Electronic Supplementary Material (ESI) for RSC Advances.

A three-dimensional metal-organic framework for guest-free ultra-low dielectric material

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1. Experimental

1.1. Chemicals and reagents

Thee reagents and solvents were purchased from commercial sources and used without further purification.

1.2. Physical measurements

Elemental analyses (C, H and N) were performed with an Elementar Vario EL III analytical instrument. IR spectra were recorded on a Bruker Vector 22 Fourier Transform Infrared Spectrometer (170SX) (KBr disc). Thermogravimetric (TG) experiment was performed with a TA2000/2960 thermogravimetric analyzer from 30 to 800°C at a warming rate of 10 K/min under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. Powder X-ray diffraction (PXRD) data for the as-prepared was collected using Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA with Cu K radiation λ = 1.5418 Å at ambient temperature. Temperature and frequency dependent dielectric constant, ε', and dielectric loss, tan(δ), measurements were carried out employing Concept 80 system (Novocontrol, Germany); the powdered pellet, with a thickness of ca. 0.48 mm, was coated by gold films on the opposite surfaces and sandwiched by the copper electrodes and the ac frequencies span from 100 Hz to 10^6 Hz.

X-ray crystallography. Selected crystals of **1** at room temperature were centered on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector and a graphite monochromated Mo Kα (λ = 0.71073 Å). The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis.[1] Structures were solved by the direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program.[2] The non-Hydrogen atoms were anisotropically refined using the full-matrix least-squares method on F^2. The crystallographic details about data collection, structural refinement are summarized in Table S1.

References:

1. *CrysAlis V1.171*, Oxford Diffraction Ltd., Poland, 2004.
2. G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal structure, University of Göttingen, Germany, 1997.

1.3. Preparations for 1

The synthesis procedure of compound **1** is in following described: First, the $Zn(NO_3)_2{\cdot}6H_2O$ (0.075 g) and 4,4'-biphenyldicarboxylic acid (0.120 g) were dissolved in 10ml DMF. The mixture were stirred for 1h, then 0.021 g dimethylamine hydrochloride was added and stirred another 1h. The mixture were sealed in Teflon-lined autoclave and heated to 100 ℃ for 72h. Colorless needle-shape crystals were obtained in solution. The crystal was washed with DMF and acetone and dried in air.

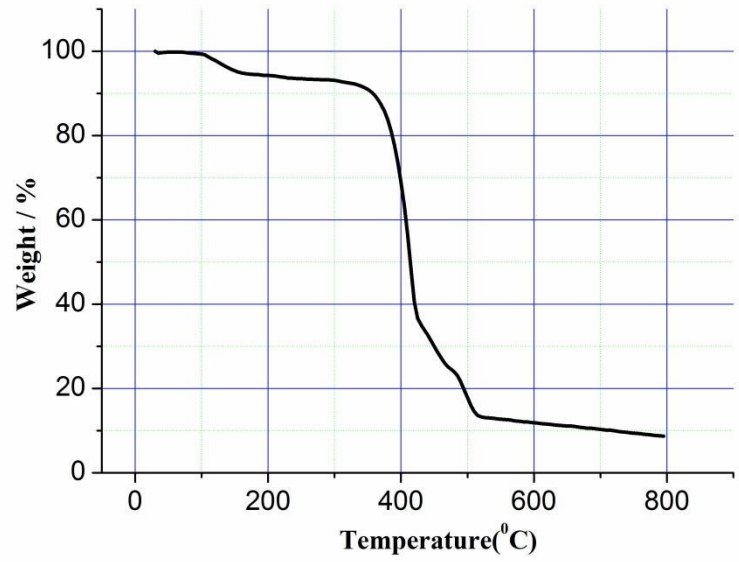

Figure S1 TG curves of compound **1**.

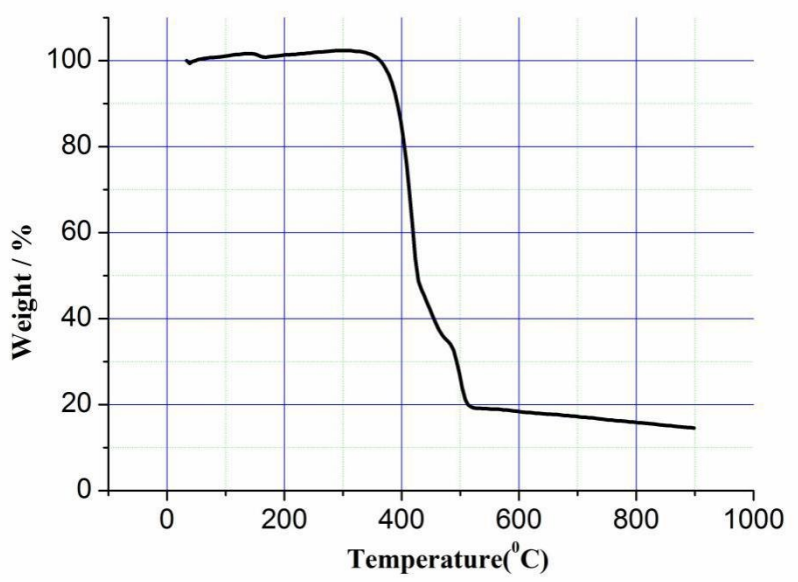

Figure S2 TG curves of compound **1'** showing high thermal stability.

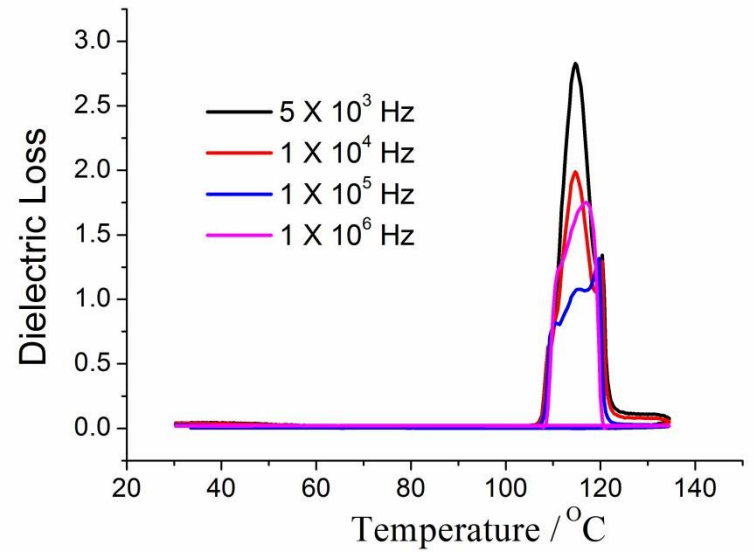

Figure S3 Temperature-dependent dielectric loss of **1** in the temperature range of 30-135^{O}C.

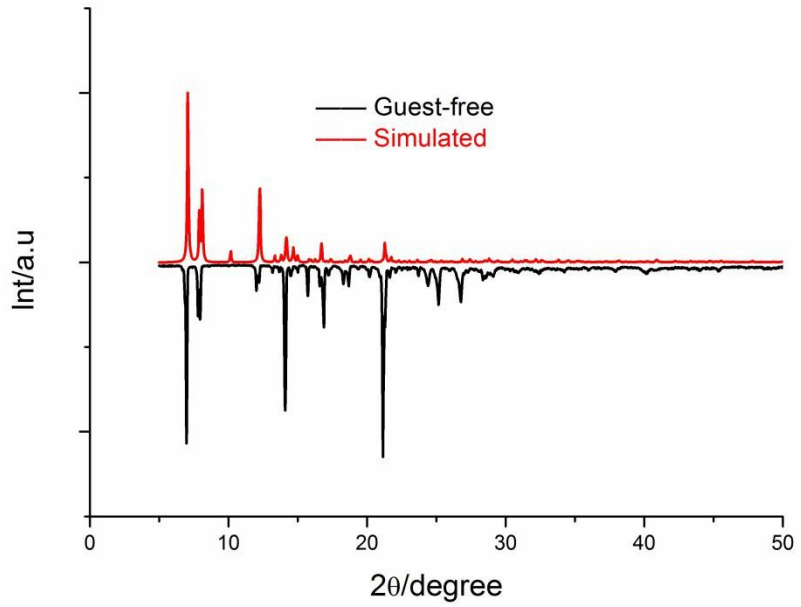

Figure S4 Powder X-ray diffraction patterns for sample of **1'**, confirming the sample **1** is stable after removing DMF (Black lines: experimental patterns of **1'**; red lines: simulated profiles of **1**).

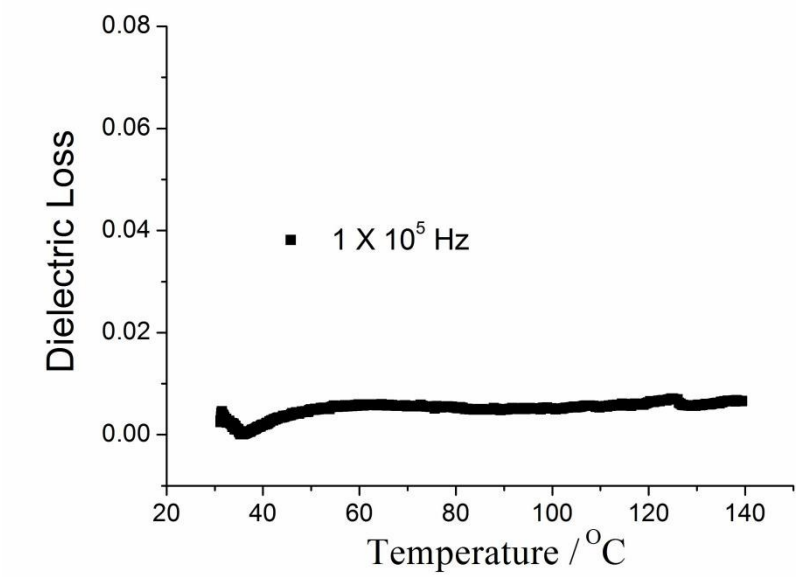

Figure S5 Temperature-dependent dielectric loss at 10^5Hz of **1**′

Table S1 Crystal and structural refinement data for compound **1**

Complex	**1**
Molecular formula	$C_{60}H_{48}N_2O_{16}Zn_3$
Space group	Pna21
Crystal system	orthorhombic
Temp/K	100(2)
Wavelength (Å)	0.71073
a/Å	24.7046(12)
b/Å	14.5230(9)
c/Å	22.3879(12)
α/°	90
β/°	90
γ/°	90
V/Å^3. Z	8032.4(8)
μ/mm^{-1}	0.939
ρ/g cm^{-3}	1.033
F000	2560
Index ranges	-29 ≤ h ≤29
	-17 ≤ k ≤ 13
	-26 ≤ l ≤ 22
R_1	0.0540
wR_2	0.0764

Table S2 Comparison of reported low-k MOFs (f≤0.1MHz) (ref 17a)		
MOF	k	Ref.
{(Zn(MeIM)$_2$}[a](ZIF-8)	≈2.4	[17a]
{[Sr$_2$(1,3-bdc)$_2$(H$_2$O)$_2$] ●H$_2$O}$_n$[b]	≈2.4	[15c]
{[Pb(Tab)2(4,4'-bipy)] (PF6)2 ●2MeCN}[c]	≈2.5	[16d]
{[Zn$_2$(L-trp)$_2$(bpe)$_2$(H$_2$O)$_2$] ●2H$_2$O●2NO$_3$}$_n$[d]	≈2.5	[16a]
{Mn$_2$(D-cam)$_2$(2-Hpao)$_4$}$_n$[e]	≈2.8	[16e]
{[Co$_2$(D-cam)$_2$-(3-abpt)$_2$(H$_2$O)$_3$]n●5n●H$_2$O}[e]	≈3.0	[16e]
{[Pb(Tab)$_2$]$_2$(PF$_6$)$_4$] ●2MeCN●DMF}[c]	≈3.0	[16d]
{[Ni$_2$(bbim)(H$_2$bbim)$_4$] ●2CH$_3$COO●CH$_3$CN}$_2$[f]	≈4.8	[16b]
[Sr(μ-BDC)]$_n$[g]	≈4.9	[17b]
{[(C$_3$H$_7$)$_2$NH2][Cr$_7$NiF$_8$(O$_2$C$_4$H$_5$)16]-MMA}	≈5.0	[17c]
[Zn(TMPT$_)2$]$_n$[h]	≈6.0	[17d]
[Cu$_2$(EBTC)]$_n$[i]	≈6.2	[17e]

[a] MeIM=2-methylimidazolate

[b] 1,3-bdc=benzene-1,3-dicarboxylicacid

[c] Tab=4-(trimethylammonio) benzenethiolate 4,4-bipy=4,4-bipyridine

[d] L-trp= L-tryptophan bpe=1,2-bis(4-pyridyl)ethylene

[e] D-cam= D(+)-camphoric acid 2-Hpao=2-pyridinealdoxime

3-abpt=4-amino-3,5-bis(3- pyridyl)-1,2,4-triazole

[f] H2bbim=bisbenzimidazole [g] BDC= benzene-1,4-dicarboxylate

[h] TMPT=5-(4-[(1H-1,2,4-triazol-1-yl)methyl]phenyl)-2H-tetrazole

[i] EBTC=1,1'-ethynebenzene-3,3',5,5'-tet-racarboxylate