SUPPORTING INFORMATION

In situ preparation of highly luminescent Sb³⁺/Mn²⁺ codoped Cs₂KInCl₆ lead-free double perovskite in PVDF matrix and application to white light emitting diode and anti-counterfeiting

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| Positio | Peak1 | Peak1 PL | Peak2 | Peak2 PL | FWHM | CIE |
|---------|------------|-----------|------------|-----------|----------|------------------|
| n | wavelength | intensity | Wavelength | intensity | | |
| | (nm) | | (nm) | | | |
| 1 | 501 | 906059.1 | 633 | 702325.1 | 230.6416 | (0.3357, 0.3833) |
| 2 | 500 | 943006.4 | 634 | 724365.4 | 232.7982 | (0.3333, 0.3800) |
| 3 | 501 | 953537.7 | 634 | 775487.4 | 231.0202 | (0.3396, 0.3822) |
| 4 | 501 | 1008074.3 | 634 | 835016.5 | 229.9310 | (0.3415, 0.3832) |
| 5 | 501 | 1028279.9 | 634 | 862647.2 | 232.2089 | (0.3424, 0.3825) |
| 6 | 501 | 1054715.6 | 633 | 839332.0 | 230.0910 | (0.3380, 0.3830) |
| 7 | 500 | 1066223.9 | 634 | 887090.8 | 232.7456 | (0.3399, 0.3779) |
| 8 | 500 | 1070569.8 | 634 | 852467.1 | 231.8963 | (0.3360, 0.3793) |
| 9 | 500 | 1071127.5 | 633 | 875282.5 | 231.1717 | (0.3388, 0.3801) |
| 10 | 500 | 1075901.7 | 633 | 886219.9 | 234.4710 | (0.3398, 0.3801) |
| 11 | 501 | 1096263.9 | 633 | 881045.3 | 230.9752 | (0.3388, 0.3830) |
| 12 | 501 | 1096271.3 | 632 | 932813.7 | 232.2579 | (0.3441, 0.3833) |
| 13 | 501 | 1104425.1 | 632 | 898658.9 | 232.8296 | (0.3390, 0.3806) |
| 14 | 502 | 1137986.1 | 634 | 952250.0 | 232.7614 | (0.3438, 0.3849) |
| 15 | 501 | 1142087.1 | 632 | 903584.3 | 230.7596 | (0.3379, 0.3834) |
| 16 | 501 | 1181506.1 | 634 | 981440.0 | 232.5075 | (0.3395, 0.3791) |

Table S1. The positions, PL intensities, FWHM and CIE coordinates of the dual peaks in different regions of the $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1.

Table S2. Weight percentage and atomic percentage of partial relevant elements in $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1.

| Element | Weight % | Atomic % |
|---------|----------|----------|
| F (K) | 85.93 | 94.92 |
| Cs (L) | 4.00 | 0.63 |
| K (K) | 0.83 | 0.45 |
| In (L) | 2.17 | 0.40 |
| Cl (K) | 5.08 | 3.01 |
| Sb (L) | 0.80 | 0.14 |
| Mn (K) | 1.18 | 0.45 |

| Mn to Sb ratio | A ₁ (%) | τ_1 (ms) | A ₂ (%) | τ ₂ (ms) | $	au_{ave}$ (ms) |
|-------------------|--------------------|---------------|--------------------|---------------------|------------------|
| 8:1 | 0.248 | 2.558 | 0.721 | 15.813 | 15.114 |
| 12:1 | 0.265 | 1.062 | 0.651 | 14.522 | 14.134 |
| 16:1 | 0.294 | 3.689 | 0.621 | 16.155 | 14.941 |
| 20:1 | 0.388 | 1.310 | 0.533 | 14.759 | 13.944 |

Table S3. Bi-exponential fitting results of decay curves for Sb^{3+}/Mn^{2+} co-doped $Cs_2KInCl_6/PVDF$ composite films

Table S4. Comparison of optical properties of the other perovskite/polymer composite

 films by in situ stratety.

| Composite film | Color | PLQY (%) | Ref |
|--|--------|----------|-----------|
| MAPbBr ₃ /PVDF | green | 94.6 | 1 |
| CsPbBr ₃ /PVDF | green | 65 | 2 |
| Mn ²⁺ doped MAPbCl ₃ /PVDF | red | 22.8 | 3 |
| MAPbBr ₃ /pHEA | green | 11 | 4 |
| MAPbBr ₃ /PAN | green | 71 | 5 |
| MAPbBr ₃ /PVA | green | 95.3 | 6 |
| Cd ²⁺ doped FAPbBr ₃ /PVDF | green | 74.4 | 7 |
| Cs ₃ Cu ₂ I ₅ /PMMA | blue | 64 | 8 |
| Cs2Na0.8Ag0.2BiCl6/PMMA | orange | 21.52 | 9 |
| Sb ³⁺ /Mn ²⁺ co-doped | white | 86.98 | This work |
| Cs ₂ KInCl ₆ /PVDF | | | |



Fig. S1 The photograph of $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1 obtained by direct heating at 100°C under sunlight.



Fig. S2 SEM image of Cs₂KInCl₆/PVDF composite film with Mn to Sb ratio of 16:1 obtained by direct heating at 100°C.



Fig. S3 Transmission spectrum of pure PVDF film and composite films.



Fig. S4 PL spectra of different regions of the $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1.



Fig. S5 (a) Raman spectrum of pure PVDF film, undoped, Sb³⁺ doped and co-doped Cs₂KInCl₆/PVDF composite films. (b) Raman spectrum of pure PVDF film, undoped, Sb³⁺ doped and co-doped Cs₂KInCl₆/PVDF composite films at 50 and 400 cm⁻¹.



Fig. S6 SEM image of pure PVDF film.



Fig. S7 PLE spectra of $Cs_2KInCl_6/PVDF$ composite films with single Sb^{3+} doped and co-doped.



Fig. S8 (a) and (b). Absorption spectrum of pure PVDF film and $Cs_2KInCl_6/PVDF$ composite film.



Fig. S9 (a), (b) and (c). PL spectrum of pure PVDF film, $Cs_2KInCl_6/PVDF$ composite film and Mn^{2+} doped $Cs_2KInCl_6/PVDF$ composite film.



Fig. S10 PLQY of $Cs_2KInCl_6/PVDF$ composite films with different Sb content in precursor.



Fig. S11 PLQY of 0.5%Sb: Cs₂KInCl₆/PVDF composite film.



Fig. S12 PL intensity of $Cs_2KInCl_6/PVDF$ composite films with different Mn/Sb feeding ratio.



Fig. S13 PLQY of Cs₂KInCl₆/PVDF composite film with Mn to Sb ratio of 16:1.



Fig. S14 (a) Pseudo-color maps of temperature-dependent PL spectra of the Sb³⁺ doped Cs2KInCl6/PVDF composite film (λ_{ex} =320nm). And its corresponding (b) PL intensity versus 1/T and fitting results. (c) Fwhm versus temperature and the fitting results. (d) Schematic diagram of photophysical processes.



Fig. S15 (a) Stability of $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1 under heating. (b) Thermogravimetric analysis thermogram of $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1.



Fig. S16 Stability of $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1 under illumination.



Fig. S17 Variable excitation spectrum of $Cs_2KInCl_6/PVDF$ composite film with Mn to Sb ratio of 16:1

References

1. Q. C. Zhou, Z. L. Bai, W. G. Lu, Y. T. Wang, B. S. Zou and H. Z. Zhong, *Adv. Mater.*, 2016, **28**, 9163-+.

2. P. T. Liang, P. Zhang, A. Z. Pan, K. Yan, Y. S. Zhu, M. Y. Yang and L. He, *ACS Appl. Mater. Interfaces*, 2019, **11**, 22786-22793.

3. X. W. Bai, L. Q. Meng, N. Zhou, J. J. Zheng, X. F. Yu, P. K. Chu, J. J. Xiao, B. S. Zou and J. Li, *J. Colloid Interface Sci.*, 2022, **606**, 1163-1169.

4. D. R. Wang, Y. Q. Bao, J. J. Cui, L. F. Chao, L. Gu, W. Hui, Y. Shen, B. Zhang, Y. H. Chen and L. Song, *Adv. Funct. Mater.*, 2023, **33**, 10.

5. R. Cheng, Z. B. Liang, L. L. Zhu, H. Li, Y. Zhang, C. F. Wang and S. Chen, *Angew. Chem.-Int. Edit.*, 2022, **61**, 11.

6. H. Zhang, S. Cao, J. L. Jiang, Q. Sun, J. Z. Liu, D. L. Ou, J. L. Zhao, W. Y. Yang,
H. Fu and J. J. Zheng, *Chem. Eng. J.*, 2023, 462, 10.

7. J. Z. Liu, H. Fu, Z. T. Du, D. L. Ou, S. X. Li, Q. C. Chen, W. Y. Yang, J. L. Zhao and J. J. Zheng, *J. Mater. Chem. C*, 2022, **10**, 17512-17520.

 W. Zhou, X. D. Zhu, J. Yu, D. D. Mou, H. X. Li, L. Y. Kong, T. C. Lang, L. L. Peng,
 W. B. Chen, X. H. Xu and B. T. Liu, *ACS Appl. Mater. Interfaces*, 2023, 15, 38741-38749.

9. J. D. Shi, M. Q. Wang, C. Zhang, J. N. Wang, Y. Zhou, Y. L. Xu, N. V. Gaponenko and A. S. Bhatti, *ACS Appl. Mater. Interfaces*, 2023, **15**, 12383-12392.