Exploring the Photoactive Properties of Promising MXenes for Water Splitting

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Fig. S1. Phonons spectra along the **Γ→K→M→Γ k**-points paths for the distorted phases of the S- and Se-terminated MXenes.

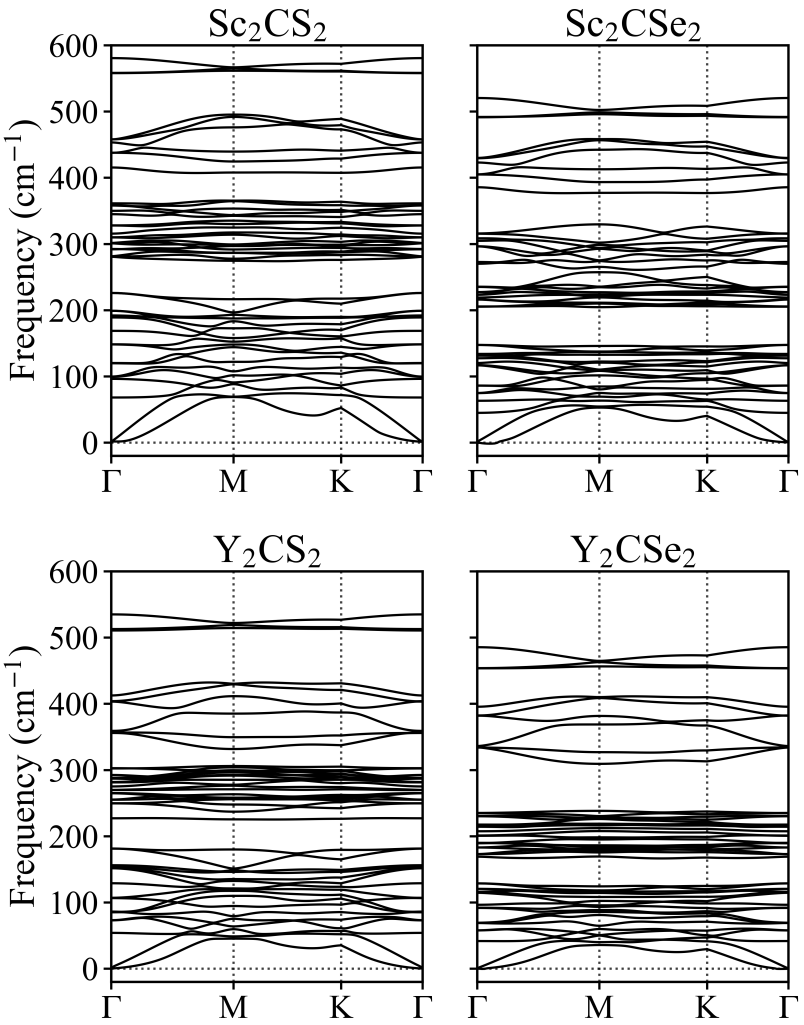

Fig. S2 Phonons spectra along the **Γ→K→M→Γ k**-points path for the Zr_2CO_2 MXene in the excited triplet state.

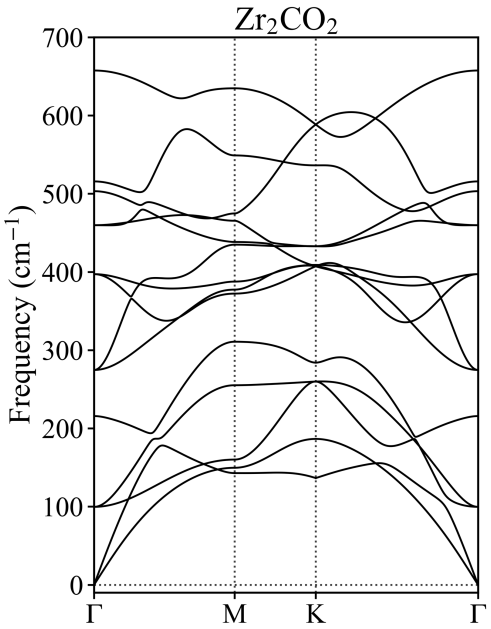

Fig. S3. PBE0 Bandstructure and density of states (DOS) for the distorted MXenes structures, both projected onto the different atomic contributions. In grey, blue, and red are marked the TM, X, and T contributions, respectively, while in the case of the DOS, black denotes the total sum. The green arrow marks the bandgap, with its correspondent value, given in eV. The energies, E, also given in eV, are referenced to the Fermi level, E_F, here placed at the valence band maximum (VBM).

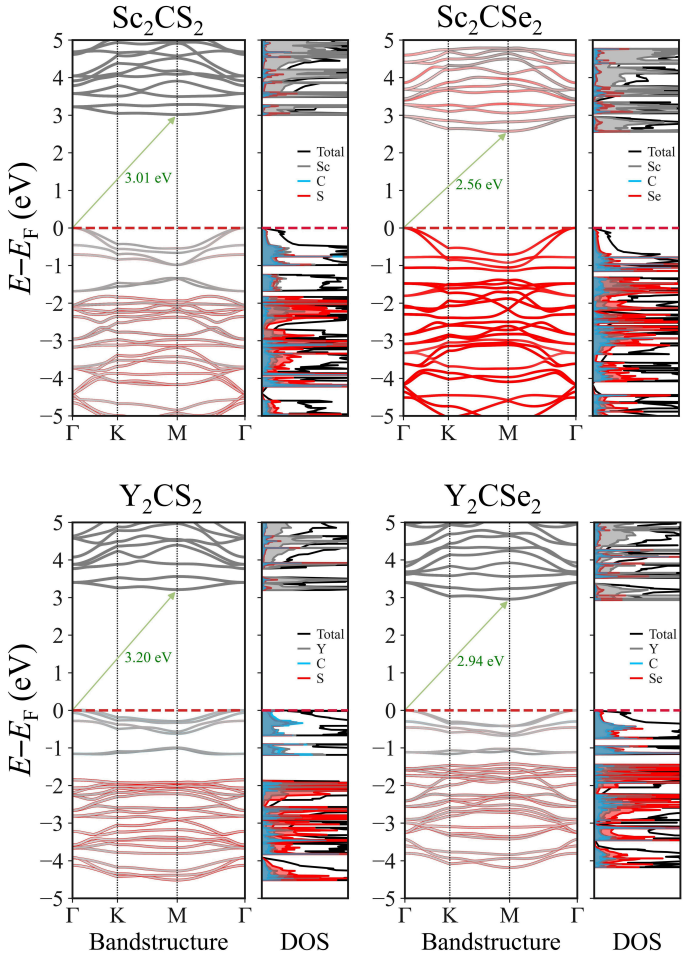

Fig. S4. VBM and conduction band minimum (CBM) alignments of the distorted chalcogen-terminated MXenes with respect to the water splitting redox potentials at $pH = 0$ (dashed black lines) and $pH = 7$ (grey dashed lines). The blue and orange bars represent the VB and CB, respectively. Since these are Janus materials, each surface has his own band alignment, the darker blue/orange, compels the average of both while the bars above and below it denote the CBM (light blue) or VBM (light orange), of the H_X and H_M surface, respectively.

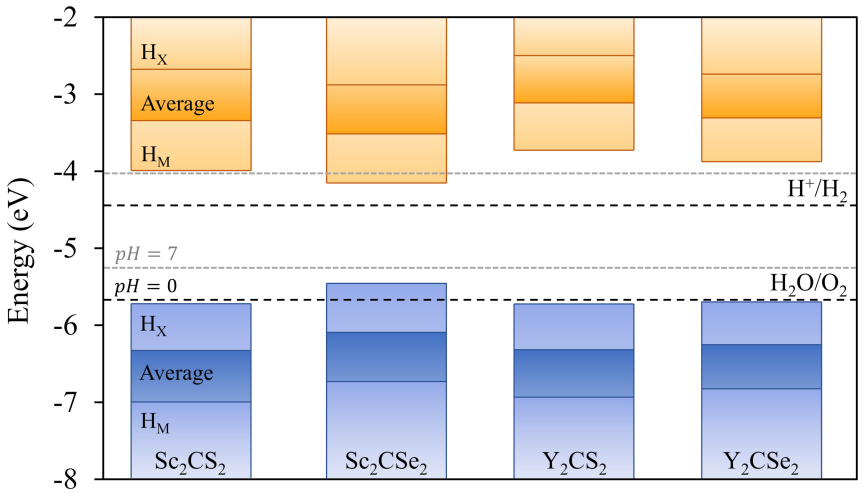

Fig. S5. Side views of partial charge densities for the VBM (blue) and CBM (orange) for the ten studied regular MXenes.

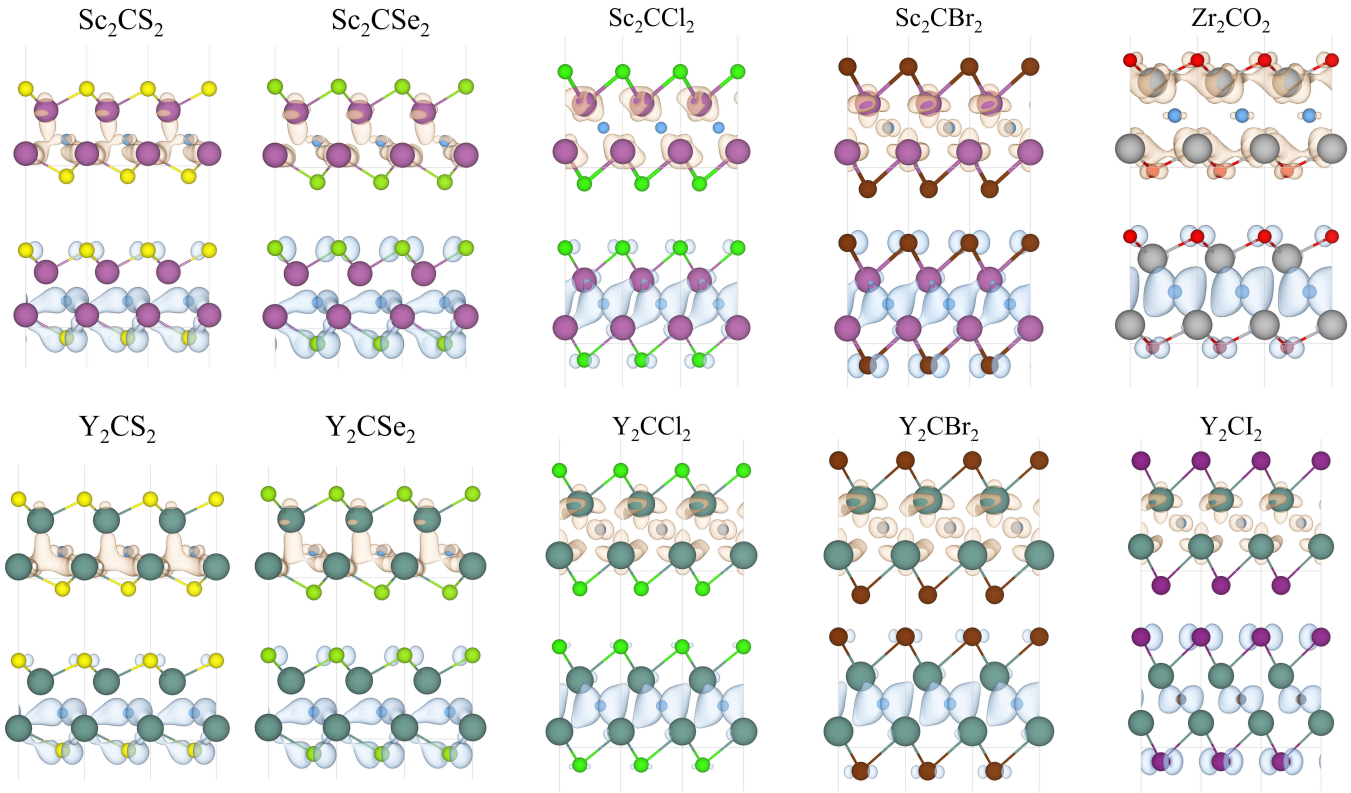

Fig. S6. (a) Partial charge densities for the VBM (blue) and CBM (orange) for the 4 distorted MXenes structures. (b) Spatial overlap, $\hat{S}_{ab}$, percentage between the VBM and CBM charge densities for the distorted MXenes.

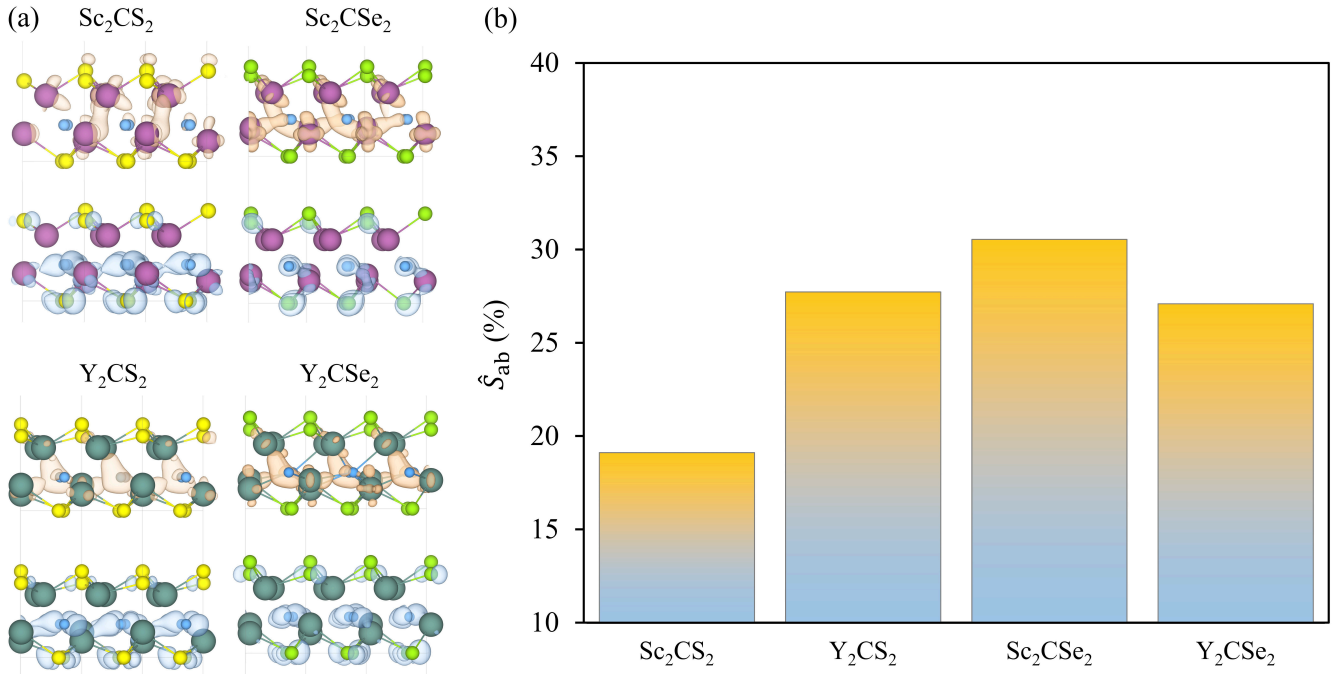

Fig. S7. (a) Total energy, and (b) band edge positions, both in eV, as a function of uniaxial strain along *x* and *y* directions, for the exemplary case of Y_2CCl_2 MXene, with distinction for bands associated to photogenerated electron, *e*, or heavy, h^H, or light, h^L, holes.

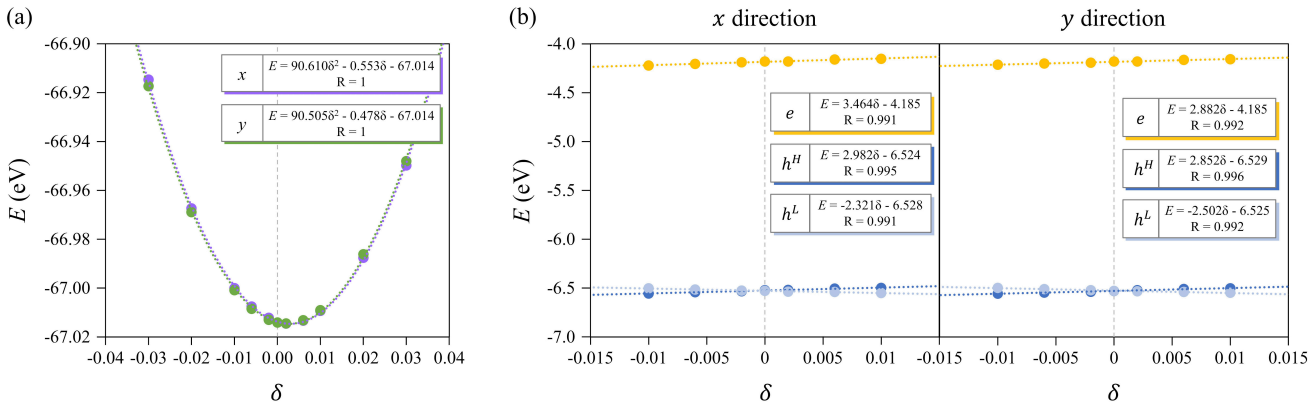

Table S1. Charge carrier properties for the distorted MXenes, where m_i^* is the carrier effective mass along the *i* transport direction, as a fraction w.r.t the free electron. $C_{2D,i}$ is the elastic constant along the *i* transport direction in units of $N \cdot m^{-1}$, $E_{d,i}$ is the deformation potential constant along *x* and *y* directions, in units of eV, and μ_i is the carrier mobility, in $cm^2 \cdot V^{-1} \cdot s^{-1}$ at $T = 300$ K. The *e*, h^H, and h^L carriers denote the electron, heavy hole, and light hole, respectively.

MXene	Carrier	m_x^*	m_y^*	$C_{2D,x}$	$C_{2D,y}$	$E_{d,x}$	$E_{d,y}$	μ_x	μ_y
	e	5.90	4.73			-0.33	1.77	530.57	22.75
d-Sc_2CS_2	h^H	0.85	0.83	84.48	83.81	3.83	3.87	171.52	171.65
	h^L	0.54	0.54			-0.85	-0.91	8492.93	7414.90
	e	2.17	1.87			0.79	2.79	590.98	55.04
d-Y_2CS_2	h^H	1.38	1.48	75.10	76.12	4.62	4.25	38.31	42.70
	h^L	1.34	1.33			1.18	0.98	642.05	954.56
	e	1.88	3.76			-0.95	1.83	316.53	42.21
d-Sc_2CSe_2	h^H	0.71	0.68	66.15	66.16	3.18	3.17	284.10	295.53
	h^L	0.38	0.37			-2.32	-2.29	1868.35	1959.07
	e	1.42	1.94			2.13	1.63	115.98	146.83
d-Y_2CSe_2	h^H	0.92	0.99	58.36	58.67	3.19	3.14	138.07	134.13
	h^L	0.84	0.81			-1.00	-0.90	1784.75	2316.87

Fig. S8. Charge carrier mobility, μ, in $cm^2 \cdot V^{-1} \cdot s^{-1}$ for the electrons and heavy holes along the x (zigzag) and y (armchair) directions for the distorted MXenes. The orange and blue bars indicate the electron and heavy hole mobilities.

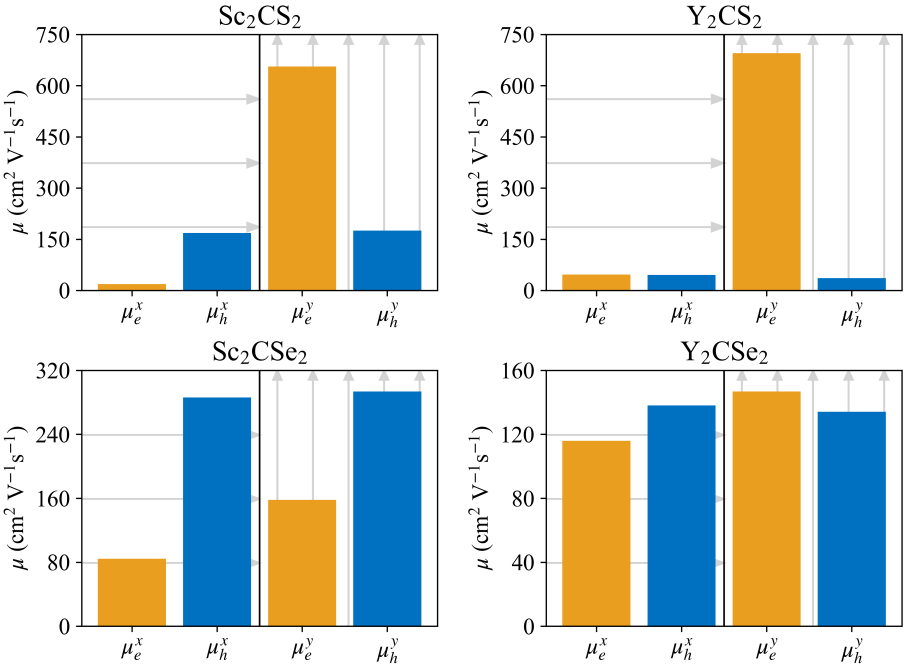

Fig. S9. Imaginary part of the dielectric function, ε_i, in arbitrary units, as a function of the photon energy, ω, in eV. The dotted lines in the chalcogen-terminated MXenes represent the distorted structure values. The Zr_2CO_2 values have been scaled down by a 2.5 factor for comparison purposes.

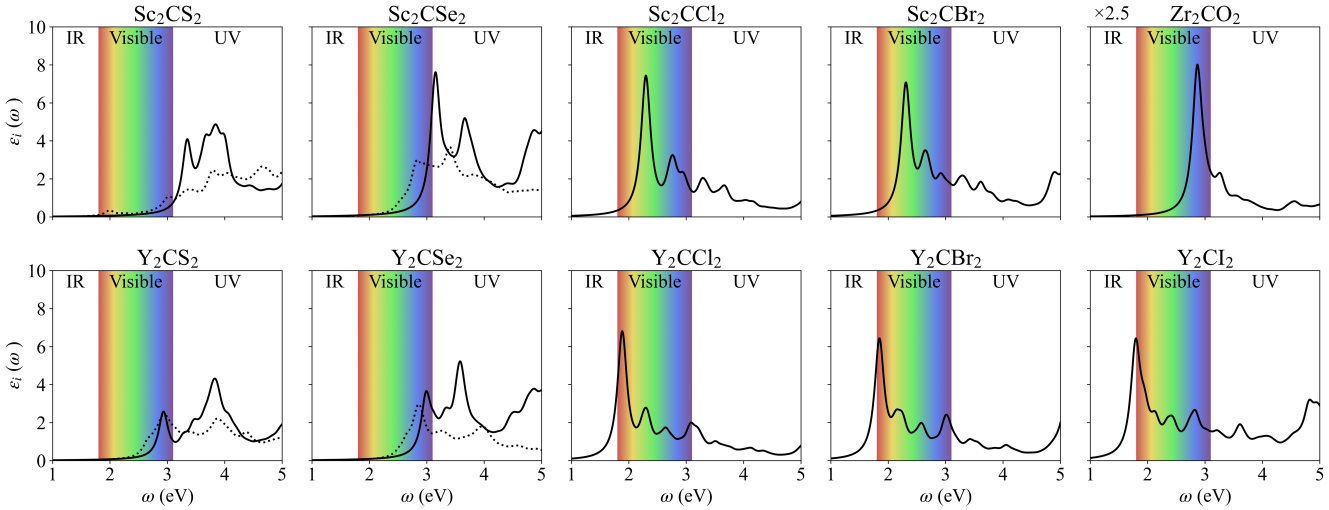

Table S2. Solar-to-hydrogen (STH) efficiency parameters, with Δϕ being the difference between the vacuum energies at the two surfaces of Janus MXenes, χ_{H_2} and χ_{O_2} being the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) overpotentials at *pH* = 7, respectively, all given in eV, and η_{abs}, η_{cu}, η_{STH} and η'_{STH} representing the efficiency of light absorption, carrier utilization, STH, and corrected STH, respectively, given in percentage.

MXene	$\Delta\phi$	χ_{H_2}	χ_{O_2}	η_{abs}	η_{cu}	η_{STH}	η'_{STH}
Zr_2CO_2	0.00	0.11	0.92	8.3	30.3	2.5	2.5
Sc_2CS_2	1.20	1.35	1.85	2.6	34.4	0.9	0.9
Y_2CS_2	0.83	1.48	1.54	7.2	37.9	2.7	2.7
Sc_2CSe_2	1.19	1.34	1.37	4.1	35.7	1.5	1.4
Y_2CSe_2	0.91	1.44	1.45	6.2	37.2	2.3	2.3
Sc_2CCl_2	0.00	-0.19	1.44	—	—	—	—
Y_2CCl_2	0.00	-0.07	1.27	—	—	—	—
Sc_2CBr_2	0.00	-0.05	1.13	—	—	—	—
Y_2CBr_2	0.00	-0.05	1.18	—	—	—	—
Y_2CI_2	0.00	0.15	0.56	46.6	46.0	21.4	21.4
d-Sc_2CS_2	1.31	1.35	1.73	7.3	37.9	2.8	2.7
d-Y_2CS_2	1.24	1.54	1.67	13.4	40.8	5.5	5.2
d-Sc_2CSe_2	1.29	1.16	1.46	16.7	42.1	7.0	6.5
d-Y_2CSe_2	1.14	1.29	1.56	13.4	40.8	5.5	5.2