Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Thermochromism of bromotellurates (IV): experimental insights

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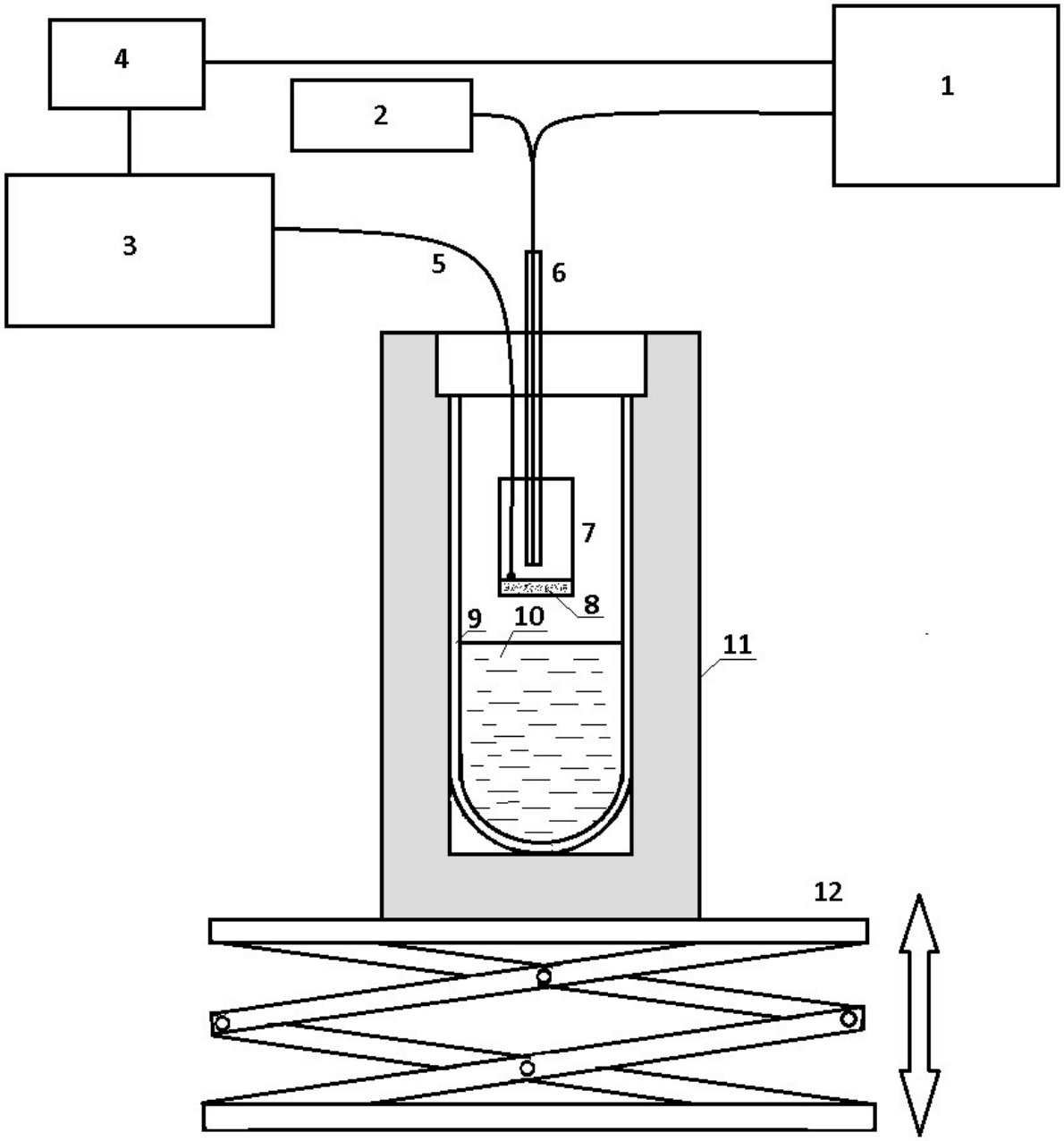

Figure 1S. Setup use for diffuse reflectance spectra measurements at different temperatures. (1) Kolibri-2 Spectrometer, (2) D/W lamp (AvaLight-DHS), (3) Thermometer, (4) PC, (5) Thermocouple, (6) Fiber optic cable (Ocean Optics, QR-400-7), (7) Sealed cell, (8) Sample, (9) Dewar vessel, (10) liquid nitrogen, (11) Protecting casing, (12) scissors jack

X-Ray Crystallography. Diffraction data for single-crystals of **2, 9, 10, 13** and **14** were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [*]. The structures were solved by dual space algorithm (SHELXT [**]) and refined by the full-matrix least squares technique (SHELXL [***]) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic cations were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table S1. CCDC 1878422-1878426 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif.

[*] CrysAlisPro 1.171.38.41. Rigaku Oxford Diffraction. 2015.

[**] Sheldrick G.M. // *Acta Cryst.*, 2015, A71, 3.

[***] Sheldrick G.M. // *Acta Cryst.*, 2015, C71, 3.

Table 1S. Crystal data and structure refinement for **2, 9, 10, 13** and **14**

Identification code	**2**	**9**	**10**	**13**	**14**
Empirical formula	$C_{14}H_{20.5}Br_6N_2O_{0.25}Te$	$C_{10}H_{14}Br_6I_2N_2O_2Te$	$C_{10}H_{10}Br_6Cl_2N_2Te$	$C_{12}H_{18}Br_8N_2O_2Te$	$C_{10}H_{12}Br_6Cl_4N_2O_2Te$
M, g/mol	827.88	1055.09	836.16	989.16	941.08
Crystal system	*Monoclinic*	*Triclinic*	*Triclinic*	*Monoclinic*	*Monoclinic*
Space group	*C*2/*c*	*P*−1	*P*−1	$P2_1/n$	$P2_1/n$
a, Å	15.3224(4)	7.6363(5)	7.3223(5)	9.7234(5)	8.6178(4)
b, Å	13.0117(4)	11.3319(7)	8.3339(6)	11.0724(5)	12.9085(6)
c, Å	23.4808(7)	14.0460(10)	9.0497(6)	12.1082(7)	10.8436(5)
α, deg.	90	95.738(5)	74.694(6)	90	90
β, deg.	94.188(3)	93.775(5)	70.263(5)	109.028(6)	98.779(4)
γ, deg.	90	103.128(5)	83.031(6)	90	90
V, Å^3	4668.9(2)	1172.83(14)	501.05(6)	1232.36(12)	1192.14(10)
Z	8	2	1	2	2
D(calc.), g/cm^3	2.356	2.988	2.771	2.666	2.622
μ, mm^{-1}	11.546	14.128	13.707	14.186	11.76
F(000)	3060	944	380	904	864
Crystal size, mm	0.31 × 0.28 × 0.25	0.30 × 0.25 × 0.10	0.39 × 0.23 × 0.10	0.47 × 0.12 × 0.10	0.21 × 0.15 × 0.12
θ range for data collection, deg.	3.40–28.94	3.28–28.87	3.62–29.05	3.56–28.87	3.28–28.85
Index ranges	$-20 \le h \le 15$, $-17 \le k \le 17$, $-31 \le l \le 26$	$-10 \le h \le 10$, $-15 \le k \le 15$, $-16 \le l \le 17$	$-6 \le h \le 10$, $-11 \le k \le 11$, $-9 \le l \le 12$	$-11 \le h \le 13$, $-8 \le k \le 14$, $-15 \le l \le 15$	$-7 \le h \le 11$, $-17 \le k \le 13$, $-14 \le l \le 12$
Reflections collected / independent	12214 / 5127	10349 / 5087	3754 / 2201	5857 / 2725	5336 / 2627

R_{int}	0.0169	0.0318	0.0266	0.0270	0.0255
Reflections with $I > 2\sigma(I)$	4778	4280	1905	2266	2283
Goodness-of-fit on F^2	1.233	0.998	1.040	0.972	1.027
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0274$, $wR_2 = 0.0625$	$R_1 = 0.0326$, $wR_2 = 0.0631$	$R_1 = 0.0352$, $wR_2 = 0.0741$	$R_1 = 0.0281$, $wR_2 = 0.0429$	$R_1 = 0.0274$, $wR_2 = 0.0508$
R indices (all data)	$R_1 = 0.0303$, $wR_2 = 0.0632$	$R_1 = 0.0428$, $wR_2 = 0.0667$	$R_1 = 0.0427$, $wR_2 = 0.0783$	$R_1 = 0.0399$, $wR_2 = 0.0460$	$R_1 = 0.0352$, $wR_2 = 0.0527$
Largest diff. peak / hole, e/Å^3	0.804 / −0.628	1.114 / −1.492	0.952 / −1.538	0.692 / −0.813	0.502 / −0.589

Preparation of 2

116 mg (0.5 mmol) of 1,2-dimethylpyridinium iodide were dissolved in 5 ml of water; 100 mg of $AgNO_3$ were added and the mixture was stirred for 15 min. Precipitate of AgI was filtered off; several drops of HBr were added and solution was filtered again. After that, 5 ml of 2M HBr were added (solution 1). Separately, 40 mg (0.25 mmol) of TeO_2 were dissolved in 5 ml of 2M HBr at 70°C; then solution 1 was added. The mixture was slowly cooled to r.t; after partial evaporation of solvent, there forms orange crystalline precipitate of **2**. Yield 81%. The sample was dried in air for 1 h. For $C_{14}H_{20}N_2TeBr_6$ calcd, %: C 20.4; H 2.5; N 3.4; found, %: C 20.1; H 2.8; N 3.3.

Preparation of 9, 10, 13 or 14

40 mg (0.25 mmol) of TeO_2 were dissolved in 3 ml of 2M HBr at 70°C; then, solution of 3-IPy (**9,** 54 mg), 2-ClPy (**10**, 47 mcl), 2-Br-5-MePy (**13**, 52 mg) or 3,5-ClPy (**14**, 74 mg) in 5 ml of 2M HBr was added. The mixtures were kept at 70°C for 20 min and then cooled to r.t.; after partial evaporation of solvent, there forms orange crystalline precipitates. The samples was dried in air for 1 h. Yield: 70% (**9**), 73% (**10**), 72% (**13**) and 69% (**14**). In all cases, EA data are consistent with calculated values.

Complex	C, H, N, calcd/found, %
9	11.8, 1.0, 2.7 / 11.6. 1.1, 2.8
10	14.4, 1.2, 3.4 / 14.3, 1.3, 3.3
13	15.1, 1.5, 2.9 / 15.0, 1.4, 2.8
14	13.3, 0.9, 3.1 / 12.8, 1.0, 2.9

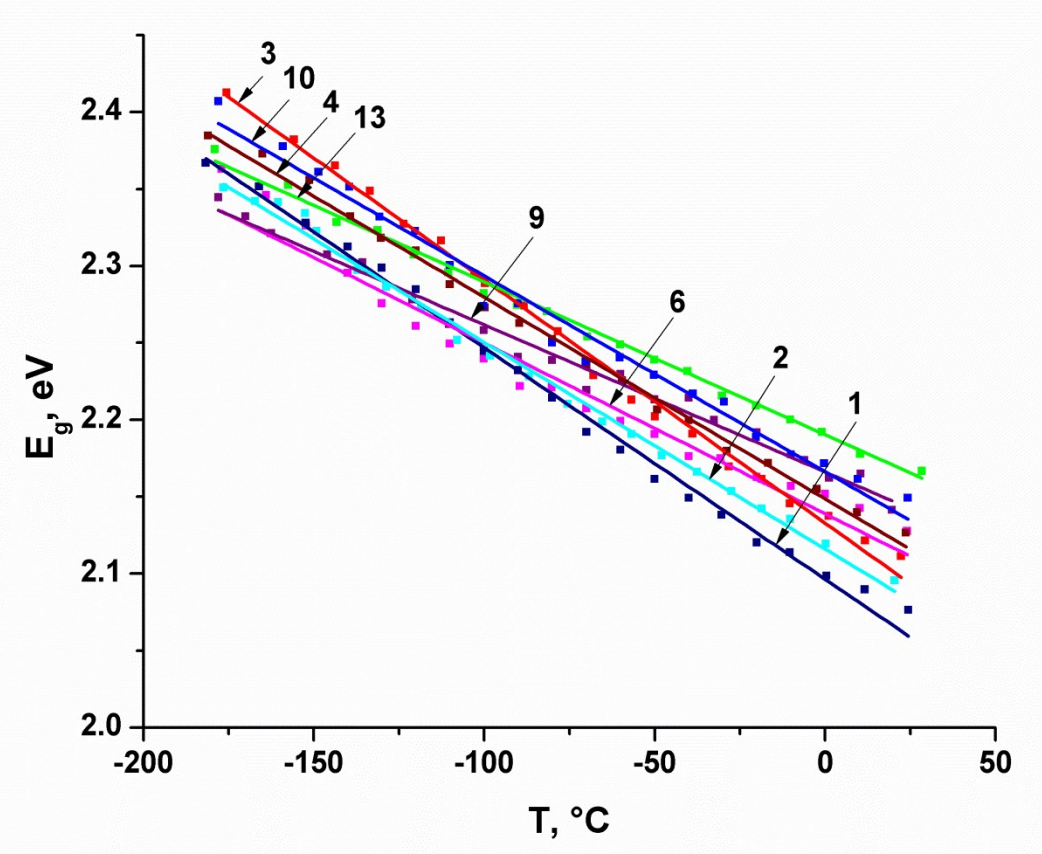

Figure 2S. Temperature dependencies of E_g; numbers correspond to the Table 1 in main text

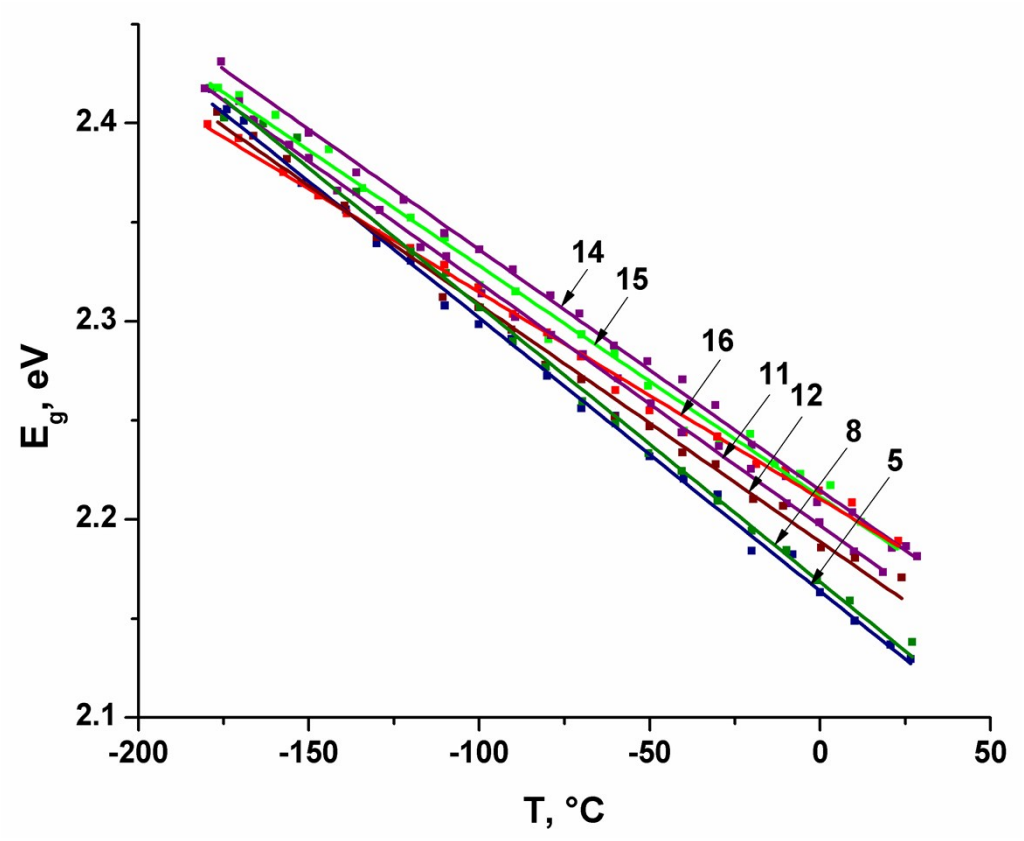

Figure 3S. Temperature dependencies of E_g; numbers correspond to the Table 1 in main text

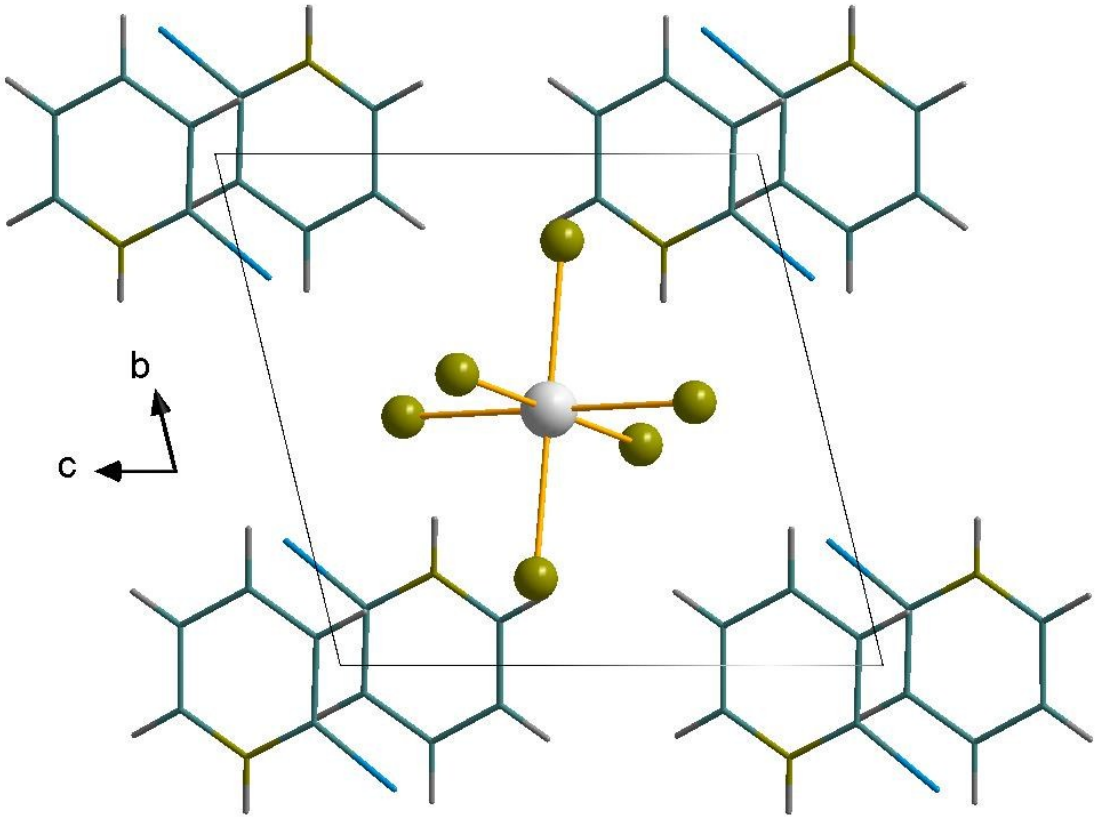

Figure 4S. Crystal packing in the structure of **10**

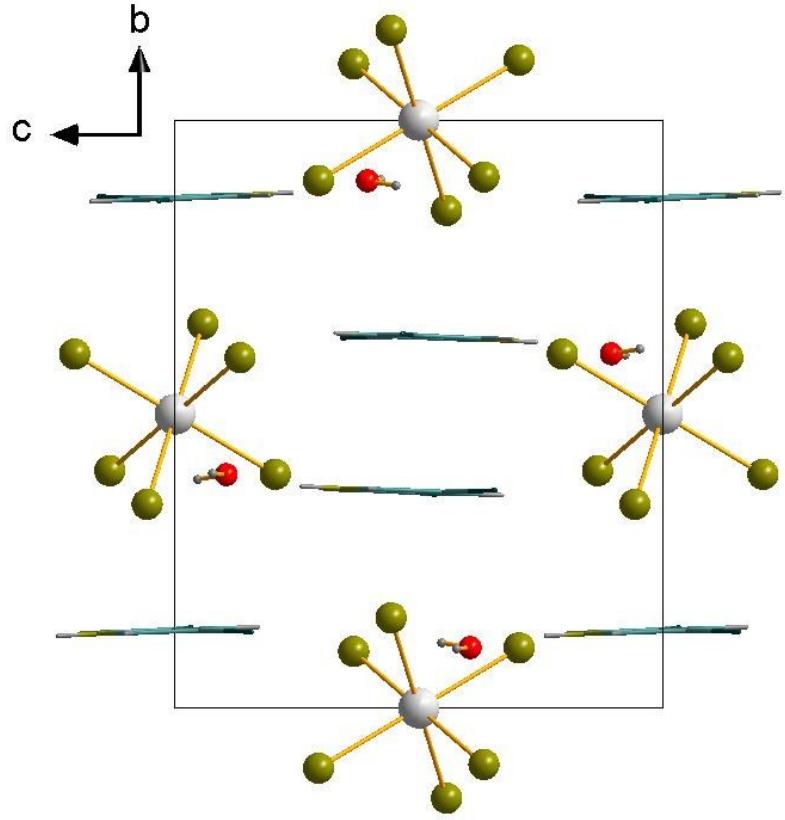

Figure 5S. Crystal packing in the structure of **14**

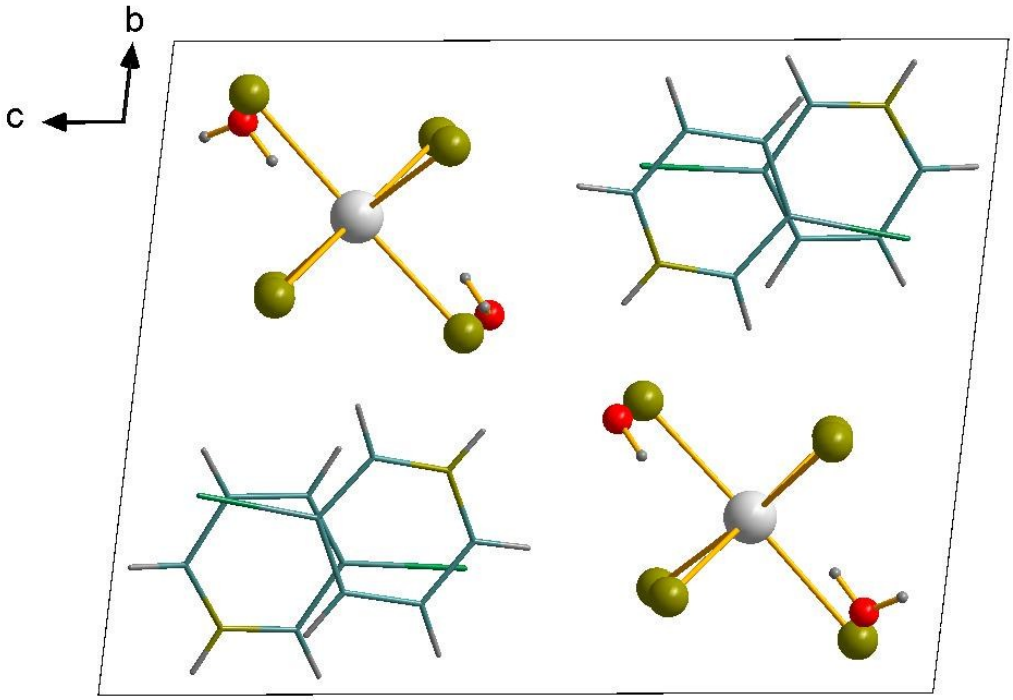

Figure 6S. Crystal packing in the structure of **9**

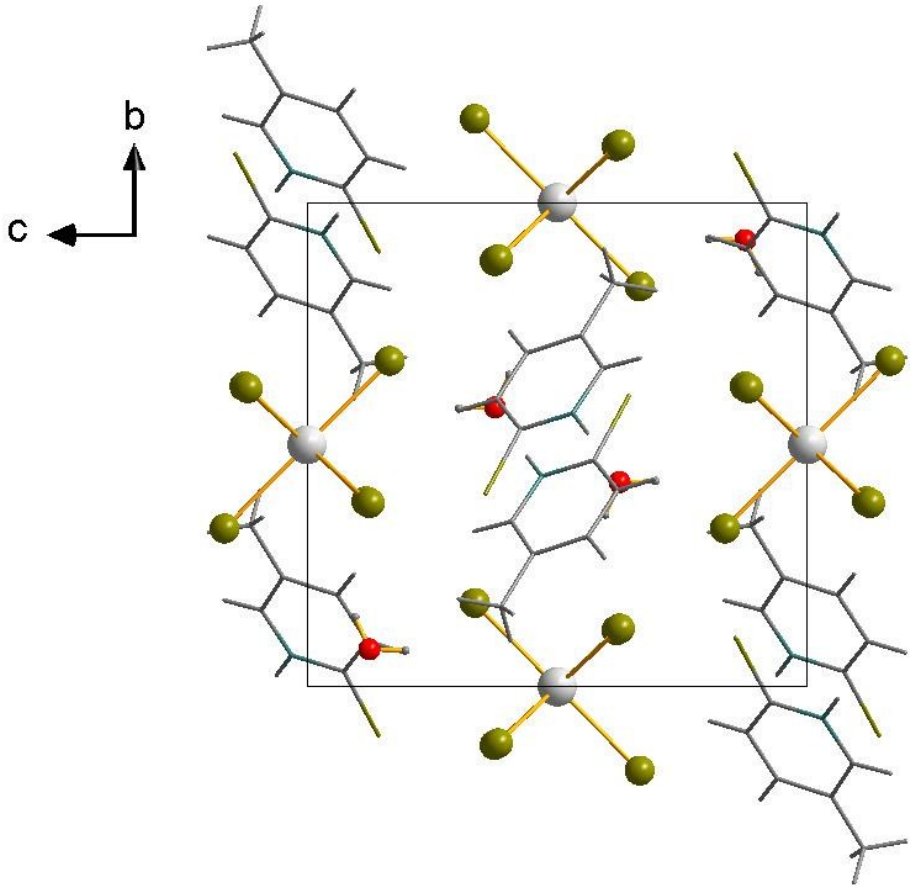

Figure 7S. Crystal packing in the structure of **13**