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

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The design and synthesis of low dielectric constant (low-\(k\)) materials has been a subject of interest in terms of their potential for use in high performance electronic devices. Materials with extremely low-dielectric constants have been targeted as interlayer dielectrics (ILD) because they decrease the cross-talk noise, propagation delay, and power dissipation in microelectronics applications. The International Technology Roadmap for Semiconductors (ITRS), 2010–2020, projects 1.01, the partial replacement of solid network with air or vacuum appears to be the more intuitive and direct option to meet the demands for use as stable low-\(k\) materials.‡ MOFs have been extensively studied over the past decade for their potential for use in high performance electronic devices. However, these theoretical calculations did not take into account the orientational and ionic contributions to the molecular polarizability, which drastically contribute to the dielectric constant. These theoretical results encouraged us to search for new MOFs materials with experimentally ultra-low \(k\) values.

In this work, we report on the preparation of a MOF, \([\text{NH}_2(\text{CH}_3)_2][\text{Zn}_3(\text{bpdc})_4]\)·3DMF (1), which have 3D frameworks with high thermal stability (Fig. S1‡) and a ultra-low \(k\) values of its guest-free sample 1’. The 1’ possesses a very low \(k\) values of 1.80 (at 100 kHz) and high thermal stability at temperatures up to 360 °C (Fig. S2†), making it a potential candidate for use as an ILD. To the best of our knowledge, to date, the \(k\) values of 1’ is the lowest value for MOFs reported. Furthermore, compound 1 shows dielectric relaxation and anomalies in the temperature range of 35−140 °C. Dielectric relaxation and anomalies of 1 is related to reorientation of the dipole moments of surface absorbed water and guest DMF molecules, respectively.

The compound 1 was obtained from the solvothermal reaction of Zn(NO₃)₂·6H₂O, H₂bpdc and [NH₂(CH₃)₂]Cl in DMF. X-ray crystallographic analysis reveals that it crystallizes in the space group Pna₂₁.‡ The asymmetric unit contains of three

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‡ Crystal data for compound 1, space group Pna₂₁, \(a = 24.7046(12) \text{ Å}, b = 14.5230(9) \text{ Å}, c = 22.3879(12) \text{ Å}, \alpha = \beta = \gamma = 90.00°, V = 8032.4(8) \text{ Å}³, Z = 4, D₄ = 1.033 g cm⁻³, Mu = 0.939 mm (see ESI).
crystallographically distinct Zn$^{2+}$ ions, four deprotonated bpdc$^{2-}$ ligands, two [NH$_2$(CH$_3$)$_2$]$^+$ ions and three free DMF molecules. Three crystallographically independent Zn$^{2+}$ ions have two coordination modes (Fig. 1a). The Zn(1) and Zn(3) adopts a four-coordinated and formed slightly distorted tetrahedral geometry, and the Zn(2) adopts a six-coordinated geometry. O13 and O16 atoms originated from monodentate coordination of the bpdc$^{2-}$ ligands and the other oxygen atoms are coordinated by μ2-modes bpdc$^{2-}$ ligands to Zn$^{2+}$ ions. The shortest and longest Zn–O distance is 1.881(10) and 2.088(9) Å, respectively. Each Zn(2) atom is connected Zn(1) atom and Zn(3) atom by three bridged bidentate bpdc$^{2-}$ ligands to form trinuclear building blocks. As shown in Fig. 1b, trinuclear building blocks are further linked together by bpdc$^{2-}$ ligands make up the 3D anionic framework with two different channels, and the channels is occupied by [NH$_2$(CH$_3$)$_2$]$^+$ ions and disordered DMF guest molecules. Parallel to the ac plane, the monodentate bpdc$^{2-}$ ligands bridge trinuclear building blocks to afford layers stacking, and the layers are pillared by bidentate bpdc$^{2-}$ ligands to give rise to a regular 3D network (Fig. 1c), and channel dimensions is about 13 × 18 Å along the b-axis direction. The triangle cage was formed along the c-axis direction with small channel (Fig. 1d). Overall, two individual triangle cage are independent interpenetrated to form the entire framework of 1 (Fig. 1e). It should be noted that although the framework of 1 is interpenetration networks, it is still highly porous. After the removal of solvent molecules in the channels, the accessible volume of 1 is 40.2%.

The temperature dependent dielectric properties were investigated in the temperature range of 30–135 °C, and two-step dielectric relaxation were observed. As show in Fig. 2a, it is clear that compound 1 shows the first step dielectric relaxation in the temperature range of 30–80 °C. When 1 was heated from 30 to 37 °C, the dielectric constant progressive increased and reaches a maximum of 174.4 at $10^3$ Hz. Further increase in temperature results in the dielectric constant of 1 slowly decreasing and dielectric peak disappears. The first step dielectric relaxation is due to the relaxation of absorbed water molecules in the sample surface. The dielectric relaxation signal was not observed in the cooling process (from 95 °C to 30 °C) for losing surface water (Fig. 2b). The $\kappa$ value is directly related to the polarization phenomena. The higher the polarization, the greater the increase in $\kappa$ value will be. Usually, the MOF materials with low $\kappa$ value feature the reorientational motions of polar guest molecules being restricted at low temperature or frameworks solvent-free. However, for 1, the thermally assisted dynamical dipole motion due to polar DMF molecules is appeared. The guest molecules get enough excitation thermal energy to be able to obey the change under the external electric field more easily in the high temperature regime, and the reorientational dynamics of guest molecules is activated above 105 °C. This in return enhances their contribution to the polarization leading to an sharp increase of dielectric permittivity value. At $f = 10^5$ Hz, the dielectric constant reaches a maximum of 237, and then sharply decreased when the temperature increased. In the following cooling process, a very low $\kappa$ value was observed and no dielectric relaxation was occurred (Fig. 2c). The second step dielectric relaxation at different frequency are shown in Fig. 2d, which can be ascribed to the guest polar DMF reorientational motions. In addition, the dielectric loss values shows similar features in the selected frequency range (Fig. S3†).

Removing polar guest molecules from the framework may be decreases the polarization and the possibility of any type of hydrogen bonding or ionic interactions between the framework and guest molecular, hence, the $\kappa$ value will also decreases. The guest-free sample 1$^*$ were obtained by simply heating method. The PXRD patterns of the 1 match well with the 1$^*$ (Fig. S4†), thus demonstrating the phase were unaltered. The dielectric properties of guest-free sample 1$^*$ were investigated. As shown in Fig. 3, after removing the polar DMF molecules, a very low $\kappa$ value of 1.78 at 100 kHz at 40 °C with a low dielectric loss (0.005) was observed (Fig. S5†). It is very interesting as the temperature increase from 40 to 130 °C, $\kappa$ value increases very slowly. $\kappa$ value is 1.99 at 130 °C. With the ac electric field frequency increasing, the $\kappa$ value slightly decrease (Fig. 3a). It is noteworthy that, to date, dielectric investigations of MOFs have received relatively little attention, although a few exciting examples have been reported. Only a limited number of MOFs have been reported to

![Figure 1](image1.png)

**Fig. 1** Structure of 1 (a) trinuclear metal cluster building blocks; (b) 3D anionic framework with two different channels; (c) regular channel along the b-axis direction; (d) the triangle cage along the c-axis direction; (e) two independent interpenetrated triangle cage.
Conclusions

In conclusion, we have presented a 3D MOFs [NH$_2$(CH$_3$)$_2$]$_2$-Zn$_3$(bpdc)$_4$:3DMF (I) and its guest-free framework (I'). I possesses two types of cavities, which are occupied by counter ions and the polar solvents DMF, and shows two-step dielectric relaxations which is related to reorientation of the dipole moment of surface absorbed water and guest DMF molecules. Two step relaxation were not observed in guest-free framework I'. I' shows quite low $\kappa$ value (to the best of our knowledge, the $\kappa$ values of I' is the lowest value for MOFs reported to date) and high thermal stability. The ultra-low $\kappa$ value exhibits no significant change over a wide temperature range (40–130 °C). The ultra-low dielectric constant of I' can be attributed to the highly porous and small counter ions in the channels. The foregoing results discussed in this work provide an effective path towards achieving remarkable new applications for dielectric MOFs in the future.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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