Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Revealing the structure−property relationships of covalent organic frameworks for CO_2 capture from postcombustion gas: a multi-scale computational study

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1. Physicochemical properties of the 46 COFs Studied in This Work

Table S1. Physicochemical properties of the 46 COFs studied in this work

COF ID	Names	Dimensions [a]	Unit cells[a] (Å)	Pore sizes[a] (Å)	V_{free} [b] (cm^3/g)	φ [b]	S_{acc} [b] (m^2/g)	ΔQ_{st}^0 [c] (kJ/mol)
1	COF-1[1]	2D	a = b = 15.6529, c = 6.7005	7.0	0.55	0.52	221	10.4
2	COF-5[1]	2D	a = b = 29.7010, c = 3.46020	27.0	1.24	0.72	1697	7.6
3	COF-6[2]	2D	a = b = 15.0911, c = 3.59880	8.6	0.55	0.53	1123	7.1
4	COF-8[2]	2D	a = b = 22.7331, c = 3.47640	16.4	0.93	0.65	1551	6.3
5	COF-10[2]	2D	a = b = 37.8099, c = 3.47630	31.7	1.74	0.78	1919	6.5
6	COF-11Å[3]	2D	a = b = 20.8120, c = 3.38500	11.0	0.35	0.40	299	5.0
7	COF-14Å[3]	2D	a = b = 20.8120, c = 3.38500	14.0	0.34	0.48	520	6.3
8	COF-16Å[3]	2D	a = b = 20.8120, c = 3.38500	16.0	0.61	0.57	1359	10.0
9	COF-18Å[3]	2D	a = b = 20.8120, c = 3.38500	18.0	0.77	0.63	1478	7.4
10	PPy-COF[4]	2D	a = b = 22.1629, c = 3.42066	17.3	0.65	0.57	1214	5.4
11	TP-COF[5]	2D	a = b = 37.5412, c = 3.37840	32.6	1.42	0.75	1724	8.0
12	COF-42[6]	2D	a = b = 29.9768, c = 4.05000	28.0	1.28	0.72	2575	9.0
13	COF-43[6]	2D	a = b = 45.8877, c = 3.97840	35.0	2.34	0.81	2551	21.6
14	CTF-1[7]	2D	a = b = 14.5740, c = 3.40400	12.0	0.48	0.49	919	5.3
15	CTF-2-AA[8]	2D	a = b = 18.3600, c = 3.36000	18.0	0.60	0.54	1185	5.0
16	CTF-2-AB[8]	2D	a = b = 18.3600, c = 6.72000	18.0	0.60	0.54	443	13.3
17	BLP-2H[9]	2D	a = b = 15.2905, c = 3.45790	6.4	0.56	0.50	1077	5.2
18	ZnPc-Py COF[10]	2D	a = b = 26.9800, c = 3.33800	27.0	0.85	0.66	1334	10.7

19	2D-NiPc-BTDA COF[11]	2D	a = b = 46.4916, c = 3.40493	19.0	0.69	0.62	1243	8.3
20	TpPa-1[12]	2D	a = b = 22.5560, c = 3.40000	18.3	0.92	0.65	1600	25.8
21	TpPa-2[12]	2D	a = b = 22.5060, c = 3.50000	15.0	0.77	0.60	1521	9.2
22	TpBD[13]	2D	a = b = 29.2871, c = 3.25000	23.1	1.18	0.70	1657	24.4
23	TpPa-F_4[14]	2D	a = b = 22.1200, c = 3.28000	17.0	0.58	0.59	1072	7.6
24	TPBD-ME_2[14]	2D	a = b = 29.2800, c = 3.2500	23.0	1.02	0.66	1494	6.2
25	TpBD-$(NO_2)_2$[14]	2D	a = b = 31.5400, c = 3.4900	22.0	1.12	0.70	1624	9.8
26	DAAQ-TFP COF[15]	2D	a = b = 29.8330, c = 3.62140	23.0	1.19	0.73	1687	23.9
27	COF-366[16]	2D	a = b = 25.4170, c = 12.3770	20.0	2.23	0.81	4035	17.5
28	COF-66[16]	2D	a = b = 28.9840, c = 3.81300	23.0	1.24	0.72	1700	6.1
29	ILCOF-1[17]	2D	a = 34.7756, b = 34.1644, c = 6.57870	23.2	2.54	0.82	3765	25.2
30	TT-COF[18]	2D	a = b = 32.8400, c = 3.45000	30.0	1.30	0.75	1622	8.6
31	Star-COF-1[19]	2D	a = b = 38.5200, c = 3.38000	39.0	1.22	0.71	1334	4.3
32	Star-COF-2[19]	2D	a = b = 46.3300, c = 3.42000	46.0	1.51	0.75	1458	5.6
33	Star-COF-3[19]	2D	a = b = 46.8300, c = 3.41000	47.0	1.71	0.77	1545	4.2
34	Pc-PBBA COF[20]	2D	a = b = 22.8500, c = 3.34000	21.2	0.81	0.64	1328	6.0
35	COF-LZU1[21]	2D	a = b = 22.0400, c = 3.72900	18.0	1.21	0.69	2130	4.6
36	COF-102[22]	3D	a = b = c = 27.1771	8.9	1.86	0.78	5005	4.9
37	COF-103[22]	3D	a = b = c = 28.2477	9.6	2.05	0.80	5204	4.6
38	COF-105[22]	3D	a = b = c = 44.8860	18.3	5.17	0.91	6637	4.1
39	COF-108[22]	3D	a = b = c = 28.4010	15.2/29.6	5.37	0.92	6409	5.1

40	COF-202[23]	3D	a = b = c = 30.1051	11.0	1.37	0.72	4151	7.6
41	NPN-1[24]	3D	a = b = 13.1545, c = 7.98180	7.3×3.3	0.48	0.50	605	11.2
42	NPN-2[24]	3D	a = b = 13.4210, c = 8.52800	7.8×3.4	0.54	0.53	918	10.5
43	NPN-3[24]	3D	a = b = 15.7703, c = 7.07170	5.2×5.2	0.46	0.48	877	8.1
44	COF-300[25]	3D	a = b = 28.1270, c = 8.87900	7.8	1.31	72	3094	13.0
45	CTC-COF[26]	3D	a = b = 25.0645, c = 4.29890	22.0	0.89	64	1450	6.4
46	COF-320[27]	3D	a = 27.9300, b = 31.3100, c = 7.89000	11.5	0.87	61	1659	4.6

[a] Obtained from the experimental data.

[b] Calculated with the Materials Studio package.

[c] Obtained from molecular simulations.

The accessible surface area (S_{acc}) and the total free volume (V_{free}) of each COF material were estimated using the "Atoms Volume & Surfaces" calculation within the Materials Studio package.[28] The porosity was obtained from the ratio of free volume V_{free} to the total volume per unit cell. The accessible surface area (S_{acc}) was calculated by a probe molecule with diameter equal to the kinetic diameter of N_2 (0.368 nm), while a probe size of 0.0 nm was applied to determine the absolute amount of volume not occupied by the framework atoms.

2. Force field parameters for the COFs

Table S2. Lennard-Jones parameters for the framework atoms of the COFs

Atoms	C	O	H	N	F	B	Si	S	Zn	Ni[a]
σ (Å)	3.47	3.03	2.85	3.26	3.09	3.58	3.80	3.59	4.04	2.52
ε/k_B (K)	47.86	48.16	7.650	38.95	36.48	47.81	156.0	173.1	27.68	7.549

[a] Taken from the UFF force field[29] (they are missing in the Dreiding force field).

3. Model clusters and atomic partial charges for the COFs

COF-1

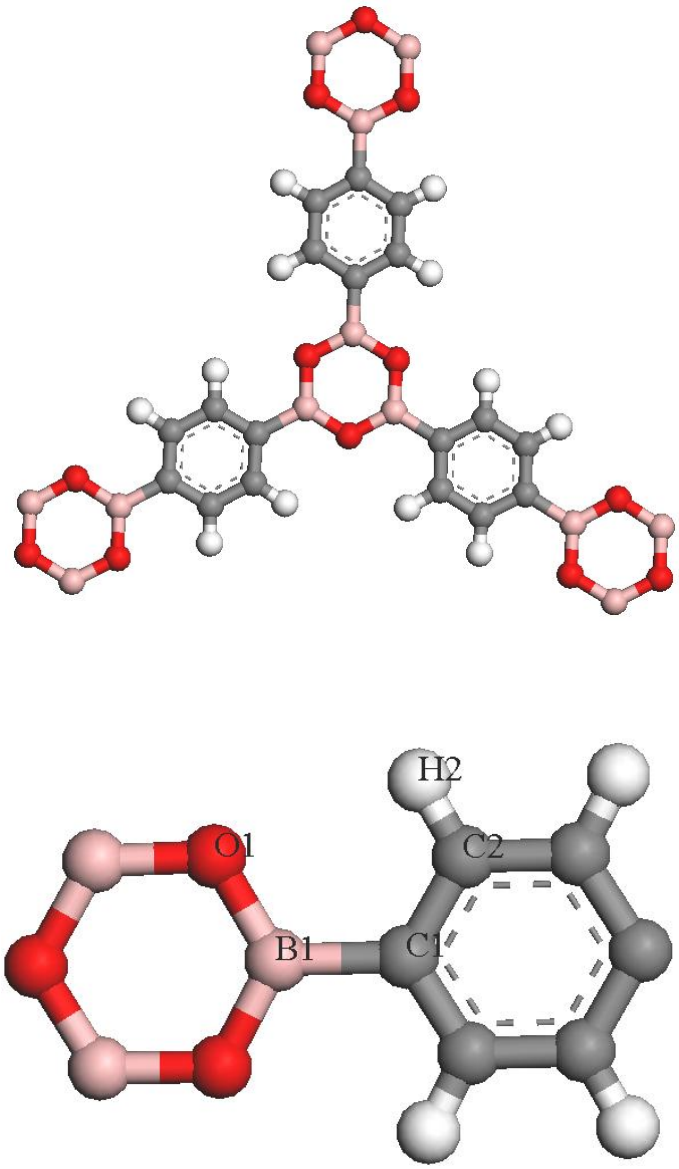

Fig. S1. Model cluster used for calculating the partial charges for each atom of COF-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S3. Atomic partial charges for the COF-1 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**H2**
Charge (*e*)	0.700	-0.587	-0.157	-0.084	0.106

COF-5

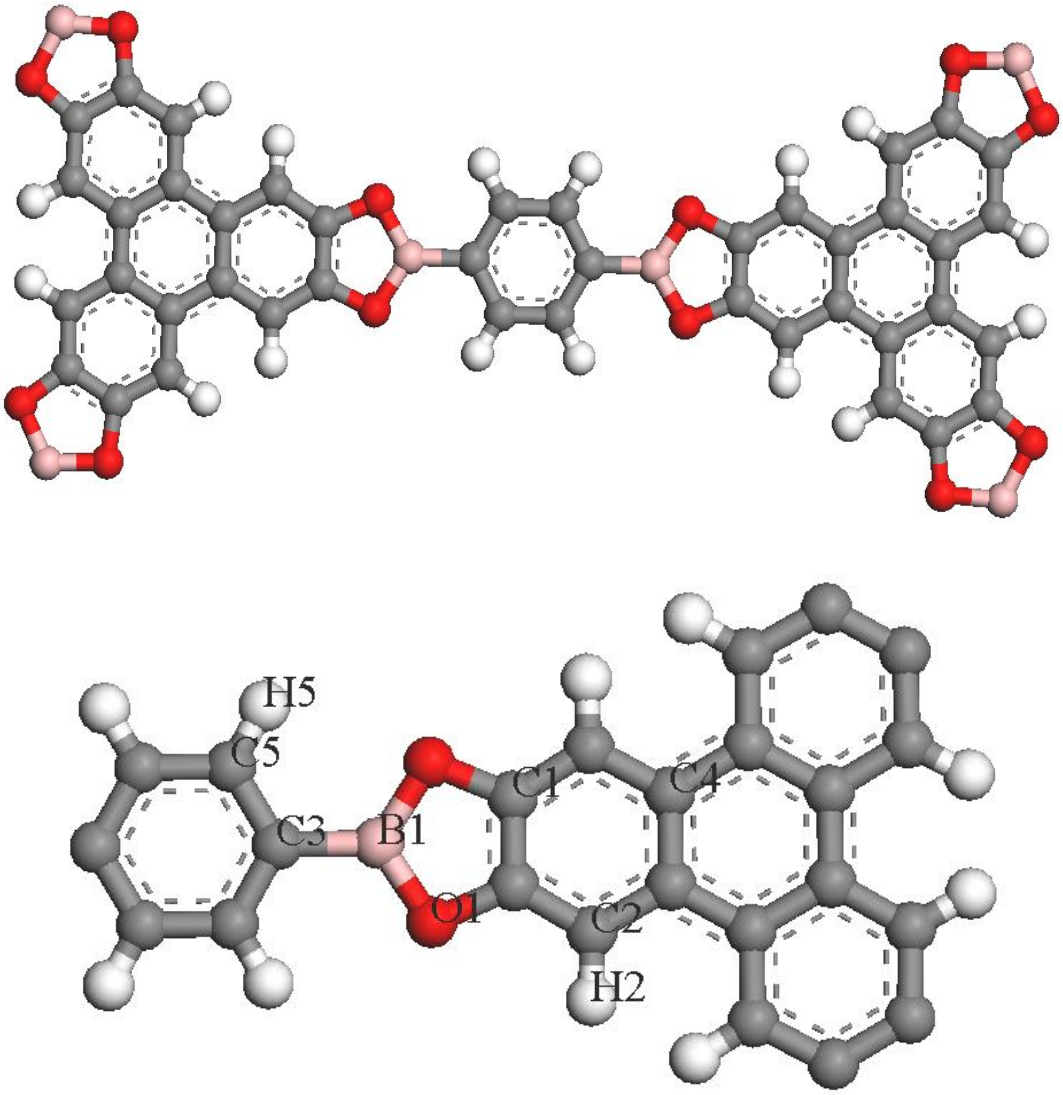

Fig. S2. Model cluster used for calculating the partial charges for each atom of COF-5. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S4. Atomic partial charges for the COF-5 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H1**	**H2**
Charge (*e*)	0.660	-0.401	0.219	-0.179	-0.158	0.057	-0.086	0.106	0.073

COF-6

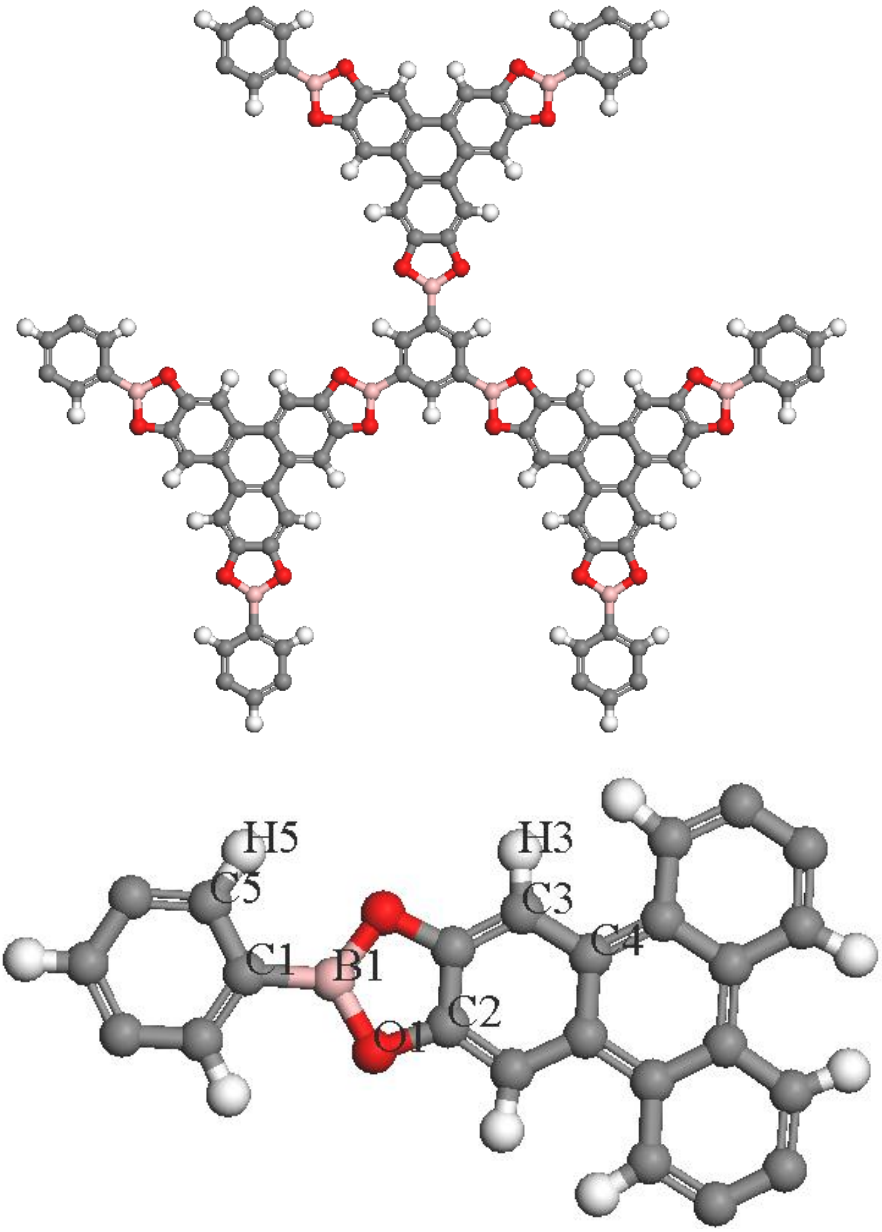

Fig. S3. Model cluster used for calculating the partial charges for each atom of COF-6. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S5. Atomic partial charges for the COF-6 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H1**	**H2**
Charge (*e*)	0.547	-0.396	-0.127	0.265	-0.343	0.044	-0.045	0.192	0.101

COF-8

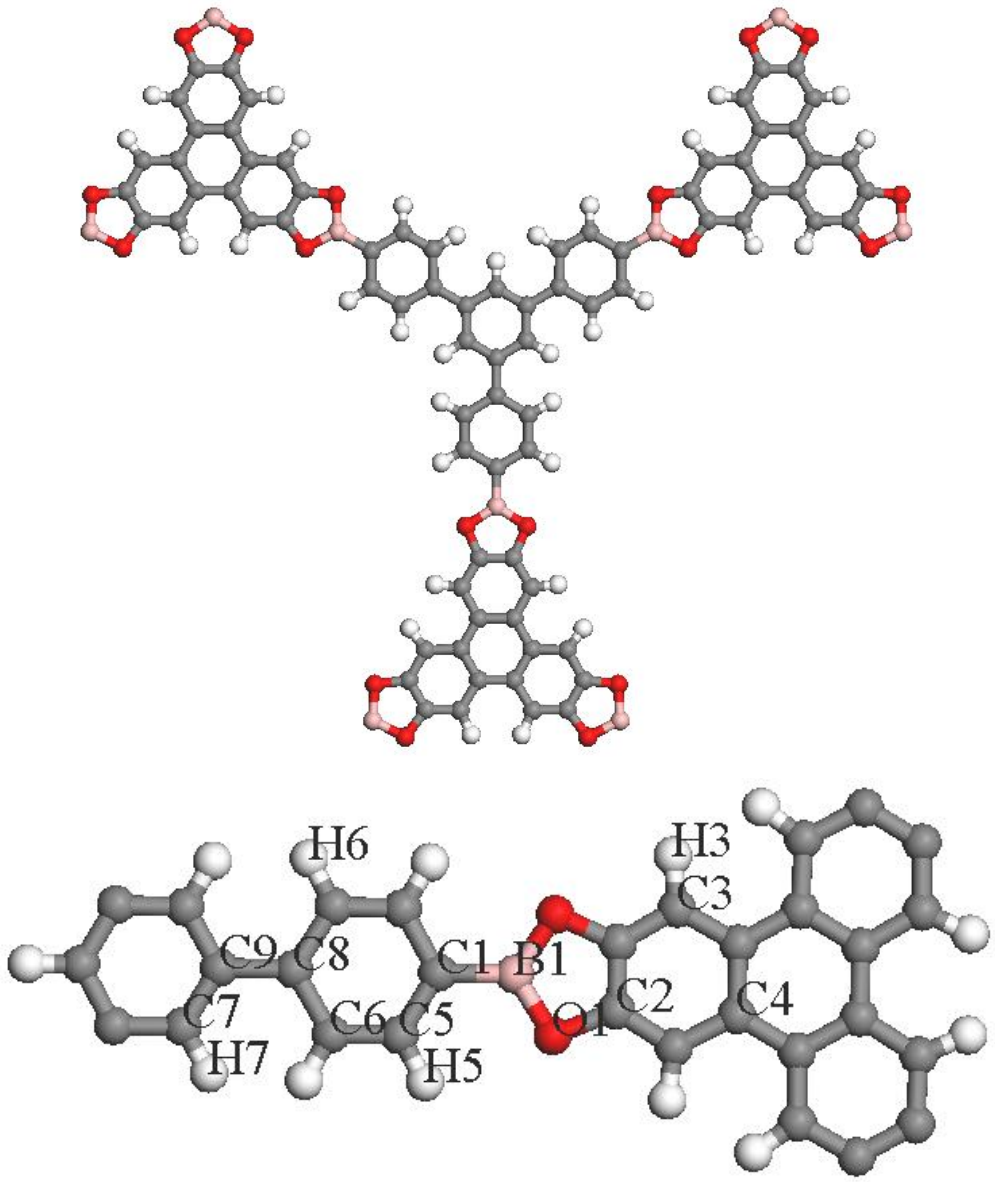

Fig. S4. Model cluster used for calculating the partial charges for each atom of COF-8. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S6. Atomic partial charges for the COF-8 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.681	-0.422	-0.189	0.226	-0.181	0.034	-0.105	-0.164	-0.089
Atomic types	**C8**	**C9**	**H1**	**H2**	**H3**	**H4**			
Charge (*e*)	0.043	0.037	0.124	0.085	0.130	0.063			

COF-10

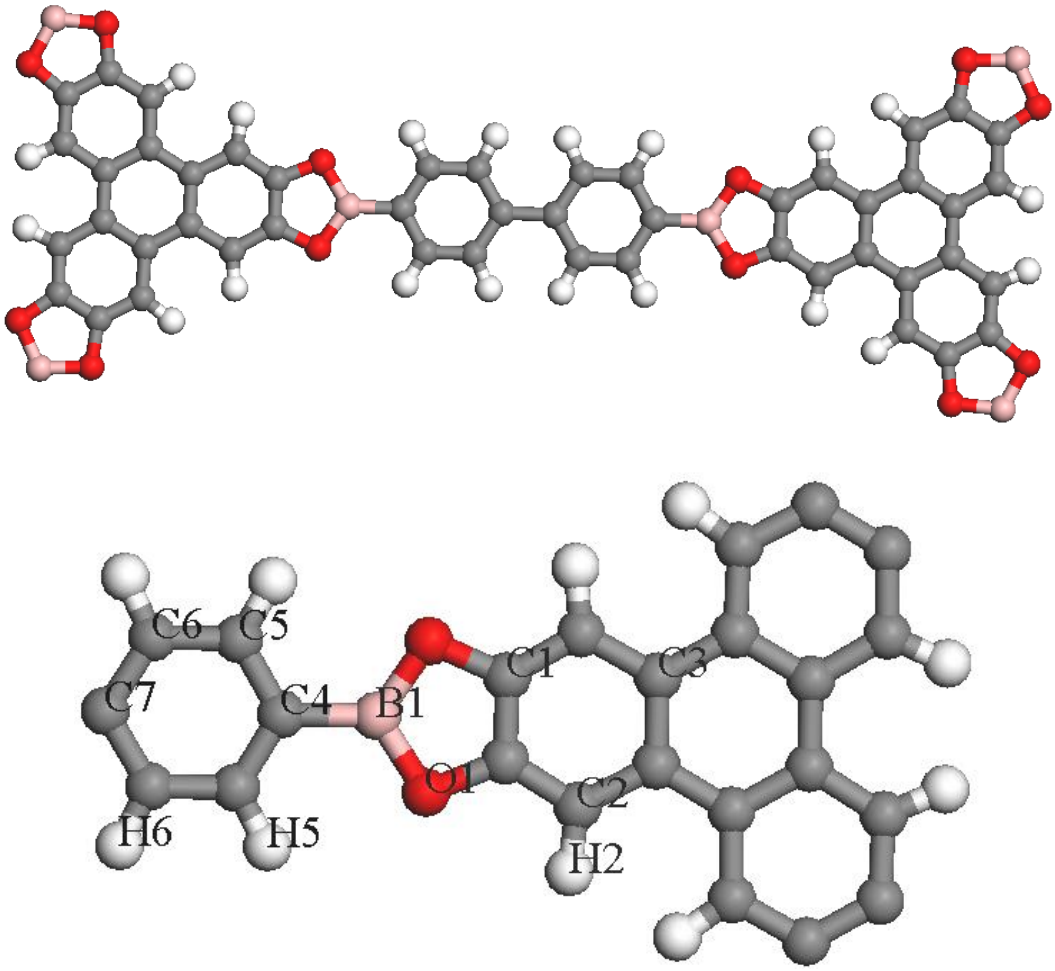

Fig. S5. Model cluster used for calculating the partial charges for each atom of COF-10. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S7. Atomic partial charges for the COF-10 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.696	-0.410	0.220	-0.139	0.040	-0.185	-0.140	-0.140	0.040
Atomic types	**H2**	**H5**	**H6**						
Charge (*e*)	0.108	0.103	0.093						

COF-11Å

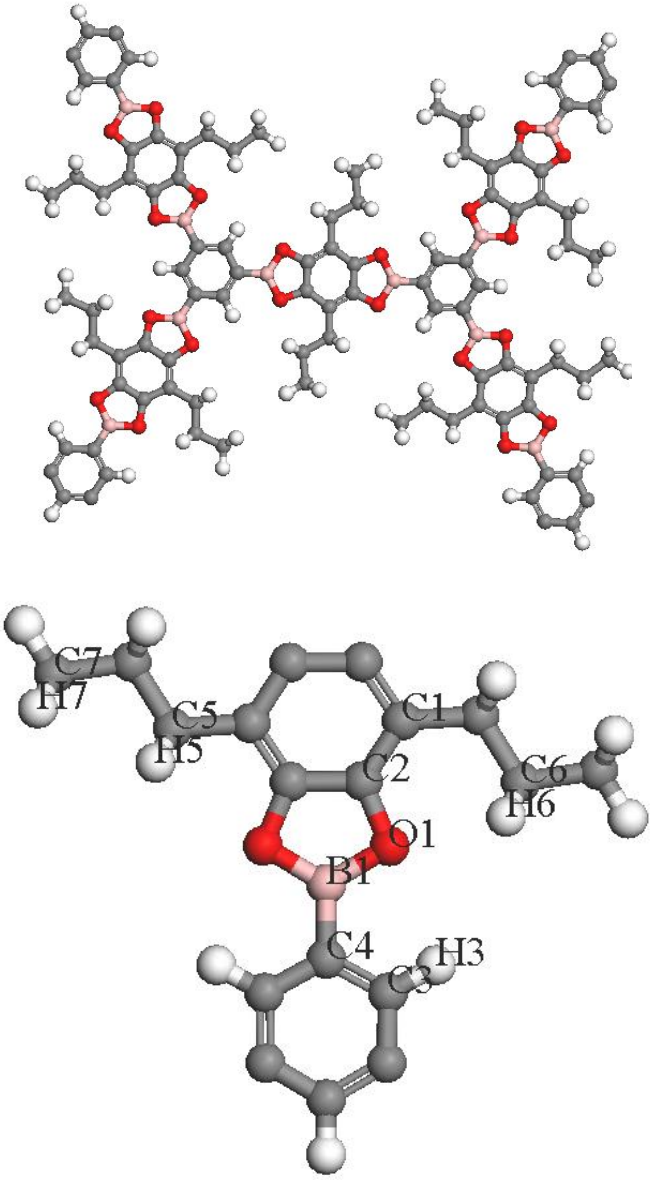

Fig. S6. Model cluster used for calculating the partial charges for each atom of COF-11Å. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S8. Atomic partial charges for the COF-11Å structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.503	-0.355	-0.140	0.003	0.271	-0.440	0.167	0.047	-0.278
Atomic types	**H2**	**H5**	**H6**	**H7**					
Charge (*e*)	0.066	0.011	0.019	0.060					

COF-14Å

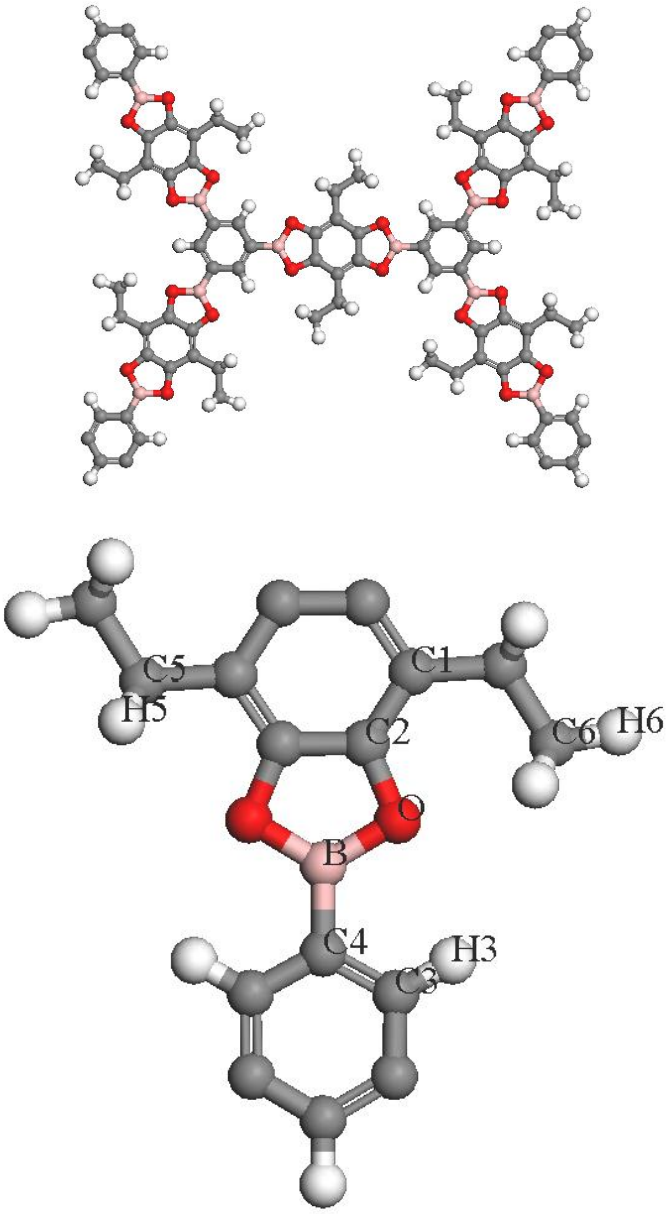

Fig. S7. Model cluster used for calculating the partial charges for each atom of COF-14Å. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S9. Atomic partial charges for the COF-14Å structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**H3**
Charge (*e*)	0.389	-0.256	-0.398	0.191	-0.238	0.064	0.433	-0.565	0.134
Atomic types	**H5**	**H6**							
Charge (*e*)	-0.013	0.129							

COF-16Å

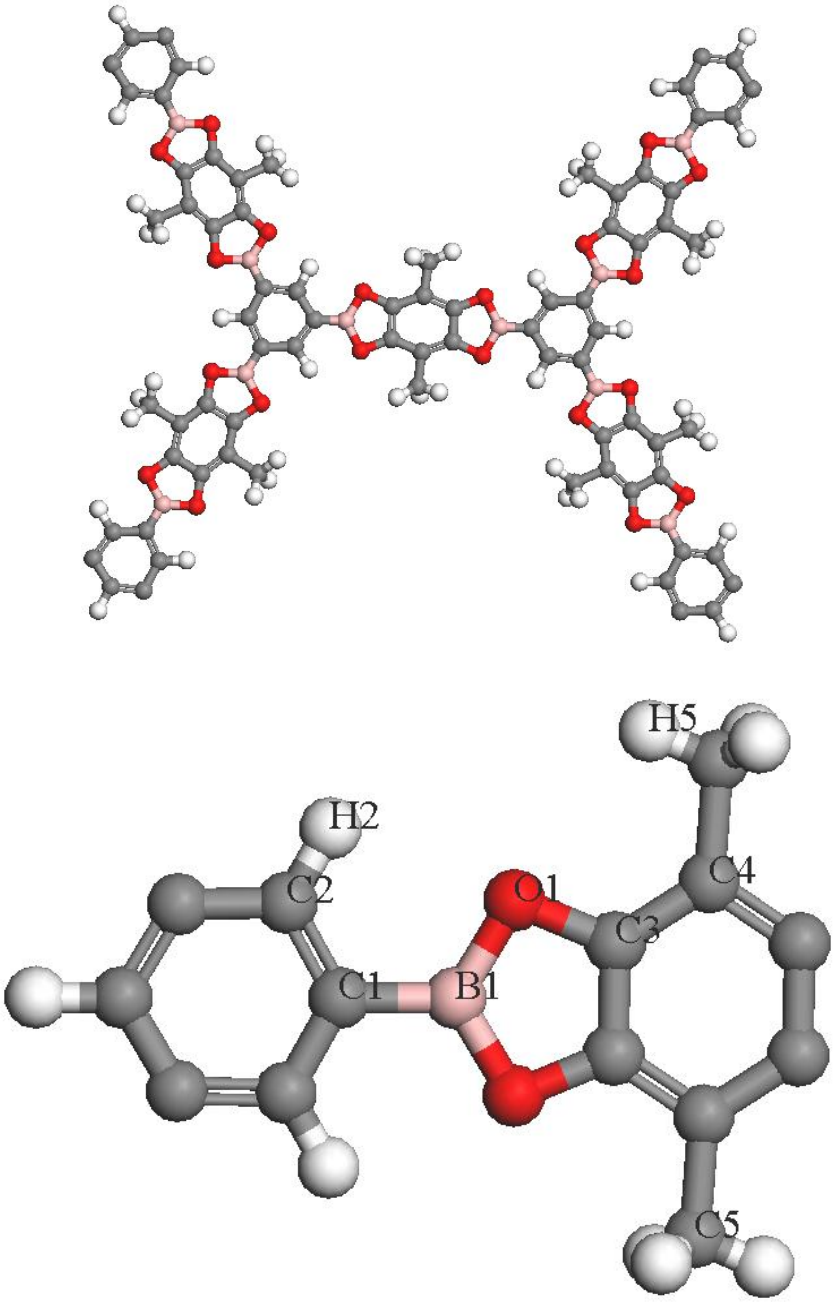

Fig. S8. Model cluster used for calculating the partial charges for each atom of COF-16Å. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S10. Atomic partial charges for the COF-16Å structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H2**	**H5**
Charge (*e*)	0.515	-0.258	-0.243	0.118	0.131	-0.205	0.029	0.007	0.011

COF-18Å

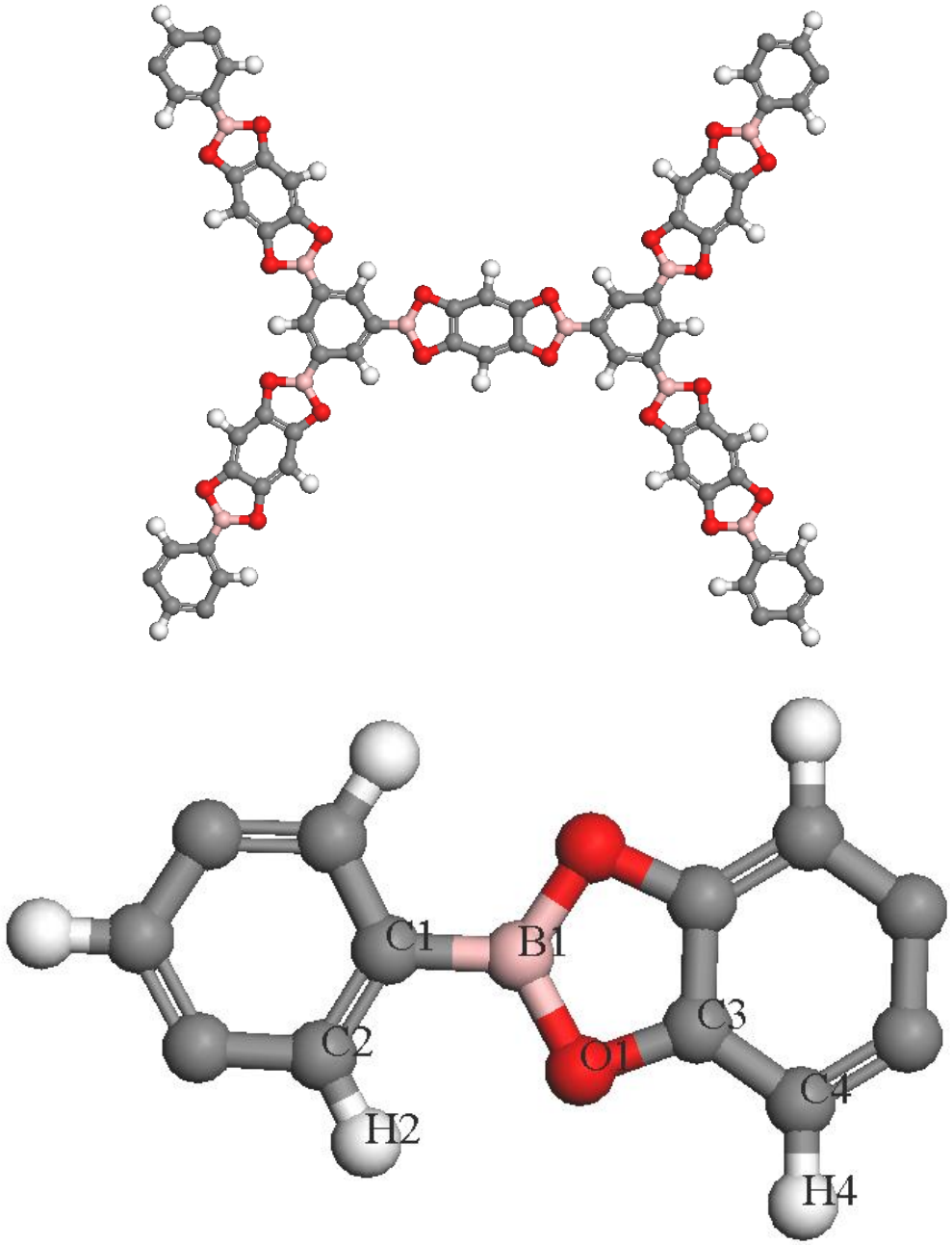

Fig. S9. Model cluster used for calculating the partial charges for each atom of COF-18Å. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S11. Atomic partial charges for the COF-18Å structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**H2**	**H4**
Charge (*e*)	0.506	-0.356	-0.176	0.052	0.303	-0.513	0.054	0.183

COF-42

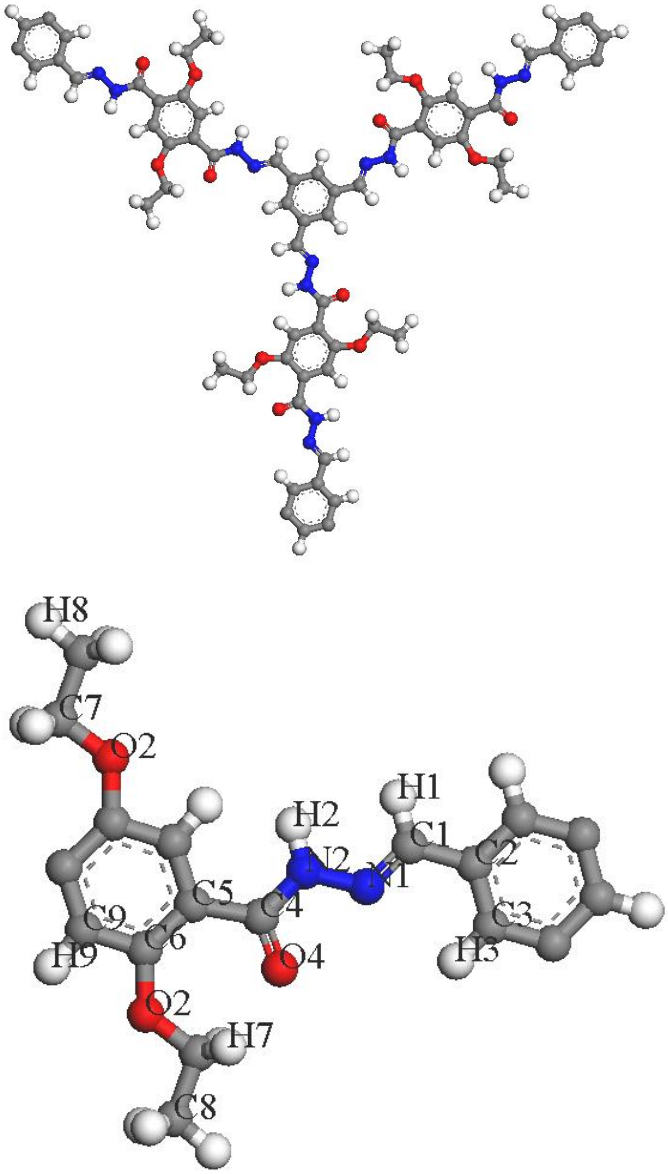

Fig. S10. Model cluster used for calculating the partial charges for each atom of COF-42. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S12. Atomic partial charges for the COF-42 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**N2**	**O2**	**O4**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Charge (*e*)	-0.202	-0.307	-0.488	-0.609	0.130	-0.056	-0.017	0.736	-0.245	0.518
Atomic types	**C7**	**C8**	**C9**	**H1**	**H2**	**H3**	**H7**	**H8**	**H9**	
Charge (*e*)	0.503	-0.350	-0.372	0.088	0.274	0.048	-0.008	0.072	0.149	

COF-43

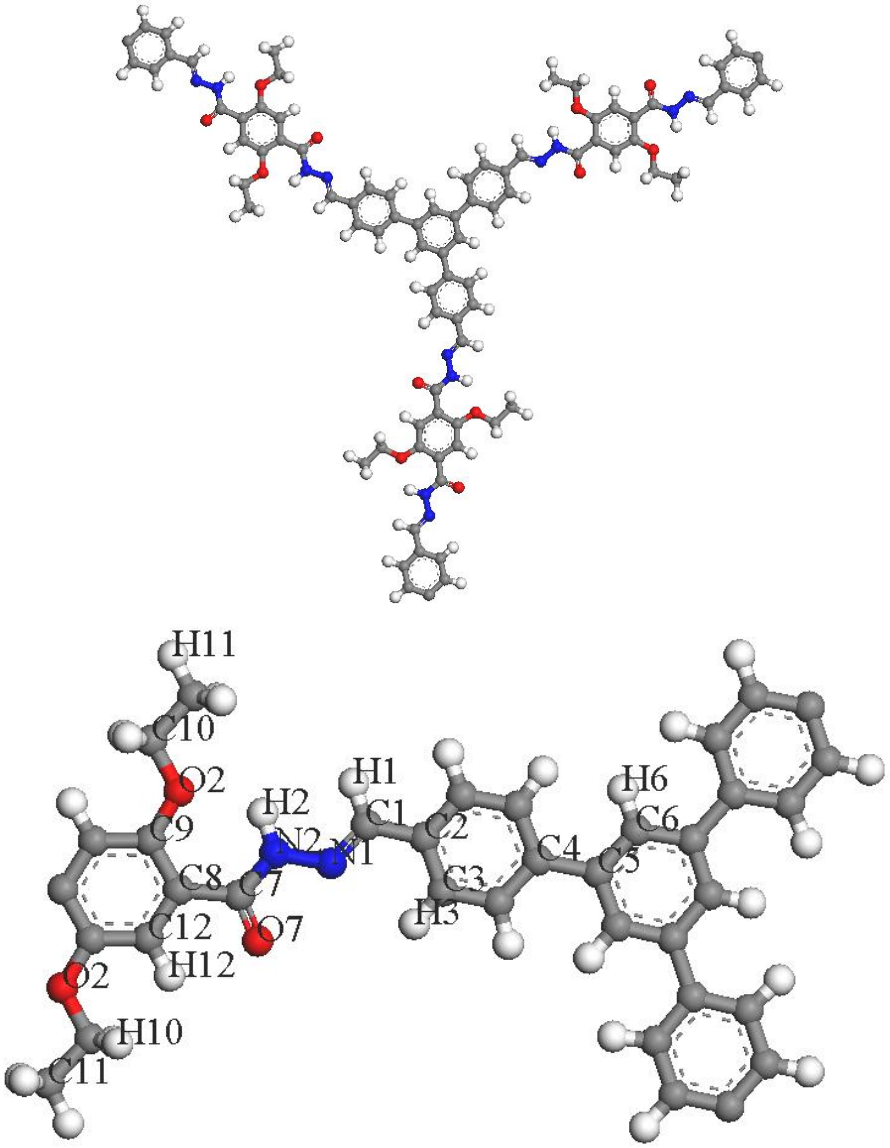

Fig. S11. Model cluster used for calculating the partial charges for each atom of COF-43. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S13. Atomic partial charges for the COF-43 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**N2**	**O2**	**O7**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
Charge (*e*)	-0.216	-0.300	-0.483	-0.574	0.107	-0.028	-0.138	0.129	0.046	-0.182	0.697	-0.286
Atomic types	**C9**	**C10**	**C11**	**C12**	**H1**	**H2**	**H3**	**H6**	**H10**	**H11**	**H12**	
Charge (*e*)	0.280	0.506	-0.261	-0.086	0.085	0.295	0.115	0.120	**-0.043**	**0.063**	**0.120**	

TT-COF

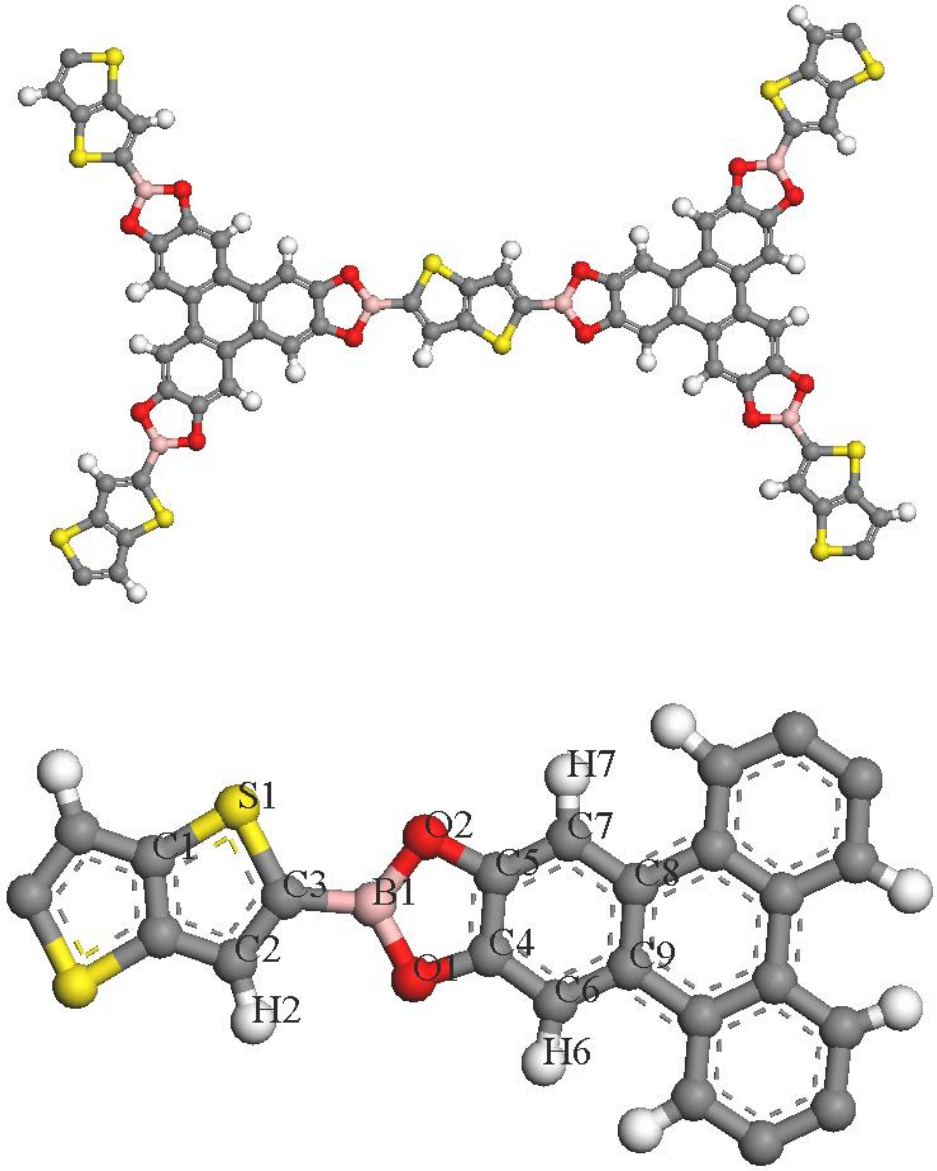

Fig. S12. Model cluster used for calculating the partial charges for each atom of TT-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S14. Atomic partial charges for the TT-COF structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**O2**	**S1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Charge (*e*)	0.670	-0.463	-0.345	0.015	0.157	-0.225	-0.291	0.351	0.093	-0.405
Atomic types	**C7**	**C8**	**C9**	**H2**	**H6**	**H7**				
Charge (*e*)	-0.210	-0.036	0.114	0.201	0.209	0.165				

ZnPc-Py-COF

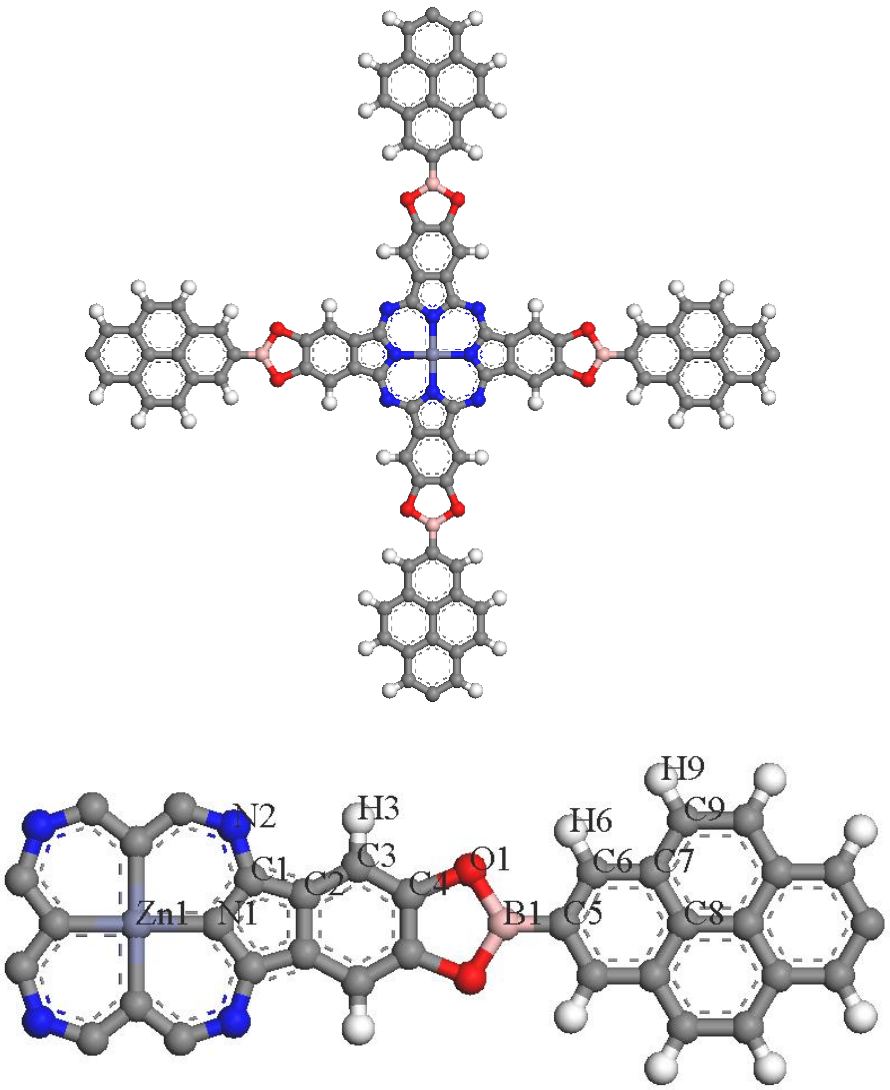

Fig. S13. Model cluster used for calculating the partial charges for each atom of ZnPc-Py-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S15. Atomic partial charges for the ZnPc-Py-COF structure derived on DFT/B3LYP Level.

Atomic types	**Zn1**	**N1**	**N2**	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**
Charge (*e*)	0.884	-0.675	-0.762	0.585	-0.475	0.709	-0.139	-0.219	0.252	-0.057
Atomic types	**C6**	**C7**	**C8**	**C9**	**H3**	**H6**	**H9**			
Charge (*e*)	-0.266	0.227	-0.292	-0.049	0.150	0.155	0.145			

2D-NiPc-BTDA-COF

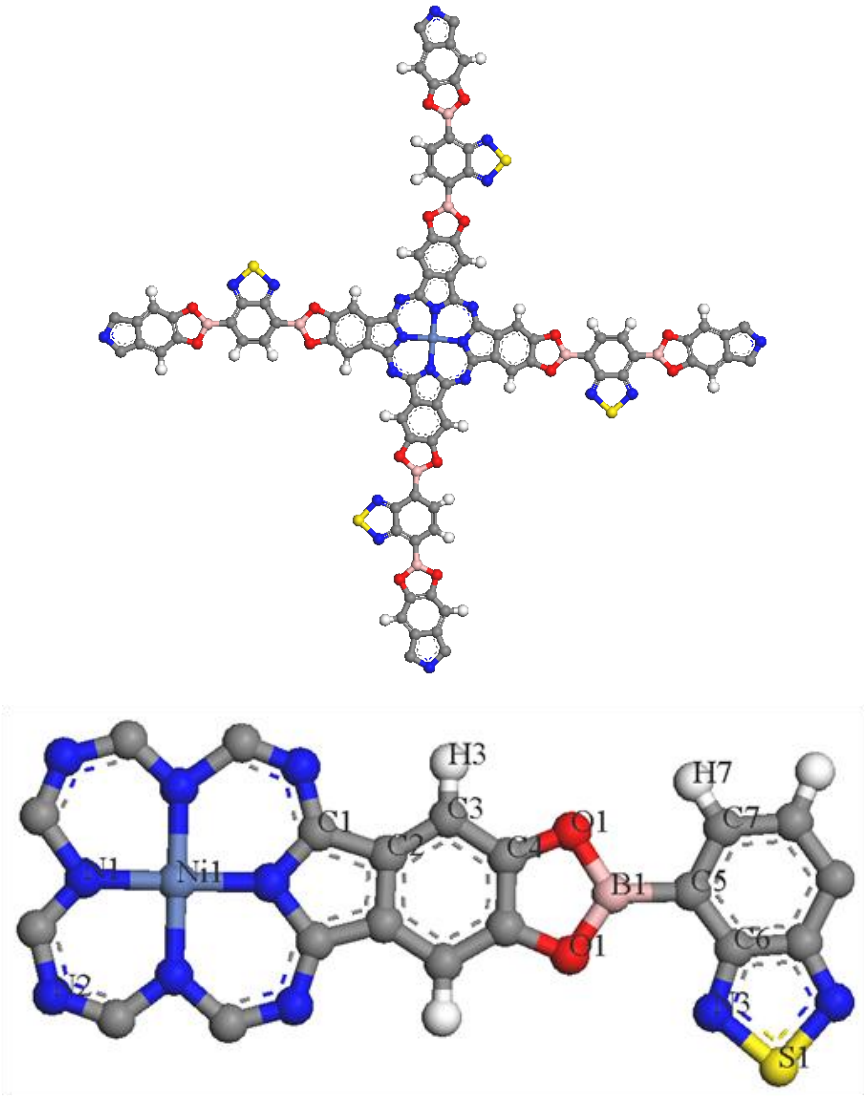

Fig. S14. Model cluster used for calculating the partial charges for each atom of 2D-NiPc-BTDA-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S16. Atomic partial charges for the 2D-NiPc-BTDA-COF structure derived on DFT/B3LYP Level.

Atomic types	**Ni1**	**N1**	**N2**	**N3**	**B1**	**O1**	**S1**	**C1**	**C2**	**C3**
Charge (*e*)	0.316	-0.460	-0.644	-0.417	0.697	-0.445	0.296	0.614	-0.165	-0.190
Atomic types	**C4**	**C5**	**C6**	**C7**	**H3**	**H7**				
Charge (*e*)	0.257	-0.343	0.392	-0.048	0.166	0.122				

Pc-PBBA-COF

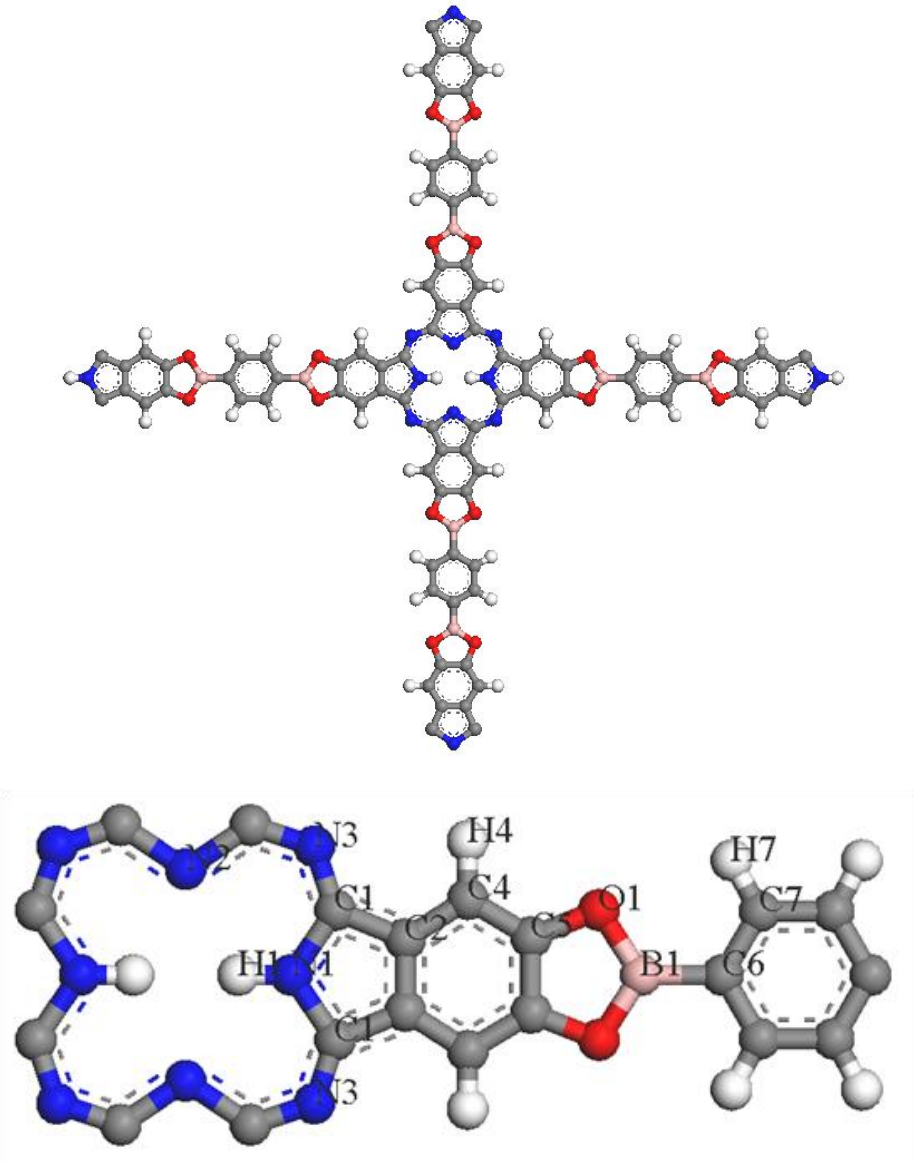

Fig. S15. Model cluster used for calculating the partial charges for each atom of Pc-PBBA-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S17. Atomic partial charges for the Pc-PBBA-COF structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**N2**	**N3**	**B1**	**O1**	**C1**	**C2**	**C4**	**C5**
Charge (*e*)	-0.676	-0.792	-0.690	0.519	-0.394	0.738	-0.146	-0.257	0.280
Atomic types	**C6**	**C7**	**H1**	**H4**	**H7**				
Charge (*e*)	-0.065	-0.100	0.358	0.168	0.106				

COF-LZU1

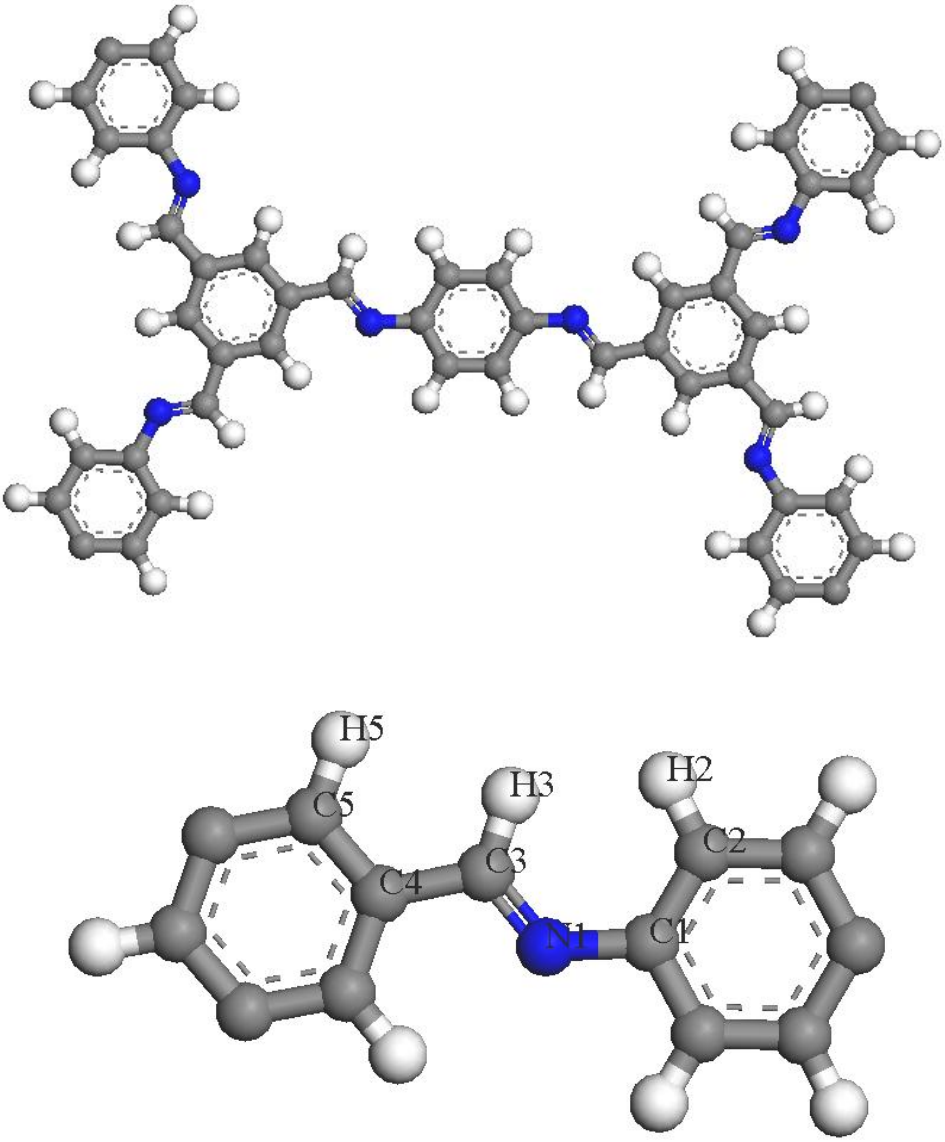

Fig. S16. Model cluster used for calculating the partial charges for each atom of COF-LZU1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S18. Atomic partial charges for the COF-LZU1 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H2**	**H3**	**H5**
Charge (*e*)	-0.483	0.409	-0.241	0.217	0.012	-0.101	0.152	0.048	0.076

BLP-2H

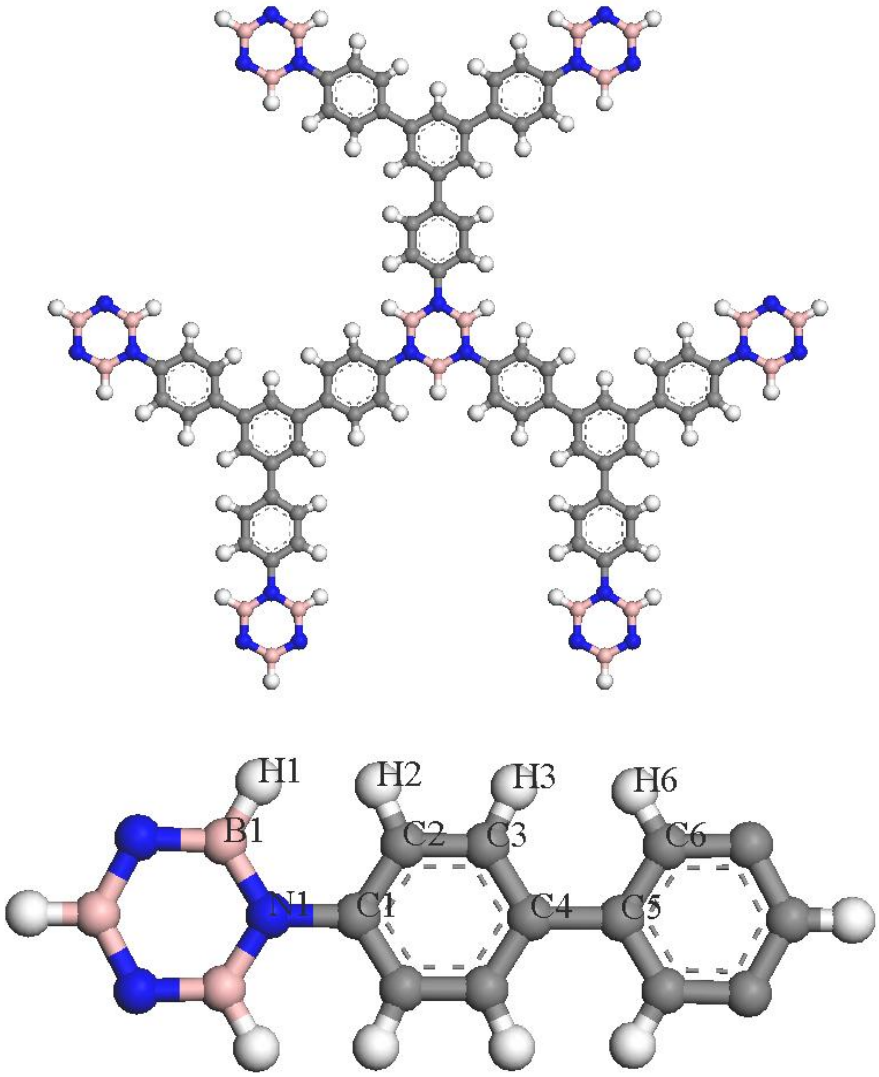

Fig. S17. Model cluster used for calculating the partial charges for each atom of BLP-2H. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S19. Atomic partial charges for the BLP-2H structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**B1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**H1**
Charge (*e*)	-0.357	0.373	0.288	-0.265	-0.155	0.085	0.051	-0.196	-0.115
Atomic types	**H2**	**H3**	**H6**						
Charge (*e*)	0.158	0.136	0.123						

IL-COF-1

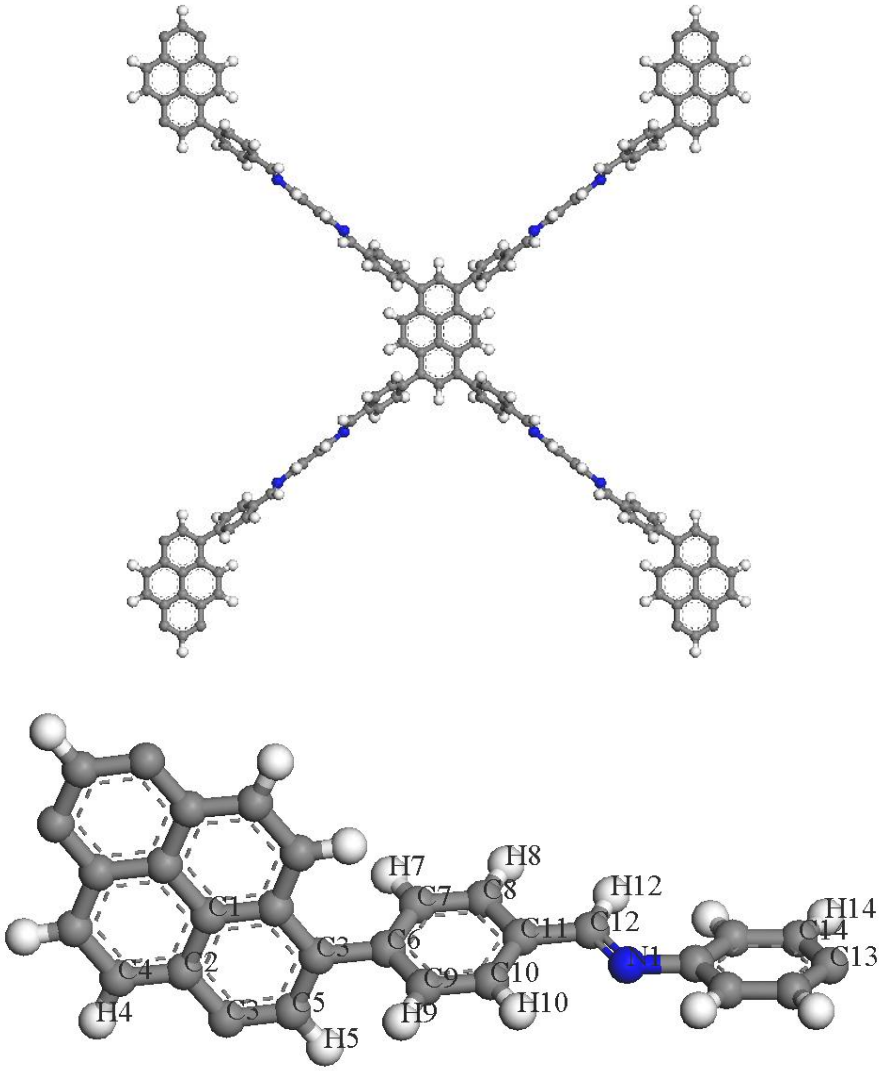

Fig. S18. Model cluster used for calculating the partial charges for each atom of IL-COF-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S20. Atomic partial charges for the IL-COF-1 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**
Charge (*e*)	-0.547	-0.005	0.121	-0.083	-0.230	-0.182	0.286	-0.194	-0.146	-0.273	0.008	-0.081
Atomic types	**C12**	**C13**	**C14**	**H4**	**H5**	**H7**	**H8**	**H9**	**H10**	**H12**	**H14**	
Charge (*e*)	0.321	0.425	-0.248	0.143	0.111	0.117	0.121	0.142	0.085	0.013	0.153	

COF-66

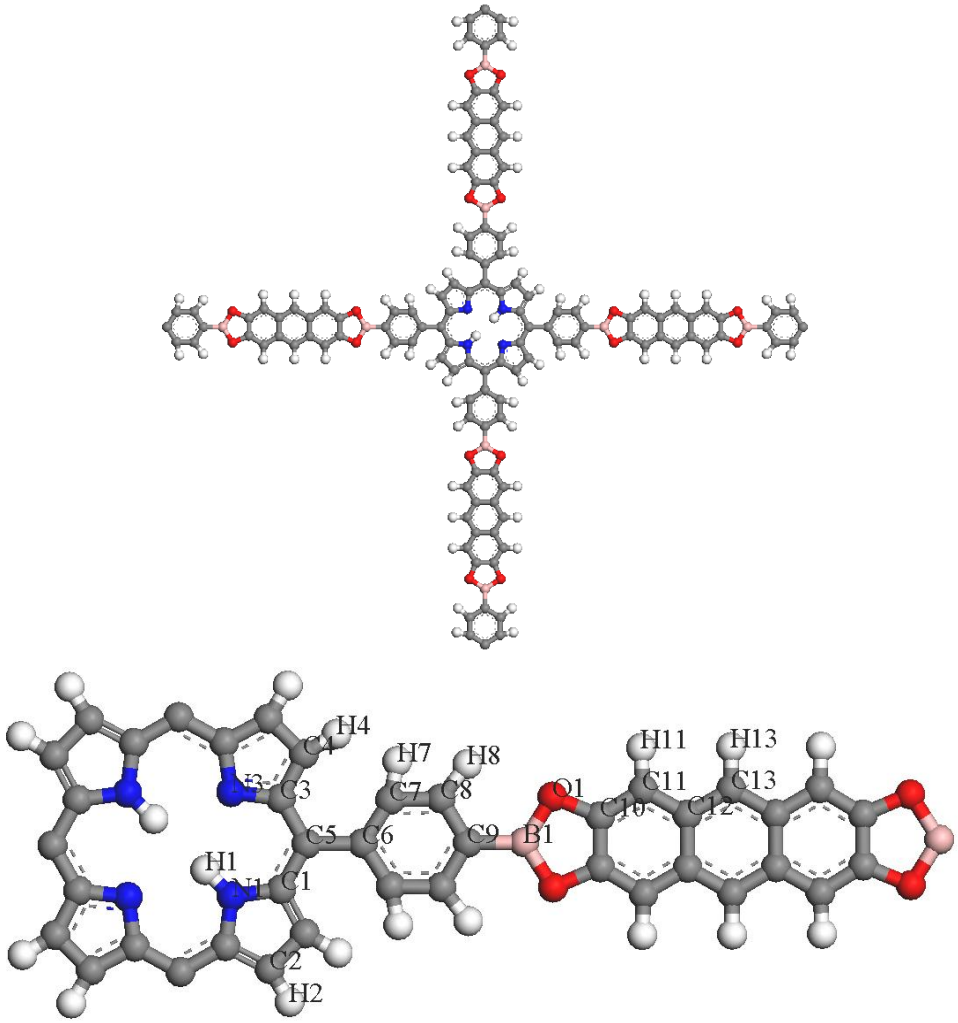

Fig. S19. Model cluster used for calculating the partial charges for each atom of COF-66. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S21. Atomic partial charges for the COF-66 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**N3**	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Charge (*e*)	-0.543	-0.801	0.544	-0.402	0.642	-0.409	0.768	-0.446	-0.685	0.629
Atomic types	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**H1**	**H2**	**H4**
Charge (*e*)	-0.401	-0.038	-0.152	0.294	-0.380	0.131	-0.229	0.344	0.210	0.210
Atomic types	**H7**	**H8**	**H11**	**H13**						
Charge (*e*)	0.200	0.074	0.170	0.122						

COF-366

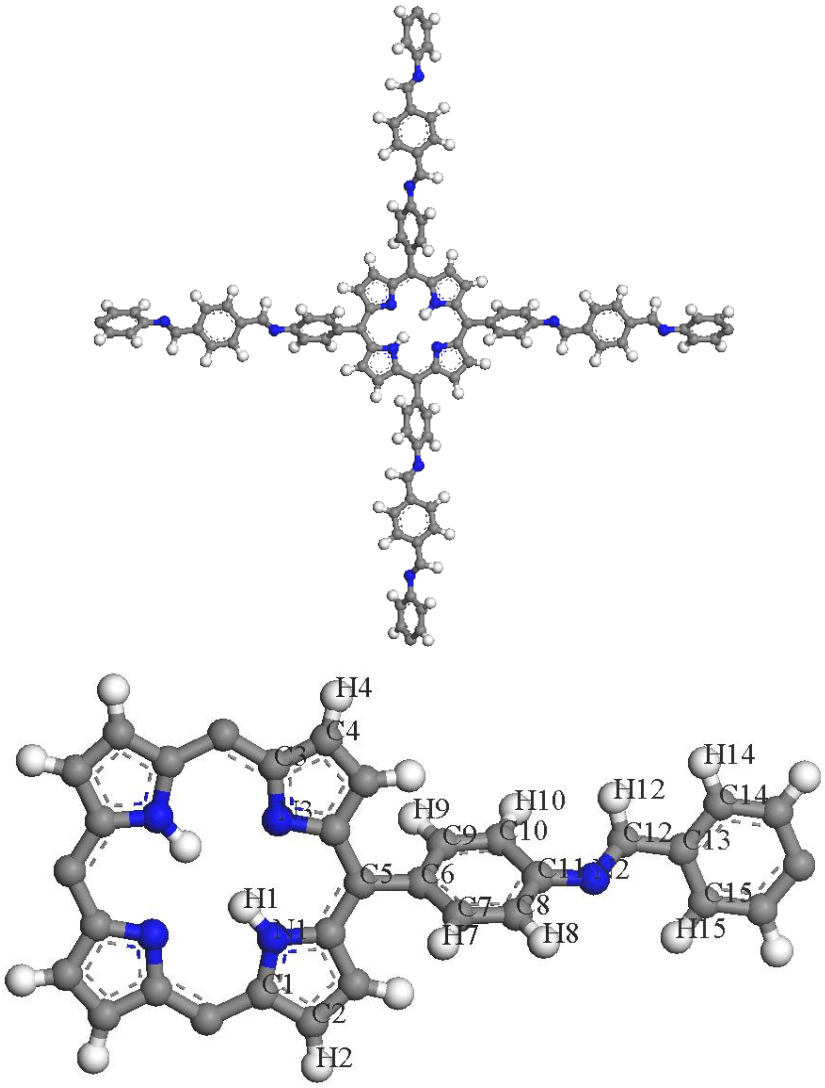

Fig. S20. Model cluster used for calculating the partial charges for each atom of COF-366. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S22. Atomic partial charges for the COF-366 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**N2**	**N3**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (e)	-0.306	-0.386	-0.607	0.292	-0.237	0.431	-0.282	-0.254	0.058	-0.022
Atomic types	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**C15**	**H1**	**H2**
Charge (e)	-0.334	-0.138	-0.220	0.413	0.051	0.043	-0.117	-0.088	0.271	0.163
Atomic types	**H4**	**H7**	**H8**	**H9**	**H10**	**H12**	**H14**	**H15**		
Charge (e)	0.159	0.124	0.124	0.124	0.124	0.097	0.103	0.093		

CTF-1

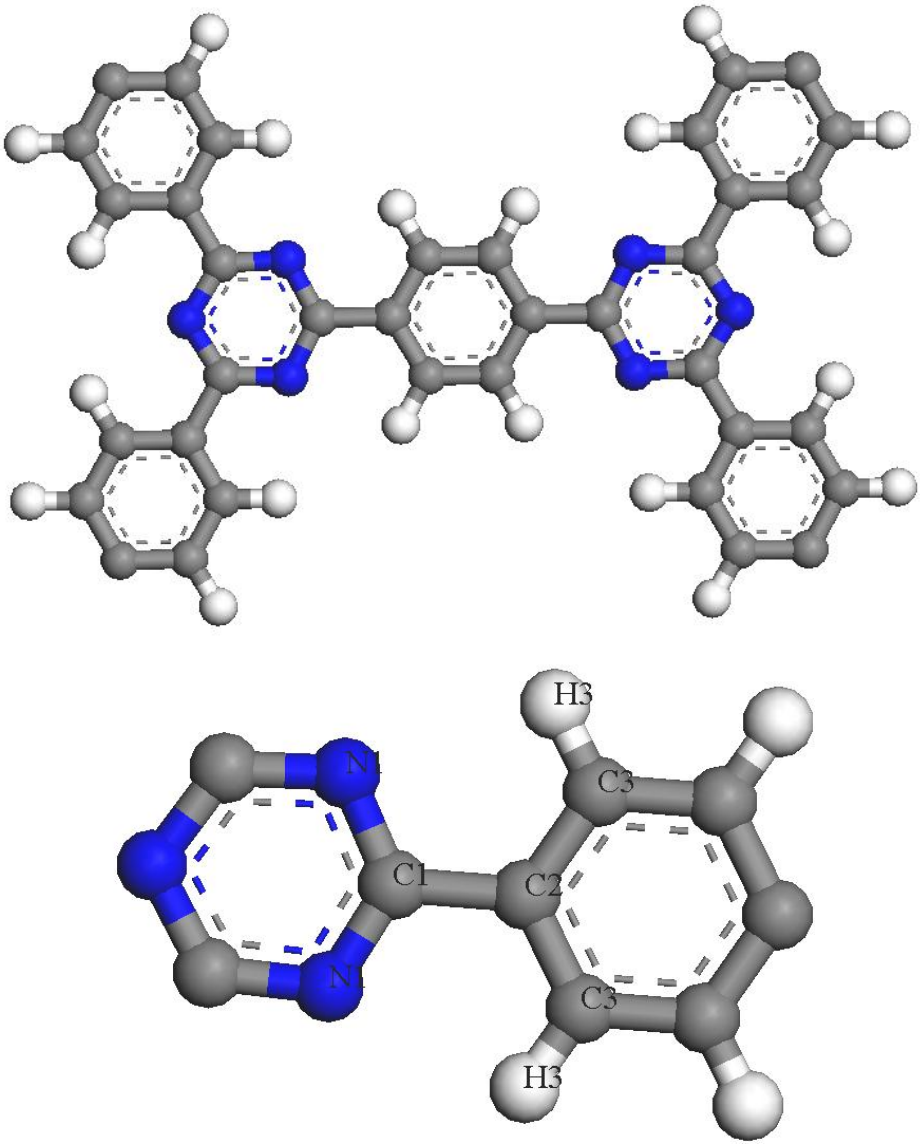

Fig. S21. Model cluster used for calculating the partial charges for each atom of CTF-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S23. Atomic partial charges for the CTF-1 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**H3**
Charge (*e*)	-0.704	0.737	-0.051	-0.106	0.115

CTF-2

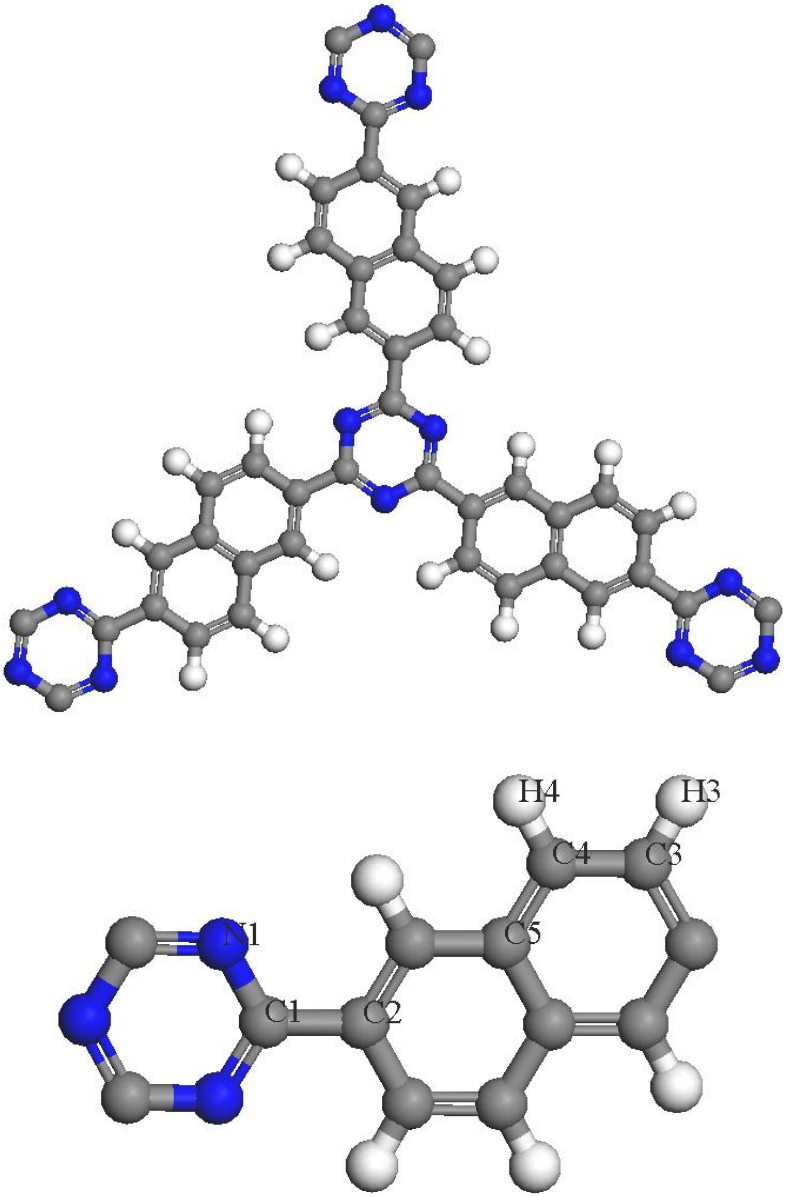

Fig. S22. Model cluster used for calculating the partial charges for each atom of CTF-2. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S24. Atomic partial charges for the CTF-2 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H3**	**H4**
Charge (e)	-0.782	0.853	-0.139	-0.108	-0.266	0.237	0.121	0.151

PPy-COF

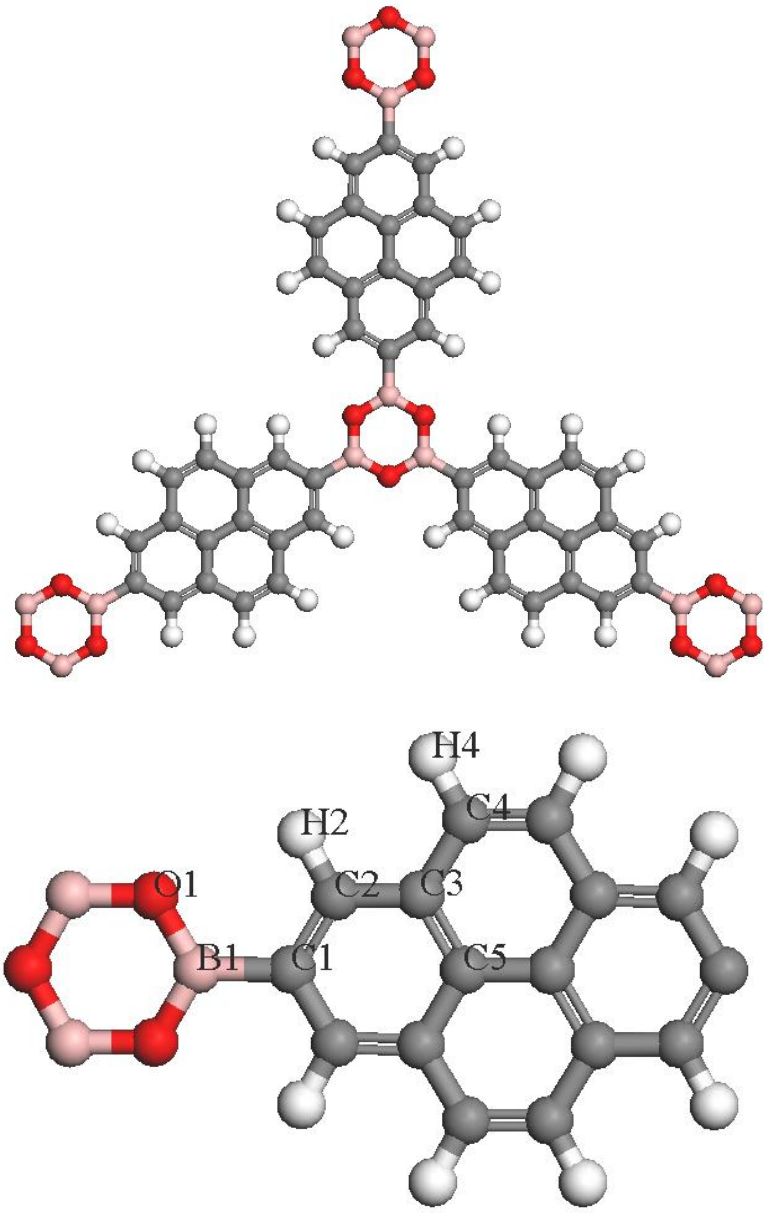

Fig. S23. Model cluster used for calculating the partial charges for each atom of PPy-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S25. Atomic partial charges for the PPy-COF structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H2**	**H4**
Charge (*e*)	-0.782	-0.593	-0.102	-0.278	0.237	-0.231	-0.039	0.129	0.135

TP-COF

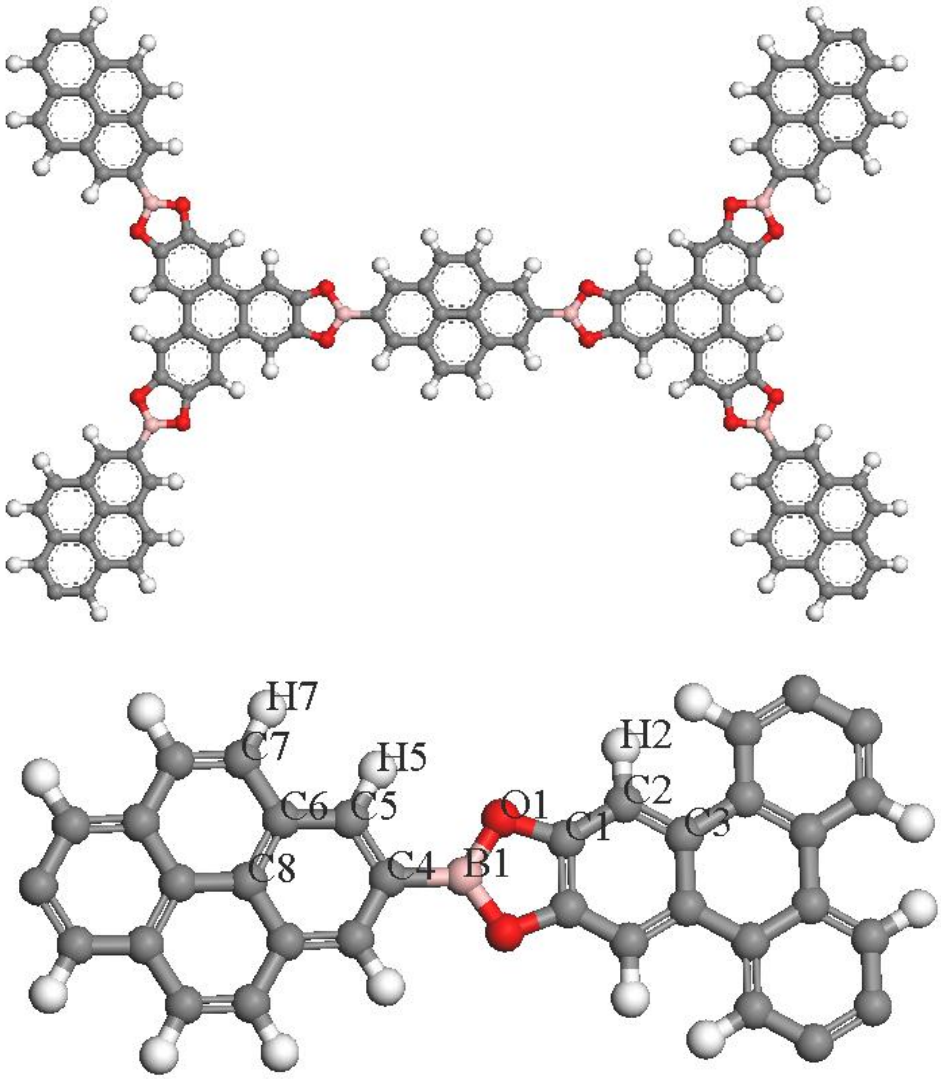

Fig. S24. Model cluster used for calculating the partial charges for each atom of TP-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S26. Atomic partial charges for the TP-COF structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (e)	0.632	-0.411	0.260	-0.327	0.045	-0.128	-0.226	0.200	-0.224
Atomic types	**C8**	**H2**	**H5**	**H7**					
Charge (e)	-0.020	0.176	0.125	0.140					

Star-COF-1

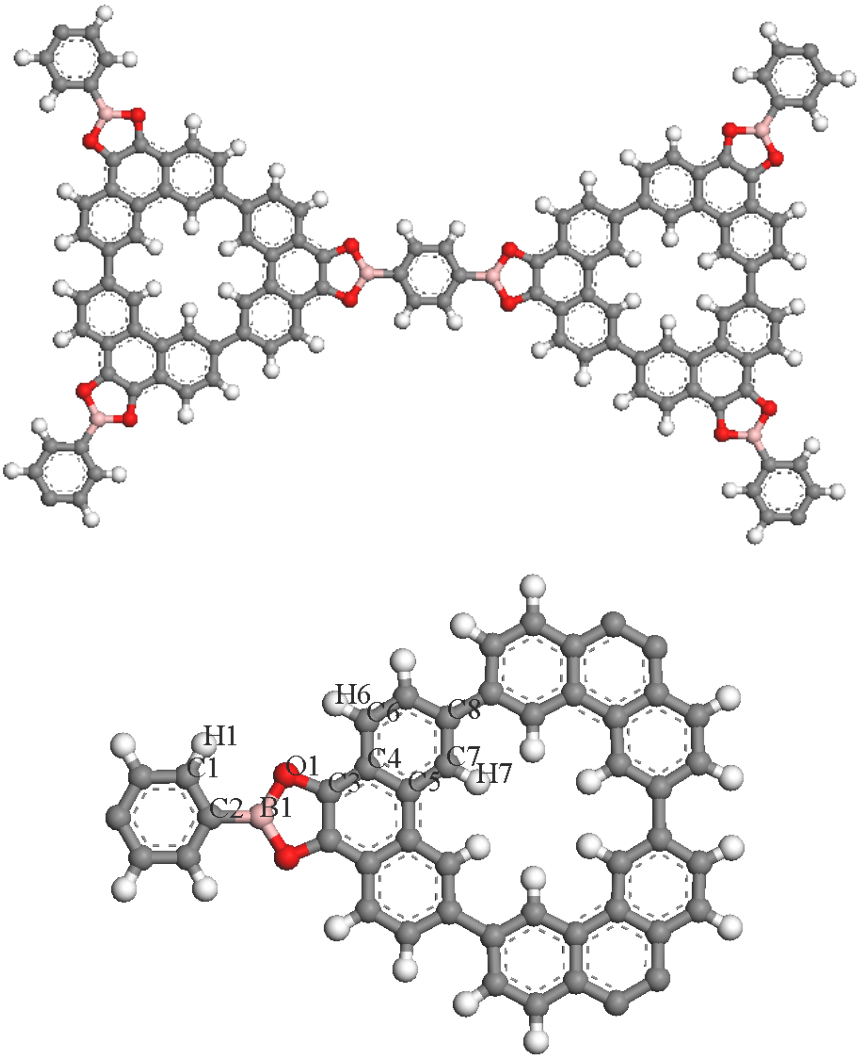

Fig. S25. Model cluster used for calculating the partial charges for each atom of Star-COF-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S27. Atomic partial charges for the Star-COF-1 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.534	-0.342	-0.085	-0.116	0.112	0.045	0.008	-0.145	-0.185
Atomic types	**C8**	**H1**	**H6**	**H7**					
Charge (*e*)	0.075	0.101	0.128	0.132					

Star-COF-2

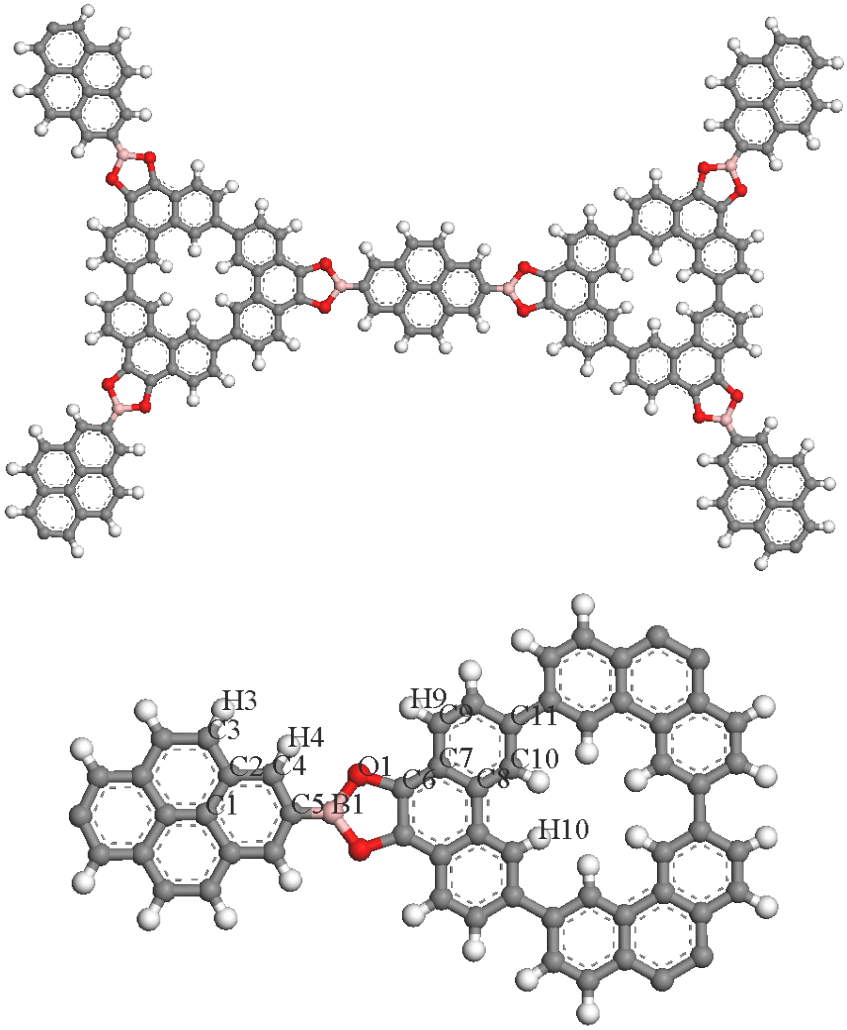

Fig. S26. Model cluster used for calculating the partial charges for each atom of Star-COF-2. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S28. Atomic partial charges for the Star-COF-2 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.590	-0.424	-0.018	0.195	-0.245	-0.244	-0.080	0.092	0.045
Atomic types	**C8**	**C9**	**C10**	**C11**	**H3**	**H4**	**H9**	**H10**	
Charge (*e*)	0.018	-0.096	-0.189	0.053	0.168	0.168	0.126	0.138	

Star-COF-3

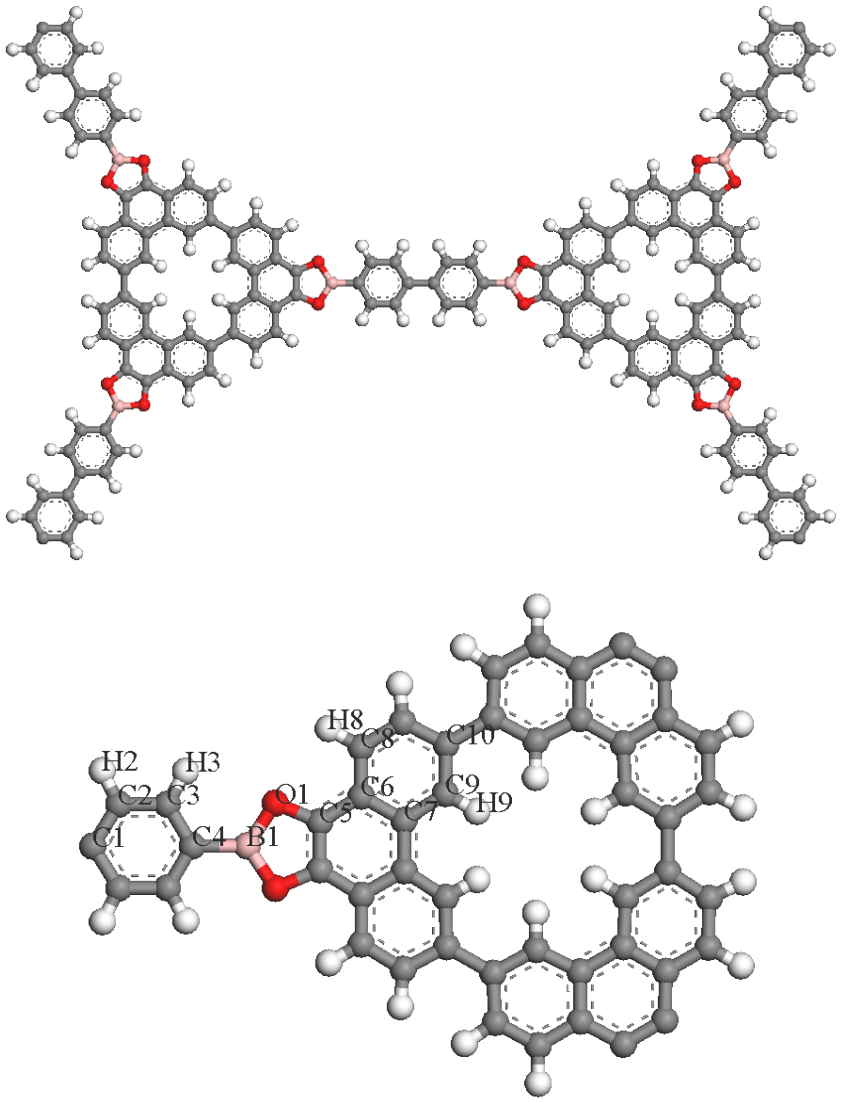

Fig. S27. Model cluster used for calculating the partial charges for each atom of Star-COF-3. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S29. Atomic partial charges for the Star-COF-3 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.551	-0.358	0.102	-0.187	-0.053	-0.165	0.130	0.033	0.013
Atomic types	**C8**	**C9**	**C10**	**H2**	**H3**	**H8**	**H9**		
Charge (*e*)	-0.138	-0.190	0.076	0.127	0.097	0.130	0.133		

TpPa-1

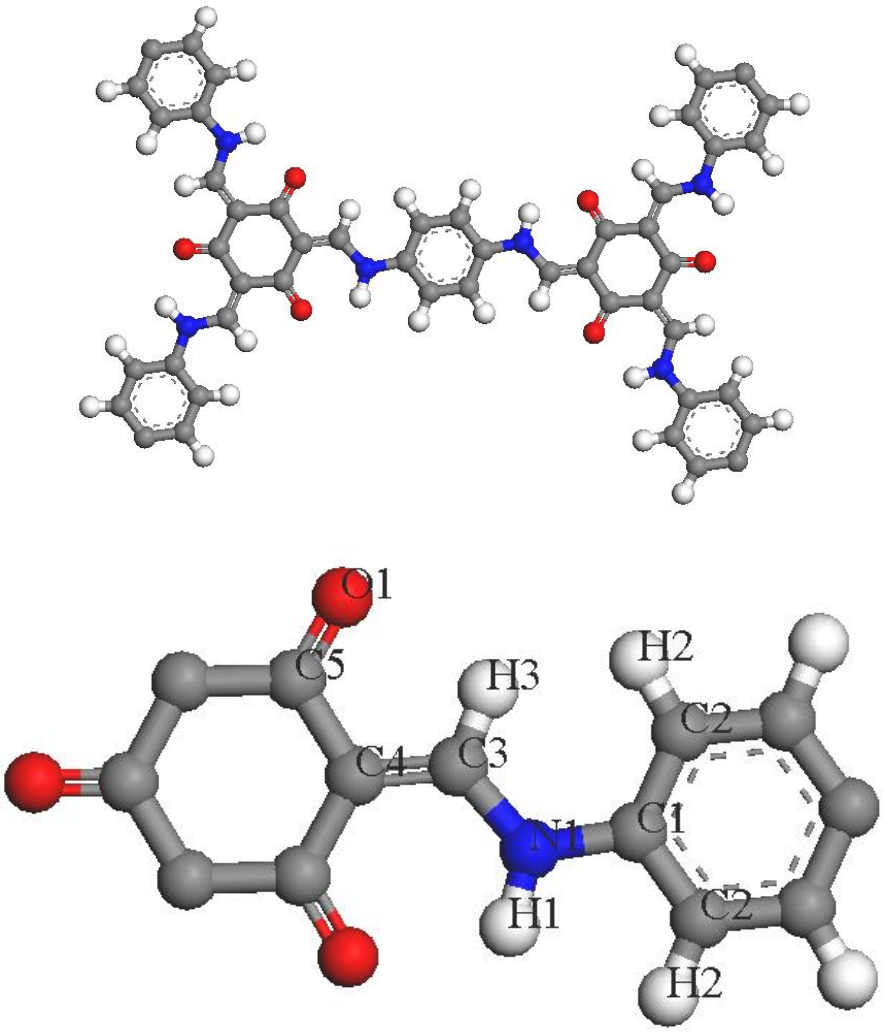

Fig. S28. Model cluster used for calculating the partial charges for each atom of TpPa-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S30. Atomic partial charges for the TpPa-1 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H1**
Charge (*e*)	-0.459	-0.639	0.270	-0.228	0.313	-0.685	0.860	0.372
Atomic types	**H2**	**H3**						
Charge (*e*)	0.161	0.102						

TpPa-2

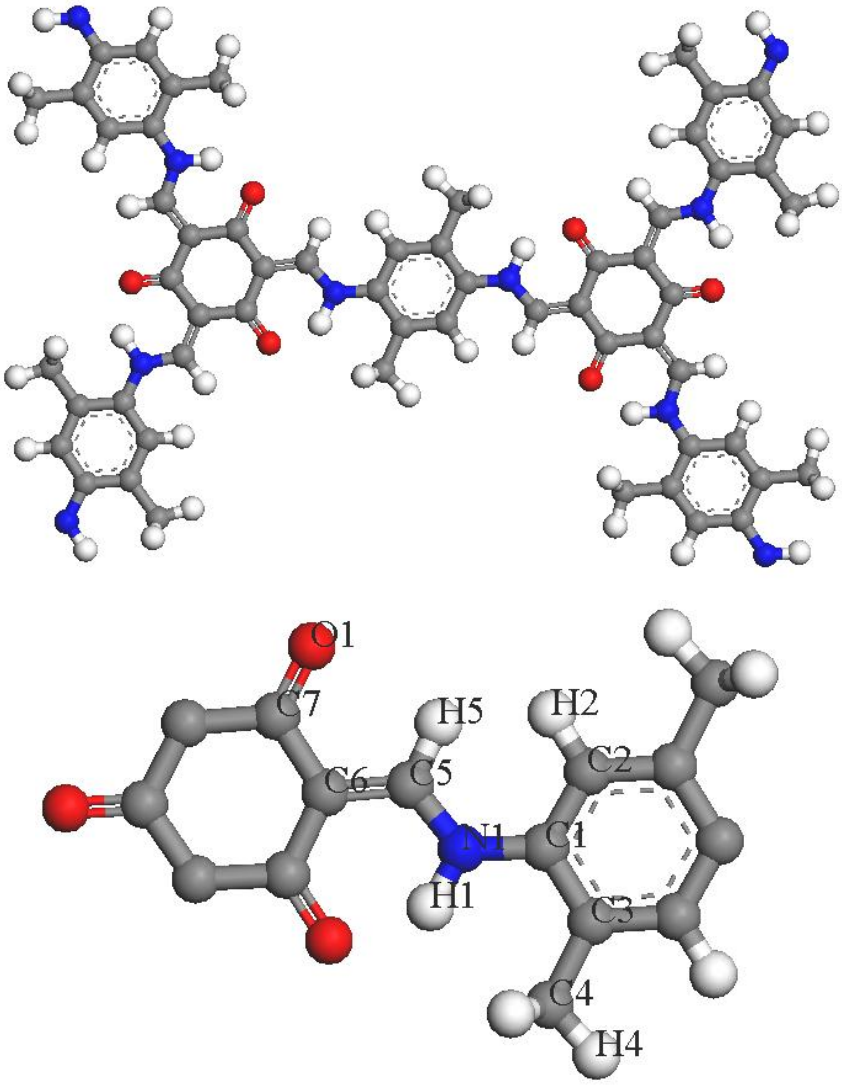

Fig. S29. Model cluster used for calculating the partial charges for each atom of TpPa-2. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S31. Atomic partial charges for the TpPa-2 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	-0.348	-0.676	0.179	-0.345	0.063	-0.169	0.246	-0.603	0.754
Atomic types	**H1**	**H2**	**H4**	**H5**					
Charge (*e*)	0.403	0.196	0.061	0.117					

DAAQ-TFP COF

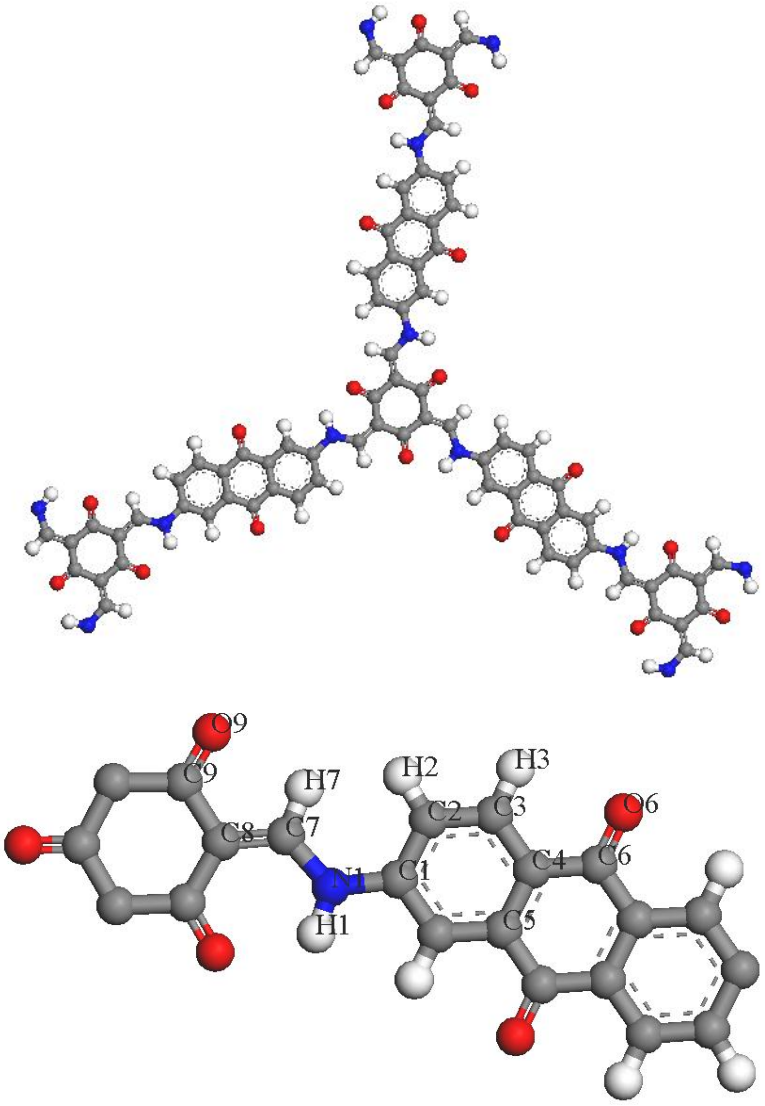

Fig. S30. Model cluster used for calculating the partial charges for each atom of DAAQ-TFP COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S31. Atomic partial charges for the DAAQ-TFP COF structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O6**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
Charge (*e*)	-0.517	-0.563	0.362	-0.248	0.031	-0.198	-0.064	0.660	0.406	-0.768
Atomic types	**C9**	**H1**	**H2**	**H3**	**H7**	**O9**				
Charge (*e*)	0.947	0.391	0.142	0.100	0.088	-0.663				

TpBD

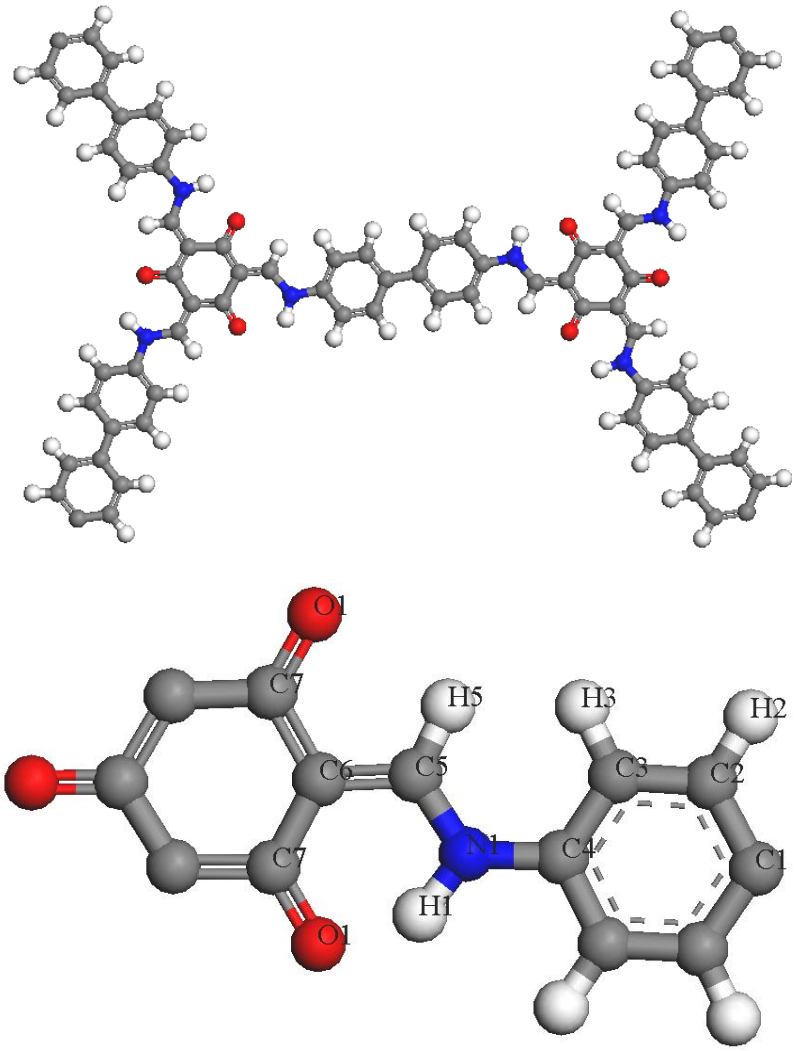

Fig. S31. Model cluster used for calculating the partial charges for each atom of TpBD. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S33. Atomic partial charges for the TpBD structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	-0.517	-0.705	0.045	-0.110	-0.293	0.405	0.315	-0.602	0.759
Atomic types	**H1**	**H2**	**H3**	**H5**					
Charge (*e*)	0.450	0.120	0.152	0.112					

TpPa-4F

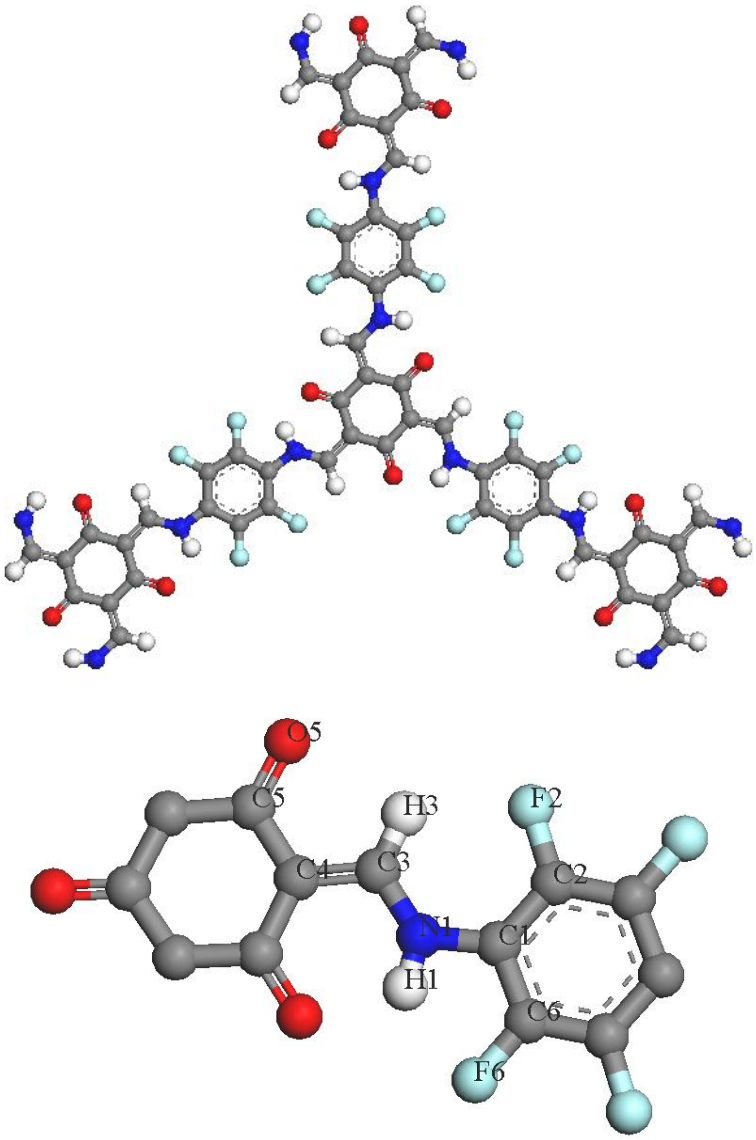

Fig. S32. Model cluster used for calculating the partial charges for each atom of TpPa-4F. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S34. Atomic partial charges for the TpPa-4F structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O5**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**F2**
Charge (*e*)	-0.067	-0.672	-0.220	0.288	0.116	-0.532	0.726	0.103	-0.184
Atomic types	**F6**	**H1**	**H3**						
Charge (*e*)	-0.129	0.370	0.201						

TpBD-$(NO_2)_2$

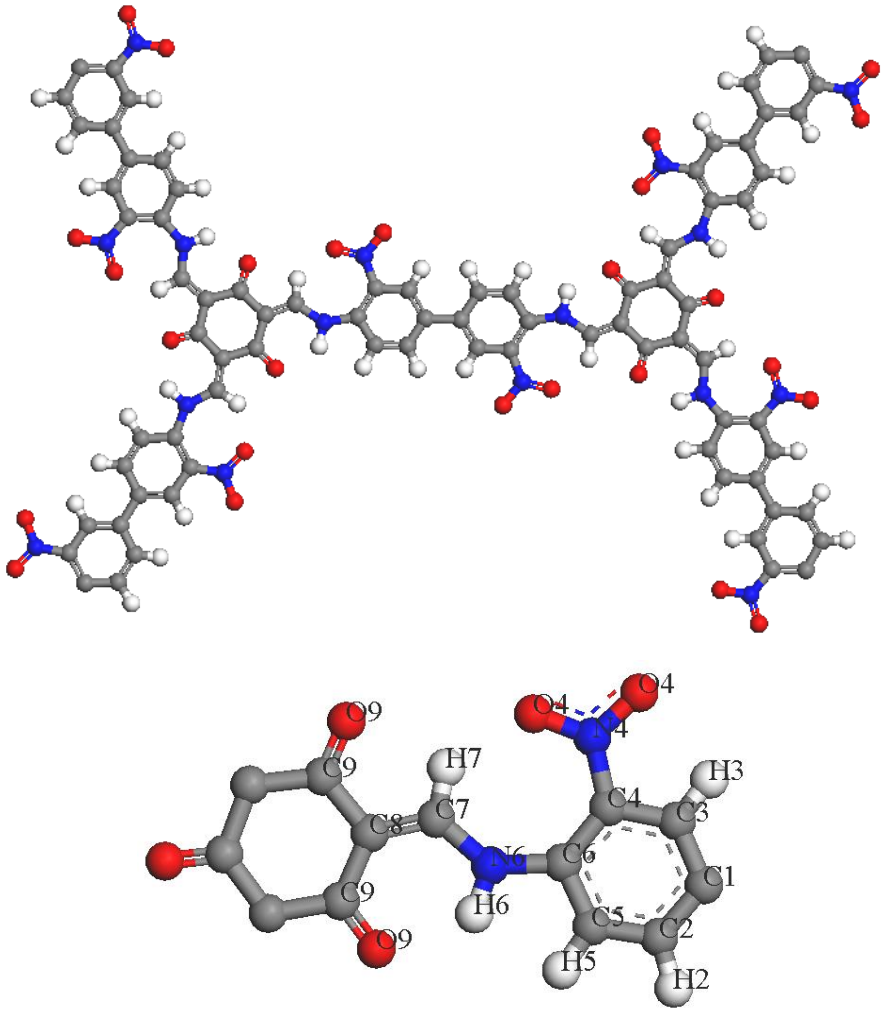

Fig. S33. Model cluster used for calculating the partial charges for each atom of TpBD-$(NO_2)_2$. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S35. Atomic partial charges for the TpBD-$(NO_2)_2$ structure derived on DFT/B3LYP Level.

Atomic types	**N4**	**N6**	**O4**	**O9**	**C1**	**C2**	**C3**	**C4**	**C5**
Charge (*e*)	0.637	-0.347	-0.420	-0.562	0.070	-0.073	-0.217	0.023	-0.272
Atomic types	**C6**	**C7**	**C8**	**C9**	**H2**	**H3**	**H5**	**H6**	**H7**
Charge (*e*)	0.210	0.134	-0.495	0.685	0.157	0.157	0.178	0.335	0.220

TpBD-Me_2

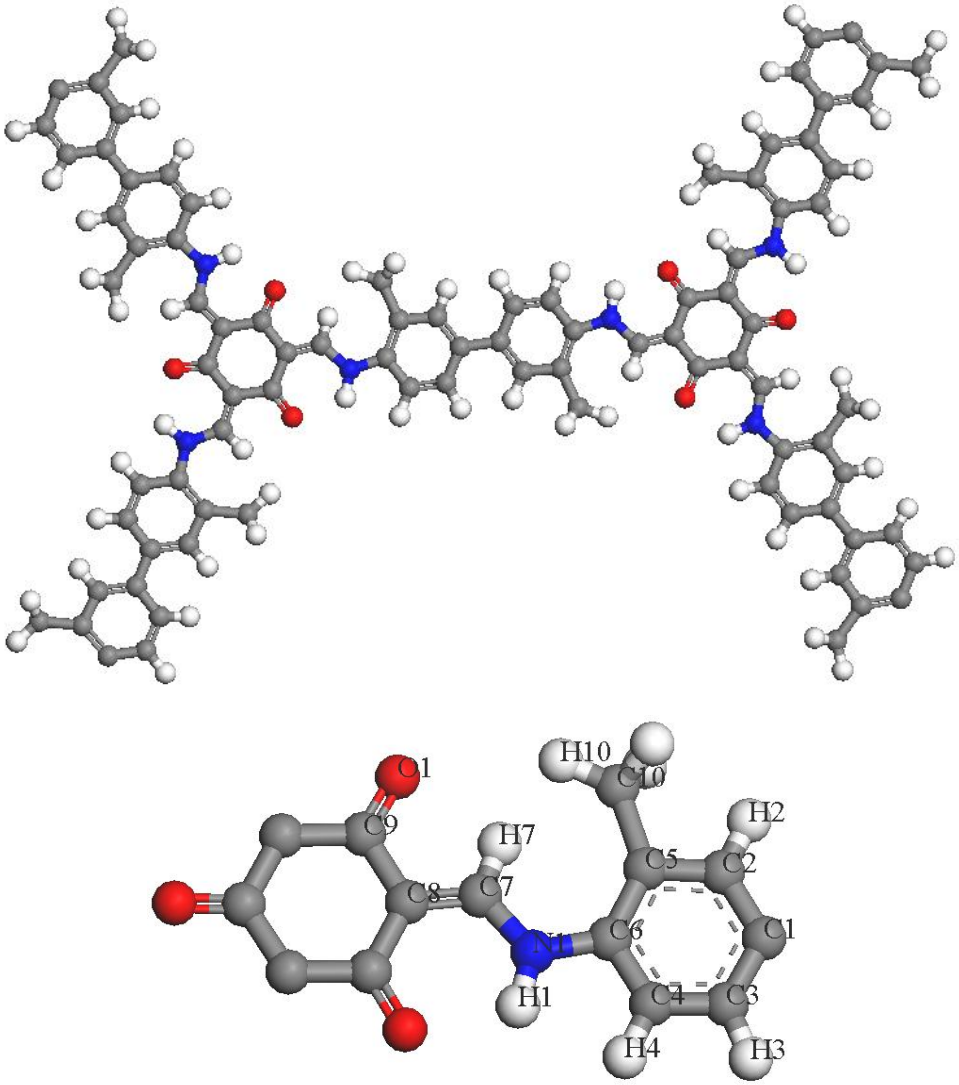

Fig. S34. Model cluster used for calculating the partial charges for each atom of TpBD-Me_2. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S36. Atomic partial charges for the TpBD-Me_2 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	-0.383	-0.676	0.120	-0.398	-0.186	-0.234	0.237	0.102	0.261
Atomic types	**C8**	**C9**	**C10**	**H1**	**H2**	**H3**	**H4**	**H7**	**H10**
Charge (*e*)	-0.663	0.804	-0.578	0.350	0.203	0.119	0.140	0.350	0.144

COF-102

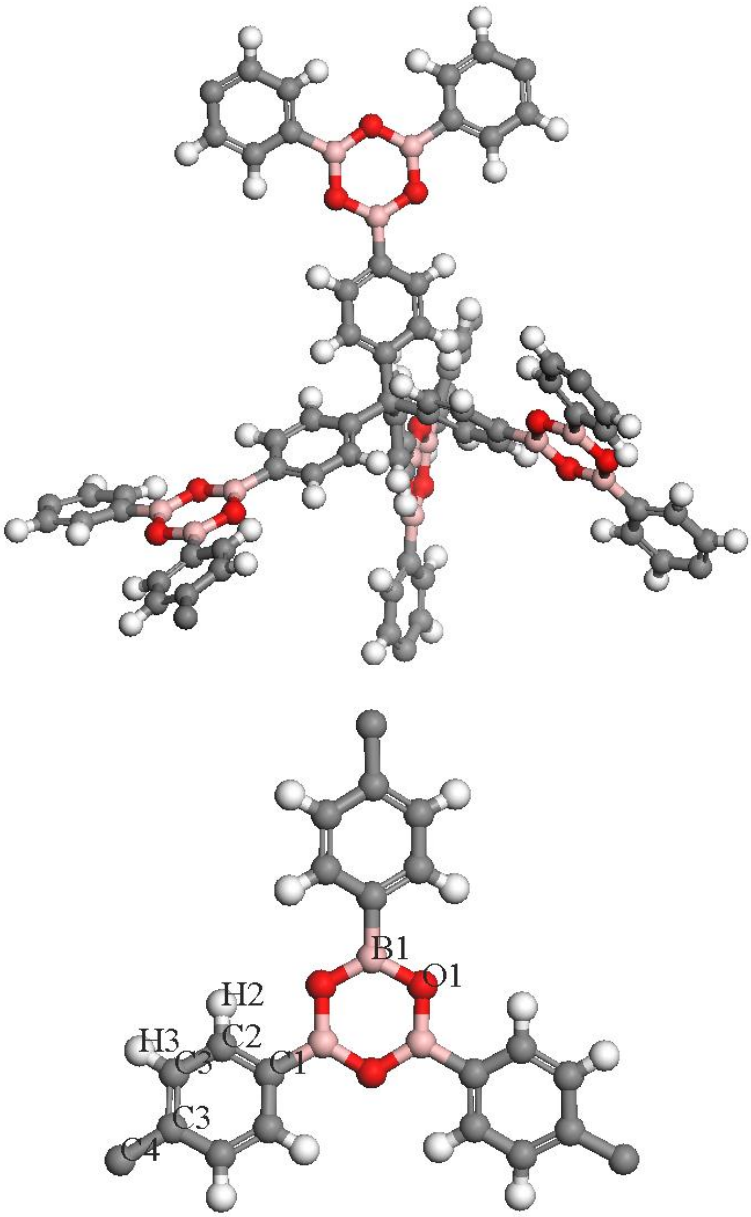

Fig. S35. Model cluster used for calculating the partial charges for each atom of COF-102. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S37. Atomic partial charges for the COF-102 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**H2**	**H3**
Charge (*e*)	0.787	-0.650	-0.176	-0.088	-0.123	0.070	-0.124	0.099	0.112

COF-103

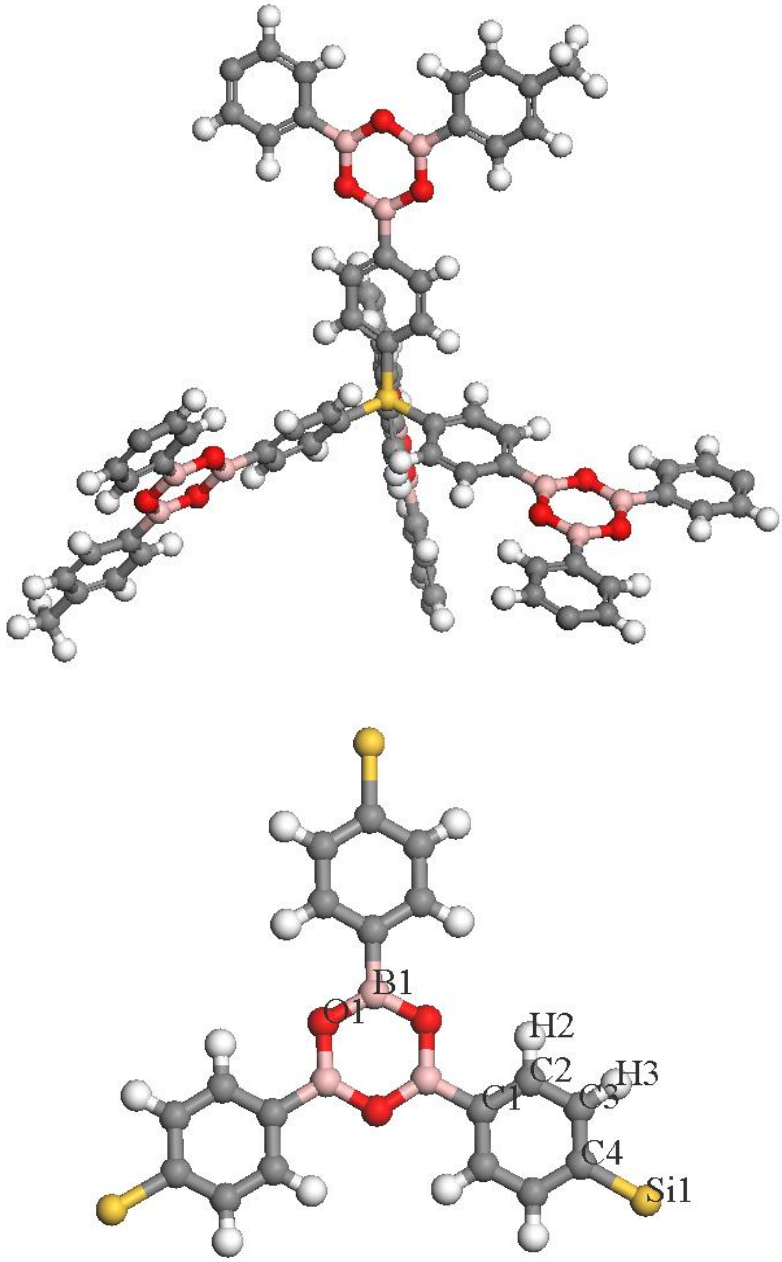

Fig. S36. Model cluster used for calculating the partial charges for each atom of COF-103. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S38. Atomic partial charges for the COF-103 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**Si1**	**H2**	**H3**
Charge (*e*)	0.755	-0.614	-0.228	-0.073	-0.202	0.262	-0.276	0.115	0.107

COF-105

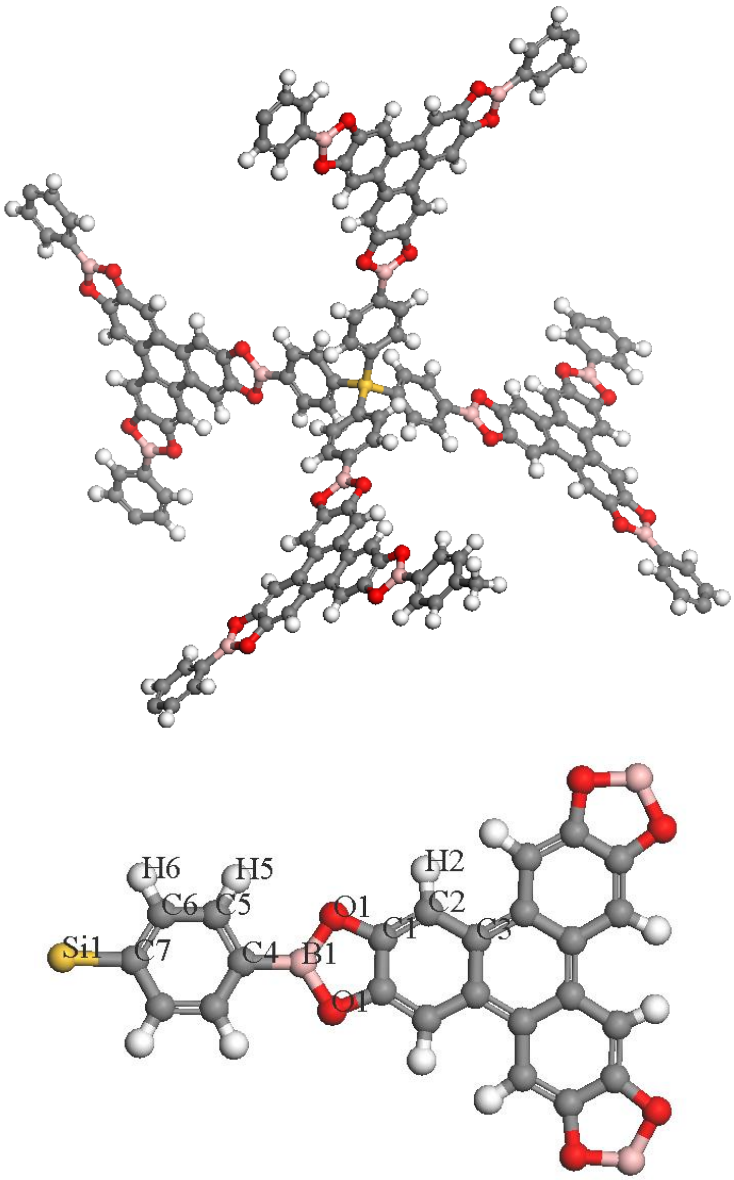

Fig. S37. Model cluster used for calculating the partial charges for each atom of COF-105. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S39. Atomic partial charges for the COF-105 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.599	-0.417	0.257	-0.331	0.043	-0.176	-0.067	-0.191	0.118
Atomic types	**Si1**	**H2**	**H5**	**H6**					
Charge (*e*)	0.116	0.196	0.111	0.114					

COF-108

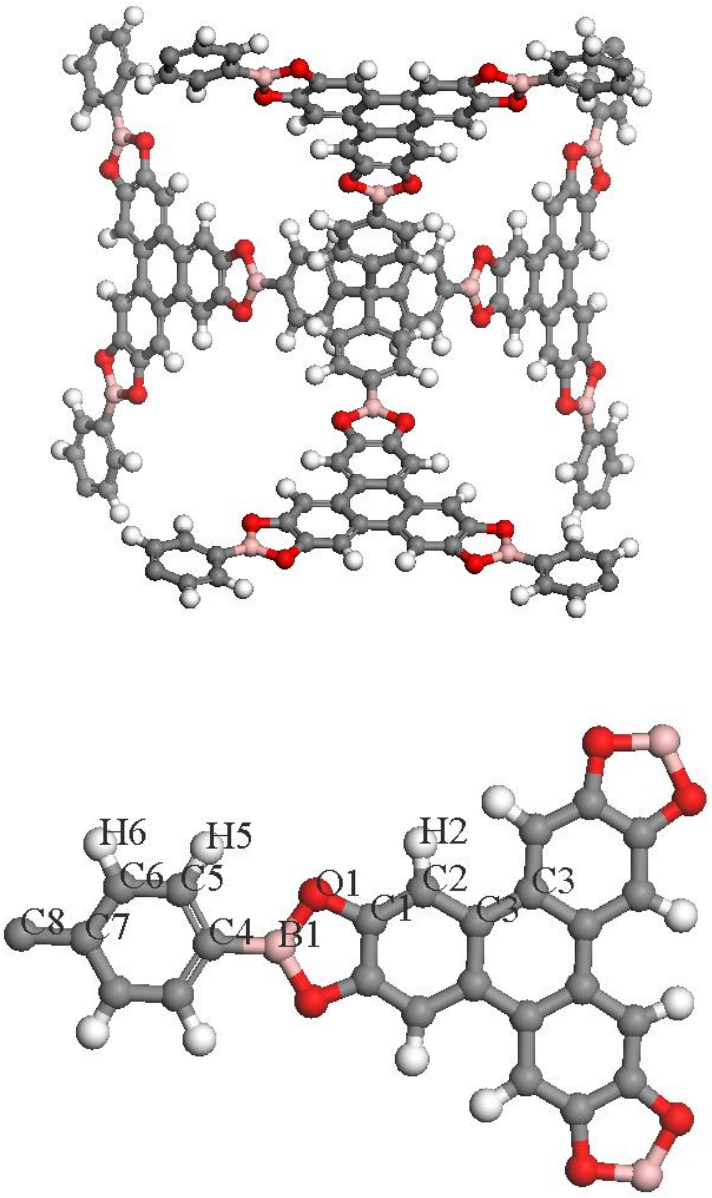

Fig. S38. Model cluster used for calculating the partial charges for each atom of COF-108. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S40. Atomic partial charges for the COF-108 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.610	-0.418	0.260	-0.332	0.045	-0.165	-0.104	-0.154	0.156
Atomic types	**C8**	**H2**	**H5**	**H6**					
Charge (*e*)	0.076	0.190	0.110	0.093					

COF-202

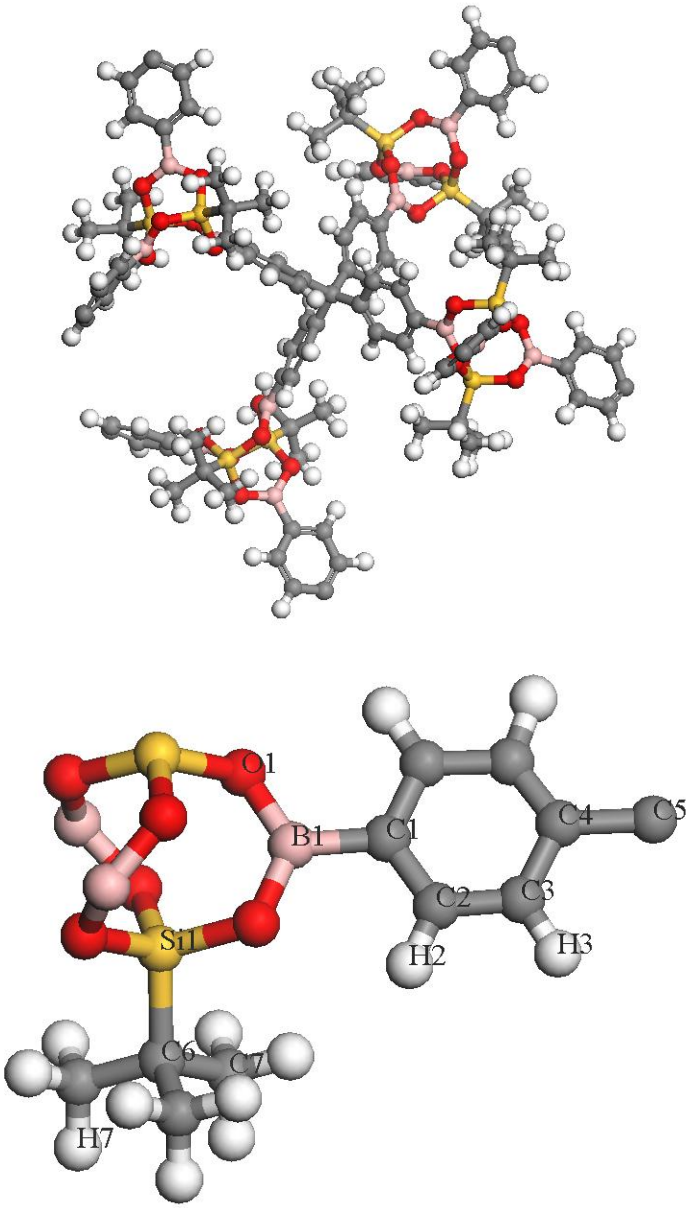

Fig. S39. Model cluster used for calculating the partial charges for each atom of COF-202. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S41. Atomic partial charges for the COF-202 structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Charge (*e*)	0.754	-0.631	-0.209	-0.111	-0.197	0.327	-0.384	0.552	-0.323
Atomic types	**Si1**	**H2**	**H3**	**H7**					
Charge (*e*)	0.918	0.136	0.098	0.050					

CTC-COF

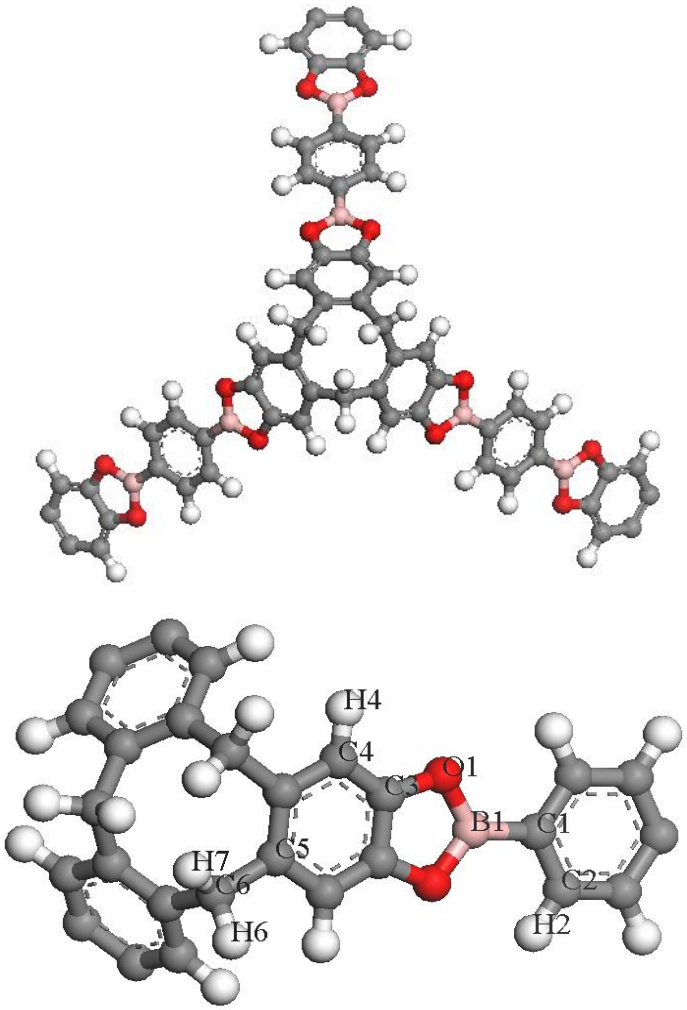

Fig. S40. Model cluster used for calculating the partial charges for each atom of CTC-COF. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S42. Atomic partial charges for the CTC-COF structure derived on DFT/B3LYP Level.

Atomic types	**B1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Charge (*e*)	0.587	-0.411	-0.127	-0.080	0.276	-0.358	0.030	0.024
Atomic types	**H2**	**H4**	**H6**	**H7**				
Charge (*e*)	0.090	0.090	0.003	0.029				

COF-300

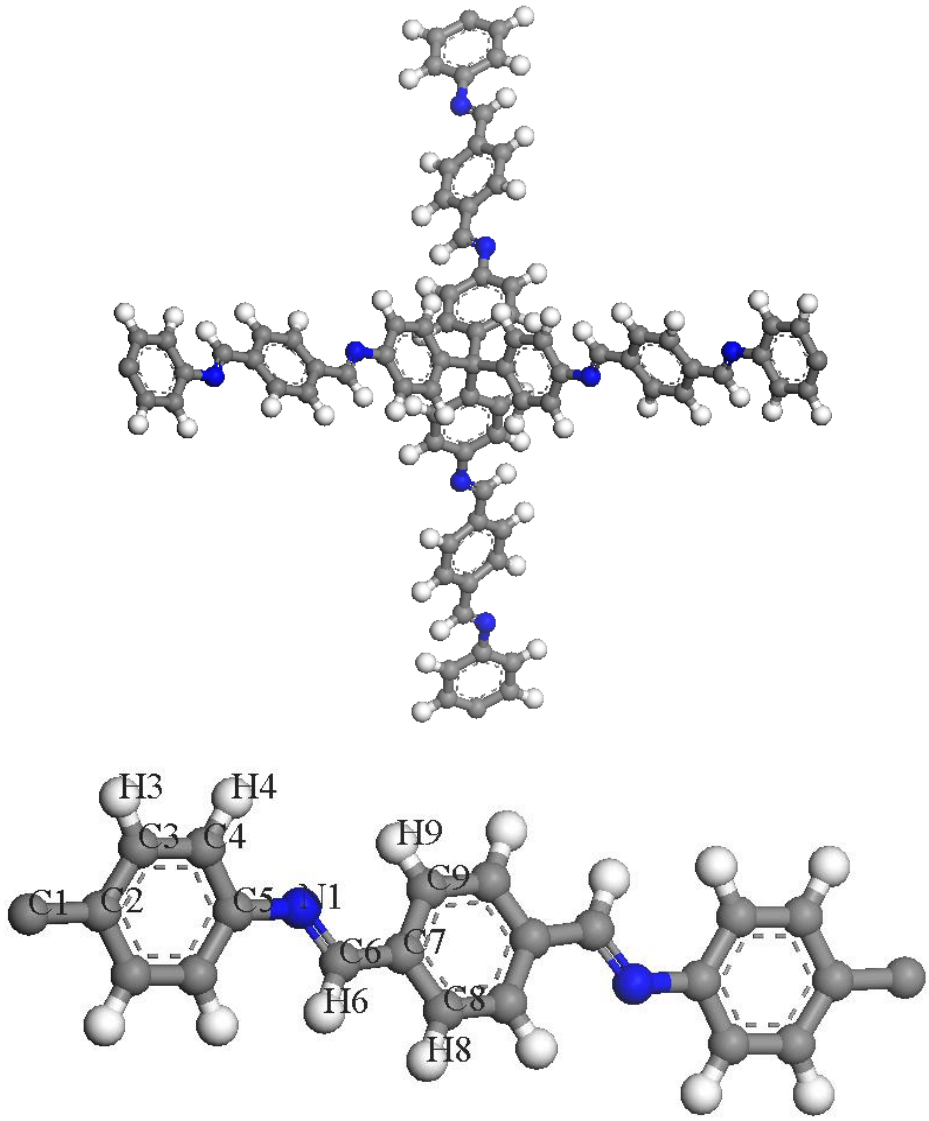

Fig. S41. Model cluster used for calculating the partial charges for each atom of COF-300. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S43. Atomic partial charges for the COF-300 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
Charge (*e*)	-0.455	0.024	0.069	-0.090	-0.341	0.453	0.193	0.024	-0.161
Atomic types	**C9**	**H3**	**H4**	**H6**	**H8**	**H9**			
Charge (*e*)	-0.023	0. 105	0.169	0.028	0.130	0.075			

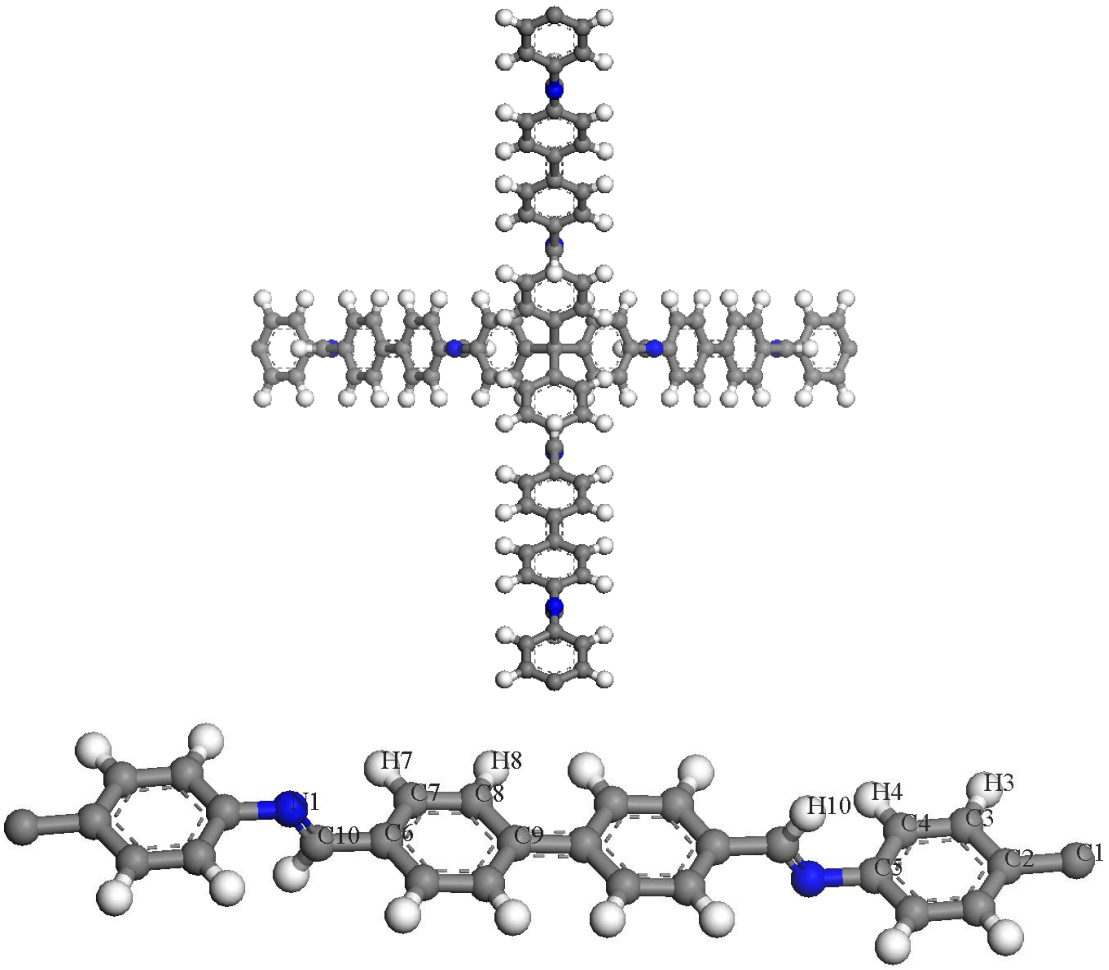

Fig. S42. Model cluster used for calculating the partial charges for each atom of COF-320. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S44. Atomic partial charges for the COF-320 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
Charge (*e*)	-0.619	0.240	0.014	-0.130	-0.355	0.546	-0.035	-0.125	-0.151
Atomic types	**C9**	**C10**	**H3**	**H4**	**H7**	**H8**	**H10**		
Charge (*e*)	0.069	0.473	0.128	0.170	0.108	0.126	-0.05		

NPN-1

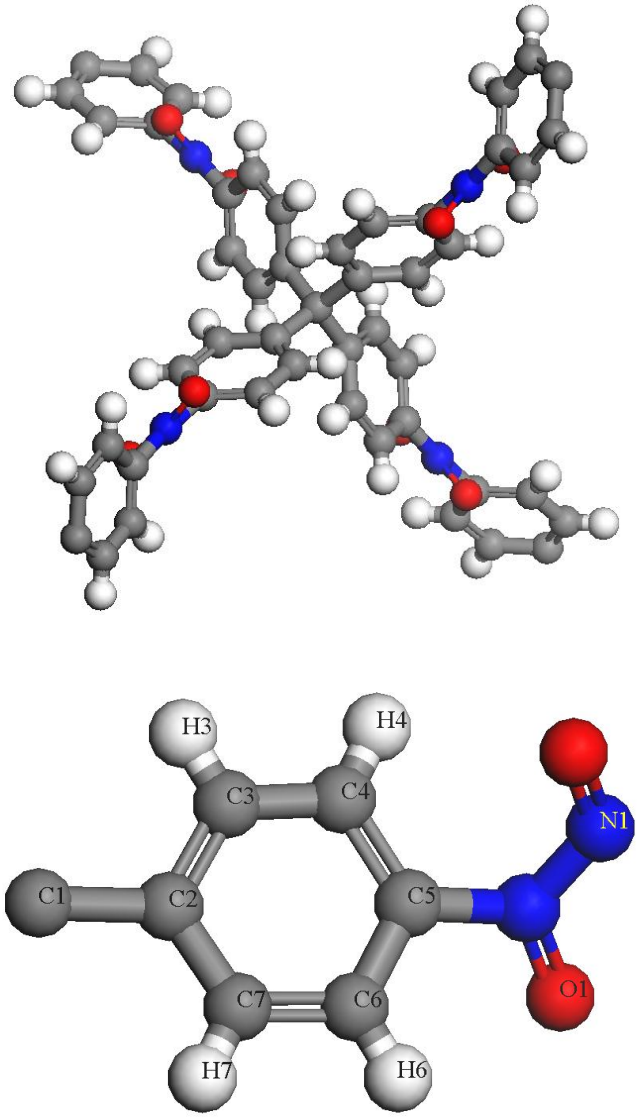

Fig. S43. Model cluster used for calculating the partial charges for each atom of NPN-1. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S45. Atomic partial charges for the NPN-1 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**H3**
Charge (*e*)	0.386	-0.516	0.064	0.080	0.022	-0.210	-0.080	0.005	0.065
Atomic types	**H4**	**H5**							
Charge (*e*)	0.144	0.154							

NPN-2

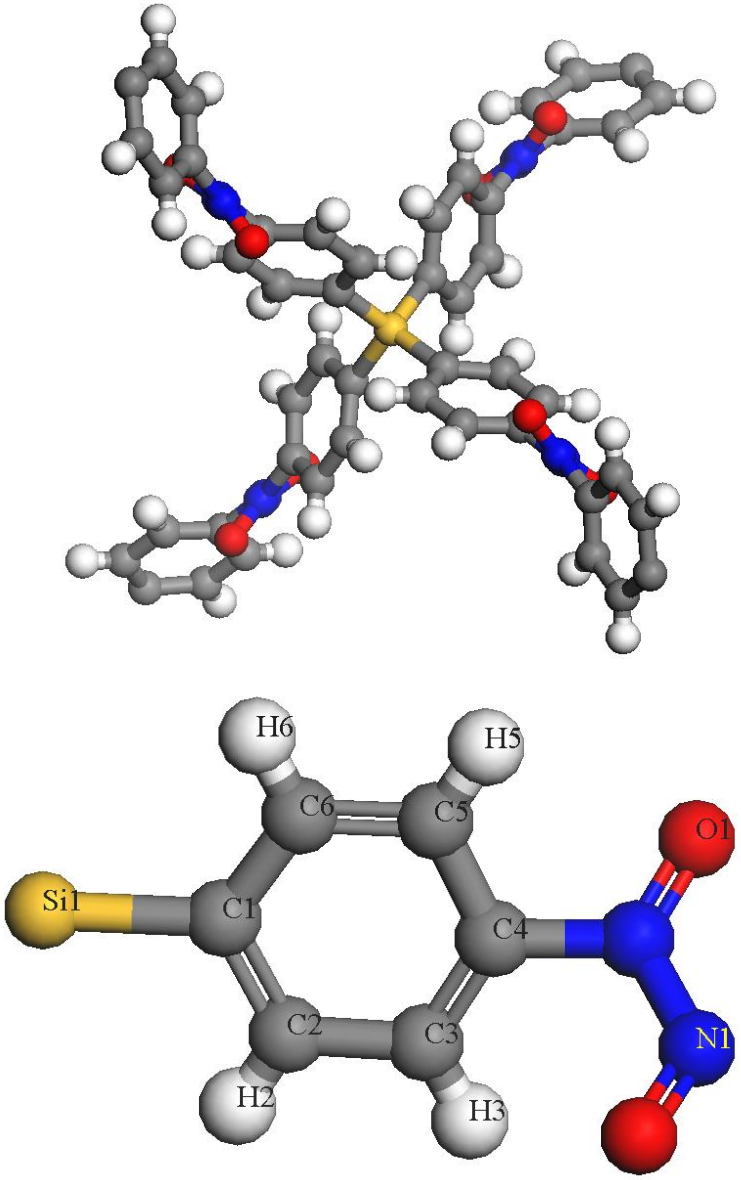

Fig. S44. Model cluster used for calculating the partial charges for each atom of NPN-2. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S46. Atomic partial charges for the NPN-2 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**H2**
Charge (*e*)	0.372	-0.499	-0.060	-0.006	-0.214	-0.156	-0.104	0.062	0.099
Atomic types	**H3**	**Si1**							
Charge (*e*)	0.157	0.372							

NPN-3

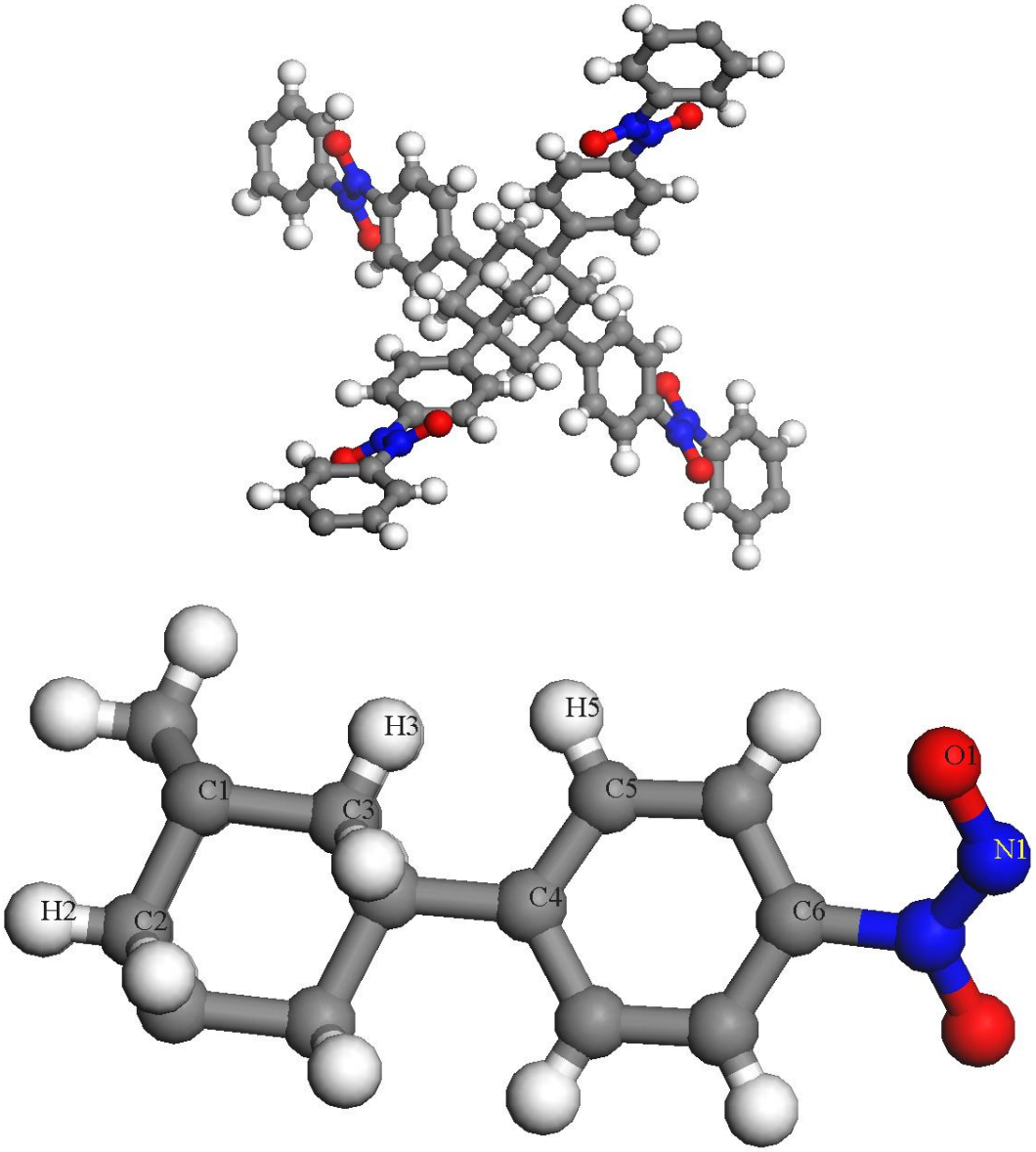

Fig. S45. Model cluster used for calculating the partial charges for each atom of NPN-3. The terminations of the cluster were saturated with methyl groups to minimize the boundary effects.

Table S47. Atomic partial charges for the NPN-3 structure derived on DFT/B3LYP Level.

Atomic types	**N1**	**O1**	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**H2**
Charge (*e*)	0.342	-0.508	-0.060	0.339	-0.191	0.012	-0.012	-0.164	0.091
Atomic types	**H3**	**H5**							
Charge (*e*)	-0.035	0.151							

4. Separation properties of the top 4 COFs

Table S48. Calculated results of the four evaluation criteria of the top 4 COFs.

Materials	S	ΔN_{CO_2} (mol kg^{-1})	S_{sp}	R (%)
TaPa-1	84	1.77	1075	87.6
CTF-2-AB	66	2.32	861	85.8
NPN-1	49	2.33	562	86.0
DAAQ-TFP COF	44	1.10	340	89.3

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