

Supporting Information

Organic Anion Template: a 24-Nuclearity Silver Cluster Encapsulating a Squarate Dimer

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Materials and Methods.

All of the reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. Diffuse reflectance spectra were collected on a finely ground sample with a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere; the spectra were measured from 200 to 800 nm by using barium sulfate (BaSO_4) as a standard with 100% reflectance. The ^{13}C cross-polarized magic-angle spinning (CPMAS) experiments were performed for **1**. Solid NMR spectra were recorded on Bruker Biospin Avance 400 MHz NMR spectrometer (Avance III, Bruker Biospin, Switzerland), operating at 400.2 MHz for ^1H frequency and 100.6 MHz for ^{13}C using Bruker 4.0 mm DVT probe. All spectra were recorded at 12.0 kHz Magic Angle Spinning (MAS) frequency. CPMAS experiments for **1** were performed at 25 $^\circ\text{C}$. The ^{13}C CPMAS spectra were recorded with spectral width of 500 ppm, 2k data points, and 7k scans.

X-ray Crystallography. Intensity data of $1 \cdot 2\text{CH}_3\text{CN}$ were collected on an Oxford Gemini S Ultra system (Mo $\text{K}\alpha$). Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by direct methods, and non-hydrogen atoms except disordered components were refined anisotropically by least-squares on F_2 using the SHELXTL program. The hydrogen atoms of organic ligands were generated geometrically, while no attempt was made to locate hydrogen atoms of solvent molecules.

Characterization

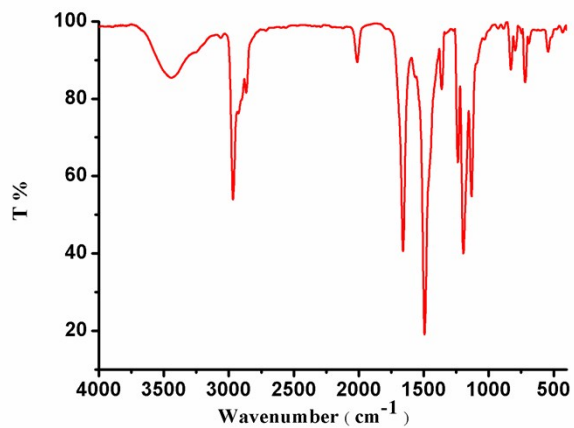


Figure S1. The IR spectrum of **1**.

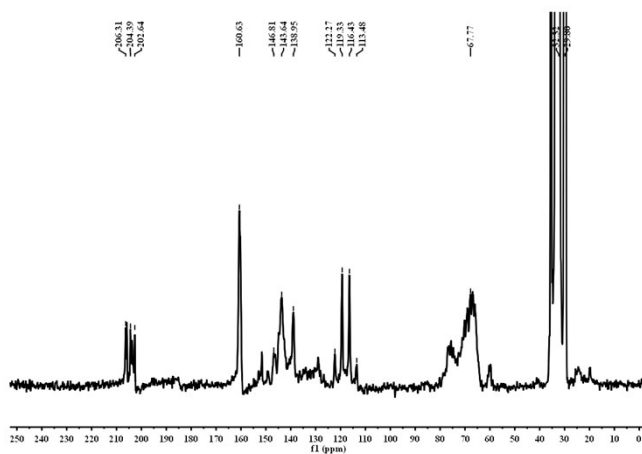


Figure S2. Solid-state ¹³C NMR spectrum of **1**. 204.4 (m, C₄O₄²⁻), 160.6 (s, CF₃COO⁻), 143.6 (m, C≡Cbu^l), 122.3, 119.3, 116.4, 113.5 (q, CF₃), 67.8 (m, C≡Cbu^l), 32.3 (m, CH₃ and C(CH₃)₃) ppm.

Table S1. Crystal data and structure refinement for **1**.

<i>Compound</i>	1
Chemical formula	C ₁₁₆ H ₁₅₀ F ₁₂ N ₂ O ₁₆ Ag ₂₄
Formula weight	4645.25
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> , Å	23.5527(7)
<i>b</i> , Å	20.9694(8)
<i>c</i> , Å	29.3460(9)
<i>α</i> , deg	90
<i>β</i> , deg	95.231(3)
<i>γ</i> , deg	90
<i>V</i> , Å ³	14433.2(8)
<i>Z</i>	4
ρ_{calc} , g/cm ³	2.135
μ , mm ⁻¹	3.238
Reflections collected	68602
Independent reflections	28306
<i>R</i> _{int}	0.0437
Reflections <i>I</i> > 2σ(<i>I</i>)	28306
Parameters	1720
GOF on <i>F</i> ²	1.054
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0489 / 0.0860
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (<i>all</i>)	0.0762 / 0.0937

$$^a R_1 = [\sum \text{abs}(\text{abs}(\text{Fo}) - \text{abs}(\text{Fc}))] / [\sum \text{abs}(\text{Fo})]. \quad ^b wR_2 = [\sum (w(\text{Fo}^2 - \text{Fc}^2)^2) / \sum (w(\text{Fo}^2)^2)]^{0.5}.$$

Table S2. Mean deviation from planes [Å], the dihedral angles [°] of the four parallel planes and the mean interplanar separations for **1**.^[a]

Mean deviation from planes [Å]			
Plane 1	0.0025	Plane 2	0.0082
Plane 3	0.0074	Plane 4	0.0020
The dihedral angles [°]			
$\alpha_{1,2}$	178.31(0.14)	$\alpha_{1,3}$	177.07(0.14)
$\alpha_{1,4}$	176.54(0.03)	$\alpha_{2,3}$	176.49(0.19)
$\alpha_{2,4}$	176.99(0.14)	$\alpha_{3,4}$	178.04(0.14)
Mean interplanar separation [Å]			
<i>d</i> _{1,2}	2.957	<i>d</i> _{2,3}	3.108
<i>d</i> _{3,4}	2.961	<i>d</i> _{1,4}	9.022

[a] The mean interplanar separation are calculated by Mercury with the mean distance between the atom in one plane and the other.

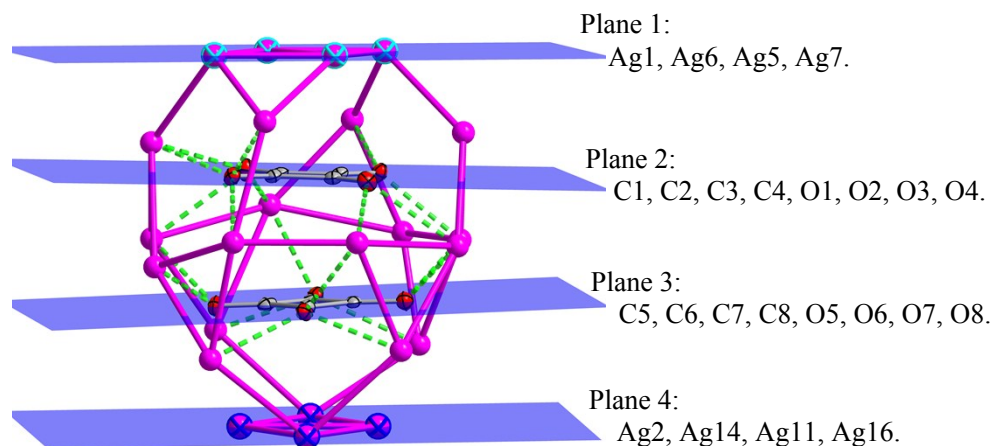


Figure S3. The locations of four nearly parallel planes in the core structure of cluster **1**.

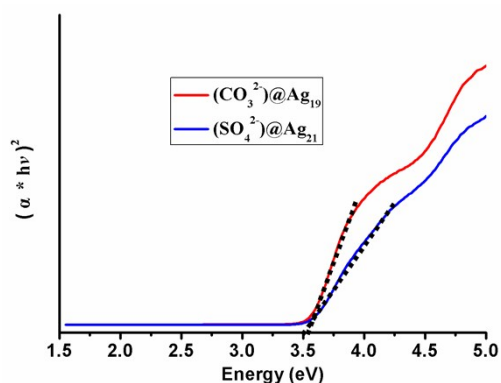


Figure S4. The solid UV-vis diffuse reflectance spectra of $[\text{Ag}_{19}(\text{C}\equiv\text{C}'\text{Bu})_{16}(\text{CO}_3^{2-})]\text{BF}_4$ ($(\text{CO}_3^{2-})@Ag_{19}$) and $[\text{Ag}_{21}(\text{C}\equiv\text{C}'\text{Bu})_{18}(\text{SO}_4)]\text{BF}_4$ ($(\text{SO}_4^{2-})@Ag_{21}$).

Table S3. Selected Bond lengths [\AA] and angles [$^\circ$] for **1**.

Bond lengths [\AA]			
O(1)-Ag(15)	2.800(4)	O(5)-Ag(3)	2.809(4)
O(1)-Ag(20)	2.687(4)	O(5)-Ag(10)	2.653(4)
O(1)-Ag(21)	2.828(4)	O(5)-Ag(19)	2.609(4)
O(2)-Ag(9)	2.417(4)	O(6)-Ag(4)	2.442(4)
O(2)-Ag(12)	2.833(4)	O(6)-Ag(12)	2.779(4)
O(2)-Ag(20)	2.816(4)	O(7)-Ag(9)	2.806(4)
O(3)-Ag(8)	2.550(4)	O(7)-Ag(22)	2.846(4)
O(3)-Ag(17)	2.592(4)	O(7)-Ag(23)	2.645(4)
O(4)-Ag(3)	2.560(4)	O(8)-Ag(8)	2.578(5)
O(4)-Ag(13)	2.682(4)	O(8)-Ag(13)	2.624(5)
C(1)-O(1)	1.263(7)	C(2)-O(2)	1.265(7)
C(3)-O(3)	1.269(7)	C(4)-O(4)	1.263(7)

C(5)-O(5)	1.263(7)	C(6)-O(6)	1.254(8)
C(7)-O(7)	1.257(7)	C(8)-O(8)	1.253(8)
C(1)-C(4)	1.450(9)	C(1)-C(2)	1.453(8)
C(2)-C(3)	1.442(9)	C(3)-C(4)	1.456(8)
C(5)-C(8)	1.451(9)	C(5)-C(6)	1.468(9)
C(6)-C(7)	1.460(9)	C(7)-C(8)	1.480(9)

Angles [°]

O(1)-C(1)-C(4)	135.8(6)	O(1)-C(1)-C(2)	134.4(6)
O(2)-C(2)-C(3)	136.3(6)	O(2)-C(2)-C(1)	133.3(6)
O(3)-C(3)-C(2)	133.9(6)	O(3)-C(3)-C(4)	136.2(6)
O(4)-C(4)-C(1)	136.4(6)	O(4)-C(4)-C(3)	133.7(6)
O(5)-C(5)-C(8)	134.8(6)	O(5)-C(5)-C(6)	134.4(6)
O(6)-C(6)-C(7)	134.6(6)	O(6)-C(6)-C(5)	135.8(6)
O(7)-C(7)-C(6)	134.8(6)	O(7)-C(7)-C(8)	135.2(6)
O(8)-C(8)-C(5)	135.5(6)	O(8)-C(8)-C(7)	134.8(6)
C(4)-C(1)-C(2)	89.8(5)	C(3)-C(2)-C(1)	90.4(5)
C(2)-C(3)-C(4)	89.9(5)	C(1)-C(4)-C(3)	89.9(5)
C(8)-C(5)-C(6)	90.8(5)	C(7)-C(6)-C(5)	89.7(5)
C(6)-C(7)-C(8)	89.9(5)	C(5)-C(8)-C(7)	89.6(5)
