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

Supporting Information

Zn(II)-based metal–organic framework: an exceptionally thermal stable, guest-free low dielectric material

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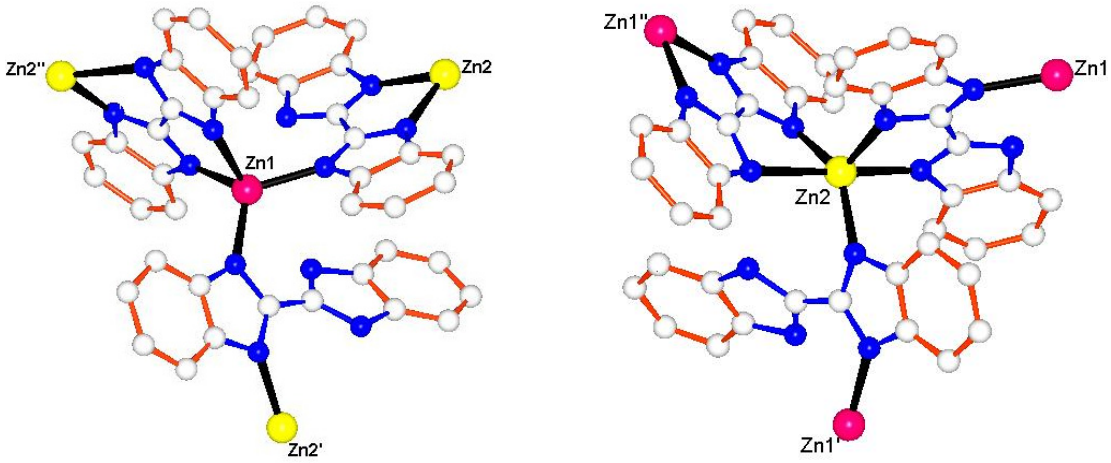
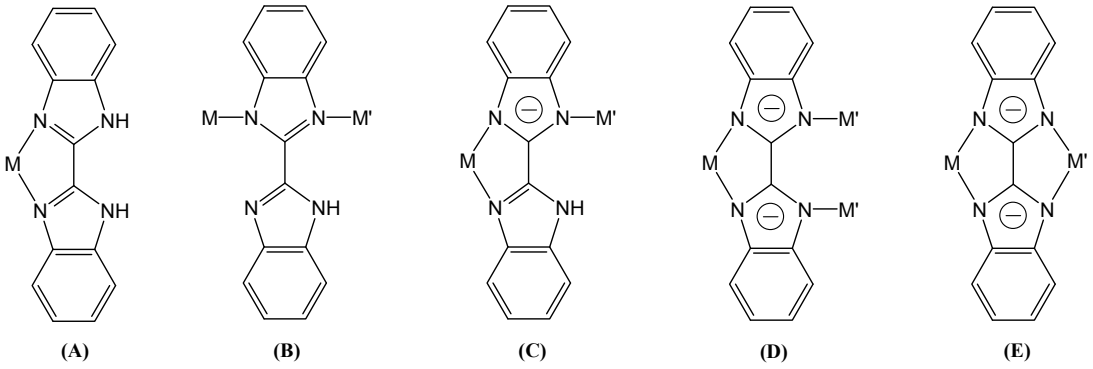


Figure S1. The coordination modes of the $bbim^{2-}$ ligand, in Zn(1) and Zn(2).



Scheme S1. Possible coordination modes of H_2bbim.

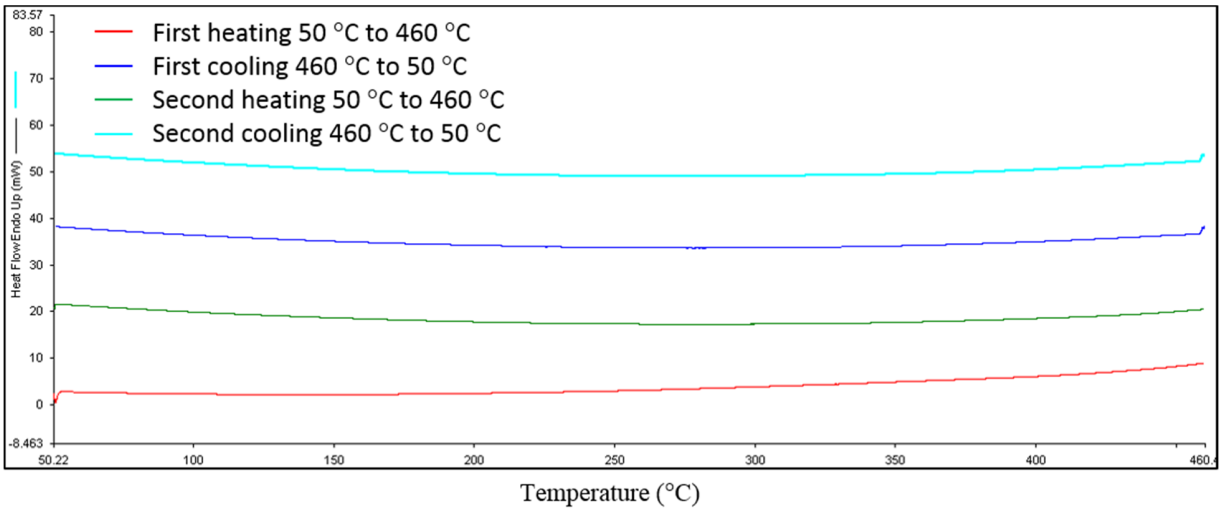


Figure S2. The DSC traces of successive heating/cooling runs for compound **1**. The following cool/heat cycle confirms the stability of compound up to 460 °C. The heating rate is 10 °C/min.

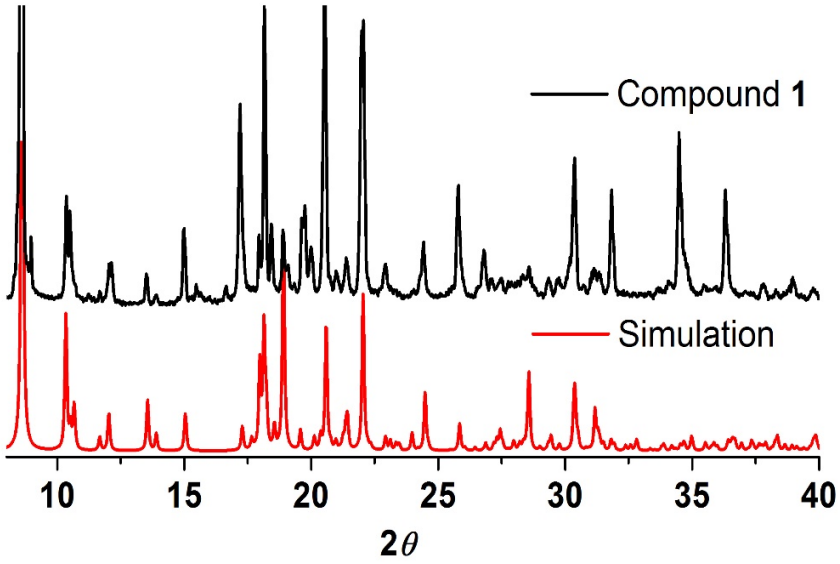


Figure S3. The PXRD pattern for compound **1**.

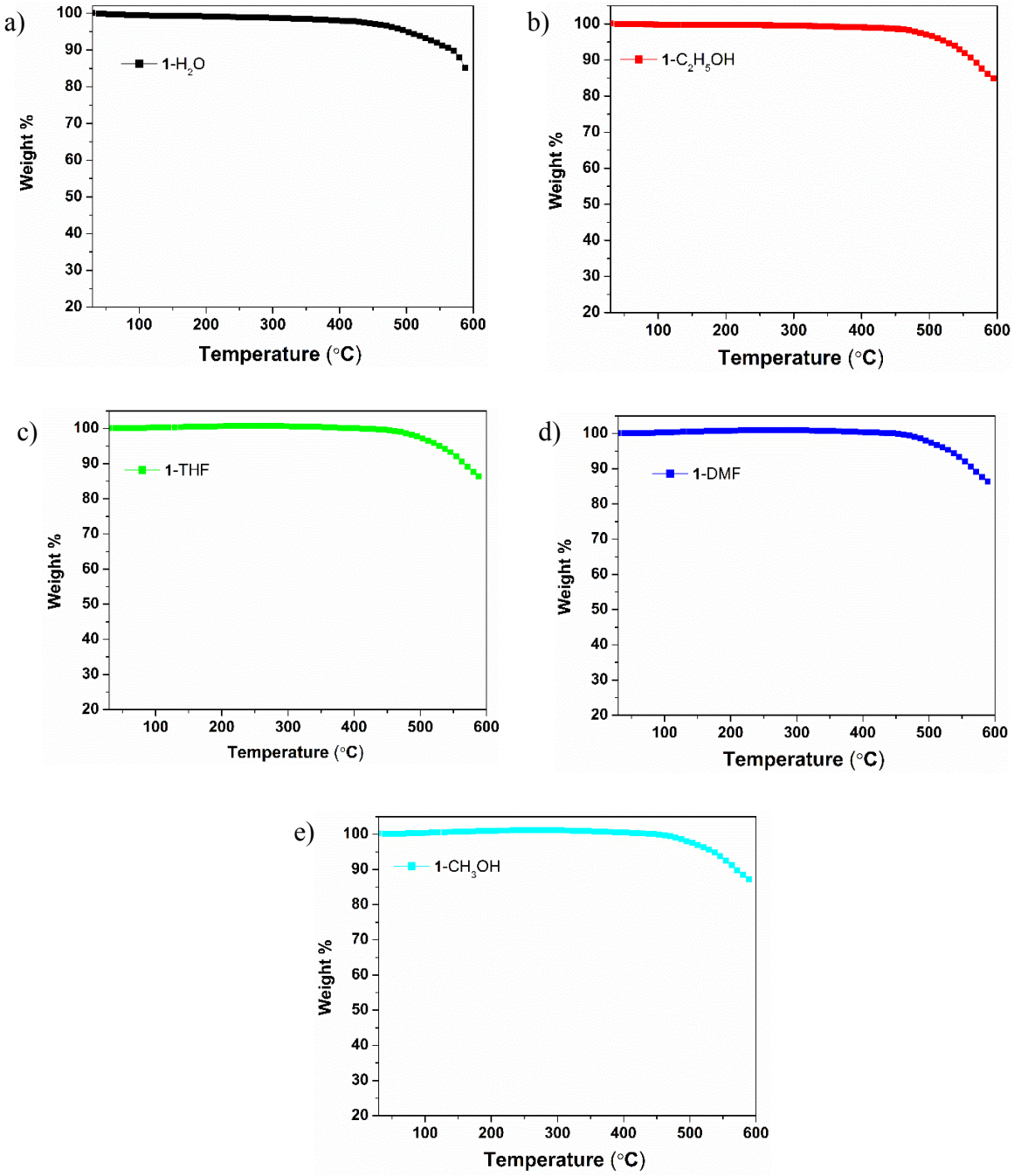


Figure S4. a) The thermogravimetric analysis of compound **1** treated with water, b) compound **1** treated with ethanol, c) compound **1** treated with tetrahydrofuran (THF), d) compound **1** treated with dimethylformamide (DMF), e) compound **1** treated with methanol.

Table S1. Crystallographic data and structural refinement of **1**.

Empirical formula	C42 H26 N12 Zn2	
Formula weight	829.49	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*1	
Unit cell dimensions	a = 9.6285(3) Å	α = 99.852(2)°
	b = 9.8729(3) Å	β = 96.899(2)°
	c = 10.6722(4) Å	γ = 116.498(2)°
Volume	872.06(5) Å^3	
Z	1	
Density (calculated)	1.579 Mg/m^3	
Absorption coefficient	1.428 mm^{-1}	
F(000)	422	
Crystal size	0.40 x 0.21 x 0.05 mm^3	
Theta range for data collection	2.38 to 25.64°	
Reflections collected	10529	
Independent reflections	5839 [R(int) = 0.0724]	
Max. and min. transmission	0.9320 and 0.5989	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5839 / 3 / 505	
Goodness-of-fit on F^2	1.029	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0532, wR2 = 0.1330	
R indices (all data)	R1 = 0.0679, wR2 = 0.1619	

Supplementary Results for Theoretical Calculation.

In Table S2, we list the HOMO and LUMO energies, band gap, electronic polarizabilities and dielectric constants calculated with the long-range corrected density functional ωPBEh (range-separation parameter set as 0.15) and the commonly used hybrid density functional B3LYP, with the same settings in the basis set and effective core potentials (6-31g* and LANL2DZ for Zn). It can be seen that the HOMO-LUMO energy gap for B3LYP is much lower, leading to a higher polarizability and electronic dielectric constant (3.17). Even though the dielectric constant deriving from B3LYP functional is closer to the experimental value (3.05), it is clearly an overestimated value due to the erroneously low bandgap predicted. The molecular structure employed is listed in Table S3.

Table S2. Additional results from DFT calculation.[a]

Density functional	E_{HOMO}	E_{LUMO}	E_g	Averaged polarizability	Dielectric Constant
B3LYP	-9.44	-6.53	2.91	926	3.17
ωPBEh	-11.04	-5.19	5.85	730	2.48

[a] Listed are the energy of HOMO (E_{HOMO}), LUMO (E_{LUMO}) and their difference (E_g) in units of eV. The averaged polarizability was calculated to be 1/3 of the trace of the electronic polarizability tensor, in the units of $Å^3$.

Table S3. Molecular Structure employed in the calculation, in their xyz coordinates, in the units of Å.

Zn	-2.896998	-0.199095	0.044962
N	-4.293363	0.324410	-1.342903
C	-4.525512	1.583906	-1.779157
N	-5.741969	1.766240	-2.334916
H	-6.093101	2.649806	-2.679866
C	-6.363648	0.530897	-2.230669
C	-5.468590	-0.344722	-1.659027
C	-7.640009	0.121874	-2.625792

H	-8.342376	0.814524	-3.078331
C	-7.975659	-1.194529	-2.396595
H	-8.962469	-1.544542	-2.684696
C	-7.065734	-2.095593	-1.855555
H	-7.362429	-3.134576	-1.737616
C	-5.810895	-1.706130	-1.462493
H	-5.085769	-2.415425	-1.088492
C	-3.560498	2.658015	-1.688768
N	-3.858474	3.926009	-1.543694
N	-2.219962	2.399983	-1.855813
H	-1.797375	1.480664	-1.989630
C	-1.591662	3.637107	-1.822498
C	-0.261345	3.997202	-1.978836
H	0.509058	3.255887	-2.172022
C	0.032891	5.342229	-1.906588
H	1.055644	5.679528	-2.028622
C	-2.630871	4.576742	-1.617211
C	-2.292566	5.919577	-1.533406
H	-3.061422	6.668853	-1.369973
C	-0.979716	6.271569	-1.672086
H	-0.711469	7.323084	-1.614888
N	-3.238856	-2.139034	0.582788
C	-4.233800	-2.267803	1.473753
N	-4.639621	-3.549364	1.682459
H	-5.340923	-3.890647	2.323639
C	-3.820962	-4.315111	0.858348
C	-2.961836	-3.440346	0.164777
C	-2.059297	-3.937609	-0.774057
H	-1.426451	-3.264269	-1.340528
C	-2.031687	-5.296888	-0.986656
H	-1.347669	-5.705906	-1.723826
C	-3.781805	-5.694684	0.638366
H	-4.443377	-6.372575	1.169940
C	-2.872608	-6.161772	-0.278356
H	-2.823530	-7.228826	-0.475471
C	-4.794680	-1.053496	2.017882

N	-4.316611	0.108036	1.642744
N	-5.842944	-0.961782	2.887370
H	-6.370816	-1.711339	3.309901
C	-5.133928	1.060242	2.256036
C	-5.122983	2.449144	2.188112
H	-4.404394	2.972154	1.564339
C	-6.066815	3.130798	2.905326
H	-6.085137	4.215438	2.860130
C	-6.077436	0.406838	3.064455
C	-7.034518	1.089503	3.772867
H	-7.772505	0.568804	4.377191
C	-7.030270	2.469154	3.697730
H	-7.768624	3.044580	4.245294
N	-1.241351	-0.483421	-1.612861
C	-0.147316	-0.517135	-0.854051
N	0.941894	-1.130635	-1.333564
C	-0.804095	-1.138822	-2.752386
C	0.529657	-1.535670	-2.597762
C	1.209425	-2.209618	-3.618768
H	2.244078	-2.515538	-3.494153
C	0.540301	-2.412886	-4.805237
H	1.048802	-2.910450	-5.626281
C	-1.485914	-1.367902	-3.955372
H	-2.516560	-1.048160	-4.078034
C	-0.802113	-2.005413	-4.978630
H	-1.295927	-2.188775	-5.927847
C	-0.124542	0.136992	0.433284
N	1.012823	0.272946	1.117001
N	-1.239655	0.610005	0.999281
C	-0.774300	1.142598	2.200467
C	-1.435141	1.795222	3.212405
H	-2.503122	1.979554	3.148230
C	-0.723864	2.202603	4.313902
H	-1.230621	2.714457	5.126219
C	0.609807	0.927350	2.287733
C	1.341087	1.336885	3.400880

H	2.409725	1.150681	3.463967
C	0.655688	1.968690	4.400002
H	1.191034	2.299741	5.285730
H	2.140935	1.856474	0.639896
N	2.703692	2.612448	0.262923
C	3.751964	2.520757	-0.606572
N	4.230027	3.682273	-0.981706
C	3.412717	4.634475	-0.368415
C	3.423659	6.023380	-0.436337
H	4.161551	6.538668	-1.043442
C	2.479829	6.705034	0.280874
H	2.467025	7.790784	0.243928
C	2.469212	3.981072	0.440006
C	1.512124	4.663742	1.148416
H	0.777563	4.141887	1.755227
C	1.516371	6.043387	1.073282
H	0.779806	6.620133	1.622409
C	4.312852	1.306414	-1.150698
N	5.307789	1.435196	-2.041668
H	5.682587	2.331625	-2.328829
N	3.907011	0.024873	-0.941983
C	4.725682	-0.740863	-1.766100
C	5.584813	0.133893	-2.459683
C	6.487342	-0.363373	-3.398504
H	7.146060	0.300988	-3.949976
C	6.514956	-1.722650	-3.611105
H	7.207685	-2.132979	-4.339203
C	4.764842	-2.120451	-1.986090
H	4.095708	-2.796199	-1.462085
C	5.674032	-2.587542	-2.902805
H	5.729699	-3.654195	-3.103024
Zn	2.444749	-0.833294	0.114375
N	2.962044	-2.457714	1.093538
C	4.178502	-2.640034	1.649295
N	4.410645	-3.899550	2.085553
H	5.176201	-4.220889	2.661009

C	2.340368	-3.693051	1.197787
C	3.235420	-4.568684	1.769437
C	1.064001	-4.102079	0.802662
H	0.370320	-3.399836	0.357398
C	0.728353	-5.418482	1.031861
H	-0.261388	-5.766043	0.762143
C	1.638278	-6.319546	1.572901
H	1.341259	-7.355162	1.712096
C	2.893118	-5.930078	1.965959
H	3.597068	-6.630809	2.404632
C	5.143509	-1.565947	1.739686
N	4.845539	-0.297939	1.884764
N	6.484049	-1.823967	1.572646
H	6.903098	-2.696133	1.282723
C	7.112352	-0.586848	1.605950
C	8.442663	-0.226751	1.449622
H	9.218075	-0.968853	1.281520
C	8.736903	1.118276	1.521867
H	9.763302	1.453384	1.411831
C	6.073136	0.352793	1.811245
C	6.411444	1.695625	1.895049
H	5.647698	2.445999	2.076465
C	7.724295	2.047617	1.756369
H	7.992166	3.098454	1.823202