Supplementary data for

Embedded Lanthanoid Ions Modulated Periodic Luminescence of Transition Metal Dichalcogenide Monolayers Prepared from Liquid Precursor

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Figure S1. Pictorial drawing of two-step thermolysis process to systhesize Ln^{3+} -doped MoS₂. Sublimated sulfur powder is put in a porcelain boat and placed upstream of the tube furnace airflow. The silicon slice spin-coated with the precursor is horizontally set on another boat in the middle of the tubular furnace. In the first step, the Ar containing 5% H2 is used as the carrier gas. After 20 min of gas washing, the flow rate was changed to 120 sccm. Heat the furnace tube to 500 °C, the heating rate is set to 30 °C / min, holding 0.5 h. In the second step, the carrier gas is changed to high-purity argon with the same flow rate. The furnace temperature is raised to 850 °C, and the upstream sulfur powder is heated at 200 °C to evaporate and keep for 15 min.



Figure S2. Characterization of monolayer Er^{3+} -doped MoS₂. (a) HADDF-STEM images of the Er^{3+} -doped MoS₂. Er atoms are marked with yellow circles. (b) Intensity profile of the selected area marked in (a). Er atom shows much stronger intensity compared to Mo and S. (c) EDS spectrum of Er^{3+} -doped MoS₂. (e) EDS analysis mapping images of S, Mo, and Er in the same collected area in (c).



S3. XPS results of the Ln³⁺-doped MoS₂ monolayers.

Figure S3. XPS results of the MoS₂ monolayers with dopants of : (a)Ce³, (b)Pr³⁺, (c)Nd³⁺, (d)Sm³⁺, (e)Eu³⁺, (f)Gd³⁺, (g)Tb³⁺, (h)Dy³⁺, (i)Ho³⁺, (j)Er³⁺, (k)Tm³⁺, (l)Yb³⁺, (m)Lu³⁺. In each section, the left figure is the comparison of Mo 3d, S 2s measured from Ln³⁺-doped and pristine MoS₂, and the right figure shows the scan of d core level of the lanthanoid element in Ln³⁺-doped MoS₂.

The change of embedded lanthanoid elements would result in different peak shifts in XPS. As shown in Table S1, compared to the XPS peaks in pristine MoS_2 , the Mo $3d_{5/2}$, Mo $3d_{3/2}$, and S 2s peaks of all Ln^{3+} -doped samples drift to the lower energy. Interestingly, the offsets present a double symmetry along with the lanthanoid family. It illustrates that the perturbation of doped lanthanoid ions to the matrix chemical environment only depends on the element itself when neglecting the concentration effect and lattice distortion. On the other hand, the significant movements to the standards in peaks of d core level from lanthanoids are reflected in Table S2.¹ It can indicate that the crystal field of two-dimensional materials can effectively stretch atomic orbitals of lanthanoid elements to produce deformation and promote energy level splitting.²

Sample	S 2s peak		Mo 3d _{5/2} peak		Mo 3d _{3/2} peak	
	Postion (eV)	Shift (eV)	Postion (eV)	Shift (eV)	Postion (eV)	Shift (eV)
La ³⁺ -doped	226.9	-0.2	229.7	-0.3	232.9	-0.2
Ce ³⁺ -doped	226.9	-0.2	229.6	-0.4	232.8	-0.3
Pr ³⁺ -doped	226.5	-0.6	229.4	-0.6	232.6	-0.5
Nd ³⁺ -doped	226.7	-0.4	229.4	-0.6	232.6	-0.5
Sm ³⁺ -doped	226.9	-0.2	229.7	-0.3	232.9	-0.2
Eu ³⁺ -doped	227.0	-0.1	229.8	-0.2	232.9	-0.2
Gd ³⁺ -doped	226.8	-0.3	229.6	-0.4	232.8	-0.3
Tb ³⁺ -doped	226.6	-0.5	229.7	-0.3	232.9	-0.2
Dy ³⁺ -doped	226.8	-0.3	229.7	-0.3	232.9	-0.2
Ho ³⁺ -doped	226.8	-0.3	229.6	-0.4	232.9	-0.2
Er ³⁺ -doped	227.0	-0.1	229.7	-0.3	232.9	-0.2
Tm ³⁺ -doped	226.8	-0.3	229.6	-0.4	232.7	-0.4
Yb ³⁺ -doped	226.8	-0.3	229.6	-0.4	232.7	-0.4
Lu ³⁺ -doped	226.9	-0.2	229.7	-0.3	232.9	-0.2

Table S1. Comparison of XPS peaks of Mo $3d_{5/2}$, Mo $3d_{5/2}$, and S 2s measured from Ln^{3+} -doped and pristine MoS₂.

Sample	Peak	Experimental (eV)	Standard (eV)	Shift (eV)	Peak	Experimental (eV)	Standard (eV)	Shift (eV)
La ³⁺ -doped	3d _{5/2}	837.0	835.0	2.0	3d _{3/2}	853.9	853.0	0.9
Ce ³⁺ -doped	3d _{5/2}	879.8	884.0	-4.2	3d _{3/2}	904.1	902.0	2.1
Pr ³⁺ -doped	3d _{5/2}	937.1	931.8	5.3	3d _{3/2}	941.6	952.2	-10.6
Nd ³⁺ -doped	3d _{5/2}	979.2	981.0	-1.8	3d _{3/2}	1000.9	1003.0	-2.1
Sm ³⁺ -doped	3d _{5/2}	1086.9	1081.0	5.9	3d _{3/2}	1107.1	1108.0	-0.9
Eu ³⁺ -doped	3d _{5/2}	1134.4	1126.0	8.4	3d _{3/2}	1157.0	1155.0	2.0
Gd ³⁺ -doped	4d	154.7	141.0	13.7				
Tb ³⁺ -doped	3d _{5/2}	1240.0	1242.1	-2.1	3d _{3/2}	1265.0	1276.7	-11.7
Dy ³⁺ -doped	3d _{5/2}	1304.1	1296.2	7.9	3d _{3/2}	1335.1	1335.1	0.0
Ho ³⁺ -doped	4d _{5/2}	162.4	159.6	2.8	4d _{3/2}	163.6	161.0	2.6
Er ³⁺ -doped	4d _{5/2}	168.2	167.3	0.9	4d _{3/2}	172.9	169.3	3.6
Tm ³⁺ -doped	4d	179.1	175.4	3.7				
Yb ³⁺ -doped	4d _{5/2}	185.7	185.0	0.7	4d _{3/2}	190.4	190.9	-0.5
Lu ³⁺ -doped	4d _{5/2}	198.8	196.0	2.8	4d _{3/2}	207.0	205.8	1.2

Table S2. Comparison of XPS peaks d core level of lanthanoid measured from Ln³⁺-doped and the standard data.¹



Figure S4. Schematic of the transient reflectance (TR) spectroscopy. A femtosecond pump pulse excites the MoS_2 monolayer, while a delayed broadband probe pulse monitors the changes in the optical transmission spectrum as a function of delay.



S5. TR measurements of the pristine and Ln³⁺-doped MoS₂ monolayers.

Figure S5. TR mapping of MoS_2 monolayers with dopants of (a) none, (b) La^{3+} , (c) Ce^{3+} , (d) Pr^{3+} , (e) Nd^{3+} , (f) Sm^{3+} , (g) Eu^{3+} , (h) Gd^{3+} , (i) Tb^{3+} , (j) Dy^{3+} , (k) Ho^3 , (l) Er^{3+} , (m) Tm^3 , (n) Yb^{3+} , (o) Lu^{3+} . The relative absorption intensity in all the spectra was standardized.

The transient reflectance (TR) spectra reveal the effect of lanthanoid doping on MoS_2 monolayers in the entire luminescence process. Figure S2 shows the standardized TR contour plots of the pristine and Ln^{3+} -doped MoS_2 , it is intuitive to distinguish their discrepancies, attributing to the different energy band renormalizations by diverse lanthanoid doping. The data at the same acquisition time (1ps) were selected to extract the TR spectrum of each sample and the kinetic of the A exciton peak. The decay curves were fitted by the double exponential. The wavelength position and lifetime of A exciton extracted in TR spectra are listed in Table S3. The ultrafast τ_1 stands for the non-radiative scattering process in the conduction band, while the τ_2 is recognized for the lifetime of the exciton.³ Similarly, the results show periodicity, which is consistent with the regularity in the PL spectra, reflecting the law of lanthanoids.

Table S3. The wavelength positions and lifetimes of A exciton peak collected in the TR spectra of Ln^{3+} -doped and pristine MoS₂.

Sample	Peak position (nm)	Peak intensity (a.u.)	$\tau_1(ps)$	$\tau_2(ps)$
Pristine	690.4	0.0039	0.90	17.17
La ³⁺ -doped	689.1	0.0076	1.54	16.09
Ce ³⁺ -doped	680.3	0.0046	0.72	14.89
Pr ³⁺ -doped	677.8	0.0048	0.96	18.25
Nd ³⁺ -doped	671.6	0.0068	0.81	18.19
Sm ³⁺ -doped	675.3	0.0061	0.94	20.86
Eu ³⁺ -doped	676.6	0.0060	1.70	25.15
Gd ³⁺ -doped	672.8	0.0054	0.95	23.20
Tb ³⁺ -doped	686.6	0.0077	1.29	16.36
Dy ³⁺ -doped	681.6	0.0047	0.90	21.87
Ho ³⁺ -doped	674.1	0.0078	0.88	25.33
Er ³⁺ -doped	670.3	0.0095	0.92	19.52
Tm ³⁺ -doped	684.1	0.0070	1.06	14.70
Yb ³⁺ -doped	685.4	0.0065	0.91	11.46
Lu ³⁺ -doped	687.9	0.0055	0.80	10.88

References

- 1 B. V. Crist, Handbook of Monochromatic XPS Spectra; John Wiley & Sons, New York, 2000.
- D. Xu, W. Y. Chen, M. Q. Zeng, H. F. Xue, Y. X. Chen, X. H. Sang, Y. Xiao, T. Zhang, R. R. Unocic, K. Xiao and L. Fu, *Angew. Chem.-Int. Edit.*, 2018, 57, 755-759.
- 3 H. Y. Shi, R. S. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing and L. B. Huang, *ACS Nano*, 2013, 7, 1072-1080.