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SUPPORTING INFORMATION

Improving LMOF Luminescence Quantum Yield through Guest-Mediated Rigidification

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S1. LMOF-263 single crystal data

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically, then constrained and refined using a riding model. Displacement parameter restraints were used in the modeling of the disorder in the bipyridine ligand. Once the modelling of the framework was complete attempts were made to locate the solvent molecules (DMA) and water. However, no meaningful molecules could be found in the difference map, so SQUEEZE was used. SQUEEZE reported Solvent Accessible Volume of 2361 Å3, and Electrons Found in S.A.V. to be 570. This number of electrons would equate to around 12 DMA molecules. As this was approximated from x-ray data and could be partially due to the presence of water, the 12 DMA have not been included in the chemical formula.

Table S1. Single crystal data for LMOF-263 at 100 K

Compound	LMOF-263
Formula	$C_{64}H_{40}N_2O_8Zn_2$
M	1002.07
Crystal system	Triclinic
Space group	P -1
a/Å	13.9511(6)
b/Å	16.5329(7)
c/Å	20.1599(9)
α/o	89.937(3)
β/o	82.221(2)
γ/o	88.827(2)
V, Å^3	4606.16(35)
Z	2
Temperature (K)	100
λ(radiation wavelength) Å	0.7749
D, g/cm^3	0.722459
Reflections collected	39877
R1[a] [I > 2σ(*I*)]	0.0607
wR2[b] [I > 2σ(*I*)]	0.1779
Goodness-of-fit	0.983
CCDC No.	1947629

[a] $R1 = \sum|F_o - F_c| / \sum|F_o|$

[b] $wR2 = \sum[w(F_o^2 - F_c^2)^2] / w(F_o^2)^2]^{1/2}$

S2. Photoluminescence data

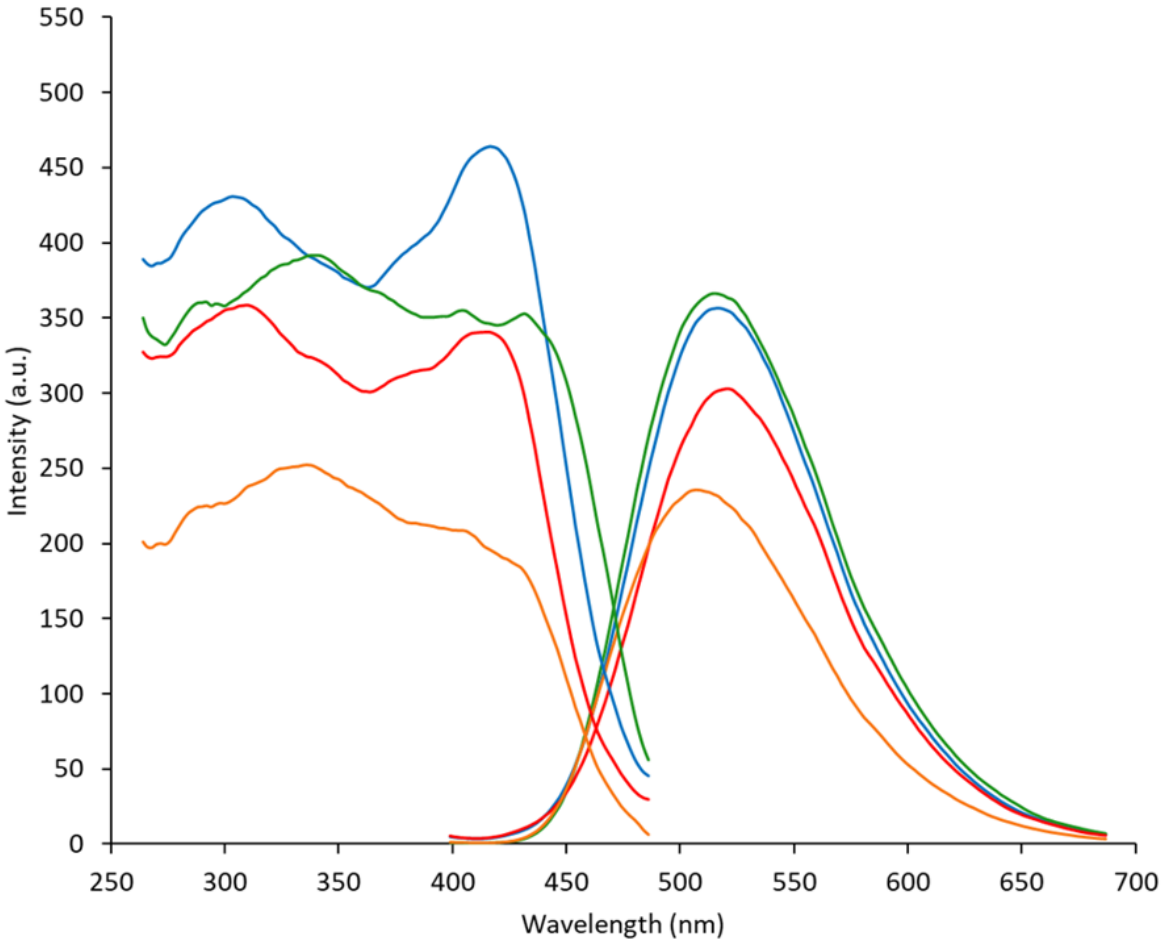

Figure S1. Excitation (left) and emission (right) spectra of outgassed LMOF-236 (blue), outgassed LMOF-301 (red), pentane-solvated LMOF-236 (green), and pentane-solvated LMOF-301 (gold). Excitation spectra were monitored at 520 nm emission, and emission spectra were collected under 455 nm excitation.

Table S2. Ligand quantum yield data

S3. Thermogravimetric analysis

All thermogravimetric analysis data was collected using a TA Instruments Q5000 TGA. Samples were loaded into a Pt pan and heated under a constant dry N2 flow of 20 mL/min. The temperature was gradually increased from ambient to 600 °C at a constant rate of 10 °C/min.

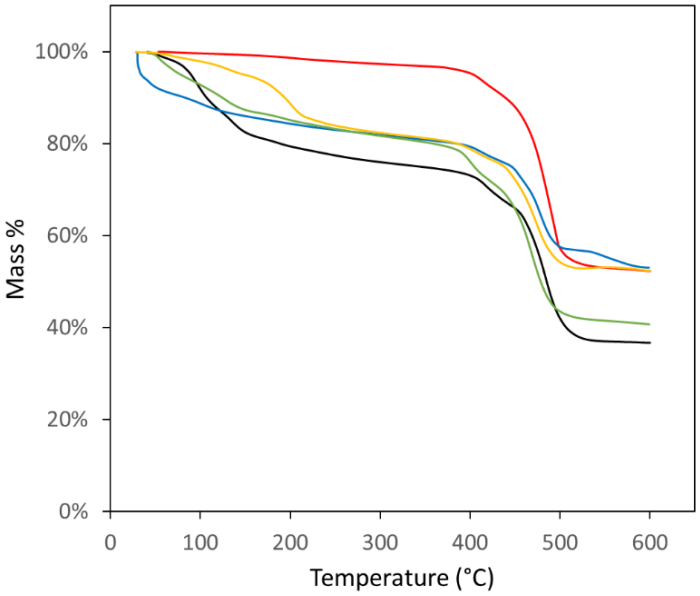

Figure S2. Thermogravimetric analysis data for LMOF-236 as made (black), outgassed (red), pentane-loaded (blue), cyclohexane-loaded (green), n-dodecane-loaded (yellow).

Ligand	Internal quantum yield
H_4tcbpe	62.3%
H_4tcbpe-F	46.5 %

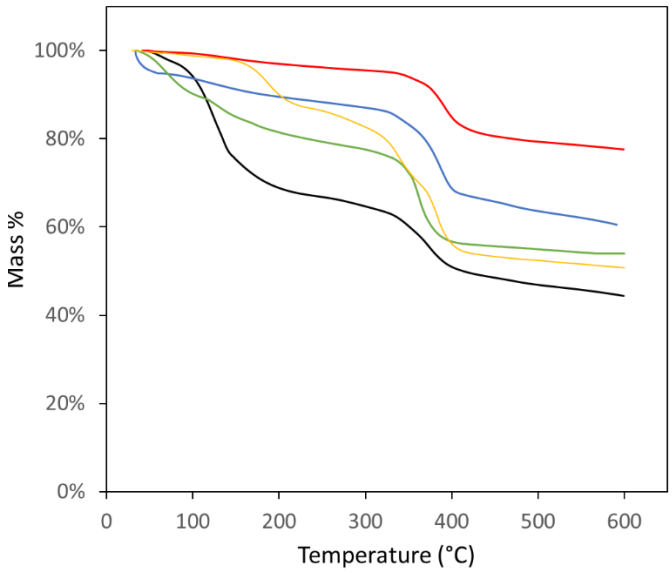

Figure S3. Thermogravimetric analysis data for LMOF-301 as made (black), outgassed (red), pentane-loaded (blue), cyclohexane-loaded (green), n-dodecane-loaded (yellow).

S4. Powder X-ray diffraction

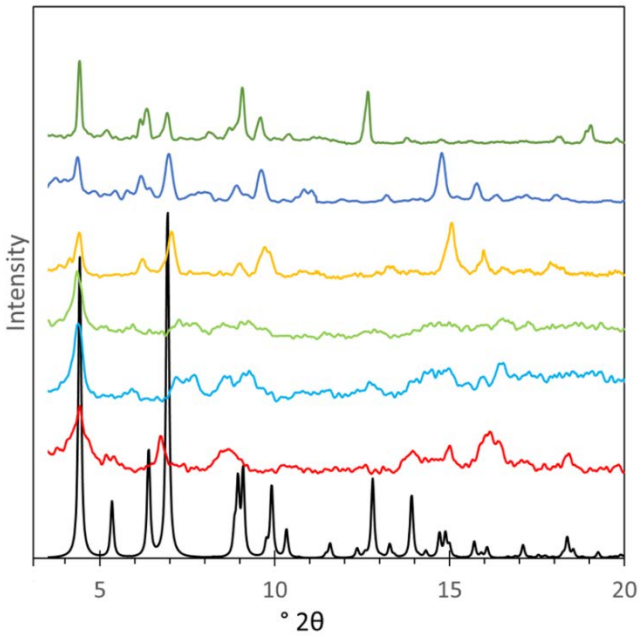

Figure S4. Powder X-ray diffraction patterns for as-made LMOF-263 (dark green), benzene-loaded LMOF-263 (dark blue), toluene-loaded LMOF-263 (gold), cyclohexane-loaded LMOF-263 (light green), n-dodecane-loaded LMOF-263 (light blue), and ethyl acetate-loaded LMOF-263 (red). The simulated pattern for LMOF-263 is shown in black.

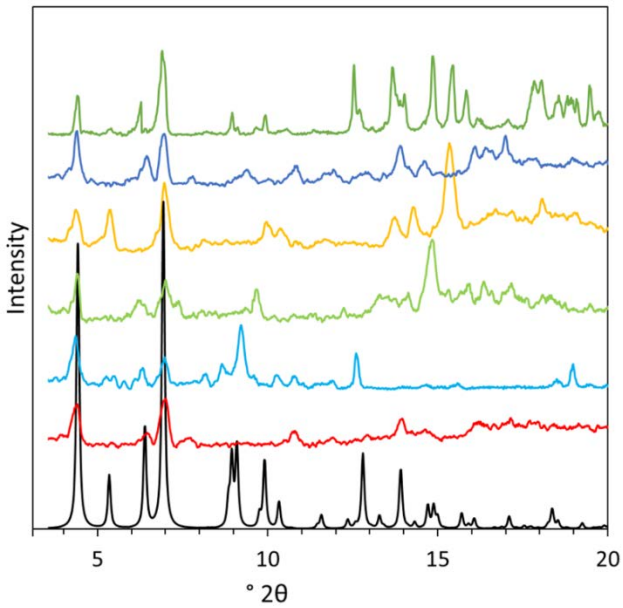

Figure S5. Powder X-ray diffraction patterns for as-made LMOF-301 (dark green), benzene-loaded LMOF-301 (dark blue), toluene-loaded LMOF-301 (gold), cyclohexane-loaded LMOF-301 (light green), n-dodecane-loaded LMOF-301 (light blue), and ethyl acetate-loaded LMOF-301 (red). The simulated pattern for LMOF-301 is shown in black.