Supporting Information for

## Ag(I)-Mediated Formation of Pyrodiphosphonate Coupled with C-C

## **Bond Cleavage of Acetonitrile**

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**Materials.** Acetonitrile was A. R. grade except for the special statement and was dried with 4 Å molecular silicate sieve prior to use. Sliver nitrate was A. R. grade and used without purification. All manipulations were performed under dried conditions. Elemental analyses for C, H and N were determined using a PE 2400 elemental analyzer. The IR spectra were recorded on a Bruker VECTOR 22 IR spectrometer with pressed KBr pellets in the 400-4000 cm<sup>-1</sup> region. Powder X-ray diffraction patterns were recorded on a SHIMADZU XRD-6000 instrument using Cu-K $\alpha$  radiation. Liquid state <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker Advance DPX 500 spectrometer. The ESI-MS spectra were recorded on a Thermo SCIENTIFIC LCQFLEET XP ion trap mass spectrometer.

Experimental Section. Phenylphosphonic acid (H<sub>2</sub>L), 3-thienylphosphinic acid (3-TPA) and

naphthylphosphonic acid (NPA) were synthesized according the classical procedure known as

Arbuzov-type reaction.<sup>1</sup>

[Ag<sub>3</sub>(ppp)](CN) 1: To 6.5 mL of CH<sub>3</sub>CN was added AgNO<sub>3</sub> (0.340 g, 2.0 mmol) and H<sub>2</sub>L (0.158 g, 1.0 mmol), then the mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 48 hours. After slow cooling to room temperature, colorless needle-like crystals were obtained, which were collected, washed with CH<sub>3</sub>CN and dried in air. Yield: 0.156 g (36.2 % based on AgNO<sub>3</sub>).. Elemental analysis calcd (%) for C<sub>13</sub>H<sub>10</sub>NO<sub>5</sub>P<sub>2</sub>Ag<sub>3</sub>: C, 24.18; H, 1.56; N, 2.17; found: C, 24.11; H, 1.47; N, 2.18. The presence of CN<sup>-</sup> is further confirmed by the weak peak at 2249 cm<sup>-1</sup> in the IR spectrum.

[Ag<sub>3</sub>(ptp)](CN) 2: To 6.5 mL of CH<sub>3</sub>CN was added AgNO<sub>3</sub> (0.034 g, 0.2 mmol) and 3-TPA (0.033 g, 0.2 mmol), then the mixture was transferred to a Teflon-lined autoclave and kept at 120  $^{\circ}$ C for 48 hours. After slow cooling to room temperature, pale yellow lamina crystals accompanying with a small amount of brown powder were obtained. The crystals were collected manually, washed with CH<sub>3</sub>CN and dried in air. Yield: 0.016 g (36.5 % based on AgNO<sub>3</sub>). Elemental analysis calcd (%) for C<sub>9</sub>H<sub>6</sub>NO<sub>5</sub>P<sub>2</sub>S<sub>2</sub>Ag<sub>3</sub>: C, 16.43; H, 0.92; N, 2.13; found: C, 16.27; H, 0.87; N, 2.11.

[Ag<sub>5</sub>(pnp)<sub>2</sub>](CN) 3: To 6.5 mL of CH<sub>3</sub>CN was added AgNO<sub>3</sub> (0.026 g, 0.15 mmol) and NPA (0.021 g, 0.10 mmol), then the mixture was transferred to a Teflon-lined autoclave and kept at 140 °C for 72 hours. After slow cooling to room temperature, a few yellow block crystals with large unknown brown-black powder were obtained. The crystal suited for X-ray single crystal diffraction was picked out and characterized. The yield is about 2 % based on AgNO<sub>3</sub>. Elemental

analyses isn't carried out for the crystals are few and obtained accompanying with a large sum of brown powder.

AgCN 4: To 50 mL of CH<sub>3</sub>CN was added AgNO<sub>3</sub> (2.616 g, 15.4 mmol), then the mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 48 hours. After slow cooling to room temperature a white powder (4) was obtained, which was collected by filtration, washed with CH<sub>3</sub>CN and dried in desiccator. Yield: 0.115 g 5.6 % based on AgNO<sub>3</sub>. Elemental analysis calcd (%) for AgCN: C, 8.97; N, 10.46; found: C, 8.99; N, 10.41.

**X-ray Crystallography**. Crystals of dimensions 0.26 x 0.24 x 0.22 mm<sup>3</sup> for **1**, 0.30 x 0.26 x 0.24 mm<sup>3</sup> for **2** and 0.27 x 0.21 x 0.12 mm<sup>3</sup> for **3** were selected for indexing and intensity data collection at room temperature on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation. The data were integrated using the Siemens SAINT program<sup>2</sup>, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Absorption corrections were applied. The structures were solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares using SHELXTL<sup>3</sup>. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. The H atoms were placed in calculated positions allowed to ride on their respective parent atoms. Selected bond lengths and angles are given in Tables S1-S3 for compounds **1-3**, respectively.

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Ag1-X	2.181(10)	Ag2-Ag3A	3.008(1)
Ag1-O4B	2.322(6)	Ag2-Ag2B	3.299(2)
Ag1-O2A	2.365(7)	C1-P1	1.790(11)
Ag1-01	2.425(7)	C7-P2	1.767(10)
Ag2-O5A	2.297(7)	O1-P1	1.467(8)
Ag2-O2B	2.322(7)	O2-P1	1.499(7)
Ag2-O1	2.333(7)	O3-P1	1.589(7)
Ag2-O4	2.494(6)	O3-P2	1.618(7)
Ag3-O5	2.197(7)	O4-P2	1.520(7)
Ag3-X′C	2.322(11)	O5-P2	1.508(7)
Ag1-Ag2	3.082(1)	X-X'	1.047(14)
Ag1-Ag3B	3.090(1)		
X-Ag(1)-O4B	125.0(3)	P1-O2-Ag2B	115.0(4)
X-Ag1-O2A	113.5(3)	P1-O2-Ag1E	130.9(4)
X-Ag1-O1	107.9(3)	P2-O4-Ag1B	114.0(4)
O4B-Ag1-O2A	109.4(2)	P2-O4-Ag2	126.6(4)
O4B-Ag1-O1	94.6(3)	P2-O5-Ag3	129.2(5)
O2A-Ag1-O1	102.2(2)	P2-O5-Ag2E	126.4(4)
O5A-Ag2-O2B	89.9(3)	P1-O3-P2	128.6(5)
O5A-Ag2-O1	120.9(3)	Ag2-Ag1-Ag3B	119.3(0)
O5A-Ag2-O4	94.6(2)	Ag3A-Ag2-Ag1	160.5(0)
O2B-Ag2-O1	145.3(3)	Ag2E-Ag3-Ag1B	79.6(0)
O2B-Ag2-O4	107.7(2)	Ag1-X-X'	169.3(10)
O1-Ag2-O4	86.9(2)	Ag3-X'C-XC	174.5(10)

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O5-Ag3-X'C	164.4(3)	X-Ag1-Ag3B	82.1(2)	
P1-O1-Ag2	120.8(4)	X'C-Ag3-Ag1B	105.5(3)	
P1-O1-Ag1	139.9(5)			
<sup><i>a</i></sup> Symmetry codes: A: $x + 1$ , v, z: B: $-x + 2$ , $-v$ , $-z + 1$ : C: $x - 1$ , $v - 1$ , z: D: $1 - x$ , $-v$ , $1$				
– z; E: x - 1, y, z.				
Table S2. Selected	Bond Lengths [Å	] and Angles [°] for Compo	bund $2^a$	
Ag1-X	2.005(9)	Ag1-Ag3D	3.366(1)	
Ag1-O4	2.283(7)	Ag2-Ag2A	3.223(2)	
Ag1-O1A	2.428(7)	P1-O1	1.483(7)	
Ag2-O1A	2.304(7)	P1-O2	1.504(7)	
Ag2-O2	2.359(6)	O3-P1	1.614(8)	
Ag2-O5B	2.482(7)	O3-P2	1.612(7)	
Ag3-X′C	2.066(10)	O4-P2	1.489(7)	
Ag3-O5	2.182(7)	O5-P2	1.457(8)	
Ag1-Ag3	3.068(1)	P1-C1	1.764(10)	
Ag1-Ag2	3.202(1)	C5-P2	1.779(11)	
Ag2-Ag3B	3.176(1)	X-X'	1.134(15)	
X-Ag1-O4	155.0(4)	P2-O3-P1	127.7(5)	
X-Ag1-O1A	115.7(3)	Ag1-X-X'	172.9(9)	
04-Ag1-01A	89.2(2)	Ag3-X'C-XC	167.7(10)	
O1A-Ag2-O2	155.3(2)	X'C-Ag3-Ag1	106.8(3)	
O1A-Ag2-O5B	120.4(3)	X-Ag1-Ag3	77.7(3)	
O2-Ag2-O5B	84.2(3)	Ag3-Ag1-Ag2	96.9(0)	
X'C-Ag3-O5	169.7(3)	Ag3B-Ag2-Ag1	170.9(0)	
P1-O1-Ag2A	121.3(4)	Ag1-Ag3-Ag2B	91.7(0)	
P1-O1-Ag1A	132.1(4)	Ag1-Ag2-Ag2A	80.7(4)	
P1-O2-Ag2	114.4(3)	Ag3B -Ag2-Ag2A	101.4(1)	
P2-O4-Ag1	121.1(4)	Ag2-Ag1-Ag3D	97.8 (1)	
P2-O5-Ag3	128.6(5)	Ag2B-Ag3-Ag1E	78.9(1)	
P2-O5-Ag2B	120.6(4)			

<sup>*a*</sup> Symmetry codes: A: -x + 1, -y, -z; B: -x + 2, -y, -z; C: -x + 2, -y + 1, -z; D: x - 1, y, z; E: x + 1, y, z.

**Table S3.** Selected Bond Lengths [Å] and Angles [°] for Compound  $3^a$ 

		<u>-]</u>		
Ag1-X	2.080(7)	Ag3-Ag2A	3.279(9)	
Ag1-O2	2.163(6)	X-X'F	1.109(2)	
Ag2-O4	2.532(6)	C1-P1	1.801(8)	
Ag2-O3C	2.189(6)	C11-P2	1.824(9)	
Ag2-O5B	2.476(5)	O1-P2	1.608(6)	
Ag2-O5D	2.376(6)	O1-P1	1.612(6)	
Ag3-O4A	2.215(6)	O2-P1	1.484(6)	
Ag3-O4	2.215(6)	O3-P1	1.488(6)	
Ag1-Ag1E	3.313(1)	O4-P2	1.451(6)	

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Ag3-Ag2	3.274(9)	O5-P2	1.485(7)
X-Ag1-O2	152.6(3)	P2-O1-P1	135.3(4)
O3C-Ag2-O5D	164.4(2)	P1-O2-Ag1	124.8(3)
O3C-Ag2-O5B	124.7(2)	P1-O3-Ag2D	145.6(4)
O3C-Ag2-O4	99.4(2)	P2-O4-Ag3	120.9(4)
O5D-Ag2-O5B	70.3(2)	P2-O4-Ag2	141.7(3)
O5D-Ag2-O4	83.1(2)	P2-O5-Ag2C	139.2(3)
O5B-Ag2-O4	91.2(2)	P2-O5-Ag2B	112.3(3)
O4A-Ag3-O4	173.9(3)	X-Ag1-Ag1E	67.2(2)
Ag2-Ag3-Ag2A	73.6(1)	O2-Ag1-Ag1E	121.03(15)
X'F-X-Ag1	171.3(5)		

<sup>*a*</sup> Symmetry codes: A: -x, y, -z + 1/2; B: -x, -y + 1,-z + 1; C: x, -y + 1,z + 1/2; D: x, -y + 1, z - 1/2; E: -x, -y, -z; F: -x, y, -z - 1/2; G: x, -y, z - 1/2.



Scheme S1 The coordination modes of the pyrophosphonates: (a) ppp<sup>2-</sup>; (b) ptp<sup>2-</sup>; (c) pnp<sup>2-</sup>.



Fig. S1 (a) The inorganic layer of 1 derived from infinite stair-like "silver chains" and CN<sup>-</sup> groups. The symmetry

codes are the same as those in Table S1.

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Fig. S1 (b) Packing diagram of 1 along the *a*-axis. The hydrogen atoms are ommited for clarity.



**Fig. S2** (a) The layer structure of **2**, made up of infinite "cationic columns"  $\{[Ag_3(ptp)]^+\}_{\infty}$  and cyanide groups.

All H atoms are omitted for clarity.



Fig. S2 (b) The inorganic layer of 2 derived from infinite stair-like "silver chains" and CN<sup>-</sup> groups. The symmetry

codes are the same as those in Table S2.



Fig. S2 (c) Packing diagram of 2 along the *a*-axis. The hydrogen atoms are ommited for clarity.



Fig. S3 (a) A "broad column" viewed along the c-axis in 3. The hydrogen atoms are ommited for clarity.



**Fig. S3** (b) Packing diagram of **3** along the *c*-axis. The layer extended in the *bc* plane is made up of "broad columns" connected by inter-column Ag…Ag interactions. The hydrogen atoms are ommitted for clarity.



**Fig. S4** ESI mass spectra of the resulting solution, which were obtained by treating  $H_2L$  with M ( $C_{AgNO3} = 0.038$  mol·L<sup>-1</sup>) in the molar ratio of 2:1 in CH<sub>3</sub>CN after 3 h (top), and heating  $H_2L$  in CH<sub>3</sub>CN after 48 h (bottom).



**Fig. S5** The IR spectra of the solid products obtained by reacting  $H_2L$  with AgNO<sub>3</sub> in a molar ratio of 2:1 in acetonitrile at 120 °C for different time: (A) 1 day, (B) 2 days, (C) 4 days and (D) 7 days. For the convenience of comparison, the IR spectrum of crystals **1** (1) is also given. The characteristic peaks: the peaks in the range of 1250-950 cm<sup>-1</sup> in spectrum 1 suggest the existence of phosphonate group; the strong splitting peaks at 2139 and 2161 cm<sup>-1</sup> in spectrum 4 (IR spectrum of compound **4**) suggest the existence of cyanide group. The slight difference in the range of 1250-950 cm<sup>-1</sup> between spectrum B and 4 suggests that AgCN began to convert to  $[Ag_3(ppp)](CN)$  in about two days, and the highly resemblance of spectrum D and 1 reveal that AgCN is almost totally converted into  $[Ag_3(ppp)](CN)$  after 7 days.



**Fig. S6** The <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of the filtrate, which was obtained by treating pure compound **4** with NaBr in the molar ratio of 2:3 in  $D_2O-d_2$ .



**Fig. S7** (a) The <sup>1</sup>H NMR spectrum of solution 1 on a Bruker Advance DPX 500 spectrometer shows the impurity in the region of methyl and methylene. The impure proton resonance's intensity is equal to 1.23 when the proton resonance's intensity of CH<sub>3</sub>CN is named to 100. Solution 1 was prepared by removing of 200  $\mu$ L of acetonitrile (HPLC Grade), which was heated at 120 °C for 48 h under solvothermal conditions prior to use, to 550  $\mu$ L of CD<sub>3</sub>CN-*d*<sub>3</sub>.



**Fig. S7** (b) The <sup>1</sup>H NMR spectrum of solution 2 on a Bruker Advance DPX 500 spectrometer shows the proton resonance's intensity in the region of methyl and methylene has increased 60 % compared with that in Fig. S7(a) (the proton resonance's intensity of CH<sub>3</sub>CN is named to 100). This result indicates that the C-C bond of CH<sub>3</sub>CN has been cleaved. Solution 2 was prepared by removing of 200  $\mu$ L of resulting acetonitrile solution, which was obtained by heating acetonitrile (HPLC Grade) solution of silver(I) nitrate ( $C_{AgNO3} = 0.308 \text{ mol·L}^{-1}$ ) at 120 °C for 48 h under solvothermal conditions, to 550  $\mu$ L of CD<sub>3</sub>CN-d<sub>3</sub>.



**Fig. S7** (c) The <sup>1</sup>H NMR spectrum of solution 3 on a Bruker Advance DPX 500 spectrometer shows the proton resonance's intensity in the region of methyl and methylene has increased 96 % compared with that in Fig. S7(a) (the proton resonance's intensity of CH<sub>3</sub>CN is named to 100). This result indicates that the C-C bond cleavage of CH<sub>3</sub>CN has been increased comparing with that without H<sub>2</sub>L (Fig S7(b)). Solution 3 was prepared by removing of 200  $\mu$ L of resulting acetonitrile solution, which was obtained by reacting H<sub>2</sub>L with AgNO<sub>3</sub> ( $C_{AgNO3} = 0.308$  mol·L<sup>-1</sup>) in the molar ratio of 2:1 in acetonitrile (HPLC Grade) at 120 °C for 48 h under solvothermal conditions, to 550  $\mu$ L of CD<sub>3</sub>CN-*d*<sub>3</sub>.



**Fig. S7** (d) The <sup>1</sup>H NMR spectrum of solution 4 on a Bruker Advance DPX 500 spectrometer shows the proton resonance's intensity in the region of methyl and methylene has increased 156 % compared with that in Fig. S7(a) (the proton resonance's intensity of CH<sub>3</sub>CN is named to 100). This result indicates that with the compound **1** was generated, the more C-C bond of acetonitrile had been cleaved. Solution 4 was prepared by removing of 200  $\mu$ L of resulting acetonitrile solution (the resulting solution to obtain compound **1**), which was obtained by reacting H<sub>2</sub>L with AgNO<sub>3</sub> ( $C_{AgNO3} = 0.308 \text{ mol·L}^{-1}$ ) in the molar ratio of 1:2 in acetonitrile (HPLC Grade) at 120 °C for 48 h under solvothermal conditions, to 550  $\mu$ L of CD<sub>3</sub>CN-d<sub>3</sub>.

For comparison, the chemical shift and relative intensity of the proton signal in the region of methyl and methylene are presented in the following table. The proton resonance's intensity of CH<sub>3</sub>CN is named to 100,  $C_{AgNO3} = 0.308 \text{ mol}\cdot\text{L}^{-1}$ .

Sample	Chemical Shift ( $\delta$ ) / ppm	<b>Relative Intensity</b>
HPLC CH <sub>3</sub> CN	3.07	1.23
AgNO <sub>3</sub>	3.10	1.97
$H_2L:M = 2:1$	3.13	2.41
$H_2L:M = 1:2$	3.13	3.15



**Fig. S8** The ESI mass spectra of the resulting solutions, which were obtained by reacting H<sub>2</sub>L with AgCN (4) in the molar ratio of 2:1 at 120 °C for 3 h, 12 h, 2 d, 4 d and 7d (from bottom to top in turn) under solvothermal conditions, respectively. The spectra reveal that the pyrophenylphosphonate (HPPP<sup>-</sup>, m/z 297) was generated after 3 h and its amount was increased firstly along with the increase of the reacting time, and then it was kept invariable about 4 days later. ( $C_{AgCN} = 0.038 \text{ mol·L}^{-1}$ )



**Fig. S9** The IR spectra of AgCN (**4**) and the resulting solid substances. The solid substances were obtained by reacting H<sub>2</sub>L with AgCN (**4**) in the molar ratio of 2:1 in acetonitrile at 120 °C for 12 h, 2 d, 4 d and 7d under solvothermal conditions, respectively (from bottom to top in turn). The high resemblance of them indicates that the solid substance is still AgCN (**4**) and no compound **1** was generated even after 7 day. ( $C_{AgCN} = 0.038 \text{ mol·L}^{-1}$ ).

## References

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