Electronic Supplementary Information

Tunable luminescent lead bromide complexes

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I. Materials and Methods

i. Preparation of the lead halides in poly(ethylene glycol) Lead bromide, lead chloride, tetrabutylammonium bromide (TBABr), tetrabutylammonium chloride (TBACl), dimethylsulfoxide (DMSO), Poly(ethylene glycol) (PEG) 200 and 400 are purchased from Sigma-Aldrich. Tri-ethylene glycol and PEG 600 are purchased from Alfa Aesar. Butylammonium bromide is from Dyesol and methylammonium bromide is from Lumtec. Every solute, alkylammonium halide or lead halide, is dissolved and stirred overnight in DMSO-PEG co-solvent (1:10 volume ratio) except lead bromide in PEG (In Figure 1). For perfect solvation, lead halide solution is diluted until 62.5 mM (1/16 M). All procedures are processed in air

ii. Preparation of white-emissive metallogel 4,4'-Bis(9-ethyl-3-carbazovinylene)-1,1'-biphenyl (BCzVBi) is purchased from Lumtec. This blue-emissive organic dye is dispersed in tetrabutylammonium lead bromide based yellow-emissive metallogel with DMSO-PEG 600 co-solvent. These yellow-emissive agents, yellow metallogels (YGs) are obtained by stoichiometric control of TBABr and lead bromide. (TBABr : lead bromide = 0.5:1 in YG 1, 1:1 in YG 2) with consistent concentration of lead bromide, 62.5 mM. For the phase-transition to gel, temperature is decreased under 15℃. All procedures are processed in air

II. Characterization

i. Photoluminescent excitation and emission spectra measurement The PL spectra were collected using a Xe lamp coupled to a monochromator as the excitation source and a spectrometer (Hamamatsu C9920-02 with a Hamamatsu PMA-11 optical detector). The wavelength of excitation sources were 365 nm and 340 nm for bromides and chlorides. PLQY values were obtained using a Xe lamp coupled to a monochromator as the excitation source and an integrating sphere coupled to a same spectrometer. The instrumental error is ≈1%. The PL excitation spectra were collected by Edinburgh FLS1000 using a µF2 Xe lamp and single-photon counting vis-PMT 980.

ii. Photoluminescence decay time measurement PL decays were measured using a compact fluorescence lifetime spectrometer C11367, Quantaurus Tau. The excitation sources were, consistently 365 nm and 340 nm LEDs for bromide and chloride, respectively. PL lifetime measurement software U11487 was used to register the data. the PL decays were fitted with a biexponential function.

III. Simulation

Density Functional Theory-calculation All the calculations are carried out using Gaussian09 program at the level of m06-2x/def2-tzvp for all atoms and SDD pseudopotential for Pb atoms with dispersion correction GD3 method. The optimized structures are further examined by frequency analysis to confirm that true local minima are achieved. In addition, quantum theory of atom in molecule (QTAIM) is applied to visualize bonds.

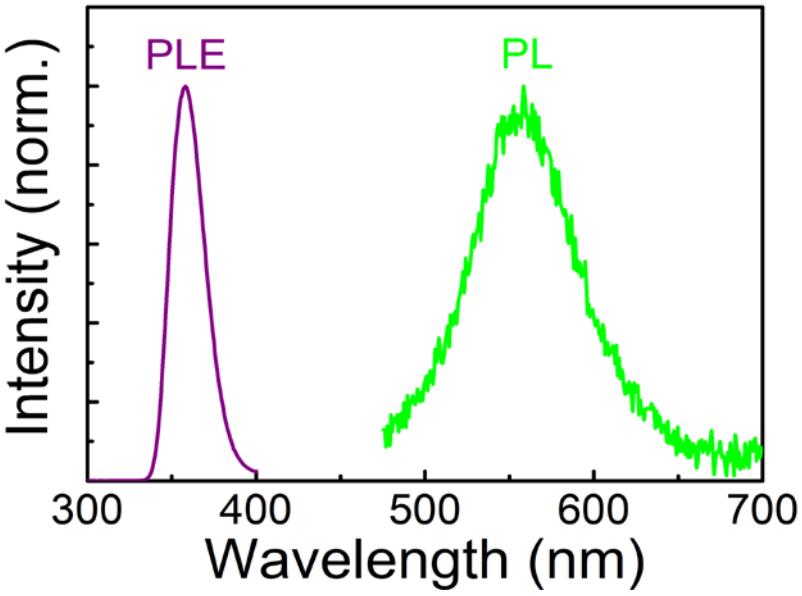

Fig. S1. Photoluminescent and excitation spectra of DMSO

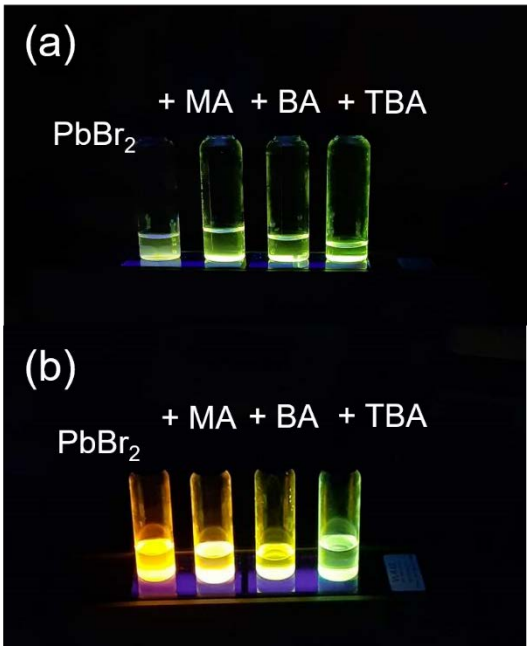

Fig. S2. (a) Luminescent lead bromide and perovskite precursor solutions in DMSO and (b) DMSO-PEG co-solvent on UV lamp

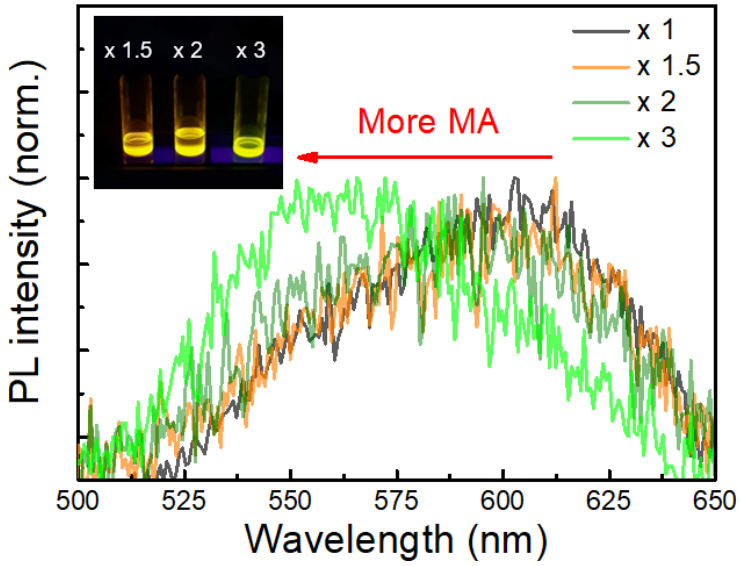

Fig. S3. Excess MABr concentration-dependant photoluminescent spectra

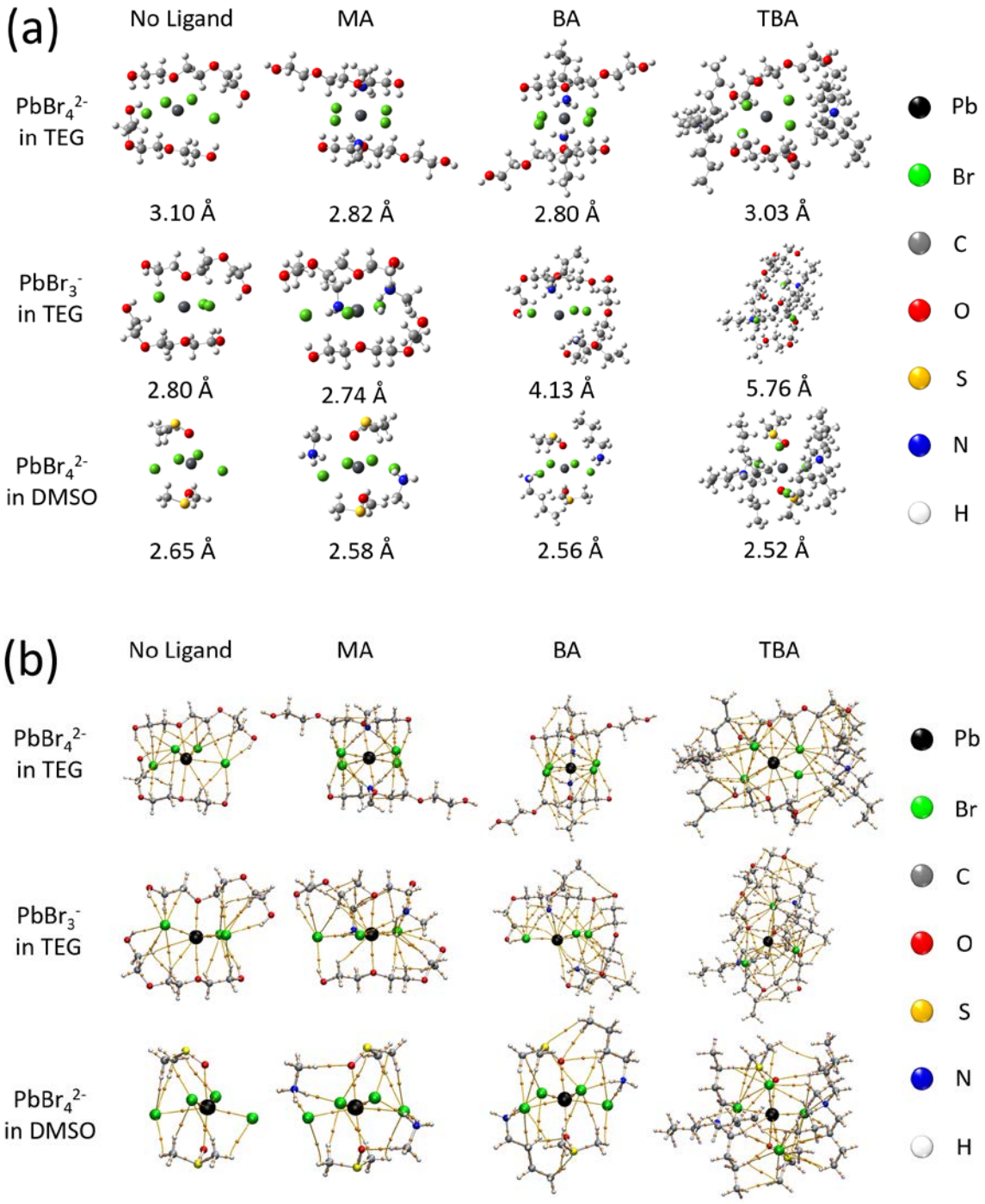

Fig. S4. (a) Theoretical calculation of Pb-O distances in lead bromide-solvent system with and without various ligands. (b) Visualized interaction via Quantum theory of atom in molecule (QTAIM).

Note: The covalent bonds are visualized as white lines while the chemical interactions are yellow. The calculations show that $PbBr_3^-$ in TEG is not stable in the presence of large ligands. The Br anion dissociates in those systems.

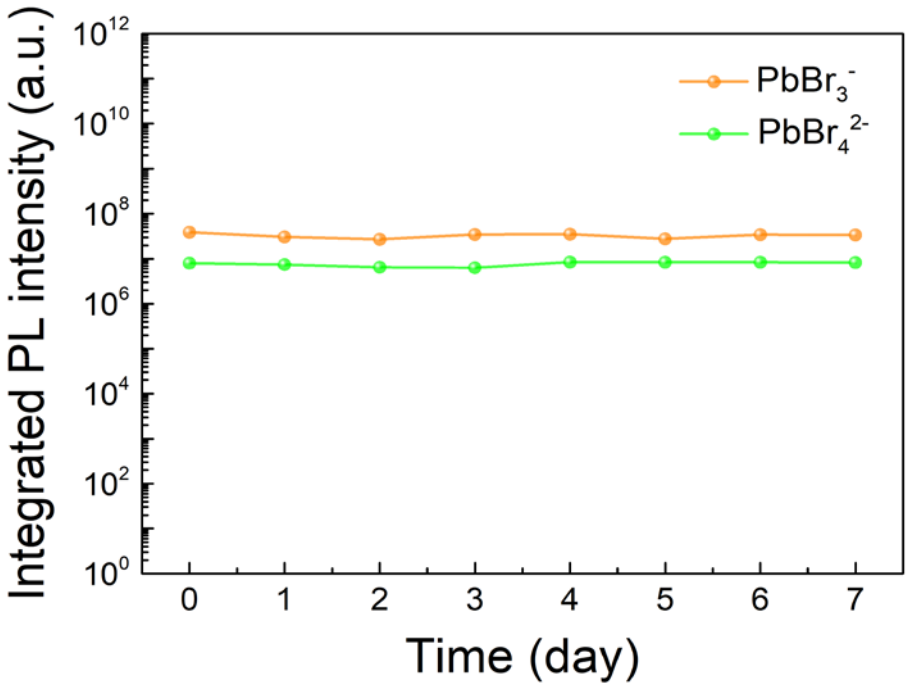

Fig. S5. PL stability of $PbBr_3^-$ and $PbBr_4^{2-}$ complexes

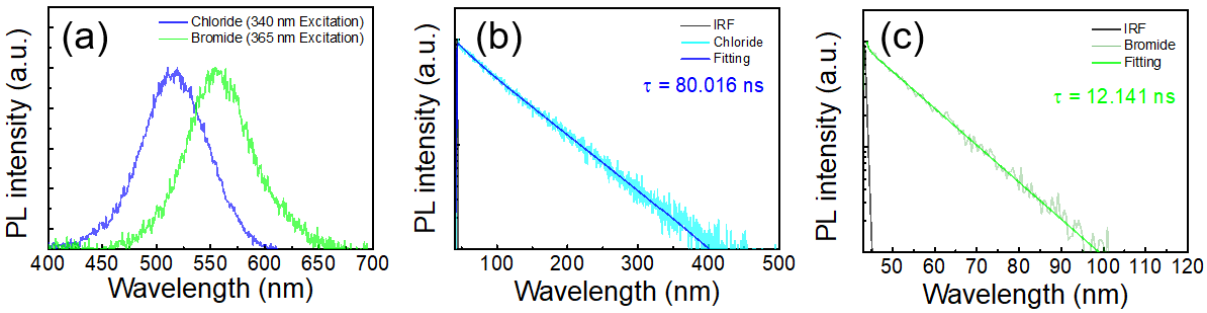

Fig. S6. (a) Photoluminescent spectra of lead chloride + TBACl and lead bromide + TBABr (TBAX is 2-fold to lead halide). Decay curves of (b) chloride and (c) bromide.

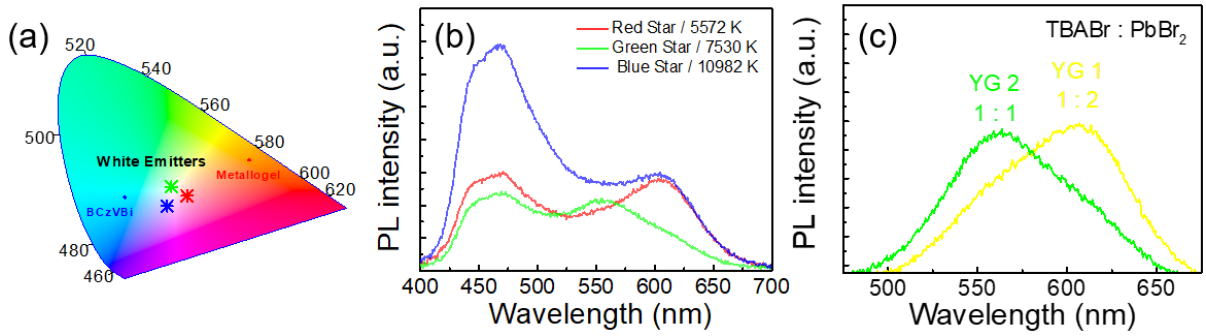

Figure S7. (a) Emissive character of BCzVBi, yellow metallogel and white metallogel set on CIE coordinate. PL spectra of (b) white-emissive metallogel set and (c) yellow-emissive metallogel set.

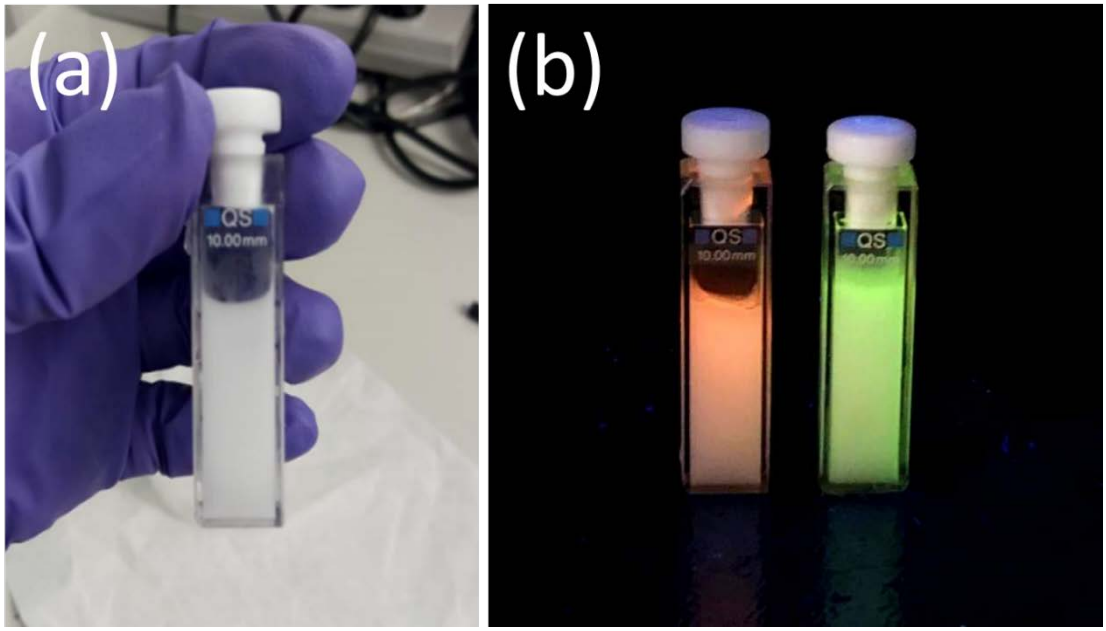

Figure S8. Gel phase sample at 0 °C for optical characterizations. (a) under white light illumination and (b) under UV illumination for a sample without (orange fluorescence) and with alkylammonium bromide (green fluorescence).

Table S1. PLQY Table

Solute	Solvent	PLQY (%)	Note
$PbBr_2$	DMF	1.6	
$PbBr_2$	DMSO	0.7	
$PbBr_2$ + 2MABr	DMSO	1.1	
$PbBr_2$ + 2BABr	DMSO	1.0	
$PbBr_2$ + 2TBABr	DMSO	2.1	
$PbBr_2$	TEG	9.3	
$PbBr_2$	PEG 200	12.3	
$PbBr_2$	PEG 400	16.6	
$PbBr_2$	PEG 600	23.4	- Due to the phase transition of PEG 600 on 15℃, measurements are conducted over 20℃. - The volume ratio between DMSO and PEG 600 in co-solvent is 1:10. - DMSO decreases PLQY of PEG-based solution (refer to $PbBr_2$ in DMSO and DMSO + PEG 600). - Pure $PbCl_2$ is unable to be dissolved in PEG. - The PLQY of white-emissive metallogel (W1-3) is highly dependent on the concentration of BCzVBi dye.
$PbBr_2$	DMSO + PEG 600	2.1	
$PbBr_2$ + 1.5MABr	DMSO + PEG 600	2.7	
$PbBr_2$ + 2MABr	DMSO + PEG 600	2.5	
$PbBr_2$ + 3MABr	DMSO + PEG 600	2.0	
$PbBr_2$ + 2BABr	DMSO + PEG 600	2.2	
$PbBr_2$ + 2TBABr	DMSO + PEG 600	2.7	
$PbCl_2$ + 2TBACl	DMSO + PEG 600	7.4	
YG1 set	DMSO + PEG 600	4.0	
YG2 set	DMSO + PEG 600	3.7	
W1 set	DMSO + PEG 600	7.4	
W2 set	DMSO + PEG 600	5.4	
W3 set	DMSO + PEG 600	9.2	

Table S2. Color of White emitters

	Concentration of BCzVBi	CIE coordinate (CIE_x, CIE_y)	Color temperature (T_c)
W1 (Red Star)	0.125 g/l in YG 1	0.331, 0.311	5572 K
W2 (Green Star)	0.625 g/l in YG 2	0.291, 0.345	7530 K
W3 (Blue Star)	1.250 g/l in YG 1	0.280, 0.273	10982 K

Color temperature (T_c) set is calculated by McCamy's approximation which is shown below.

$$n = \frac{(CIE_x - 0.3320)}{(0.1858 - CIE_y)}$$

$$T_c\,(\mathrm{K}) = 437\,n^3 + 3601\,n^2 + 6861\,n + 5517$$