Electronic Supplementary Material (ESI) for Chemical Communications

Temperature-dependent Conductivity of $Emim^+$ ($Emim^+$ = 1-ethyl-3-methyl imidazolium) Confined in Channels of a Metal–organic Framework

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Measure Method and Apparatus. All reagents were of commercial origin and were used as received. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectra were recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curves were prepared on a SDT Q600 Thermal Analyzer. The DSC measurement was carried out with a NETZSCH DSC 200F3 analyzer. The X-ray powder diffractometry (XRPD) study was performed on Panalytical X-Pert pro diffractometer with Cu-Kα radiation. AC impedance and dielectric properties measures were performed by use of 2-wire mode on the WAYNE KERR 6500B High Frequency LCR Meter . The frequency range for AC impedance measures is from 1 KHz to 120 MHz. The amplitude of AC source is 1V. The crystal sizes for measures along [110] direction and c axis are 1.05 mm × 0.69 mm × 0.78 mm and 0.37 mm × 0.56 mm × 0.30 mm, respectively. Two test lines were fixed on the sample via electric glue and connected with the apparatus. The temperature-controlled apparatus is Sigma/Delta instrument.

Synthesis of compound 1. 0.249 g $Co(OOCCH_3)_2{\cdot}4H_2O$ and 0.165 g 2,2',4,4'-biphenyl tetracarboxylic acid were mixed in 1.2g 1-ethyl-3-methyl imidazolium bromide. Then the mixture was subsequently sealed to a 25 mL Teflon-lined Parr at 160 ^oC for about a week and cooled to room temprature at a rate of $3^oC{\cdot}h^{-1}$. The purple crystals were obtained with 32.5% yield (based on 2,2',4,4'-biphenyl tetracarboxylic sodium). Anal. Calcd. (Found) for $C_{50}H_{45}N_6O_{16}NaCo_2$ (**1**): C, 53.25(52.85); N, 7.45(7.26); H, 3.99(4.13). IR Spectra for **1** (KBr, cm^{-1}): 1612.1(s), 1542.1(s), 1381.5(s), 1434.1(s), 1172.9(s), 3102.9(m), 1204.3(m), 1047.3(m), 783.1(m), 724.7(m), 848.8(w), 783.1(w), 525.1(w).

Single-crystal X-ray structure determination: Data collections were performed on a Rigaku R-AXIS RAPID IP diffractometer at 173 K for **1.** Empirical absorption corrections were applied. The structure was solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. The hydrogen atoms of organic ligand were generated geometrically (C-H, 0.96 Å; N-H, 0.90 Å).

Crystal data for compound 1 at 173 K: $[Co_2Na(bptc)_2][EMIm]_3$, monoclinic, space group $C2/c$, a = 21.518(4) Å, b = 11.737(2) Å, c = 19.301(4) Å, β = 94.14(3)°, V = 4861.7(17) Å^3, Z = 4, ρ_{calcd} = 1.539 g·cm^{-3}, Mr = 1126.77, Of the 19930 reflections collected, 4774 are independent (R_{int} = 0.0470) and 4092 are observed ($I > 2\sigma(I)$). On the basis of all these data and 344 refined parameters, R_1(obs.) = 0.0533 and wR_2(all data) = 0.1595 were obtained.

Crystal data for compound 1 at RT: $[Co_2Na(bptc)_2][EMIm]_3$, monoclinic, space group $C2/c$, a = 21.5119(5) Å, b = 11.8062(3) Å, c = 19.4114(5) Å, β = 94.591(2)°, V = 4914.2(2) Å^3, Z = 4, ρ_{calcd} = 1.523 g·cm^{-3}, Mr = 1126.77, Of the 17459 reflections collected, 4828 are independent (R_{int} = 0.0313) and 4152 are observed ($I > 2\sigma(I)$). On the basis of all these data and 344 refined parameters, R_1(obs.) = 0.0504 and wR_2(all data) = 0.1113 were obtained.

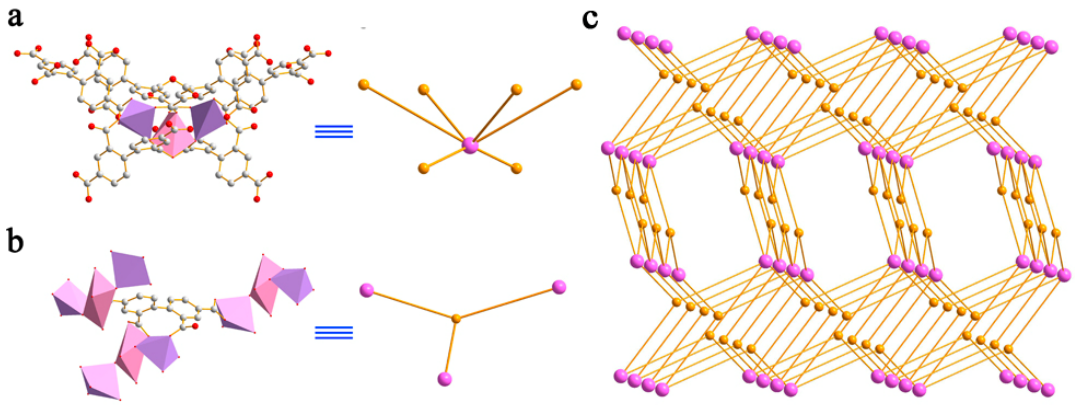

Fig. S1. (a) Coordination geometry of $[Co_2Na(O_2CR)_6]$ unit in 1; (b) The bptc^{4-} ligand serve as 3-connected nodes; and (c) Schematic representation of the topology in **1**. The yellow ball represents the bptc^{4-} ligand, while the purple ball represents the $[Co_2Na(O_2CR)_6]$ unit.

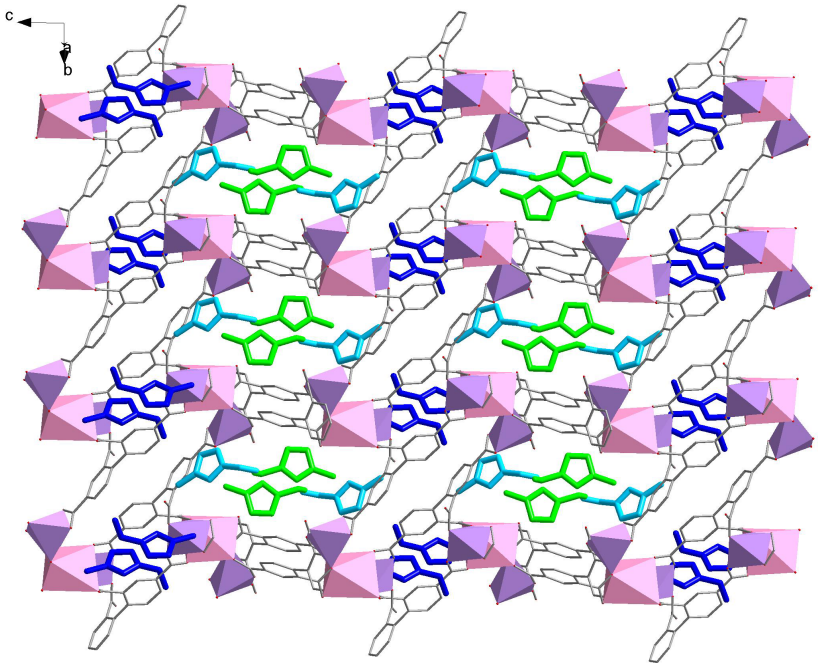

Fig. S2 Polyhedral view of the structure of **1** along [110] direction.

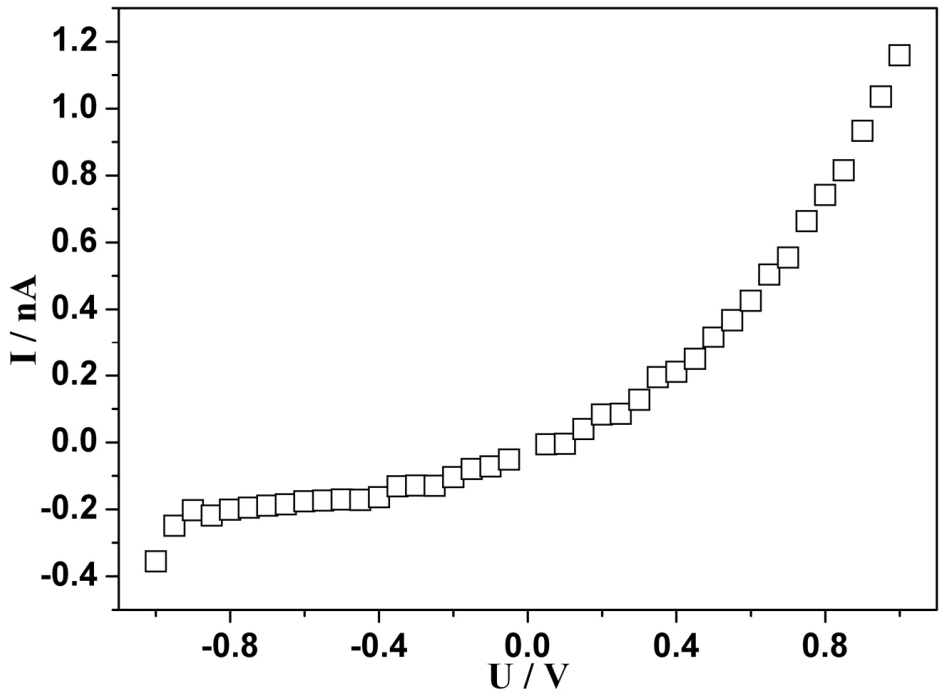

Fig. S3 DC plot of pellet with the size 2.38 mm×3.04 mm×0.31 mm in the direct electric field from -1 to 1 V.

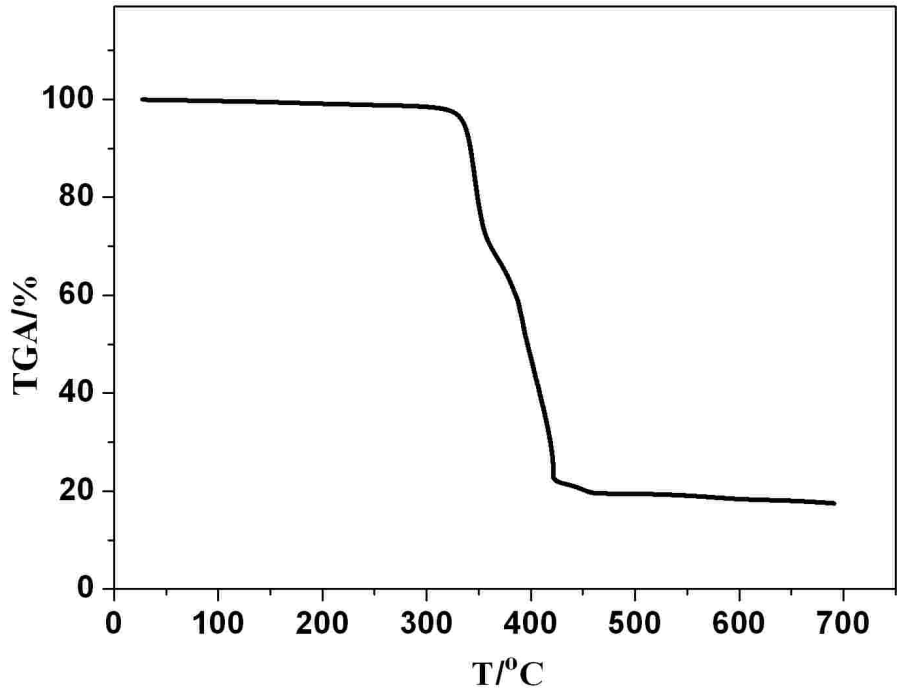

Fig. S4 TGA curve for compound **1** at the range from room temperature to 700°C.

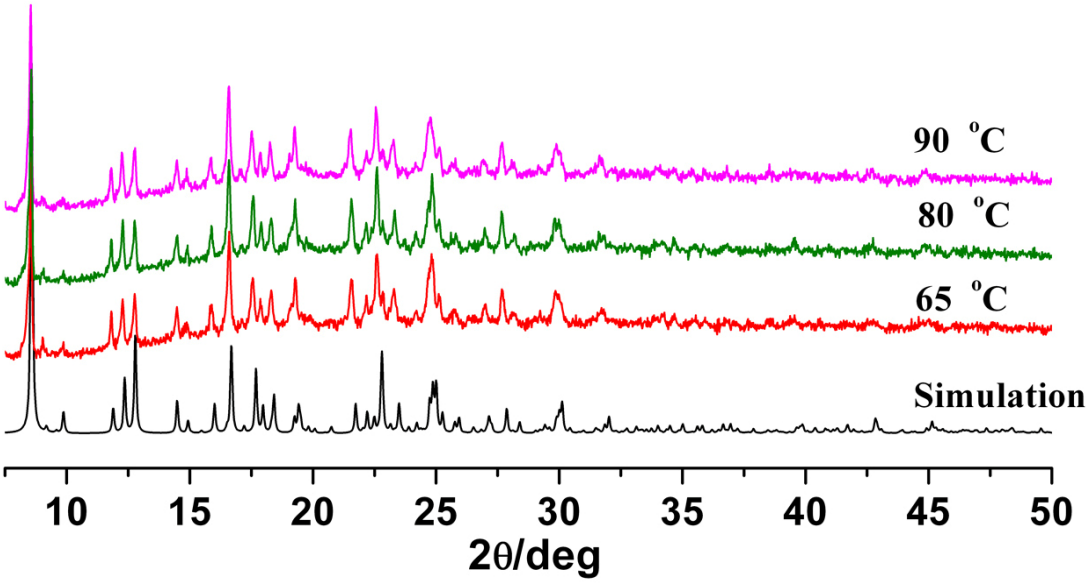

Fig. S5 PXRD patterns of **1** at 65°C, 80°C, 90°C and the corresponding simulation according to single crystal structural determinations.