Two low-dimensional metal halides: ionothermal synthesis, photoluminescence, and nonlinear optical properties†

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Physical measurements:

Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. Diffuse reflectance spectra were recorded at room temperature on a Shimadzu UV-2600 UV-vis spectrophotometer in the wavelength range of 200-800 nm. $BaSO_4$ powder was used as 100% reflectance reference. The photoluminescent spectrum was measured on a Fluoromax-4 fluorescence spectrometer (Horiba Jobin Yvon-Edison) with a calibrated integrating sphere system. Structural measurements were performed on an Agilent Xcalibur Eos Gemini diffractometer at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL program package.[1] All non-hydrogen framework atoms were refined anisotropically.

Theoretical Calculations:

The first principles calculations for $(C_6H_{11}N_2)PbBr_3$ were performed using the full-potential projector augmented wave (PAW) method,[2] as implemented in the Vienna ab initio Simulation Package (VASP) package.[3] The exchange-correlation (XC) interaction was treated by the Perdew-Burke-Ernaerhof (PAW-PBE)[4] functional. The band structure and density of states (DOS)/partial DOS (PDOS) were computed. Moreover, the kinetic energy cutoff of 400 eV was chosen and the k-point sampling in the Brilliouin zone was used to be 4 × 4 × 2. The birefringence and electron-density difference (EDD) are calculated by Materials Studio (MS), under the Nom conserving pseudopotentials, the kinetic cutoff energy set as 720 eV and the k-point sampling in the Brilliouin zone was performed using 3 × 3 × 2. In all calculations, the Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation (GGA) was adopted.[5] The rest parameters used in the calculations were set by the default values of the CASTEP.

Reference

1. G. M. Sheldrick, Acta Cryst., Sect. A, 2008, 64, 112.

2. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.

3. (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758; (c) G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169; (d) G. Kresse, VASP, 5.3.5; http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html, 2014.

4. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

5. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

Synthesis

Synthesis of $(C_7H_{13}N_2)_2MnCl_4$ (**1**): A mixture of $MnCl_2·4H_2O$ (0.198 g) and 1-ethyl-2, 3-dimethylmidazolium chloride (0.408 g) was sealed in a 25 mL Teflon-coated steel autoclave and heated at 150 °C for 5 days. The autoclave was subsequently allowed to cool to room temperature. Green flake crystals were washed with ethanol, recovered by filtration, and finally dried at ambient temperature (88% yield based on manganese).

Synthesis of $(C_6H_{11}N_2)PbBr_3$ (**2**): A mixture of $PbBr_2$ (0.375 g) and 1-ethyl-3-methyl imidazolium bromide (0.382 g) was sealed in a 25 ml Teflon-coated steel autoclave and heated at 150 °C for 5 days. The autoclave was subsequently allowed to cool to room temperature. Colorless needle crystals were washed with ethanol, recovered by filtration, and finally dried at ambient temperature (50% yield based on lead).

Table S1. Calculation of dipole moment for $PbBr_6$ polyhedra and net dipole moment for a unit cell in compound **2** (D = Debyes).

$(C_6H_{11}N_2)PbBr_3$				
Polar unit (a unit cell)	Dipole moment (D)			
$PbBr_6$	x-component	y-component	z-component	total magnitude
	1.086420005	-7.592411387	0.019251211	7.669771164
	1.086420005	-7.592411387	0.019251211	7.669771164
	-22.52075554	6.09962745	-0.125129467	23.3324997
	-1.085537276	7.594388913	0.018601518	7.671602189
	-1.085815976	-7.592693668	-0.019086086	7.669964651
	1.087160108	-7.66494073	-40.91735896	41.64328875
	-22.64699027	6.12101551	-48.21718785	53.62135958
	Ux	Uy	Uz	Ut
Total	-45.16551895	-3.035013912	-89.24090963	100.0653555
Cell Volume	1239.15Å^3			

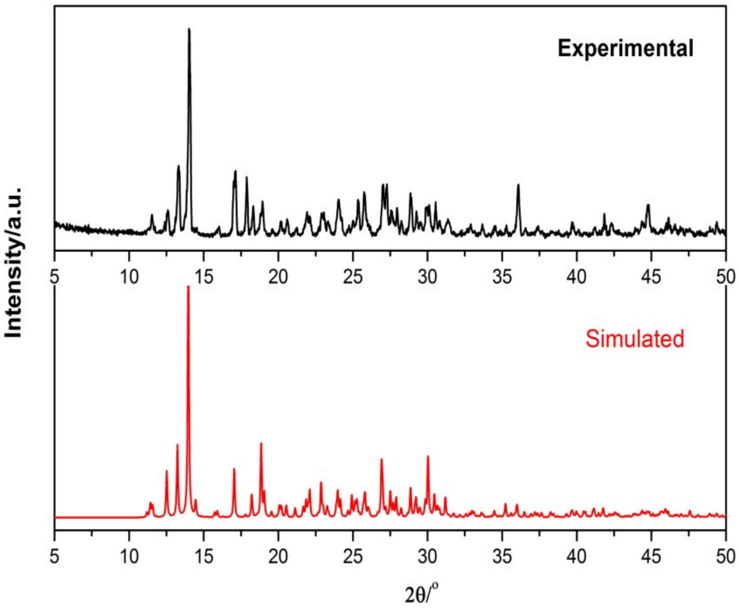


Fig. S1. Experimental and simulated powder XRD patterns of compound **1**.

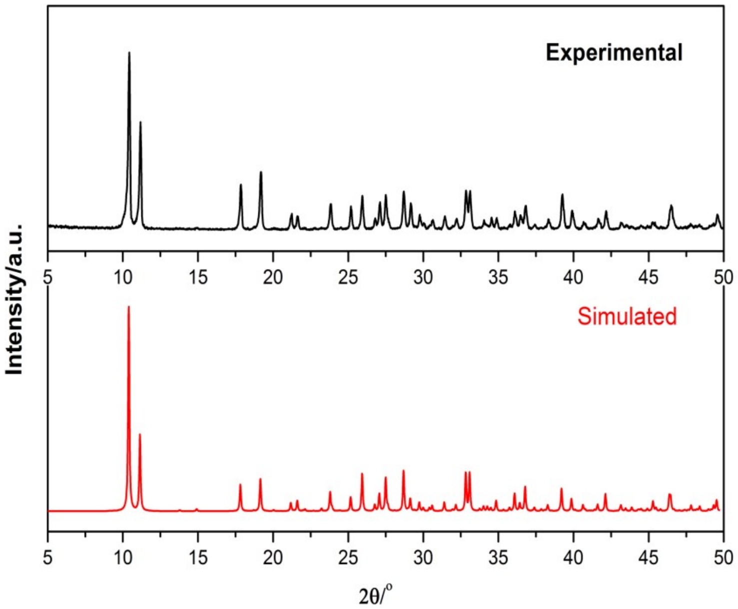


Fig. S2. Experimental and simulated powder XRD patterns of compound **2**.

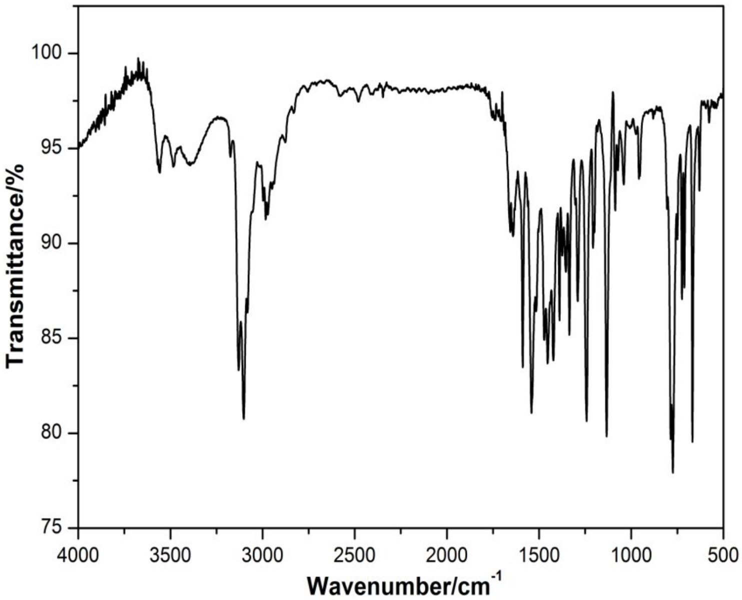


Fig. S3. The IR spectrum of compound **1**.

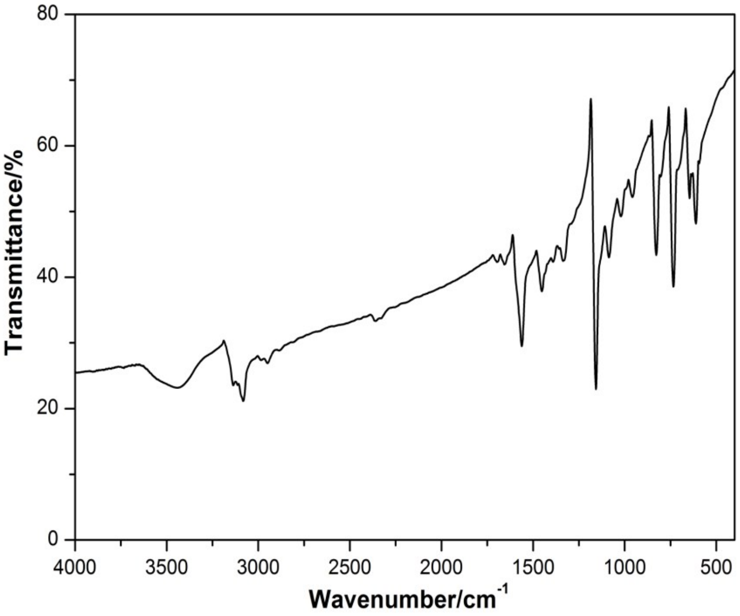


Fig. S4. The IR spectrum of compound **2**.

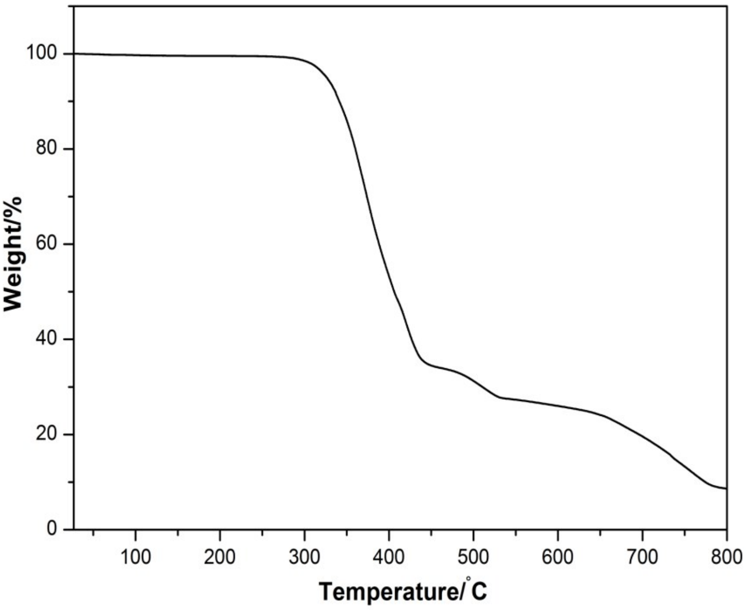


Fig. S5. The TGA curve of compound **1**.

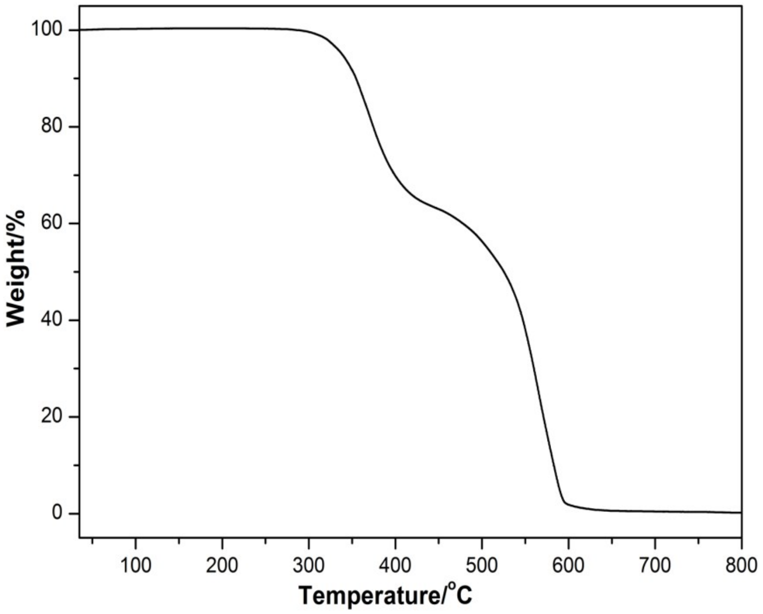


Fig. S6. The TGA curve of compound **2**.

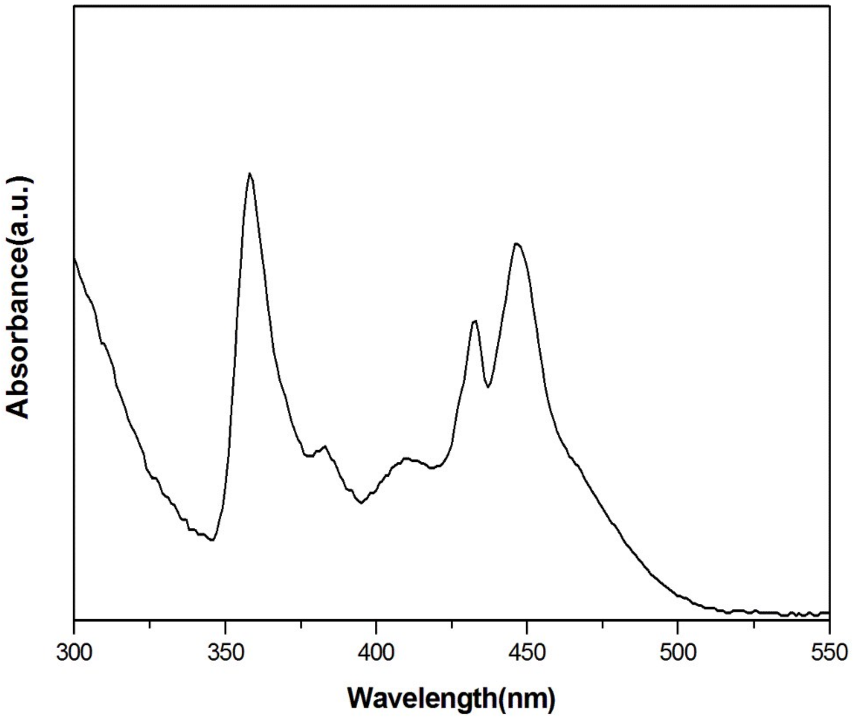
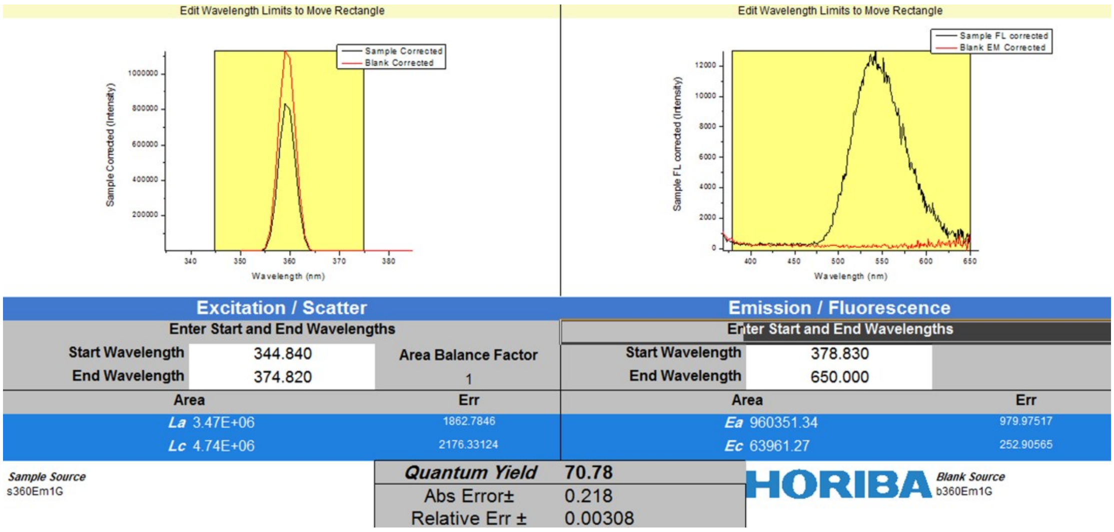


Fig. S7. UV-vis absorption spectrum of compound **1**.



Excitation / Scatter

Enter Start and End Wavelengths

Start Wavelength 344.840

End Wavelength 374.820

Area Balance Factor 1

Area	Err
La 3.47E+06	1862.7846
Lc 4.74E+06	2176.33124

Emission / Fluorescence

Enter Start and End Wavelengths

Start Wavelength 378.830

End Wavelength 650.000

Area	Err
Ea 960351.34	979.97517
Ec 63961.27	252.90565

Sample Source
s360Em1G

Quantum Yield	70.78
Abs Error±	0.218
Relative Err ±	0.00308

Blank Source
b360Em1G

Fig. S8. The quantum yield of compound **1**.

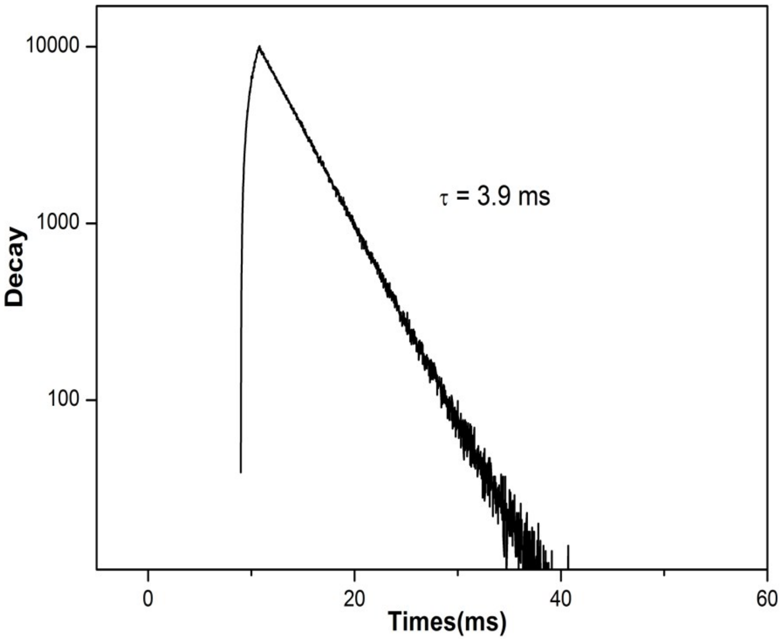


Fig. S9. The lifetime of compound **1**.

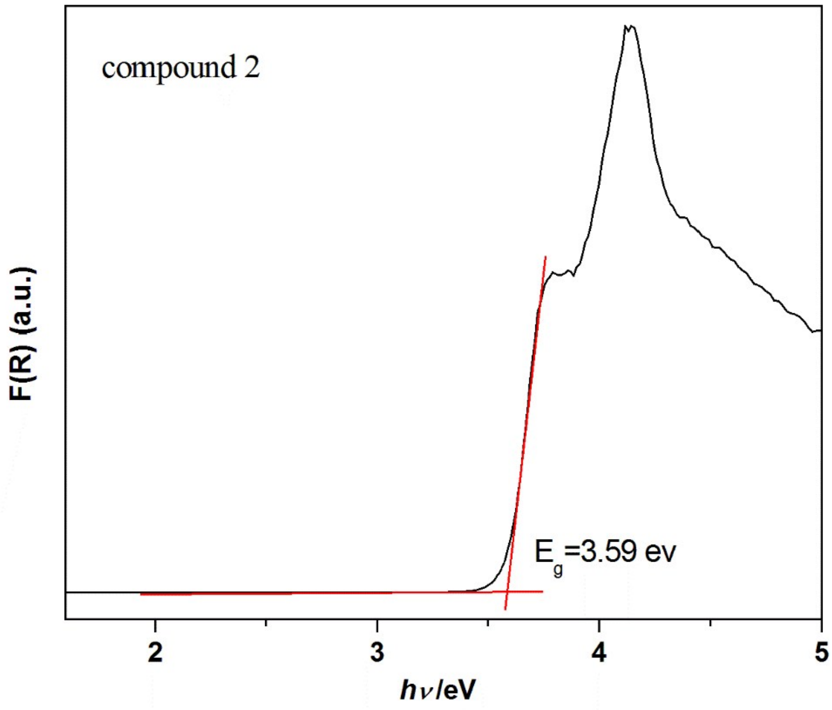


Fig. S10. A plot of *F(R)* versus *hv* for the band gap energy.

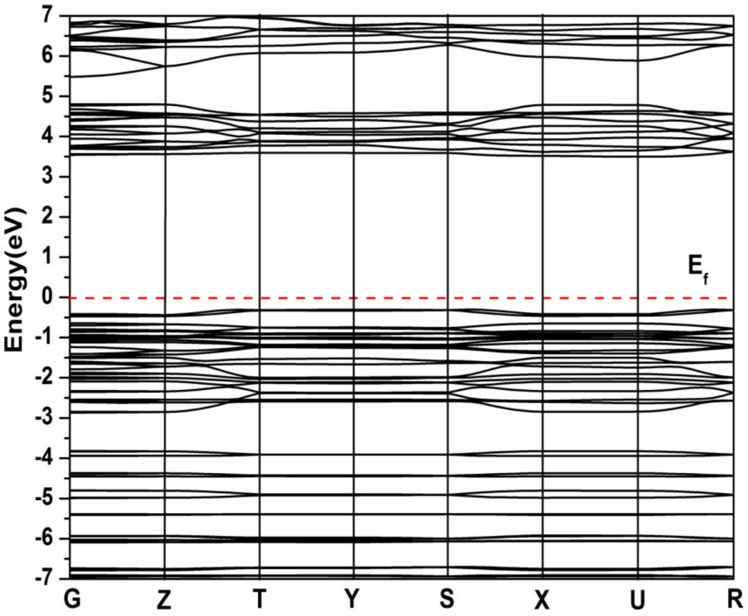


Fig. S11. Calculated band structure for compound **2** (the Ferm level is set at 0 eV).

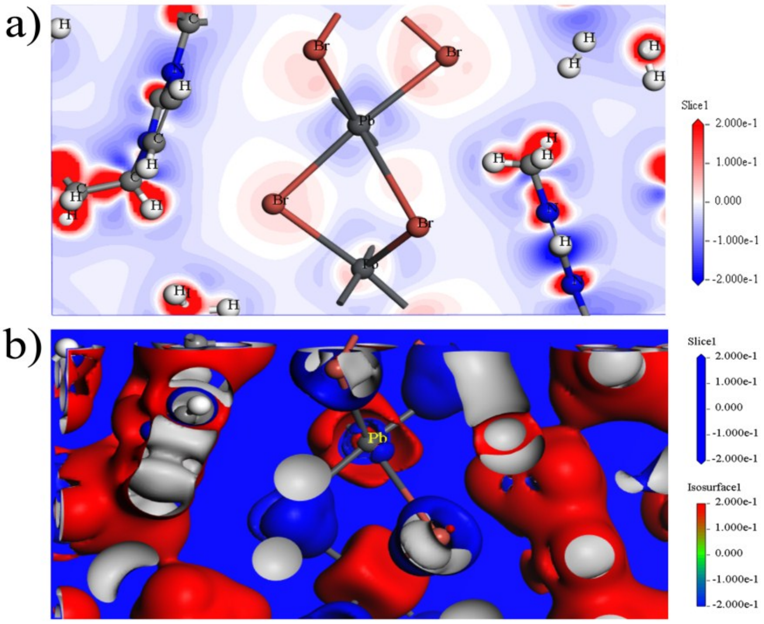


Fig. S12. (a) and (b) Electron-density difference map of compound **2**.

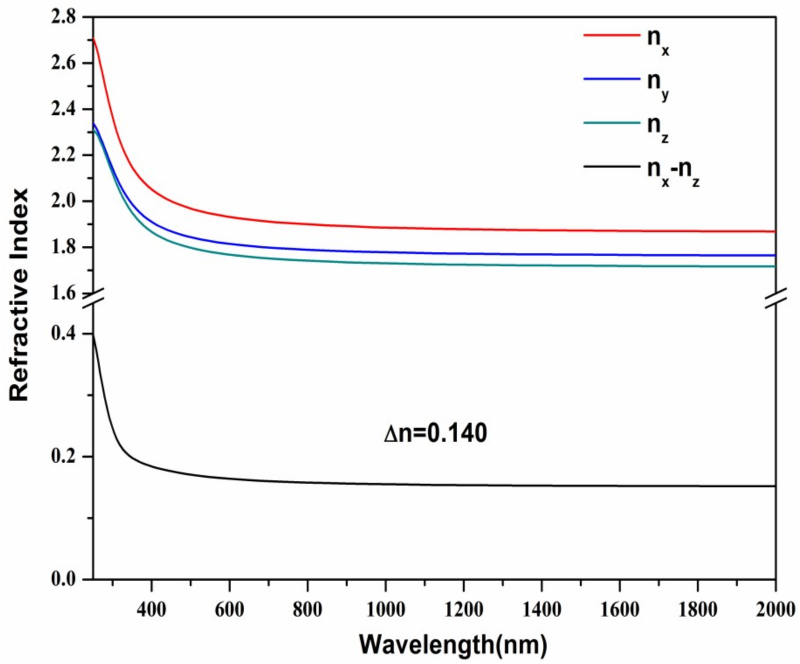


Fig. S13. Calculated refractive indexes for compound **2**.

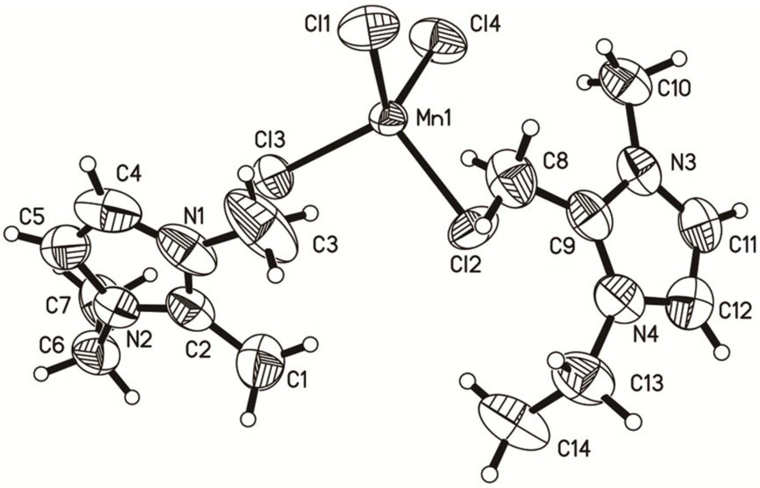


Fig. S14. ORTEP view of the asymmetric unit of compound **1**, showing the labeling scheme and the 50 % probability displacement ellipsoids.

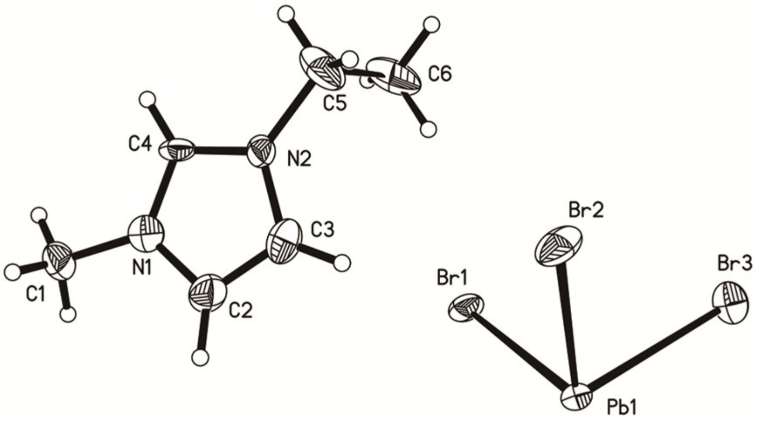


Fig. S15. ORTEP view of the asymmetric unit of compound **2**, showing the labeling scheme and the 50 % probability displacement ellipsoids.

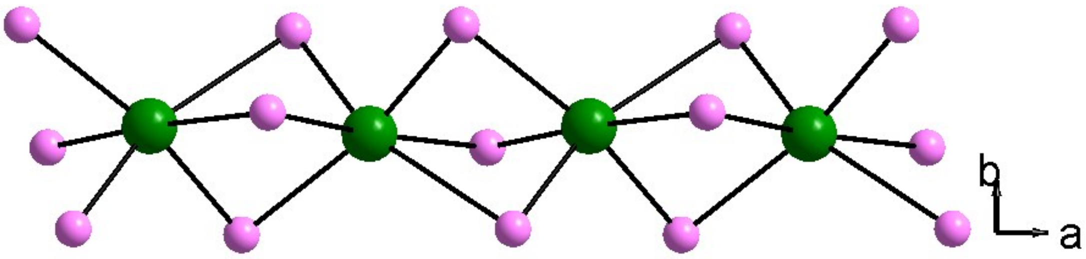


Fig. S16. Ball-and-stick representation of the chain-like structure of compound **2**.

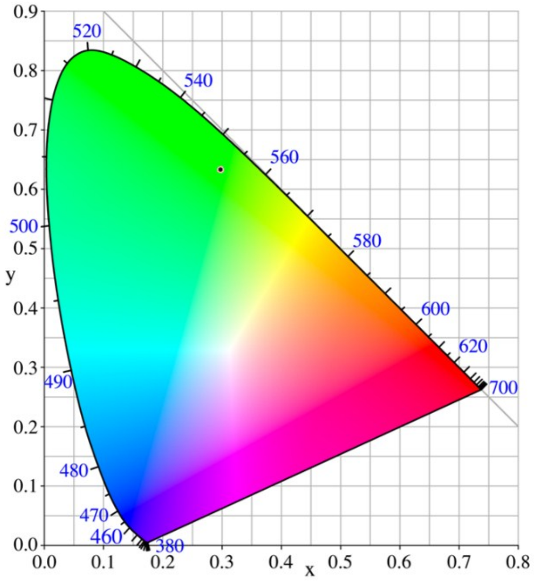


Fig. S17. CIE chromaticity diagram of compound **1**.