

Electronic supplementary information (ESI)

Two hybrid transition metal triphosphonates decorated with tripodal imidazole ligand: synthesis, structures and properties

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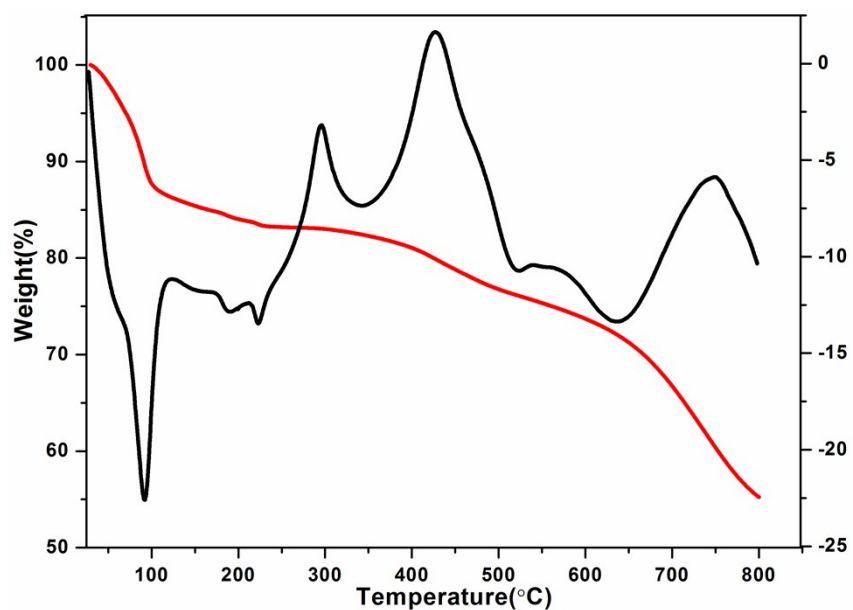


Fig. S1 TGA (thermogravimetric analysis, red) and DTA (differential thermal analysis, black) curves for **1**.

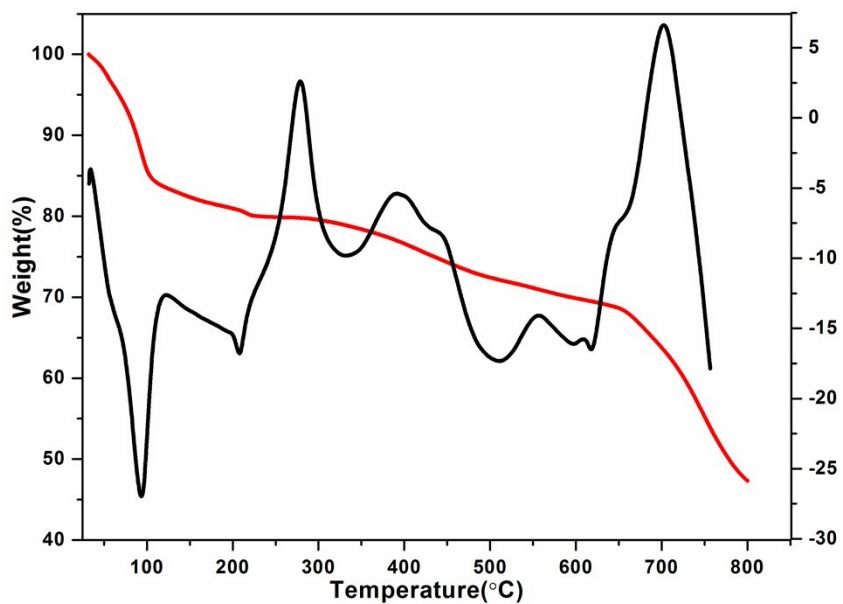


Fig. S2 TGA (red) and DTA (black) curves for **2**.

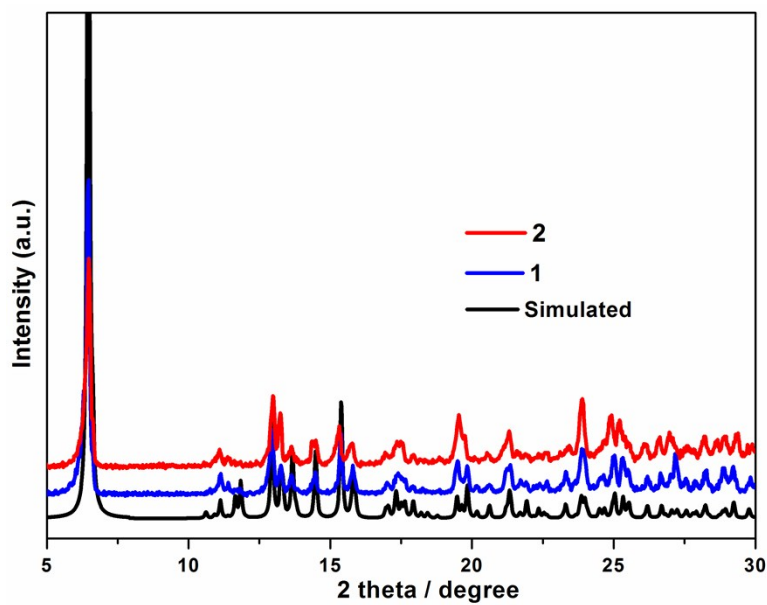


Fig. S3 PXRD patterns of **1** and **2**.

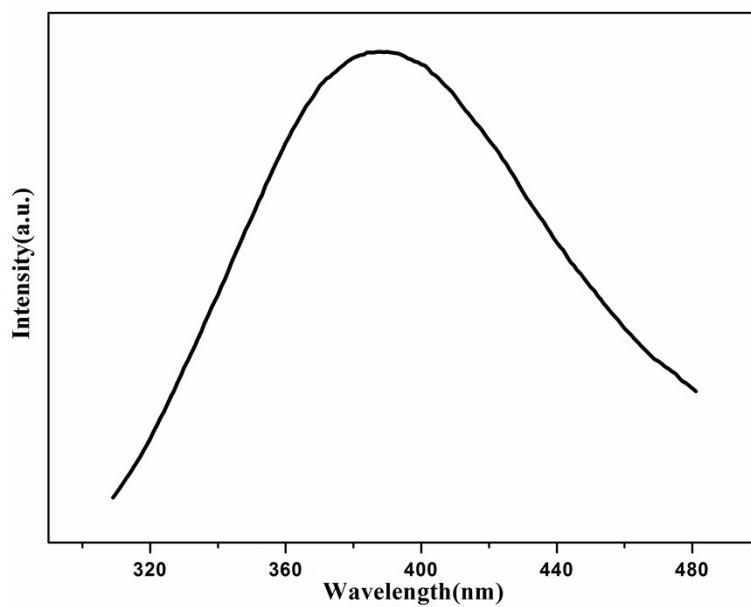


Fig. S4 Emission spectra of tib ligand in the solid state at room temperature with excitation at 260 nm.

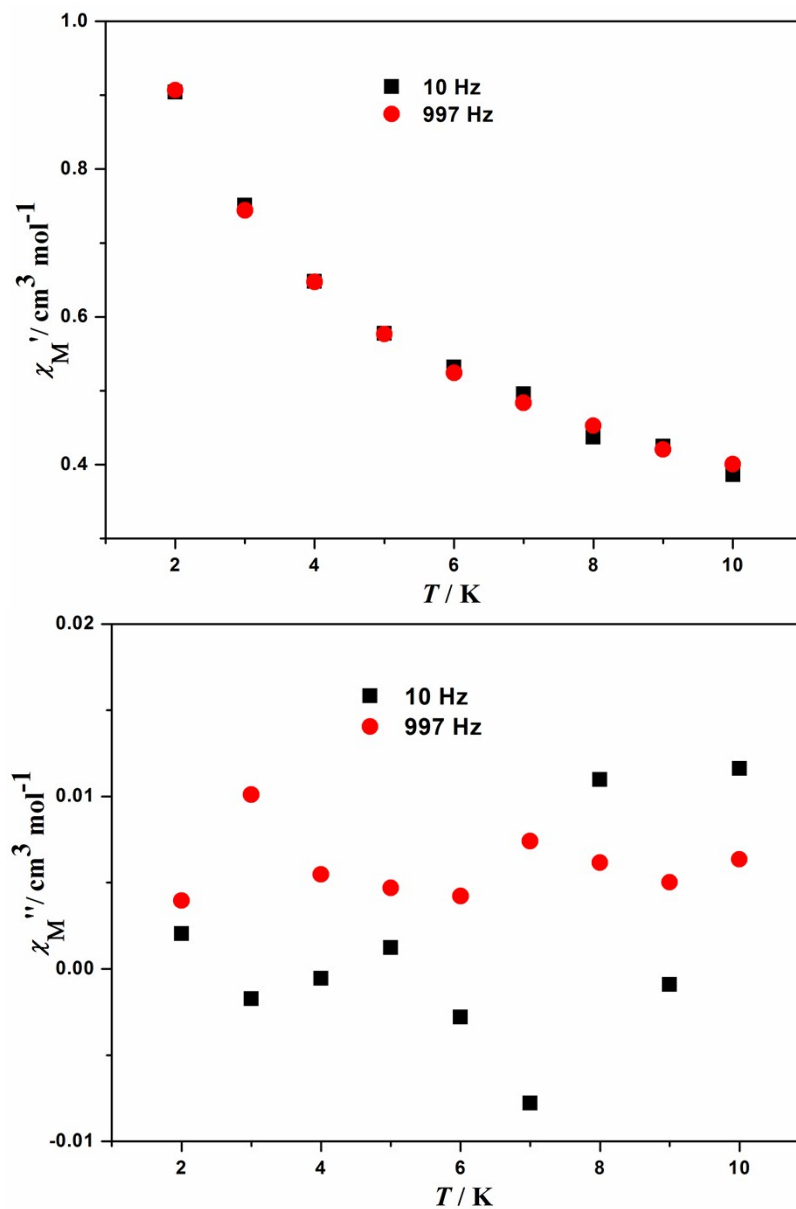


Fig. S5 Temperature dependence of the AC χ_M at 10 and 997 Hz with zero DC field for **2**.

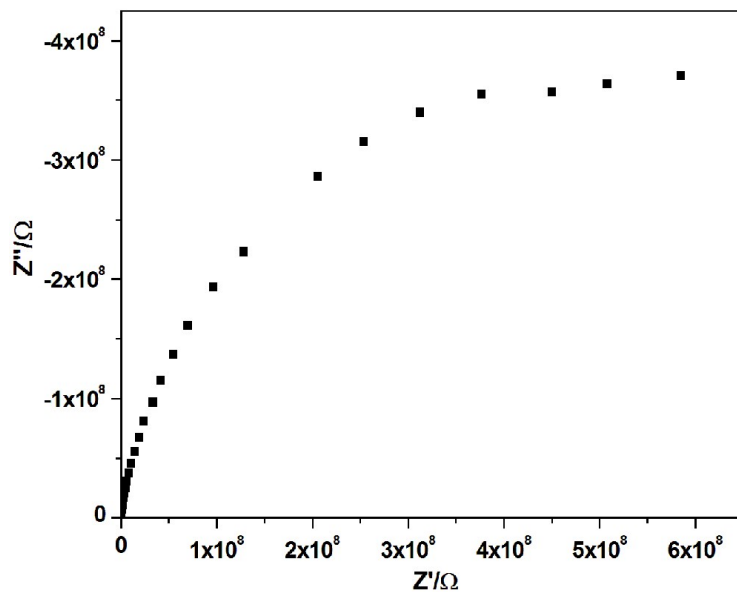


Fig. S6 Nyquist plot of compound **2** at 20°C and 30% relative humidity.

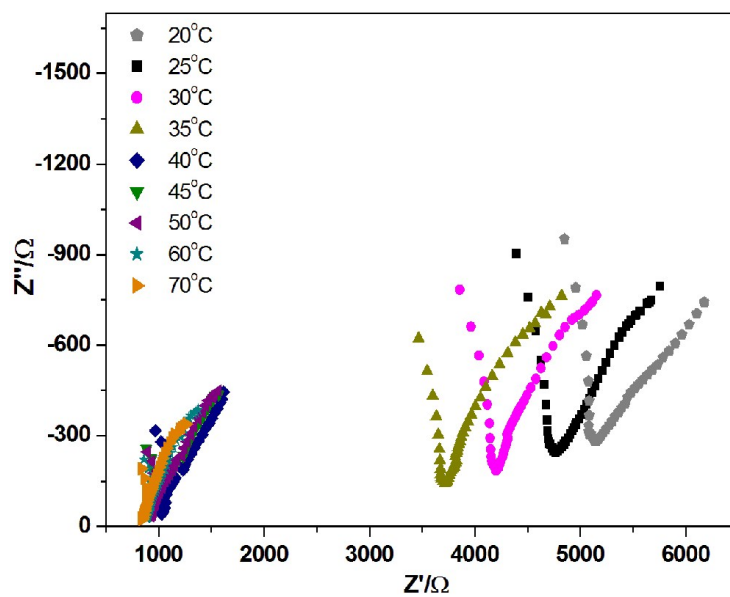


Fig. S7 The variable-temperature ac impedance spectra of **2** at 100% relative humidity.

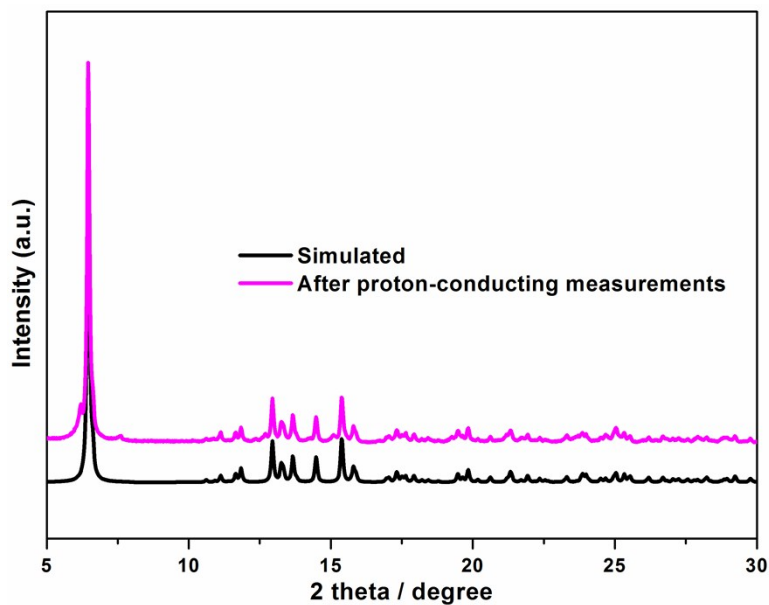


Fig. S8 The PXRD patterns of **2** after proton-conducting measurements.

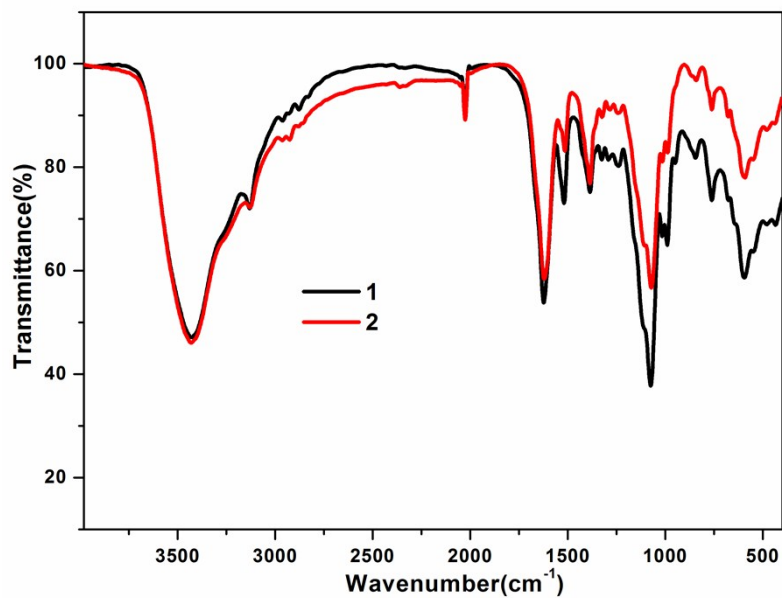


Fig. S9 IR patterns of **1** and **2**.

Table S1. Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|---------------------|-----------|---------------------|-----------|
| Zn(1)-O(7)#6 | 1.926(2) | Zn(2)-N(7) | 2.322(3) |
| Zn(1)-O(8)#5 | 1.938(2) | Zn(2)-N(2)#1 | 2.058(3) |
| Zn(1)-O(2) | 1.945(2) | Zn(3)-O(1) | 1.929(2) |
| Zn(1)#4-O(7) | 1.926(2) | Zn(3)#3-O(4) | 1.940(2) |
| Zn(1)#5-O(8) | 1.938(2) | Zn(3)#4-O(5) | 1.963(2) |
| Zn(1)-N(1) | 2.004(3) | Zn(3)-O(4)#3 | 1.940(2) |
| Zn(2)-O(9) | 1.970(2) | Zn(3)-O(5)#6 | 1.963(2) |
| Zn(2)-O(6) | 2.034(2) | Zn(3)-N(3)#7 | 1.996(3) |
| Zn(2)-O(3) | 2.010(2) | Zn(3)#2-N(3) | 1.996(3) |
| Zn(2)#1-N(2) | 2.058(3) | | |
| O(7)#6-Zn(1)-O(8)#5 | 114.22(9) | O(6)-Zn(2)-N(2)#1 | 96.78(1) |
| O(7)#6-Zn(1)-O(2) | 109.91(1) | O(9)-Zn(2)-N(7) | 84.72(8) |
| O(8)#5-Zn(1)-O(2) | 104.46(1) | O(3)-Zn(2)-N(7) | 83.37(8) |
| O(7)#6-Zn(1)-N(1) | 98.73(1) | O(6)-Zn(2)-N(7) | 82.88(8) |
| O(8)#5-Zn(1)-N(1) | 107.33(1) | N(2)#1-Zn(2)-N(7) | 175.12(9) |
| O(2)-Zn(1)-N(1) | 122.60(1) | O(1)-Zn(3)-O(4)#3 | 109.37(1) |
| O(9)-Zn(2)-O(3) | 122.99(9) | O(1)-Zn(3)-O(5)#6 | 116.42(1) |
| O(9)-Zn(2)-O(6) | 117.80(1) | O(4)#3-Zn(3)-O(5)#6 | 104.28(1) |
| O(3)-Zn(2)-O(6) | 115.61(1) | O(1)-Zn(3)-N(3)#7 | 102.87(1) |
| O(9)-Zn(2)-N(2)#1 | 99.69(1) | O(4)#3-Zn(3)-N(3)#7 | 114.14(1) |
| O(3)-Zn(2)-N(2)#1 | 92.43(1) | O(5)#6-Zn(3)-N(3)#7 | 110.14(1) |

^aSymmetry codes: #1: -x+2, -y+1, -z; #2: x, y+1, z-1; #3: -x+1, -y, -z+1; #4: x-1, y, z; #5: -x+1, -y+1, -z+1; #6: x+1, y, z; #7: x, y-1, z+1.

Table S2. Selected bond lengths (Å) and angles (°) for **2**

| | | | |
|--------------|-----------|---------------------|-----------|
| Co(1)-O(9) | 1.981(2) | Co(2)-O(1)#3 | 1.969(2) |
| Co(1)-O(6) | 2.000(2) | Co(2)-N(7)#4 | 2.021(3) |
| Co(1)-O(3) | 2.028(2) | Co(3)-O(7)#3 | 1.933(2) |
| Co(1)-N(5)#1 | 2.080(3) | Co(3)-O(8)#5 | 1.946(2) |
| Co(1)-N(1) | 2.268(3) | Co(3)-O(5) | 1.952(2) |
| Co(2)-O(4) | 1.940(2) | Co(3)-N(2) | 2.016(3) |
| Co(2)-O(2)#2 | 1.953(2) | | |
| 123.23(1) | 123.23(1) | O(4)-Co(2)-O(1)#3 | 117.65(1) |
| 117.33(1) | 117.33(1) | O(2)#2-Co(2)-O(1)#3 | 105.55(1) |
| 116.64(1) | 116.64(1) | O(4)-Co(2)-N(7)#4 | 100.75(1) |
| 98.03(1) | 98.03(1) | O(2)#2-Co(2)-N(7)#4 | 112.97(1) |
| 92.14(1) | 92.14(1) | O(1)#3-Co(2)-N(7)#4 | 108.95(1) |
| 96.57(1) | 96.57(1) | O(7)#3-Co(3)-O(8)#5 | 116.11(1) |
| 85.64(9) | 85.64(9) | O(7)#3-Co(3)-O(5) | 109.92(1) |
| 84.07(9) | 84.07(9) | O(8)#5-Co(3)-O(5) | 105.42(1) |
| 83.52(9) | 83.52(9) | O(7)#3-Co(3)-N(2) | 98.19(1) |
| 175.78(1) | 175.78(1) | O(8)#5-Co(3)-N(2) | 106.16(1) |
| 111.17(1) | 111.17(1) | O(5)-Co(3)-N(2) | 121.57(1) |

^aSymmetry codes: #1: -x+1, -y+1, -z; #2: -x, -y, -z+1; #3: x+1, y, z; #4: x, y-1, z+1; #5: -x, -y+1, -z+1; #6: x, y+1, z-1; #7: x-1, y, z.