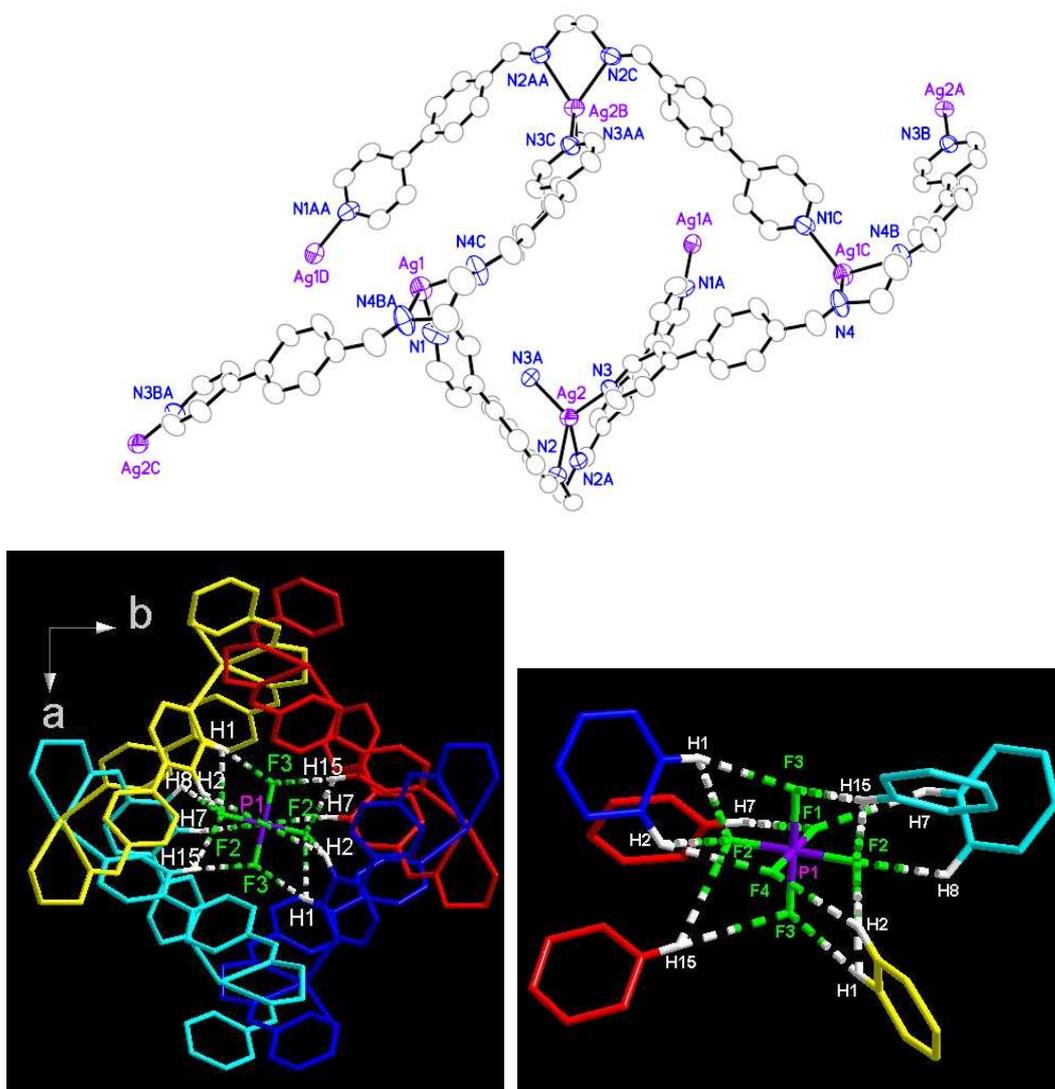


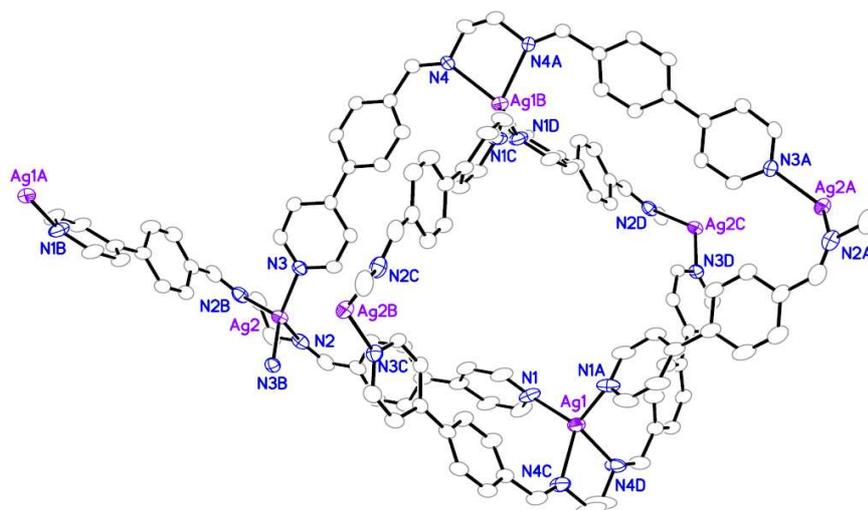
**Supporting Information For**  
**1D Independent Nano-Sized Metal-Organic Tube: Anion Exchange,  
Separation and Anion-Responsive Luminescence**

Chao Fang, Qi-Kui Liu, Jian-Ping Ma, and Yu-Bin Dong\*

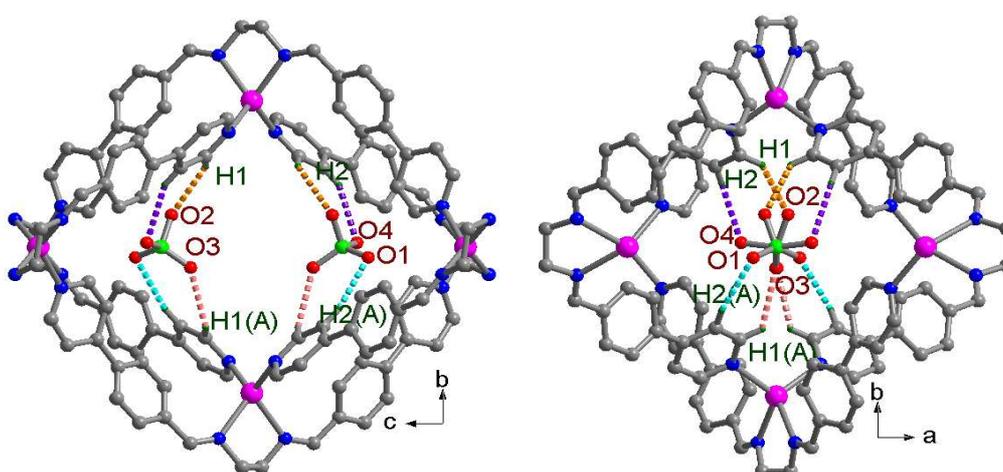
College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, People's Republic of China. Email: [yubindong@sdu.edu.cn](mailto:yubindong@sdu.edu.cn)



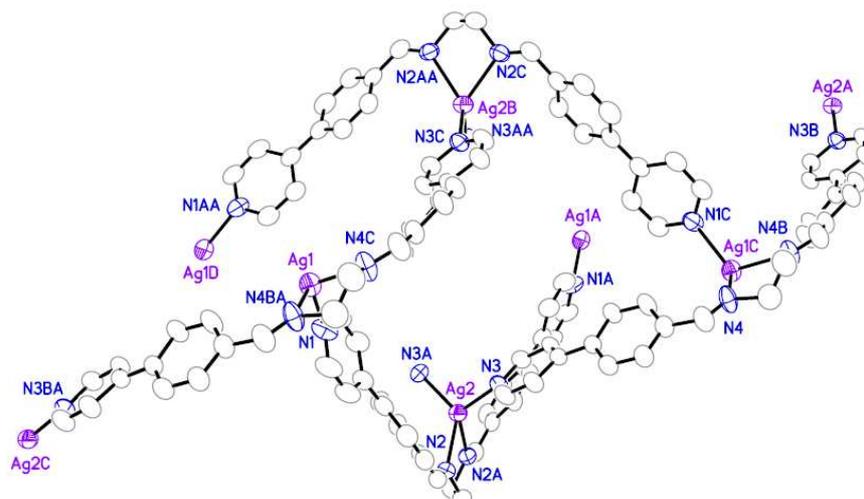
**Figure S1.** Up: The ORTEP figure of **1**. Bottom: The H-bonding interactions of P(1)F<sub>6</sub><sup>-</sup> in the framework of **2**. F(1)⋯H(7) = 2.856 Å, F(2)⋯H(1) = 2.675 Å, F(2)⋯H(2) = 2.718 Å, F(2)⋯H(15) = 2.792 Å, F(2)⋯H(8) = 2.590 Å, F(2)⋯H(15) = 2.792 Å, F(3)⋯H(1) = 2.522 Å, F(3)⋯H(15) = 2.777 Å, F(4)⋯H(2) = 2.718 Å, F(2)⋯H(1) = 2.675 Å.



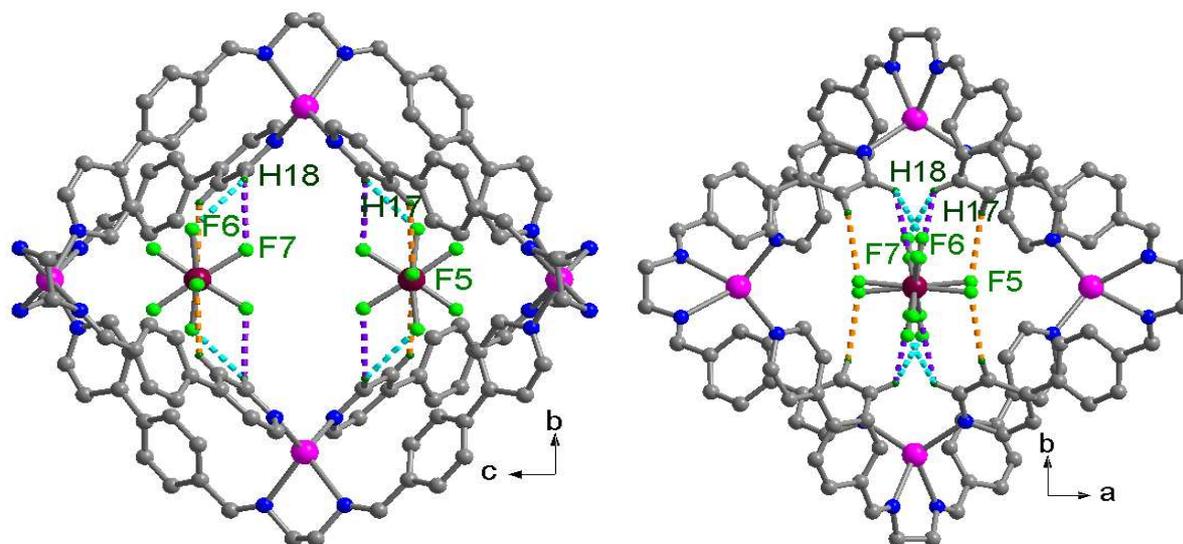
**Figure S2.** The ORTEP figure of **2**.



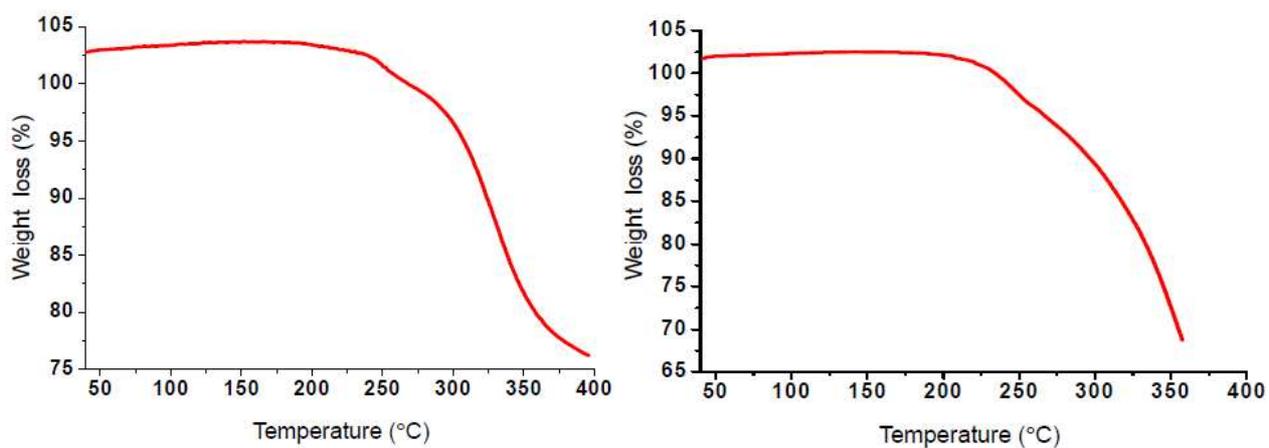
**Figure S3.** The H-bonding interactions of  $\text{ClO}_4^-$  in the framework of **2**.  $\text{H}(2\text{A})\cdots\text{O}(1) = 2.654 \text{ \AA}$ ,  $\text{H}(1)\cdots\text{O}(2) = 2.558 \text{ \AA}$ ,  $\text{H}(1\text{A})\cdots\text{O}(3) = 2.555 \text{ \AA}$ ,  $\text{H}(2)\cdots\text{O}(4) = 2.553 \text{ \AA}$ .



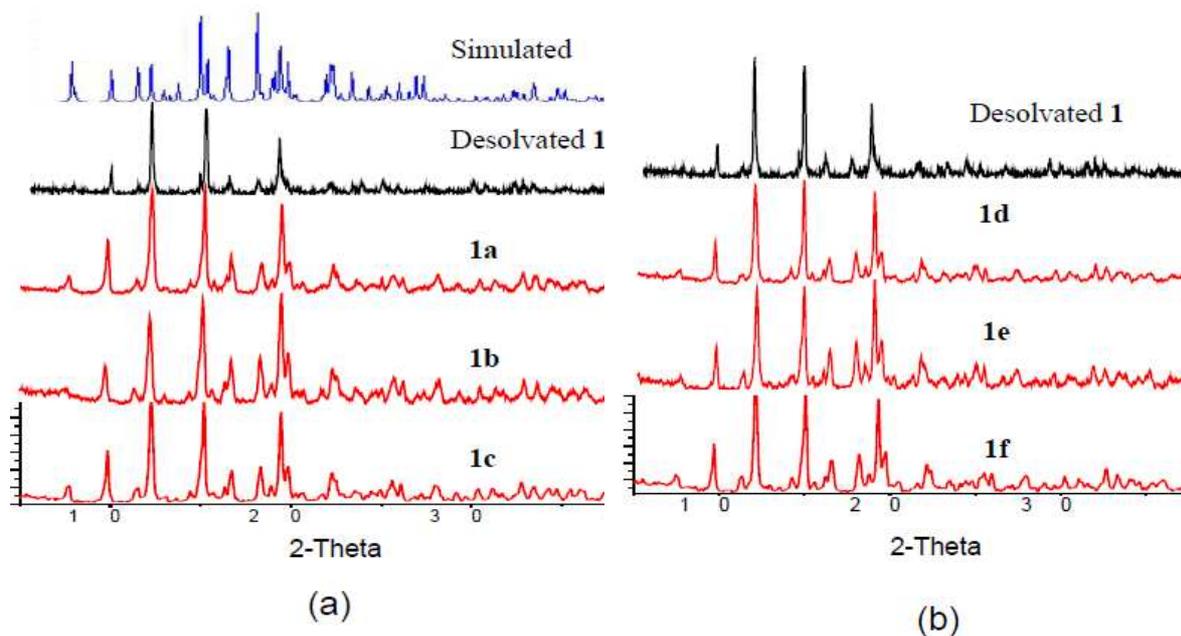
**Figure S4.** The ORTEP figure of **3**.



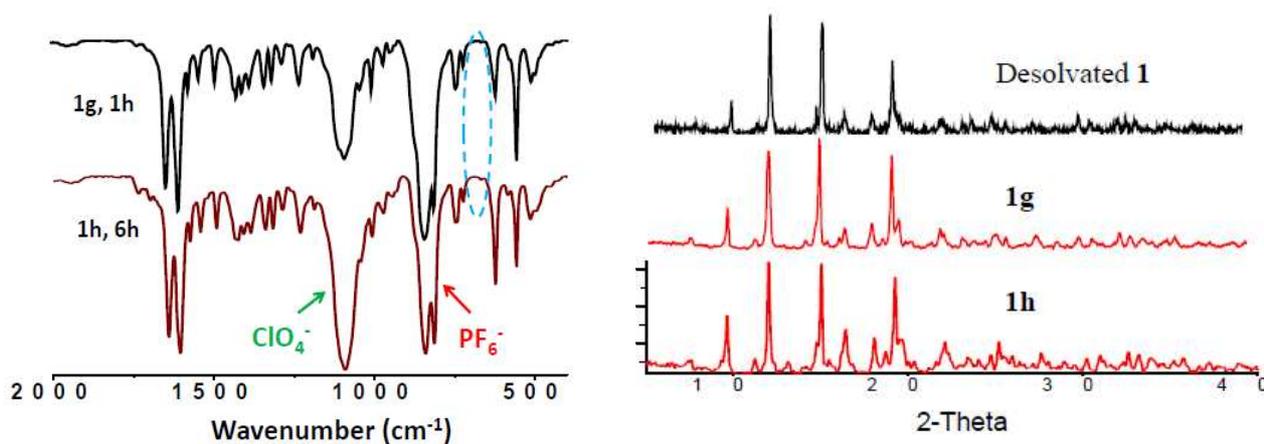
**Figure S5.** The H-bonding interactions of  $\text{SbF}_6^-$  in the framework of **3**.  $\text{H}(17)\cdots\text{F}(5) = 2.50 \text{ \AA}$ ,  $\text{H}(18)\cdots\text{F}(6) = 2.502 \text{ \AA}$ ,  $\text{H}(18)\cdots\text{F}(7) = 2.483 \text{ \AA}$ .



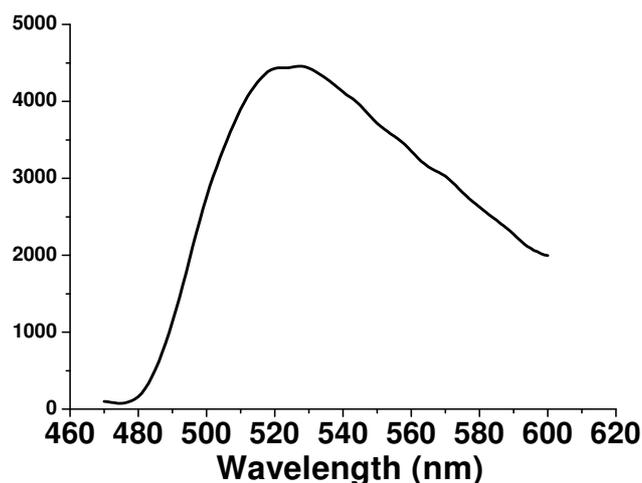
**Figure S6.** TGA traces of the desolvated **2** (left) and **3** (right). No guest mass loss was detected.



**Figure S7.** (a) XRPD patterns of the simulated, desolvated **1** and **1a-1c**. (b) XRPD patterns of the desolvated **1** and **1d-1f**.



**Figure S8.** Left: The IR spectra of **1** stirred in a THF/MeOH ( $v : v = 1 : 1$ ) solution of equimolar  $\text{NH}_4\text{SbF}_6$  and  $\text{NaClO}_4$  at 1 (**1g**) and 6h (**1h**). Only characteristic bands of  $\text{ClO}_4^-$  and  $\text{PF}_6^-$  were found in the spectra. Right: XRPD patterns of the desolvated **1**, **1g** and **1h**. The ion chromatography analysis suggested that 61.32 % of  $\text{PF}_6^-$  anions were replaced by  $\text{ClO}_4^-$  to generate a mixed anion compound (**1h**).



**Figure S9.** The solid-State emission spectrum of **L** (528 nm upon excited at 448 nm).

**Experimental Section.** Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000  $\text{cm}^{-1}$  range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. All fluorescence measurements were carried out on a Cary Eclipse Spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . X-ray Powder diffraction (XRPD) patterns were recorded on a D8 ADVANCE X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) over a range of  $5^{\circ} < 2\theta < 40^{\circ}$  in 0.1  $^{\circ}$  step with a 1-s counting time per step. Simulation was generated based on the single crystal data using the Mercury software. The desolvated sample of **1** and anion-exchanged samples of **1a-1f** were mounted on clear cellophane tape and XRPD data were collected after mounting. Data are shown in Figure S7.

**Synthesis of L.** A solution of 4-(4-pyridyl)benzaldehyde (1.83 g, 10 mmol),  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  (0.30 g, 5 mmol) and several drops of  $\text{HCOOH}$  in EtOH (25 mL) was stirred at room temperature for 8 h to afford light yellow crystalline solids of **L** (1.39 g). Yield, 71%. Mp: 210-212  $^{\circ}\text{C}$ . IR (KBr pellet,  $\text{cm}^{-1}$ ):

2841(m), 1642(s), 1593(s), 1488(m), 1406(m), 1239(w), 1182 (w), 1029(m), 810(s), 741(m), 501(m).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ , 25 °C, TMS, ppm): 8.64-7.73 (AA'BB', 8H,  $-\text{C}_6\text{H}_4$ ), 8.42 (s, 2H,  $-\text{CH}=\text{N}-$ ), 7.86 (s, 8H,  $-\text{C}_6\text{H}_4$ ), 3.94 (s, 4H,  $-\text{CH}_2-$ ). Elemental analysis (%) calcd for  $\text{C}_{26}\text{H}_{22}\text{N}_4$ : C 80.00, H 5.64, N 14.36; Found: C 79.66, H 5.81, N 14.05.

**Synthesis of 1.** A solution of  $\text{AgPF}_6$  (6.3 mg, 0.025 mmol) in MeOH (6 mL) was layered onto a solution of **L** (9.8 mg, 0.025 mmol) in THF (8 mL). The solutions were left for about 5 days at room temperature, and colorless crystals were obtained. Yield, 45 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3421(br), 1643(s), 1605(s), 1542(w), 1491(w), 1432(m), 1316(m), 1231(m), 1073(w), 1010(w), 835(s), 557(s), 513(w). Elemental analysis (%) calcd for  $\text{C}_{52}\text{H}_{44}\text{N}_8\text{Ag}_2\text{P}_2\text{F}_{12}$ (desolvated): C 48.54, H 3.45, N 8.71; Found: C 48.79, H 3.27, N 8.32.

**Synthesis of 2.** A solution of  $\text{AgClO}_4$  (5.2 mg, 0.025 mmol) in MeOH (6 mL) was layered onto a solution of **L** (9.8 mg, 0.025 mmol) in THF (8 mL). The solutions were left for about 5 days at room temperature, and colorless crystals were obtained. Yield, 40 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3422(br), 1639(s), 1601(s), 1541(w), 1490(w), 1421(m), 1405 (m), 1337(m), 1318(m), 1227(w), 1088(s), 1006(w), 811(s), 742(m), 623(s), 568(w), 515(m). Elemental analysis (%) calcd for  $\text{C}_{52}\text{H}_{44}\text{N}_8\text{Ag}_2\text{Cl}_2\text{O}_8$ (desolvated): C 52.24, H 3.71, N 9.37; Found: C 52.56, H 3.35, N 9.01.

**Synthesis of 3.** A solution of  $\text{AgSbF}_6$  (8.6 mg, 0.025 mmol) in MeOH (6 mL) was layered onto a solution of **L** (9.8 mg, 0.025 mmol) in THF (8 mL). The solutions were left for about 5 days at room temperature, and colorless crystals were obtained. Yield, 41 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3421(br), 1642(s), 1603(s), 1541(w), 1492(w), 1425(m), 1316(m), 1230(m), 1070(w), 1006(w), 815(s), 743(w), 657(s), 502(w). Elemental analysis (%) calcd for  $\text{C}_{52}\text{H}_{44}\text{Ag}_2\text{F}_{12}\text{N}_8\text{Sb}_2$ (desolvated): C 42.54, H 3.02, N 7.65; Found: C 42.62, H 3.36, N 7.63.

**Single-crystal analysis.** For **1-3**, X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.<sup>1</sup> Corrections for incident and diffracted beam absorption effects were applied using SADABS.<sup>1</sup> None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against  $F^2$  by the full-matrix least squares technique. Crystal data, data collection parameters, and refinement statistics are listed in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 838061, 838062 and 838063. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Table S1** Crystal data of 1-3

No.	1	2	3
empirical formula	C <sub>54</sub> H <sub>44</sub> Ag <sub>2</sub> F <sub>12</sub> N <sub>8</sub> O <sub>2</sub> P <sub>2</sub>	C <sub>55</sub> H <sub>48</sub> Ag <sub>2</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>9.50</sub>	C <sub>53</sub> H <sub>50</sub> Ag <sub>2</sub> F <sub>12</sub> N <sub>8</sub> O <sub>2</sub> Sb <sub>2</sub>
Formula weight	1342.65	1259.65	1518.25
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
<i>a</i> (Å)	23.533(4)	22.456(4)	24.238(4)
<i>b</i> (Å)	29.906(4)	29.527(6)	30.052(6)
<i>c</i> (Å)	15.980(2)	16.123(3)	15.646(3)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	90	90
$\gamma$ (°)	90	90	90
Volume (Å <sup>3</sup> )	11246(3)	10690(4)	11396(4)
space group	<i>Ccca</i>	<i>Ccca</i>	<i>Ccca</i>
Z value	8	8	8
Density(g cm <sup>-1</sup> )	1.586	1.565	1.770
$\mu$ (Mo-K $\alpha$ )(mm <sup>-1</sup> )	0.841	0.898	1.702
temp(K)	298(2)	173(2)	293(2)
Data / restraints / parameters	4981 / 32 / 383	5039 / 0 / 403	5374 / 22 / 391
Final R indices [I>2sigma(I)]: R; Rw	0.0644; 0.1937	0.0566; 0.1257	0.0502; 0.1288

**References**

- (1) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.
- (2) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool. University of Utrecht, Utrecht, the Netherlands, 1998.