Supplementary Information

Controlling the gate-sorption properties of solid solutions of Werner complexes by varying component ratios

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1. ATR-IR spectra

**Fig. S1.** ATR-IR spectra of α-PAC-2-PF$_6$/CF$_3$SO$_3$ (x = @) (red, x = 1; blue, x = 0.75; green, x = 0.50; purple, x = 0.25; black, x = 0).

**Fig. S2.** Plot of x vs $I(847\text{cm}^{-1})/I(1448\text{cm}^{-1})$, where $I(847\text{cm}^{-1})$ and $I(1448\text{cm}^{-1})$ are intensities at each wavenumber. The bands at 847 and 1448 cm$^{-1}$ are assigned as a PF$_6^-$ $\nu_3$ vibration and a pyridine ring stretching vibration, respectively.$^{1,2}$ The solid line represents the least-squares linear fit.
2. TG analysis

![Graph showing TG curves of α-PAC-2-PF₆/CF₃SO₃ (x = @) (red, x = 1; blue, x = 0.75; green, x = 0.50; purple, x = 0.25; black, x = 0).

Fig. S3. TG curves of α-PAC-2-PF₆/CF₃SO₃ (x = @) (red, x = 1; blue, x = 0.75; green, x = 0.50; purple, x = 0.25; black, x = 0).
3. UV-vis spectra

**Fig. S4.** UV-vis spectra of α-PAC-2-PF$_6$ (red) and α-PAC-2-CF$_3$SO$_3$ (blue) in acetone solution (thick lines) and solid state (thin lines).
4. Powder X-ray diffraction patterns

Table S1. Unit cell parameters for \( \alpha\text{-PAC-2-PF}_6\text{/CF}_3\text{SO}_3 \ (x = @) \) derived from Pawley fitting.

<table>
<thead>
<tr>
<th>x</th>
<th>( a ) / Å</th>
<th>( b ) / Å</th>
<th>( c ) / Å</th>
<th>( \beta ) / °</th>
<th>( V ) / Å(^3)</th>
<th>( R_p ) / %</th>
<th>( R_{wp} ) / %</th>
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<tr>
<td>0</td>
<td>10.546(2)</td>
<td>16.272(3)</td>
<td>16.851(3)</td>
<td>-</td>
<td>2892(1)</td>
<td>5.13</td>
<td>7.48</td>
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<td>0.25</td>
<td>10.553(5)</td>
<td>16.253(5)</td>
<td>16.818(8)</td>
<td>-</td>
<td>2885(2)</td>
<td>8.66</td>
<td>12.45</td>
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<td>0.25</td>
<td>10.571(1)</td>
<td>14.81(2)</td>
<td>18.30(2)</td>
<td>92.17(5)</td>
<td>2864(5)</td>
<td>8.18</td>
<td>12.62</td>
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<tr>
<td>0.5</td>
<td>10.462(5)</td>
<td>14.473(6)</td>
<td>18.213(8)</td>
<td>91.57(2)</td>
<td>2757(2)</td>
<td>3.00</td>
<td>4.07</td>
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<tr>
<td>0.75</td>
<td>10.482(5)</td>
<td>14.436(6)</td>
<td>17.953(6)</td>
<td>91.94(2)</td>
<td>2715(2)</td>
<td>3.14</td>
<td>4.31</td>
</tr>
<tr>
<td>1</td>
<td>10.434(6)</td>
<td>14.323(7)</td>
<td>17.622(8)</td>
<td>92.03(2)</td>
<td>2632(2)</td>
<td>3.72</td>
<td>5.43</td>
</tr>
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Fig. S5. Pawley fit of the PXRD pattern of \( \alpha\text{-PAC-2-PF}_6\text{/CF}_3\text{SO}_3 \ (x = 1) \). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be \( P2_1/c \) by the indexing routine of the TOPAS program package.
**Fig. S6.** Pawley fit of the PXRD pattern of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$ (x = 0.75). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be $P2_1/c$ by the indexing routine of the TOPAS program package.

**Fig. S7.** Pawley fit of the PXRD pattern of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$ (x = 0.5). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be $P2_1/c$ by the indexing routine of the TOPAS program package.
**Fig. S8.** Pawley fit of the PXRD pattern of α-PAC-2-PF₆/CF₃SO₃ (x = 0.25). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be $P2_1/c$ by the indexing routine of the TOPAS program package.

**Fig. S9.** Pawley fit of the PXRD pattern of α-PAC-2-PF₆/CF₃SO₃ (x = 0.25). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be $Pbcn$ by the indexing routine of the TOPAS program package.
Fig. S10. Pawley fit of the PXRD pattern of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$ ($x = 0$). The blue, red, and green lines represent the experimental, calculated and difference profile, respectively. The space group was determined to be $Pbcn$ by the indexing routine of the TOPAS program package.

Fig. S11. Composition ratio-dependent cell parameters of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$ ($x = @$). Red, green, purple, and blue symbols indicate $a$, $b$, $c$, and $V$, respectively.
Fig. S12. PXRD patterns of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$($x = 0.75$) before (red) and after (blue) an exposure to a saturated acetone vapor.

Fig. S13. PXRD patterns of $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$($x = 0.5$) before (red) and after (blue) an exposure to a saturated acetone vapor.
Fig. S14. PXRD patterns of α-PAC-2-PF$_6$/CF$_3$SO$_3$(x = 0.25) before (red) and after (blue) an exposure to a saturated acetone vapor.
5. Acetone sorption properties

Fig. S15. Acetone adsorption/desorption isotherms (adsorption, closed symbols; desorption, open symbols) in $\alpha$-PAC-2-PF$_6$/CF$_3$SO$_3$ ($x = 0.75$) at 288 K. The solid and dashed lines indicate the adsorption/desorption isotherms of physical mixture ($\alpha$-PAC-2-PF$_6$ : $\alpha$-PAC-2-CF$_3$SO$_3$ = 0.75 : 0.25) calculated using the acetone adsorption/desorption data of pure $\alpha$-PAC-2-PF$_6$ and $\alpha$-PAC-2-CF$_3$SO$_3$. 
Fig. S16. Acetone adsorption/desorption isotherms (adsorption, closed symbols; desorption, open symbols) in \( \textit{a-PAC-2-PF}_6/\textit{CF}_3\textit{SO}_3 \) (\( \textit{x} = 0.5 \)) at 288 K. The solid and dashed lines indicate the adsorption/desorption isotherms of physical mixture (\( \textit{a-PAC-2-PF}_6 : \textit{a-PAC-2-CF}_3\textit{SO}_3 = 0.5 : 0.5 \)) calculated using the acetone adsorption/desorption data of pure \( \textit{a-PAC-2-PF}_6 \) and \( \textit{a-PAC-2-CF}_3\textit{SO}_3 \).
**Fig. S17.** Acetone adsorption/desorption isotherms (adsorption, closed symbols; desorption, open symbols) in $a$-PAC-2-PF$_6$/CF$_3$SO$_3$ ($x = 0.25$) at 288 K. The solid and dashed lines indicate the adsorption/desorption isotherms of physical mixture ($a$-PAC-2-PF$_6$: $a$-PAC-2-CF$_3$SO$_3 = 0.25 : 0.75$) calculated using the acetone adsorption/desorption data of pure $a$-PAC-2-PF$_6$ and $a$-PAC-2-CF$_3$SO$_3$. 
6. Theoretical calculations

![Diagram](image)

$E_b = -7.7 \text{ kcal/mol}$

$E_b = -4.1 \text{ kcal/mol}$

$E_b = -3.1 \text{ kcal/mol}$

**Fig. S18.** Optimized structures of (a) $\{\text{Cu(PF}_{6})_{2}(\text{py})_{4}\} \cdot \text{acetone}$, (b) $\{\text{Cu(CF}_{3}\text{SO}_{3})_{2}(\text{py})_{4}\} \cdot \text{acetone}$ with the interaction between acetone and F/O atoms of CF$_3$SO$_3$ anion, and (c) $\{\text{Cu(CF}_{3}\text{SO}_{3})_{2}(\text{py})_{4}\} \cdot \text{acetone}$ with the interaction between
acetone and F atom of CF₃SO₃. The binding energy of acetone for [Cu(PF₆)₂(py)₄] was larger than those for [Cu(CF₃SO₃)₂(py)₄].
7. References
