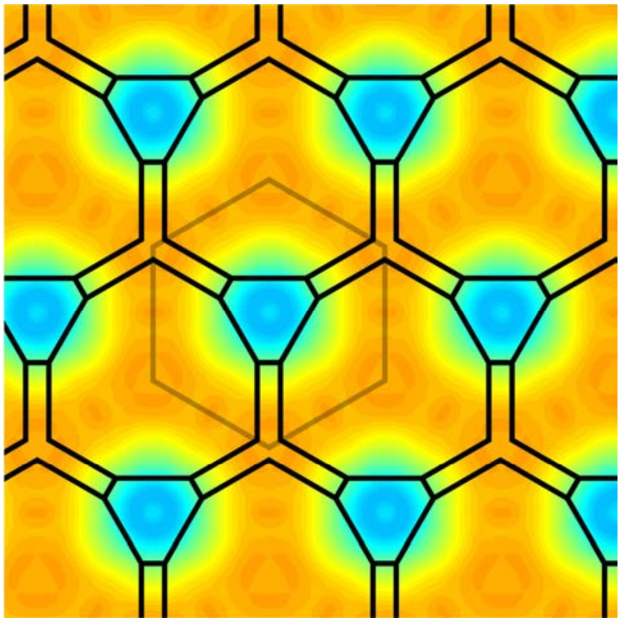

**Hexahydroxytriphenylene-
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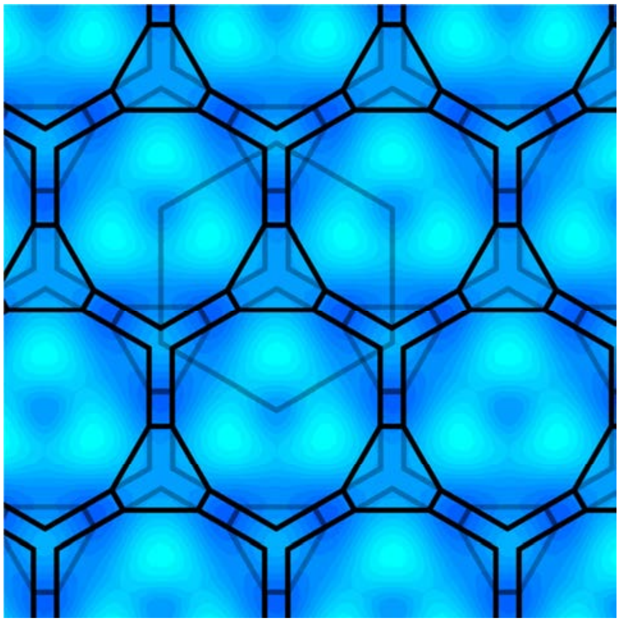
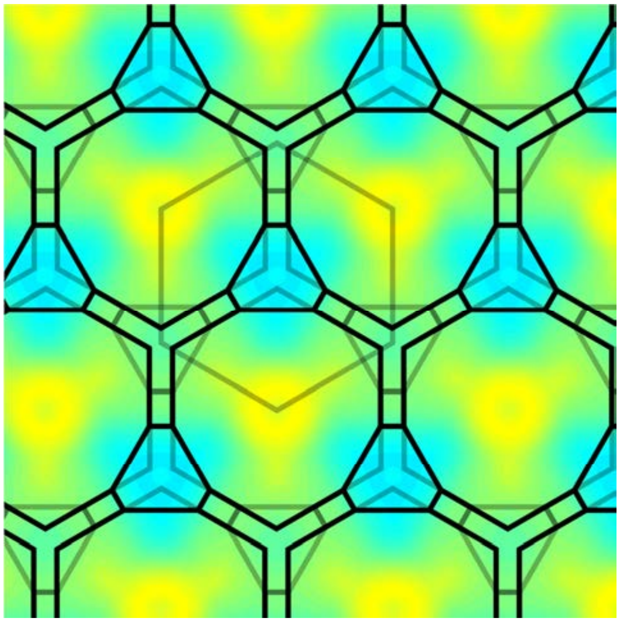
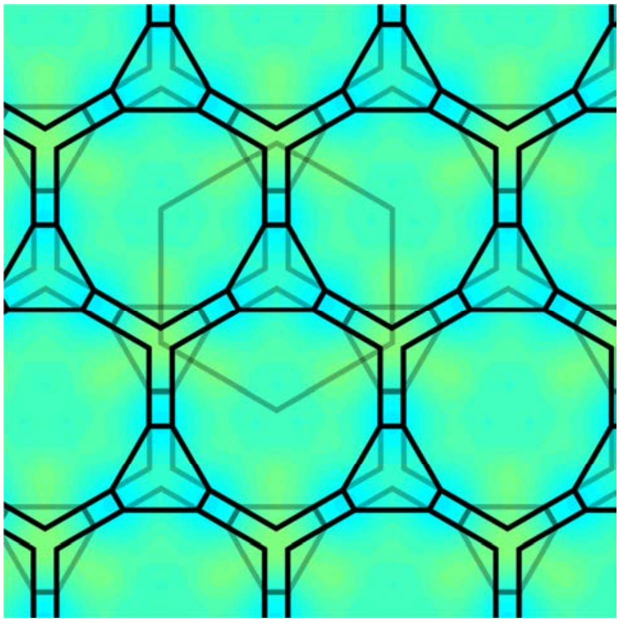
Topology C



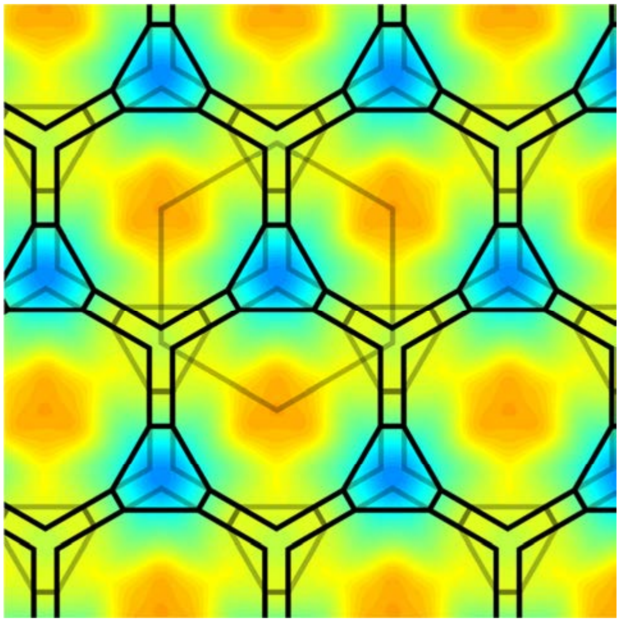
Boroxine-1,3,5-Benzene



Boroxine-1,3,5-Triphenylbenzene



Hexahydroxybenzene-1,3,5-Benzene



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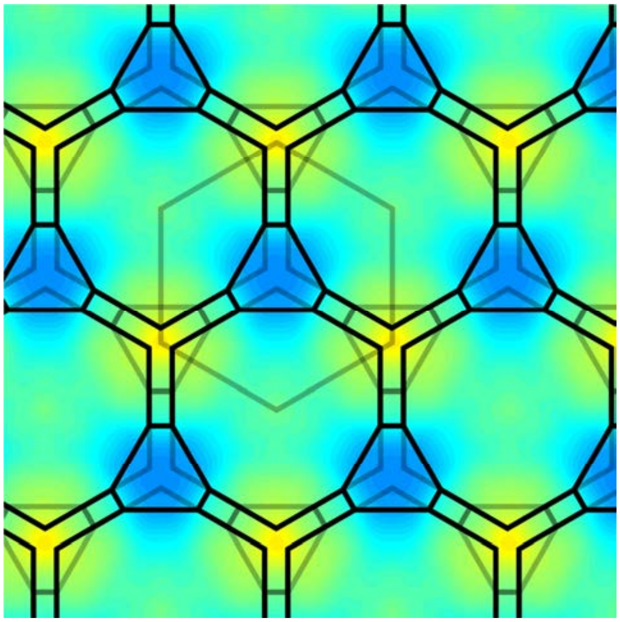
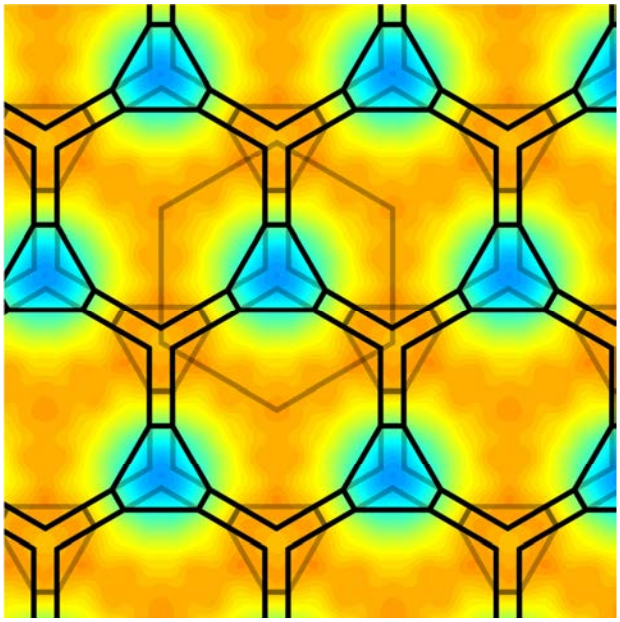
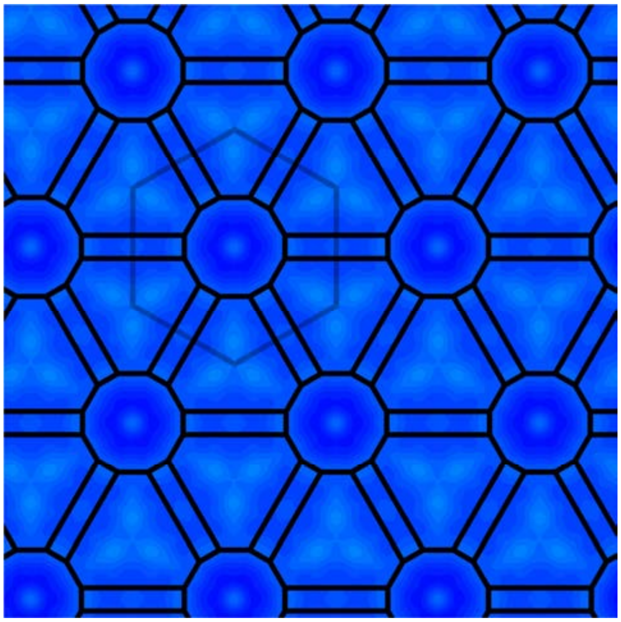


Hexahydroxytriphenylene-1,3,5-Benzene

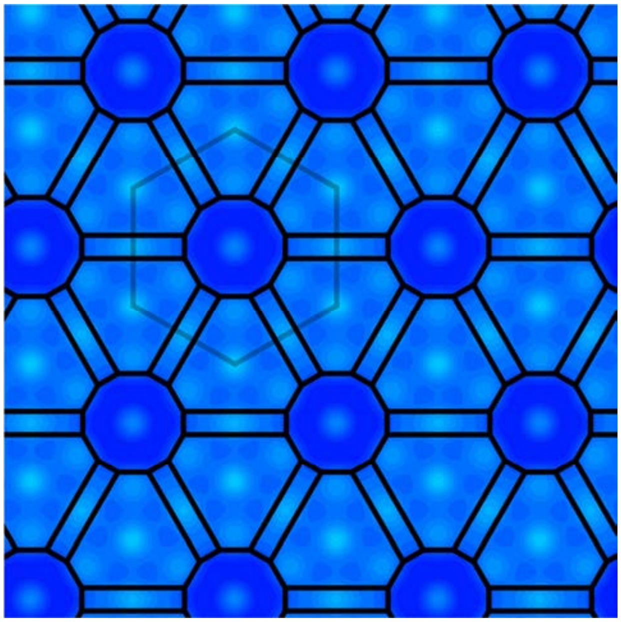


Hexahydroxytriphenylene-1,3,5-Triphenylbenzene

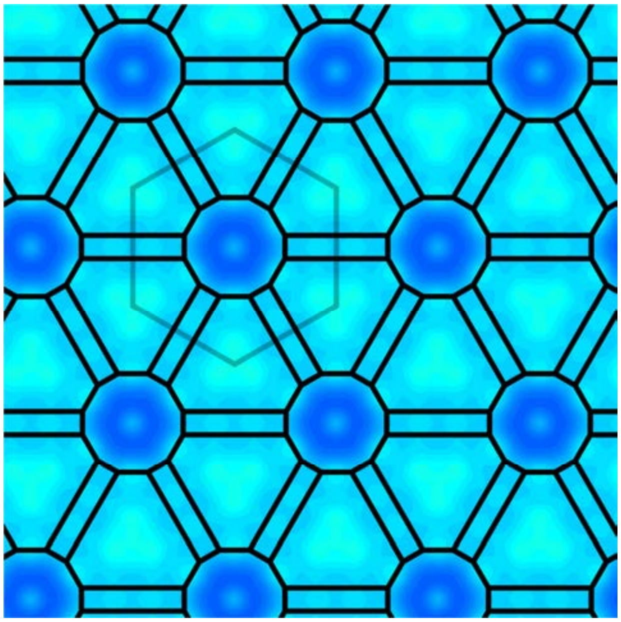
Topology D



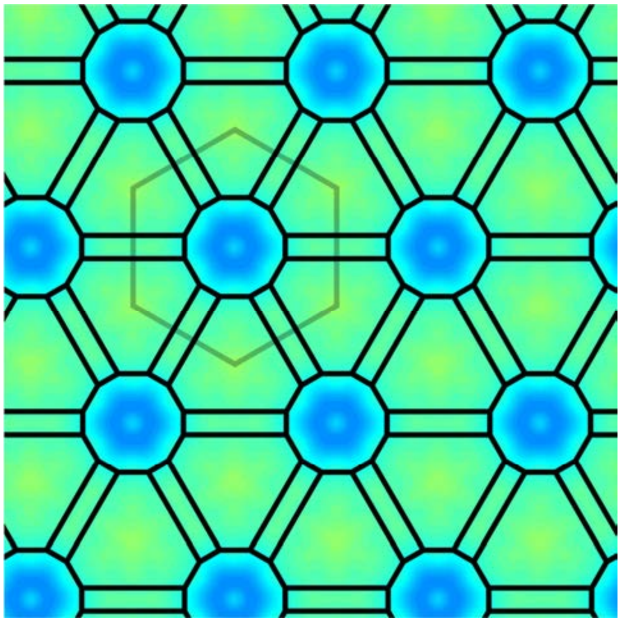
Dodecahydroxycoronene-Pyrene



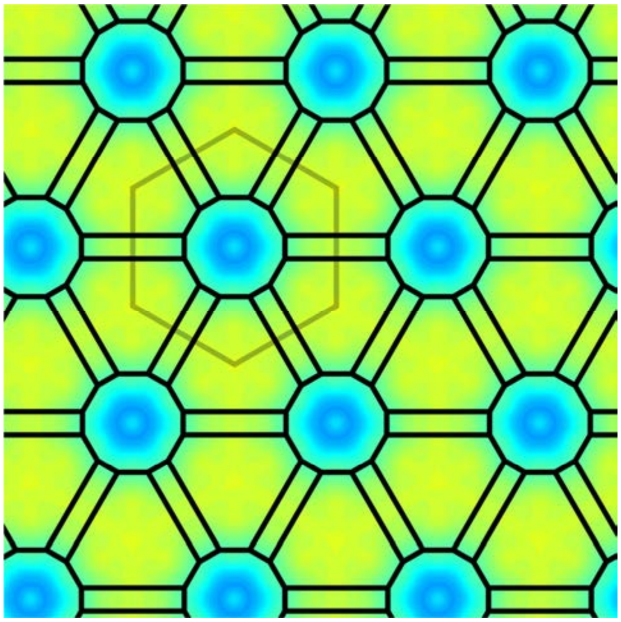
Dodecahydroxycoronene-Phenylene



Dodecahydroxycoronene-Biphenyl

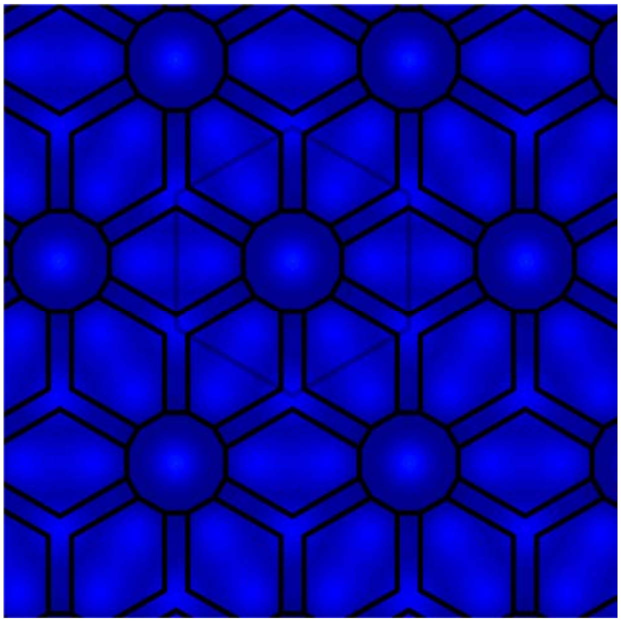


Dodecahydroxycoronene-Diphenylacetylene

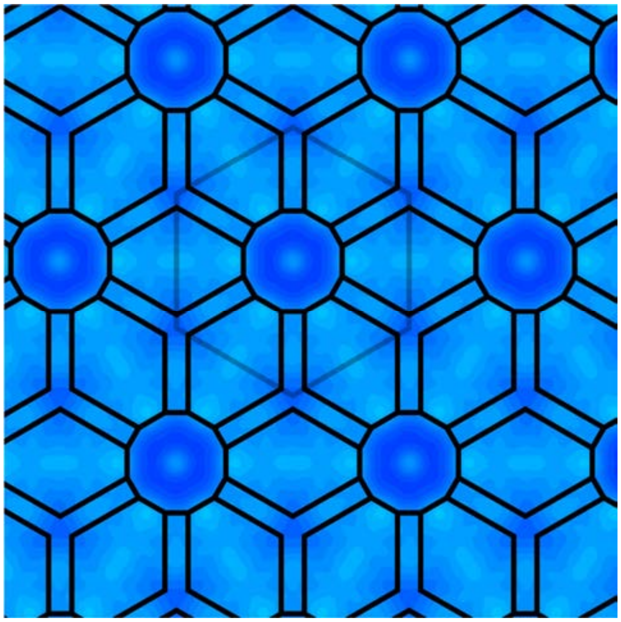


Dodecahydroxycoronene-Diphenylbutadiyne

Topology E

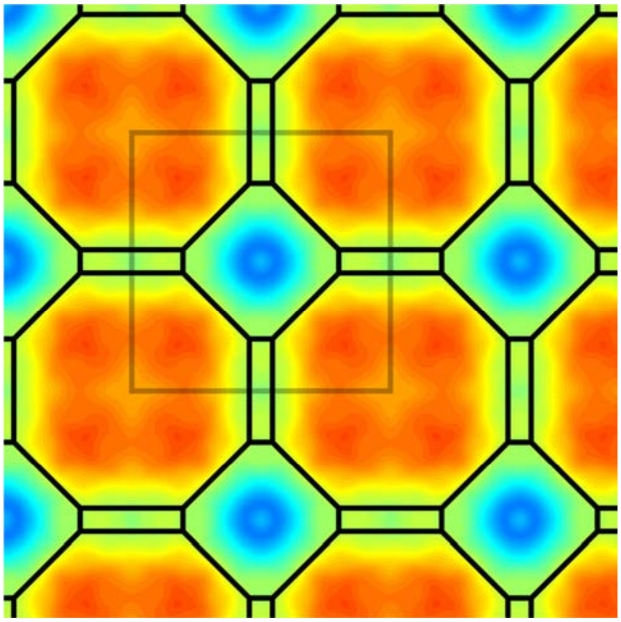


**Dodecahydroxycoronene-
1,3,5-Benzene**

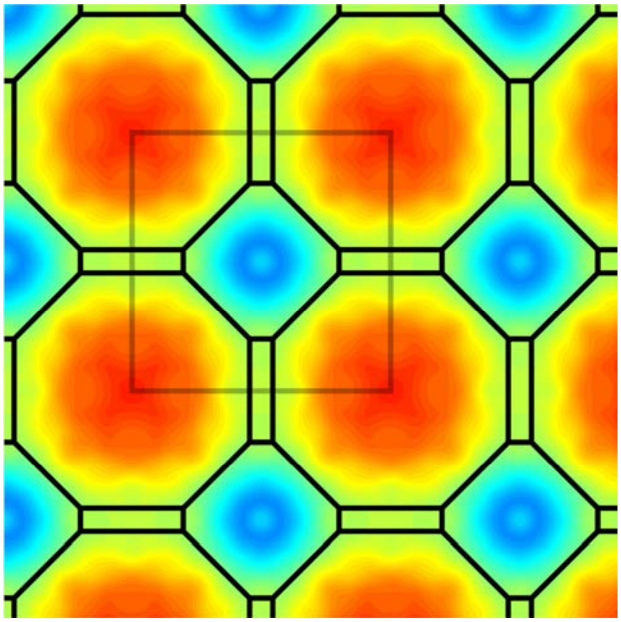


**Dodecahydroxycoronene-
1,3,5-Triphenylbenzene**

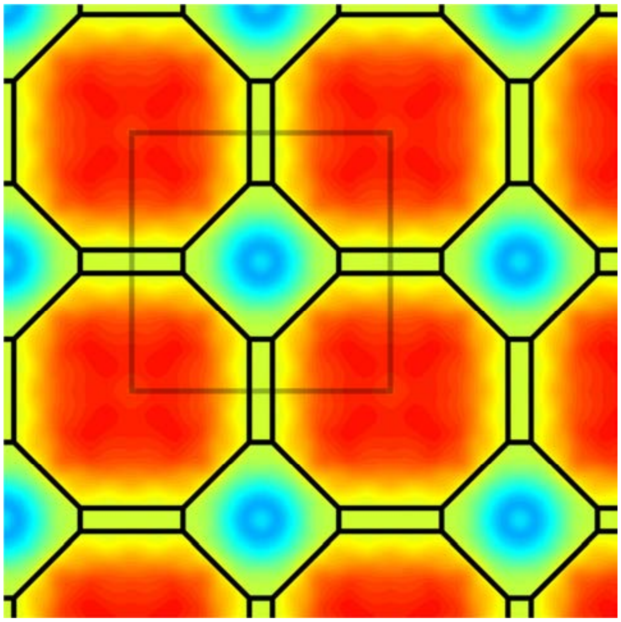
Topology F



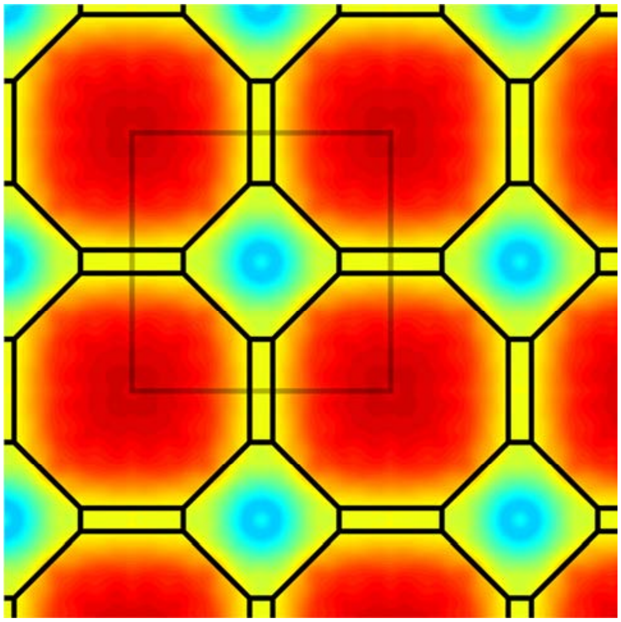
Phthalocyanine-Pyrene



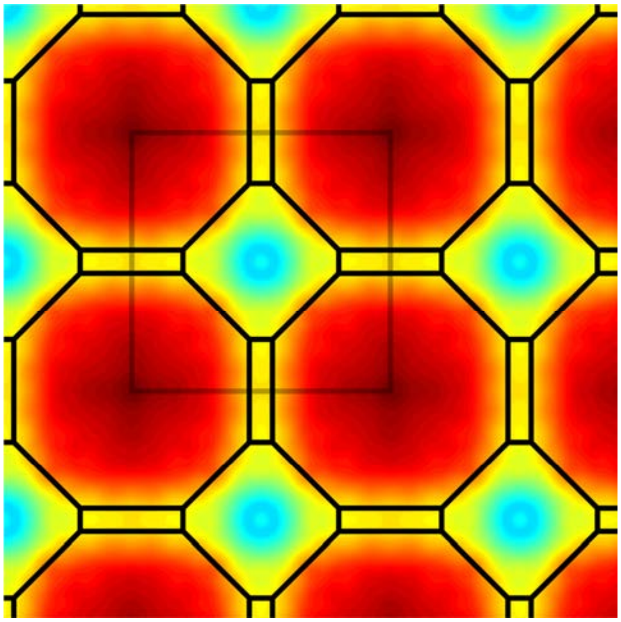
Phthalocyanine-Phenylene



Phthalocyanine-Biphenyl



Phthalocyanine-Diphenylacetylene



Phthalocyanine-Diphenylbutadiyne

TABLES

Table S1. Compilation of synthesized COFs and not-yet-synthesized COFs in literature.

	B	**TPB**	**Py**	**Ph**	**BP**	**DPA**	**DPB**
Boroxine	–	–	PPy-COF[4]	COF-1[1]	–	–	–
HHB	–	–	–	–	–	–	–
HHTP	COF-6[2]	COF-8[2]	TP-COF[3]	COF-5[1]	COF-10[2]	–	HHTP-DPB[6]
DHC	–	–	–	–	–	–	–
Pc	[redacted]	[redacted]	–	Pc-PBBA[5]	–	–	–

Table S2. Well depths of the lowest lying potential energy wells on the PES. Units of meV/atom. The subscript r denotes rotated configurations.

	B	**B_r**	**TPB**	**TPB_r**	**Py**	**Ph**	**BP**	**DPA**	**DPB**
BRX	2.9[§]	1.1[†]	4.6	4.1	8.4	5.3	8.1	10.2	10.3
HHB	3.1	1.5[†]	8.7	9.7	11.2	10.0	11.3	12.6	12.5
HHTP	7.4	5.2	11.2	12.4	14.6	13.9	15.5	14.8	14.2
DHC	1.2	–	2.4	–	1.9	2.4	3.4	5.7	8.1
Pc	–	–	–	–	9.0	8.6	8.3	8.6	9.2

[†] between close lowest lying sites. [§] lowest lying sites located at staggered positions (region **2**)

Table S3.1. Ratio between the ranges of dispersion and electrostatic interaction energies. The subscript r denotes rotated configurations.

	B	**B_r**	**TPB**	**TPB_r**	**Py**	**Ph**	**BP**	**DPA**	**DPB**
BRX	0.2	0.1	1.6	1.3	3.0	1.1	2.8	3.3	3.6
HHB	0.8	0.8	3.5	3.6	6.6	3.9	5.0	5.4	6.4
HHTP	3.2	3.2	5.1	6.9	8.1	6.4	6.7	7.9	8.3
DHC	0.3	–	1.1	–	1.0	0.9	1.7	2.7	3.5
Pc	–	–	–	–	6.1	5.2	6.4	7.0	8.0

Table S3.2. Range of the dispersion interaction energies in units of meV/atom. The subscript r denotes rotated configurations.

	B	**B_r**	**TPB**	**TPB_r**	**Py**	**Ph**	**BP**	**DPA**	**DPB**
BRX	1.5	1.6	6.4	7.4	10.8	5.2	11.3	11.6	13.1
HHB	3.7	4.4	10.2	12.1	16.6	12.1	15.0	14.5	15.6
HHTP	8.4	10.4	12.7	13.1	18.2	15.7	16.3	17.0	18.1
DHC	1.3	–	3.5	–	3.0	2.9	5.2	7.2	9.4
Pc	–	–	–	–	16.4	16.8	16.9	17.8	19.6

Table S3.3. Range of the electrostatic interaction energies in units of meV/atom. The subscript r denotes rotated configurations.

	B	**B$_r$**	**TPB**	**TPB$_r$**	**Py**	**Ph**	**BP**	**DPA**	**DPB**
BRX	6.2	11.2	4.1	5.6	3.6	4.7	4.1	3.5	3.6
HHB	4.5	5.3	3.0	3.3	2.5	3.1	3.0	2.7	2.5
HHTP	2.6	3.2	2.5	1.9	2.2	2.5	2.4	2.2	2.2
DHC	3.9	–	3.0	–	3.1	3.3	3.1	2.7	2.6
Pc	–	–	–	–	2.7	3.2	2.6	2.5	2.5

Table S4. Comparison of preferred lateral offsets of representative COF layers computed by MM and DFT.

	MM	**DFT**	**Error**
BRX-Ph (COF-1)	2.1 Å	1.9 Å	-0.2 Å
BRX-Py	1.7 Å	1.5 Å	-0.2 Å
BRX-DPB	1.7 Å	1.6 Å	-0.1 Å
HHTP-Ph (COF-5)	1.6 Å	1.7 Å	0.1 Å
HHTP-Py	1.6 Å	1.7 Å	0.1 Å
HHTP-DPB	1.6 Å	1.7 Å	0.1 Å
Pc-Ph	1.7 Å	1.7 Å	0.0 Å
DHC-Ph	2.5 Å	1.8 Å	-0.7 Å

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