Supplementary Information

for

Highly luminescent silver-based MOFs: Scalable eco-friendly synthesis paving the way for photonics sensors and electroluminescent devices

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Scheme S1. Schematic representation of the (A) binuclear Ag₂(BDC)₂ building units (CCDC 198096) [1] and (B) the interweaved 2D layers giving rise to the dense 3D framework of OX-2 MOF.



Figure S1. FTIR spectra of $OX-2_m$ (black line), $OX-2_{m:1/2}$ (red line), $OX-2_{DMF}$ (blue line) and $OX-2_w$ (green line).



Figure S2. FESEM micrographs of (A) $OX-2_m$ and (B) $OX-2_{DMF}$ MOFs.



Figure S3. (A-B) AFM topography images of the elongated nanoplates of $OX-2_w$. (C-D) Thickness profiles of the $OX-2_w$ elongated nanoplates obtained from the AFM image in (A) and (B) respectively, showing a thickness of tens of nm.



Figure S4. FESEM-EDX micrographs of (A-C) $OX-2_{m:1/2}$ and (D-F) $OX-2_w$, showing the "flower" shaped crystals and the homogeneously distributed elongated nanoplates, respectively.



Table S1. Representation of the %weight and %at>omic of C, Ag and O elements estimated from the EDX maps corresponding to the FESEM micrographs.

Materials (micrograph)	Element	% weight	% atomic	
OV 2	С	23	41	
OA-2m:1/2	Ag	5	1	
Figures 2 E-G	0	5	6	
$OX-2_{m:1/2}$	С	33	52	
Micron-sized "columns"	Ag	0.43	0.08	
Figures 2 H-J	0	3.5	4	
OX-2 _{m:1/2}	С	16	30	
"Flower"-shaped crystals	Ag	5	1	
Figures S4 A-C	0	4	6	
	C	40		
OX-2w	C	40	66	
Elongated nanoplates	Ag	22	4	
Figures S4 D-F	0	6	8	

Figure S5. Nanosecond-picosecond emission decays of (A) BDC linker, (B) $OX-2_{DMF}$, (C) $OX-2_m$, (D) $OX-2_{m:1/2}$ and (E) $OX-2_w$ in solid-state. The observation wavelengths are indicated as inset and the samples were excited at 365 nm. The solid lines are from the best-fit using a multiexponential function.



Table S2. Values of time constants (τ_i), pre-exponential factors (a_i) and normalized (to 100) fractional contributions ($c_i = \tau_i a_i$) obtained from the fit of the emission decays of the BDC linker in solid-state upon excitation at 365 nm and for the observation wavelength (λ obs) indicated.

Sample	λ obs / nm	τ_1 / ns	a ₁	c ₁	τ_2 / ns	a ₂	c ₂	τ_3 / ns	a 3	c ₃
	485	1.7	0.080	41	4.2	0.037	46	16.5	0.002	12
BDC	520	1.7	0.074	35	4.2	0.042	49	16.5	0.004	16
	560	1.7	0.069	32	4.2	0.044	50	16.5	0.004	18

Table S3. Values of time constants (τ_i), pre-exponential factors (a_i), and normalized (to 100) fractional contributions ($c_i = \tau_i a_i$) obtained from the fit of the emission decays of OX-2_m, OX-2_{m:1/2}, OX-2_{DMF} and OX-2_w in solid-state upon excitation at 365 nm and observation as indicated.

Sample	λ obs / nm	$ au_1$ / ps	a ₁	c ₁	τ_2 / ns	a ₂	c ₂
	485	540	0.151	73	3.4	0.09	27
OX-2 _m	520	540	0.098	57	3.4	0.012	43
	560	540	0.080	42	3.4	0.017	58
	485	350	0.103	67	2.0	0.009	33
OX-2 _{m:1/2}	520	350	0.094	54	2.0	0.014	46
	560	350	0.090	52	2.0	0.014	48
	485	540	0.049	61	3.0	0.006	39
OX-2 _{DMF}	520	540	0.051	61	3.0	0.006	39
	560	540	0.048	57	3.0	0.006	43
OX-2 _w	485	540	0.126	58	3.5	0.014	42
	520	540	0.066	44	3.5	0.013	56
	560	540	0.047	32	3.5	0.016	68

Figure S6. Comparison of the PXRD patterns of the $[Ag-(BDC)_{1/2}]_n$ reported [1] and those of OX-2_w MOFs obtained through a small scale synthesis (hundreds of mg) and a scale-up synthesis (10 g).





Figure S7. Excitation-emission map of the OX-2_w obtained through our scale-up method.

Figure S8. PXRD patterns of $OX-2_w$ after being soaked in water for different time intervals, ranging from 1 to 21 days.



Figure S9. PXRD patterns of OX- 2_w MOF as-synthetized and after being exposed to ambient conditions in the lab (day light, ~40% humidity, etc) for 70 days.



Figure S10. Emission of spectra of OX- 2_w MOF before and after being exposed to ambient conditions in the laboratory (day light, ~40% humidity, etc) for up to 70 days. The inset shows a minimal decrease in the quantum yield values from 60% to 57%.



Figure S11. (A-B) PXRD patterns and emission spectra of OX-2 pellets compressed at different pressures for the second time. (C-D) PXRD patterns and emission spectra of OX-2 powders obtaining by grinding the former pellets.





Figure S12. Deconvoluted electroluminescence spectra and their fits of the (A) OX-2 and (B) OX-2 / PVK LED devices at different applied voltages (indicated as inset).

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Leaching Experiments

To test the chemical stability of $OX-2_w$, we have performed leaching experiments in order to quantify the amount of BDC linkers being released from the framework over time. To this end, we have poured 500 mg of $OX-2_w$ in 30 mL of water for a few days. During those days, the UV-vis absorption spectra of some aliquots of the supernatant were recorded to estimate the amount of BDC linker released into the solution.

As a reference and for comparing the chemical decomposition of $OX-2_w$, we have prepared a solution of 11 mg of BDC linker in 30 mL of water which corresponds to a 5% decomposition of the MOF. This calculation was made by taking into account the following steps:

• The chemical formula of OX-2 MOF is $[Ag_2BDC]_n$, which gives a total molecular weight of 380 g/mol. From there, 216 g/mol (56%) corresponds to Ag_2 atoms, while 164 g/mol (44%) to the BDC linker.

• This means that in the prepared solution (500 mg of OX-2 in 30mL water), 220 mg of BDC molecules (500 mg x 0.44) would be released if the MOF completely degraded.

• Therefore, for an estimated MOF decomposition of 5%, a solution of 11 mg of BDC linker was dissolved in 30 mL of water.

The UV-vis absorption spectra of the different aliquots of the supernatant collected from the OX-2_w suspension over time (see Figure S13) compared to the absorption of the prepared BDC solution (simulating a 5% decomposition) is ~45 times lower, the data reveal that the degradation of OX-2_w in water is negligible ($\leq 0.1\%$) over this time.

Figure S13. Absorption spectra of the BDC solution prepared for simulating a 5% of MOF degradation and the different aliquots of the supernatant collected over time from a suspension of 500 mg of OX-2 in 30 mL of water.



Reference:

[1] D. Sun; Cao, R.; Bi, W.; Weng, J.; Hong, M.; Liang, Y., Inorg. Chim. Acta 357 (2004) 991-1001.