

Supporting Information

**Anti-Counterfeiting Quick Response Code with Emission Color of
Invisible Metal-Organic Frameworks as Encoding Information**

Yong-Mei Wang[†], Xue-Tao Tian[†], Hui Zhang[†], Zhong-Rui Yang[†], Xue-Bo Yin^{*,†,§}

[†]State Key Laboratory of Medicinal Chemical Biology and Tianjin Key Laboratory of Biosensing and Molecular Recognition, College of Chemistry, Nankai University, Tianjin, 300071, China

[§]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China

^{*}E-mail: xbyin@nankai.edu.cn; [Fax: +86-22-23503034](tel:+86-22-23503034)

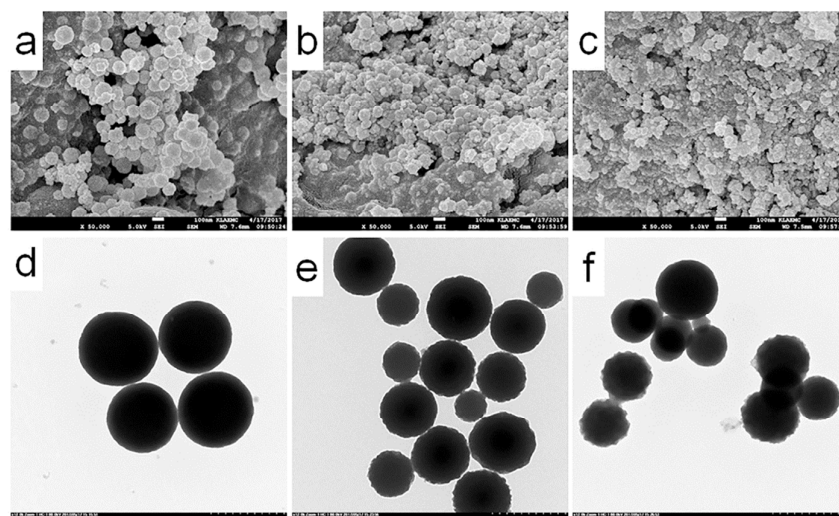


Figure S1. Ln-MOFs synthesized with (a) 5-bop and Eu^{3+} , (b) 5-bop and Tb^{3+} , (c) 5-bop and Dy^{3+} , (d) 1,3- H_2BDC and Eu^{3+} , (e) 1,3- H_2BDC and Tb^{3+} , (f) 1,3- H_2BDC and Dy^{3+} .

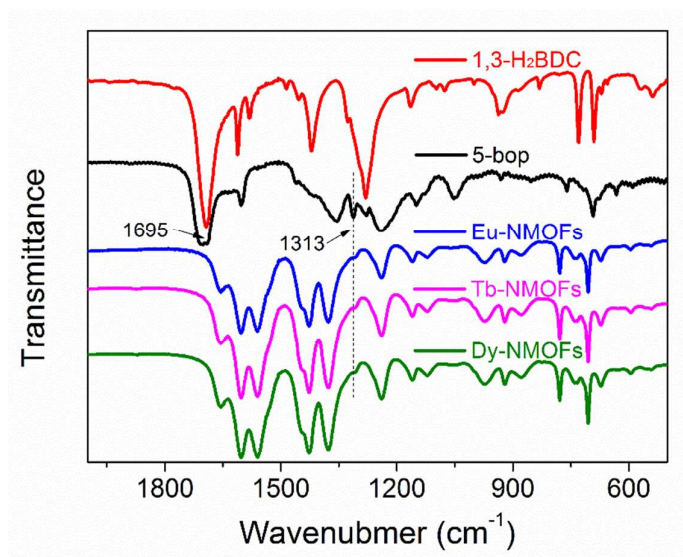


Figure S2. Fourier transform infrared spectra (FTIR) of 1,3- H_2BDC , 5-bop, and Ln-MOFs.

Table S1. Crystallographic data collection and refinement of Eu-SMOFs.

Compound	Eu-SMOFs
Chemical formula	C ₂₄ H ₁₆ Eu ₂ O ₁₄
Formula mass	832.29 g/mol
Crystal system	Monoclinic
Space group	p 21/n
Unit cell dimensions	a = 13.320(3) Å, α = 90.000° b = 14.481(3) Å, β = 104.377(4)° c = 13.459(3) Å, γ = 90.000°
Cell Volume	2514.8 (8) Å ³
Z	4
Temperature	113(2) K
Wavelength	0.17073 Å
Crystal size	0.12 × 0.18 × 0.2 mm ³
Calculated Density	2.19817 g/cm ⁻³
F(000)	1592.0
Absorption coefficient	5.017 mm ⁻¹
R (int)	0.030
Goodness of fit on F ²	1.0070
Limiting indices	-17 ≤ h ≤ 17, -18 ≤ k ≤ 17, -17 ≤ l ≤ 17
Final R indices I>2σ(I)	R 1a = 0.0377, wR 2b = 0.0780
R indices (all data)	R 1 = 0.0477, wR 2 = 0.0842

Table S2. Crystallographic data collection and refinement of Tb-SMOFs.

Compound	Tb-SMOFs
Chemical formula	C ₂₄ H ₁₈ Tb ₂ O ₁₅
Formula mass	864.22g/mol
Crystal system	Monoclinic
Space group	p 21/n
Unit cell dimensions	a = 10.537(2) Å, α = 90.000° b = 14.162(3) Å, β = 97.364(5)° c = 16.923(3) Å, γ = 90.000°
Cell Volume	2506.3(9)Å ³
Z	4
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal size	0.12 × 0.18 × 0.2 mm ³
Calculated Density	2.290 g/cm ⁻³
F(000)	1648
Absorption coefficient	5.678 mm ⁻¹
R (int)	0.0386
Goodness of fit on F ²	0.984
Limiting indices	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Final R indices I>2sigma(I)	R 1a = 0.0175, wR 2b = 0.0368
R indices (all data)	R 1 = 0.0151, wR 2 = 0.0363

Table S3. Crystallographic data collection and refinement of Dy-SMOFs.

Compound	Dy-SMOFs
Chemical formula	C ₄₈ H ₃₆ Dy ₄ O ₃₀
Formula mass	1742.77 g/mol
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 10.5772(19) Å α = 90 °. b = 14.206(3) Å β = 97.363(7) °. c = 16.976(4) Å γ = 90 °.
Cell Volume	2529.7(9) Å ³
Z	2
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal size	0.18 x 0.10 x 0.10 mm
Calculated Density	2.288 g/m ³
F(000)	1656
Absorption coefficient	5.941 mm ⁻¹
R (int)	0.0293
Goodness of fit on F ²	1.015
Limiting indices	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -22 ≤ l ≤ 21
Final R indices I>2σ(I)	R1 = 0.0114, wR2 = 0.0285
R indices (all data)	R1 = 0.0131, wR2 = 0.0288

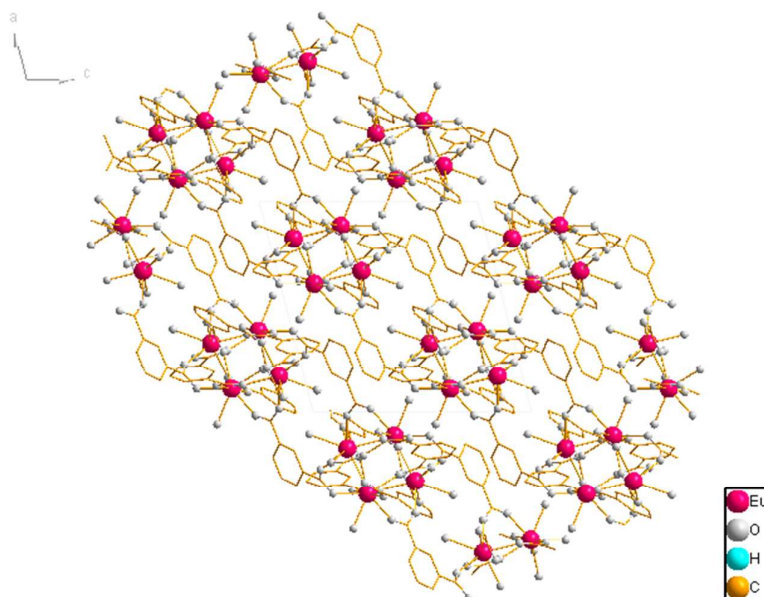


Figure S3. The 3D framework structure of Eu-SMOFs.

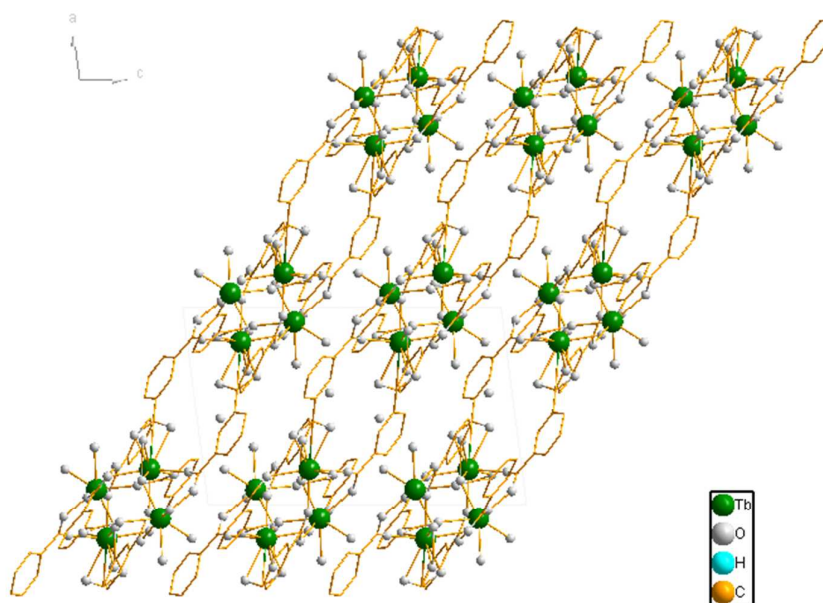


Figure S4. The 3D framework structure of Tb-SMOFs.

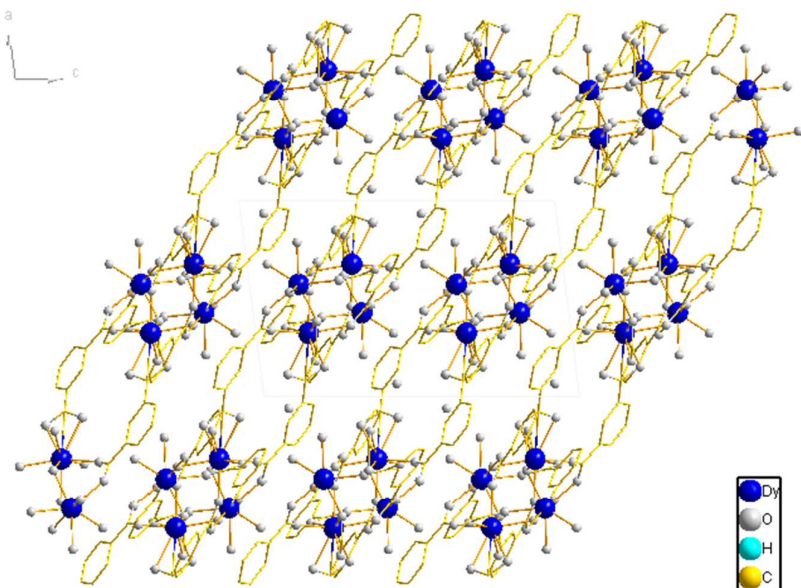


Figure S5. The 3D framework structure of Dy-SMOFs.

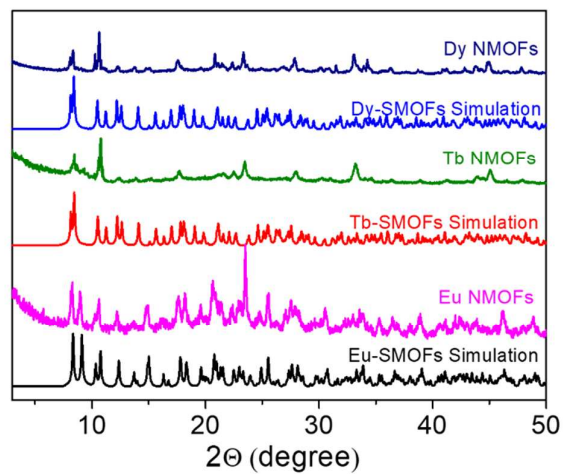


Figure S6. The powder diffraction pattern (PXRD) comparison of the nanosized Ln-NMOFs and simulation from $\text{Eu}_2(1,3\text{-H}_2\text{BDC})_3(\text{H}_2\text{O})_2$, $\text{Tb}_2(1,3\text{-H}_2\text{BDC})_3(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ and $\text{Dy}_4(1,3\text{-H}_2\text{BDC})_6(\text{H}_2\text{O})_4 \cdot (\text{H}_2\text{O})_2$ of CIF.

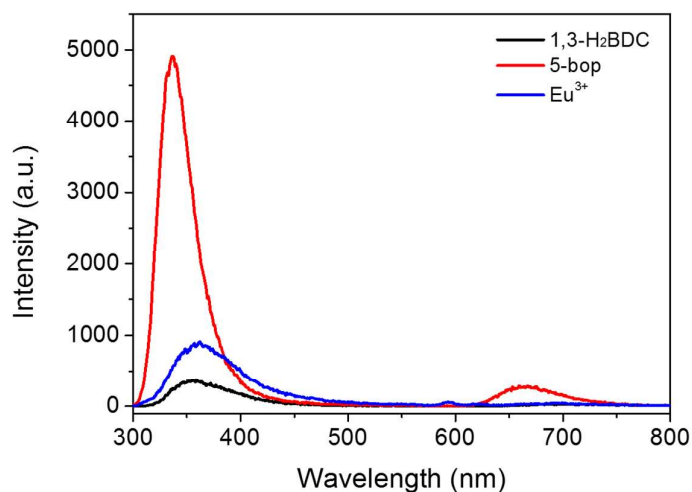


Figure S7. The fluorescence spectra of 1,3-H₂BDC, 5-bop and Eu³⁺.

Table S4. The energy level S₁ and T₁ of 5-bop and 1,3-H₂BDC.

	S ₁ (cm ⁻¹)	T ₁ (cm ⁻¹)	Energy gap between T ₁ and Ln ³⁺ ions (cm ⁻¹)		
			Eu ³⁺ ⁵ D ₀ , 18674 cm ⁻¹	Tb ³⁺ ⁵ D ₄ , 20500 cm ⁻¹	Dy ³⁺ ⁴ F _{2/9} , 22000 cm ⁻¹
5-bop	35335	23923	5249	3423	1923
1,3-H ₂ BDC	35714	22831	4157	2331	831

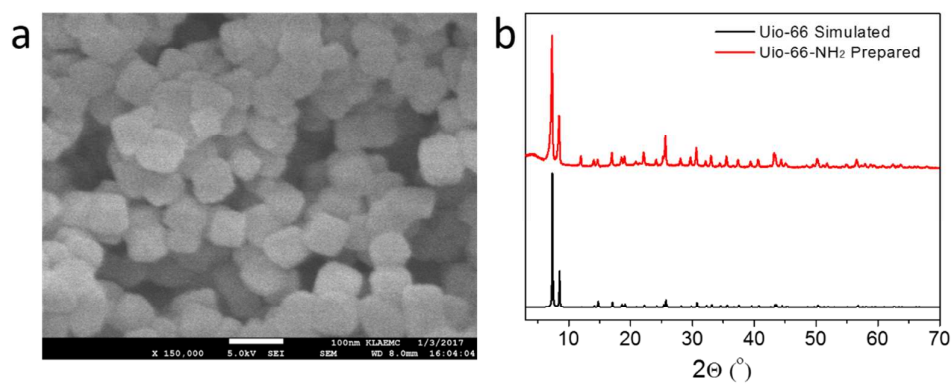


Figure S8. (a) Scanning electron microscope (SEM) image of Uio-66-NH₂. (b) The powder diffraction pattern (PXRD) comparison of the nanoscale Uio-66-NH₂ and simulation from Uio-66 of CIF.

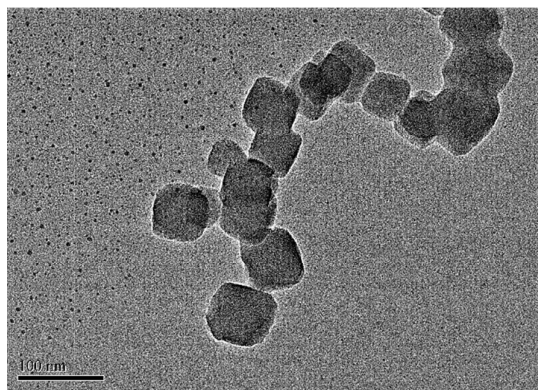


Figure S9. The TEM image of prepared UiO-66-NH₂.

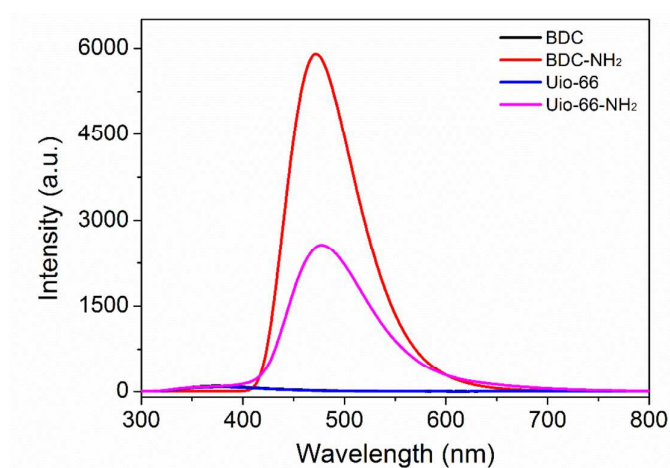


Figure S10. The fluorescence spectra of BDC, BDC-NH₂, and UiO-66-NH₂.

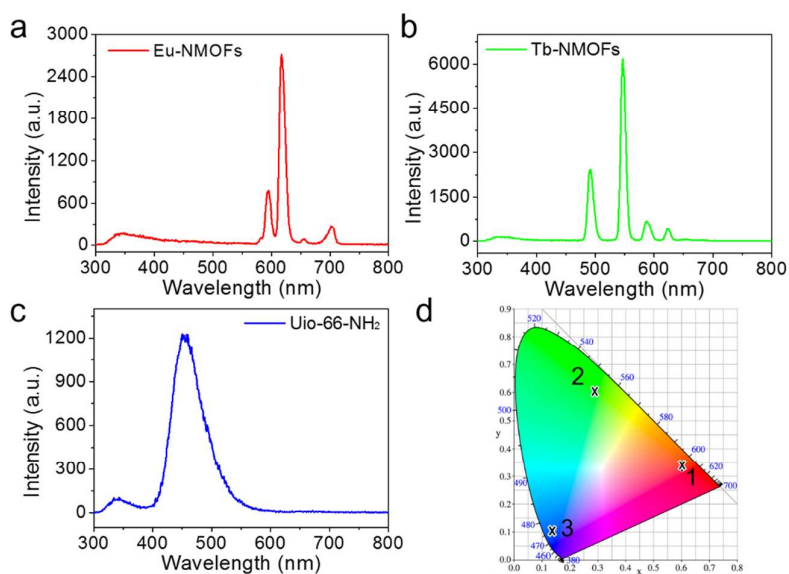


Figure S11. Luminescence spectrum of (a) Eu-NMOFs, (b) Tb-NMOFs, (c) UiO-66-NH₂ under 275 nm excitation, and (d) CIE chromaticity coordinates for luminescence of (1) Eu-NMOFs, (2) Tb-NMOFs, (3) UiO-66-NH₂.

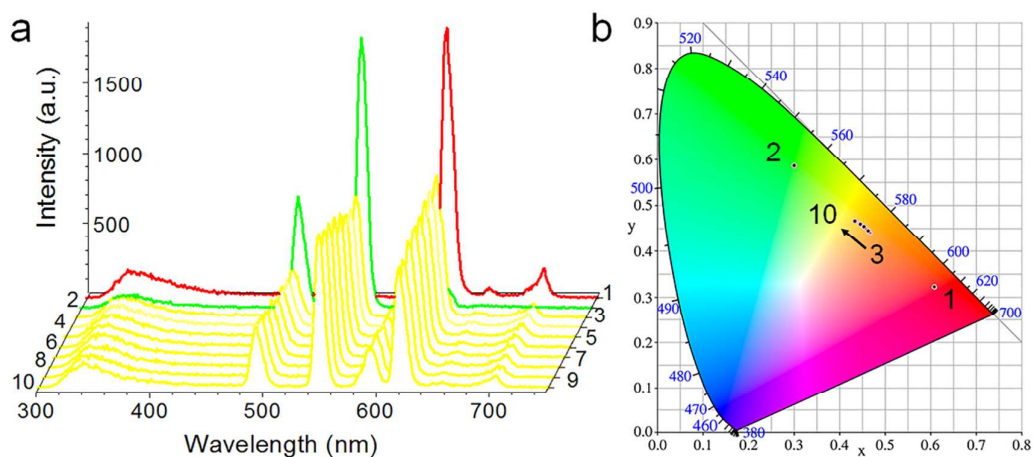


Figure S12. (a) Luminescence spectra of physically mixed Eu-NMOFs and Tb-NMOFs physically mixed with ratio of (1) 1:0, (2) 0:1, (3) 1:1, (4) 1:1.001, (5) 1:1.01, (6) 1:1.1, (7) 1:2, (8) 1:1.3, (9) 1:1.4, and (10) 1:1.5 under the excitation at 275-nm; (b) CIE chromaticity coordinates of the emissions of the mixed NMOFs. The labels from “1” to “10” corresponding to the samples listed in a.



Figure S13. Image of the printed acronym of ‘Nankai University’ with the invisible RGB-emitting NMOF inks on paper under 275 nm UV light.

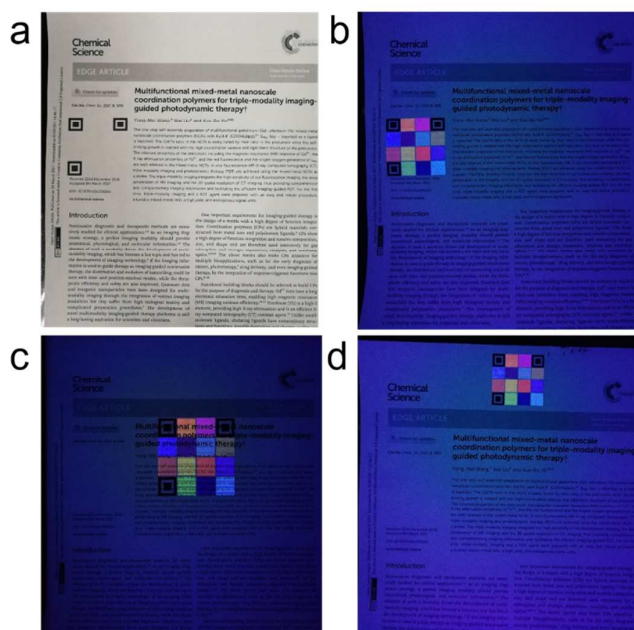


Figure S14. Images of the printed 4*4 QR code on a piece of paper with printed documents under (a) daylight and (b-d) 275 nm UV light.

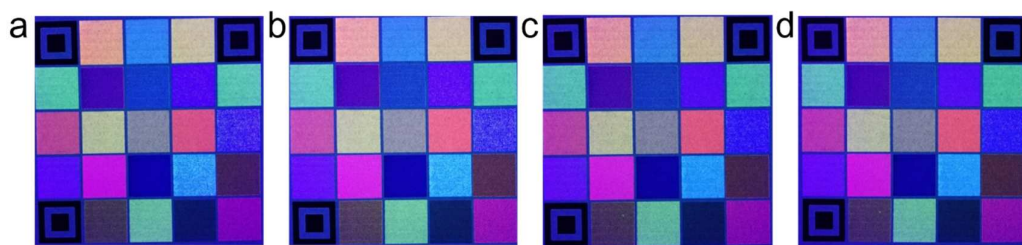


Figure S15. Images of the printed QR code patterns photographed (a) instantly, (b) one day, (c) one week, and (d) one month after printing under 275 nm UV light.