Supporting information

SUPRAMOLECULAR AGGREGATION OF YTTRIUM THIOCYANATE WITH 4,4'-BIPYRIDINE

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Table S1. **.** Thermodynamic functions of $[Y(H_2O)_3EtOH(bpy)(NCS)_3]\cdot bpy$ (**1**) and $[Y(H_2O)_5(NCS)_3]\cdot H_2O$

T, K	$[Y(H_2O)_3EtOH(bpy)(NCS)_3]\cdot bpy$				$[Y(H_2O)_5(NCS)_3]\cdot H_2O$			
	$C_p^0(T)$	$S^0(T)$	$\Phi^0(T)$	$H^0(T)-H^0(0)$	$C_p^0(T)$	$S^0(T)$	$\Phi^0(T)$	$H^0(T)-H^0(0)$
	J/(K mol)			J/mol	J/(K mol)			J/mol
10	12.80	4.095	0.9315	31.63	8.665	3.286	0.8405	24.45
15	30.79	12.53	3.286	138.7	17.58	8.419	2.470	89.24
20	52.55	24.30	7.008	345.8	29.69	15.06	4.754	206.1
25	76.63	38.58	11.86	668.1	43.02	23.13	7.602	388.1
30	101.6	54.75	17.64	1113	55.67	32.10	10.93	635.1
35	125.9	72.25	24.18	1683	67.98	41.60	14.63	944.2
40	148.5	90.56	31.33	2369	80.37	51.49	18.61	1315
45	169.3	109.3	38.94	3164	92.89	61.68	22.83	1748
50	188.7	128.1	46.92	4060	105.3	72.11	27.23	2244
60	225.0	165.8	63.59	6131	128.8	93.42	36.48	3416
70	260.0	203.1	80.86	8556	148.9	114.8	46.15	4808
80	292.8	240.0	98.45	11320	167.7	135.9	56.06	6391
90	320.2	276.1	116.2	14390	181.6	156.5	66.08	8140
100	343.6	311.1	133.9	17710	196.0	176.4	76.13	10030
110	365.8	344.9	151.6	21260	211.6	195.8	86.13	12060
120	387.4	377.6	169.1	25030	227.7	214.9	96.06	14260
130	408.8	409.5	186.3	29010	243.8	233.8	105.9	16620
140	430.5	440.6	203.4	33210	259.6	252.4	115.7	19140
150	452.5	471.0	220.2	37620	274.8	270.9	125.5	21810
160	474.4	500.9	236.8	42250	289.3	289.1	135.1	24630
170	495.7	530.3	253.2	47110	303.2	307.0	144.7	27590
180	515.9	559.2	269.4	52160	316.6	324.7	154.2	30690
190	535.0	587.7	285.4	57420	329.5	342.2	163.6	33920
200	553.9	615.6	301.3	62860	342.0	359.4	173.0	37280
210	573.5	643.1	316.9	68500	354.2	376.4	182.3	40760
220	594.6	670.2	332.3	74340	366.1	393.2	191.5	44370
230	618.9	697.2	347.6	80400	377.7	409.7	200.6	48080
240	652.0	724.2	362.7	86740	388.8	426.0	209.7	51920
250	656.8	750.8	377.7	93260	399.5	442.1	218.6	55860
260	677.2	776.9	392.6	99930	409.7	458.0	227.5	59900
270	697.0	802.9	407.3	106800.	419.5	473.6	236.4	64050
280	716.7	828.6	421.9	113900	429.3	489.0	245.1	68300
290	736.1	854.0	436.3	121100	439.3	504.3	253.8	72640
298.15	751.9	874.7	448.0	127200	447.7	516.6	260.8	76250

Table S2. Crystal data and structure refinement statistics for **1**–**7**.

Identification code	**1**
Empirical formula	C25 H28 N7 O4 S3 Y
Formula weight	675.63
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 13.6795(5) Å
	b = 14.0922(6) Å
	c = 15.6687(7) Å
Volume	3020.5(2) $Å^3$
Z	4
Density (calculated)	1.486 Mg/m^3
Absorption coefficient	2.181 mm^{-1}
F(000)	1384
Crystal size	0.25 x 0.2 x 0.15 mm^3
Theta range for data collection	2.449 to 27.492°.
Index ranges	-9<=h<=17, -18<=k<=6, -20<=l<=20
Reflections collected	12585
Independent reflections	6571 [R(int) = 0.0594]
Completeness to theta = 25.242°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6291
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6571 / 8 / 375
Goodness-of-fit on F^2	0.955
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.0756
R indices (all data)	R1 = 0.0937, wR2 = 0.0897
Absolute structure parameter	0.312(9)
Largest diff. peak and hole	0.603 and -0.366 $e.Å^{-3}$

Identification code	**2**
Empirical formula	C52 H60 N14 O8 S6 Y2
Formula weight	1379.32
Temperature	150(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 15.0003(12) Å
	b = 15.3686(9) Å β= 112.679(2)°.
	c = 15.1311(8) Å
Volume	3218.5(4) $Å^3$
Z	2
Density (calculated)	1.423 Mg/m^3
Absorption coefficient	2.048 mm^{-1}
F(000)	1416
Crystal size	0.28 x 0.2 x 0.12 mm^3
Theta range for data collection	2.651 to 29.998°.
Index ranges	-17<=h<=21, 0<=k<=21, -17<=l<=21
Reflections collected	9082
Independent reflections	9082 [R(int) = ?]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746154 and 0.526187
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9082 / 0 / 370
Goodness-of-fit on F^2	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1332
R indices (all data)	R1 = 0.1045, wR2 = 0.1552
Largest diff. peak and hole	1.963 and -1.062 $e.Å^{-3}$

Identification code	**3**
Empirical formula	C48 H46 N16 O6 S8 Y2
Formula weight	1377.31
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 13.995(4) Å
	b = 15.465(4) Å β= 114.419(4)°.
	c = 15.478(4) Å
Volume	3050.3(14) $Å^3$
Z	2
Density (calculated)	1.500 Mg/m^3
Absorption coefficient	2.226 mm^{-1}
F(000)	1400

Crystal size	0.35 x 0.28 x 0.25 mm^3
Theta range for data collection	2.560 to 25.997°.
Index ranges	-17<=h<=17, -19<=k<=19, -19<=l<=19
Reflections collected	34920
Independent reflections	5981 [R(int) = 0.0479]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6379 and 0.5564
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5981 / 0 / 361
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1333
R indices (all data)	R1 = 0.0784, wR2 = 0.1575
Largest diff. peak and hole	1.060 and -0.537 e.$Å^{-3}$

Identification code	**4**
Empirical formula	C34 H35 N10 O5 S4 Y
Formula weight	880.87
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.8885(6) Å
	b = 15.5251(9) Å β= 102.245(2)°.
	c = 22.7683(11) Å
Volume	4106.7(4) $Å^3$
Z	4
Density (calculated)	1.425 Mg/m^3
Absorption coefficient	1.675 mm^{-1}
F(000)	1808
Crystal size	0.32 x 0.15 x 0.12 mm^3
Theta range for data collection	2.513 to 25.999°.
Index ranges	-14<=h<=14, -19<=k<=18, -27<=l<=28
Reflections collected	27236
Independent reflections	8062 [R(int) = 0.0558]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.5805
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	8062 / 0 / 475
Goodness-of-fit on F^2	0.937
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.0939
R indices (all data)	R1 = 0.1064, wR2 = 0.1179
Largest diff. peak and hole	0.356 and -0.344 e.Å^{-3}

Identification code	**5**
Empirical formula	C46 H37 N14 O S6 Y
Formula weight	1083.16
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 14.7890(9) Å
	b = 18.1748(12) Å β= 106.229(2)°.
	c = 19.6738(12) Å
Volume	5077.3(6) Å^3
Z	4
Density (calculated)	1.417 Mg/m^3
Absorption coefficient	1.446 mm^{-1}
F(000)	2216
Crystal size	0.32 x 0.24 x 0.2 mm^3
Theta range for data collection	2.156 to 26.499°.
Index ranges	-18<=h<=16, -22<=k<=22, -24<=l<=24
Reflections collected	30301
Independent reflections	10458 [R(int) = 0.0482]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6291
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10458 / 0 / 625
Goodness-of-fit on F^2	0.989
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.0875
R indices (all data)	R1 = 0.0872, wR2 = 0.1040
Largest diff. peak and hole	0.457 and -0.361 e.Å^{-3}

Identification code	**6**
Empirical formula	C34 H29 N10 O2 S4 Y
Formula weight	826.82
Temperature	296(2) K

Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 9.362(10) Å
	b = 21.55(2) Å β= 98.64(2)°.
	c = 19.379(16) Å
Volume	3865(6) $Å^3$
Z	4
Density (calculated)	1.421 Mg/m^3
Absorption coefficient	1.769 mm^{-1}
F(000)	1688
Crystal size	0.25 x 0.15 x 0.01 mm^3
Theta range for data collection	2.584 to 22.496°.
Index ranges	-8<=h<=10, -23<=k<=23, -20<=l<=18
Reflections collected	17204
Independent reflections	5034 [R(int) = 0.1299]
Completeness to theta = 22.496°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.3494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5034 / 30 / 455
Goodness-of-fit on F^2	1.517
Final R indices [I>2sigma(I)]	R1 = 0.1286, wR2 = 0.2860
R indices (all data)	R1 = 0.1759, wR2 = 0.3007
Largest diff. peak and hole	1.005 and -1.981 $e.Å^{-3}$

Identification code	**7**
Empirical formula	C47 H44 N15 O4 S7 Y
Formula weight	1196.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P n
Unit cell dimensions	a = 10.922(5) Å
	b = 17.836(11) Å β= 98.157(18)°.
	c = 28.622(18) Å
Volume	5519(5) $Å^3$
Z	4
Density (calculated)	1.440 Mg/m^3
Absorption coefficient	1.378 mm^{-1}

F(000)	2456
Crystal size	0.3 x 0.04 x 0.02 mm^3
Theta range for data collection	2.284 to 20.000°.
Index ranges	-7<=h<=10, -11<=k<=17, -26<=l<=27
Reflections collected	8435
Independent reflections	7133 [R(int) = 0.1319]
Completeness to theta = 20.000°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6456 and 0.4639
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7133 / 1449 / 578
Goodness-of-fit on F^2	0.884
Final R indices [I>2sigma(I)]	R1 = 0.0889, wR2 = 0.1724
R indices (all data)	R1 = 0.2513, wR2 = 0.2255
Absolute structure parameter	0.02(2)
Largest diff. peak and hole	0.462 and -0.474 e.$Å^{-3}$

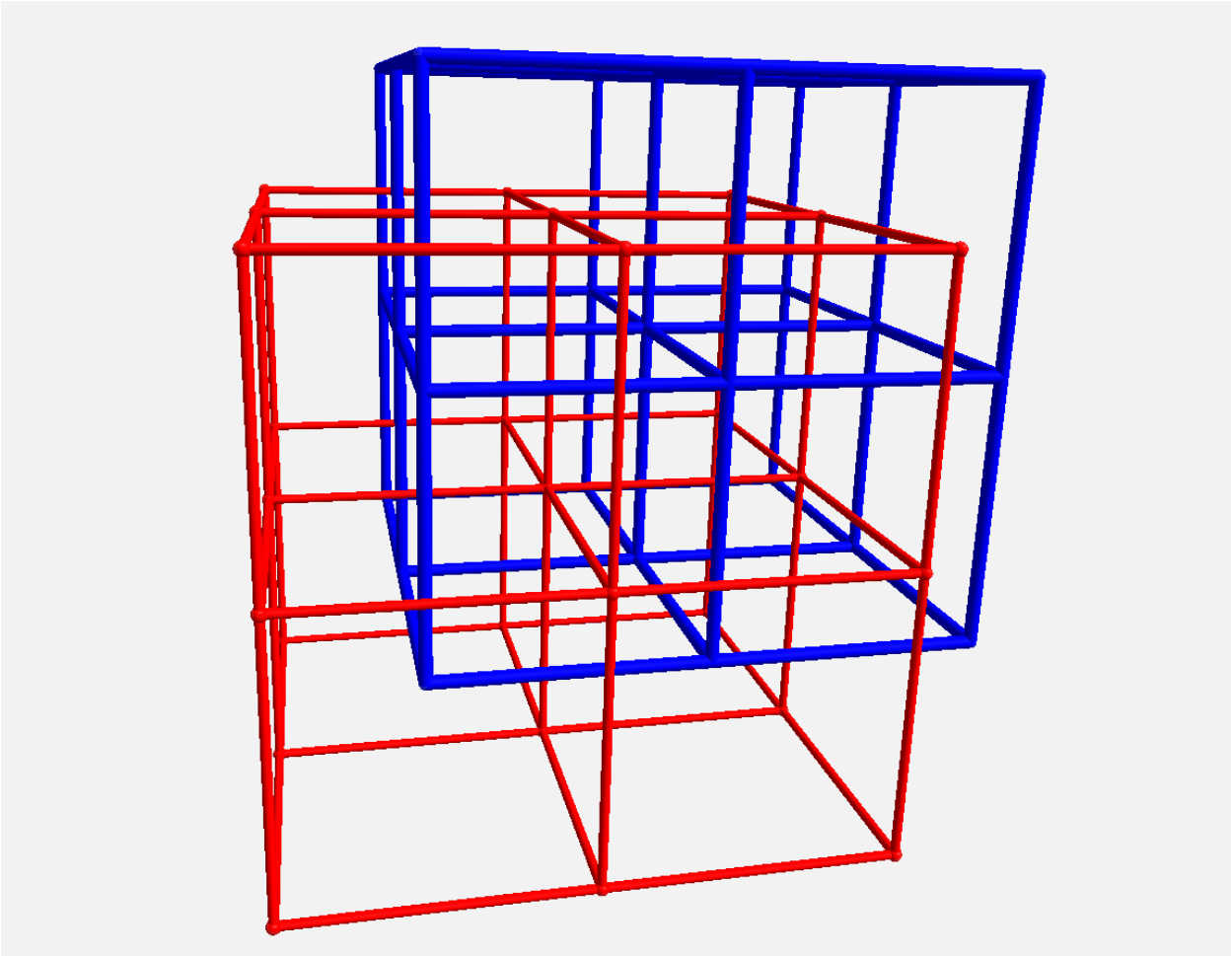

Fig. S1. Iinterpenetrating network.

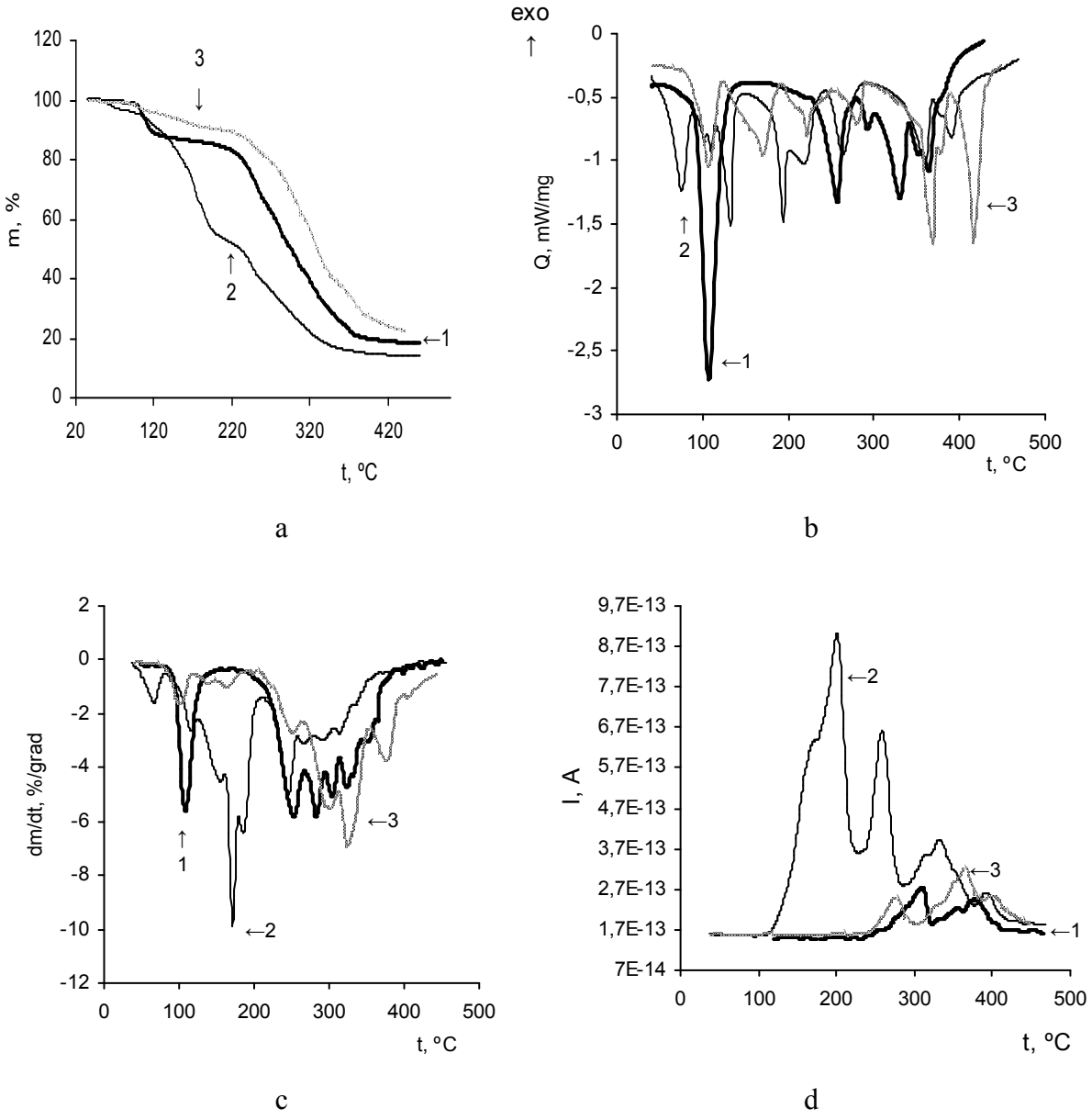

Fig. S2. TG (a), DSC (b), DTGA (c) curves and the temperature dependence of the ionic current in the mass spectra of the gases that evolved during thermogravimetry: m/z=156 (d) for compounds: **1**, bold curves; **2**, thin curves; and **3**, dashed curves.