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Electronic supplementary information for the manuscript:

“Tellurium complex polyhalides: narrow bandgap photoactive materials for electronic applications”

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Experimental

Synthetic procedures

$(TMA)_2TeBr_6I_2$ (1)

40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 15 ml of 2M HBr; 77 mg (0,5 mmol) of tetramethylammonium bromide dissolved in 5 ml of 2M HBr were added into the reaction mixture. After that it was kept at 70°C for 2 hours. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 68 %.

Elemental analysis for $C_8H_{24}N_2I_2TeBr_6$ calculated, %: C 9.5; H 2.4; N 2.8; found, %: C 9.6; H 2.4; N 2.6.

FTIR (KBr, cm^{-1}): 946, 1284, 1413, 1443, 1477, 1727, 2930, 3019.

$Py_2TeBr_6I_2$ (2)

40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 8 ml of 2M HBr; 40 μl (0.5 mmol) of pyridine dissolved in 2 ml of 2M HBr were added into the reaction mixture. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 65%.

Elemental analysis for $C_{10}H_{12}N_2I_2TeBr_6$ calculated, %: C 11.8; H 1.2; N 2.7; found, %: C 11.5; H 1.1; N 2.8.

FTIR (KBr, cm^{-1}): 470, 518, 647, 697, 734, 765, 1194, 1240, 1309, 1502, 1599, 1634, 3083, 3152, 3219, 3447.

4-$MePy_2TeBr_6I_2$ (3)

40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 8 ml of 2M HBr; 49 μl (0.5 mmol) of 4-methylpyridine dissolved in 2 ml of 2M HBr were added into the reaction mixture. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 62 %.

Elemental analysis for $C_{12}H_{16}N_2I_2TeBr_6$ calculated, %: C 13.7; H 1.5; N 2.7; found, %: C 13.4; H 1.6; N 2.6.

FTIR (KBr, cm^{-1}): 470, 518, 647, 697, 733, 765, 1196, 1240, 1310, 1366, 1503, 1599, 1635, 3082, 3151, 3220, 3434.

1-$MePy_2TeBr_6I_2$ (4)

110 mg (0.5 mmol) of 1-methylpyridinium iodide was dissolved in 4 ml of deionized water followed by the addition of 100 mg (0.6 mmol) of silver nitrate. The precipitated AgI was filtered. 2 ml of 2M HBr were added to this solution and AgBr

was filtered. 40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 8 ml of 2M HBr; previously prepared 1-methylpyridinium bromide solution was added into the reaction mixture while stirring. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 61%.

Elemental analysis for $C_{12}H_{16}N_2I_2TeBr_6$ calculated, %: C 13.7; H 1.5; N 2.7; found, %: C 13.9; H 1.7; N 2.5.

FTIR (KBr, cm^{-1}): 441, 760, 757, 1187, 1234, 1485, 1581, 1630, 3058, 3436.

3-MePyH$_2$TeBr$_6$I$_2$ (5)

40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 8 ml of 2M HBr; 49 μl (0.5 mmol) of 3-methylpyridine dissolved in 2 ml of 2M HBr were added into the reaction mixture. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 68 %.

Elemental analysis for $C_{12}H_{16}N_2I_2TeBr_6$ calculated, %: C 13.7; H 1.5; N 2.7; found, %: C 13.6; H 1.7; N 2.7.

FTIR (KBr, cm^{-1}): 455, 670, 757, 847, 1044, 1115, 1178, 1255, 1337, 1382, 1469, 1548, 1605, 1627, 3075, 3123, 3179, 3217, 3401.

1-MeDMAP$_2$TeBr$_6$I$_2$ (6)

132 mg (0.5 mmol) of 4-dimethylamine-1-methylpyridinium iodide was dissolved in 5 ml of deionized water; 100 мг (0.6 mmol) of silver nitrate were added to this solution. The precipitated AgI was filtered. 3 ml of 2M HBr were added to this solution and AgBr was filtered. 40 mg (0.25 mmol) of TeO_2 and 64 mg (0.25 mmol) I_2 were dissolved by heating at 70°C in 8 ml of 2M HBr; previously prepared 1-methylpyridinium bromide solution was added into the reaction mixture while stirring. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 72%.

Elemental analysis for $C_{16}H_{26}N_4I_2TeBr_6$ calculated, %: C 16.9; H 2.3; N 4.9; found, %: C 16.5; H 2.2; N 4.7.

FTIR (KBr, cm^{-1}): 466, 508, 707, 817, 944, 1034, 1068, 1179, 1208, 1392, 1429, 1540, 1570, 1653, 2930, 3058.

2-MePyH$_2$TeBr$_6$I$_2$ (7)

40 mg (0.25 mmol) of TeO$_2$ and 64 mg (0.25 mmol) I$_2$ were dissolved by heating at 70°C in 8 ml of 2M HBr; 49 µl (0.5 mmol) of 2-methylpyridine dissolved in 2 ml of 2M HBr were added into the reaction mixture. After that it was kept at 70°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 66%.

Elemental analysis for $C_{12}H_{16}N_2I_2TeBr_6$ calculated, %: C 13.7; H 1.5; N 2.7; found, %: C 13.6; H 1.5; N 2.6.

FTIR (KBr, cm^{-1}): 466, 540, 628, 747, 771, 1047, 1103, 1165, 1237, 1286, 1388, 1470, 1536, 1615, 1629, 2976, 3084, 3184, 3260, 3422.

1,2-DMePy$_2$TeBr$_6$I$_2$ (8)

40 mg (0.25 mmol) of TeO$_2$ and 64 mg (0.25 mmol) I$_2$ were dissolved by heating at 80°C in 8 ml of 2M HBr; 116 mg (0.5 mmol) of 1,2-dimethylpyridinium iodide dissolved in 3 ml of 2M HBr were added into the reaction mixture. After that it was kept at 80°C for 1 hour. Then, the solution was slowly cooled down to room temperature and the product precipitated as black crystals with the yield 79%.

Elemental analysis for $C_{14}H_{20}N_2I_2TeBr_6$ calculated, %: C 15.6; H 1.9; N 2.6; found, %: C 15.8; H 2.1; N 2.8.

Photodetector fabrication

Glass substrates were treated with plasma for 5 minutes and transferred in the evaporation chamber integrated in the glovebox. Gold electrodes were thermally evaporated onto the substrates at the base pressure ~ 1×10^{-5} mbar. The deposition rate was kept at ~ 0.5-1 Å/s. The channel length and width were 75 µm and 2 mm, respectively. After that the saturated solution of tellurium polyhalide in acetonitrile containing 3 mg/ml of I$_2$ was repeatedly dropcasted on the channel area to produce tellurium halide film.

Characterization techniques

X-Ray Crystallography. Diffraction data for single-crystals **1**–**7** 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 ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table S1. CCDC 2009067-2009073 contain the supplementary crystallographic data for **1-7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif.

X-ray data for single crystals of **8-9** were collected on a XCalibur diffractometer with an Atlas S2 CCD detector at 100.0(1) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined against all F 2 data (SHELXL). [G. M. Sheldrick, *Acta Cryst.*, 2015, **71**, 3–8] All nonhydrogen atoms were refined with anisotropic thermal parameters, positions of hydrogen atoms were obtained from difference Fourier syntheses and refined with riding model constraints. CCDC 2010177-2010178 contain the supplementary crystallographic data for **8-9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at http://www.ccdc.cam.ac.uk/data_request/cif.

The IR spectrum was recorded on a Scimitar FTS 2000 spectrometer in the 4000–400 cm–1 range (pellets with KBr).

Raman spectra were collected using a LabRAM HR Evolution (Horiba) spectrometer with the excitation by the 633 nm line of the He-Ne laser. The spectra at room temperatures were obtained in the backscattering geometry with a Raman microscope. The laser beam was focused to a diameter of 2 micrometers using a LMPlan FL 50x/0.50 Olympus objective. The spectral resolution was 0.7 cm-1. The laser power on the sample surface was about 0.03 mW.

Thermal gravimetry measurements were performed using DSC-TG 3+ instrument (“Mettler Toledo”).

UV-Vis absorption spectra were recorded using ISP-REF integrating sphere (“Ocean Optics”) connected to AvaSpec-2048-2 UV-VIS fiber spectrometer. First, the integrating sphere was placed on a clean white paper and the background was recorded. After that, a powder of tellurium polyhalide was placed under the integrating sphere on the same surface and the absorption spectrum was recorded. Optical bandgap values were calculated using Tauc plot method with the assumption that the corresponding transition is direct and allowed.

Voltamperic and chronoamperic characteristics of the fabricated photodetectors were measured inside the nitrogen-filled glovebox using Kethley 2612A instrument with LabTracer software. For I-V measurements, a voltage range from 0V to 200V was selected. The I-V curves were registered twice. First time in the dark (completely covered from external light sources) and second time under the laser illumination (again, covered from external light to exclude possible noise) with the wavelength of 405 nm and the power density 0.028 W/cm^2. Transient photocurrent response curves were registered under the pulsed illumination (1 second under illumination followed by 1 second in the dark).

The photosensitivity (P), responsivity (R) and specific detectivity (D) parameters were calculated as follows:

$$P = \frac{I_{photo}}{I_{dark}},$$

$$R = \frac{I_{photo}}{P_{inc}A},$$

$$D = \frac{R\sqrt{A}}{\sqrt{2qI_{dark}}}$$

where I_{photo} and I_{dark} are current values at 200 V under illumination and in the dark, respectively, P_{inc} is incident light power density, A is the active area of the photodetector and q is the electron charge.

Table S1. Crystal data and structure refinement for **1–9**.

Identification code	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_8H_{24}Br_6I_2N_2Te$	$C_{10}H_{12}Br_6I_2N_2Te$	$C_{12}H_{16}Br_6I_2N_2Sb$	$C_{12}H_{16}Br_6I_2N_2Te$	$C_{12}H_{16}Br_6I_2N_2Te$	$C_{16}H_{26}Br_6I_2N_4Te$	$C_{12}H_{16}Br_6I_2N_2Te$	$C_7H_{10}Br_5NTe$	$C_{14}H_{20}Br_6I_2N_2Te$
M, g/mol	1009.15	1021.08	1043.28	1049.13	1049.13	1135.27	1049.13	635.31	1077.18
Temperature, K	130(2)	130(2)	130(2)	130(2)	130(2)	130(2)	130(2)	100.00(10)	100.01(10)
Crystal system	*Orthorhombic*	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Orthorhombic*	*Tetragonal*	*Monoclinic*	*Orthorhombic*	*Trigonal*
Space group	$Pca2_1$	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_12_12$	$I{-}42d$	$P2/c$	$Pnma$	$R{-}3$
a, Å	19.5489(5)	17.3679(10)	13.5904(4)	14.0719(5)	11.1296(8)	13.7588(3)	18.2998(7)	7.8698(2)	10.9687(11)
b, Å	26.1911(6)	9.7898(5)	10.0509(2)	9.7260(3)	14.5113(9)	13.7588(3)	7.6117(3)	17.3825(5)	10.9687(11)
c, Å	19.2558(4)	13.7574(8)	18.7079(6)	18.4750(6)	7.6003(5)	31.9474(10)	17.9871(7)	22.0160(6)	19.6121(19)
α, deg.	90	90	90	90	90	90	90	90	90
β, deg.	90	107.611(6)	108.138(4)	108.386(4)	90	90	100.270(4)	90	90
γ, deg.	90	90	90	90	90	90	90	90	120
V, Å^3	9859.1(4)	2229.5(2)	2428.44(13)	2399.47(15)	1227.49(14)	6047.8(3)	2465.33(17)	3011.72(14)	2043.5(5)
Z	16	4	4	4	2	8	4	8	3
D(calc.), g/cm^3	2.719	3.042	2.854	2.904	2.839	2.494	2.827	2.802	2.626
μ, mm^{-1}	13.432	14.852	13.551	13.804	13.492	10.966	13.435	15.212	12.161
F(000)	7264	1816	1876	1880	940	4144	1880	2288	1458
Crystal size, mm	0.34 × 0.30 × 0.16	0.58 × 0.28 × 0.24	0.32 × 0.25 × 0.14	0.32 × 0.32 × 0.08	0.70 × 0.29 × 0.19	0.39 × 0.31 × 0.14	0.40 × 0.26 × 0.24	0.69 × 0.13 × 0.12	0.55 × 0.09 × 0.07
θ range for data	3.35–25.35	4.11–29.04	3.62–29.12	3.58–29.02	3.35–28.96	3.37–28.89	3.39–28.98	2.98–33.87	2.98–35.57

collection, deg.									
Index ranges	$-23 \leq h \leq 17$, $-31 \leq k \leq 25$, $-23 \leq l \leq 19$	$-21 \leq h \leq 18$, $-9 \leq k \leq 12$, $-13 \leq l \leq 18$	$-18 \leq h \leq 17$, $-9 \leq k \leq 13$, $-25 \leq l \leq 16$	$-18 \leq h \leq 18$, $-12 \leq k \leq 12$, $-14 \leq l \leq 24$	$-13 \leq h \leq 10$, $-19 \leq k \leq 13$, $-6 \leq l \leq 10$	$-8 \leq h \leq 18$, $-13 \leq k \leq 17$, $-42 \leq l \leq 40$	$-16 \leq h \leq 22$, $-9 \leq k \leq 10$, $-23 \leq l \leq 23$	$-11 \leq h \leq 12$, $-27 \leq k \leq 26$, $-33 \leq l \leq 31$	$-16 \leq h \leq 8$, $-14 \leq k \leq 17$, $-31 \leq l \leq 26$
Reflections collected / independent	32037 / 15585	5205 / 2459	11488 / 5440	12231 / 5315	4253 / 2595	8004 / 3161	12446 / 5514	41313 / 5984	2915 / 1800
R_{int}	0.0339	0.0240	0.0237	0.0325	0.0343	0.0369	0.0292	0.0722	0.0358
Reflections with $I > 2\sigma(I)$	10940	2187	4596	4427	2291	2644	4478	3759	563
Goodness-of-fit on F^2	1.038	1.074	1.050	1.015	1.040	1.128	1.043	1.004	1.032
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0453$, $wR_2 = 0.0820$	$R_1 = 0.0270$, $wR_2 = 0.0570$	$R_1 = 0.0301$, $wR_2 = 0.0579$	$R_1 = 0.0338$, $wR_2 = 0.0656$	$R_1 = 0.0494$, $wR_2 = 0.1134$	$R_1 = 0.0474$, $wR_2 = 0.0932$	$R_1 = 0.0339$, $wR_2 = 0.0690$	$R_1 = 0.0835$, $wR_2 = 0.2093$	$R_1 = 0.0943$, $wR_2 = 0.1899$
R indices (all data)	$R_1 = 0.0765$, $wR_2 = 0.0908$	$R_1 = 0.0322$, $wR_2 = 0.0587$	$R_1 = 0.0401$, $wR_2 = 0.0609$	$R_1 = 0.0463$, $wR_2 = 0.0702$	$R_1 = 0.0580$, $wR_2 = 0.1198$	$R_1 = 0.0618$, $wR_2 = 0.0986$	$R_1 = 0.0486$, $wR_2 = 0.0734$	$R_1 = 0.1318$, $wR_2 = 0.2385$	$R_1 = 0.2712$, $wR_2 = 0.2911$
Largest diff. peak / hole, e/Å^3	1.787 / −0.947	0.981 / −1.529	1.518 / −1.216	1.131 / −1.725	1.894 / −1.822	1.255 / −1.236	1.319 / −1.263	4.916 / −2.600	0.808 / −0.514

Table S2 Crystal structure parameters of compounds **1-9**.

Compound	Te-Br, Å	Te-Br_I, Å	I-I (I_2), Å	$Br_I \cdots I_{I2}$, Å	Br_I-I-I,°
1	2.621-2.697	2.737-2.762	2.693-2.698	3.095-3.195	164.6-174.5
2	2.625-2.690	2.780	2.715	3.201	172.9
3	2.562-2.690	2.758-2.958	2.715	3.247-3.325	172.0-174.7
4	2.608-2.694	2.813-2.828	2.724	3.181-3.300	171.7-176.1
5	2.653-2.741	2.719	2.71	3.32-3.33	171
6	2.698	2.703	2.73-2.74	3.14-3.31	172.1-175.1
7	2.644-2.705	2.775-2.811	2.710-2.711	3.252-3.270	168.9
8	2.771	2.771	2.73	3.04	174.2
9	2.58 and 2.719-2.723*	2.916-2.918**	-	-	-

* There are two different types of non-equivalent Br atoms

** Bond length between Te and shared Br

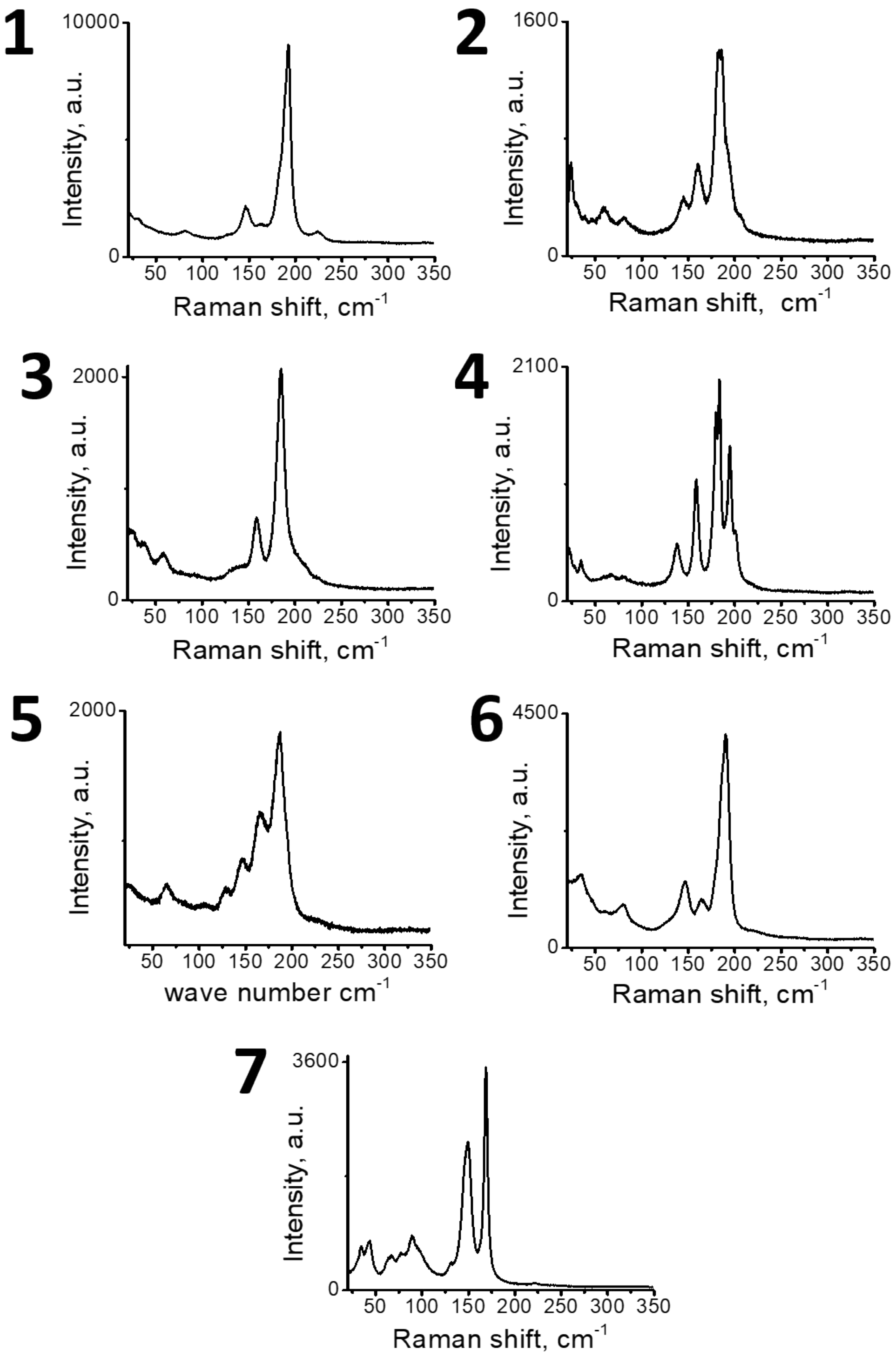

Fig. S1 Raman spectra of tellurium complex polyhalides.

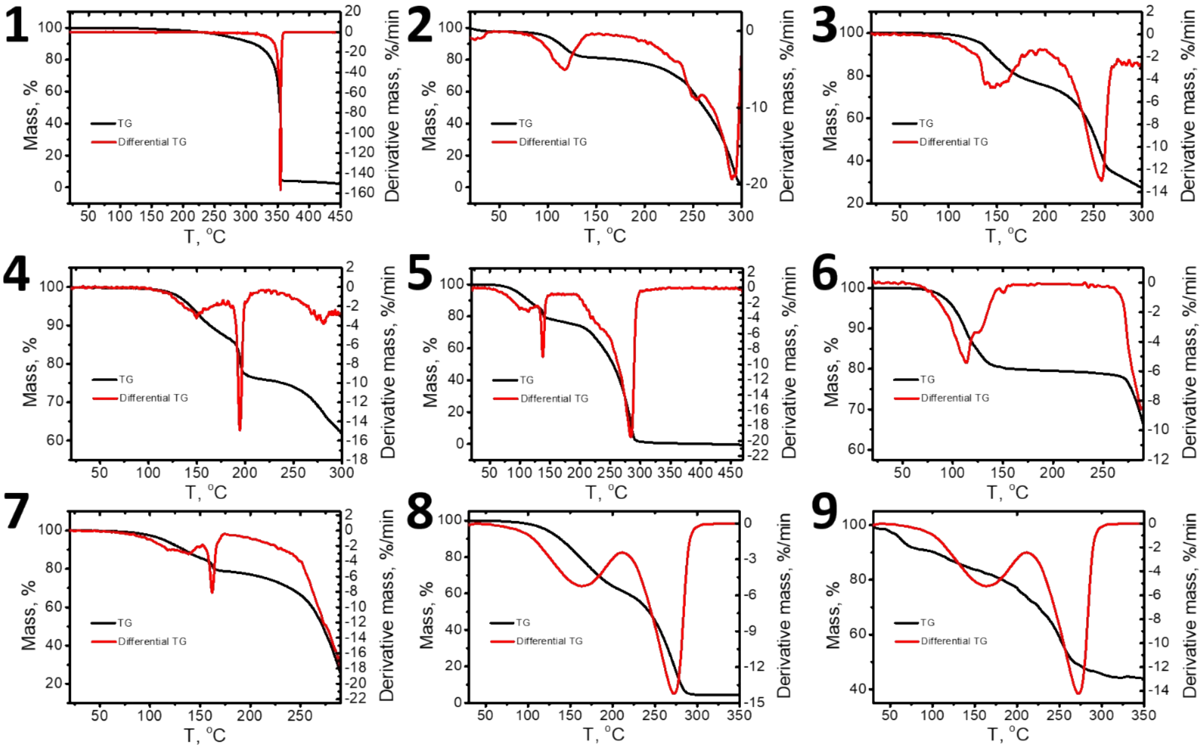

Fig. S2 Thermal gravimetry curves of tellurium complex polyhalides.

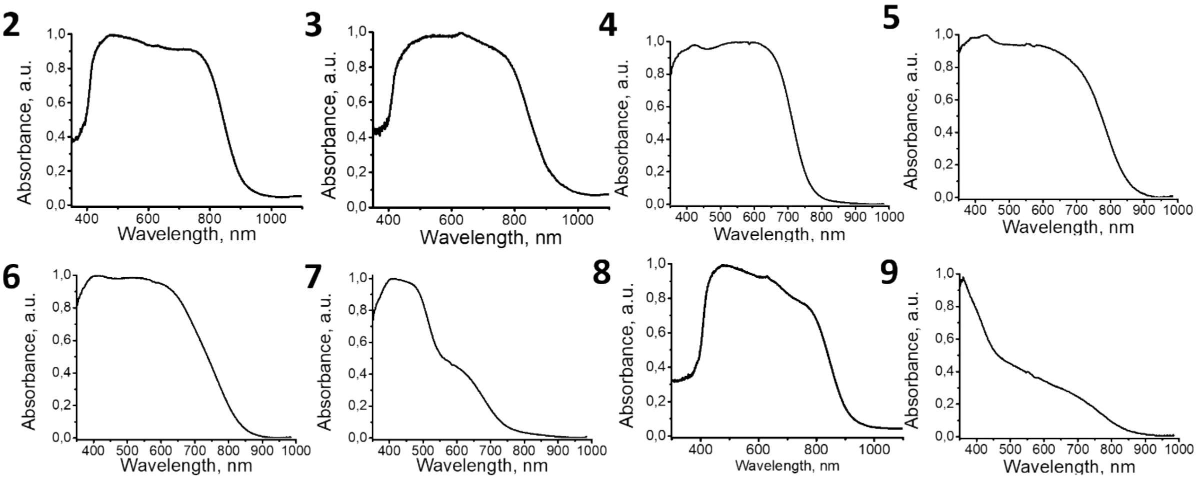

Fig. S3 UV-Vis absorption spectra of tellurium polyhalides.

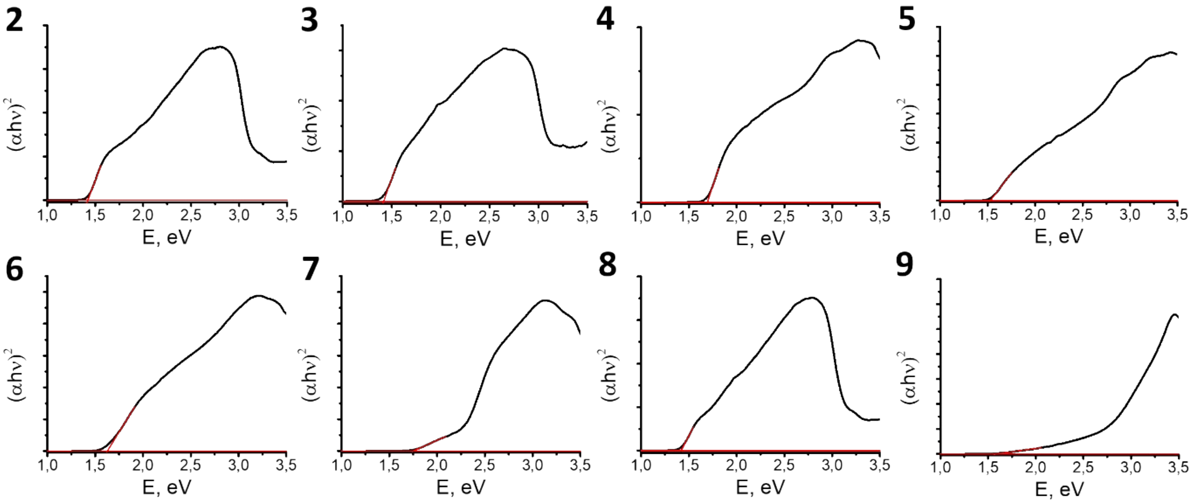

Fig. S4 Tauc plots used to determine optical bandgap values of tellurium polyhalides.

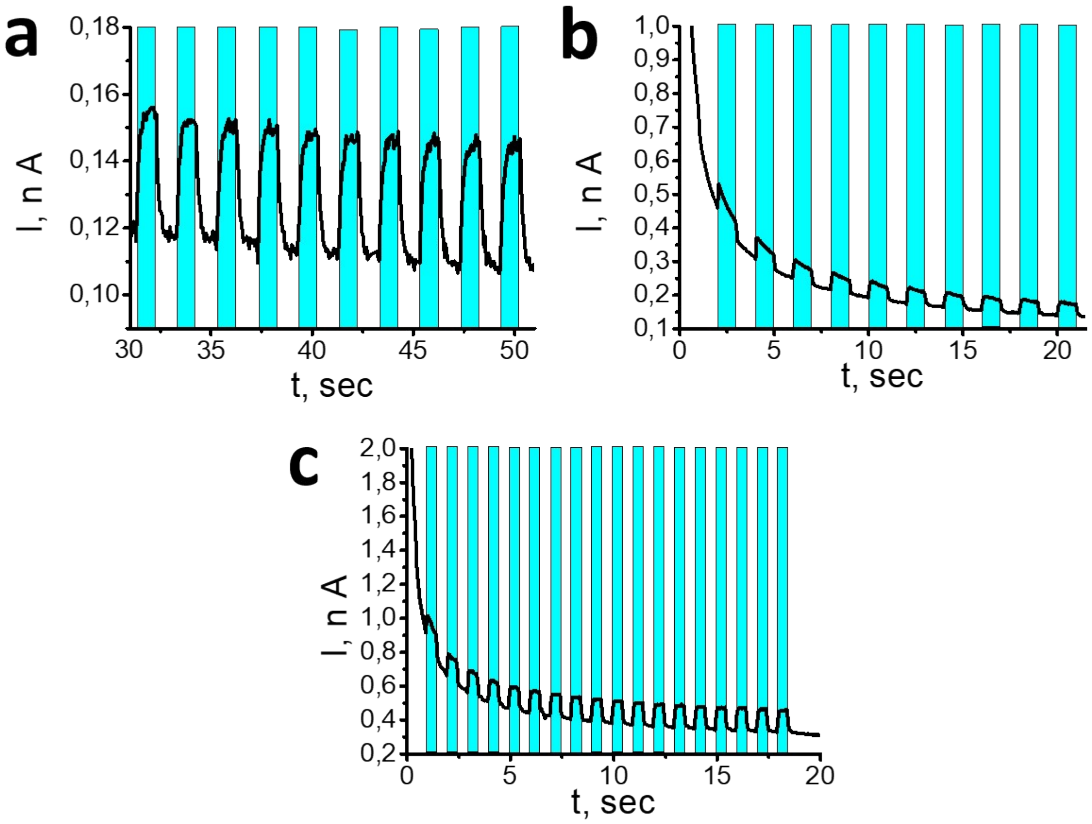

Fig. S5 Photo response of lateral devices based on compound **2** (a), **3** (b) and **9** (c). Blue rectangles illustrate light pulses.