Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information:

Band gap opening from displacive instabilities in layered covalent-organic frameworks†

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Tab. S1. Lattice parameters and space groups of **(a)** planar experimentally-reported crystal structure and **(b)** wavy relaxed structure of Tp-Azo. The lattice parameters and space groups of **(c)** planar experimentally-reported crystal structure and **(d)** wavy relaxed structure of DAAQ-TFP.

	Lattice parameters						
–	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Space group
(a) Tp-Azo[S1]	31.50	31.50	3.30	90	90	120	$P6/m$
(b) Tp-Azo*	33.28	33.36	4.23	61.71	128.44	121.17	$P\bar{1}$
(c) DAAQ-TFP[S2]	29.83	29.83	3.60	90	90	60	$P6/m$
(d) DAAQ-TFP *	30.28	30.38	4.04	68.68	56.15	60.19	$P\bar{1}$

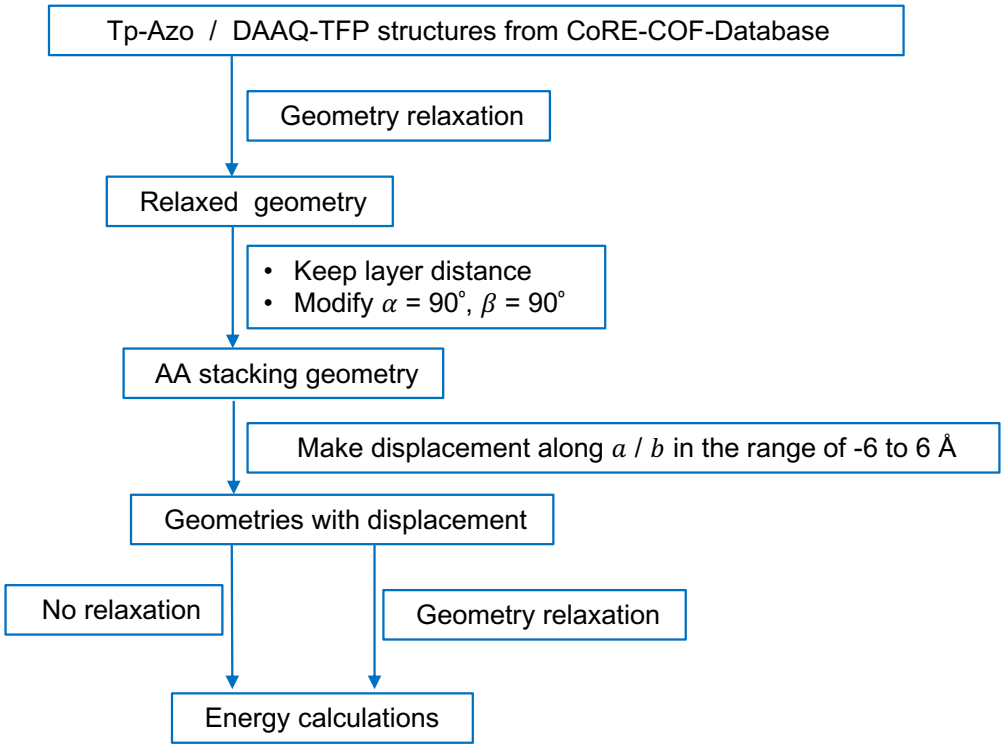

Fig. S1. Workflow of displacement process.

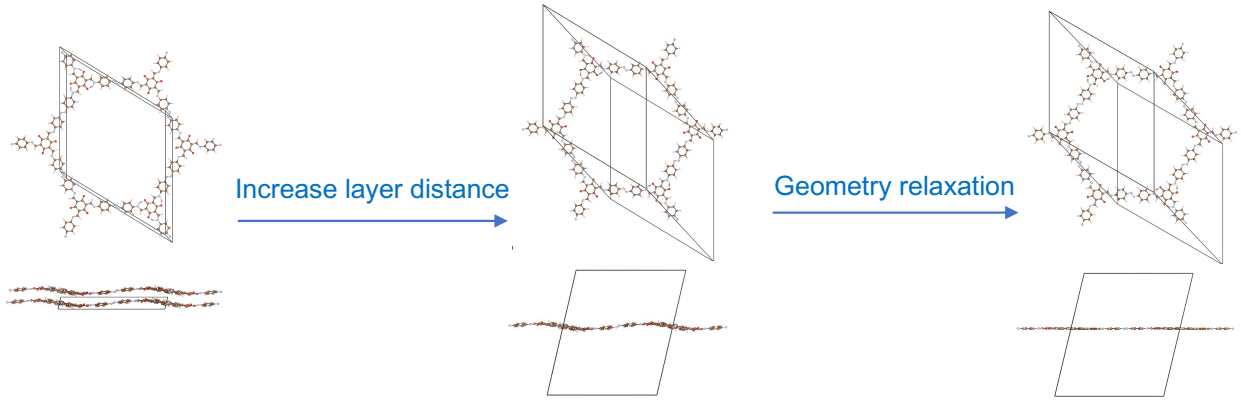

Fig. S2. Process of forming monolayer and the binding energy calculation of Tp-Azo COF. The upper figures are viewed looking down the c axis, and the lower figures are viewed along the ab plane. The layer distance in geometry relaxation keeps 30 Å.

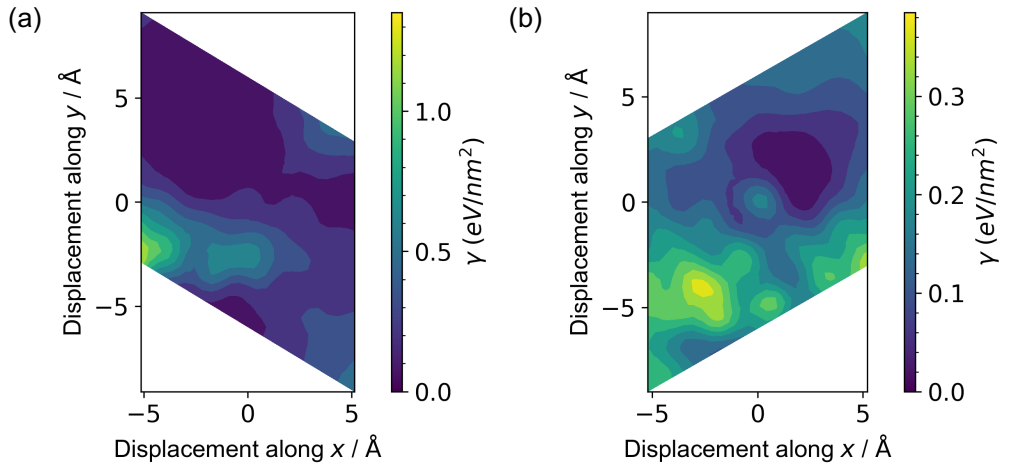

Fig. S3. Potential energy surfaces (PES) for rigid layer displacements along a and b sides of (a) Tp-Azo and (b) DAAQ-TFP. Note, the PES reported in the main text includes geometry relaxation.

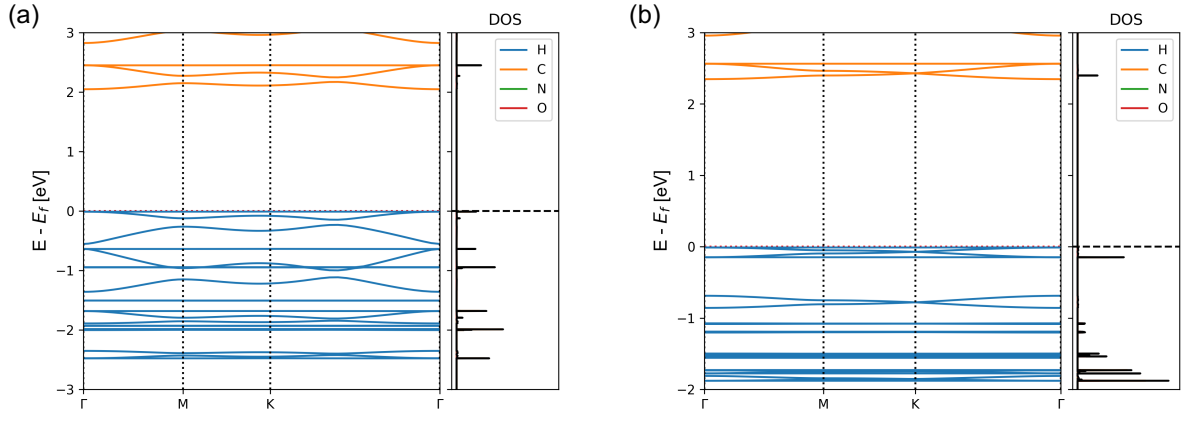

Fig. S4. Electronic band structures of monolayer Tp-Azo (a) and monolayer DAAQ-TFP (b).

References

(S1) Chandra, S.; Kundu, T.; Kandambeth, S.; BabaRao, R.; Marathe, Y.; Kunjir, S. M.; Banerjee, R. Phosphoric Acid Loaded Azo (- N N-) Based Covalent Organic Framework for Proton Conduction. *Journal of the American Chemical Society* **2014**, *136*, 6570–6573.

(S2) DeBlase, C. R.; Silberstein, K. E.; Truong, T.-T.; Abruña, H. D.; Dichtel, W. R. β-Ketoenamine-linked covalent organic frameworks capable of pseudocapacitive energy storage. *Journal of the American Chemical Society* **2013**, *135*, 16821–16824.