Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Sterically Crowded Hydrogen-Bonded Hexagonal Network Frameworks

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Contensts.

1. Computational calculation.

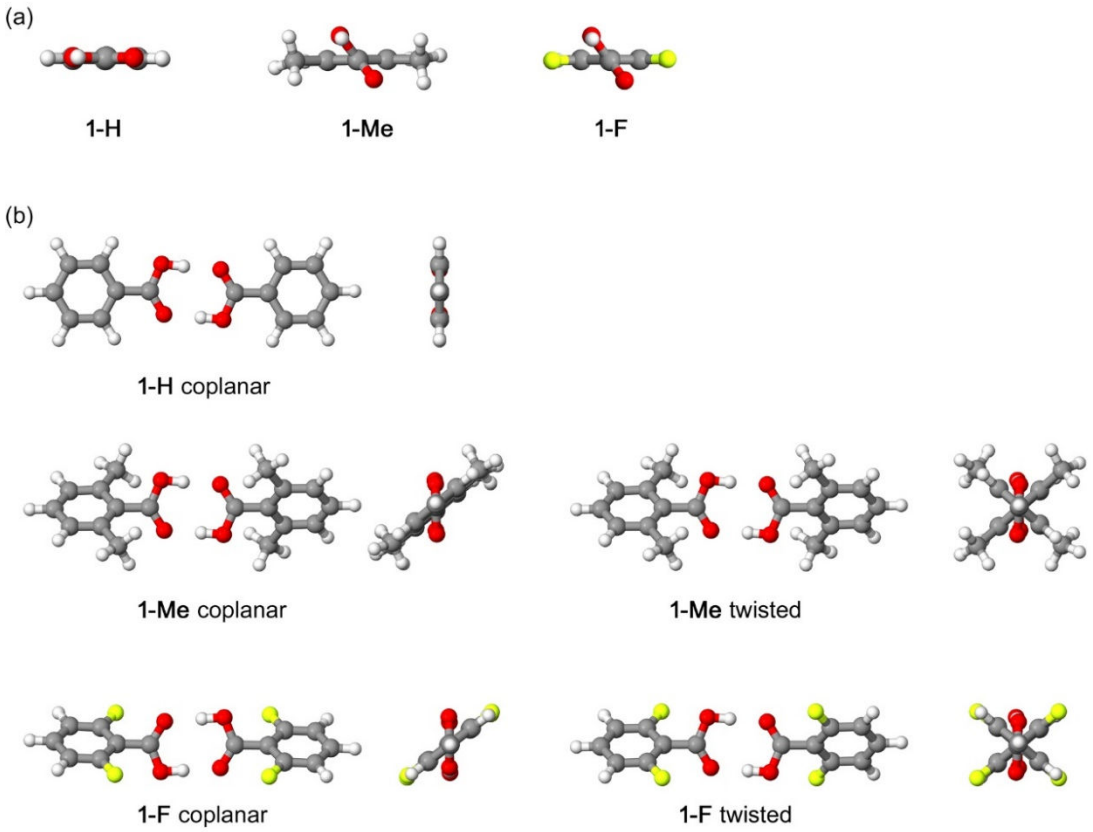

Fig. S1 Optimized geometries for (a) **1-H**, **1-Me**, **1-F** monomers, (b) **1-H** dimer and coplanar and twisted **1-Me** and **1-F** dimers.

Table S1. Atomic (ESP and Mulliken) charges on the carbonyl oxygen and the hydrogen atoms of the carboxyl groups of **1-H**, **1-Me**, and **1-F**, calculated at the MP2/6-311G**// MP2/6-311G** level.

	ESP (MK)[a]		Mulliken	
	O (C=O)	H (O-H)	O (C=O)	H (O-H)
1-H	-0.50	0.42	-0.32	0.25
1-Me	-0.50	0.39	-0.30	0.24
1-F	-0.48	0.41	-0.29	0.25

[a] Obtained by electrostatic potential fitting using Merz-Singh-Kollman scheme.

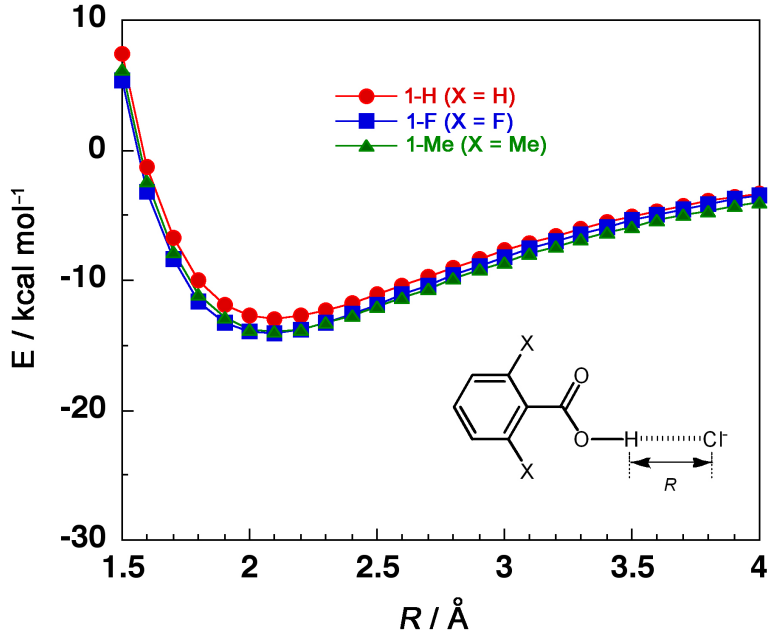

Fig. S2 Interaction energy potentials for complexes of the carboxylic acids and chloride anion. Calculation was performed at the MP2/6-311G** level.

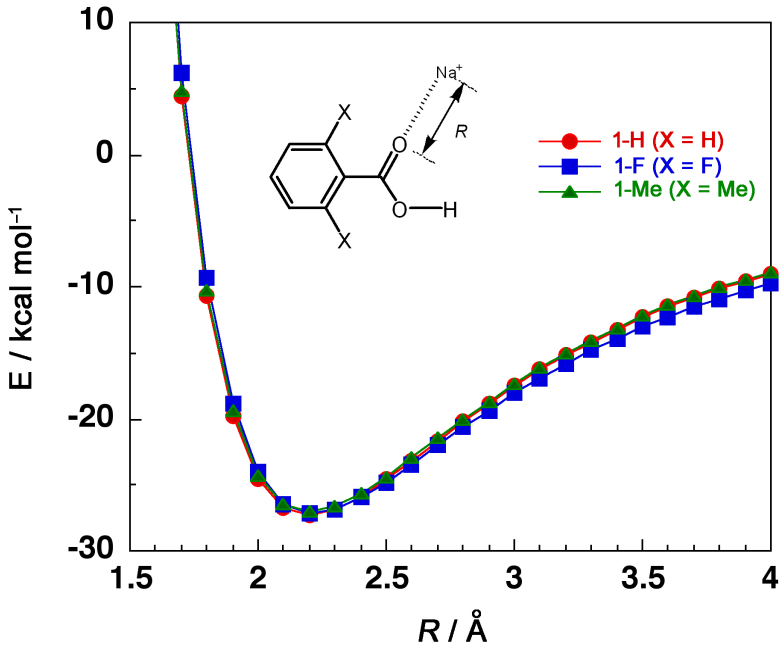

Fig. S3 Interaction energy potentials for complexes of carboxylic acids and sodium cation. Calculation was performed at the MP2/6-311G** level.

2. Stoichiometry of host and guest

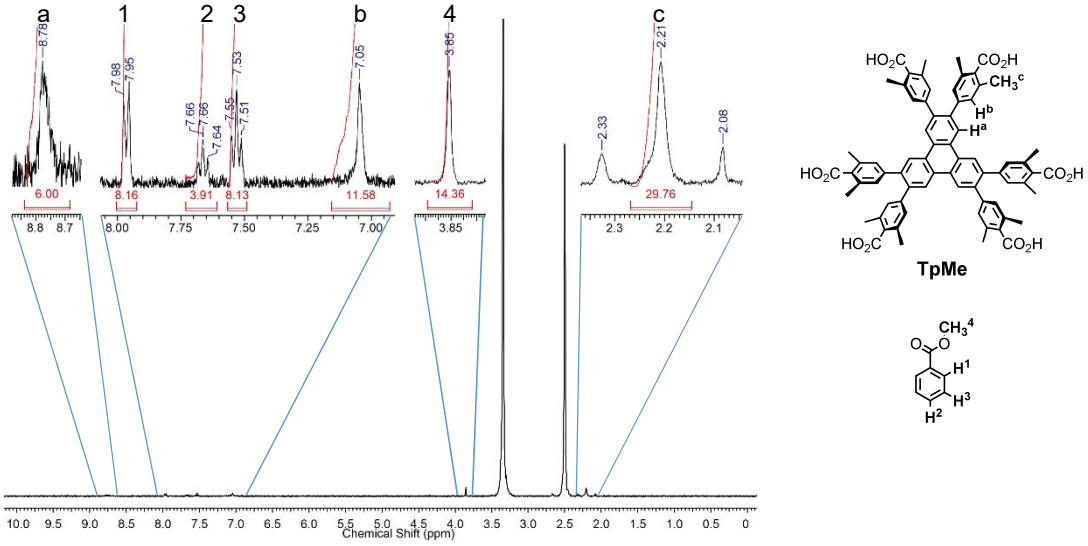

Fig. S4 ^{1}H NMR spectra of **TpMe-2Ds** dissolved in DMSO-d_6.

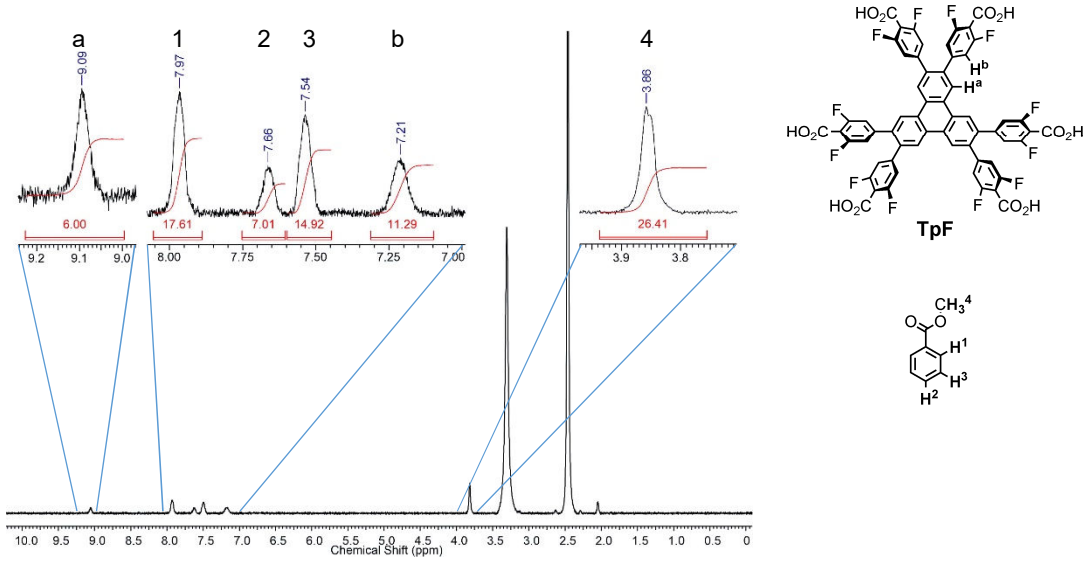

Fig. S5 ^{1}H NMR spectra of **TpMe-2Ds** dissolved in DMSO-d_6.

3. Desolvation via solvent exchanges

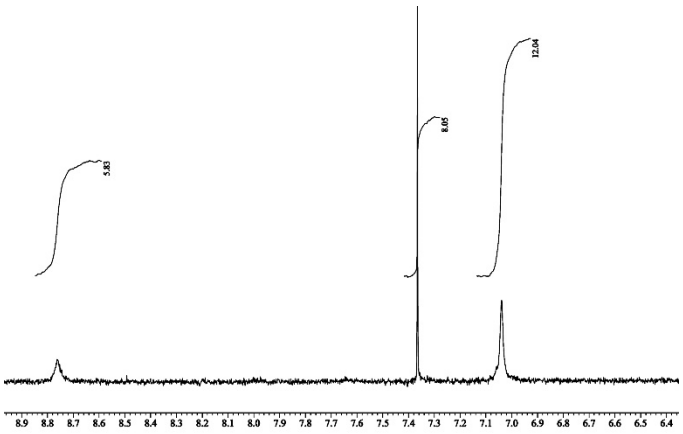

Fig. S6 [1]H NMR spectrum (400 MHz, DMDO-d_6) of **TpMe-2Ds** soaked in benzene for 48 h.

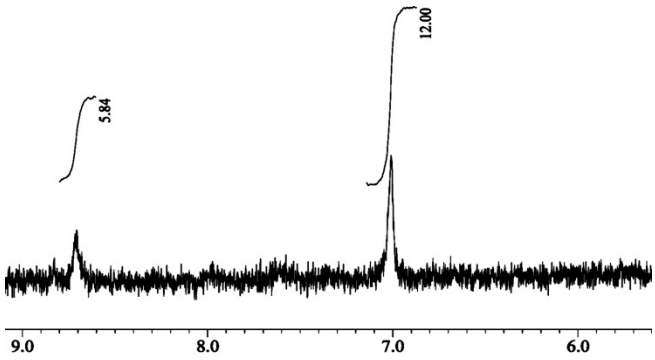

Fig. S7 [1]H NMR spectrum (400 MHz, DMDO-d_6) of **TpMe-2Ds** soaked in benzene for 48 h followed by left in vacume at 60 °C for 24 h.

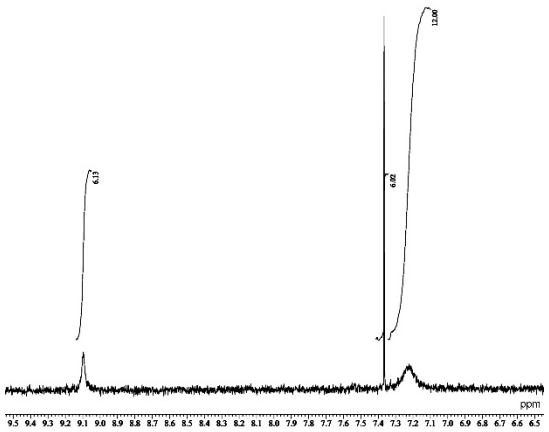

Fig. S8 [1]H NMR spectrum (400 MHz, DMDO-d_6) of **TpF-1** soaked in benzene for 48 h.

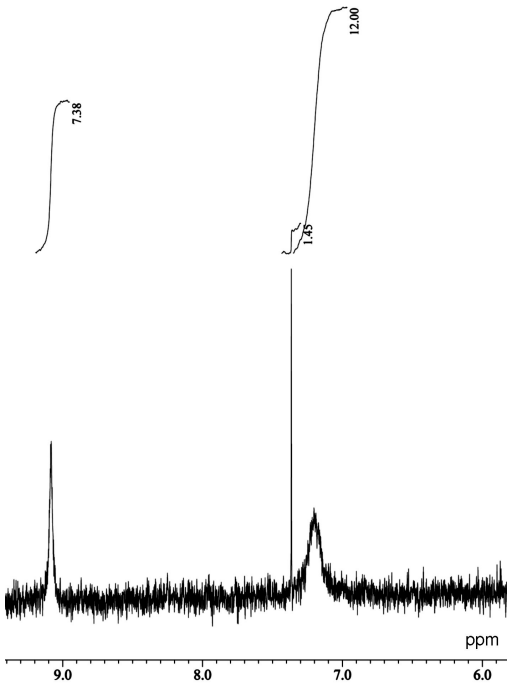

Fig. S9 ^{1}H NMR spectrum (400 MHz, DMDO-d_6) of **TpF-1** soaked in benzene for 48 h followed by left in vacume at 60 °C for 24 h.

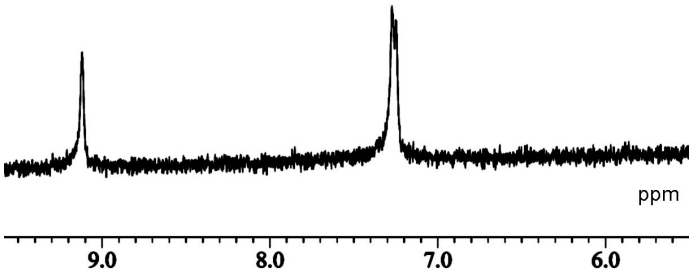

Fig. S10 ^{1}H NMR spectrum (400 MHz, DMDO-d_6) of **TpF-1** desolvated by additional heating at 100 °C for a day under vacuum condition.

4. Nonlocal density functional theory (NL-DFT) analysis

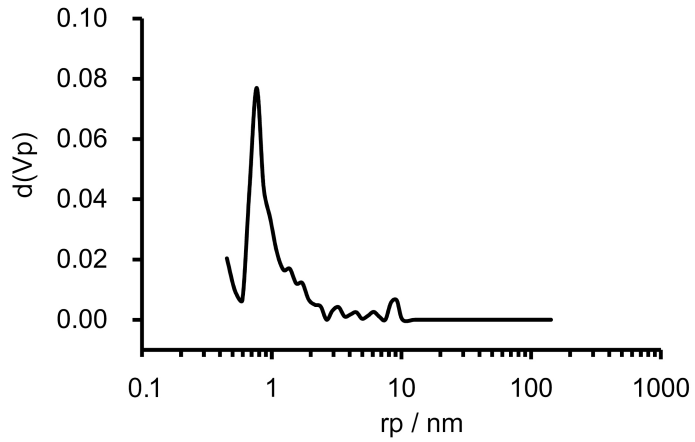

Fig S11. Pore sized distribution of **TpMe-apo**.

5. NMR spectra of the compounds newly synthesized

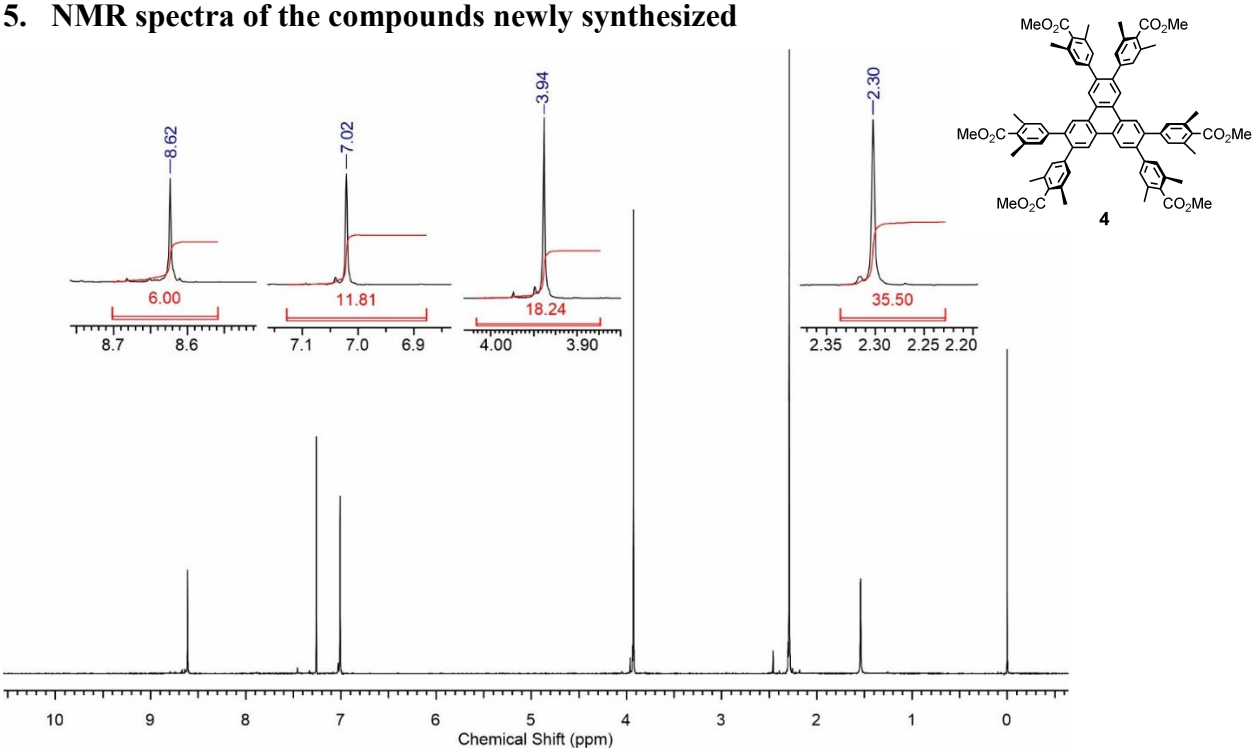

Fig. S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**.

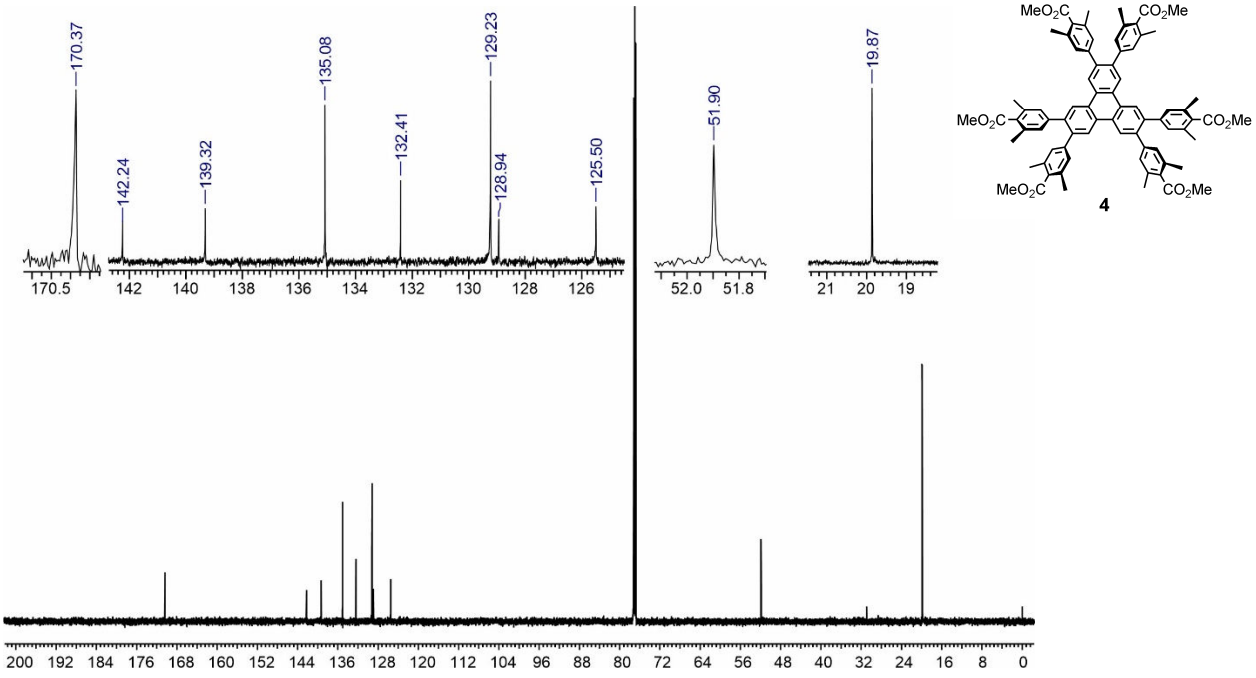

Fig. S13 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**.

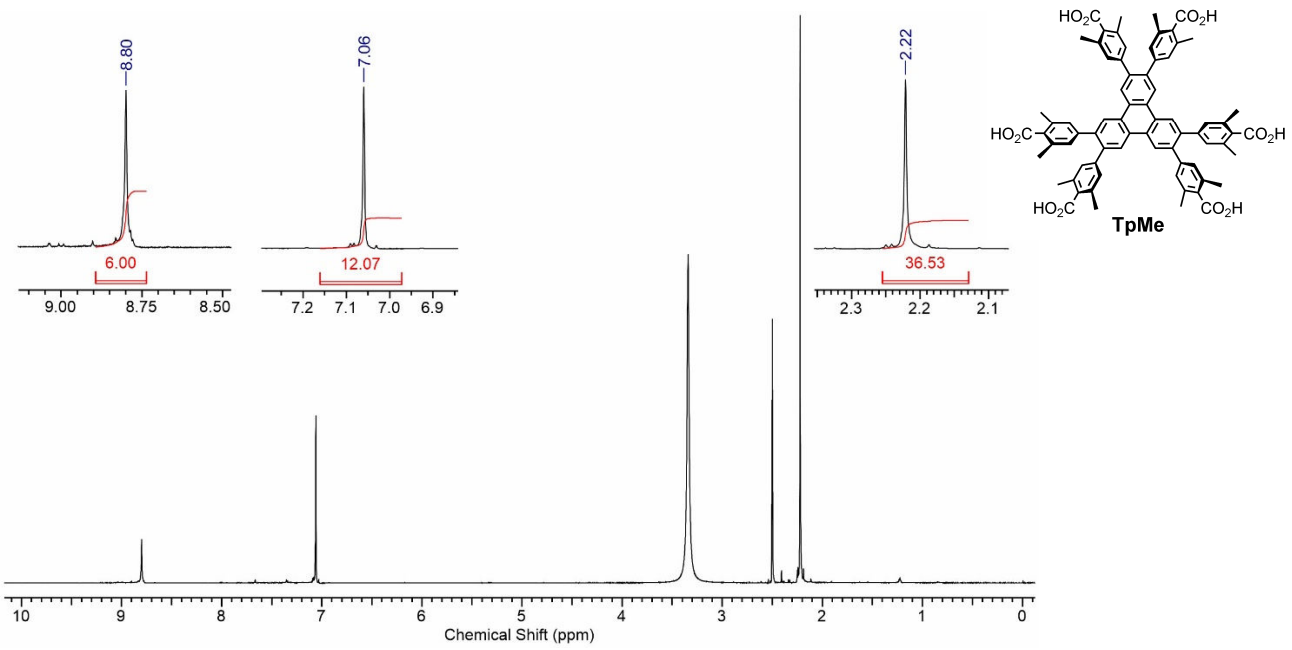

Fig. S14 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **TpMe**.

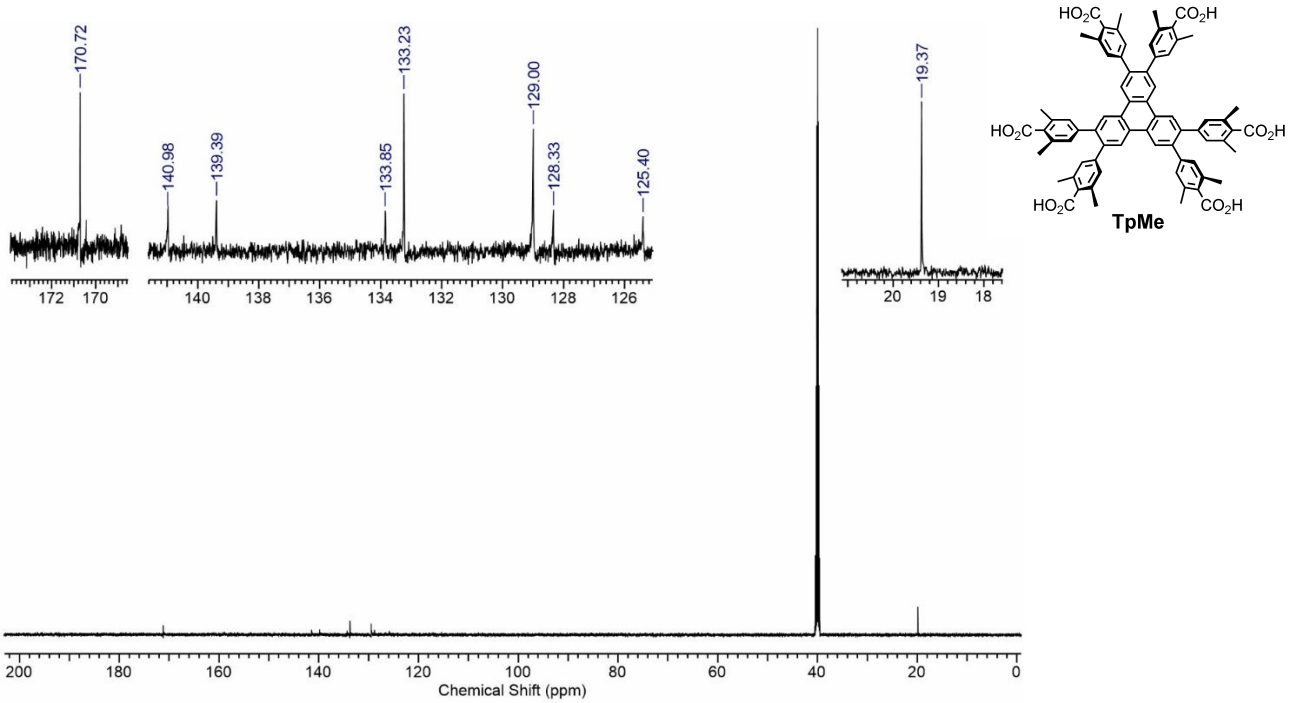

Fig. S15 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **TpMe**.

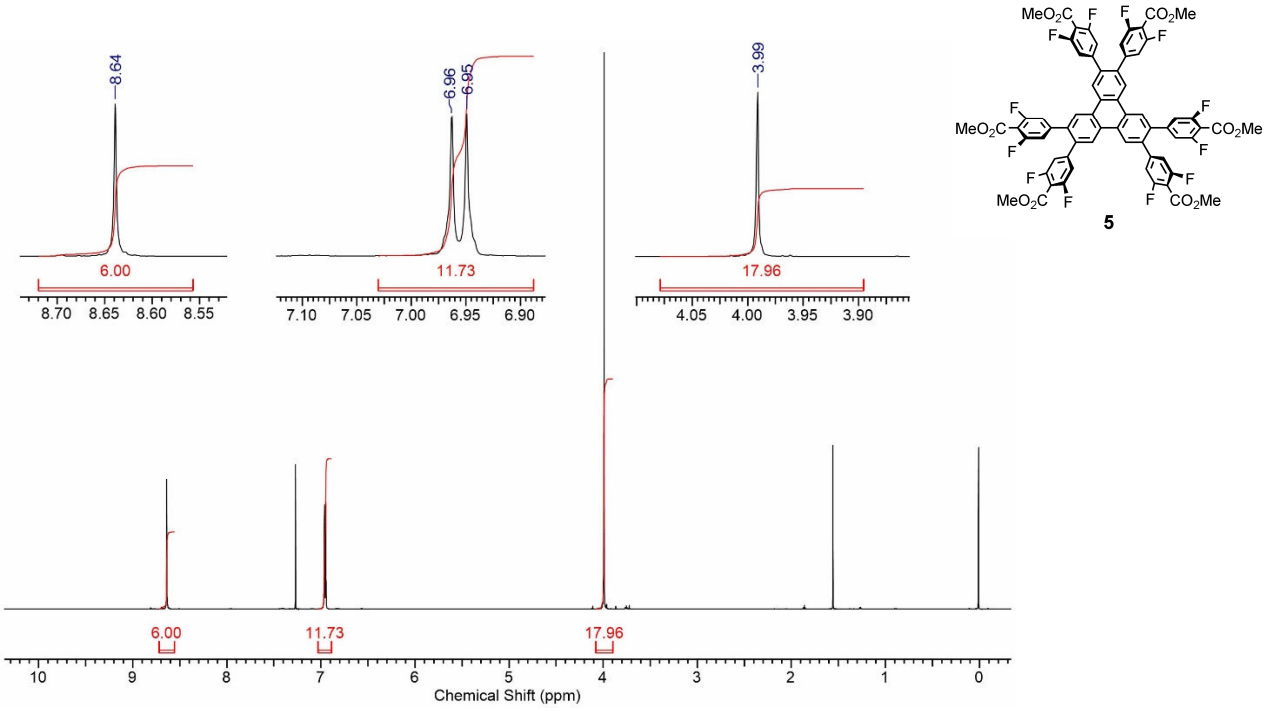

Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**.

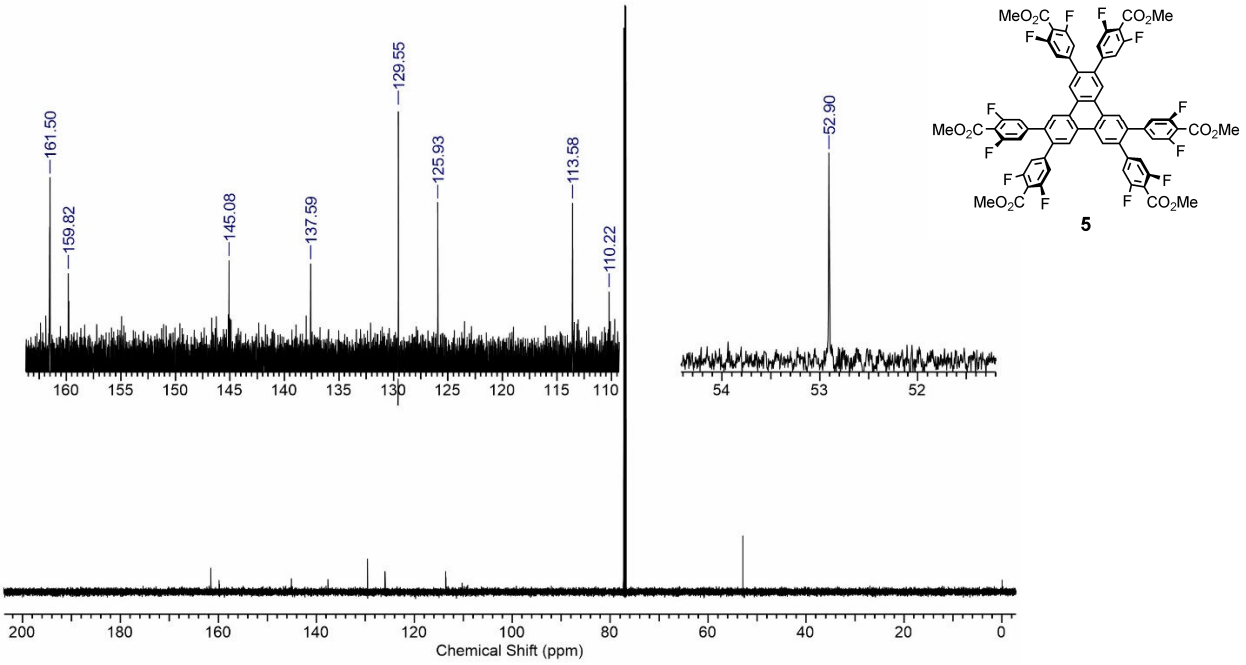

Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**.

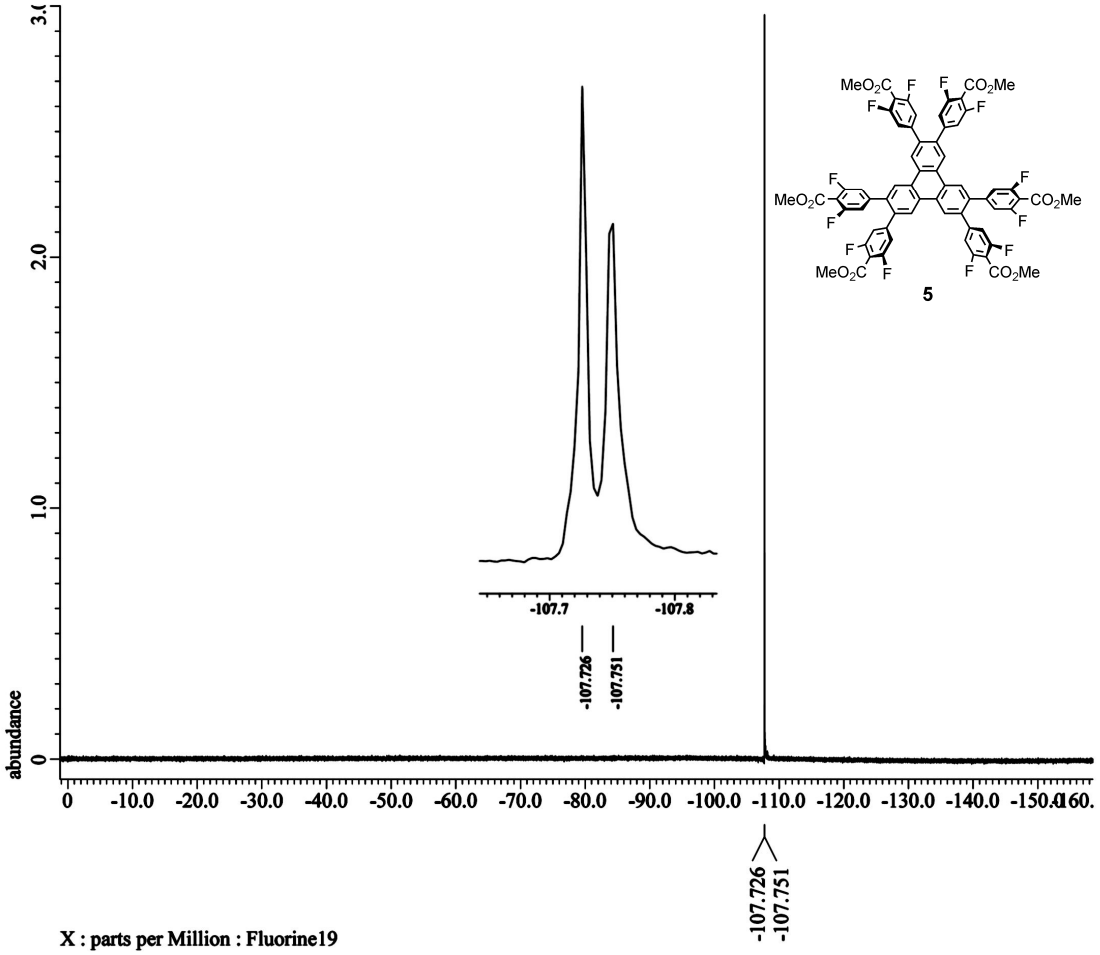

Fig. S18 ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5**.

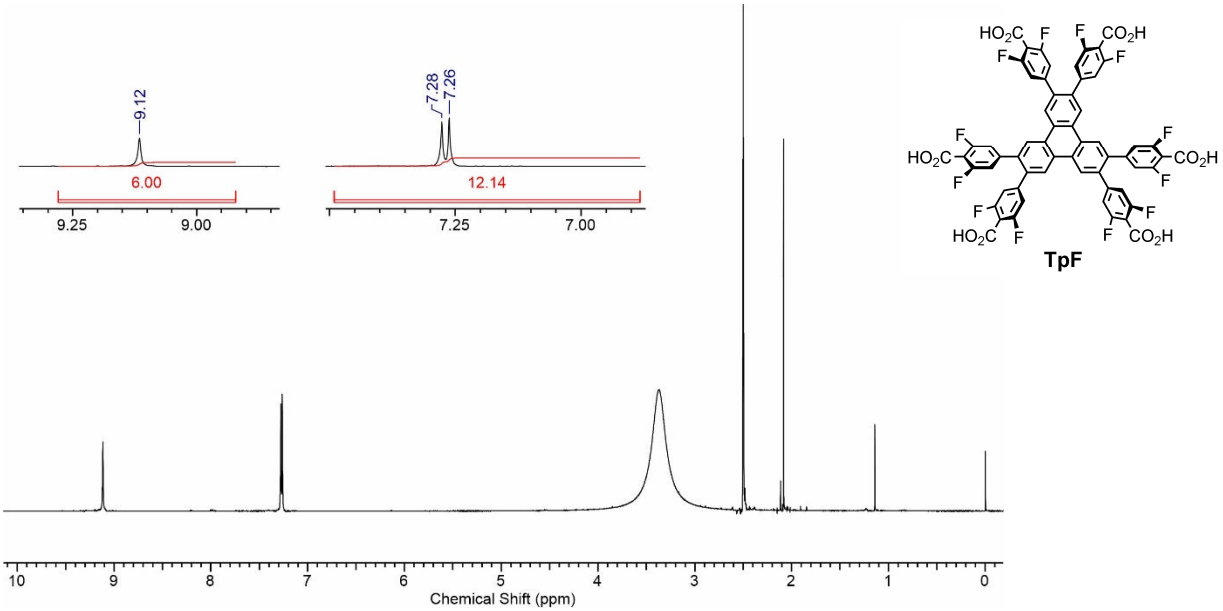

Fig. S19 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **TpF**.

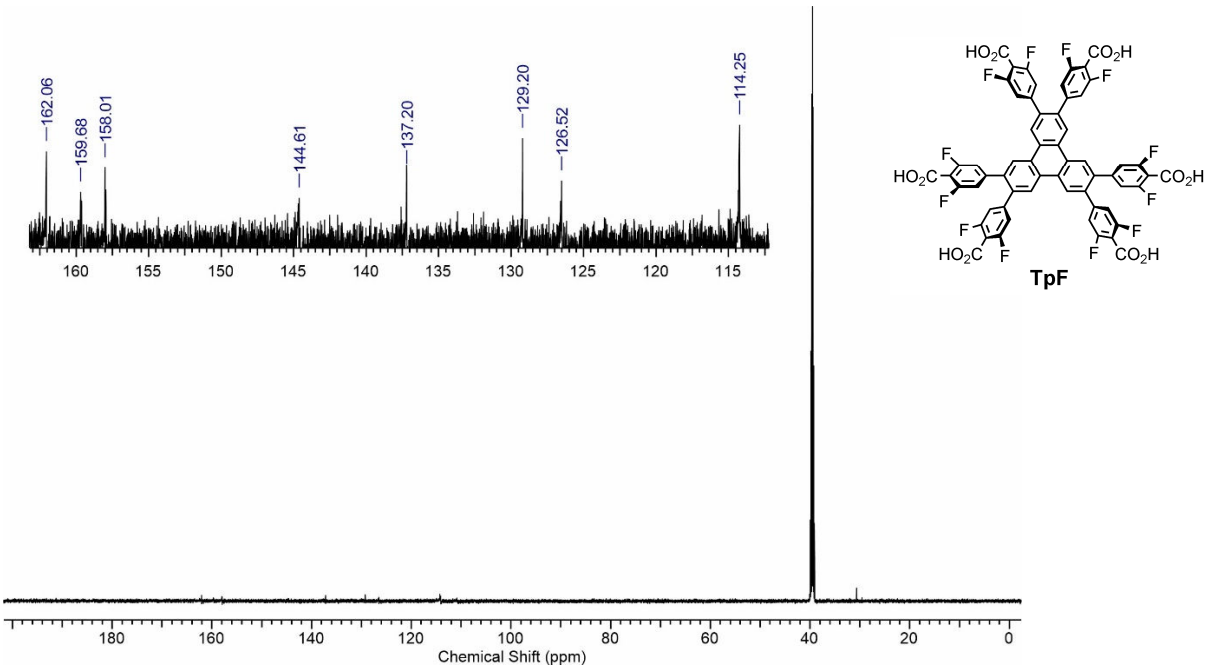

Fig. S20 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **TpF**.

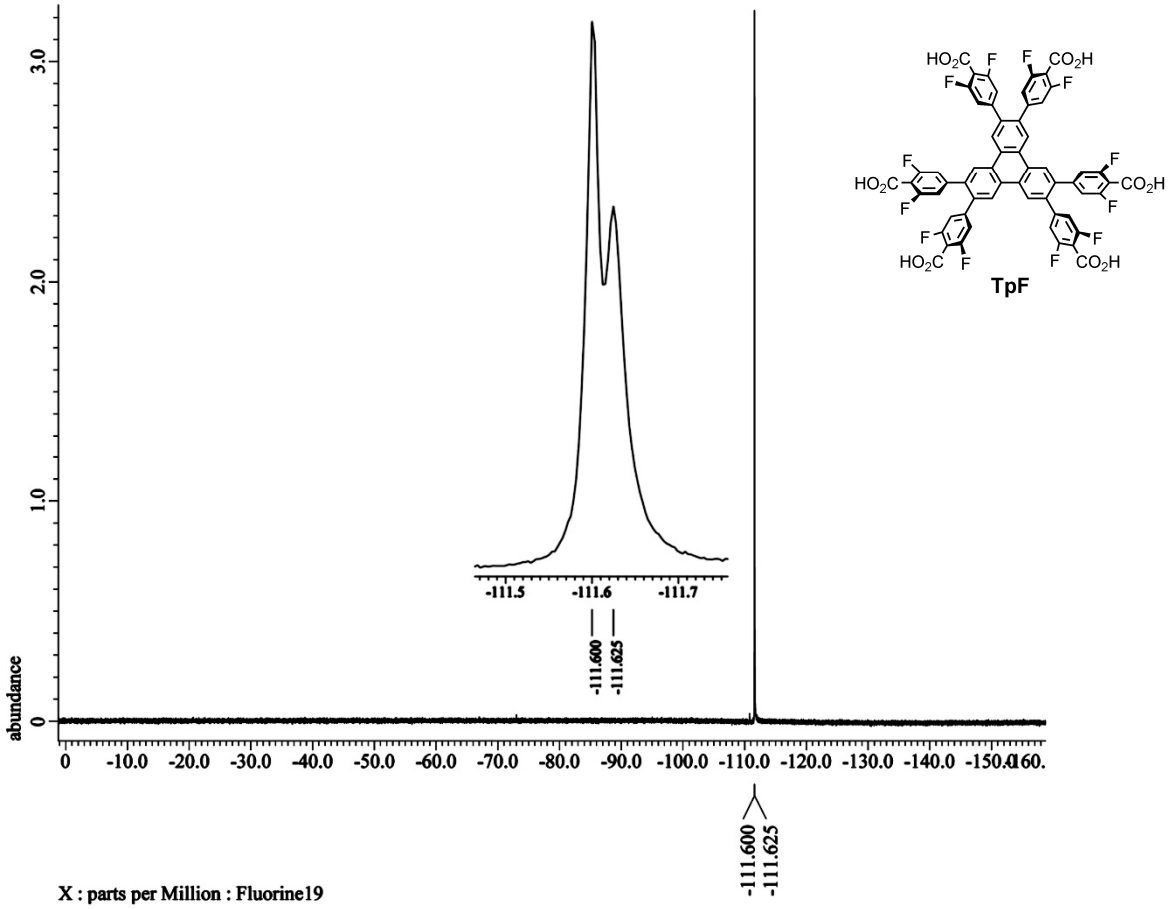

Fig. S21 ^{19}F NMR (376 MHz, DMSO-d_6) spectrum of compound **TpF**.

6. Atomic coordinates of geometrically optimized structures

Table S2. Atomic coordinate of planar **1-H**

	x	y	z
C	0.000	0.222	0.000
C	1.143	-0.589	0.000
C	1.001	-1.979	0.000
C	-0.272	-2.559	0.000
C	-1.410	-1.744	0.000
C	-1.278	-0.355	0.000
C	0.086	1.711	0.000
H	2.127	-0.133	0.000
H	1.885	-2.611	0.000
H	-0.377	-3.640	0.000
H	-2.400	-2.193	0.000
H	-2.146	0.297	0.000
O	1.366	2.157	0.000
O	-0.867	2.458	0.000
H	1.291	3.121	0.000

Table S3. Atomic coordinate of planar **1-Me**

	x	y	z
C	0.000	0.176	0.000
C	-1.183	-0.616	0.000
C	-1.048	-2.012	0.000
C	0.198	-2.633	0.000
C	1.347	-1.847	0.000
C	1.279	-0.447	0.000
C	-0.033	1.675	0.000
C	-2.602	-0.084	0.000
H	-1.950	-2.619	0.000
H	0.272	-3.717	0.000
H	2.325	-2.320	0.000
C	2.597	0.298	0.000
O	-1.283	2.204	0.000
O	0.939	2.401	0.000
H	-1.128	3.159	0.000
H	-3.295	-0.929	0.000
H	-2.804	0.532	0.878
H	-2.804	0.532	-0.878
H	3.415	-0.428	0.000
H	2.697	0.944	-0.874
H	2.697	0.944	0.874

Table S4. Atomic coordinate of twisted **1-Me**

	x	y	z
C	0.146	0.019	-0.021
C	-0.489	-1.239	-0.085
C	-1.889	-1.275	-0.064
C	-2.640	-0.102	0.038
C	-1.991	1.133	0.104
C	-0.594	1.218	0.062
C	1.635	0.118	-0.071
C	0.289	-2.53	-0.198
H	-2.392	-2.236	-0.129
H	-3.725	-0.15	0.062
H	-2.573	2.048	0.182
C	0.083	2.567	0.108
O	2.232	-0.657	0.868
O	2.265	0.815	-0.835
H	3.182	-0.53	0.729
H	0.757	-2.792	0.754
H	-0.380	-3.343	-0.494
H	1.084	-2.456	-0.945
H	0.561	2.796	-0.848
H	-0.650	3.347	0.333
H	0.862	2.599	0.875

Table S5. Atomic coordinate of planar **1-F**

	x	y	z
C	0.000	0.222	0.000
C	-1.141	-0.606	0.000
C	-1.063	-1.995	0.000
C	0.187	-2.611	0.000
C	1.346	-1.837	0.000
C	1.240	-0.449	0.000
C	-0.035	1.720	0.000
F	-2.368	-0.074	0.000
H	-1.986	-2.563	0.000
H	0.258	-3.694	0.000
H	2.336	-2.279	0.000
F	2.381	0.244	0.000
O	-1.291	2.216	0.000
O	0.944	2.430	0.000
H	-1.163	3.175	0.000

Table S6. Atomic coordinate of twisted **1-F**

	x	y	z
C	0.200	0.024	0.018
C	-0.483	-1.194	0.086
C	-1.872	-1.270	0.074
C	-2.609	-0.087	-0.023
C	-1.965	1.151	-0.097
C	-0.575	1.185	-0.069
C	1.691	0.110	0.078
F	0.227	-2.327	0.202
H	-2.348	-2.242	0.142
H	-3.693	-0.130	-0.038
H	-2.515	2.082	-0.178
F	0.047	2.369	-0.156
O	2.264	-0.671	-0.861
O	2.305	0.795	0.859
H	3.217	-0.582	-0.719

Table S7. Atomic coordinate of dimer of **1-H**

	x	y	z
C	2.899	1.801	0.000
C	2.899	3.203	0.000
C	4.115	3.892	0.000
C	5.324	3.189	0.000
C	5.318	1.789	0.000
C	4.109	1.092	0.000
C	1.626	1.027	0.000
H	1.956	3.738	0.000
H	4.118	4.978	0.000
H	6.267	3.728	0.000
H	6.257	1.242	0.000
H	4.081	0.007	0.000
O	0.540	1.781	0.000
O	1.612	-0.202	0.000
H	-0.256	1.188	0.000
C	-2.899	-1.801	0.000
C	-2.899	-3.203	0.000
C	-4.115	-3.892	0.000
C	-5.324	-3.189	0.000
C	-5.318	-1.789	0.000
C	-4.109	-1.092	0.000
C	-1.626	-1.027	0.000
H	-1.956	-3.738	0.000
H	-4.118	-4.978	0.000
H	-6.267	-3.728	0.000
H	-6.257	-1.242	0.000
H	-4.081	-0.007	0.000
O	-0.540	-1.781	0.000
O	-1.612	0.202	0.000
H	0.256	-1.188	0.000

Table S8. Atomic coordinate of twisted dimer of **1-Me**

	x	y	z
C	0.008	3.418	0.000
C	-0.797	4.124	0.920
C	-0.737	5.524	0.911
C	0.068	6.206	-0.003
C	0.849	5.488	-0.910
C	0.842	4.088	-0.920
C	-0.004	1.926	-0.012
C	-1.684	3.424	1.923
H	-1.337	6.080	1.626
H	0.092	7.293	-0.002
H	1.476	6.017	-1.624
C	1.715	3.340	-1.900
O	-1.218	1.403	-0.082
O	1.029	1.262	0.025
H	-1.138	0.414	-0.047
C	-0.008	-3.418	0.000
C	0.797	-4.124	0.920
C	0.737	-5.524	0.911
C	-0.068	-6.206	-0.003
C	-0.849	-5.488	-0.910
C	-0.842	-4.088	-0.920
C	0.004	-1.926	-0.012
C	1.685	-3.424	1.923
H	1.337	-6.080	1.626
H	-0.092	-7.293	-0.002
H	-1.476	-6.017	-1.624
C	-1.715	-3.340	-1.900
O	1.218	-1.403	-0.082
O	-1.029	-1.262	0.025
H	1.138	-0.414	-0.047
H	-2.574	3.012	1.441
H	-1.165	2.595	2.413
H	-2.000	4.130	2.695
H	2.543	2.845	-1.387
H	1.154	2.566	-2.432
H	2.124	4.034	-2.640
H	2.574	-3.012	1.441
H	1.166	-2.595	2.413
H	2.000	-4.130	2.695
H	-2.543	-2.845	-1.387
H	-1.154	-2.566	-2.432
H	-2.124	-4.034	-2.640

Table S9. Atomic coordinate of coplanar dimer of **1-Me**

	x	y	z
C	3.419	-0.001	0.005
C	4.125	-1.219	-0.077
C	5.525	-1.171	-0.107
C	6.208	0.043	-0.023
C	5.489	1.237	0.067
C	4.089	1.240	0.073
C	1.927	0.000	0.016
C	3.424	-2.556	-0.165
H	6.082	-2.102	-0.188
H	7.294	0.060	-0.037
H	6.018	2.185	0.134
C	3.341	2.550	0.150
O	1.400	-0.807	0.923
O	1.266	0.703	-0.745
H	0.411	-0.764	0.847
C	-3.419	0.001	-0.005
C	-4.088	-1.240	-0.072
C	-5.489	-1.238	-0.067
C	-6.208	-0.045	0.022
C	-5.526	1.170	0.105
C	-4.125	1.219	0.076
C	-1.927	0.001	-0.016
C	-3.339	-2.550	-0.148
H	-6.017	-2.186	-0.133
H	-7.294	-0.062	0.035
H	-6.083	2.101	0.186
C	-3.426	2.556	0.163
O	-1.400	0.807	-0.923
O	-1.266	-0.701	0.746
H	-0.411	0.765	-0.846
H	3.005	-2.845	0.803
H	2.600	-2.533	-0.884
H	4.132	-3.326	-0.484
H	2.846	2.774	-0.798
H	2.565	2.526	0.922
H	4.033	3.362	0.387
H	-2.564	-2.526	-0.920
H	-2.845	-2.773	0.800
H	-4.031	-3.362	-0.385
H	-2.602	2.534	0.883
H	-3.006	2.845	-0.804
H	-4.134	3.326	0.482

Table S10. Atomic coordinate of twisted dimer of **1-F**

	x	y	z
C	-0.007	3.403	-0.027
C	-0.751	4.142	0.898
C	-0.722	5.532	0.934
C	0.069	6.212	0.004
C	0.824	5.511	-0.940
C	0.779	4.122	-0.934
C	-0.015	1.910	-0.041
F	-1.491	3.486	1.804
H	-1.309	6.053	1.681
H	0.098	7.297	0.017
H	1.439	6.017	-1.675
F	1.487	3.445	-1.850
O	-1.230	1.406	-0.108
O	1.025	1.265	-0.001
H	-1.162	0.416	-0.069
C	0.007	-3.403	-0.027
C	0.752	-4.142	0.898
C	0.722	-5.532	0.934
C	-0.069	-6.212	0.004
C	-0.824	-5.511	-0.940
C	-0.779	-4.122	-0.934
C	0.015	-1.910	-0.042
F	1.492	-3.486	1.803
H	1.309	-6.053	1.681
H	-0.098	-7.297	0.017
H	-1.440	-6.017	-1.675
F	-1.487	-3.445	-1.850
O	1.230	-1.406	-0.108
O	-1.025	-1.265	-0.001
H	1.162	-0.416	-0.070

Table S11. Atomic coordinate of coplanar dimer of **1-F**

	x	y	z
C	3.404	0.003	-0.017
C	4.148	1.183	0.079
C	5.538	1.184	0.117
C	6.214	-0.037	0.043
C	5.508	-1.238	-0.059
C	4.118	-1.198	-0.080
C	1.911	0.003	-0.024
F	3.496	2.352	0.172
H	6.063	2.128	0.205
H	7.299	-0.052	0.066
H	6.010	-2.197	-0.124
F	3.437	-2.347	-0.196
O	1.404	0.796	-0.946
O	1.268	-0.683	0.760
H	0.415	0.771	-0.872
C	-3.404	-0.003	0.017
C	-4.118	1.198	0.079
C	-5.508	1.238	0.058
C	-6.214	0.037	-0.043
C	-5.538	-1.184	-0.116
C	-4.148	-1.183	-0.078
C	-1.911	-0.003	0.024
F	-3.437	2.347	0.195
H	-6.010	2.197	0.123
H	-7.299	0.052	-0.067
H	-6.063	-2.129	-0.204
F	-3.496	-2.352	-0.171
O	-1.404	-0.795	0.946
O	-1.268	0.683	-0.760
H	-0.415	-0.771	0.872