
Supporting Information

Degradation *versus* Expansion of the AgX Frameworks: Formation of Oligomeric and Polymeric Silver Complexes from Reactions of Bulk AgX with N- Bis(diphenylphosphanylmethyl)-2-aminopyridine

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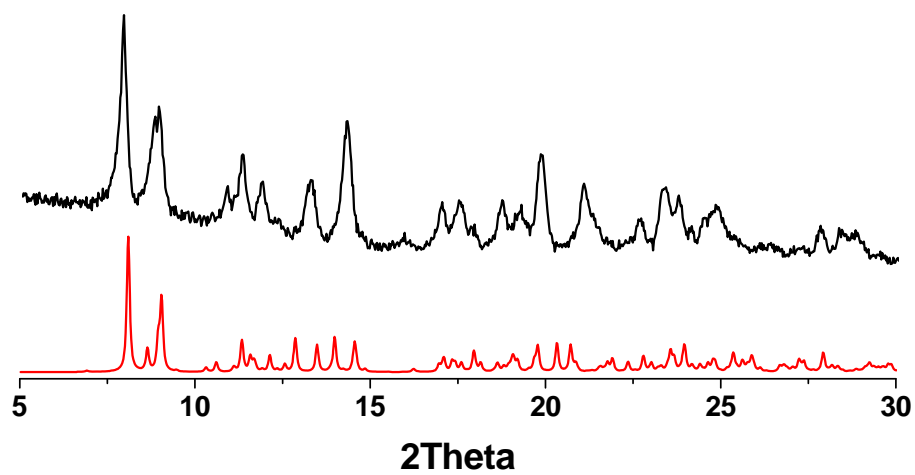
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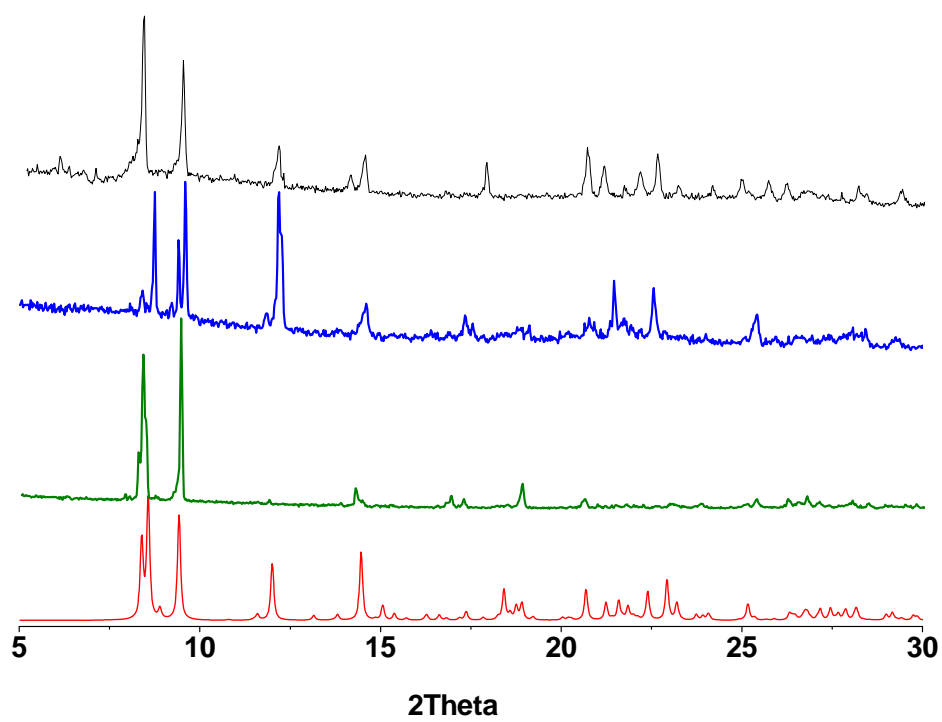
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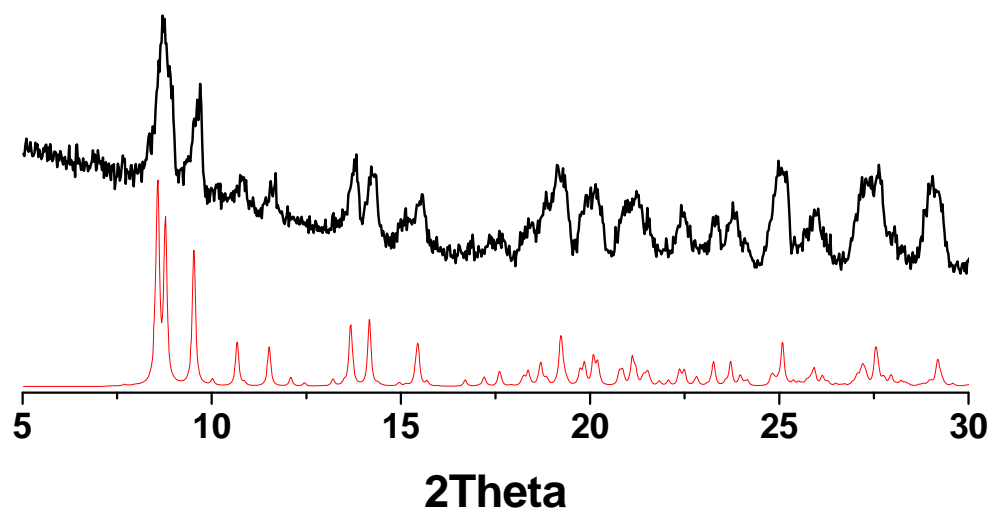
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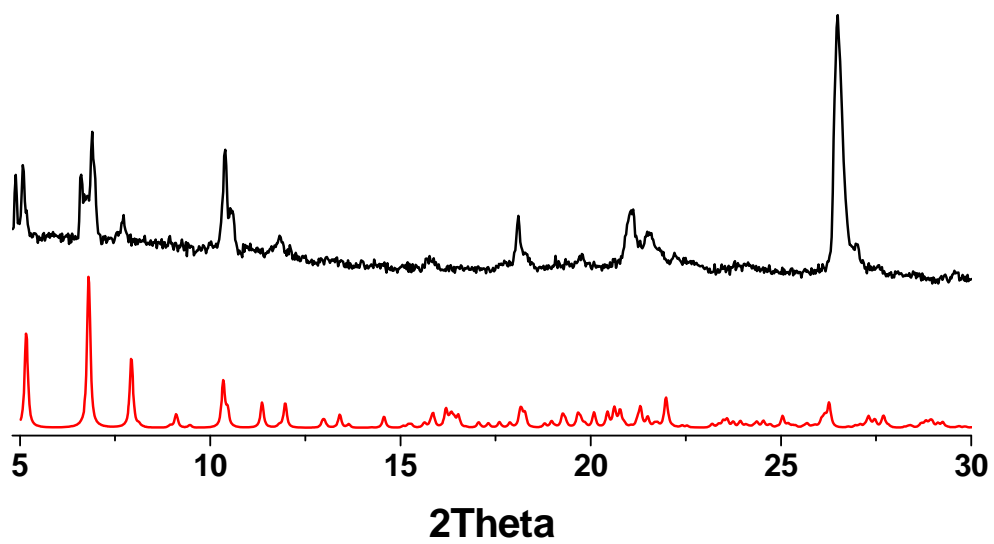
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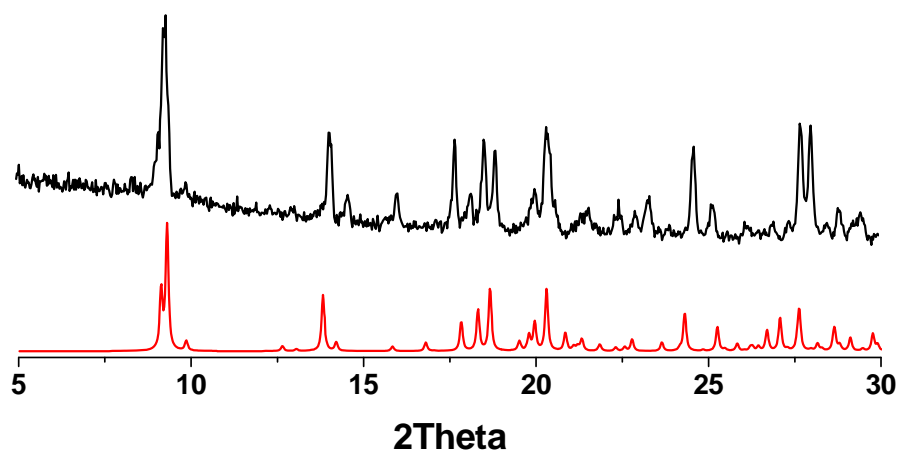
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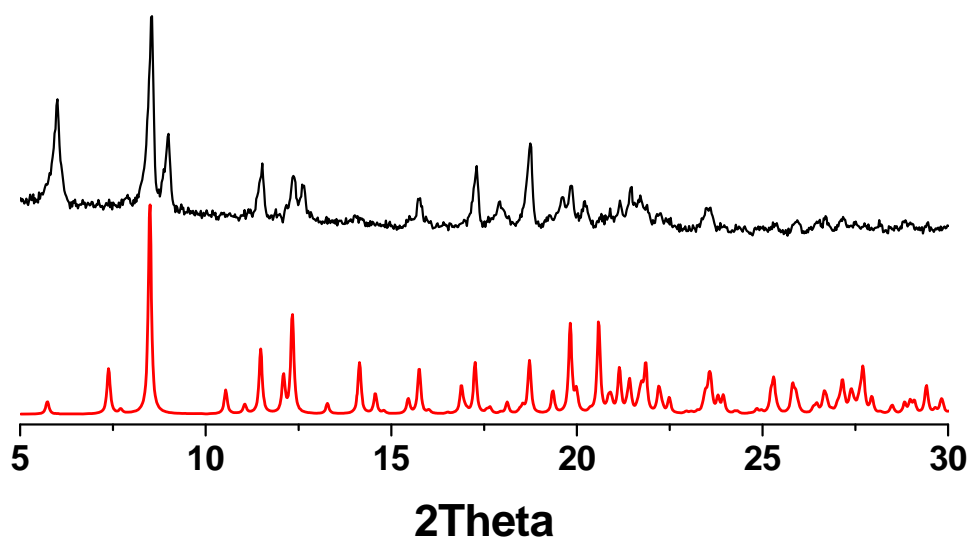
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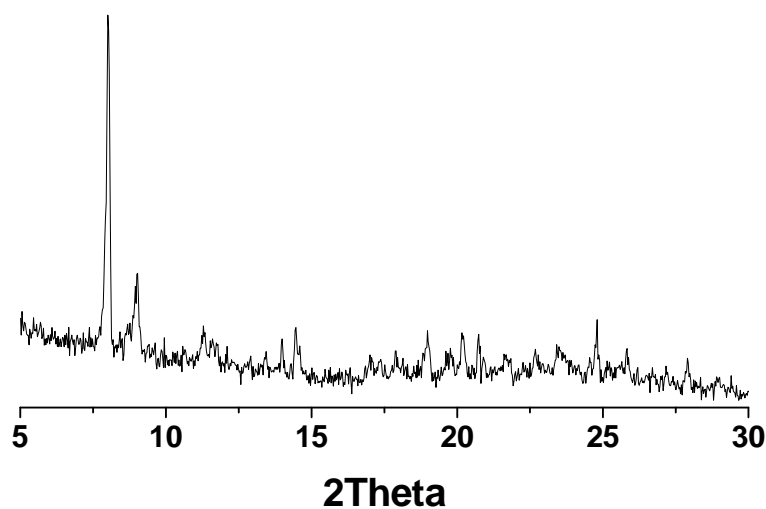
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(e)



(f)



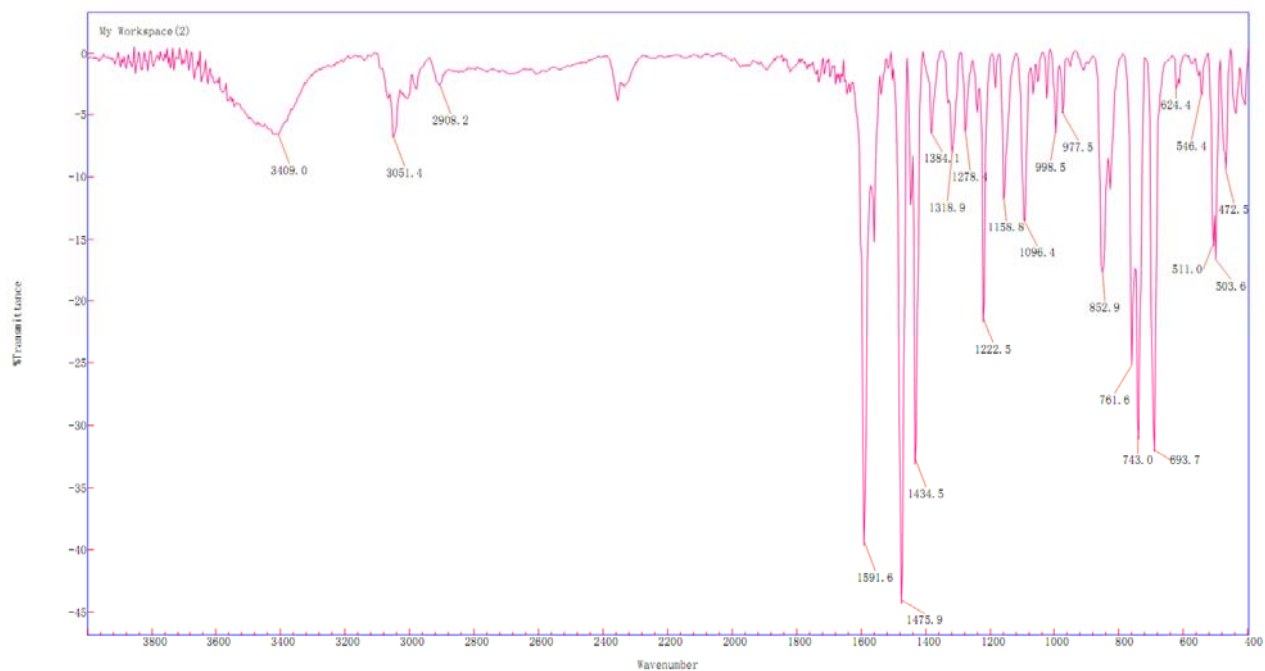
(g)

Figures S1. (a) PXRD patterns for **1**. Simulated (red) and single-phase polycrystalline sample (black) of **1**. (b) PXRD patterns for **2**, **3** and **4**. Simulated (red) of **3**, single-phase polycrystalline sample (green) of **3**, single-phase polycrystalline sample (blue) of **2** and single-phase polycrystalline sample (black) of **4**. (c) PXRD patterns for **5**. Simulated (red) and single-phase polycrystalline sample (black) of **5**. (d) PXRD patterns for **6**·CH₂Cl₂. Simulated (red) and single-phase polycrystalline sample (black) of **6**·CH₂Cl₂. (e) PXRD patterns for **7**·MeCN. Simulated (red) and single-phase polycrystalline sample (black) of **7**·MeCN. (f) PXRD patterns for **8**. Simulated (red) and single-phase polycrystalline sample (black) of **8**. (g) Observed PXRD patterns for a unknown complex obtained from refluxing a MeCN mixture containing bdppmapy and AgCN (molar ratio = 1:4).

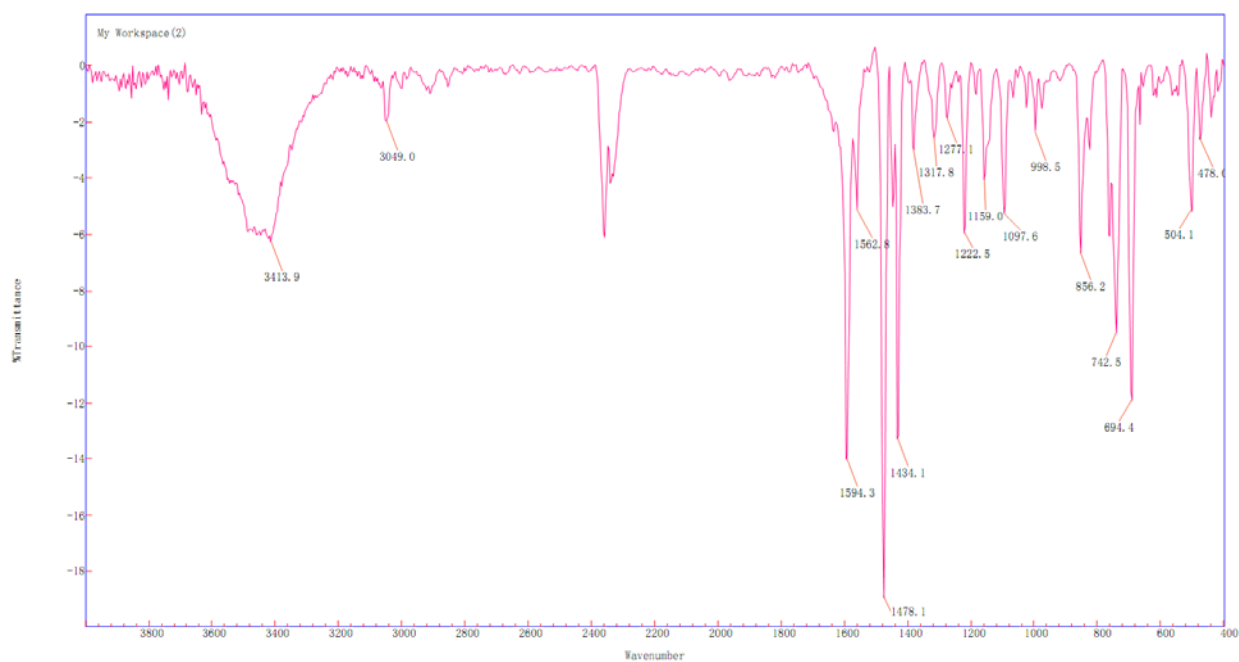
Table S1. The elemental analysis data for compounds **2-5** derived from reactions of **1** with NH_4X ($\text{X} = \text{Cl, Br, I, SCN}$) in MeCN. The numbers in parentheses are theoretical values for the C, H, N contents of **2-5**.

⁵	C	H	N
Compound 2	58.33 (58.74)	4.72 (4.45)	4.73 (4.42)
Compound 3	55.19 (54.89)	3.83 (4.16)	4.53 (4.13)
Compound 4	50.99 (51.37)	3.72 (3.75)	4.06 (3.99)
Compound 5	58.92 (58.55)	4.01 (4.30)	6.89 (6.40)

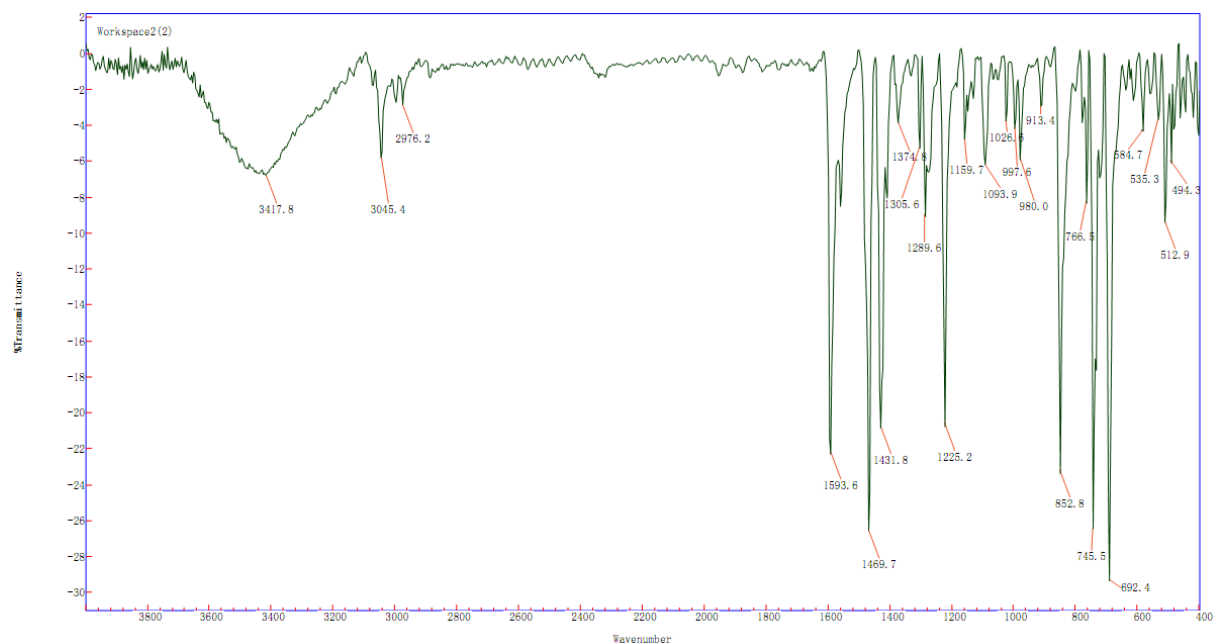
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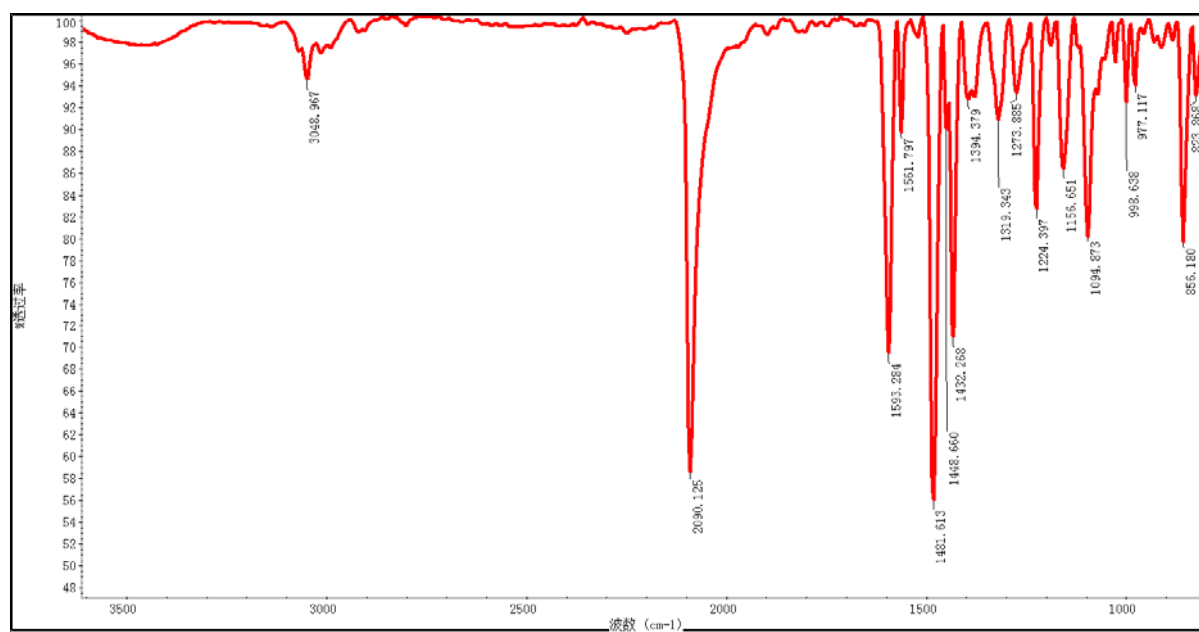
(a)



(b)

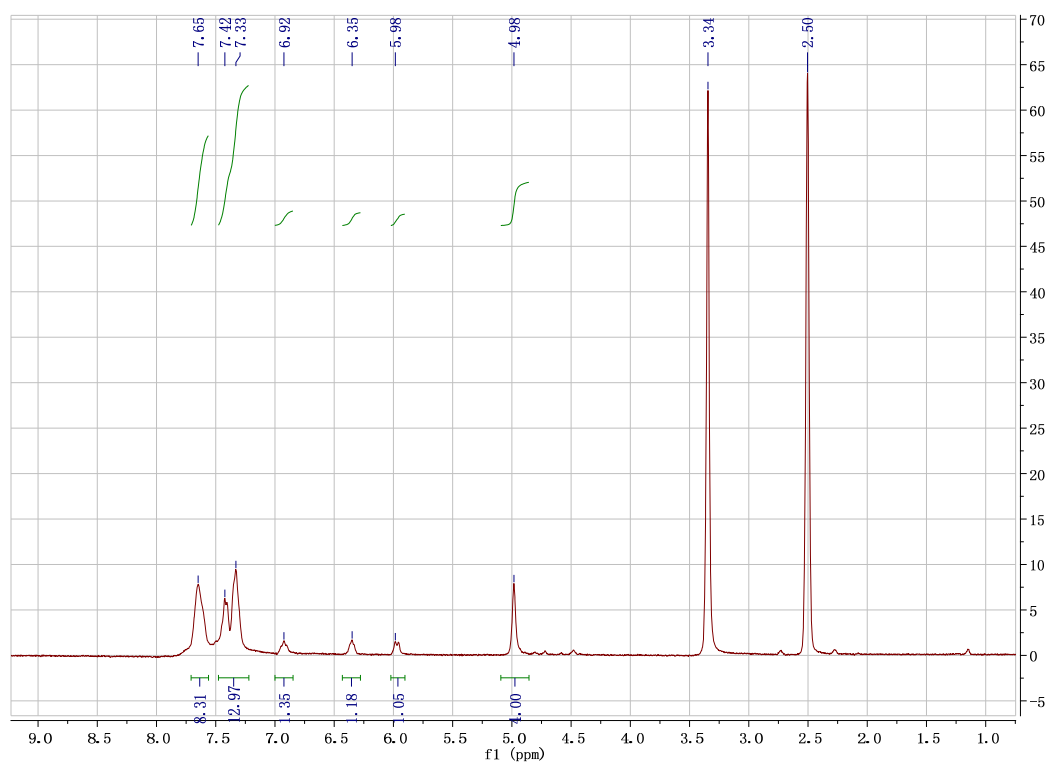


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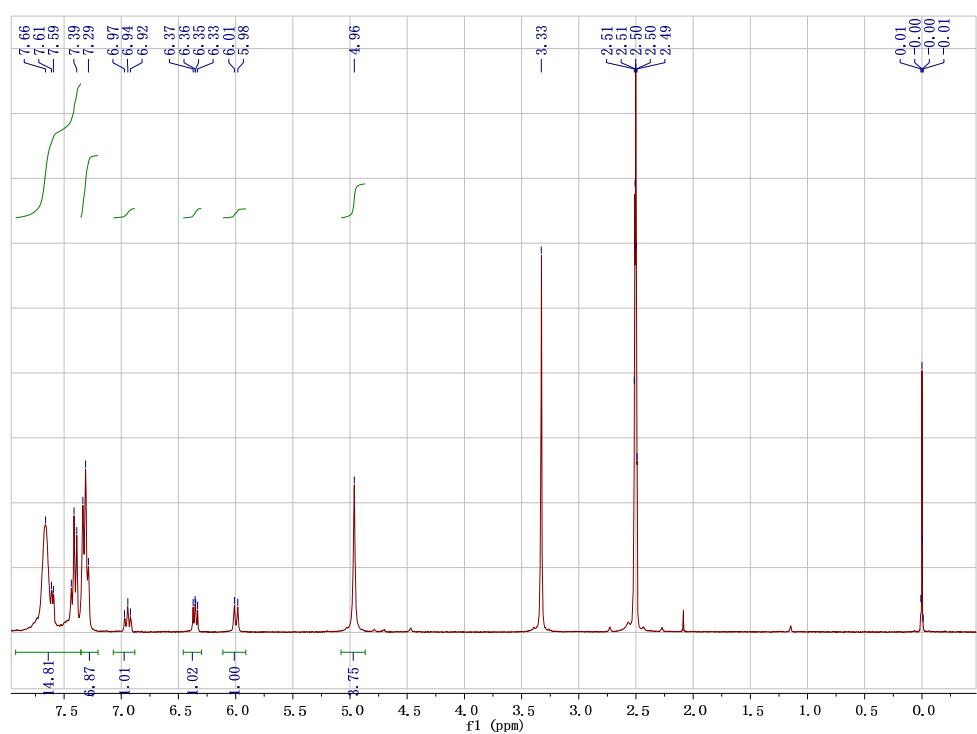


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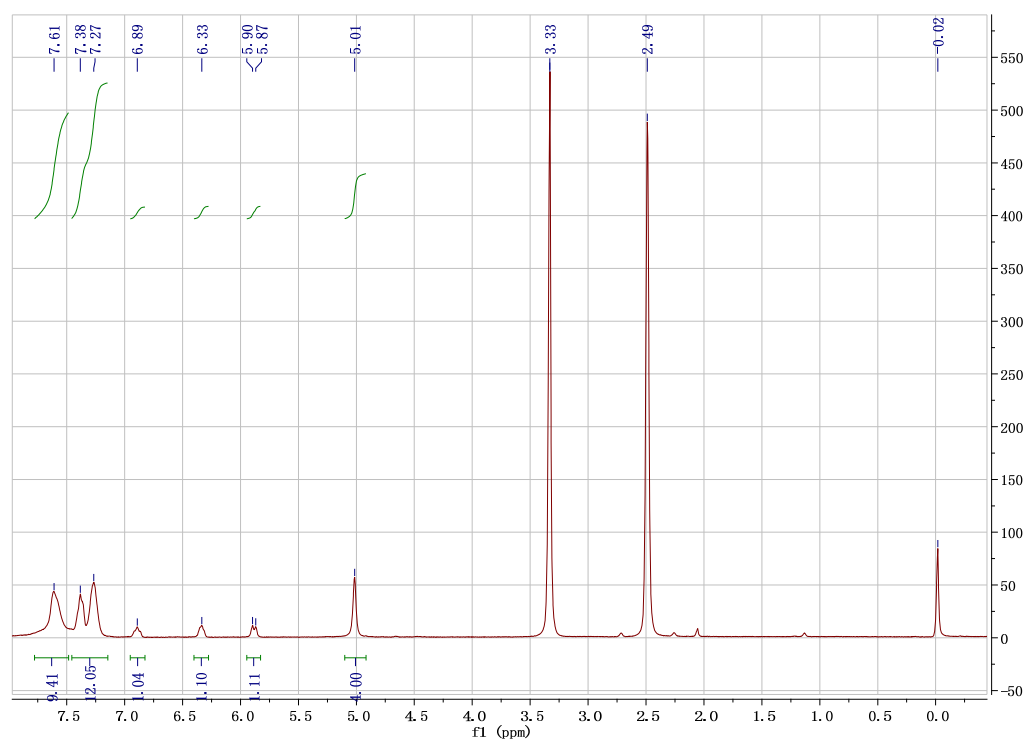
Figure S2. The IR spectra of compounds **2** (a), **3** (b), **4** (c) and **5** (d) derived from reactions of **1** with NH_4X ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) in MeCN.



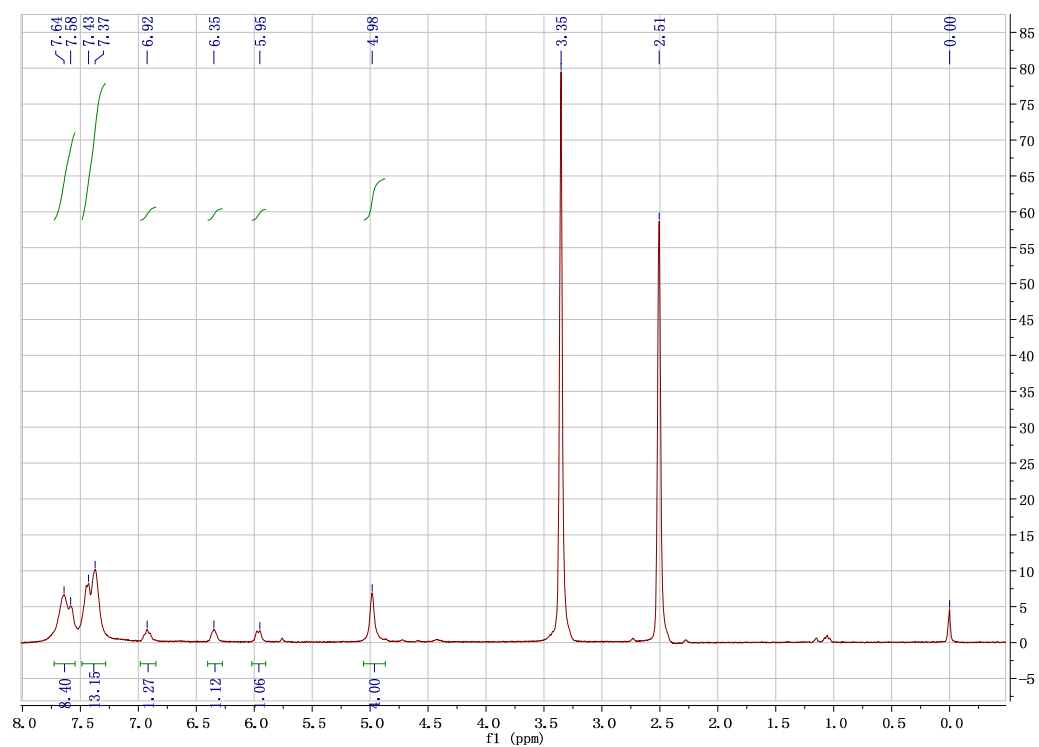
(a)



(b)

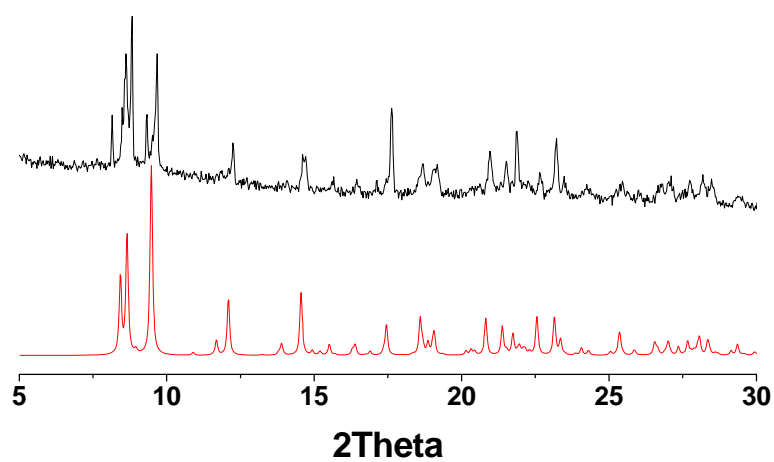


(c)

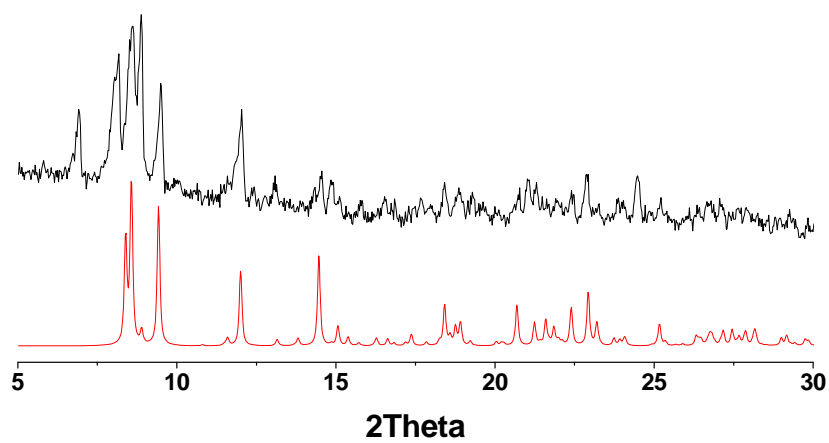


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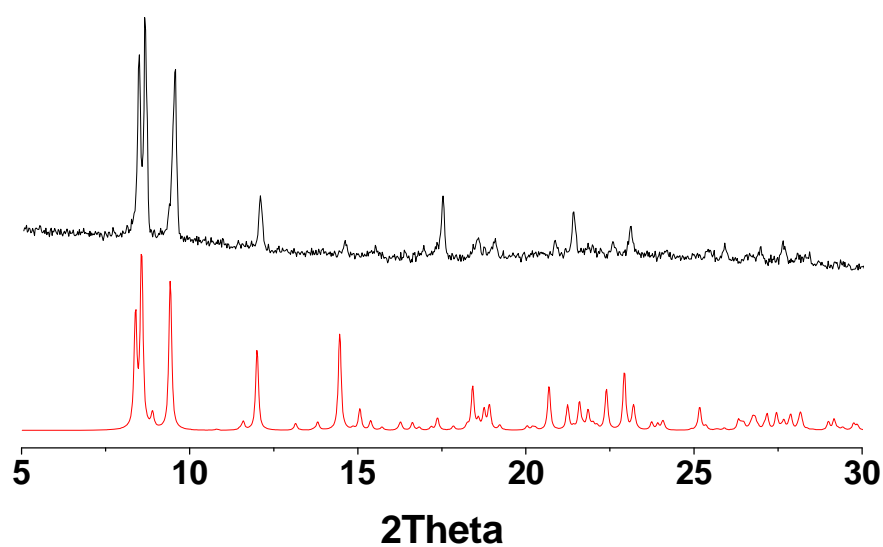
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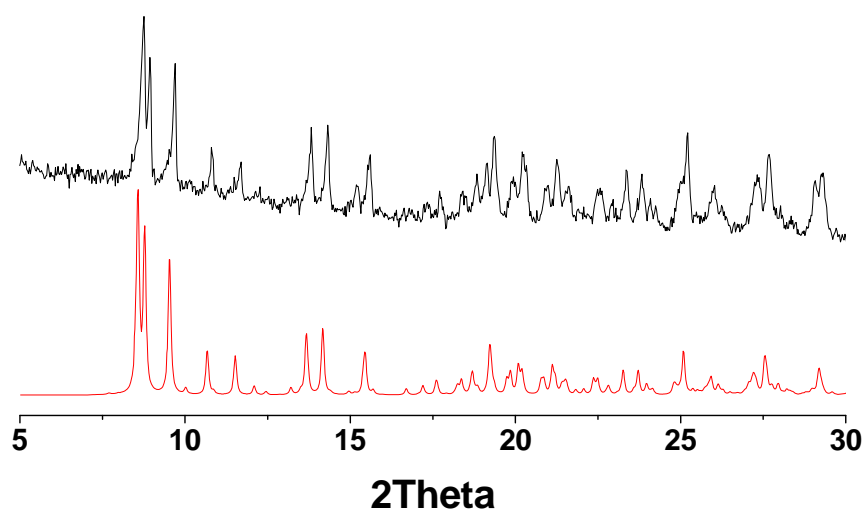
(a)



(b)



(c)



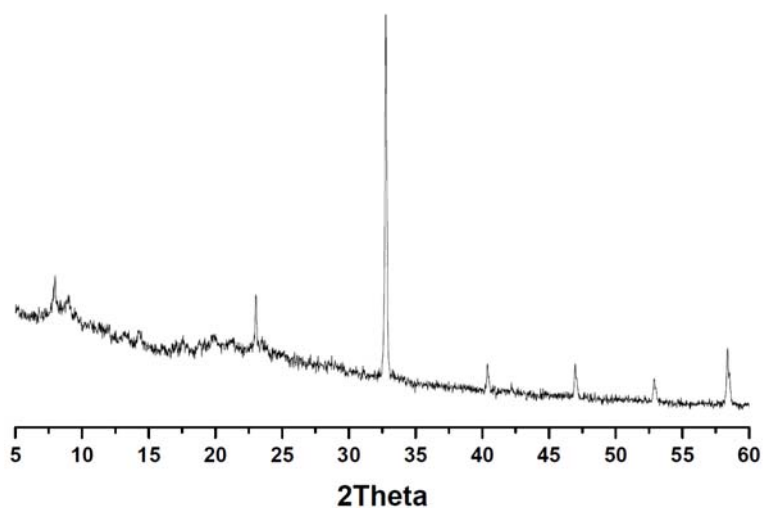
(d)

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Figure S4. The PXRD patterns of **2** (a), **3** (b), **4** (c) and **5** (d) derived from reactions of **1** with NH_4X ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) in MeCN. Simulated (red) and single-phase polycrystalline sample (black).

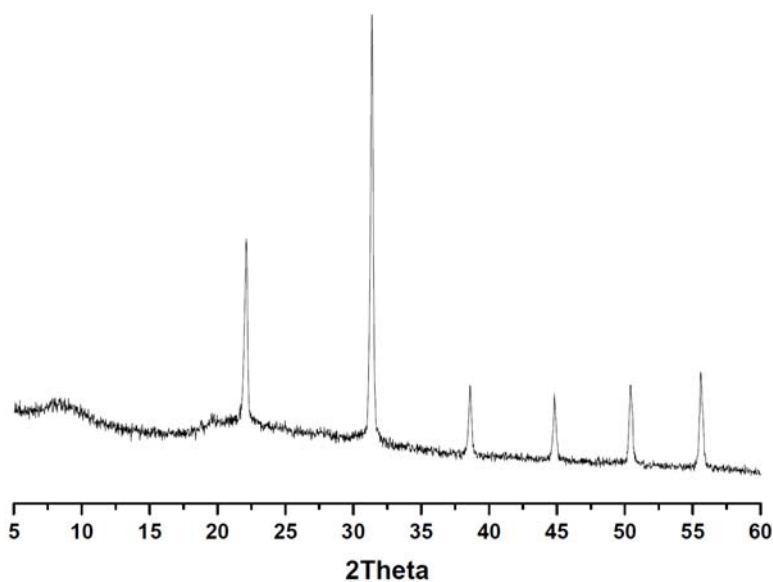
Solid state reactions of **1** with NH_4X ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) at room temperature

A mixture of powder **1** (143 mg, 0.1 mmol) and NH_4Cl (11 mg, 0.2 mmol) or NH_4Br (20 mg, 0.2 mmol) or NH_4I (29 mg, 0.2 mmol) or NH_4SCN powder (15 mg, 0.2 mmol) was placed in an agate mortar and ground at room temperature for 25 min. The resulting product was then characterized by powder X-ray diffraction (XPRD) (see below).

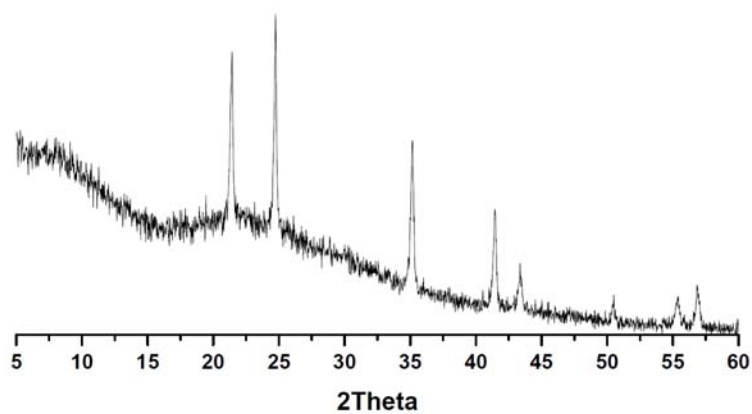


(a)

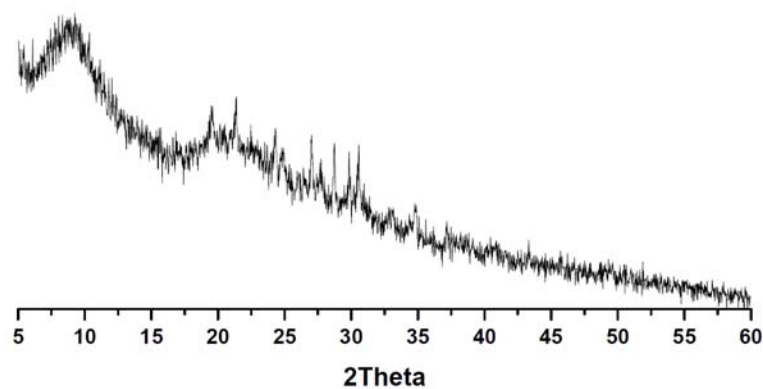
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(b)



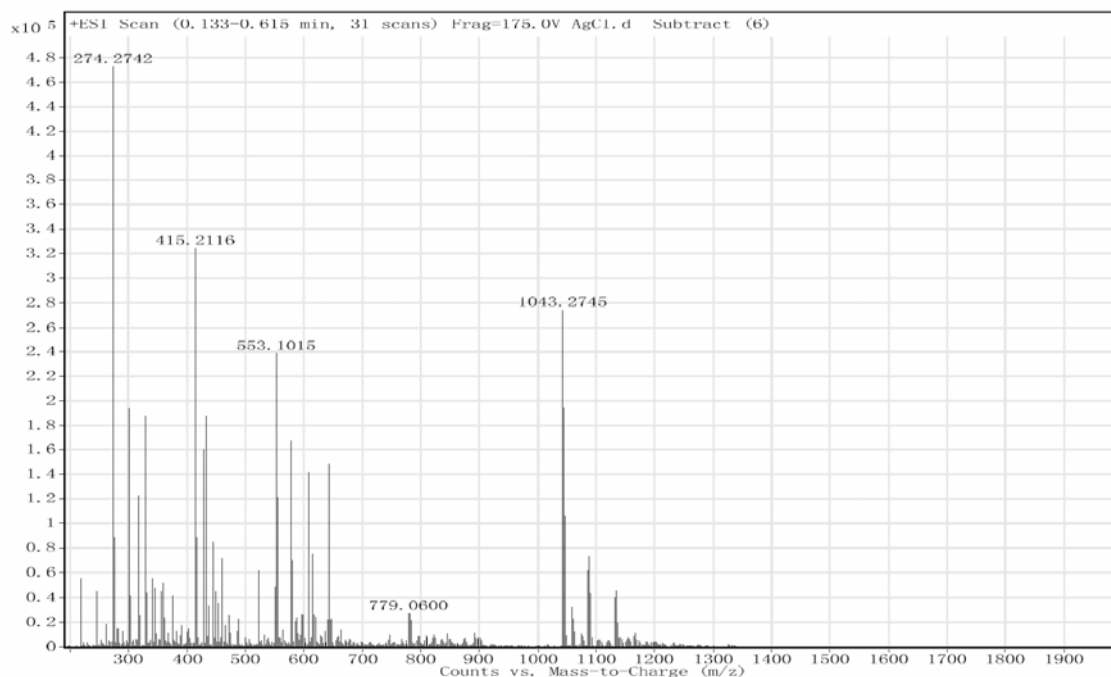
(c)



(d)

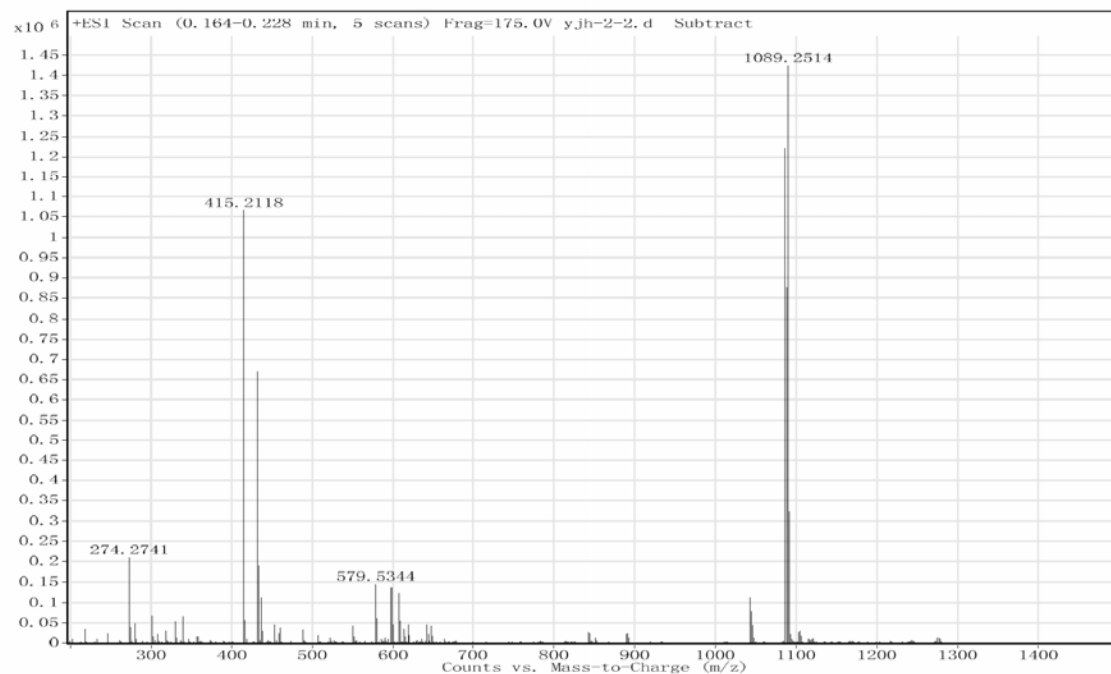
Figure S5. The observed PXRD patterns for the products derived from solid state reactions of **1** with NH_4Cl (a), NH_4Br (b), NH_4I (c) or NH_4SCN (d).

Sample Name	yjh-3	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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Data Filename	AgCl.d	ACQ Method		Comment		Acquired Time	2011-6-13 10:1



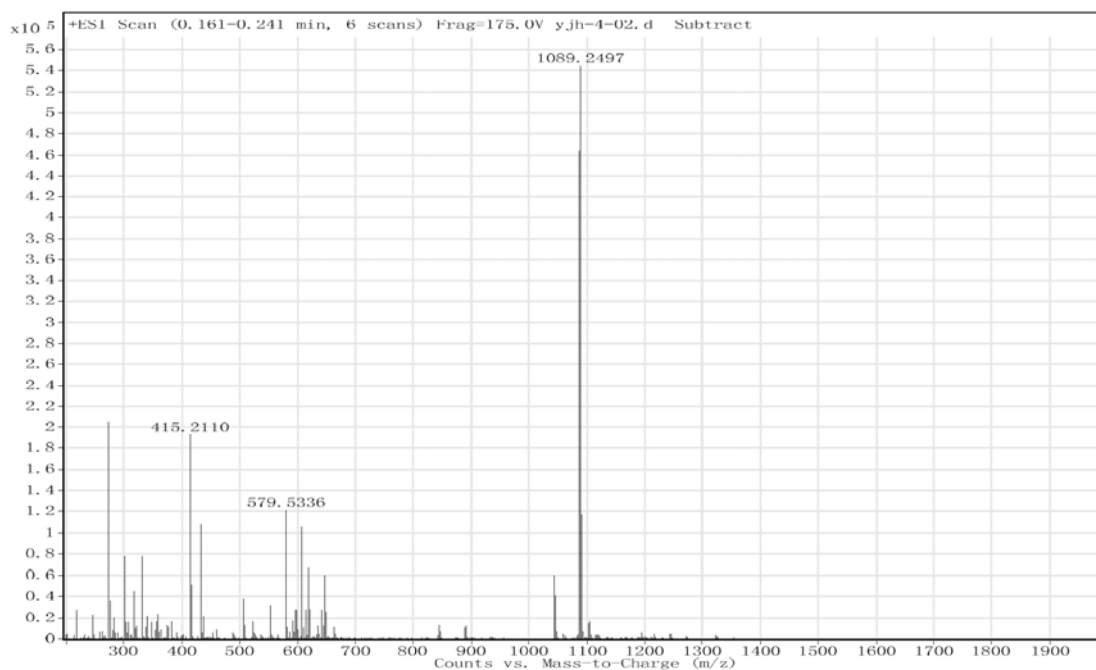
(a)

Sample Name	yjh-2	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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Data Filename	AgBr.d	ACQ Method		Comment		Acquired Time	2011-6-13 10:1



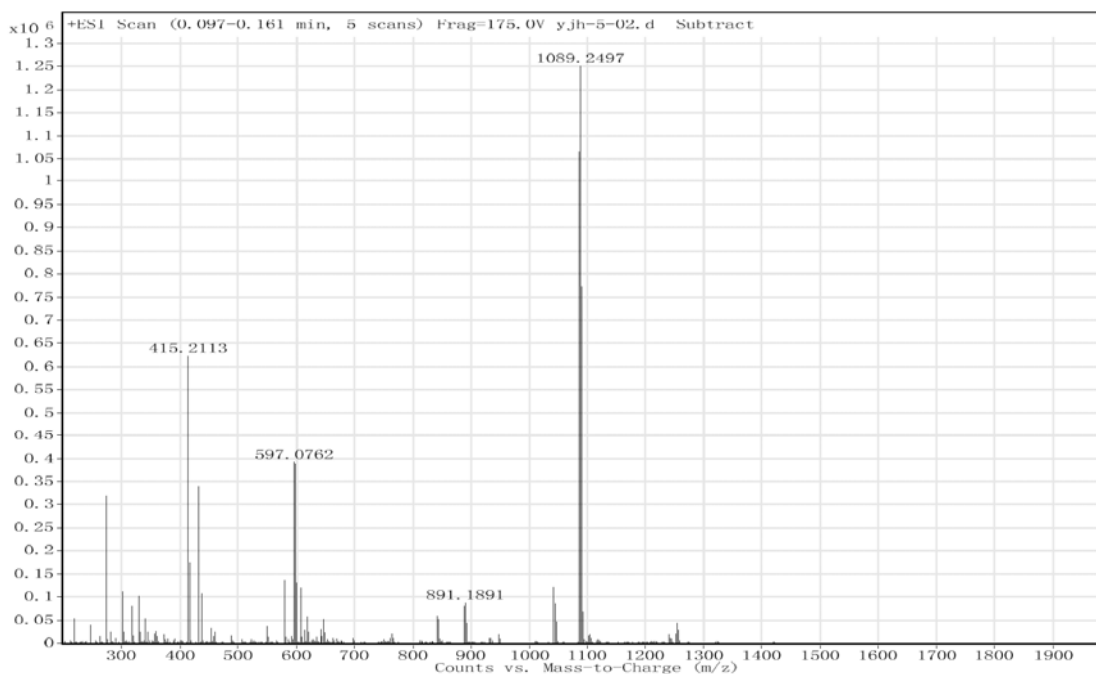
(b)

Sample Name	yjh-4	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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Data Filename	AgI.d	ACQ Method		Comment		Acquired Time	2011-6-13 10:2



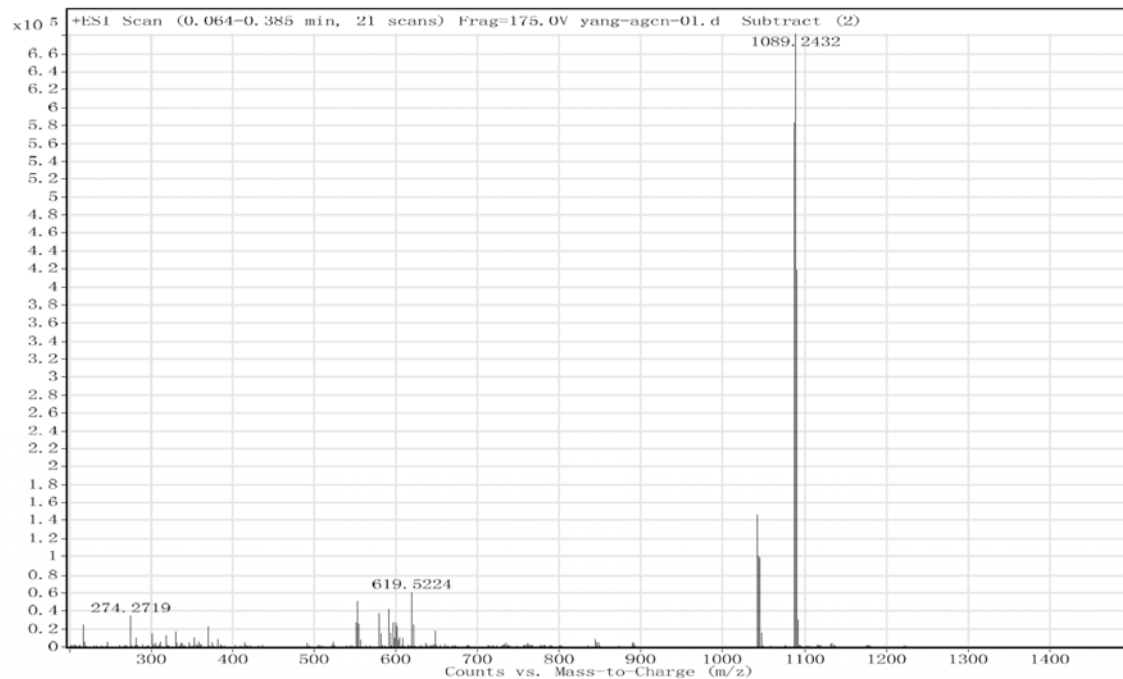
(c)

Sample Name	yjh-5	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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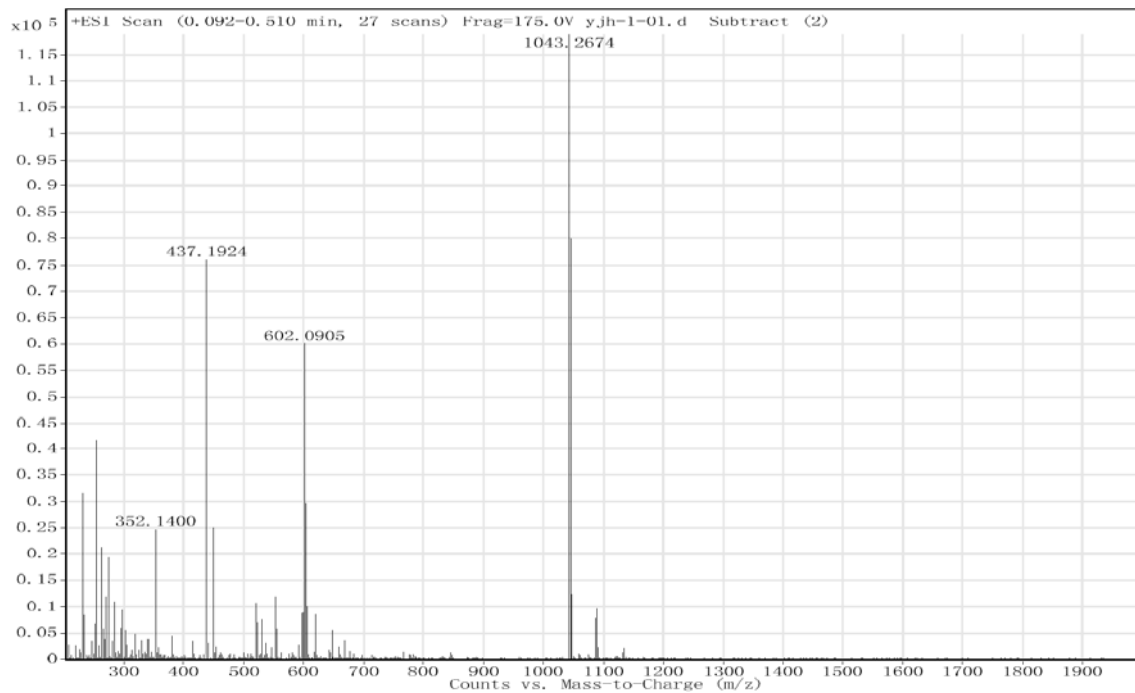
(d)

Sample Name	yang-agcn	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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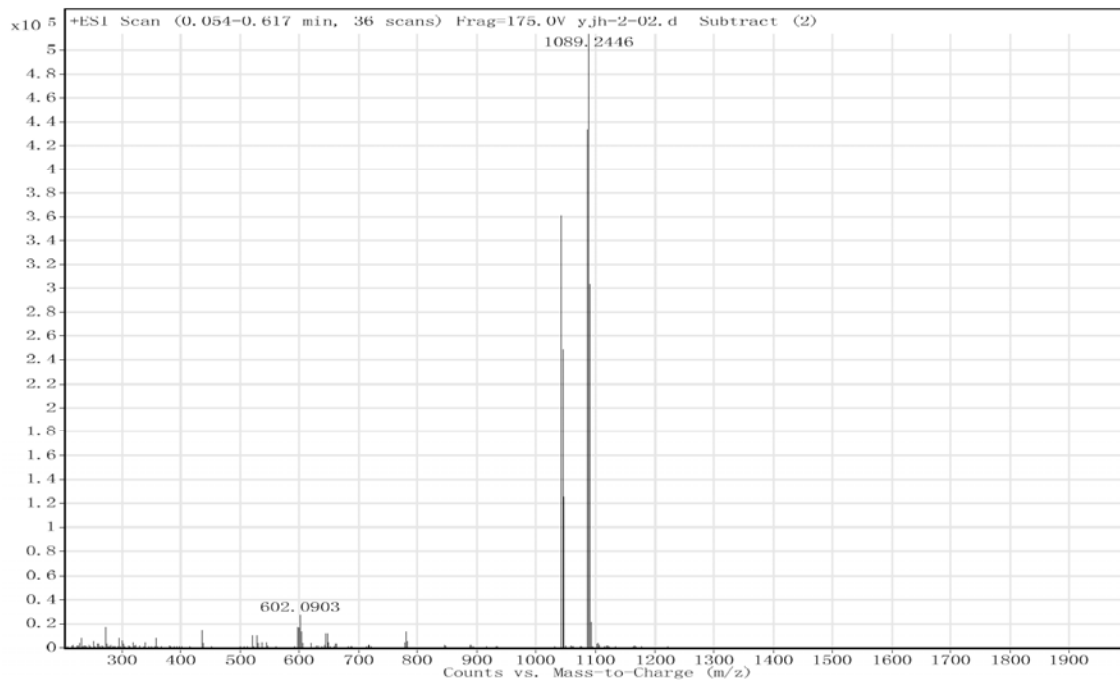
(e)

Sample Name	YJH-1	Position	Vial 1	Instrument Name	Instrument 1	User Name	
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(f)

Sample Name	YJH-2	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	0	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	yjh-2-02.d	ACQ Method		Comment		Acquired Time	2012-9-18 16:0



(g)

5

Figures S6. (a) The positive-ion ESI-MS of **2**. (b) The positive-ion ESI-MS of **3**. (c) The positive-ion ESI-MS of **4**. (d) The positive-ion ESI-MS of **5**. (e) The positive-ion ESI-MS of **6**. (f) The positive-ion ESI-MS of **7**. (g) The positive-ion ESI-MS of **8**.

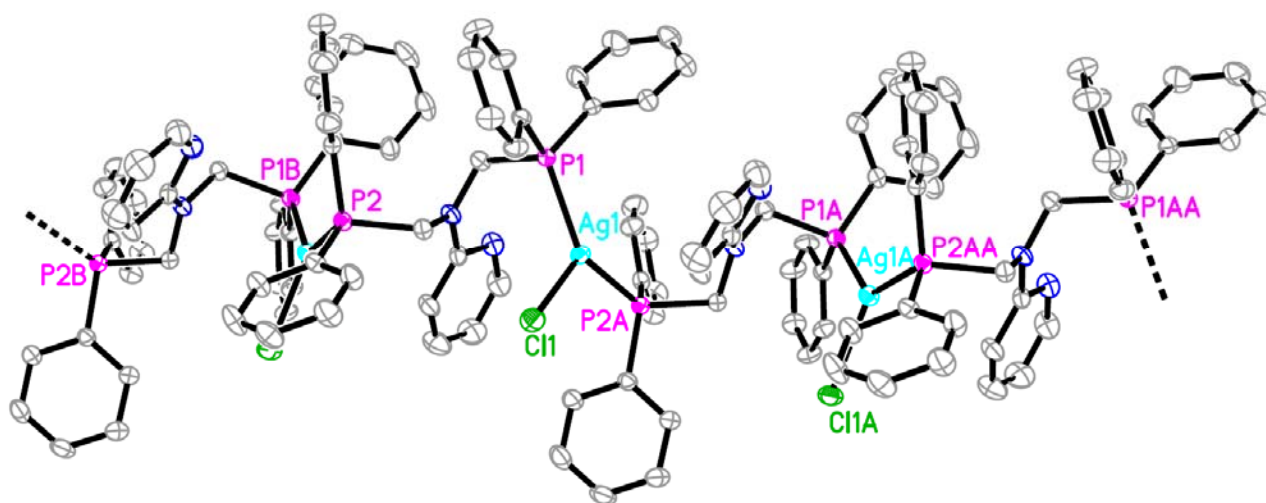


Figure S7. View of a section of the 1D chain extending along the *b* axis in **2**. All H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: $1/2 - x, 1/2 + y, z$.

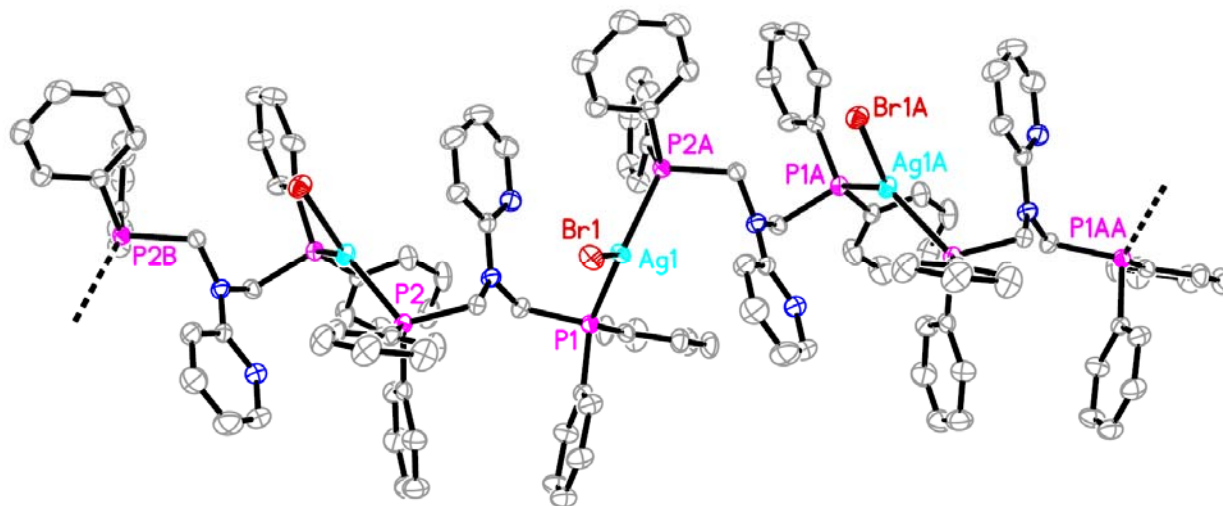
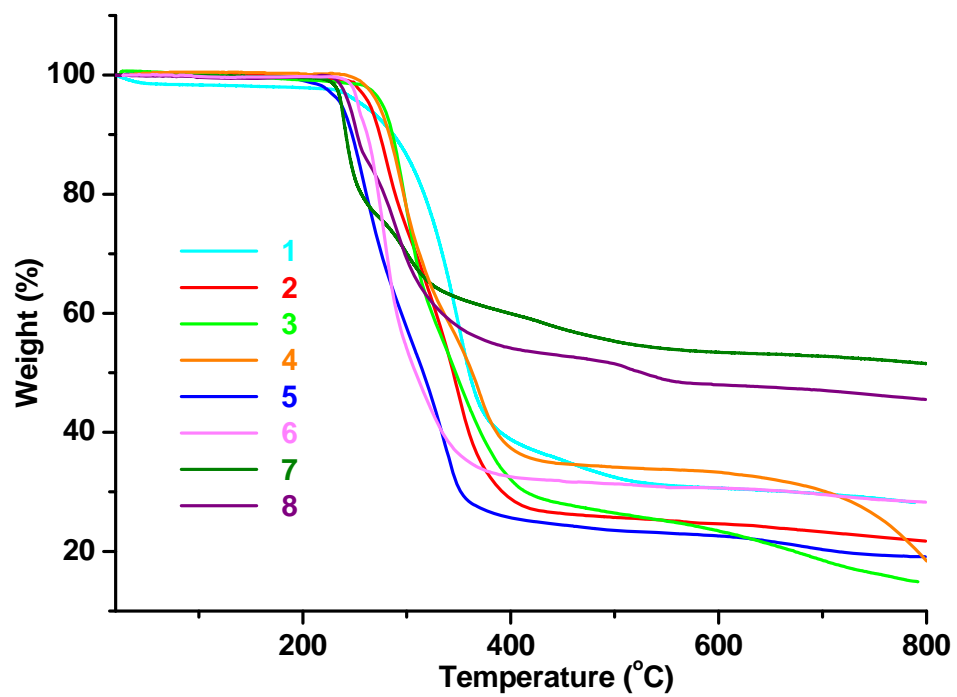


Figure S8. View of a section of the 1D chain extending along the *b* axis in **3**. All H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: $1/2 - x, 1/2 + y, z$.



Figures S9. The TGA curves for compounds **1-8**.