Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Synthesis, structure and light scattering properties of tetraalkylammonium metal isothiocyanate salts.

Didier Savard and Daniel B. Leznoff

Table S1. Comparison of the infrared data for $(Me_4N)_3[Fe(NCS)_6]$ (**7**), $(Et_4N)_3[Fe(NCS)_6]$ (**8**) and $(n\text{-}Bu_4N)_3[Ln(NCS)_6]$ (Ln = Eu(III) (**11**), Gd(III) (**12**) and Dy(III) (**13**)) with literature values for these salts.

Complex	Observed (cm^{-1})	Published	Reference
7	2073, 2058, 2023	2075, 2057, 2026	A
8	2101, 2070, 2054	2098, 2052	B
11	2047, 2037	2040	C
12	2043	2045	C
13	2054	2052	C

A. Forster, D.; Goodgame, D. M. L. *J. Chem. Soc.*, **1965**, *4*, 715
B. Bailey, R. A.; Kozak, S. L.; Michelsen, T. W.; Mills, W. N. *Coord. Chem. Rev.*, **1971**, *6*, 407
C. Burmelster, J. L.; Patterson, S. D.; Deardorff, A. E. *Inorg. Chim. Acta*, **1969**, *3*, 105

Table S2. Crystallographic data for $(NH_4)_3[Cr(NCS)_6]\cdot[(CH_3)_2CO]$ (**1b**), $(Me_4N)_3[Cr(NCS)_6]$ (**2**), $(Me_4N)_4[Mn(NCS)_6]$ (**5**), $(Et_4N)_3[Mn(NCS)_5]$ (**6**) and $(n\text{-}Bu_4N)_3[Fe(NCS)_6]$ (**9**).

Complex	**1b**	**2**	**5**	**6**	**9**
empirical formula	$C_9H_{22}CrN_{10}OS_6$	$C_{18}H_{36}CrN_9S_6$	$C_{22}H_{48}MnN_{10}S_6$	$C_{29}H_{60}Mn_1N_8S_5$	$C_{54}H_{108}FeN_9O_{0.42}S_6$
formula weight	530.73	622.94	700.01	736.11	1138.45
Temperature (K)	293	293	293	293	293
crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Cubic
space group	Pcmn	C2/c	$P2_1/n$	P-1	Pa-3
a (Å)	9.6828(16)	24.8961(10)	12.5278(6)	9.935(9)	24.1615(2)
b (Å)	14.744(2)	9.3234(4)	12.4262(6)	14.689(14)	24.1615(2)
c (Å)	16.341(3)	28.4594(12)	12.5900(6)	15.919(15)	24.1615(2)
α (deg)	90	90	90	80.442(16)	90
β (deg)	90	100.021(2)	90.076(2)	72.682(17)	90
γ (deg)	90	90	90	81.387(18)	90
V (Å^3)	2332.9(7)	6505.1(5)	1959.92(16)	2175(4)	14105.0(2)
Z	4	8	2	2	8
ρ_{calc} (g/cm^3)	1.511	1.272	1.186	1.124	1.072
μ (mm^{-1})	1.049	6.680	0.683	0.571	0.429
R $[I_o \geq 2.0\sigma(I_o)]$	0.0564	0.0521	0.0948	0.0709	0.0292
R_w $[I_o \geq 2.0\sigma(I_o)]$	0.0562	0.0557	0.0910	0.0787	0.0322

Function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0002\ F_o^2$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|^2)/\Sigma w|F_o|^2)^{1/2}$

Table S3. Crystallographic data for $(n\text{-}Bu_4N)_3[Ln(NCS)_6]$ (Ln = Eu(III) (**11**), Gd(III) (**12**) and Dy(III) (**13**)).

Compounds	**11**	**12**	**13**
empirical formula	$C_{54}H_{108}EuN_9S_6$	$C_{54}H_{108}GdN_9S_6$	$C_{54}H_{108}DyN_9S_6$
formula weight	1227.87	1233.16	1238.41
Temperature (K)	293	150	293
crystal system	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1
a (Å)	12.41400(10)	12.4039(16)	12.4126(3)
b (Å)	12.88360(10)	12.8837(16)	12.8565(3)
c (Å)	22.7811(2)	22.787(3)	22.7613(5)
α (deg)	90.9370(10)	90.877(6)	90.8850(10)
β (deg)	92.3400(10)	92.241(7)	92.3090(10)
γ (deg)	96.7250(10)	96.743(7)	96.6870(10)
V (Å^3)	3614.63(5)	3612.8(8)	3603.93(14)
Z	2	2	2
ρ_{calc} (g/cm^3)	1.127	1.171	1.141
μ (mm^{-1})	1.077	1.165	1.246
R $[I_o \geq 2.0\sigma(I_o)]$	0.0342	0.0520	0.0353
R_w $[I_o \geq 2.0\sigma(I_o)]$	0.0360	0.0504	0.0324

Function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0002\ F_o^2$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|^2)/\Sigma w|F_o|^2)^{1/2}$

Table S4. Selected bond lengths (Å) and angles (°) for $(NH_4)_3[Cr(NCS)_6]\cdot[(CH_3)_2CO]$ (**1b**), $(n\text{-}Bu_4N)_3[Cr(NCS)_6]$ (**4**), $(Me_4N)_4[Mn(NCS)_6]$ (**5**) and $(n\text{-}Bu_4N)_3[Fe(NCS)_6]$ (**9**).

Compounds	**1b**	**4**	**5**	**9**
M-N1	2.005(5)	2.057(1)	2.202(9)	2.061(3)
M-N2	1.997(4)	2.026(1)	2.214(9)	2.032(3)
M-N3	1.992(4)	--	2.223(8)	--
M-N4	2.000(5)	--	--	--
M-N1-C	177.2(5)	168.23(1)	176.7(9)	168.8(3)
M-N2-C	170.1(4)	173.95(1)	176.9(9)	173.6(3)
M-N3-C	165.8(4)	--	169.5(9)	--
M-N4-C	168.1(5)	--	--	--

Table S5. Selected bond lengths (Å) and angles (°) for $(Me_4N)_3[Cr(NCS)_6]$ (**2**).

Cr1-N1	1.999(5)
Cr1-N2	1.993(5)
Cr1-N3	1.992(5)
Cr2-N4	1.999(4)
Cr2-N5	1.993(5)
Cr2-N6	1.985(5)
Cr1-N1-C1	177.4(4)
Cr1-N2-C2	173.8(4)
Cr1-N3-C3	150.9(4)
Cr2-N4-C4	175.9(4)
Cr2-N5-C5	176.8(4)
Cr2-N6-C6	171.8(4)

Table S6. Selected bond lengths (Å) and angles (°) for $(Et_4N)_3[Mn(NCS)_5]$ (**6**).

Mn1-N1	2.216(5)	Mn1-N1-C1	171.6(4)
Mn1-N2	2.110(5)	Mn1-N2-C2	171.9(4)
Mn1-N3	2.143(4)	Mn1-N3-C3	172.7(4)
Mn1-N4	2.226(4)	Mn1-N4-C4	175.7(4)
Mn1-N5	2.173(4)	Mn1-N5-C5	166.1(4)
N1-Mn1-N2	98.3(2)	N2-Mn1-N3	110.8(2)
N1-Mn1-N3	87.8(2)	N2-Mn1-N4	91.0(2)
N1-Mn1-N4	170.3(2)	N2-Mn1-N5	116.0(2)
N1-Mn1-N5	85.9(2)	N4-Mn1-N5	87.4(2)
N3-Mn1-N4	91.5(2)	N3-Mn1-N5	133.2(2)

Table S7. Selected bond lengths (Å) and angles (°) for $(n\text{-}Bu_4N)_3[Ln(NCS)_6]$ (Ln = Eu(III) (**11**), Gd(III) (**12**) and Dy(III) (**13**)).

Compounds	**11**	**12**	**13**
M-N1	2.379(3)	2.390(4)	2.341(4)
M-N2	2.395(3)	2.395(4)	2.340(4)
M-N3	2.382(3)	2.398(4)	2.350(4)
M-N4	2.387(3)	2.365(4)	2.333(4)
M-N5	2.405(3)	2.376(4)	2.340(4)
M-N6	2.381(3)	2.396(4)	2.364(4)
M-N1-C	176.2(3)	171.3(4)	172.7(4)
M-N2-C	174.8(3)	173.9(4)	172.3(4)
M-N3-C	171.8(3)	175.3(4)	174.6(4)
M-N4-C	172.5(3)	175.6(4)	176.5(4)
M-N5-C	174.4(3)	170.7(4)	172.7(4)
M-N6-C	172.0(3)	174.5(4)	174.0(4)

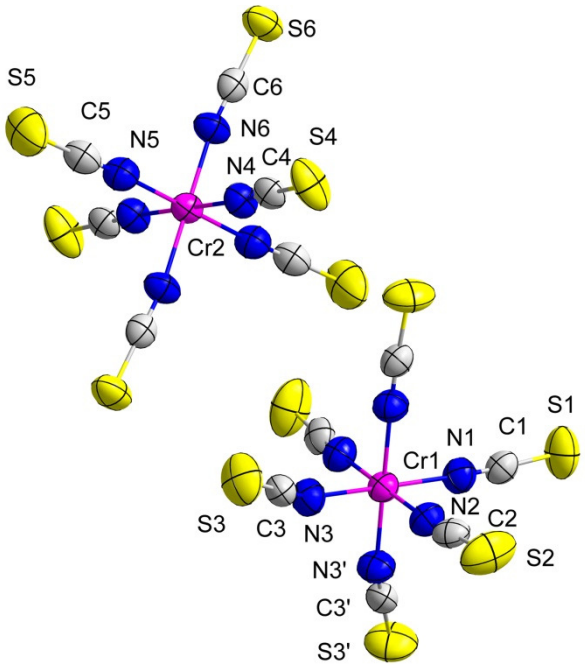

Figure S1. Crystal structure of $(Me_4N)_3[Cr(NCS)_6]$ (**2**). Thermal ellipsoids are drawn at 50% probability. Colour code: Purple (Cr), Blue (N), Yellow (S), Gray (C). Solvent molecules and hydrogen atoms have been removed for clarity.

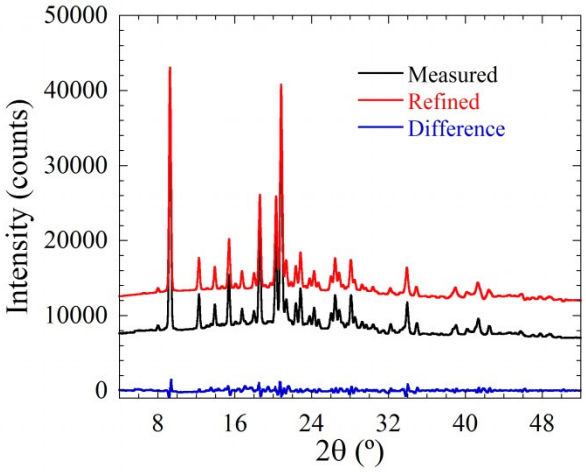

Figure S2. Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of $(Et_4N)_3[Cr(NCS)_6]$ (**3a**).

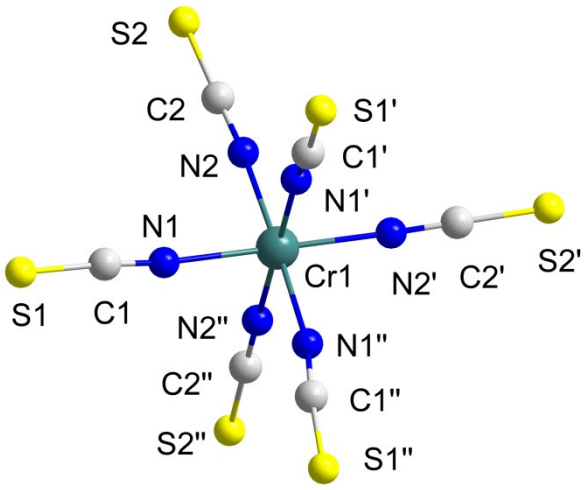

Figure S3. Generated crystal structure of $(Bu_4N)_3[Cr(NCS)_6]$ (**4**) from the Rietveld refinement. Color code: Purple (Cr), Blue (N), Yellow (S), Gray (C). Solvent molecules were removed for clarity.

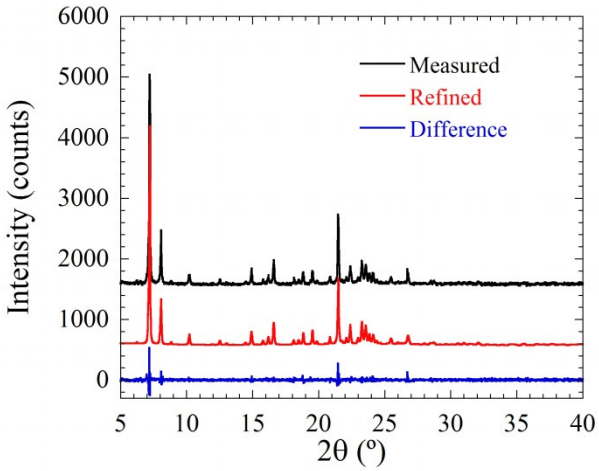

Figure S4. Measured PXRD pattern (black), calculated Rietveld refinement (red) and difference pattern (blue) of $(n\text{-}Bu_4N)_3[Cr(NCS)_6]$ (**4**).

Table S8. Rietveld refinement parameters for $(n\text{-}Bu_4N)_3[Cr(NCS)_6]$ (**4**).

System	Cubic
Space group	Pa-3
Scale	8.644e-008
Lattice parameter, α (Å)	24.442
Unit Cell Volume (Å^3)	14615
Crystal density, calculated (g cm^3)	1.638
Wt%-Rietveld	100
Rexp / Rexp ‘	8.316 / 17.065
Rwp / Rwp ‘	11.398 / 23.388
Rp / Rp ‘	8.889 / 22.824
R_{Bragg}	1.2839
GoF	1.371
DW_d	1.594

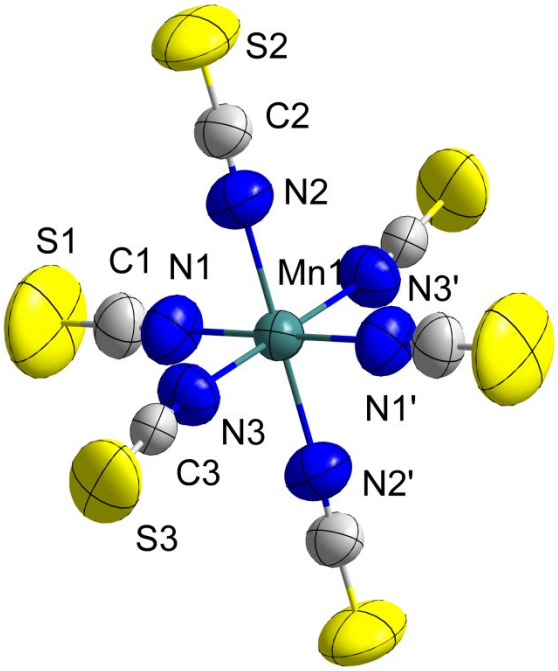

Figure S5. Crystal structure of $(Me_4N)_4[Mn(NCS)_6]$ (**5**). The thermal ellipsoids are drawn at 50% probability. Colour code: Pink (Mn), Blue (N), Yellow (S), Gray (C). Hydrogen atoms have been removed for clarity.

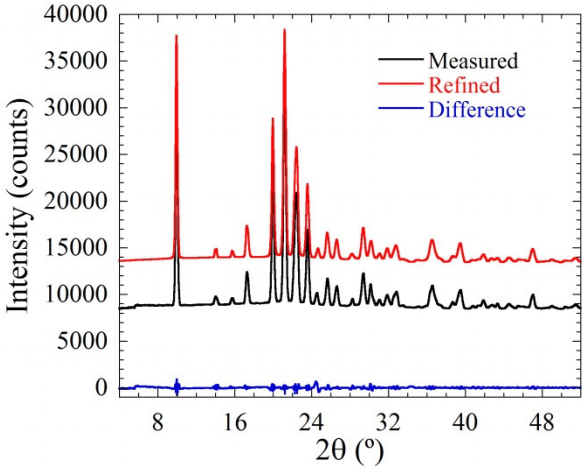

Figure S6. Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of $(Me_4N)_4[Mn(NCS)_6]$ (**5**).

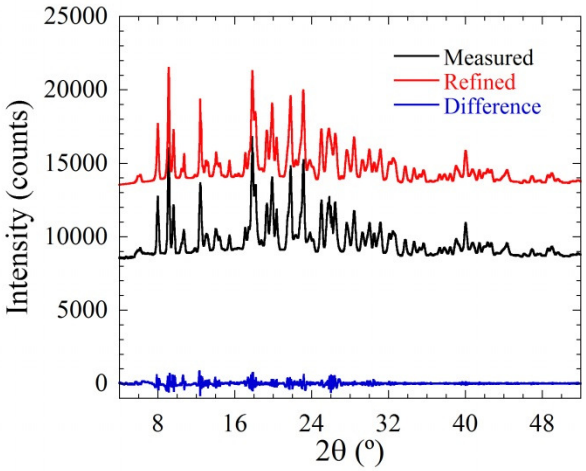

Figure S7. Measured PXRD pattern (black), Pawley refinement (red) and difference pattern (blue) of $(Et_4N)_3[Mn(NCS)_5]$ (**6**).

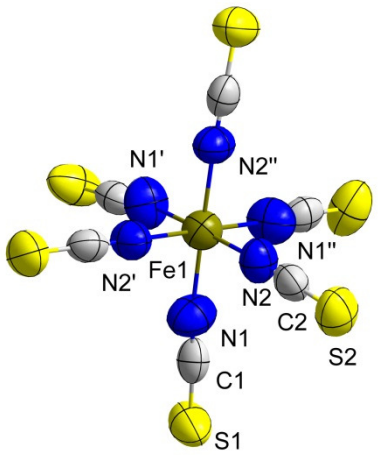

Figure S8. Crystal structure of $(n\text{-}Bu_4N)_3[Fe(NCS)_6]$ (**9**). The thermal ellipsoids are drawn at 50% probability. Colour code: Green (Fe), Blue (N), Yellow (S), Gray (C). Solvent molecules and hydrogen atoms have been removed for clarity.

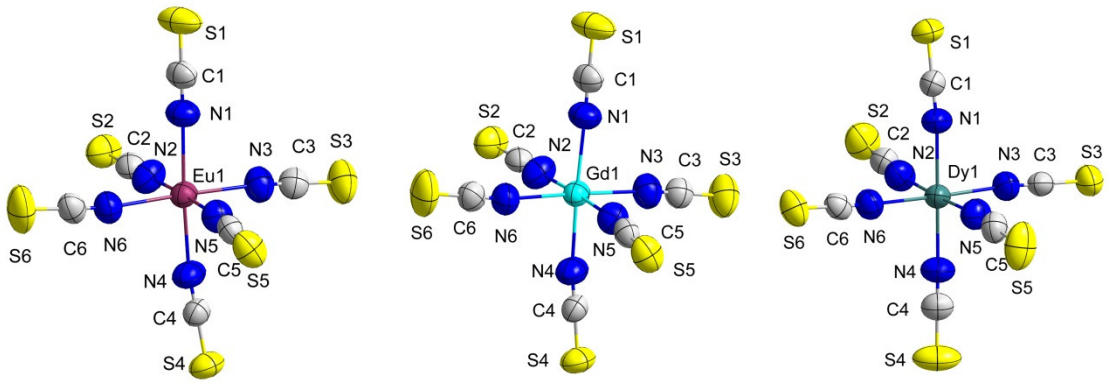

Figure S9. Crystal structure of $(n\text{-}Bu_4N)_3[Eu(NCS)_6]$ (**11**) (left), $(n\text{-}Bu_4N)_3[Gd(NCS)_6]$ (**12**) (middle) and $(n\text{-}Bu_4N)_3[Dy(NCS)_6]$ (**13**) (right). The thermal ellipsoids are drawn at 50% probability. Colour code: Purple (Eu), Light blue (Gd), Turquoise (Dy), Blue (N), Yellow (S), Gray (C).

Table S9. Pawley refinement parameters for $(Et_4N)_3[Cr(NCS)_6]$ (**3a**), $(Me_4N)_4[Mn(NCS)_6]$ (**5**) and $(Et_4N)_3[Mn(NCS)_5]$ (**6**).

Compound	**3b**	**5**	**6**
System	Cubic	Monoclinic	Triclinic
Space group	Ia-3	P21/n	P-1
a (Å)	26.92321	12.48869	9.86260
b (Å)	26.92321	12.22627	14.52658
c (Å)	26.92321	12.62604	15.70293
α (°)	90	90	80.34524
β (°)	90	90.29675	72.62981
γ (°)	90	90	81.41553
Rexp / Rexp ‘	0.754 / 5.964	0.702 / 5.574	0.501 / 1.024
Rwp / Rwp ‘	1.076 / 8.504	0.556 / 4.421	0.632 / 1.291
Rp / Rp ‘	0.727 / 10.738	0.343 / 4.648	0.335 / 0.918
GoF	1.426	0.793	1.261
DW_d	0.128	0.453	0.791

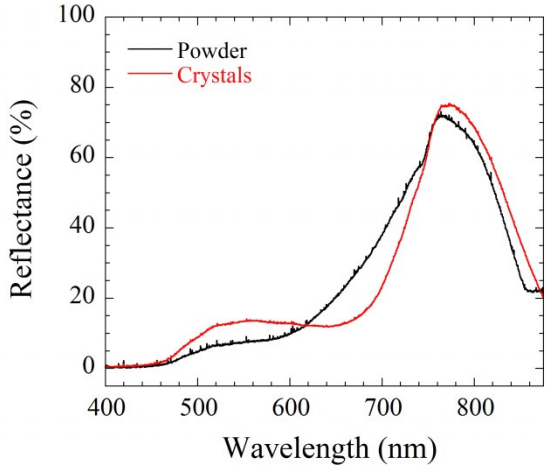

Figure S10. The solid-state visible reflectance spectra of $(Me_4N)_3[Fe(NCS)_6]$ (**7**) as powder (black) and crystals (red).

Table S10. List of restrained bond distances in **5**, **11** and **13**.

5	**11**	**13**
N5-C8	C45-C46	C25-C26
N5-C9	C21-C22	C41-C42
N5-C10	C45-C55	C13-C14
N5-C11	C21-C56	C10-C9
N4-C4		C22-C21
N4-C5		C32-C33

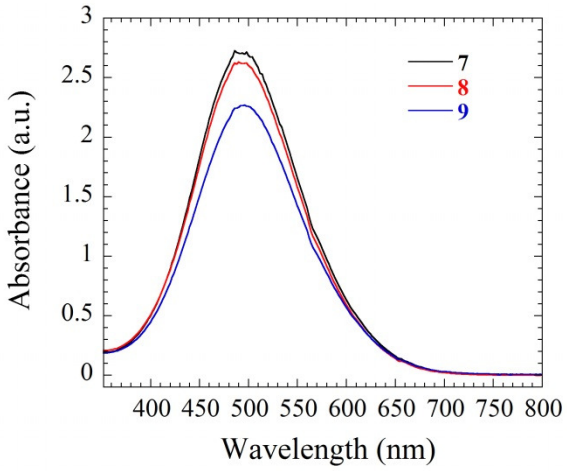

Figure S11. The solution UV-visible absorbance spectra of **7** (black), **8** (red) and **9** (blue), illustrating the identical single absorbance band at 496 nm for all three complexes.

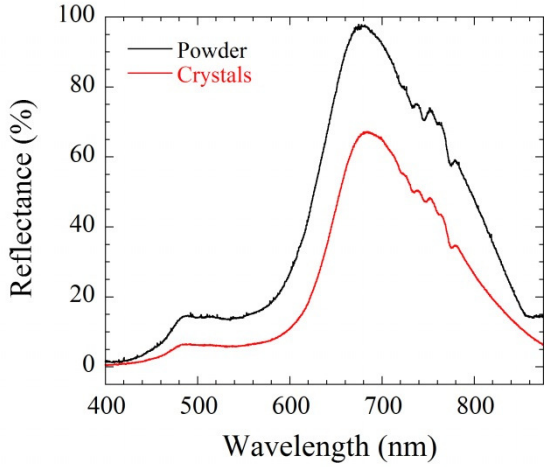

Figure S12. The solid-state visible reflectance spectra of $(n\text{-}Bu_4N)_3[Cr(NCS)_6]$ (**4**) as crystals (red) and powder (black).