Supporting Information

Achieving Unprecedented Power-Output in 4-Terminal Mirror-Symmetrical Printable Carbon $CsPbBr_3$ Solar Cells through Dual-Solvent Engineering

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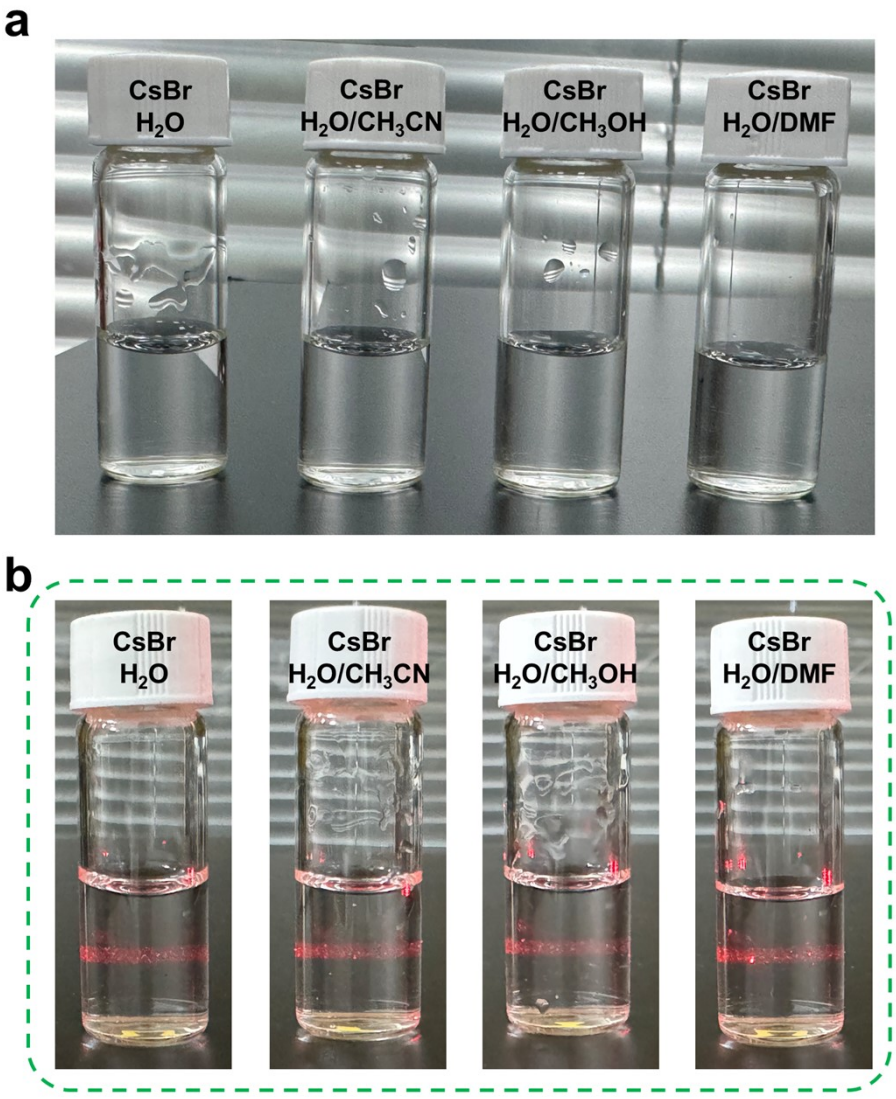

Figure S1. a) $CsBr/H_2O$ solutions containing H_2O, CH_3CN, CH_3OH, and DMF. b) Tyndall effect of CsBr solution.

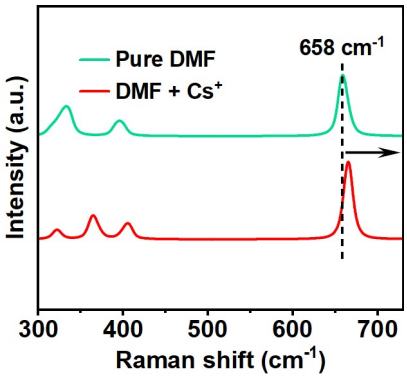

Figure S2. Raman spectrum of the interaction between Cs^+ and DMF obtained by DFT calculations.

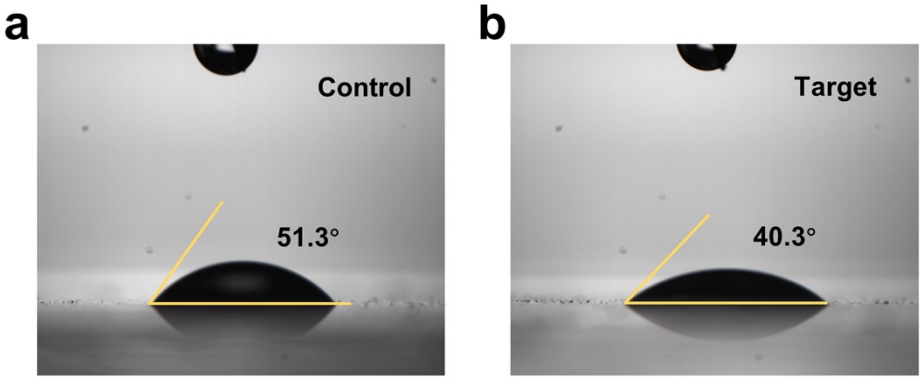

Figure S3. Contact angle test a) Control, b) Target.

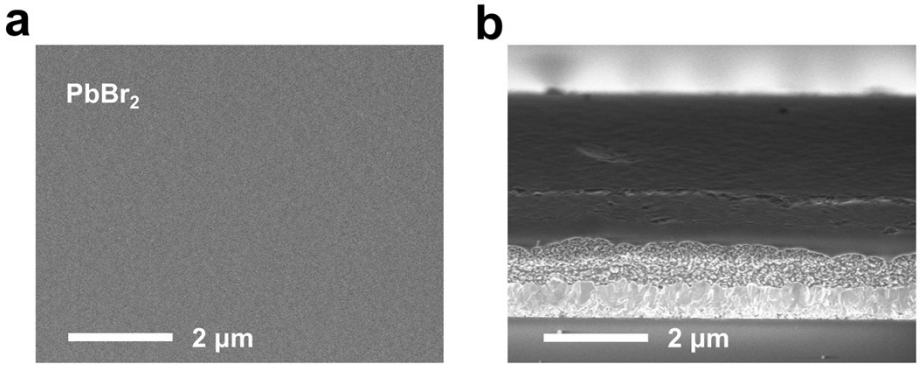

Figure S4. $PbBr_2$ film a) Surface, b) Cross-section.

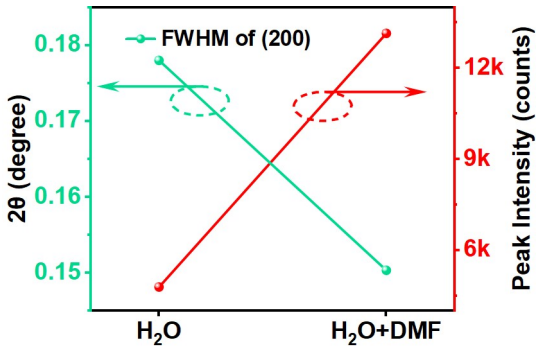

Figure S5. FWHM and intensity of the (200) diffraction peak of $CsPbBr_3$ film.

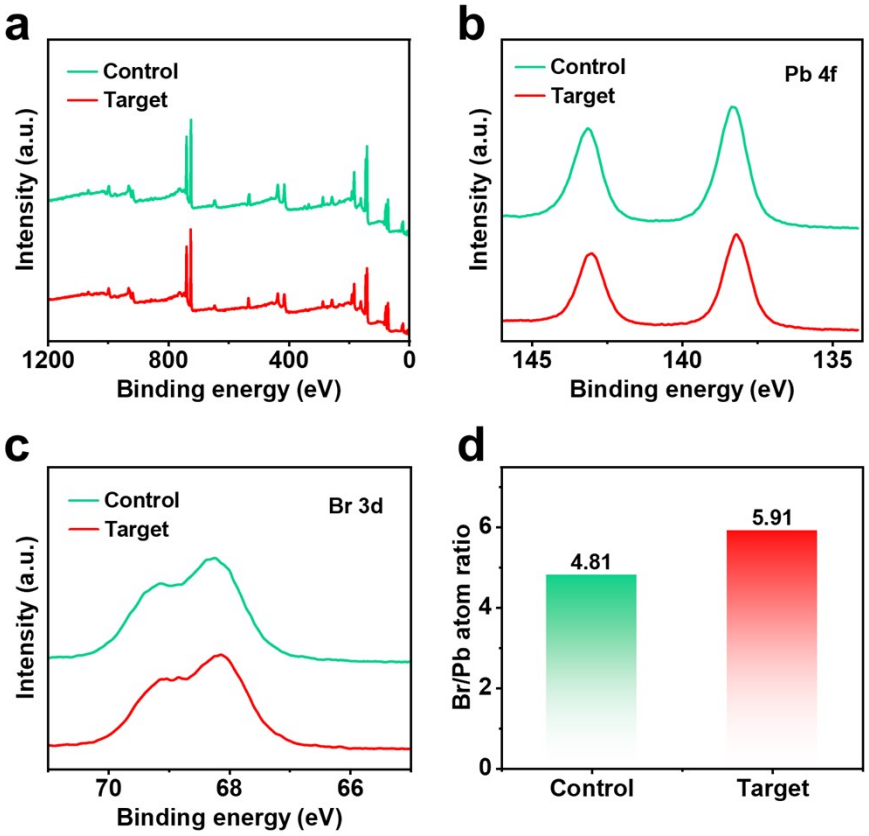

Figure S6. XPS spectra of Control and Target perovskite films: a) Full spectrum, b) Pb 4f, c) Br 3d, d) Br/Pb ratio.

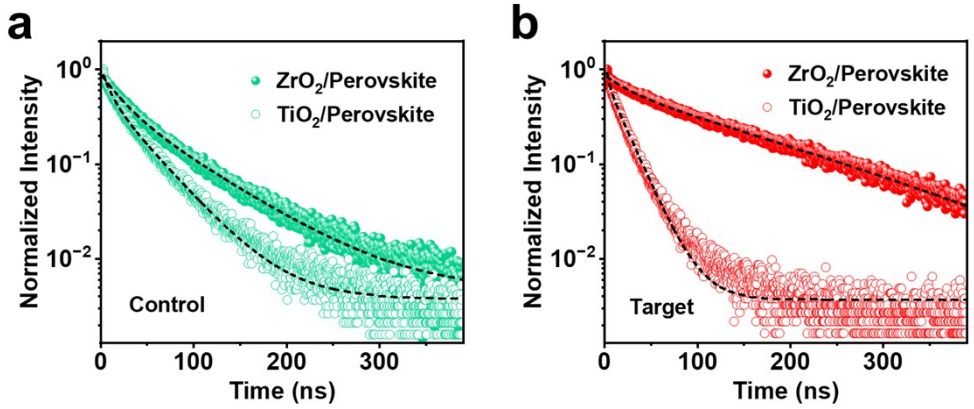

Figure S7. a) Time-resolved photoluminescence (TRPL) curve of Control and b) Target perovskite films.

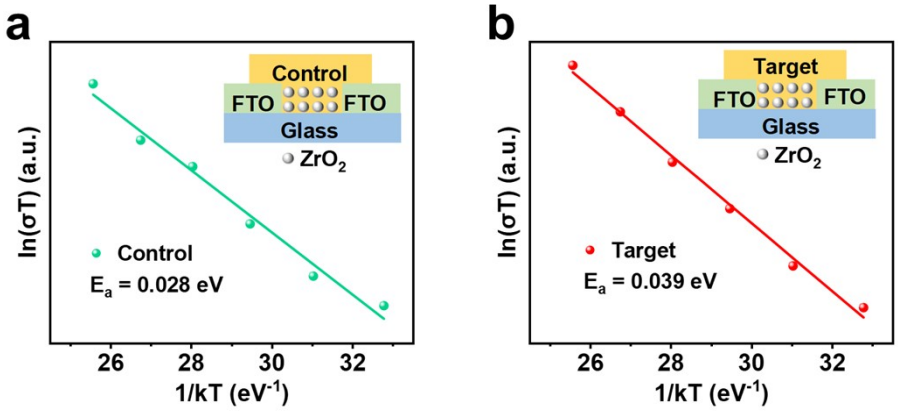

Figure S8. a) Temperature-dependent conductivity of Control and b) Target perovskite films.

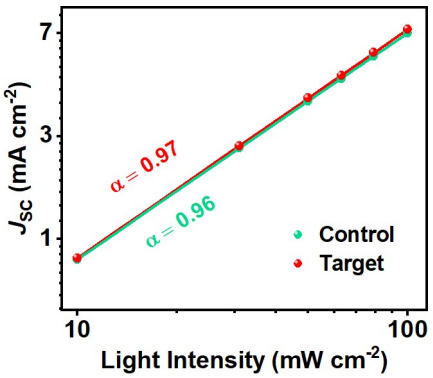

Figure S9. The relationship between the short-circuit current density (J_{SC}) of perovskite devices and light intensity.

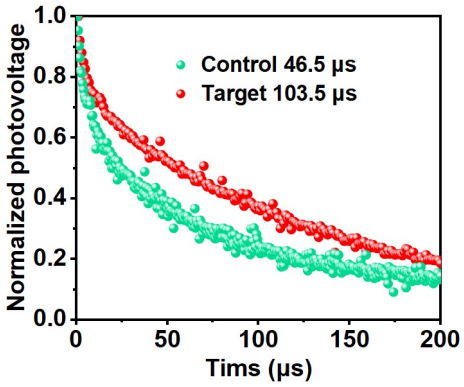

Figure S10. Transient photovoltage curve of perovskite devices.

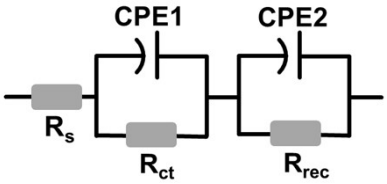

Figure S11. Equivalent circuit diagram of the EIS curve.

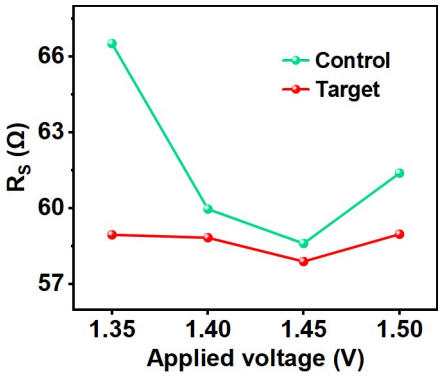

Figure S12. R_S values of Control and Target under different biases.

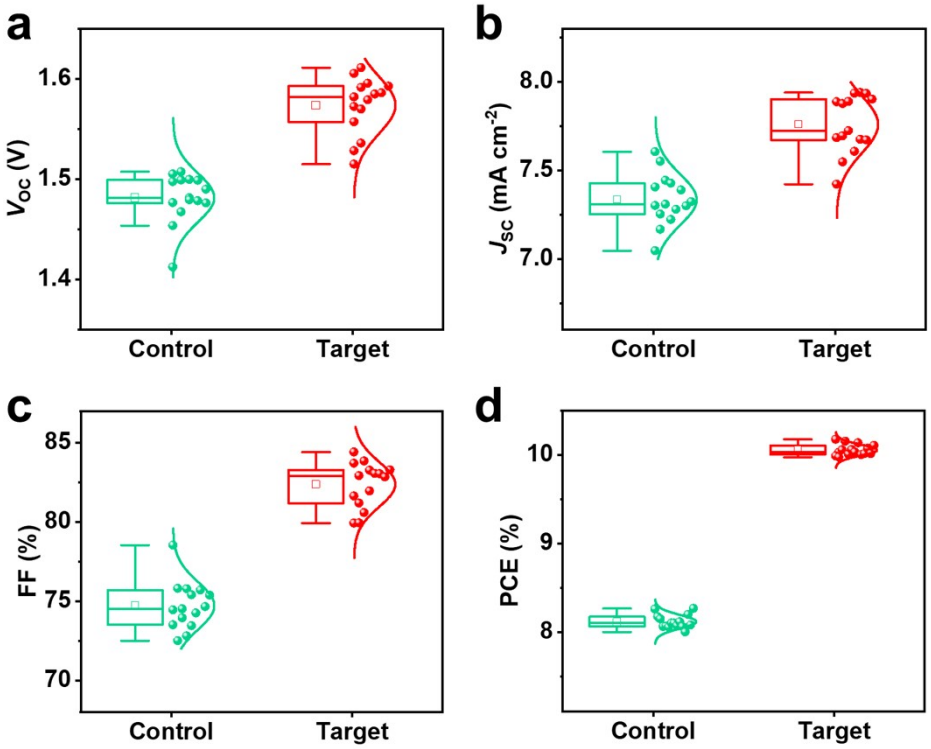

Figure S13. Statistical distribution of a) V_{OC}, b) J_{SC}, c) FF, and d) PCE of 15 cell devices each for Control and Target groups.

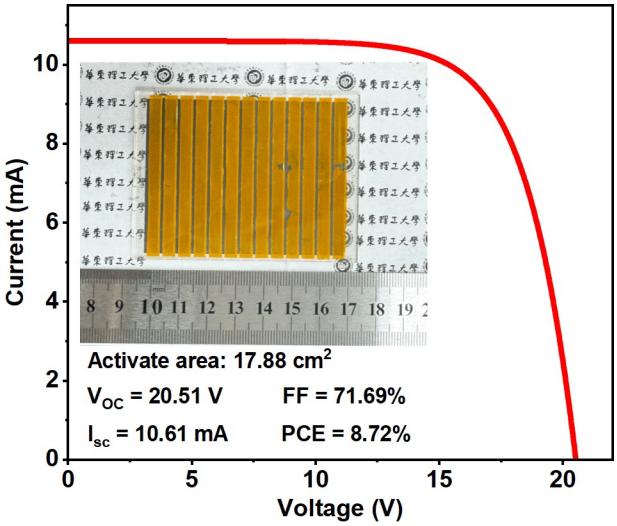

Figure S14. *J-V* curve of large-area devices.

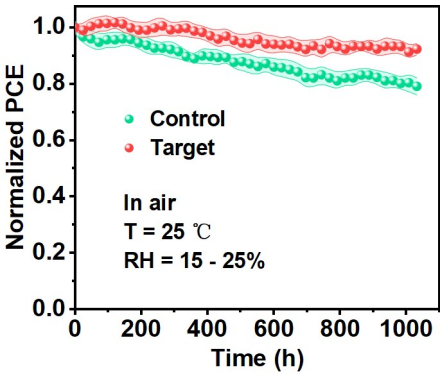

Figure S15. Stability of p-MPSC devices at 25°C.

Table S1. Values of DN and ε for different solvents.

Solvent	Dielectric constant	Donor number
H_2O	80.1	18.0
CH_3CN	37.5	14.1
CH_3OH	32.7	19.9
DMF	36.7	26.6

Table S2. Detailed parameters for fitting the TRPL curve of the perovskite film.

	A_1	τ_1 (ns)	A_2	τ_2	τ_{ave}	R^2
ZrO_2-Target	0.2471	23.76	0.6325	144.86	137.57	0.996
TiO_2-Target	0.576	3.24	0.7936	19.38	17.63	0.997
ZrO_2-Control	0.4528	21.07	0.4527	68.45	57.30	0.997
TiO_2-Control	0.4791	9.53	0.5595	39.30	34.18	0.997

Table S3. Fitting parameters of the device's EIS.

	Applied voltage (V)	R_S (Ω)	R_{ct} (Ω)	high f C (F)	R_{rec} (Ω)	low f C (F)
Target	1.35	58.96	23.40	9.14×10^{-9}	1097.00	2.85×10^{-8}
	1.40	58.84	23.00	1.11×10^{-8}	357.50	4.88×10^{-8}
	1.45	57.91	21.64	1.31×10^{-8}	131.30	1.04×10^{-7}
	1.50	58.99	16.50	1.80×10^{-8}	59.50	2.13×10^{-7}
Control	1.35	66.51	51.28	3.87×10^{-9}	740.80	3.09×10^{-8}
	1.40	59.98	55.40	2.83×10^{-9}	251.50	6.43×10^{-8}
	1.45	58.62	49.89	2.61×10^{-9}	103.60	1.43×10^{-7}
	1.50	61.4	41.02	3.20×10^{-9}	53.14	2.77×10^{-7}

Table S4. Photovoltaic performance parameters of Control and Target devices.

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	HI
Control Reverse Scan	1.50	7.41	74.46	8.26	2.30%
Control Forward Scan	1.49	7.43	73.10	8.07	
Target Reverse Scan	1.58	7.69	83.70	10.18	1.87%
Target Forward Scan	1.58	7.65	82.74	9.99	

Table S5. Photovoltaic performance in different CsBr solvents.

CsBr solution	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
H_2O	1.50	7.41	74.46	8.26
CH_3CN	1.35	4.59	63.73	3.94
CH_3CN/H_2O 0.5/9.5 (V/V)	1.50	7.14	81.96	8.77
CH_3CN/H_2O 1/9 (V/V)	1.50	7.23	81.51	8.86
CH_3CN/H_2O 2/8 (V/V)	1.51	7.08	80.32	8.62
CH_3OH	1.29	4.78	50.59	3.12
CH_3OH/H_2O 0.5/9.5 (V/V)	1.52	7.62	80.80	9.33
CH_3OH/H_2O 1/9 (V/V)	1.54	7.72	80.32	9.53
CH_3OH/H_2O 2/8 (V/V)	1.50	7.51	79.39	8.96
DMF	1.30	5.32	49.24	3.40
DMF/H_2O 0.5/9.5 (V/V)	1.59	7.70	80.55	9.83
DMF/H_2O 1/9 (V/V)	1.58	7.69	83.70	10.18
DMF/H_2O 2/8 (V/V)	1.53	7.39	80.85	9.13

Using the double exponential decay equation (Equation 1) to fit the TRPL curve in Figure S7, the carrier lifetimes τ_1 and τ_2 of the non-radiative recombination and radiative recombination processes of perovskite are obtained. Then the average carrier lifetime (τ_{ave}) is calculated with the help of Equation (2).[S1]

$$Y = A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right) + y_0 \quad (1)$$

$$\tau_{ave} = \frac{A_1{\tau_1}^2 + A_2{\tau_2}^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

Where A_1 and A_2 represent the relative amplitudes of τ_1 and τ_2, and y_0 is the offset constant of the baseline.

SCLC testing trap density (N_t) calculation Equation (3):

$$N_t = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{qL^2} \quad (3)$$

In this equation, q is the elementary charge, L is the thickness of the perovskite film, ε is the relative dielectric constant (according to the literature, the value of ε for $CsPbBr_3$ is 22 [S2]), and ε_0 is the vacuum permittivity.

tDOS testing curve fitting Equation (4).[S3]

$$N_t(E_\omega) = -\frac{V_{bi}\, dC\ \omega}{qWd\omega k_B T} \quad (4)$$

Here, ω is the angular frequency, K_B is the Boltzmann constant, T is the temperature, E_ω is the level depth, C is the capacitance, q is the elementary charge, V_{bi}, and W are the built-in potential and semiconductor depletion layer width obtained from the Mott-Schottky test, and E_ω can be obtained through Equation (5).

$$E_\omega = K_B T \times In\frac{2\beta_\rho N_V}{\omega} \quad (5)$$

Here, β_ρ is the hole capture coefficient, and N_V is the effective density of states at the valence band maximum.

The Gaussian16 software was used to perform density functional theory (DFT) calculations using the B3LYP method for H_2O, acetonitrile (CH_3CN), methanol, and N, N-dimethylformamide (DMF), where the 6-311+G(D) basis set was selected for C, H, O, and N calculations. The pseudopotential basis set LanL2DZ was used for cesium calculations, and the results were visualized using GAUSS VIEW.

REFERENCES

[S1] Z. Wu, Z. Liu, Z. Hu, Z. Hawash, L. Qiu, Y. Jiang, L. K. Ono and Y. Qi, *Adv. Mater.*, 2019, **31**, 1804284.

[S2] M. I. Saidaminov, M. A. Haque, J. Almutlaq, S. Sarmah, X.-H. Miao, R. Begum, A. A. Zhumekenov, I. Dursun, N. Cho, B. Murali, O. F. Mohammed, T. Wu and O. M. Bakr, *Adv. Opt. Mater.*, 2017, **5**, 1600704.

[S3] M. Wang, Y. Yin, W. Cai, J. Liu, Y. Han, Y. Feng, Q. Dong, Y. Wang, J. Bian and Y. Shi, *Adv. Funct. Mater.*, 2022, **32**, 2108567.