Supporting Information

Anion-dependent host–guest properties of porous assemblies of coordination complexes (PACs), $[Cu(A)_2(py)_4]$ (A = PF_6, BF_4, CF_3SO_3, and CH_3SO_3; py = pyridine), based on Werner-type copper(II) compounds in the solid state

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Table S1. P–F Bond distances (Å) for α-$[Cu(PF_6)_2(py)_4]$ (α-**PAC-2-PF$_6$**), γ-{$[Cu(PF_6)_2(py)_4]\cdot$2acetone} (γ-**PAC-2-PF$_6$**⊃2acetone), and γ-{$[Cu(PF_6)_2(py)_4]\cdot$2py} (γ-**PAC-2-PF$_6$**⊃2py).

α-**PAC-2-PF$_6$**			
P(1)–F(1)[a]	1.628(1)	P(1)–F(2)	1.583(2)
P(1)–F(3)	1.587(1)	P(1)–F(4)	1.589(1)
P(1)–F(5)	1.597(1)	P(1)–F(6)	1.590(1)
P(2)–F(7)[a]	1.627(1)	P(2)–F(8)	1.588(1)
P(2)–F(9)	1.599(1)	P(2)–F(10)	1.588(1)
P(2)–F(11)	1.605(1)	P(2)–F(12)	1.593(1)
γ-**PAC-2-PF$_6$**⊃2acetone			
P–F(1)[a]	1.630(1)	P–F(2)	1.594(1)
P–F(3)	1.596(1)	P–F(4)	1.587(1)
P–F(5)	1.593(1)	P–F(6)	1.586(1)
γ-**PAC-2-PF$_6$**⊃2py			
P–F(1)[a]	1.624(3)	P–F(2)	1.596(3)
P–F(3)	1.588(1)		

[a] These F atoms are located on the axial sites of each metal ion.

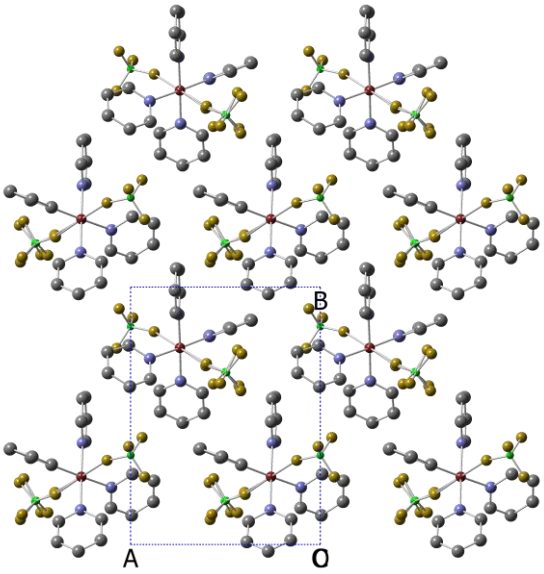

Fig. S1 Two-dimensional layer of α-**PAC-2-BF_4** in the projection along the *c*-axis. The hydrogen atoms are omitted for clarity.

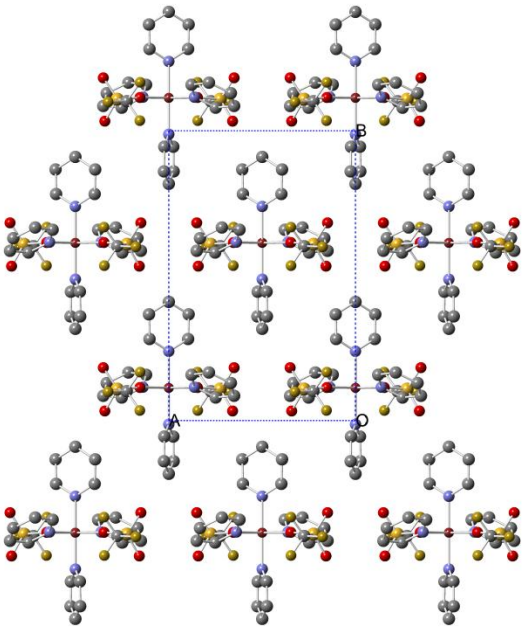

Fig. S2 Two-dimensional layer of α-**PAC-2-CF_3SO_3** in the projection along the *c*-axis. The hydrogen atoms are omitted for clarity.

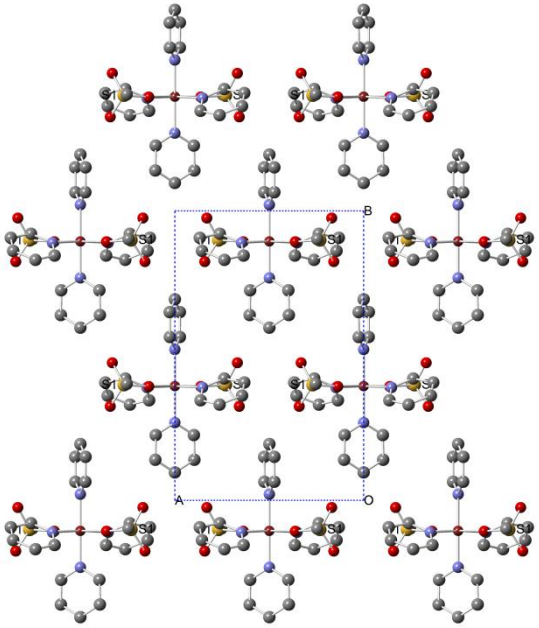

Fig. S3 Two-dimensional layer of α-**PAC-2-CH_3SO_3** in the projection along the *c*-axis. The hydrogen atoms are omitted for clarity.

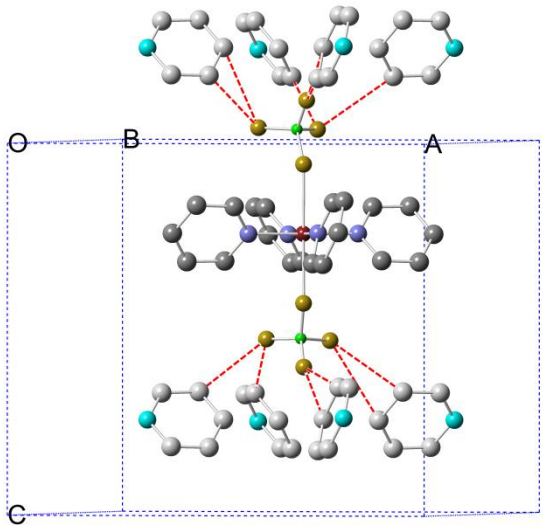

Fig. S4 View of intermolecular hydrogen-bonding interactions in γ-**PAC-2-BF_4**⊃2acetone. The py molecules of other mononuclear complexes are represented in faint colors. The hydrogen atoms are omitted for clarity.

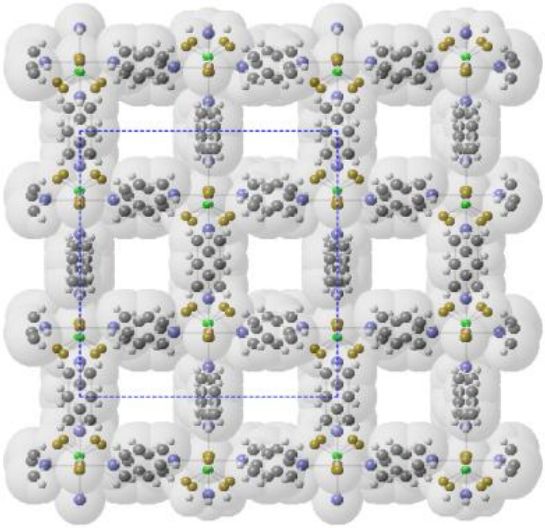

Fig. S5 Porous aggregate of γ-**PAC-2-BF$_4$**⊃2acetone in the projection along the *c*-axis. The guest molecules are omitted for clarity.

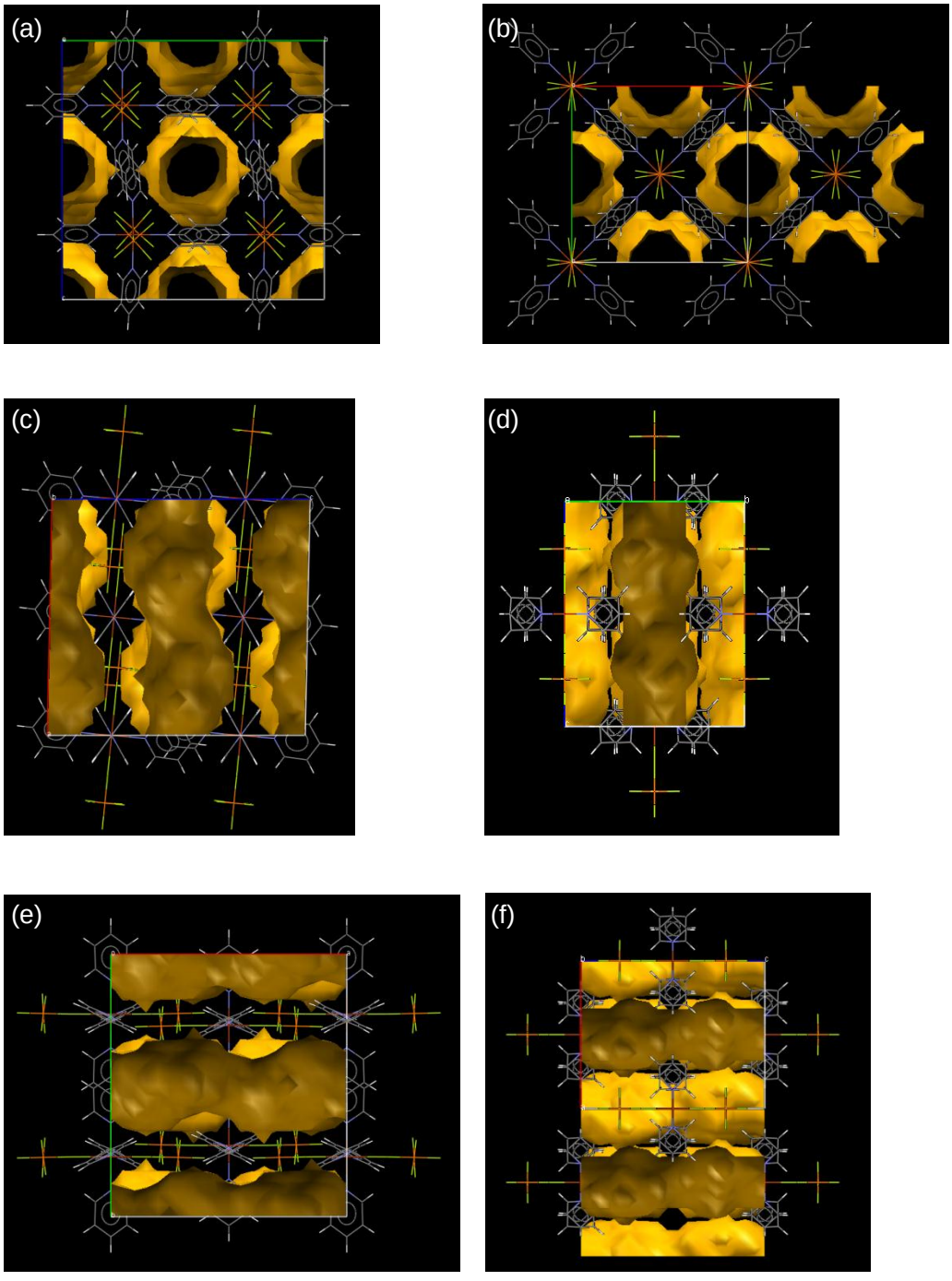

Fig. S6 One-dimensional channel structure of (a, c, and e) γ-**PAC-2-PF$_6$**⊃2acetone and (b, d, and f) γ-**PAC-2-PF$_6$**⊃2py.

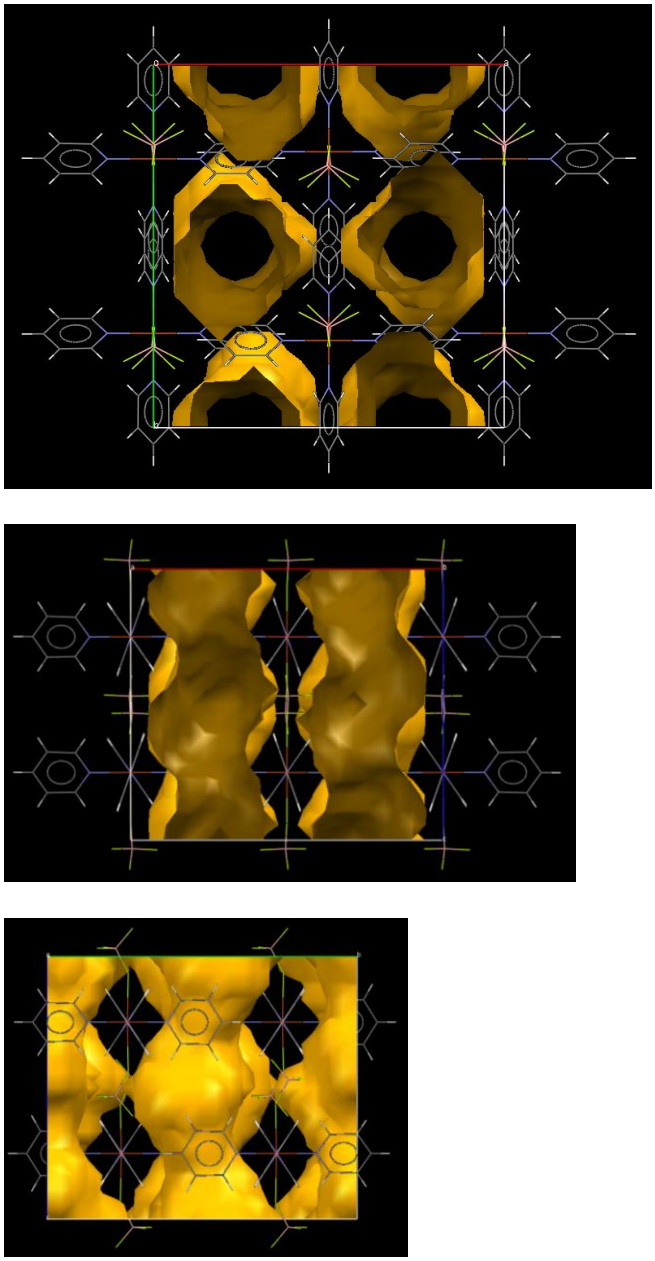

Fig. S7 One-dimensional channel structure of γ-**PAC-2-BF$_4$**⊃2acetone.

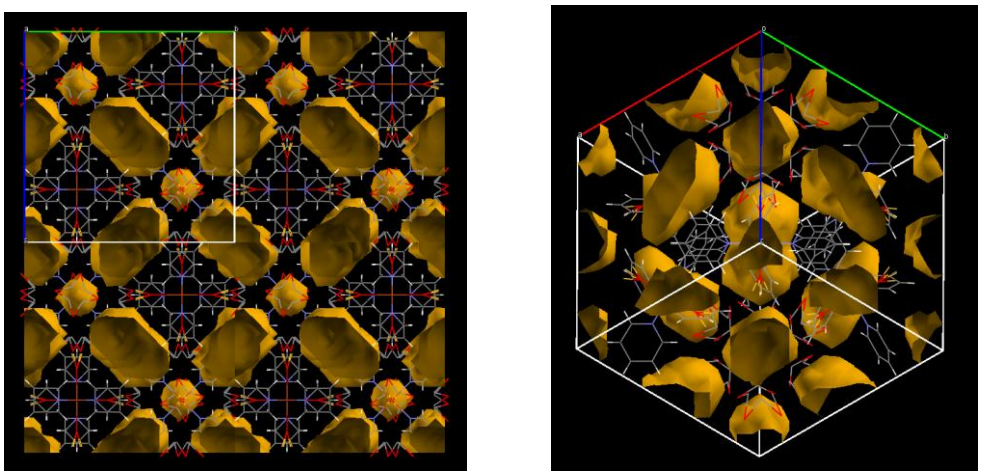

Fig. S8 Cavity structure of β-**PAC-2-CH_3SO_3**⊃2.67H_2O.

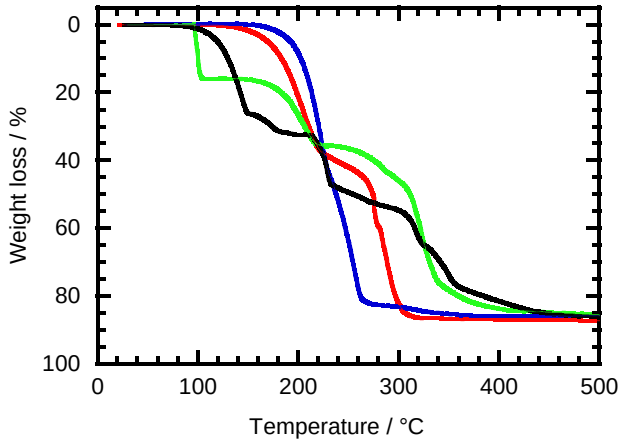

Fig. S9 TG curves of α-**PAC-2-A** (A = PF_6 (red), BF_4 (blue), CF_3SO_3 (green), and CH_3SO_3 (black)). First, all complexes lose coordinated py molecules. After that, the decomposition of anions starts, resulting in the formation of CuO as a final product.

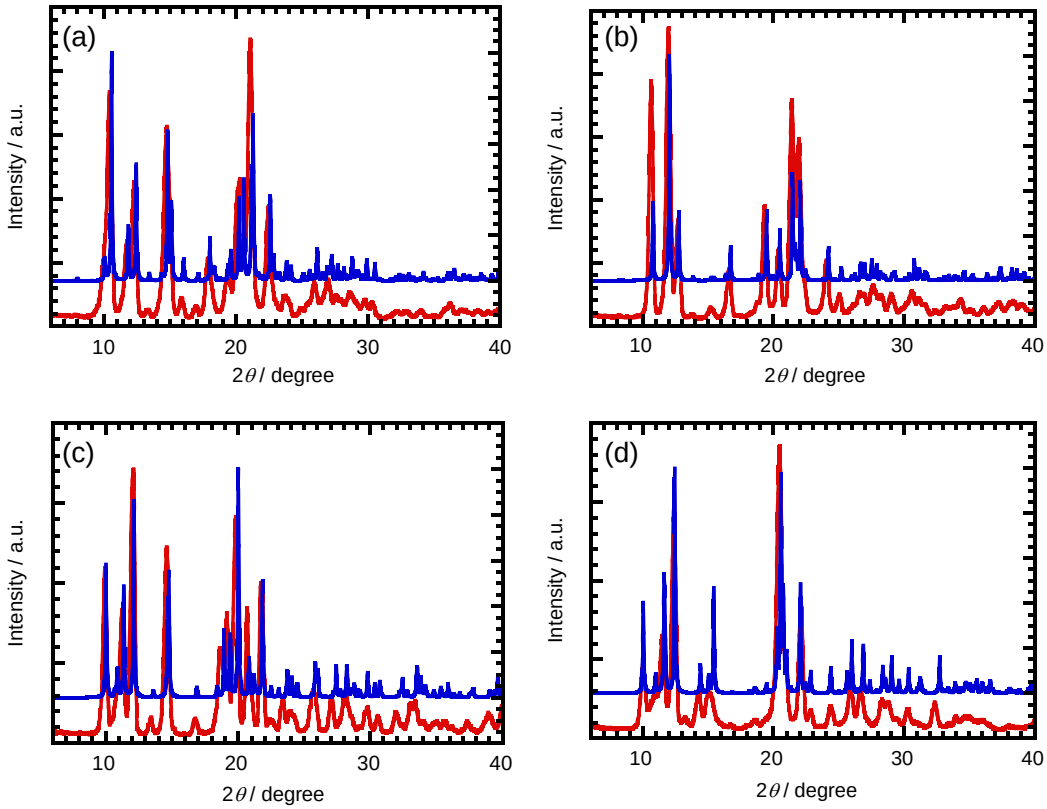

Fig. S10 The simulated (blue) and observed (red) XRPD patterns of α-**PAC-2-A** (A = (a) PF_6, (b) BF_4, (c) CF_3SO_3, and (d) CH_3SO_3).

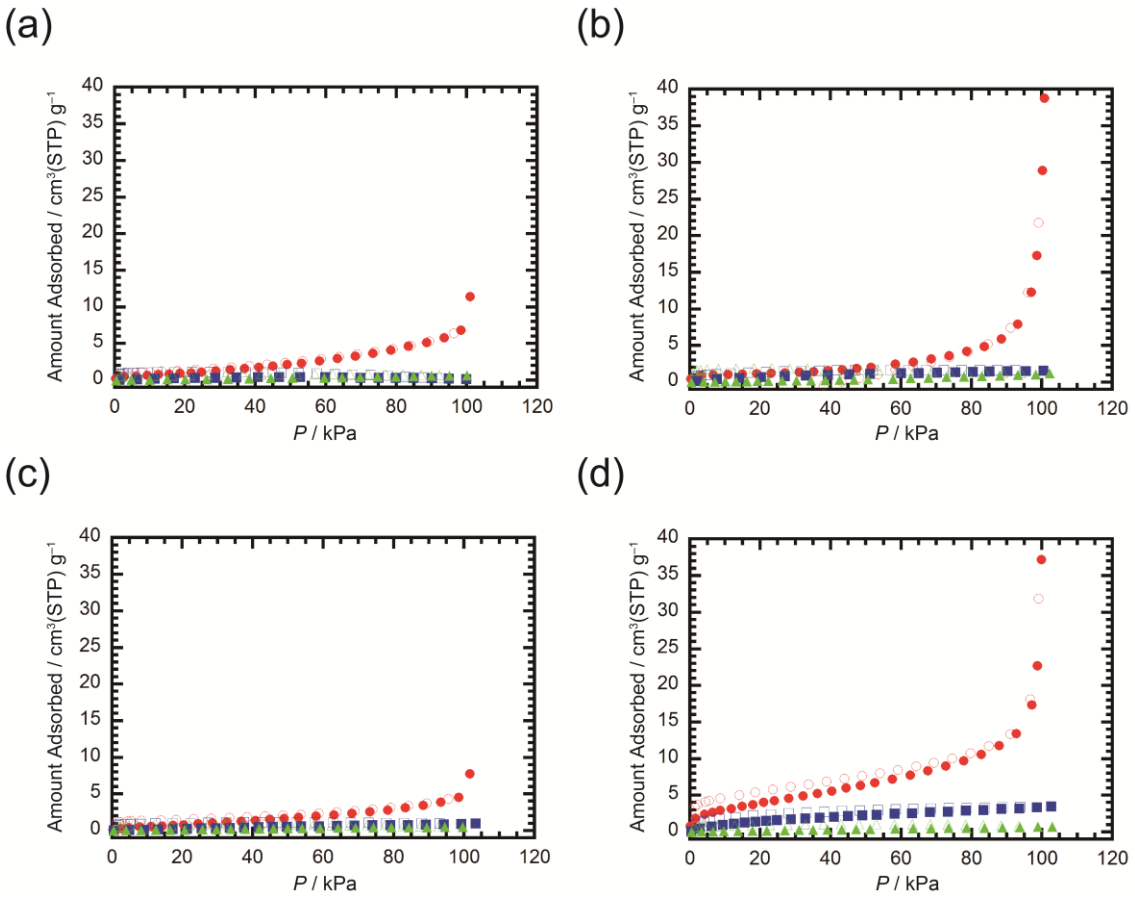

Fig. S11 Adsorption (filled symbols) and desorption (open symbols) isotherms for N_2 (77K, red) and CO_2 (195K (blue) and 273K (green)) in α-**PAC-2-A** (A = (a) PF_6, (b) BF_4, (c) CF_3SO_3, and (d) CH_3SO_3).

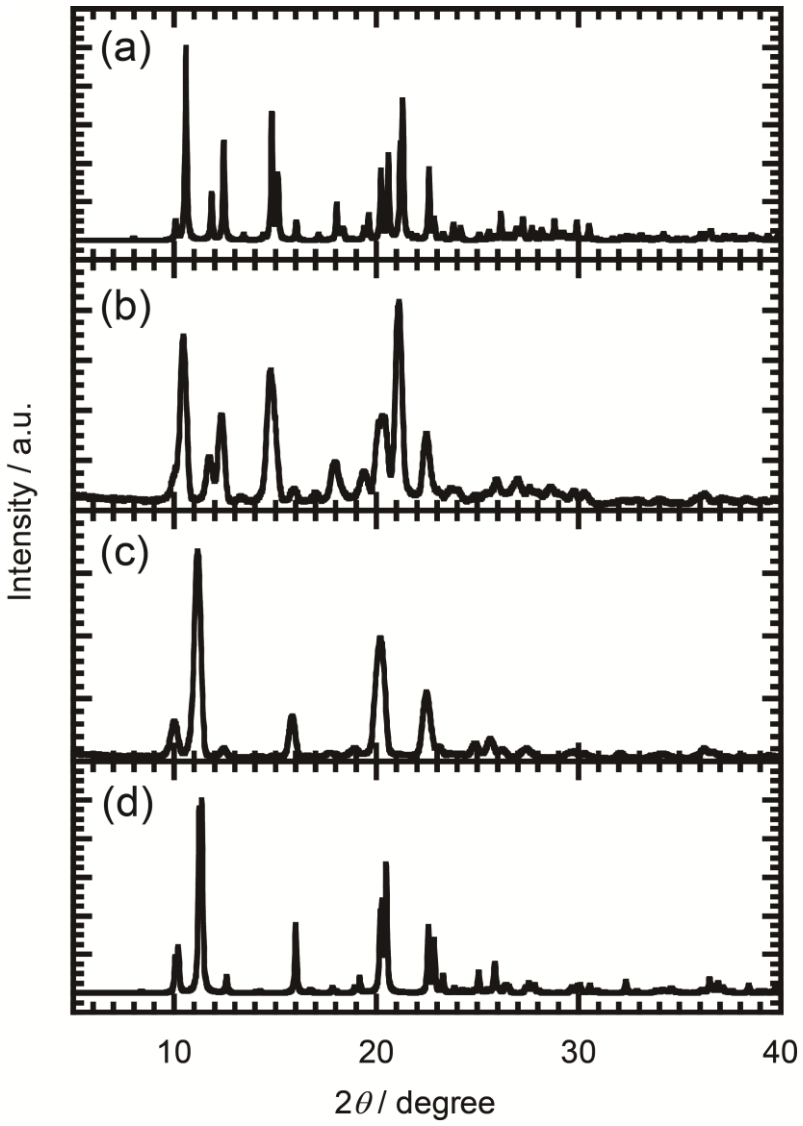

Fig. S12 XRPD patterns of (a) simulated α-**PAC-2-PF$_6$** from single-crystal analysis, (b) α-**PAC-2-PF$_6$**, (c) γ-**PAC-2-PF$_6$**⊃**x(acetone) obtained by exposure of α-**PAC-2-PF$_6$** to a saturated acetone vapor for 5 hours, and (d) simulated γ-**PAC-2-PF$_6$**⊃**2acetone from single-crystal analysis.

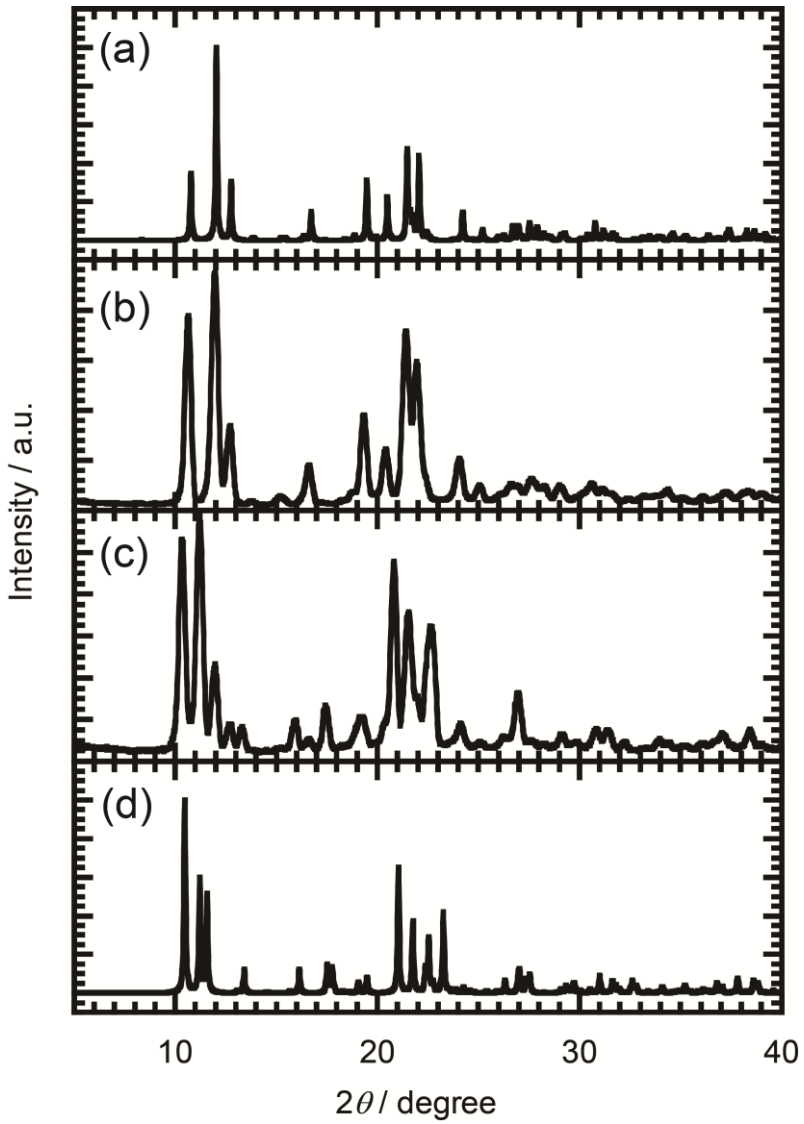

Fig. S13 XRPD patterns of (a) simulated α-**PAC-2-BF$_4$** from single-crystal analysis, (b) α-**PAC-2-BF$_4$**, (c) γ-**PAC-2-BF$_4$**⊃x(acetone) obtained by an exposure of α-**PAC-2-BF$_4$** to a saturated acetone vapor for 57.5 hours, and (d) simulated γ-**PAC-2-BF$_4$**⊃2acetone from single-crystal analysis. As you can see, α-**PAC-2-BF$_4$** remained after an exposure to a saturated acetone vapor for 57.5 hours.

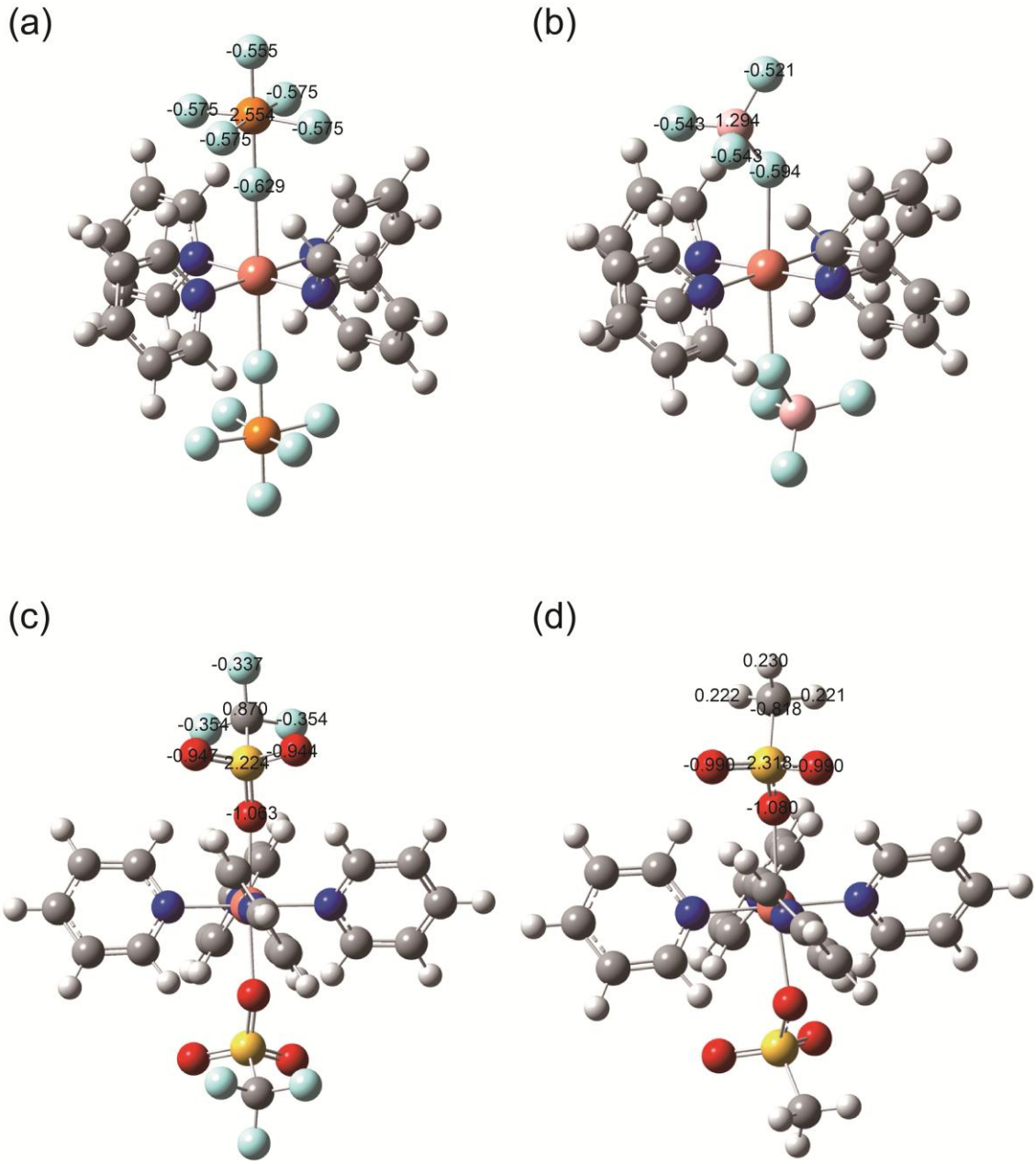

Fig. S14 NBO charges of anions in α-**PAC-2-A** (A = (a) PF_6, (b) BF_4, (c) CF_3SO_3, and (d) CH_3SO_3).