Supporting Information

Do alkyl groups on aromatic or aliphatic structure directing agents affect water stabilities and properties of hybrid iodoargentates?†

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Table S1. Selected Bond Distances (Å) and Angles (°) for **1**–**5**.

1			
Bond	(Å)	Bond	(Å)
Ag(1)-I(3)#1	2.8163(4)	I(4)-Ag(1)#4	2.9559(5)
Ag(1)-I(1)	2.8614(4)	P(1)-C(11)	1.767(3)
Ag(1)-I(2)#2	2.9269(5)	P(1)-C(21)	1.805(3)
Ag(1)-I(4)#1	2.9559(5)	P(1)-C(31)	1.810(3)
Ag(1)-Ag(2)#2	3.1344(5)	P(1)-C(1)	1.810(4)
Ag(1)-Ag(2)	3.2286(5)	C(1)-C(2)	1.466(5)
Ag(1)-Ag(3)#1	3.3121(5)	C(11)-C(12)	1.372(5)
Ag(2)-I(1)	2.8109(4)	C(11)-C(16)	1.421(5)
Ag(2)-I(4)#2	2.8118(4)	C(12)-C(13)	1.409(6)
Ag(2)-I(2)#2	2.9325(5)	C(13)-C(14)	1.365(6)
Ag(2)-I(2)	2.9395(5)	C(14)-C(15)	1.357(6)
Ag(2)-Ag(3)#2	3.0889(5)	C(15)-C(16)	1.405(5)
Ag(2)-Ag(3)	3.1282(5)	C(21)-C(22)	1.369(6)
Ag(2)-Ag(1)#3	3.1344(5)	C(21)-C(26)	1.388(6)
Ag(3)-I(3)	2.8304(5)	C(22)-C(23)	1.452(7)
Ag(3)-I(1)	2.8823(5)	C(23)-C(24)	1.321(8)

Ag(3)-I(4)	2.9319(5)	C(24)-C(25)	1.372(7)
Ag(3)-I(2)	2.9371(4)	C(25)-C(26)	1.393(5)
Ag(3)-Ag(2)#3	3.0889(5)	C(31)-C(32)	1.369(4)
Ag(3)-Ag(1)#4	3.3121(5)	C(31)-C(36)	1.376(5)
I(2)-Ag(1)#3	2.9269(5)	C(32)-C(33)	1.392(6)
I(2)-Ag(2)#3	2.9325(5)	C(33)-C(34)	1.370(6)
I(3)-Ag(1)#4	2.8163(4)	C(34)-C(35)	1.363(5)
I(4)-Ag(2)#3	2.8118(4)	C(35)-C(36)	1.372(6)

Angle	(°)	Angle	(°)
I(3)#1-Ag(1)-I(1)	117.938(15)	I(4)-Ag(3)-Ag(2)#3	55.608(10)
I(3)#1-Ag(1)-I(2)#2	112.390(14)	I(2)-Ag(3)-Ag(2)#3	58.175(11)
I(1)-Ag(1)-I(2)#2	105.275(14)	I(3)-Ag(3)-Ag(2)	153.676(13)
I(3)#1-Ag(1)-I(4)#1	99.867(14)	I(1)-Ag(3)-Ag(2)	55.582(11)
I(1)-Ag(1)-I(4)#1	110.297(14)	I(4)-Ag(3)-Ag(2)	106.191(14)
I(2)#2-Ag(1)-I(4)#1	111.123(14)	I(2)-Ag(3)-Ag(2)	57.874(11)
I(3)#1-Ag(1)-Ag(2)#2	107.268(13)	Ag(2)#3-Ag(3)-Ag(2)	87.963(10)
I(1)-Ag(1)-Ag(2)#2	134.587(13)	I(3)-Ag(3)-Ag(1)#4	53.889(10)
I(2)#2-Ag(1)-Ag(2)#2	57.897(11)	I(1)-Ag(3)-Ag(1)#4	152.835(14)
I(4)#1-Ag(1)-Ag(2)#2	54.897(11)	I(4)-Ag(3)-Ag(1)#4	56.112(11)
I(3)#1-Ag(1)-Ag(2)	155.875(17)	I(2)-Ag(3)-Ag(1)#4	99.727(14)
I(1)-Ag(1)-Ag(2)	54.572(10)	Ag(2)#3-Ag(3)-Ag(1)#4	58.515(11)
I(2)#2-Ag(1)-Ag(2)	56.647(11)	Ag(2)-Ag(3)-Ag(1)#4	146.471(14)
I(4)#1-Ag(1)-Ag(2)	104.185(14)	Ag(2)-I(1)-Ag(1)	69.382(11)
Ag(2)#2-Ag(1)-Ag(2)	85.442(10)	Ag(2)-I(1)-Ag(3)	66.648(11)
I(3)#1-Ag(1)-Ag(3)#1	54.285(10)	Ag(1)-I(1)-Ag(3)	128.725(13)
I(1)-Ag(1)-Ag(3)#1	155.736(16)	Ag(1)#3-I(2)-Ag(2)#3	66.872(11)
I(2)#2-Ag(1)-Ag(3)#1	98.587(12)	Ag(1)#3-I(2)-Ag(3)	102.230(13)
I(4)#1-Ag(1)-Ag(3)#1	55.425(12)	Ag(2)#3-I(2)-Ag(3)	63.506(11)

Ag(2)#2-Ag(1)-Ag(3)#1	57.181(10)	Ag(1)#3-I(2)-Ag(2)	64.593(12)
Ag(2)-Ag(1)-Ag(3)#1	142.612(14)	Ag(2)#3-I(2)-Ag(2)	94.658(14)
I(1)-Ag(2)-I(4)#2	115.147(14)	Ag(3)-I(2)-Ag(2)	64.326(11)
I(1)-Ag(2)-I(2)#2	106.443(12)	Ag(1)#4-I(3)-Ag(3)	71.826(12)
I(4)#2-Ag(2)-I(2)#2	115.881(14)	Ag(2)#3-I(4)-Ag(3)	65.028(11)
I(1)-Ag(2)-I(2)	109.310(14)	Ag(2)#3-I(4)-Ag(1)#4	65.782(12)
I(4)#2-Ag(2)-I(2)	115.026(14)	Ag(3)-I(4)-Ag(1)#4	68.463(12)
I(2)#2-Ag(2)-I(2)	92.605(13)	C(11)-P(1)-C(21)	109.77(16)
I(1)-Ag(2)-Ag(3)#2	144.544(17)	C(11)-P(1)-C(31)	111.26(15)
I(4)#2-Ag(2)-Ag(3)#2	59.364(11)	C(21)-P(1)-C(31)	107.44(15)
I(2)#2-Ag(2)-Ag(3)#2	58.319(9)	C(11)-P(1)-C(1)	109.07(16)
I(2)-Ag(2)-Ag(3)#2	103.536(13)	C(21)-P(1)-C(1)	109.87(15)
I(1)-Ag(2)-Ag(3)	57.770(10)	C(31)-P(1)-C(1)	109.41(18)
I(4)#2-Ag(2)-Ag(3)	114.279(14)	C(2)-C(1)-P(1)	113.9(3)
I(2)#2-Ag(2)-Ag(3)	129.030(14)	C(12)-C(11)-C(16)	118.3(3)
I(2)-Ag(2)-Ag(3)	57.800(11)	C(12)-C(11)-P(1)	120.6(3)
Ag(3)#2-Ag(2)-Ag(3)	157.489(16)	C(16)-C(11)-P(1)	121.0(2)
I(1)-Ag(2)-Ag(1)#3	147.342(14)	C(11)-C(12)-C(13)	121.9(3)
I(4)#2-Ag(2)-Ag(1)#3	59.320(12)	C(14)-C(13)-C(12)	117.9(3)
I(2)#2-Ag(2)-Ag(1)#3	104.038(12)	C(15)-C(14)-C(13)	122.7(4)
I(2)-Ag(2)-Ag(1)#3	57.510(11)	C(14)-C(15)-C(16)	119.7(4)
Ag(3)#2-Ag(2)-Ag(1)#3	64.305(11)	C(15)-C(16)-C(11)	119.3(3)
Ag(3)-Ag(2)-Ag(1)#3	93.581(14)	C(22)-C(21)-C(26)	122.5(3)
I(1)-Ag(2)-Ag(1)	56.046(10)	C(22)-C(21)-P(1)	119.8(3)
I(4)#2-Ag(2)-Ag(1)	114.067(17)	C(26)-C(21)-P(1)	117.7(2)
I(2)#2-Ag(2)-Ag(1)	56.481(10)	C(21)-C(22)-C(23)	115.5(5)
I(2)-Ag(2)-Ag(1)	129.824(14)	C(24)-C(23)-C(22)	123.7(5)
Ag(3)#2-Ag(2)-Ag(1)	92.500(13)	C(23)-C(24)-C(25)	117.8(4)
Ag(3)-Ag(2)-Ag(1)	109.084(13)	C(24)-C(25)-C(26)	122.9(5)

Ag(1)#3-Ag(2)-Ag(1)	156.361(14)	C(21)-C(26)-C(25)	117.4(4)
I(3)-Ag(3)-I(1)	113.627(13)	C(32)-C(31)-C(36)	120.2(3)
I(3)-Ag(3)-I(4)	100.113(12)	C(32)-C(31)-P(1)	121.1(3)
I(1)-Ag(3)-I(4)	110.859(15)	C(36)-C(31)-P(1)	118.6(2)
I(3)-Ag(3)-I(2)	112.700(15)	C(31)-C(32)-C(33)	119.1(3)
I(1)-Ag(3)-I(2)	107.429(12)	C(34)-C(33)-C(32)	119.8(4)
I(4)-Ag(3)-I(2)	112.110(13)	C(35)-C(34)-C(33)	120.9(4)
I(3)-Ag(3)-Ag(2)#3	108.140(15)	C(34)-C(35)-C(36)	119.4(4)
I(1)-Ag(3)-Ag(2)#3	137.968(15)	C(35)-C(36)-C(31)	120.6(3)

Symmetry transformations used to generate equivalent atoms: #1 x, y, z-1; #2 x, -y+1/2, z-1/2; #3 x, -y+1/2, z+1/2; #4 x, y, z+1.

2			
Bond	(Å)	Bond	(Å)
Ag(1)-I(3)#1	2.8149(5)	P(1)-C(13)	1.786(4)
Ag(1)-I(1)	2.8240(5)	P(1)-C(19)	1.806(4)
Ag(1)-I(4)	2.9388(5)	P(1)-C(1)	1.807(4)
Ag(1)-I(4)#1	2.9427(6)	P(1)-C(7)	1.809(4)
Ag(1)-Ag(2)#1	3.1463(6)	C(1)-C(6)	1.369(5)
Ag(1)-Ag(3)#2	3.1469(6)	C(1)-C(2)	1.392(6)
Ag(1)-Ag(3)	3.1674(6)	C(2)-C(3)	1.359(7)
Ag(1)-Ag(2)	3.2253(6)	C(3)-C(4)	1.399(7)
Ag(2)-I(2)	2.8062(5)	C(4)-C(5)	1.351(7)
Ag(2)-I(1)	2.8566(5)	C(5)-C(6)	1.368(7)
Ag(2)-I(4)	2.9289(5)	C(7)-C(8)	1.373(6)
Ag(2)-I(3)	2.9427(6)	C(7)-C(12)	1.382(6)
Ag(2)-Ag(1)#2	3.1463(6)	C(8)-C(9)	1.399(7)
Ag(2)-Ag(3)#3	3.3690(6)	C(9)-C(10)	1.384(9)
Ag(3)-I(2)#4	2.8324(5)	C(10)-C(11)	1.351(7)

Ag(3)-I(1)	2.9001(5)	C(11)-C(12)	1.366(6)
Ag(3)-I(4)#1	2.9377(5)	C(13)-C(18)	1.396(6)
Ag(3)-I(3)#4	2.9401(5)	C(13)-C(14)	1.410(6)
Ag(3)-Ag(1)#1	3.1469(6)	C(14)-C(15)	1.361(6)
Ag(3)-Ag(2)#4	3.3690(6)	C(15)-C(16)	1.355(8)
I(2)-Ag(3)#3	2.8324(5)	C(16)-C(17)	1.387(7)
I(3)-Ag(1)#2	2.8149(5)	C(17)-C(18)	1.374(7)
I(3)-Ag(3)#3	2.9401(5)	C(19)-C(20)	1.511(6)
I(4)-Ag(3)#2	2.9377(5)	C(20)-C(21)	1.525(7)
I(4)-Ag(1)#2	2.9427(6)		

Angle	(°)	Angle	(°)
I(3)#1-Ag(1)-I(1)	116.188(17)	I(3)#4-Ag(3)-Ag(1)#1	54.964(12)
I(3)#1-Ag(1)-I(4)	114.504(17)	I(2)#4-Ag(3)-Ag(1)	155.907(16)
I(1)-Ag(1)-I(4)	106.375(15)	I(1)-Ag(3)-Ag(1)	55.264(13)
I(3)#1-Ag(1)-I(4)#1	114.732(17)	I(4)#1-Ag(3)-Ag(1)	57.486(13)
I(1)-Ag(1)-I(4)#1	109.110(17)	I(3)#4-Ag(3)-Ag(1)	105.188(16)
I(4)-Ag(1)-I(4)#1	93.406(14)	Ag(1)#1-Ag(3)-Ag(1)	87.162(12)
I(3)#1-Ag(1)-Ag(2)#1	58.848(13)	I(2)#4-Ag(3)-Ag(2)#4	52.951(12)
I(1)-Ag(1)-Ag(2)#1	146.925(17)	I(1)-Ag(3)-Ag(2)#4	153.248(17)
I(4)-Ag(1)-Ag(2)#1	104.583(15)	I(4)#1-Ag(3)-Ag(2)#4	99.337(15)
I(4)#1-Ag(1)-Ag(2)#1	57.386(13)	I(3)#4-Ag(3)-Ag(2)#4	55.098(12)
I(3)#1-Ag(1)-Ag(3)#2	58.782(13)	Ag(1)#1-Ag(3)-Ag(2)#4	57.623(13)
I(1)-Ag(1)-Ag(3)#2	144.72(2)	Ag(1)-Ag(3)-Ag(2)#4	144.749(18)
I(4)-Ag(1)-Ag(3)#2	57.604(12)	Ag(1)-I(1)-Ag(2)	69.187(14)
I(4)#1-Ag(1)-Ag(3)#2	103.408(16)	Ag(1)-I(1)-Ag(3)	67.178(14)
Ag(2)#1-Ag(1)-Ag(3)#2	64.736(14)	Ag(2)-I(1)-Ag(3)	128.785(15)
I(3)#1-Ag(1)-Ag(3)	115.946(16)	Ag(2)-I(2)-Ag(3)#3	73.380(14)
I(1)-Ag(1)-Ag(3)	57.558(13)	Ag(1)#2-I(3)-Ag(3)#3	66.254(13)

I(4)-Ag(1)-Ag(3)	128.716(17)	Ag(1)#2-I(3)-Ag(2)	66.204(14)
I(4)#1-Ag(1)-Ag(3)	57.332(13)	Ag(3)#3-I(3)-Ag(2)	69.876(13)
Ag(2)#1-Ag(1)-Ag(3)	93.603(16)	Ag(2)-I(4)-Ag(3)#2	103.358(14)
Ag(3)#2-Ag(1)-Ag(3)	157.66(2)	Ag(2)-I(4)-Ag(1)	66.687(13)
I(3)#1-Ag(1)-Ag(2)	113.802(18)	Ag(3)#2-I(4)-Ag(1)	64.756(13)
I(1)-Ag(1)-Ag(2)	55.884(12)	Ag(2)-I(4)-Ag(1)#2	64.802(14)
I(4)-Ag(1)-Ag(2)	56.509(12)	Ag(3)#2-I(4)-Ag(1)#2	65.182(13)
I(4)#1-Ag(1)-Ag(2)	130.282(17)	Ag(1)-I(4)-Ag(1)#2	95.481(15)
Ag(2)#1-Ag(1)-Ag(2)	156.896(18)	C(13)-P(1)-C(19)	109.9(2)
Ag(3)#2-Ag(1)-Ag(2)	92.481(15)	C(13)-P(1)-C(1)	111.09(17)
Ag(3)-Ag(1)-Ag(2)	108.595(17)	C(19)-P(1)-C(1)	107.8(2)
I(2)-Ag(2)-I(1)	117.303(17)	C(13)-P(1)-C(7)	111.21(19)
I(2)-Ag(2)-I(4)	111.262(15)	C(19)-P(1)-C(7)	109.92(18)
I(1)-Ag(2)-I(4)	105.788(16)	C(1)-P(1)-C(7)	106.75(19)
I(2)-Ag(2)-I(3)	99.423(16)	C(6)-C(1)-C(2)	118.9(4)
I(1)-Ag(2)-I(3)	111.789(15)	C(6)-C(1)-P(1)	123.3(3)
I(4)-Ag(2)-I(3)	111.354(16)	C(2)-C(1)-P(1)	117.8(3)
I(2)-Ag(2)-Ag(1)#2	106.829(15)	C(3)-C(2)-C(1)	121.0(4)
I(1)-Ag(2)-Ag(1)#2	135.751(17)	C(2)-C(3)-C(4)	119.4(5)
I(4)-Ag(2)-Ag(1)#2	57.812(13)	C(5)-C(4)-C(3)	119.0(5)
I(3)-Ag(2)-Ag(1)#2	54.948(13)	C(4)-C(5)-C(6)	121.9(4)
I(2)-Ag(2)-Ag(1)	154.446(19)	C(5)-C(6)-C(1)	119.8(4)
I(1)-Ag(2)-Ag(1)	54.930(12)	C(8)-C(7)-C(12)	119.5(4)
I(4)-Ag(2)-Ag(1)	56.804(12)	C(8)-C(7)-P(1)	121.6(4)
I(3)-Ag(2)-Ag(1)	106.000(16)	C(12)-C(7)-P(1)	118.6(3)
Ag(1)#2-Ag(2)-Ag(1)	86.178(11)	C(7)-C(8)-C(9)	120.1(5)
I(2)-Ag(2)-Ag(3)#3	53.668(12)	C(10)-C(9)-C(8)	118.8(5)
I(1)-Ag(2)-Ag(3)#3	155.537(18)	C(11)-C(10)-C(9)	120.4(5)
I(4)-Ag(2)-Ag(3)#3	98.533(14)	C(10)-C(11)-C(12)	121.1(5)

I(3)-Ag(2)-Ag(3)#3	55.026(12)	C(11)-C(12)-C(7)	120.0(4)
Ag(1)#2-Ag(2)-Ag(3)#3	57.641(13)	C(18)-C(13)-C(14)	118.8(4)
Ag(1)-Ag(2)-Ag(3)#3	143.819(18)	C(18)-C(13)-P(1)	120.2(3)
I(2)#4-Ag(3)-I(1)	116.866(17)	C(14)-C(13)-P(1)	120.9(3)
I(2)#4-Ag(3)-I(4)#1	112.605(17)	C(15)-C(14)-C(13)	119.4(4)
I(1)-Ag(3)-I(4)#1	107.188(14)	C(16)-C(15)-C(14)	121.7(4)
I(2)#4-Ag(3)-I(3)#4	98.880(14)	C(15)-C(16)-C(17)	119.9(4)
I(1)-Ag(3)-I(3)#4	110.273(16)	C(18)-C(17)-C(16)	120.1(5)
I(4)#1-Ag(3)-I(3)#4	110.852(16)	C(17)-C(18)-C(13)	120.0(4)
I(2)#4-Ag(3)-Ag(1)#1	106.156(17)	C(20)-C(19)-P(1)	112.5(3)
I(1)-Ag(3)-Ag(1)#1	136.605(19)	C(19)-C(20)-C(21)	111.6(3)
I(4)#1-Ag(3)-Ag(1)#1	57.640(12)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z-1/2; #2 2 x, -y+1/2, z+1/2; #3 x, y, z+1; #4 x, y, z-1.

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Bond	(Å)	Bond	(Å)
Ag(1)-I(1)#1	2.8239(5)	I(5)-Ag(5)#3	2.8260(5)
Ag(1)-I(3)	2.8294(5)	I(5)-Ag(2)#3	2.8352(5)
Ag(1)-I(1)	2.8630(4)	I(6)-Ag(5)#3	2.8311(5)
Ag(1)-I(2)	2.9186(5)	P(1)-C(1)	1.787(4)
Ag(1)-Ag(3)#1	3.1964(6)	P(1)-C(13)	1.794(4)
Ag(1)-Ag(4)	3.2529(6)	P(1)-C(7)	1.798(4)
Ag(2)-I(4)	2.8290(5)	P(1)-C(19)	1.832(5)
Ag(2)-I(5)#1	2.8352(5)	C(1)-C(2)	1.392(6)
Ag(2)-I(5)	2.8756(5)	C(1)-C(6)	1.401(7)
Ag(2)-I(2)	2.9745(5)	C(2)-C(3)	1.374(7)
Ag(2)-Ag(4)	3.2845(6)	C(3)-C(4)	1.363(9)
Ag(3)-I(6)	2.8299(5)	C(4)-C(5)	1.358(9)

Ag(3)-I(1)	2.8466(5)	C(5)-C(6)	1.348(7)
Ag(3)-I(3)#2	2.8531(5)	C(7)-C(8)	1.392(6)
Ag(3)-I(2)#3	3.0039(5)	C(7)-C(12)	1.399(5)
Ag(3)-Ag(5)#3	3.1292(6)	C(8)-C(9)	1.377(7)
Ag(3)-Ag(1)#3	3.1964(6)	C(9)-C(10)	1.366(7)
Ag(4)-I(3)	2.8411(5)	C(9)-H(9A)	0.9300
Ag(4)-I(4)	2.8433(4)	C(10)-C(11)	1.384(8)
Ag(4)-I(6)	2.8661(5)	C(11)-C(12)	1.379(6)
Ag(4)-I(2)	2.9894(5)	C(13)-C(18)	1.378(5)
Ag(5)-I(5)#1	2.8260(5)	C(13)-C(14)	1.405(5)
Ag(5)-I(6)#1	2.8311(5)	C(14)-C(15)	1.369(6)
Ag(5)-I(4)#3	2.8500(5)	C(15)-C(16)	1.367(6)
Ag(5)-I(2)	2.9918(5)	C(16)-C(17)	1.372(6)
Ag(5)-Ag(3)#1	3.1292(6)	C(17)-C(18)	1.386(6)
I(1)-Ag(1)#3	2.8239(5)	C(19)-C(20)	1.417(10)
I(2)-Ag(3)#1	3.0039(5)	C(19)-C(21)	1.528(6)
I(3)-Ag(3)#4	2.8531(5)		

Angle	(°)	Angle	(°)
I(1)#1-Ag(1)-I(3)	113.087(15)	I(6)#1-Ag(5)-Ag(3)#1	56.424(12)
I(1)#1-Ag(1)-I(1)	116.072(15)	I(4)#3-Ag(5)-Ag(3)#1	105.839(14)
I(3)-Ag(1)-I(1)	104.841(15)	I(2)-Ag(5)-Ag(3)#1	58.728(12)
I(1)#1-Ag(1)-I(2)	113.423(15)	Ag(1)#3-I(1)-Ag(3)	68.622(13)
I(3)-Ag(1)-I(2)	111.777(14)	Ag(1)#3-I(1)-Ag(1)	96.349(12)
I(1)-Ag(1)-I(2)	96.265(13)	Ag(3)-I(1)-Ag(1)	101.705(13)
I(1)#1-Ag(1)-Ag(3)#1	56.024(12)	Ag(1)-I(2)-Ag(2)	124.010(13)
I(3)-Ag(1)-Ag(3)#1	144.456(15)	Ag(1)-I(2)-Ag(4)	66.804(12)
I(1)-Ag(1)-Ag(3)#1	110.101(15)	Ag(2)-I(2)-Ag(4)	66.833(12)
I(2)-Ag(1)-Ag(3)#1	58.632(11)	Ag(1)-I(2)-Ag(5)	121.178(14)

I(1)#1-Ag(1)-Ag(4)	144.064(15)	Ag(2)-I(2)-Ag(5)	70.163(12)
I(3)-Ag(1)-Ag(4)	55.163(11)	Ag(4)-I(2)-Ag(5)	128.634(13)
I(1)-Ag(1)-Ag(4)	99.816(14)	Ag(1)-I(2)-Ag(3)#1	65.310(12)
I(2)-Ag(1)-Ag(4)	57.640(11)	Ag(2)-I(2)-Ag(3)#1	124.509(13)
Ag(3)#1-Ag(1)-Ag(4)	111.197(15)	Ag(4)-I(2)-Ag(3)#1	125.222(14)
I(4)-Ag(2)-I(5)#1	118.746(15)	Ag(5)-I(2)-Ag(3)#1	62.921(12)
I(4)-Ag(2)-I(5)	110.987(16)	Ag(1)-I(3)-Ag(4)	70.012(13)
I(5)#1-Ag(2)-I(5)	113.614(16)	Ag(1)-I(3)-Ag(3)#4	101.744(14)
I(4)-Ag(2)-I(2)	110.653(15)	Ag(4)-I(3)-Ag(3)#4	99.379(13)
I(5)#1-Ag(2)-I(2)	106.925(15)	Ag(2)-I(4)-Ag(4)	70.766(13)
I(5)-Ag(2)-I(2)	92.679(12)	Ag(2)-I(4)-Ag(5)#1	99.948(15)
I(4)-Ag(2)-Ag(4)	54.821(11)	Ag(4)-I(4)-Ag(5)#1	100.098(14)
I(5)#1-Ag(2)-Ag(4)	141.748(17)	Ag(5)#3-I(5)-Ag(2)#3	74.562(13)
I(5)-Ag(2)-Ag(4)	102.239(14)	Ag(5)#3-I(5)-Ag(2)	101.925(14)
I(2)-Ag(2)-Ag(4)	56.800(11)	Ag(2)#3-I(5)-Ag(2)	99.843(13)
I(6)-Ag(3)-I(1)	112.436(15)	Ag(3)-I(6)-Ag(5)#3	67.114(13)
I(6)-Ag(3)-I(3)#2	115.879(17)	Ag(3)-I(6)-Ag(4)	96.332(15)
I(1)-Ag(3)-I(3)#2	109.424(14)	Ag(5)#3-I(6)-Ag(4)	97.509(15)
I(6)-Ag(3)-I(2)#3	113.647(15)	C(1)-P(1)-C(13)	109.85(19)
I(1)-Ag(3)-I(2)#3	110.249(16)	C(1)-P(1)-C(7)	110.06(19)
I(3)#2-Ag(3)-I(2)#3	93.769(13)	C(13)-P(1)-C(7)	109.24(18)
I(6)-Ag(3)-Ag(5)#3	56.462(12)	C(1)-P(1)-C(19)	109.1(2)
I(1)-Ag(3)-Ag(5)#3	141.831(17)	C(13)-P(1)-C(19)	107.2(2)
I(3)#2-Ag(3)-Ag(5)#3	107.695(15)	C(7)-P(1)-C(19)	111.38(19)
I(2)#3-Ag(3)-Ag(5)#3	58.350(12)	C(2)-C(1)-C(6)	118.3(4)
I(6)-Ag(3)-Ag(1)#3	142.987(16)	C(2)-C(1)-P(1)	120.2(3)
I(1)-Ag(3)-Ag(1)#3	55.353(12)	C(6)-C(1)-P(1)	121.2(4)
I(3)#2-Ag(3)-Ag(1)#3	100.779(14)	C(3)-C(2)-C(1)	119.8(5)
I(2)#3-Ag(3)-Ag(1)#3	56.058(12)	C(4)-C(3)-C(2)	120.2(6)

Ag(5)#3-Ag(3)-Ag(1)#3	108.962(16)	C(5)-C(4)-C(3)	120.5(5)
I(3)-Ag(4)-I(4)	114.304(15)	C(6)-C(5)-C(4)	120.8(6)
I(3)-Ag(4)-I(6)	112.784(15)	C(5)-C(6)-C(1)	120.3(5)
I(4)-Ag(4)-I(6)	109.938(15)	C(8)-C(7)-C(12)	119.8(4)
I(3)-Ag(4)-I(2)	109.400(15)	C(8)-C(7)-P(1)	120.8(3)
I(4)-Ag(4)-I(2)	109.826(14)	C(12)-C(7)-P(1)	119.3(3)
I(6)-Ag(4)-I(2)	99.582(13)	C(9)-C(8)-C(7)	118.8(4)
I(3)-Ag(4)-Ag(1)	54.825(11)	C(10)-C(9)-C(8)	121.7(5)
I(4)-Ag(4)-Ag(1)	139.452(16)	C(9)-C(10)-C(11)	119.7(5)
I(6)-Ag(4)-Ag(1)	109.845(14)	C(12)-C(11)-C(10)	120.0(5)
I(2)-Ag(4)-Ag(1)	55.556(11)	C(11)-C(12)-C(7)	119.8(4)
I(3)-Ag(4)-Ag(2)	139.191(16)	C(18)-C(13)-C(14)	118.4(4)
I(4)-Ag(4)-Ag(2)	54.413(11)	C(18)-C(13)-P(1)	120.9(3)
I(6)-Ag(4)-Ag(2)	107.523(15)	C(14)-C(13)-P(1)	120.6(3)
I(2)-Ag(4)-Ag(2)	56.366(11)	C(15)-C(14)-C(13)	119.8(4)
Ag(1)-Ag(4)-Ag(2)	105.492(16)	C(16)-C(15)-C(14)	120.7(4)
I(5)#1-Ag(5)-I(6)#1	114.709(15)	C(15)-C(16)-C(17)	120.8(4)
I(5)#1-Ag(5)-I(4)#3	111.987(15)	C(16)-C(17)-C(18)	118.9(4)
I(6)#1-Ag(5)-I(4)#3	113.104(17)	C(13)-C(18)-C(17)	121.3(4)
I(5)#1-Ag(5)-I(2)	106.702(16)	C(20)-C(19)-C(21)	113.9(4)
I(6)#1-Ag(5)-I(2)	113.980(15)	C(20)-C(19)-P(1)	111.8(4)
I(4)#3-Ag(5)-I(2)	94.504(13)	C(21)-C(19)-P(1)	113.1(3)
I(5)#1-Ag(5)-Ag(3)#1	140.608(18)	I(6)#1-Ag(5)-Ag(3)#1	56.424(12)

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z-1/2; #2 x, y, z+1; #3 x, -y+3/2, z+1/2; #4 x, y, z-1.

4			
Bond	(Å)	Bond	(Å)
I(1)-Ag(1)	2.8590(4)	N(1)-C(3)	1.505(7)

I(1)-Ag(1)#1	2.8590(4)	N(1)-C(1)#3	1.513(3)
I(2)-Ag(1)#2	2.8693(4)	N(1)-C(1)	1.513(3)
I(2)-Ag(1)	2.8694(4)	N(1)-C(2)	1.525(6)
Ag(1)-I(1)#1	2.8590(4)	C(1)-C(1)#4	1.497(6)
Ag(1)-I(2)#2	2.8693(4)		
Angle	(°)	Angle	(°)
Ag(1)-I(1)-Ag(1)#1	81.684(16)	C(3)-N(1)-C(1)#3	109.4(2)
Ag(1)#2-I(2)-Ag(1)	82.724(16)	C(3)-N(1)-C(1)	109.4(3)
I(1)#1-Ag(1)-I(1)	98.316(16)	C(3)-N(1)-C(2)	107.4(3)
I(1)#1-Ag(1)-I(2)#2	112.859(9)	C(1)#3-N(1)-C(1)	107.6(3)
I(1)-Ag(1)-I(2)#2	118.414(10)	C(1)#3-N(1)-C(2)	111.5(2)
I(1)#1-Ag(1)-I(2)	118.415(10)	C(1)-N(1)-C(2)	111.5(2)
I(1)-Ag(1)-I(2)	112.859(9)	C(1)#4-C(1)-N(1)	113.0(3)
I(2)#2-Ag(1)-I(2)	97.276(15)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+2, #2 -x+1, -y+1, -z+2, #3 x, -y, z, #4 -x, y, -z+1

5

Bond	(Å)	Bond	(Å)
Ag(1)-I(1)	2.8289(4)	N(2)-C(4)	1.501(4)
Ag(1)-I(2)#1	2.8363(4)	N(2)-C(5)	1.506(4)
Ag(1)-I(3)	2.8555(4)	N(2)-C(2)	1.508(4)
Ag(1)-I(2)	2.8945(4)	N(3)-C(6)	1.474(4)
Ag(1)-Ag(1)#1	3.1512(6)	C(1)-C(2)	1.504(4)
I(2)-Ag(1)#1	2.8363(4)	C(3)-C(4)	1.509(4)
N(1)-C(3)	1.487(4)	C(5)-C(6)	1.509(5)
N(1)-C(1)	1.490(4)		

Angle	(°)	Angle	(°)
I(1)-Ag(1)-I(2)#1	116.763(12)	C(3)-N(1)-C(1)	111.4(2)
I(1)-Ag(1)-I(3)	105.672(12)	C(4)-N(2)-C(5)	109.2(2)
I(2)#1-Ag(1)-I(3)	112.352(12)	C(4)-N(2)-C(2)	109.5(2)
I(1)-Ag(1)-I(2)	104.061(11)	C(5)-N(2)-C(2)	112.8(2)
I(2)#1-Ag(1)-I(2)	113.294(12)	N(1)-C(1)-C(2)	110.6(3)
I(3)-Ag(1)-I(2)	103.453(11)	C(1)-C(2)-N(2)	110.8(2)
I(1)-Ag(1)-Ag(1)#1	128.937(16)	N(1)-C(3)-C(4)	110.2(2)
I(2)#1-Ag(1)-Ag(1)#1	57.531(10)	N(2)-C(4)-C(3)	112.1(3)
I(3)-Ag(1)-Ag(1)#1	123.780(17)	N(2)-C(5)-C(6)	116.2(3)
I(2)-Ag(1)-Ag(1)#1	55.763(10)	N(3)-C(6)-C(5)	114.2(3)
Ag(1)#1-I(2)-Ag(1)	66.706(12)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y+1, -z+1.

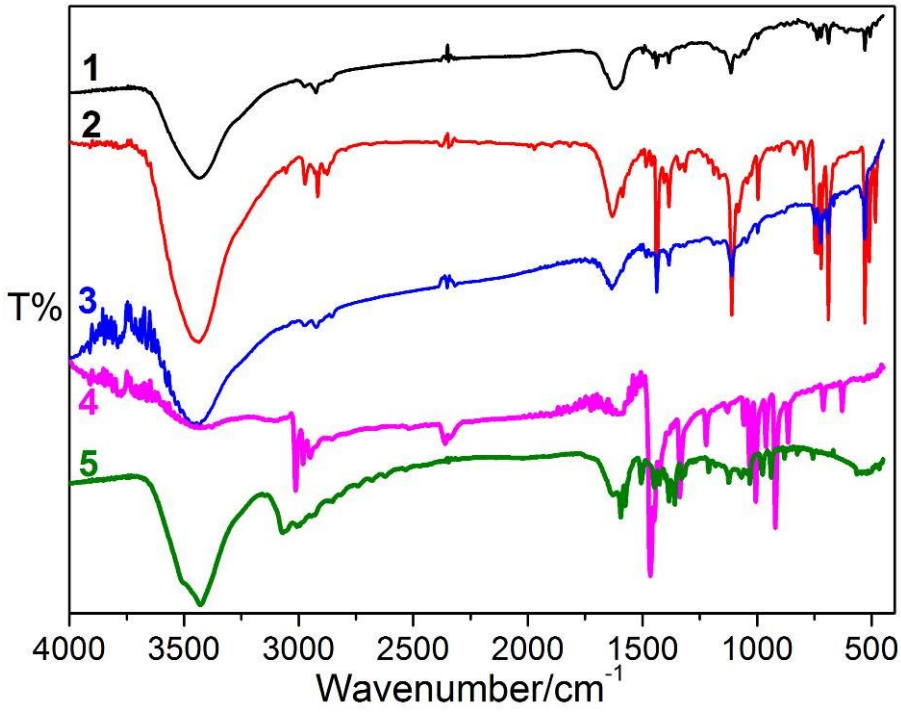
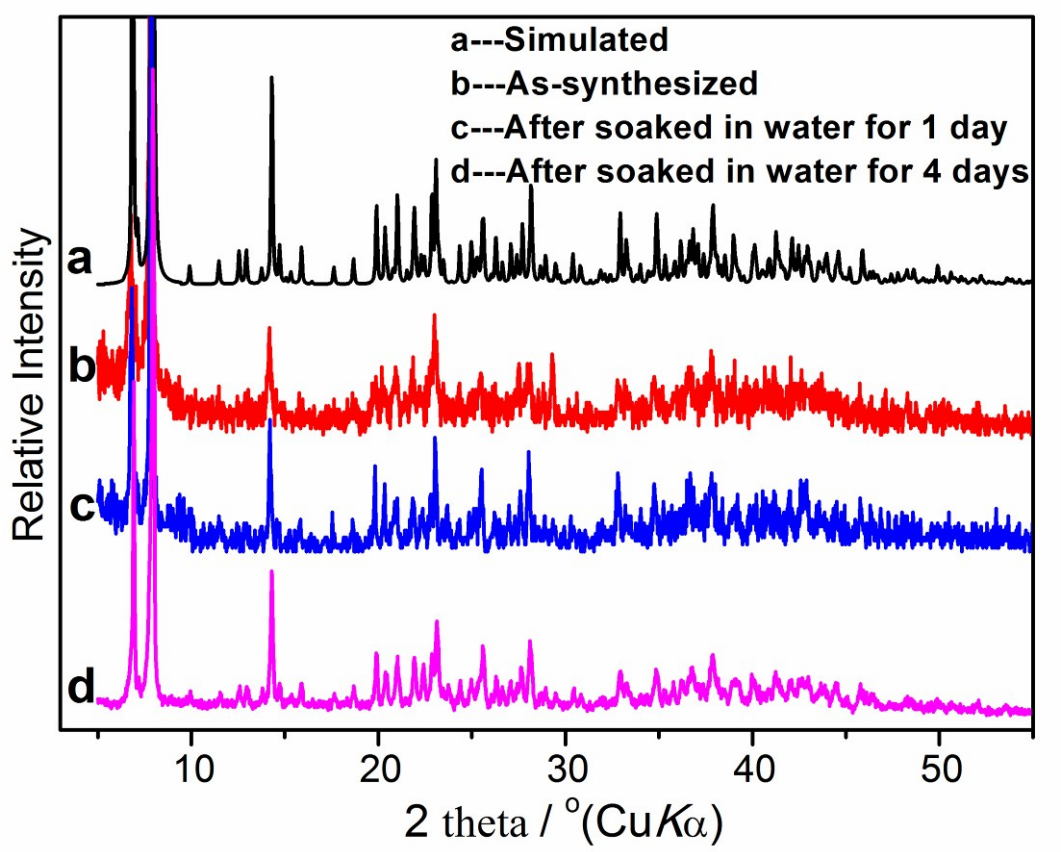


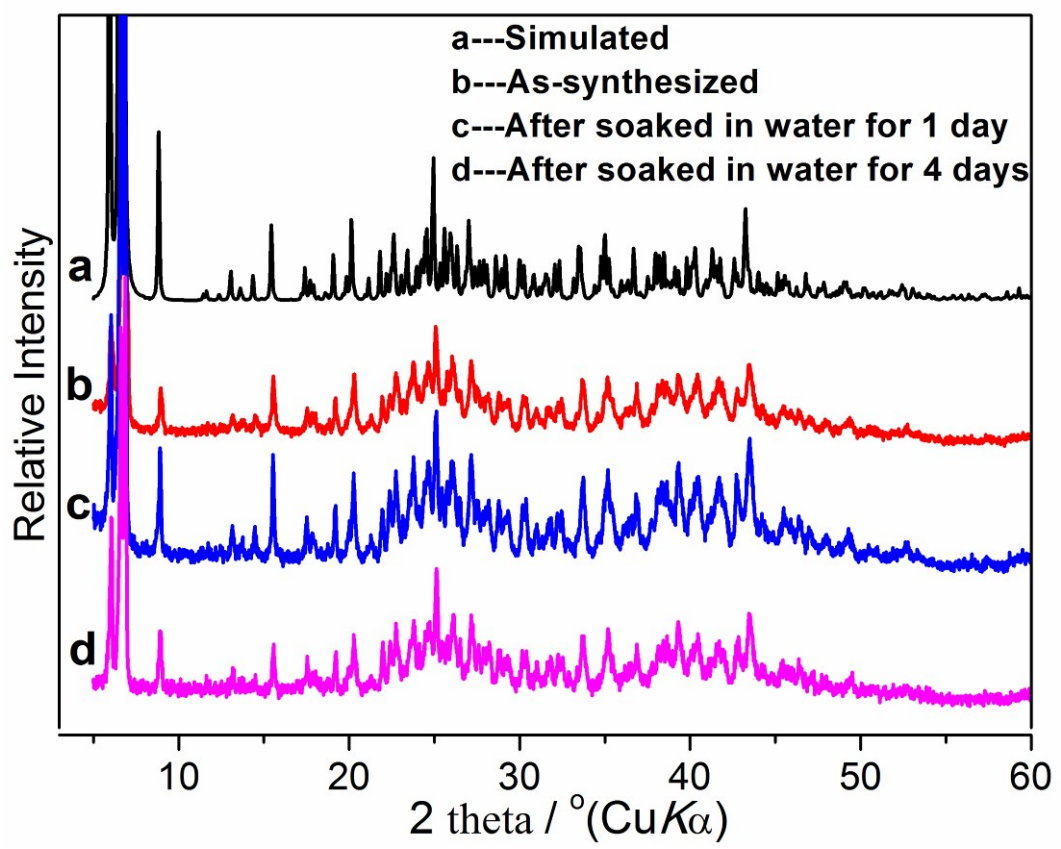
Fig. S1 IR spectra of **1**–**5**.

For **1**–**5**, the bands in the region of 3000–2850 cm^{-1} correspond to the C–H vibrations of

the alkyl group, ν(–C–H). Further, the occurrence of the characteristic band of $–CH_3$ around 1380 cm^{-1} confirms the presence of alkylation groups in **1**–**4**. As for **1**–**3**, the relatively weak bands in the region of 3013–3100 cm^{-1} correspond to the C–H vibrations of the aromatic ring hydrogen atoms, ν(=C–H). The bands of ring vibrations of the benzene rings (ν_Φ(C=C)) are observed at 1650–1450 cm^{-1}, suggesting the existence of PPh_3-derivative cations in **1**–**3**. The broad bands in the range 3530–3300 cm^{-1} for **1**–**4** are assigned to the stretching of trace water since the measurements were conducted in air, while the broad brands in the same ranges for **5** is simultaneously ascribed to the trace water in air and its lattice water molecules. For **5**, the IR bands at 3160–3020 cm^{-1} are attributed to the $N–H^+$ stretching vibration of $–NH_3^+$ group, and the bands at 2760–2250 cm^{-1} are attributed to the $N–H^+$ stretching vibrations of $>NH_2^+$ and $\geq NH^+$ groups for **5**.[1] The occurrence of these resonance signals confirms the presence of $(H_3app)^{3+}$ cation in **5**. In brief, the above results are all in agreement with the single crystal X-ray diffraction studies.



(a)



(b)

Fig. S2 The PXRD patterns of **2** (a) and **3** (b) under different conditions.

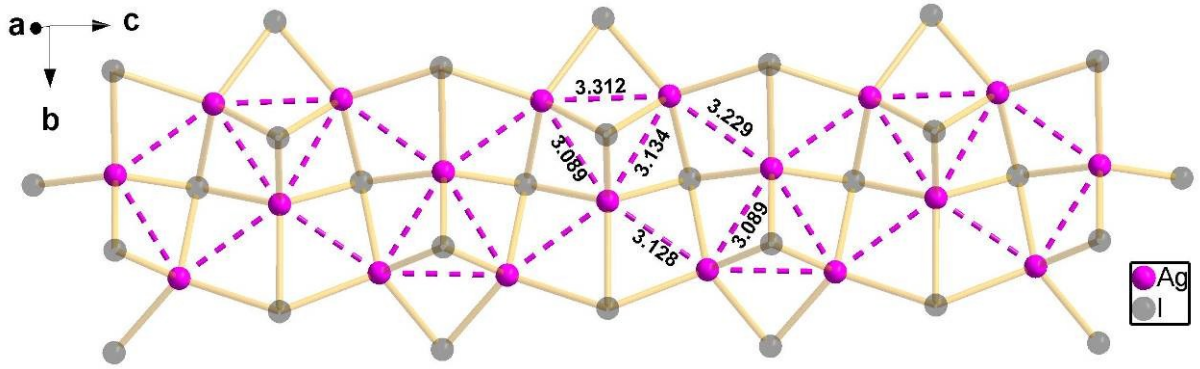


Fig. S3 The inorganic $(Ag_3I_4)^-$ anionic chain in **1** showing the intrachain Ag···Ag interactions.

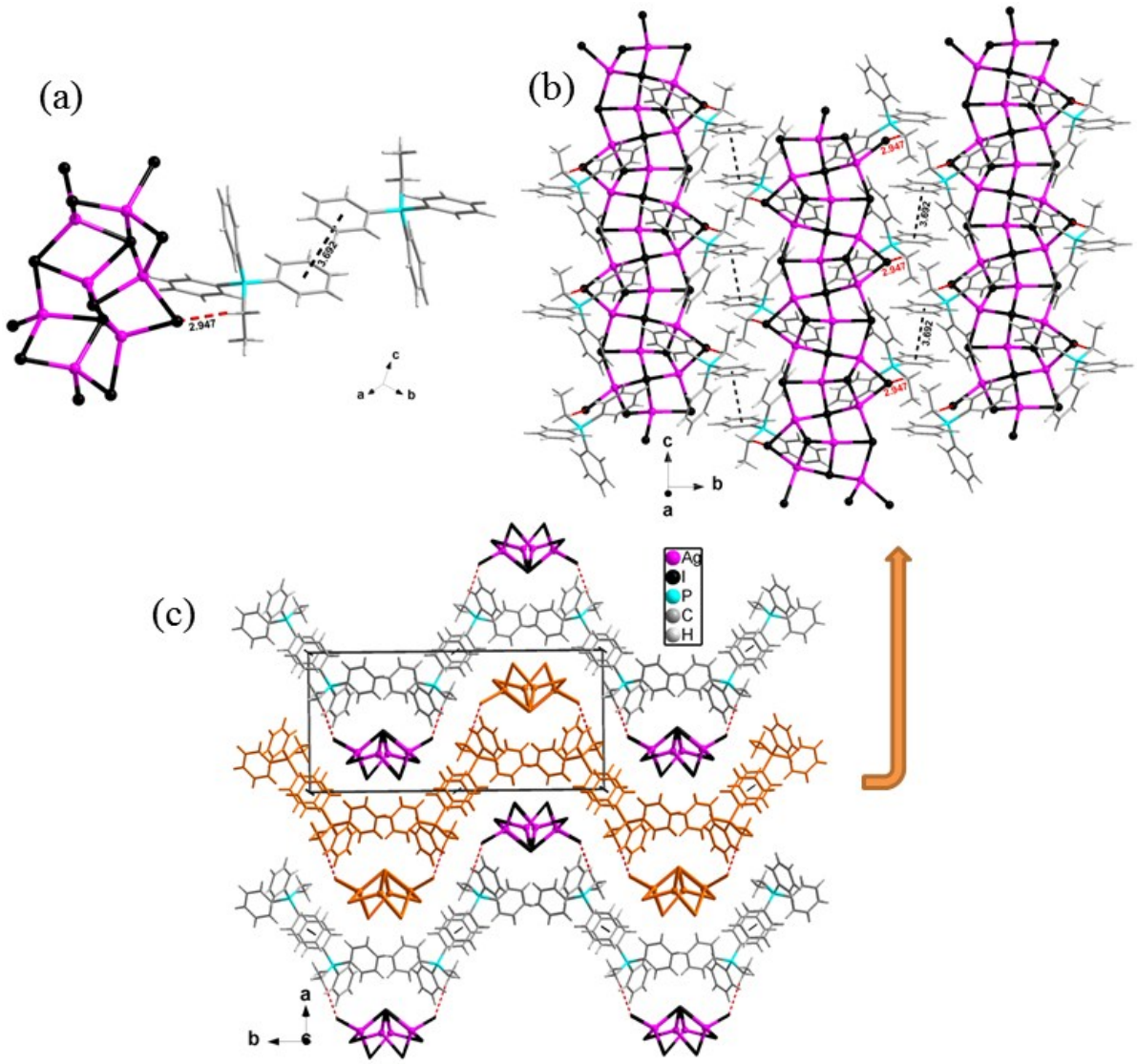


Fig. S4 (a) A close view of the C–H···I hydrogen bond (red dashed line) and the face to face π···π stacking interaction (black dashed line) in **1**. (b) The 2-D supramolecular layer formed by hydrogen bonds and face to face π···π stacking interactions. (c) The 3-D packing diagram of **1**.

Table S2. Selected Hydrogen Bonds Data for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
C1–H1B···I3	0.97	2.95	3.908(3)	171.1

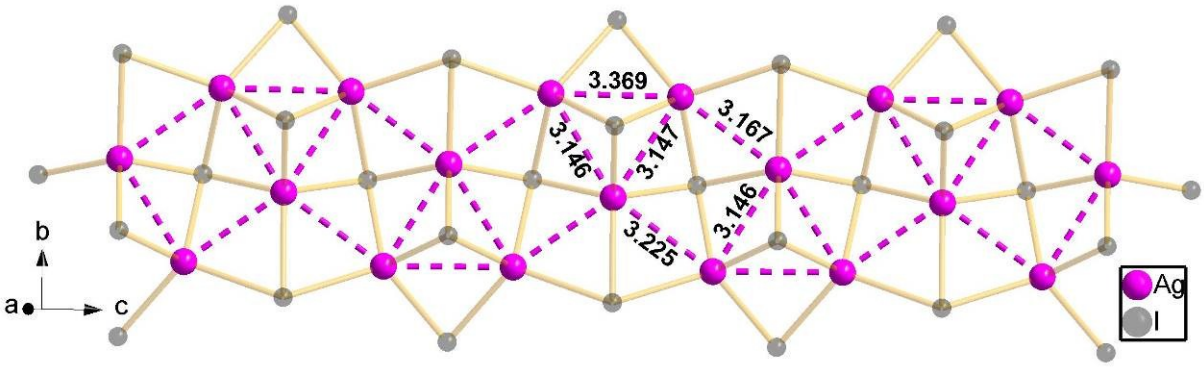


Fig. S5 The inorganic $(Ag_3I_4)^-$ anionic chain in **2** showing the intrachain Ag···Ag interactions.

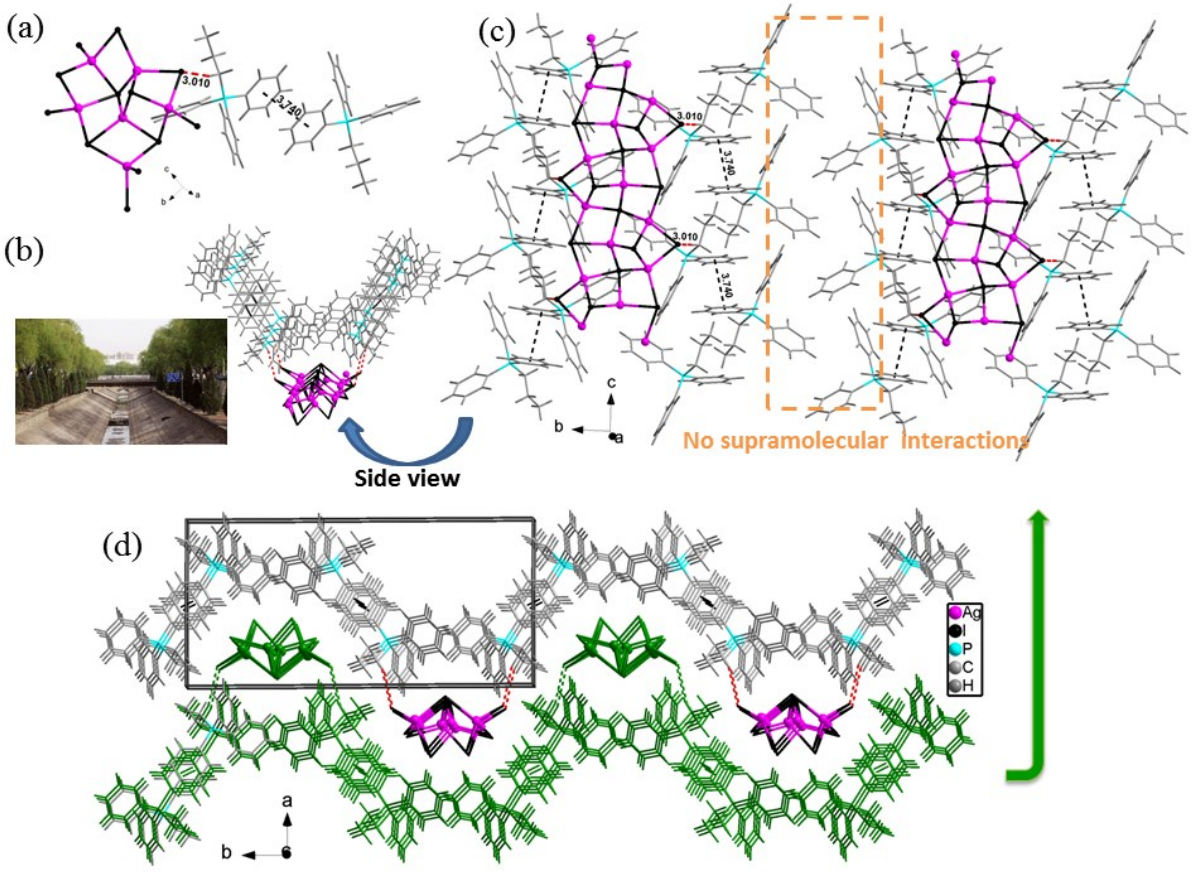


Fig. S6 (a) A close view of the C–H···I hydrogen bond (red dashed line) and the face to face π···π stacking interaction (black dashed line) in **2**. (b) The 1-D supramolecular band formed by hydrogen bonds and face to face π···π stacking interactions. (c) The 3-D packing diagram of **2**.

Table S3. Selected Hydrogen Bonds Data for **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
C19–H19B···I2[a]	0.97	3.01	3.945(4)	162.4

Symmetry code: a (-1+x, y, -1+z).

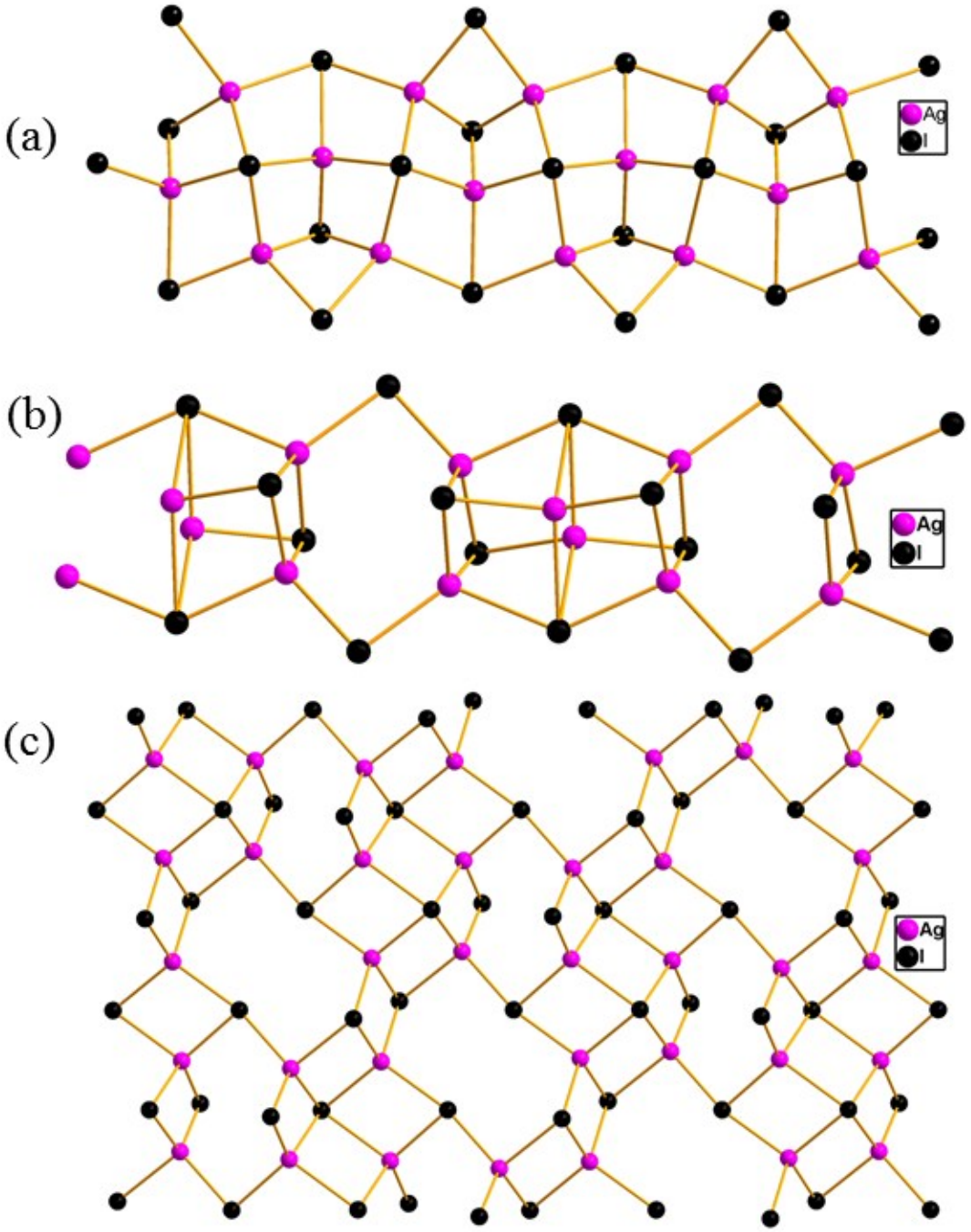


Fig. S7 (a-c) Three isomers of inorganic $(Ag_3I_4)^-$ polyanions. Type A is the one in **1** and **2**.

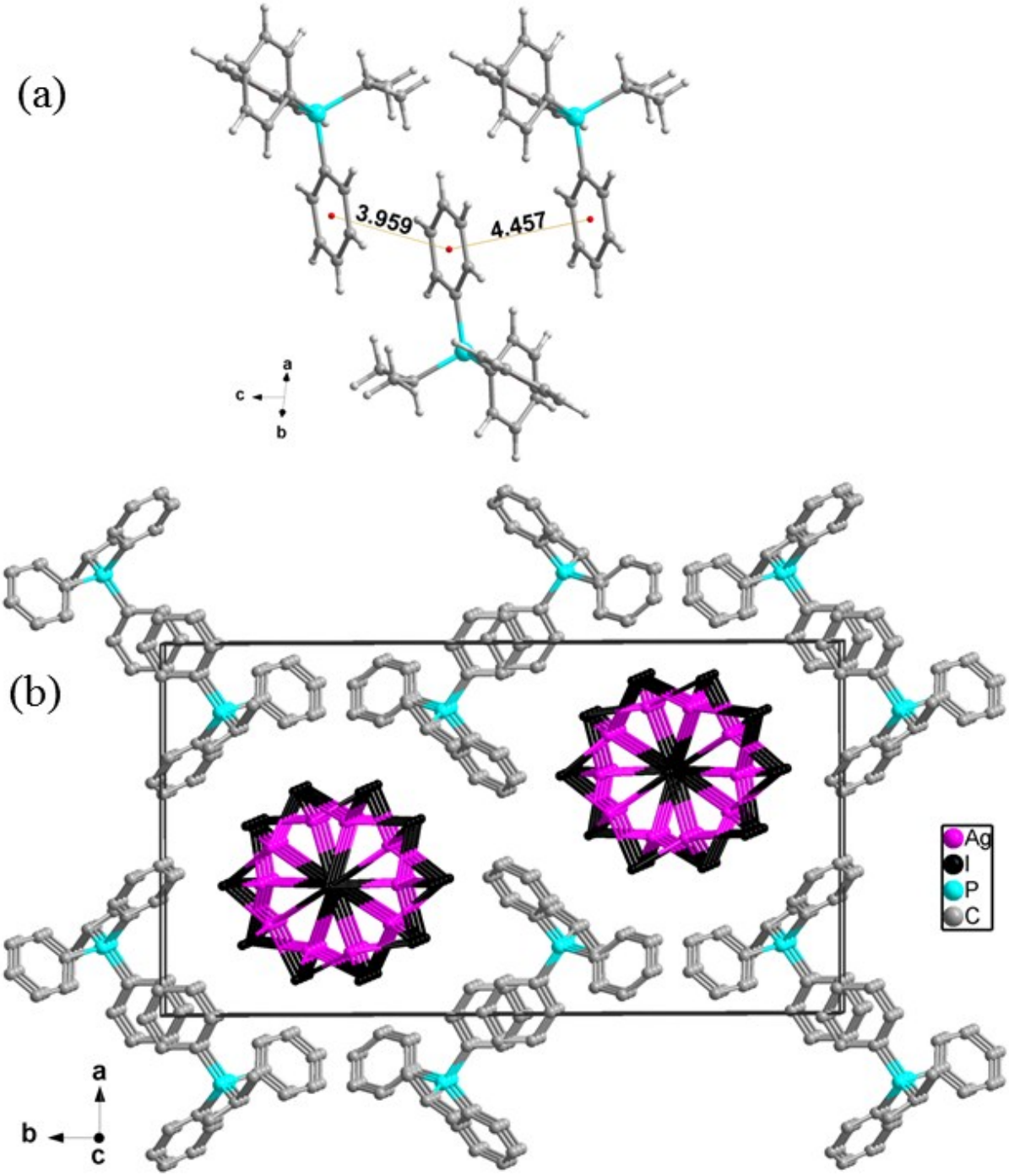


Fig. S8 (a) The nearest centroid to centroid distance between the benzene rings of two neighboring $(i\text{-PrPPh}_3)^+$ cations is 3.959 Å, indicating no significant face to face π···π stacking interactions. (b) The 3-D packing diagram of **3**. Hydrogen atoms are omitted for clarity.

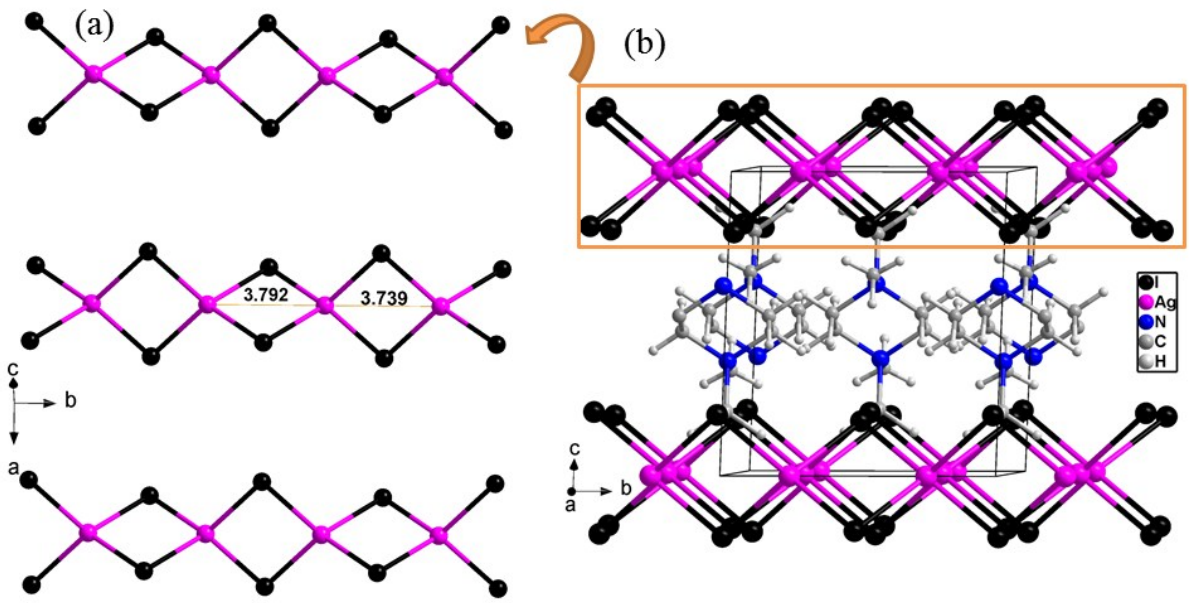


Fig. S9 (a) The α-type $(AgI_2)^-$ anionic chains arranged side by side to form a inorganic sheet parallel to the *ab* plane. (b) The 3-D packing diagram of **4**.

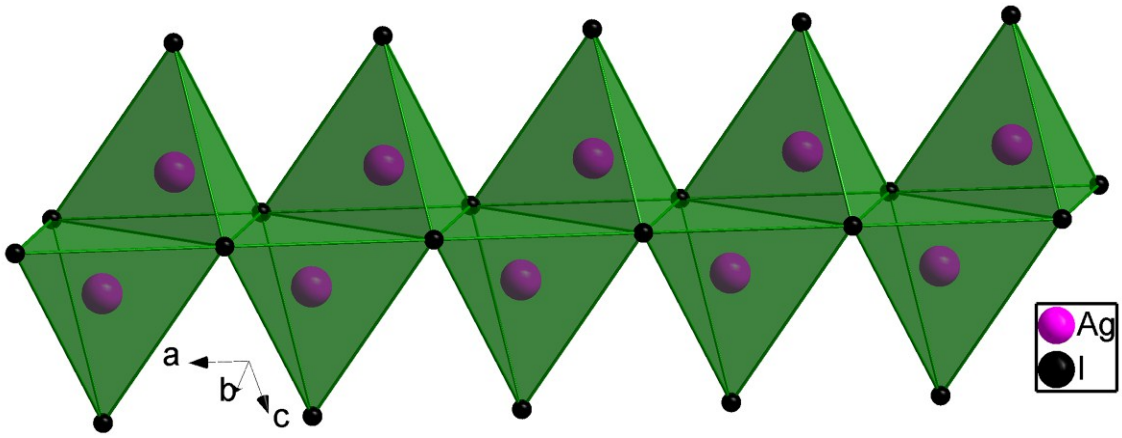


Fig. S10 The β-type $(AgI_2)^-$ chain in the literature,[1] which is built up by each tetrahedral (AgI_4) unit sharing two adjacent edges with a neighbouring (AgI_4) tetrahedron.

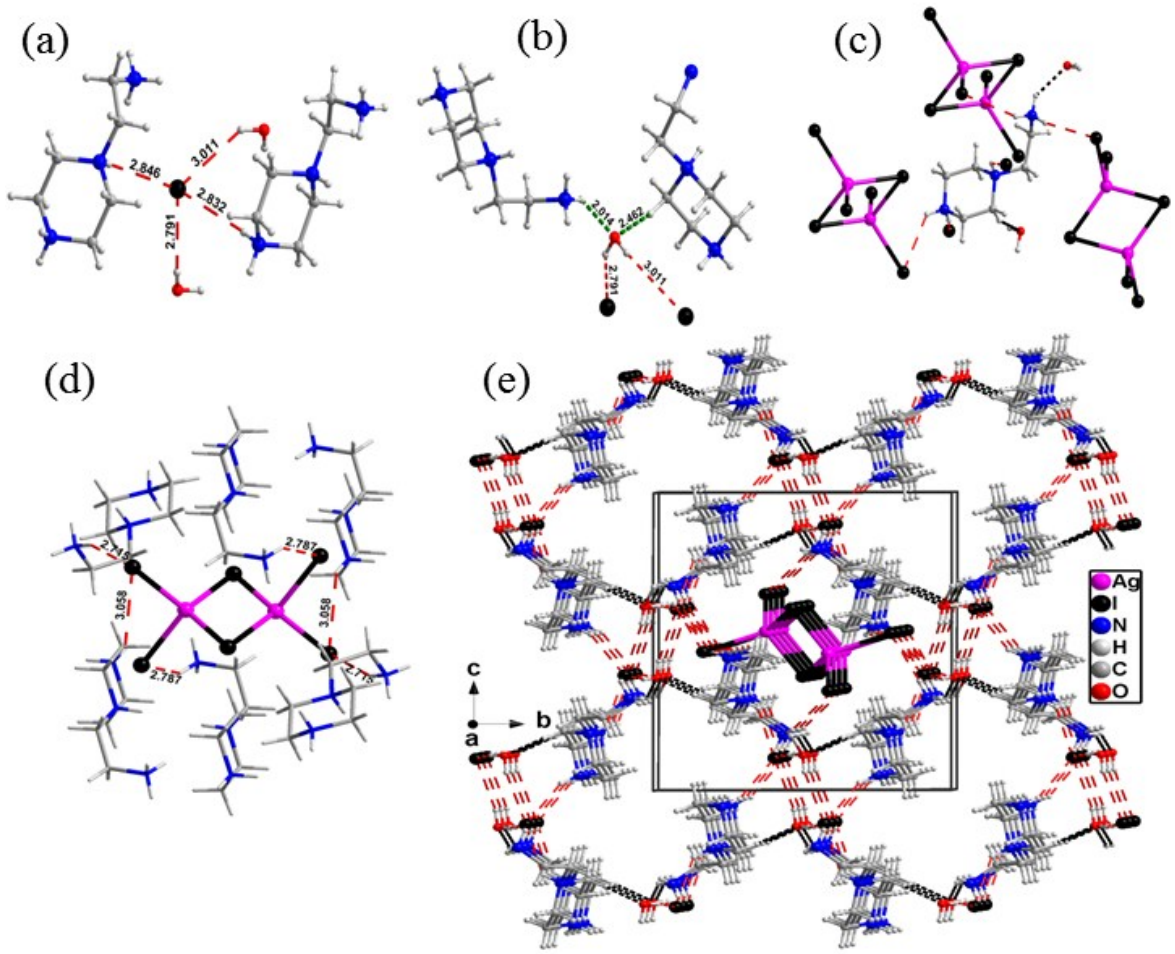


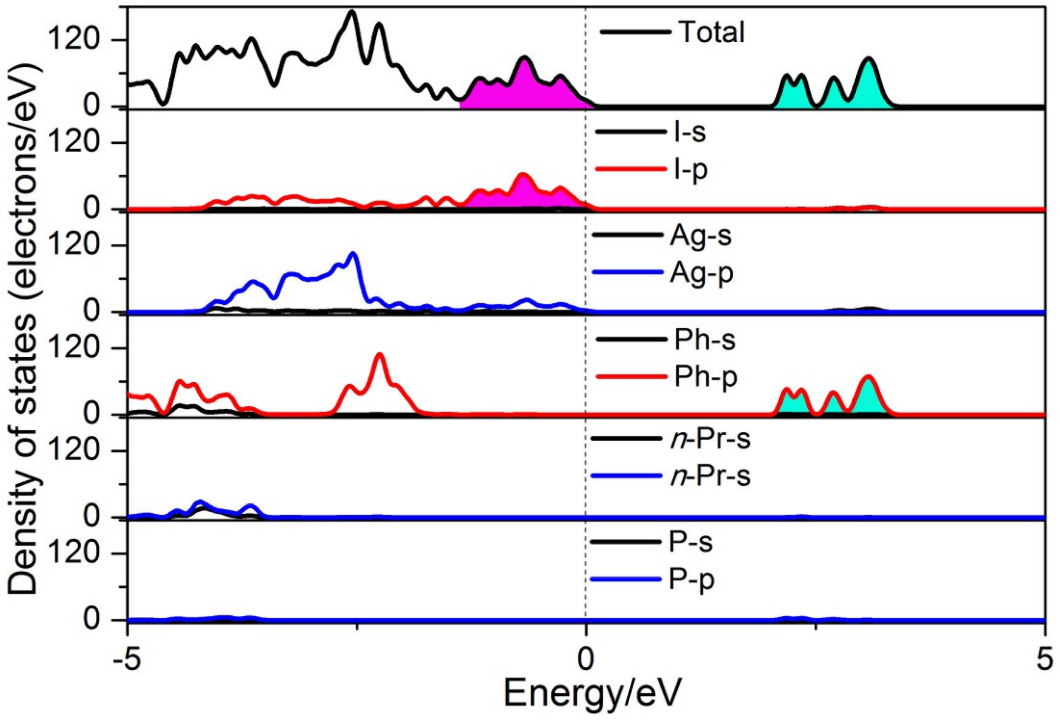
Fig. S11 (a) Each $I4^-$ ion links two $(H_3app)^{3+}$ cations and two lattice water molecules via O–H···I and N–H···I hydrogen bonds. (b) Each lattice water molecules interacts with two $(H_3app)^{3+}$ cations and two isolated I^- ions via hydrogen bonds. (c) Each $(H_3app)^{3+}$ cation connects with three $(Ag_2I_6)^{4-}$ dimers, two isolated I^- ions, and two lattice water molecules. (d) Each $(Ag_2I_6)^{4-}$ anion uses its four terminal I atoms interacting with six $(H_3app)^{3+}$ cations via N–H···I hydrogen bonds. (e) The supramolecular 3-D framework of **5** formed by N–H···I and O–H···I hydrogen bonds (red dashed lines), and C–H···O and N–H···O hydrogen bonds (black dashed lines).

Table S4. Selected Hydrogen Bonds Data for **5**.

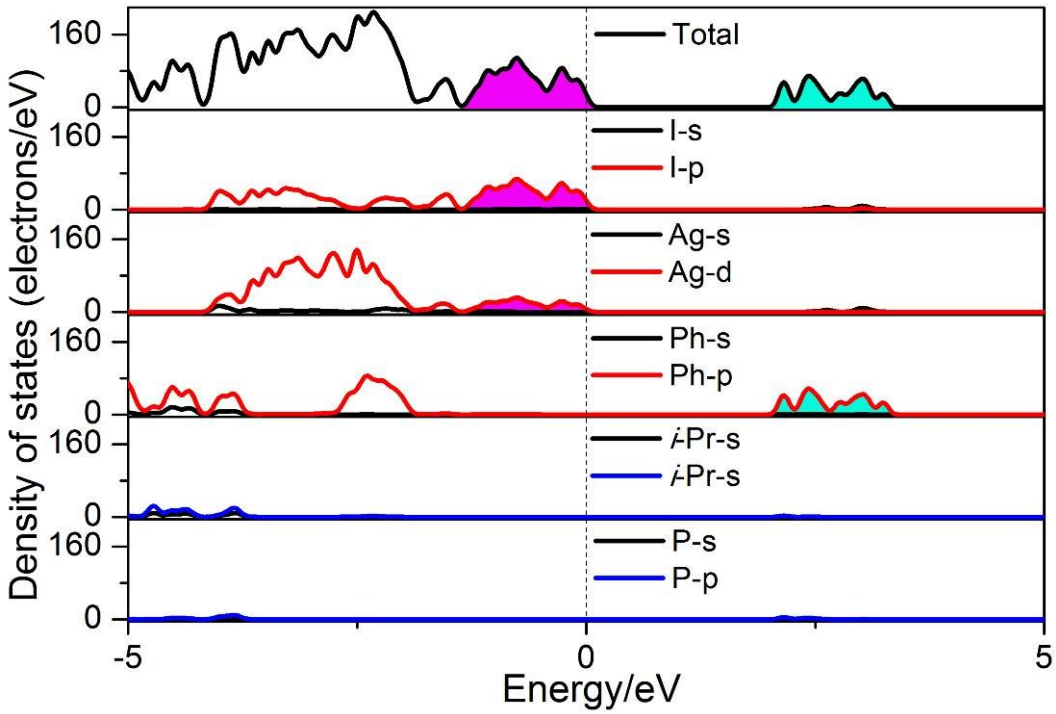
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
C4–H4B···O1W[a]	0.97	2.46	3.387(4)	159.5
N4–H8B···I4	0.89	2.84	3.661(3)	153.7

N4–H8A···I1	0.89	3.06	3.705(2)	130.5
N2–H2C···I4[b]	0.89	2.85	3.553(2)	137.2
N3–H7C···I1[c]	0.89	2.72	3.562(3)	159.4
N3–H7B···I3[d]	0089	2.79	3.520(3)	140.8
N3–H7A···O1W	0.89	2.01	2.773(4)	142.5
O1W-H1WB···I4[c]	0.85	2.79	3.573(2)	153.8
O1W-H1WA···I4[e]	0.85	3.01	3.713(2)	142

Symmetry code: a (-x, -1/2+y, 1/2-z); b (x, 1/2-y, -1/2+z); c (-1+x, 1/2-y, -1/2+z); d (1-x, 1-y, 1-z); e (-x, 1/2+y, 1/2-z).

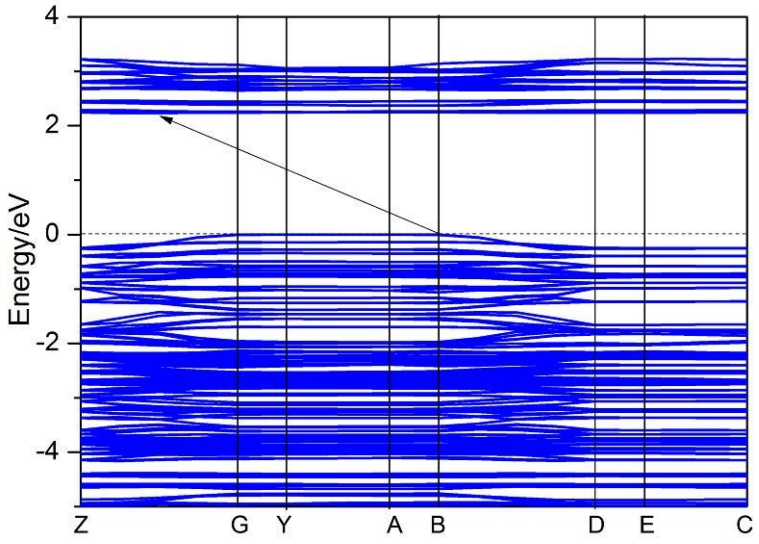


(a)

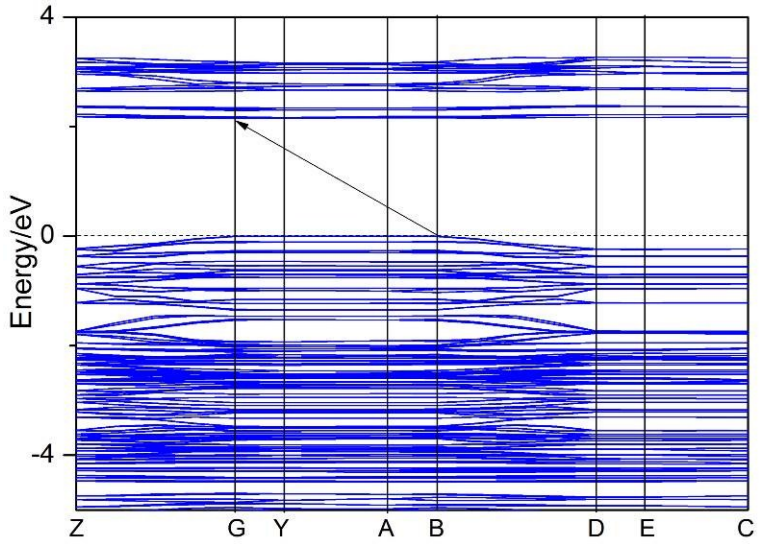


(b)

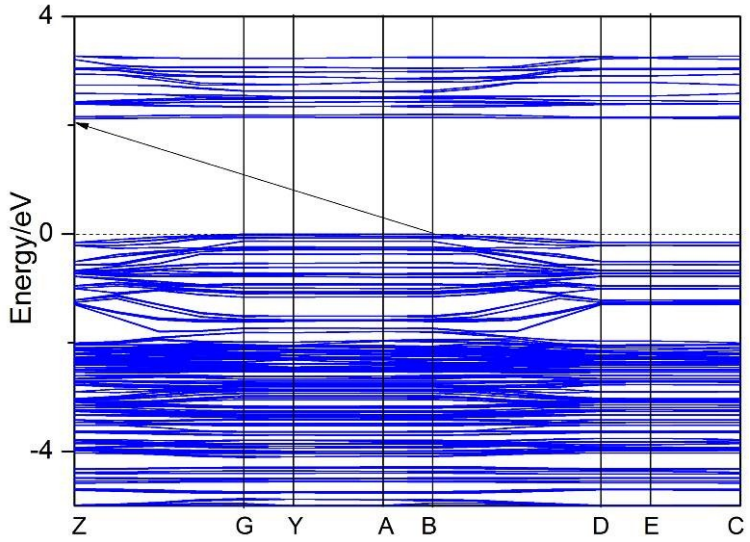
Fig. S12 Total and partial density of states of **2** (a) and **3** (b).



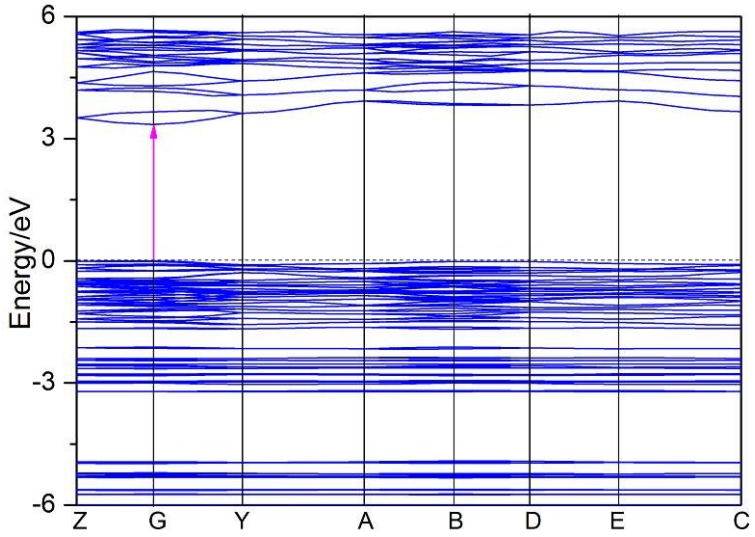
(a)


4
0
-4
Energy/eV
Z
G
Y
A
B
D
E
C

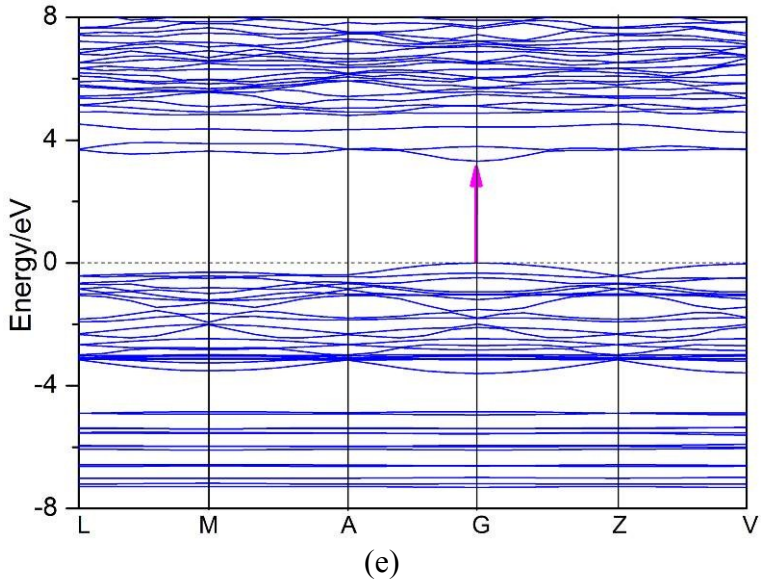
(b)


4
0
-4
Energy/eV
Z
G
Y
A
B
D
E
C

(c)


6
3
0
-3
-6
Energy/eV
Z
G
Y
A
B
D
E
C

(d)



(e)

Fig. S13 Band structures of **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e). The Fermi level is set at 0 eV.

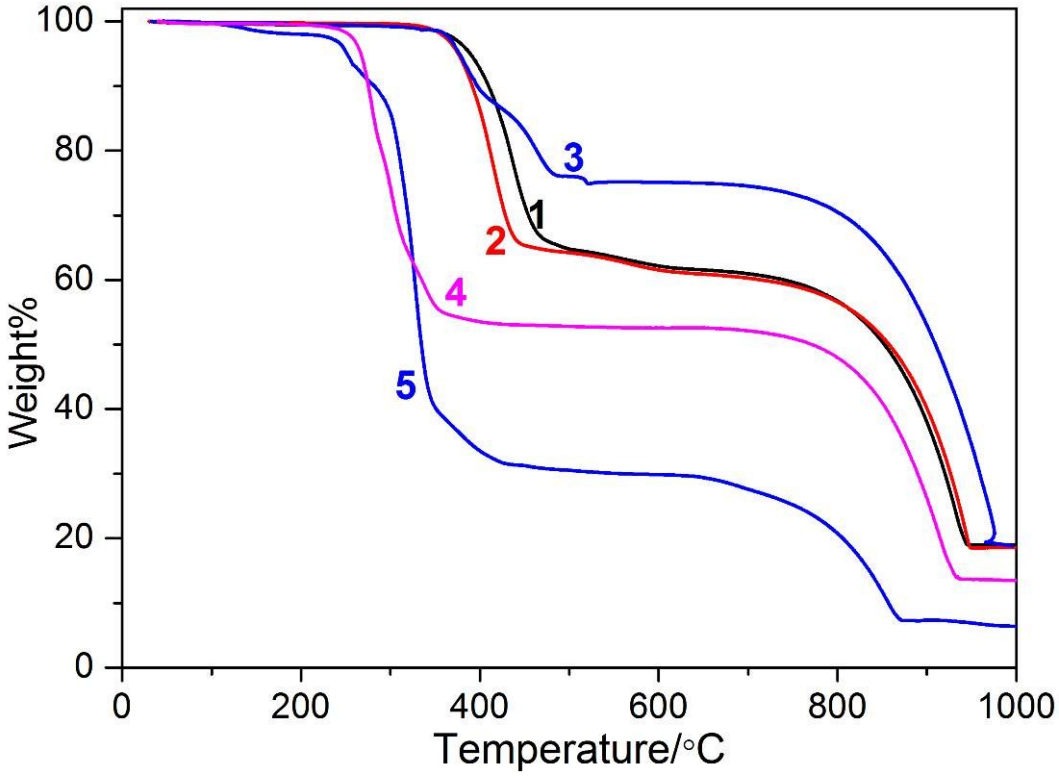


Fig. S14 TGA curves of **1**–**5**.

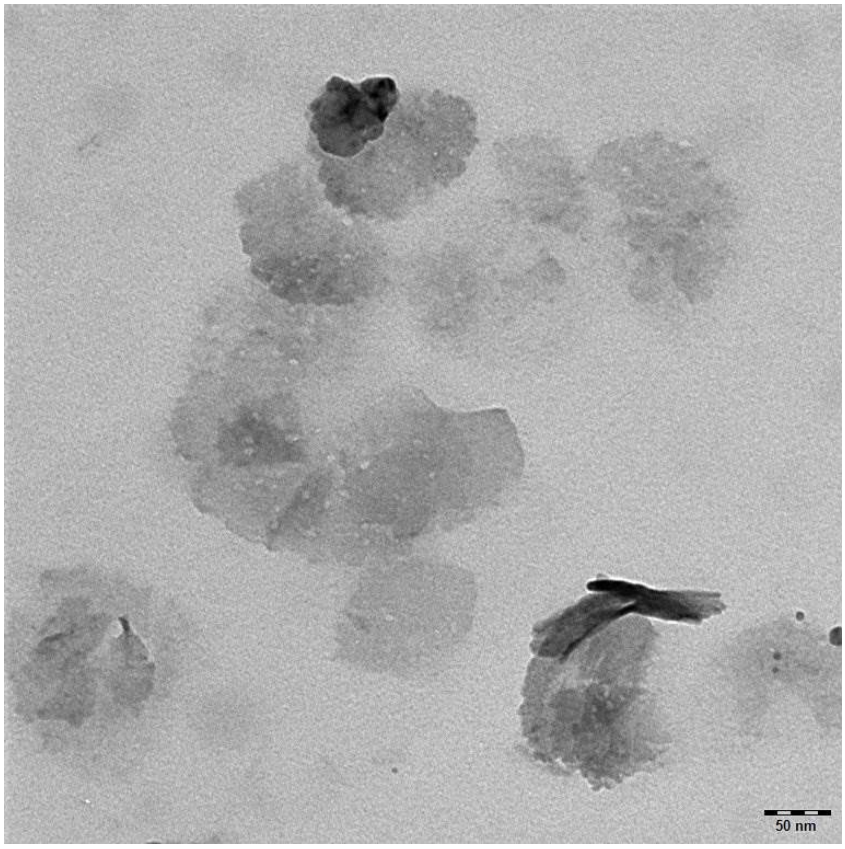
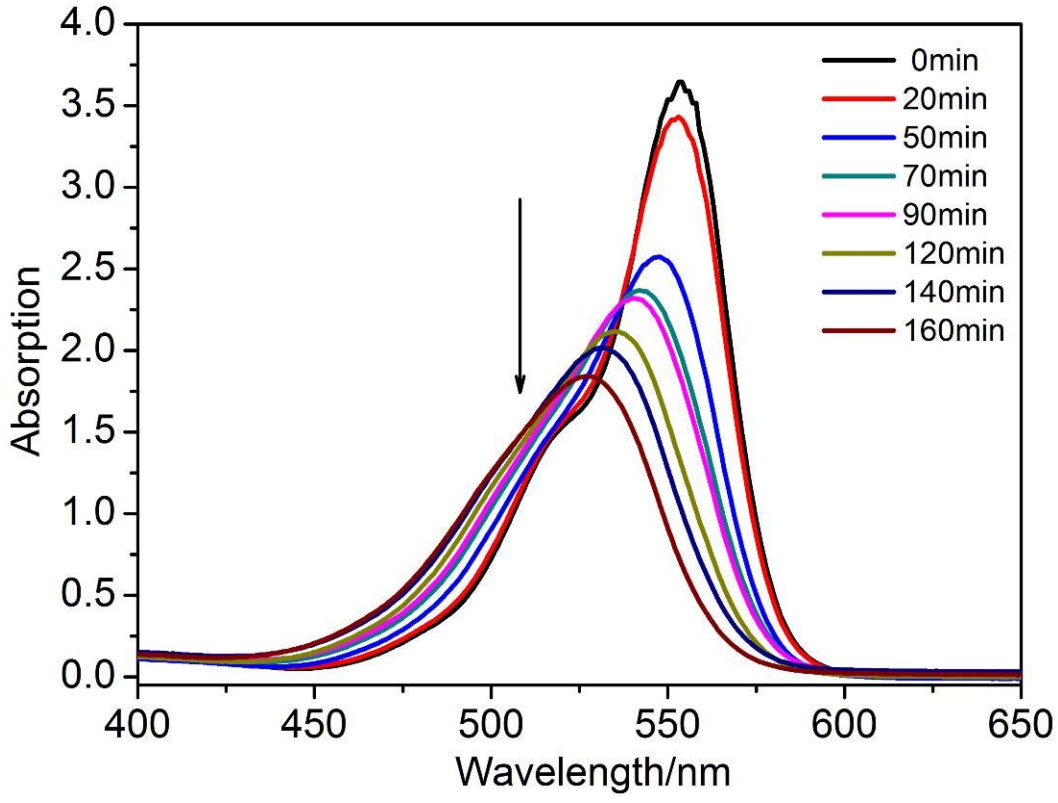
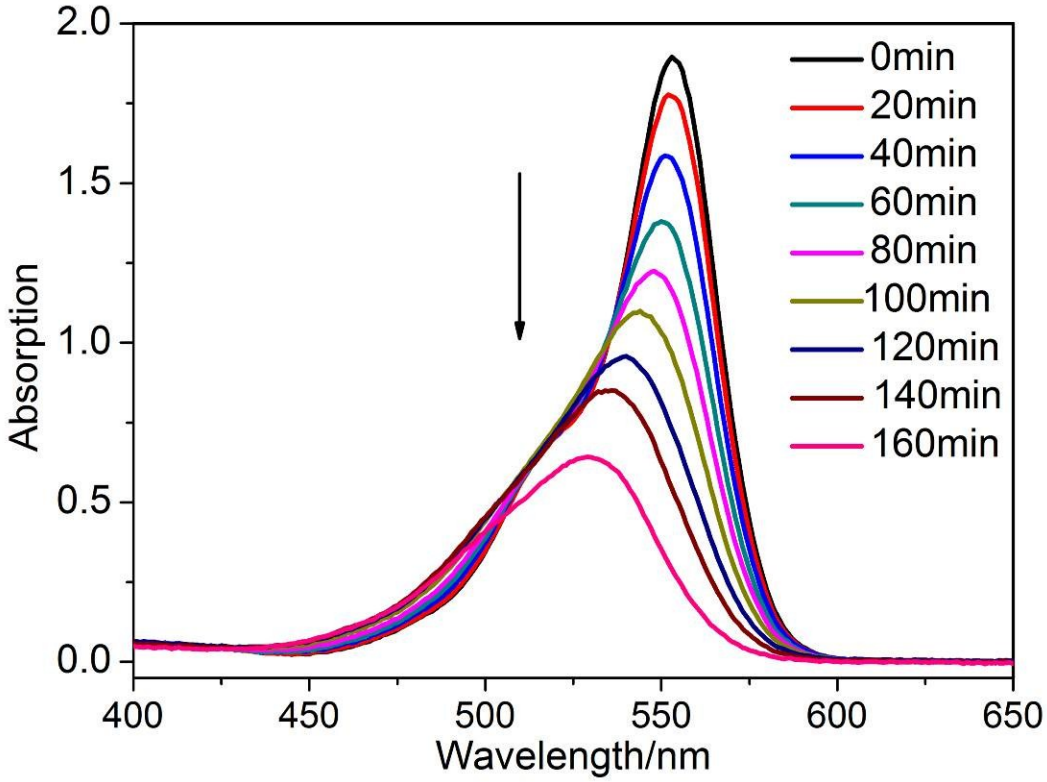


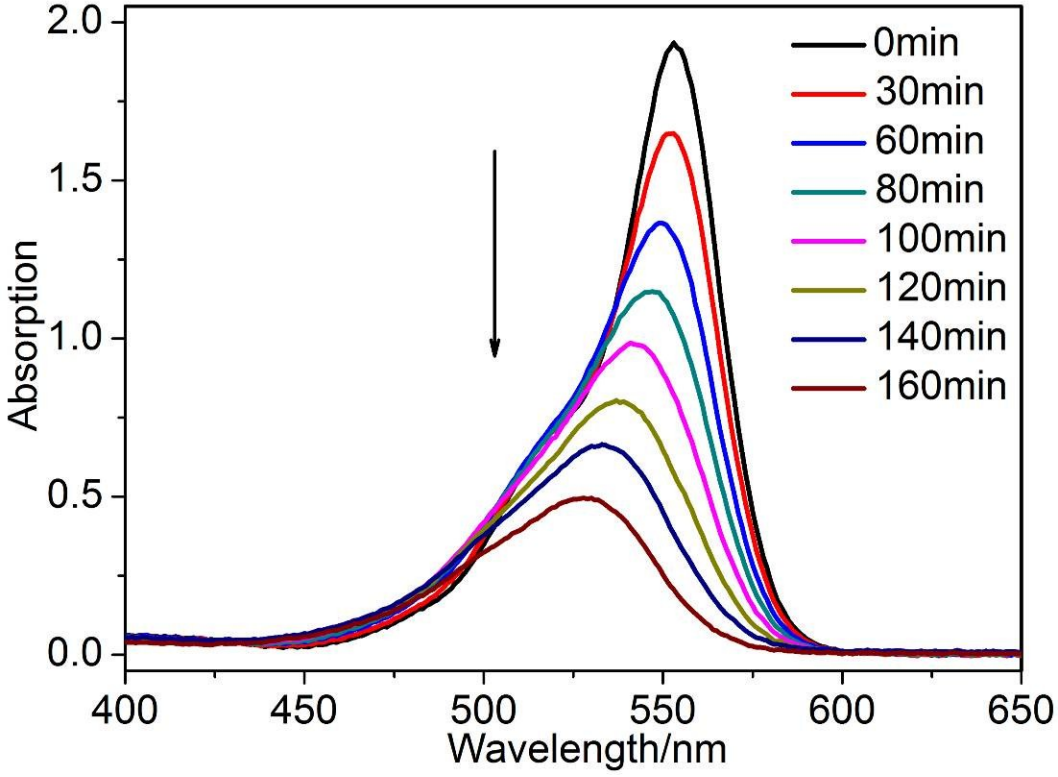
Fig. S15 The TEM image of the cubic AgI powder formed by hydrolysis reaction of **5**.



(a)



(b)



(c)

Fig. S16 Time-dependent UV-vis spectra of MhB over **1** (a) and **2** (b).

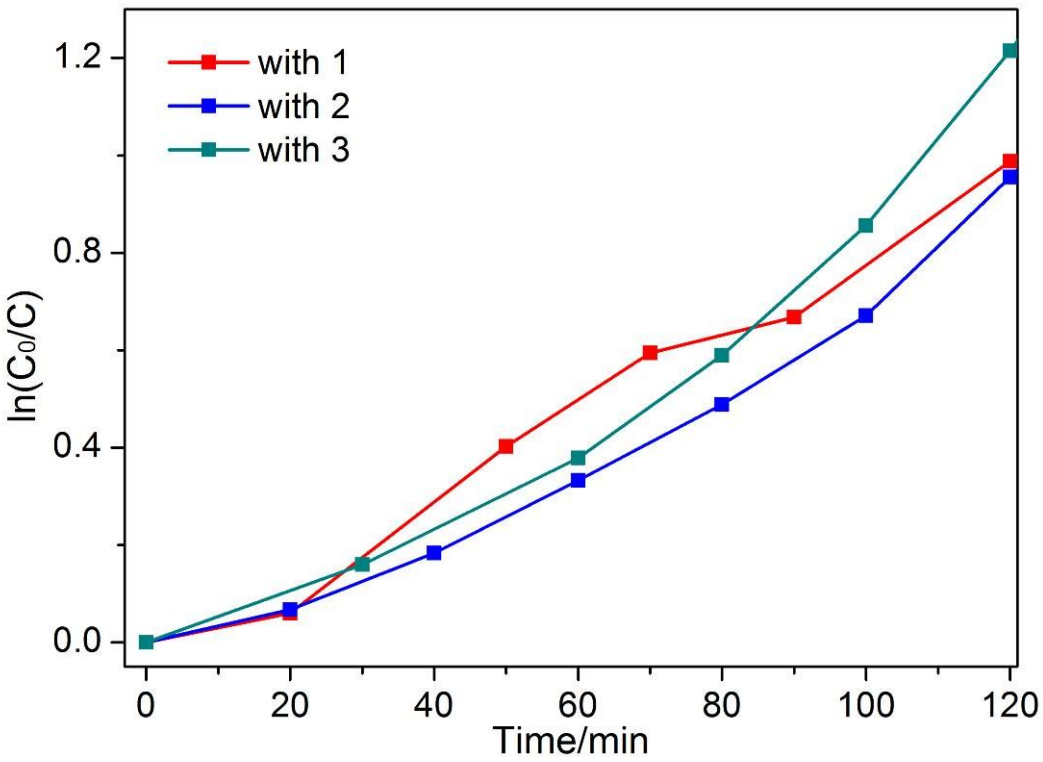
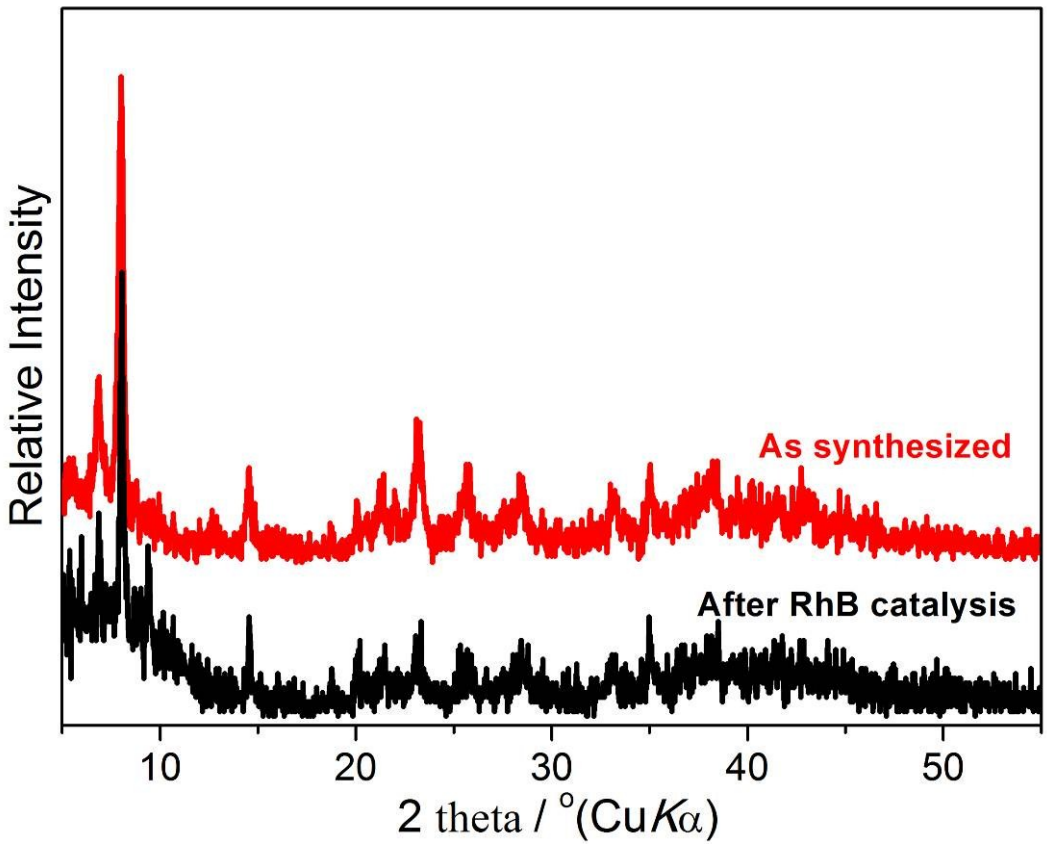
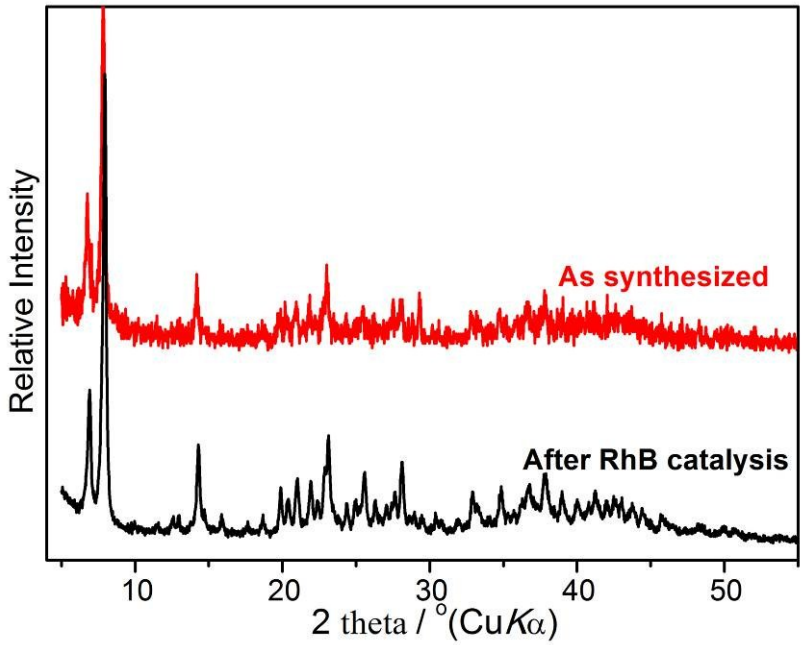


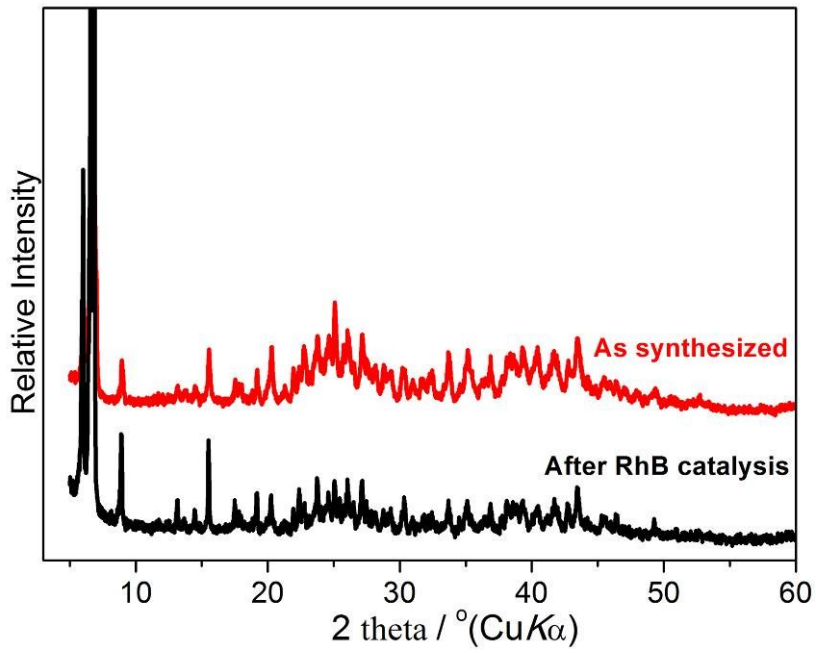
Fig. S17 The linear relationship of $\ln(C_0/C)$ over the reaction time.



(a)



(b)



(c)

Fig. S18 The PXRD patterns of **1** (a), **2** (b), and **3** (c) after photodegradation of RhB dye.

Reference:

1. G.-N. Liu, L.-L. Liu, Y.-N. Chu, Y.-Q. Sun, Z.-W. Zhang and C.-C. Li, *Eur. J. Inorg. Chem.,* 2015, 478