Synthesis, Crystal Structure, and Proton Conductivity of 1D, 2D, and 3D Zirconium Phosphonates Based on Glyphosate and Glyphosine

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Supporting Information

Table S1. Fractional atomic coordinates and isotropic atomic displacement parameters for **1**.

Atom	x/*a*	y/*b*	z/*c*	U_{iso}x100
Zr	0.8231(3)	0.0573(1)	0.6739(6)	1.8(1)
F	0.613(1)	0.0773(4)	0.583(2)	1.5(1)
O1	0.503(2)	-0.1963(4)	0.876(3)	1.5(1)
O2	0.750(2)	-0.1699(4)	1.103(3)	1.5(1)
C3	0.609(2)	-0.1637(4)	0.980(4)	1.5(1)
C4	0.541(2)	-0.1223(5)	0.984(4)	1.5(1)
N5	0.668(2)	-0.0933(4)	1.128(3)	1.5(1)
C6	0.611(2)	-0.0482(5)	1.048(3)	1.5(1)
P7	0.7782(6)	-0.0093(2)	1.173(1)	1.5(1)
O8	0.771(1)	0.0233(4)	0.953(2)	1.5(1)
O9	0.942(1)	-0.0346(4)	1.225(3)	1.5(1)
O10	0.758(1)	0.0123(3)	1.404(2)	1.5(1)
O11	0.877(2)	0.2502(4)	0.836(3)	1.5(1)
O12	0.761(2)	0.1974(4)	0.686(3)	1.5(1)
C13	0.808(2)	0.2273(4)	0.641(3)	1.5(1)
C14	0.840(2)	0.2323(4)	0.376(3)	1.5(1)
N15	0.819(1)	0.1969(5)	0.249(3)	1.5(1)
C16	0.986(2)	0.1792(4)	0.264(4)	1.5(1)
P17	0.9970(7)	0.1163(2)	0.238(1)	1.5(1)
O18	0.897(1)	0.0964(4)	0.417(2)	1.5(1)
O19	0.917(1)	0.1038(4)	-0.034(2)	1.5(1)
O20	1.190(2)	0.1009(4)	0.334(3)	1.5(1)

Table S2: Bond lengths (Å) for **1.**

Bond	Length/Å	Bond	Length/Å
Zr-F	1.853(9)	P17-O18	1.58(1)
Zr-O8	2.00(1)	P17-O19	1.48(1)
Zr-O9	2.078(9)	P17-O20	1.67(1)
Zr-O10	2.03(1)	P17-C16	2.07(1)
Zr-O18	2.09(1)	C16-N15	1.53(2)
Zr-O19	2.17(1)	N15-C14	1.33(2)
P7-O8	1.57(1)	C14-C13	1.51(1)
P7-O9	1.59(1)	C13-O11	1.28(1)
P7-O10	1.47(1)	C13-O12	1.11(1)
P7-C6	1.90(1)	H-bonds	
C6-N5	1.58(2)	N5···O20	2.79(2)
N5-C4	1.49(2)	N5···O20	3.03(2)
C4-C3	1.48(1)	N15···O1	2.66(2)
C3-O2	1.23(1)	N15···O12	2.90(2)
C3-O1	1.41(1)	O1···O11	2.45(2)

Table S3: Bong angles (°) for **1**.

Angle	Amplitude/°	Angle	Amplitude/°
F-Zr-O8	89.5(5)	O10-P7-C6	111.7(6)
F-Zr-O9	179.624(4)	P7-C6-N5	112.7(7)
F-Zr-O10	90.7(5)	C6-N5-C4	109.2(6)
F-Zr-O18	93.3(5)	N5-C4-C3	110.7(8)
F-Zr-O19	94.9(5)	C4-C3-O2	118.6(6)
O8-Zr-O9	90.3(4)	C4-C3-O1	118.8(8)
O8-Zr-O10	92.6(4)	O1-C3-O2	121.5(6)
O8-Zr-O18	173.4(5)	O18-P17-O19	106.8(5)
O8-Zr-O19	88.7(5)	O18-P17-O20	110.3(6)
O9-Zr-O10	89.0(4)	O18-P17-C16	109.2(6)
O9-Zr-O18	86.8(5)	O19-P17-O20	111.9(6)
O9-Zr-O19	85.5(4)	O19-P17-C16	108.8(6)
O10-Zr-O18	93.3(5)	O20-P17-C16	109.7(5)
O10-Zr-O19	174.3(5)	P17-C16-N15	115.4(7)
O18-Zr-O19	85.2(4)	C16-N15-C14	107.5(7)
O8-P7-O9	110.1(6)	N15-C14-C13	109.9(8)
O8-P7-O10	107.4(6)	C14-C13-O12	117.5(7)
O8-P7-C6	108.9(6)	C14-C13-O11	121.7(7)
O9-P7-O10	113.7(6)	O11-C13-O12	117.3(9)
O9-P7-C6	105.0(5)		

Table S4. Fractional atomic coordinates and isotropic atomic displacement parameters for **2**.

Atom	x/*a*	y/*b*	z/*c*	U_{iso}x100
Zr1	0.7278(9)	0.1024(3)	0.4073(3)	1.43(7)
Zr2	-0.5	1.0	0.0	1.43(7)
P1	-0.018(2)	0.8570(6)	0.0372(6)	1.43(7)
O2	0.265(3)	0.903(1)	0.042(1)	1.43(7)
O3	-0.188(2)	0.938(1)	0.036(1)	1.43(7)
O4	-0.105(4)	0.749(1)	-0.052(1)	1.43(7)
C5	-0.059(3)	0.833(2)	0.138(1)	1.43(7)
N6	0.145(2)	0.781(1)	0.1670(9)	1.43(7)
C7	0.112(3)	0.782(1)	0.266(1)	1.43(7)
P8	0.199(2)	0.9234(6)	0.3672(5)	1.43(7)
O9	-0.002(3)	1.002(1)	0.360(1)	1.43(7)
O10	0.200(3)	0.907(1)	0.4609(8)	1.43(7)
O11	0.457(2)	0.9749(9)	0.3637(9)	1.43(7)
C12	0.120(4)	0.660(1)	0.097(1)	1.43(7)
C13	0.341(3)	0.606(1)	0.118(1)	1.43(7)
O14	0.304(3)	0.507(1)	0.102(1)	1.43(7)
O15	0.549(4)	0.664(2)	0.167(1)	1.43(7)
P16	0.280(2)	0.2880(6)	0.4792(5)	1.43(7)
O17	0.361(3)	0.362(1)	0.582(1)	1.43(7)
O18	0.020(2)	0.232(1)	0.465(1)	1.43(7)
O19	0.465(3)	0.208(1)	0.4527(9)	1.43(7)
C20	0.237(3)	0.376(2)	0.403(1)	1.43(7)
N21	0.328(3)	0.339(1)	0.3164(9)	1.43(7)
C22	0.266(3)	0.228(1)	0.262(1)	1.43(7)
P23	0.564(2)	0.1899(6)	0.2310(5)	1.43(7)
O24	0.762(3)	0.302(1)	0.257(1)	1.43(7)
O25	0.662(3)	0.127(1)	0.2863(8)	1.43(7)
O26	0.537(3)	0.119(1)	0.1304(7)	1.43(7)
C27	0.275(4)	0.408(2)	0.256(1)	1.43(7)
C28	0.083(3)	0.488(2)	0.288(1)	1.43(7)
O29	0.018(4)	0.508(2)	0.362(1)	1.43(7)
O30	0.039(3)	0.548(2)	0.246(1)	1.43(7)
Ow	0.575(4)	0.373(2)	0.059(2)	1.43(7)

Table S5. Bond lengths (Å) for **2.**

Bond	Length/Å	Bond	Length/Å
Zr1-O9	2.07(1)	C13-O15	1.29(2)
Zr1-O10	2.09(1)	P16-O17	1.52(1)
Zr1-O11	1.99(1)	P16-O18	1.48(1)
Zr1-O18	2.08(1)	P16-O19	1.50(1)
Zr1-O19	2.07(1)	P16-C20	1.96(1)
Zr1-O25	2.03(1)	C20-N21	1.41(1)
Zr2-O2	2.056(9)	P23-O24	1.65(1)
Zr2-O3	2.045(9)	P23-O25	1.49(1)
Zr2-O26	2.026(9)	P23-O26	1.48(1)
P1-O2	1.57(1)	P23-C22	1.78(1)
P1-O3	1.48(1)	C22-N21	1.39(1)
P1-O4	1.57(1)	N21-C27	1.56(1)
P1-C5	1.75(1)	C27-C28	1.54(1)
C5-N6	1.58(2)	C28-O29	1.18(1)
P8-O9	1.59(1)	C28-O30	1.24(1)
P8-O10	1.55(1)	H-bonds	
P8-O11	1.51(1)	O4···Ow	2.85(3)
P8-C7	1.93(1)	O14···O30	2.69(2)
C7-N6	1.56(1)	O14···Ow	2.36(3)
N6-C12	1.55(1)	O17···O29	2.79(2)
C12-C13	1.51(2)	O24···O29	2.76(2)
C13-O14	1.24(2)		

Table S6. Bong angles (°) for **2**.

Angle	Amplitude/°	Angle	Amplitude/°
O9-Zr1-O10	90.6(4)	O9-P8-O11	108.7(6)
O9-Zr1-O11	91.5(5)	O10-P8-O11	110.0(6)
O9-Zr1-O18	87.6(5)	P8-C7-N6	114.2(7)
O9-Zr1-O19	177.5(6)	C5-N6-C7	107.7(7)
O9-Zr1-O25	92.9(5)	C5-N6-C12	109.3(8)
O10-Zr1-O11	91.0(4)	C7-N6-C12	108.3(8)
O10-Zr1-O18	83.5(5)	N6-C12-C13	111.2(8)
O10-Zr1-O19	91.1(5)	C12-C13-O14	118.5(8)
O10-Zr1-O25	174.5(6)	C12-C13-O15	120.4(9)
O11-Zr1-O18	174.3(6)	O14-C13-O15	120.0(8)
O11-Zr1-O19	90.3(5)	O17-P16-O18	110.0(6)
O11-Zr1-O25	93.2(5)	O17-P16-O19	107.7(7)
O18-Zr1-O19	90.7(4)	O17-P16-C20	110.2(7)
O18-Zr1-O25	92.4(5)	O18-P16-O19	111.4(6)
O19-Zr1-O25	85.2(4)	O18-P16-C20	101.4(6)
O2-Zr2-O3	92.2(3)	O19-P16-C20	116.0(5)
O2-Zr2-O3	87.8(3)	P16-C20-N21	116.9(7)
O2-Zr2-O26	89.0(4)	C22-P23-O24	108.1(6)
O2-Zr2-O26	91.0(4)	C22-P23-O25	109.6(6)
O3-Zr2-O26	92.1(4)	C22-P23-O26	110.5(6)
O3-Zr2-O26	87.9(4)	O24-P23-O25	109.4(6)
O2-P1-O3	111.2(6)	O24-P23-O26	111.6(6)
O2-P1-O4	111.0(6)	O25-P23-O26	107.6(2)
O2-P1-C5	111.0(6)	P23-C22-N21	102.3(7)
O3-P1-O4	109.2(7)	C20-N21-C22	115.9(8)
O3-P1-C5	104.6(6)	C20-N21-C27	114.8(6)
O4-P1-C5	109.6(7)	C22-N21-C27	110.6(9)
P1-C5-N6	112.5(6)	N21-C27-C28	115.2(6)
C7-P8-O9	110.6(6)	C27-C28-O29	120.5(8)
C7-P8-O10	107.5(6)	C27-C28-O30	118.7(7)
C7-P8-O11	110.2(5)	O29-C28-O30	119(1)
O9-P8-O10	109.9(6)		

Table S7. Fractional atomic coordinates and anisotropic atomic displacement parameters for **3**.

Atom	x/*a*	y/*b*	z/*c*	U_{ani}x100
Zr1	0.5	0.5	0.5	0.94(2)
P2	0.4912(2)	0.85359(9)	0.00393(7)	1.31(2)
P3	0.3252(2)	0.55243(7)	0.24535(8)	1.57(2)
O4	0.4846(5)	0.8087(2)	-0.0974(2)	2.30(7)
O5	0.2422(5)	0.8929(2)	0.0240(2)	1.84(6)
O6	0.6982(5)	0.9222(2)	0.0213(2)	1.98(6)
O7	0.0696(5)	0.5933(2)	0.2572(2)	2.59(7)
O8	0.2997(6)	0.4794(2)	0.1689(2)	2.28(7)
O9	0.4559(5)	0.5264(2)	0.3471(2)	2.10(6)
C10	0.5791(7)	0.7752(2)	0.1055(3)	1.53(8)
C11	0.5177(8)	0.6429(3)	0.2071(3)	1.90(8)
N12	0.4231(6)	0.6932(2)	0.1129(2)	1.35(7)
C13	0.4166(7)	0.6339(3)	0.0212(3)	1.77(8)
C14	0.1541(8)	0.6182(3)	-0.0201(4)	2.7(1)
O15	-0.0147(6)	0.6568(3)	0.0132(3)	4.8(1)
O16	0.1392(6)	0.5607(3)	-0.0934(3)	4.6(1)
Ow	0.1336(8)	0.8000(2)	0.2417(3)	4.6(1)

Table S8. Bond lengths (Å) for **3.**

Bond	Length/Å	Bond	Length/Å
Zr1-O5	2.079(3)	C11-N12	1.508(5)
Zr1-O6	2.057(3)	N12-C13	1.503(5)
Zr1-O9	2.060(3)	C13-C14	1.502(6)
P2-O4	1.501(3)	C14-O15	1.207(5)
P2-O5	1.527(3)	C14-O16	1.294(5)
P2-O6	1.525(3)	H-bonds (D-H···A)	
P2-C10	1.816(4)	O7-H7···O4	1.24(5), 1.28(5)
P3-O7	1.544(3)	N12-H12···Ow	0.99(3), 2.18(5)
P3-O8	1.487(3)	O16-H16···O7	1.0(1), 1.9(1)
P3-O9	1.517(3)	Ow-Hw1···O8	1.00(3), 1.95(4)
P3-C11	1.813(4)	Ow-Hw2···O4	0.99(5), 1.89(5)
C10-N12	1.500(5)		

Table S9. Bond angles (°) for **3.**

Angle	Amplitude/°	Angle	Amplitude/°
O5-Zr1-O6	92.9(1)	O7-P3-O9	111.3(2)
O5-Zr1-O6	87.2(1)	O7-P3-C11	106.7(2)
O5-Zr1-O9	90.9(1)	O8-P3-O9	115.2(2)
O5-Zr1-O9	89.1(1)	O8-P3-C11	112.0(2)
O6-Zr1-O9	90.5(1)	O9-P3-C11	101.9(2)
O6-Zr1-O9	89.5(1)	P3-C11-N12	116.3(3)
O4-P2-O5	112.6(2)	C10-N12-C11	108.1(3)
O4-P2-O6	112.9(2)	C10-N12-C13	113.4(3)
O4-P2-C10	111.1(2)	C11-N12-C13	111.0(3)
O5-P2-O6	111.9(2)	N12-C13-C14	109.6(3)
O5-P2- C10	107.1(2)	C13-C14-O15	121.8(4)
O6-P2- C10	100.5(2)	C13-C14-O16	111.5(4)
P2-C10-N12	117.6(3)	O15-C14-O16	126.7(4)
O7-P3-O8	109.5(2)		

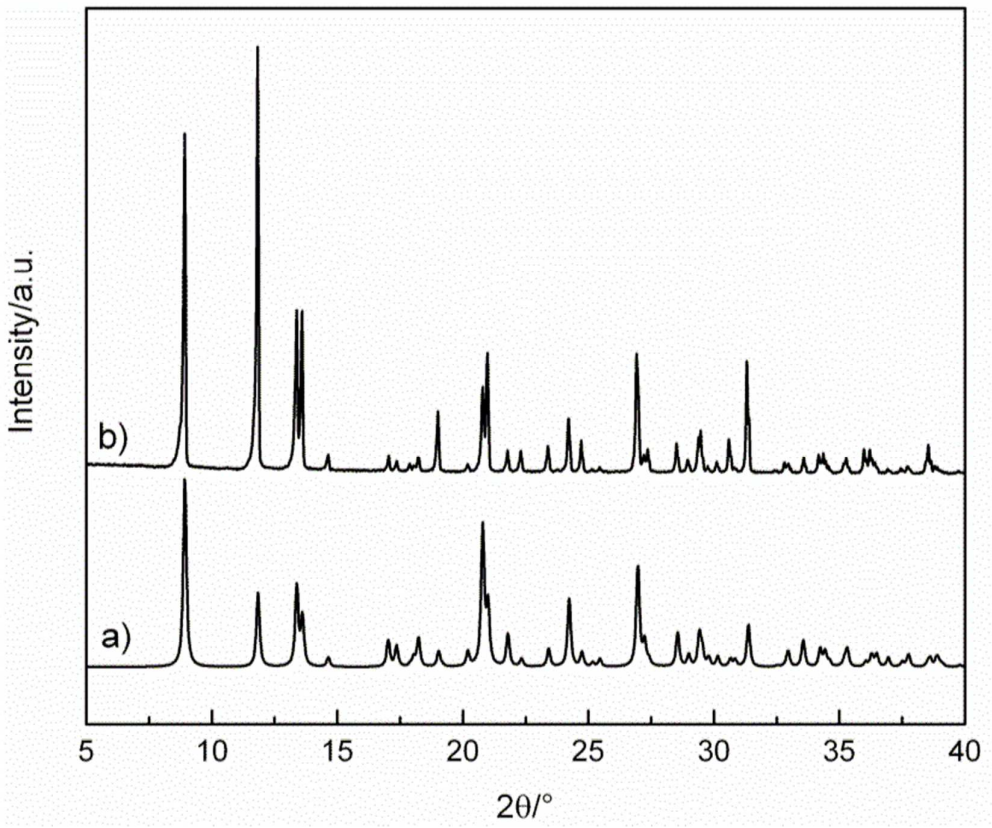

Figure S1. Comparison between the simulated (a) and the experimental (b) PXRD spectra of **3.**

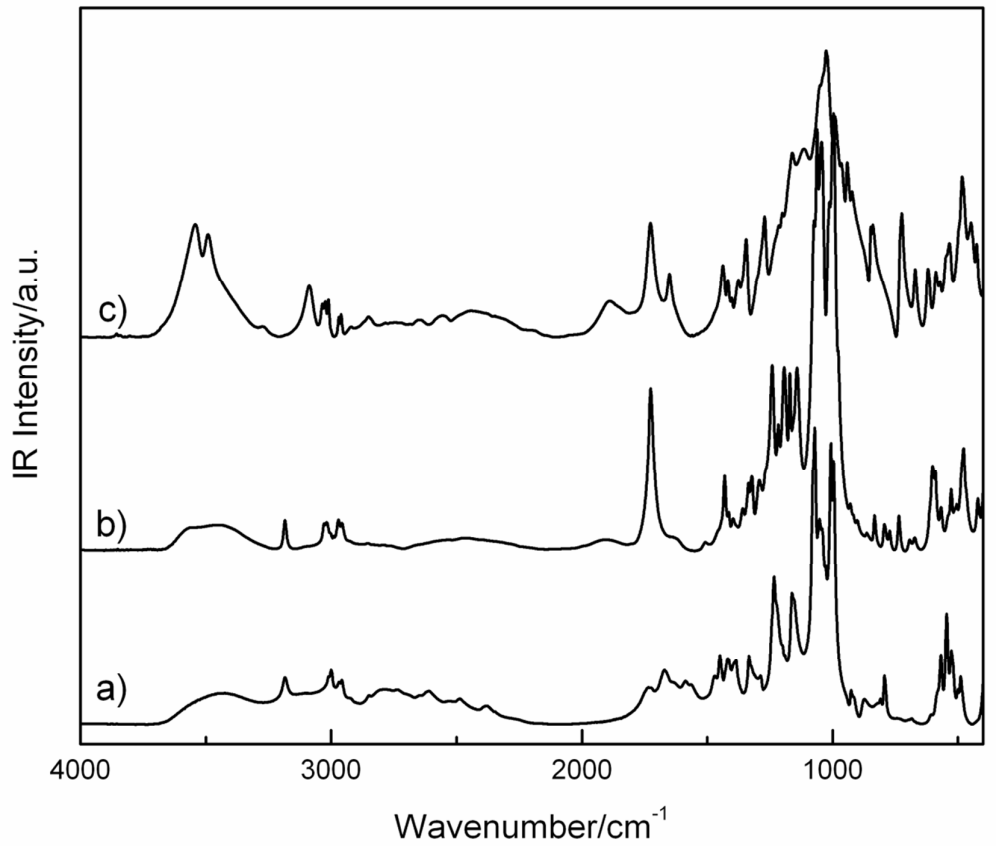

Figure S2. The FT-IR spectra of **1** (a), **2** (b), and **3** (c).

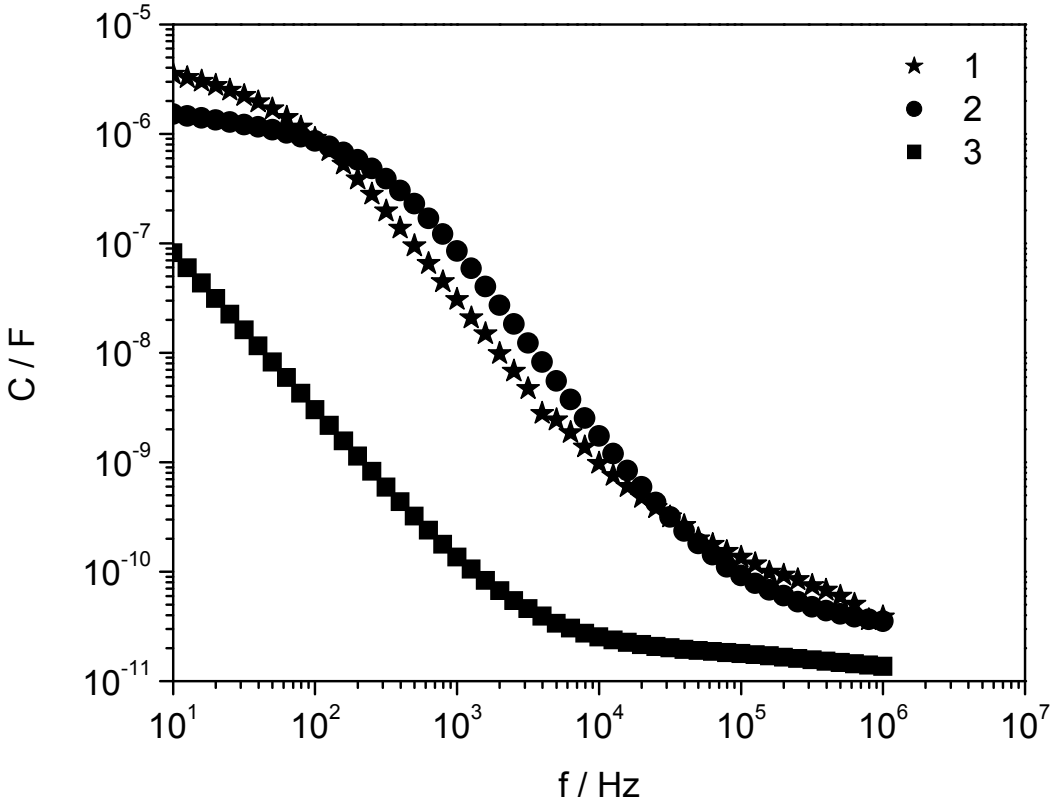

Figure S3. Equivalent parallel capacitance (C) as function of frequency (f) for **1**, **2,** and **3** samples at 100°C and 95% RH. C values were calculated from impedance data by the following equation:

$$C = -\frac{Z''}{\omega(Z'^2 + Z''^2)}$$, where ω = 2πf.

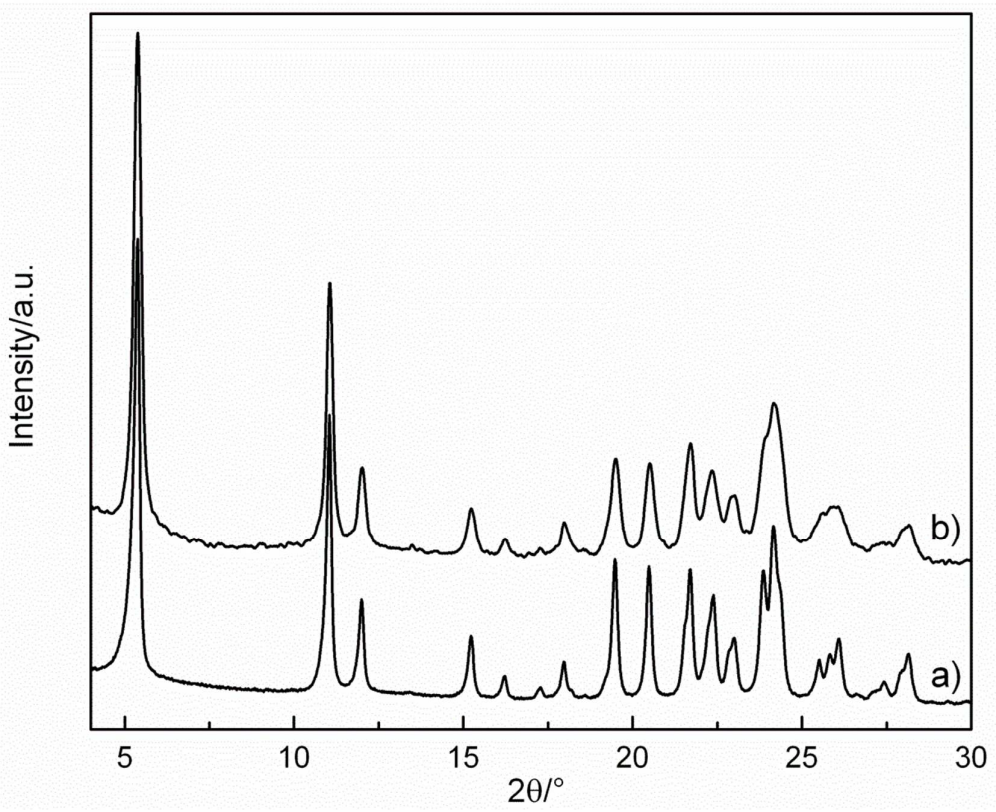

Figure S4. Comparison between the PXRD spectra of **1** as synthesized (a) and after conductivity measurement (b).

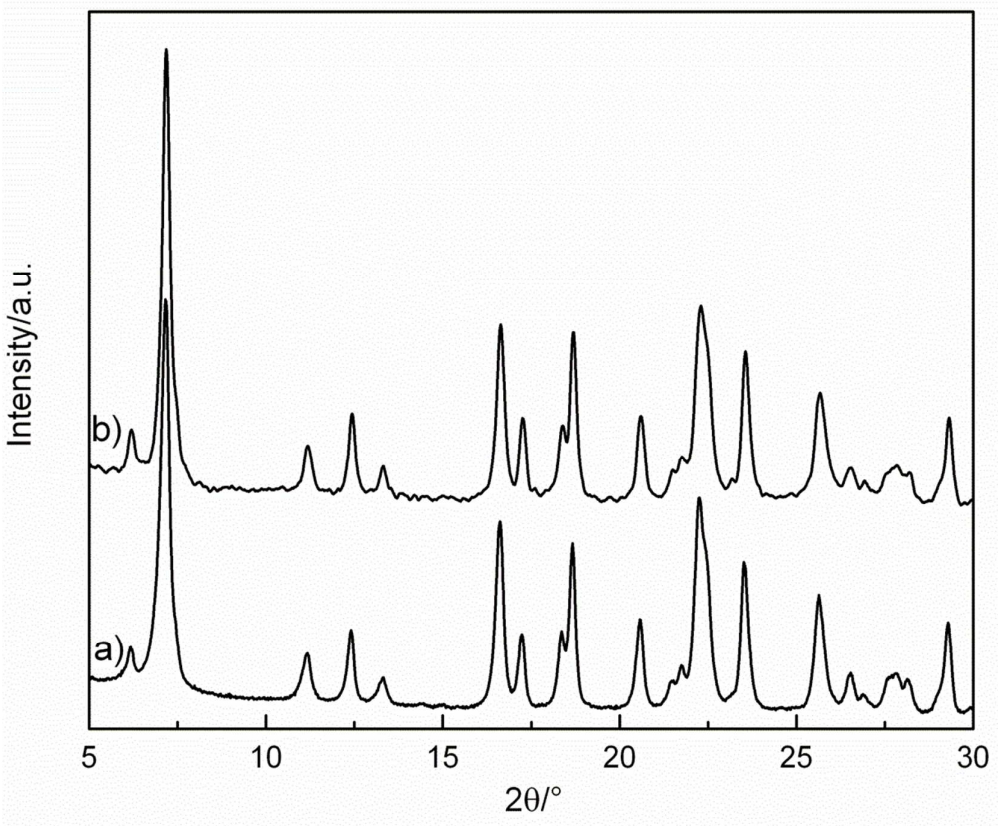

Figure S5. Comparison between the PXRD spectra of **2** as synthesized (a) and after conductivity measurement (b).

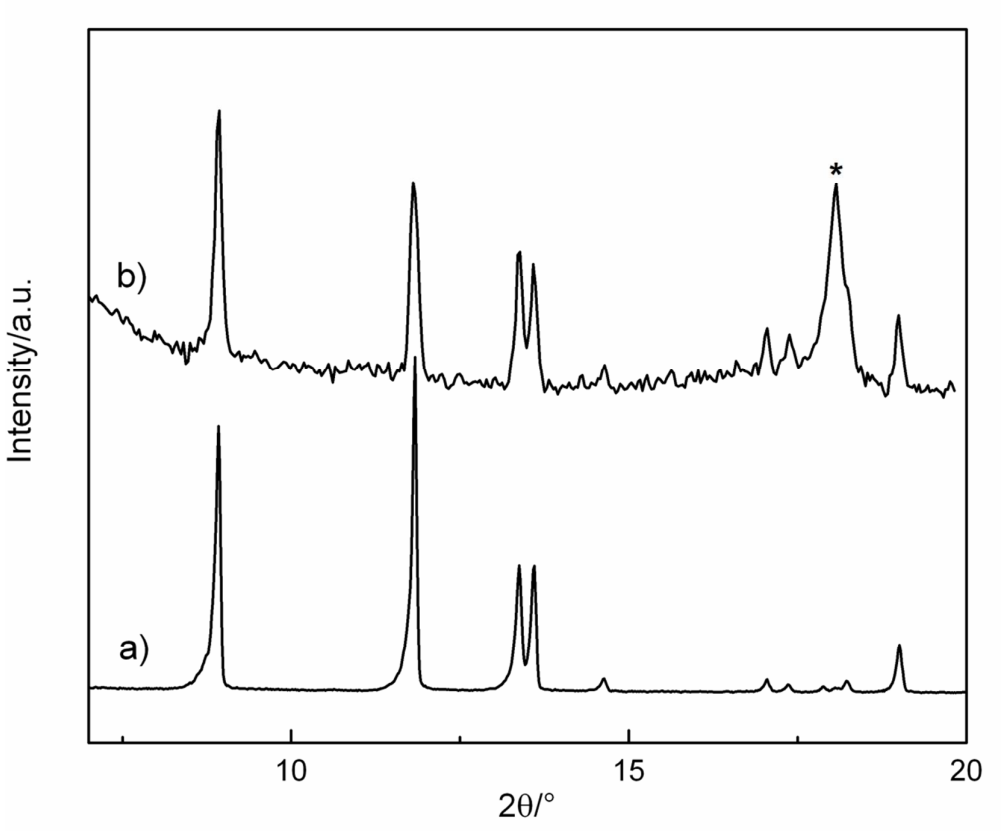

Figure S6. Comparison between the PXRD spectra of **3** as synthesized (a) and after conductivity measurement (b). The peak marked with an asterisk is due to ELAT.