

SUPPLEMENTARY INFORMATION

Nano vs. Bulk – Surfactant-controlled Photophysical and Morphological Features of Luminescent Lanthanide MOFs

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Crystal Structures

Eu³⁺-bdc and Tb³⁺-bdc

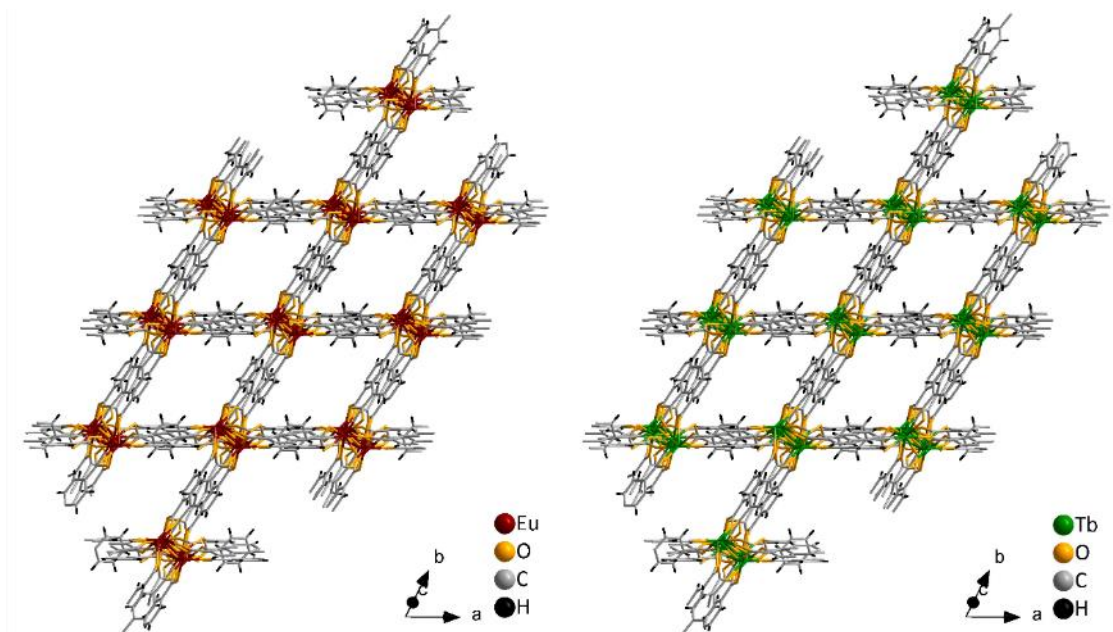


Figure SI 1 Illustrated excerpt from the crystal structure of Eu³⁺-bdc (left) and Tb³⁺-bdc (right). Atom colour code: Europium (red), Terbium (green), Oxygen (orange), Carbon (grey) and Hydrogen (black). Solvent molecules have been omitted for clarity.¹

DUT-5 and MOF-253

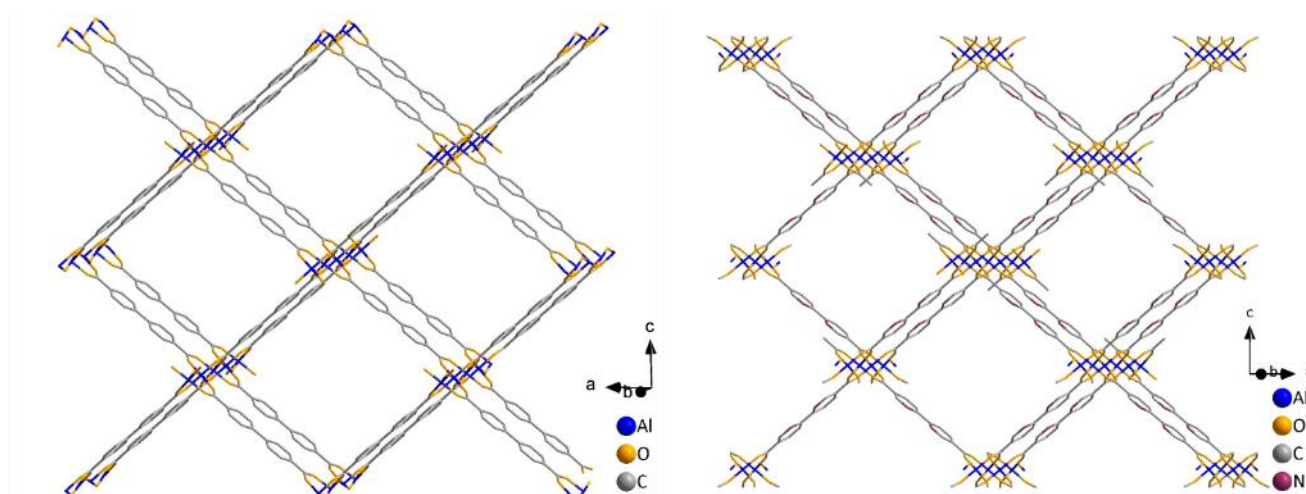


Figure SI 2 Illustrated excerpt from the crystal structure of DUT-5 and MOF-253. Atom colour code: Aluminium (blue), Oxygen (orange) and Carbon (grey). Solvent molecules and hydrogen atoms have been omitted for clarity.^{2,3}

Powder X-Ray Diffraction

PXRD patterns of Tb^{3+} -bdc, nTb^{3+} -bdc, reagents and surfactants

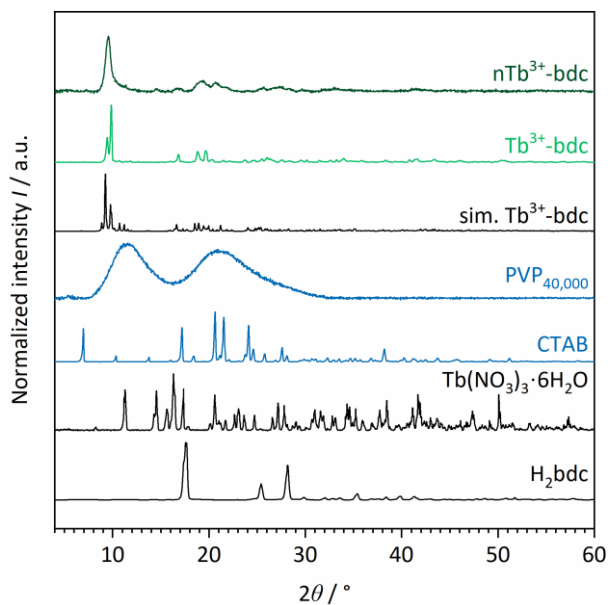


Figure SI 3 Simulated (sim.) PXRD pattern for single-crystal data of Tb^{3+} -bdc (black) and recorded PXRD patterns of Tb^{3+} -bdc (dark green), nTb^{3+} -bdc (pale green), surfactants (blue) and educts (black).

PXRD patterns of Eu^{3+} -bdc, nEu^{3+} -bdc, educts and surfactants

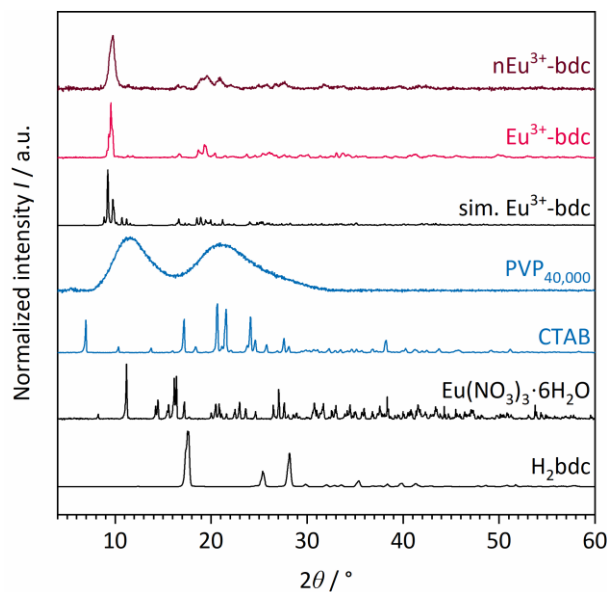


Figure SI 4 Simulated (sim.) PXRD pattern for single-crystal data of Eu^{3+} -bdc (black) and recorded PXRD patterns of Eu^{3+} -bdc (dark red), nEu^{3+} -bdc (pale red), surfactants (blue) and educts (black).

PXRD patterns of DUT-5, nDUT-5, educts and surfactants

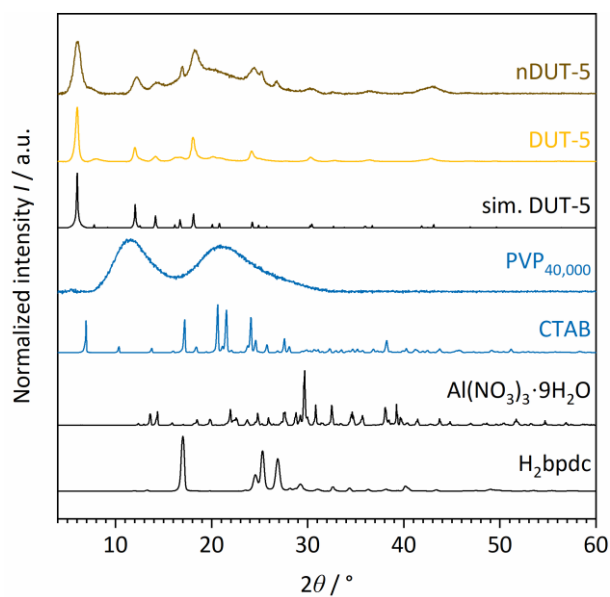


Figure SI 5 Simulated (sim.) PXRD pattern for single-crystal data of DUT-5 (black) and recorded PXRD patterns of DUT-5 (dark yellow), nDUT-5 (pale yellow), surfactants (blue) and educts (black).

PXRD patterns of MOF-253, nMOF-253, educts and surfactants

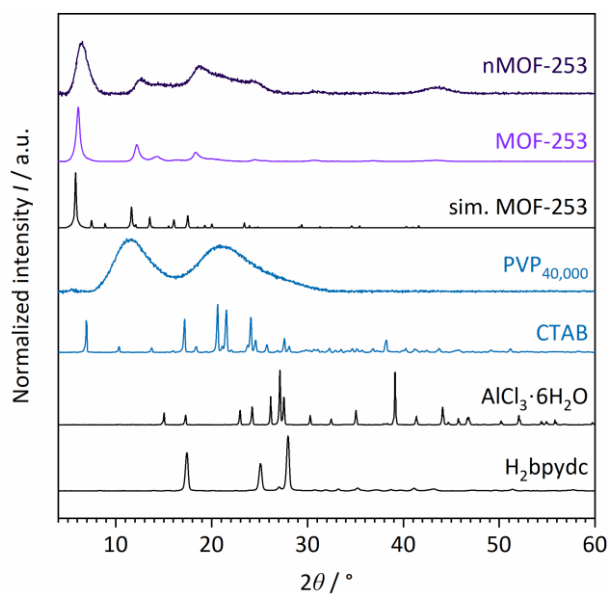


Figure SI 6 Simulated (sim.) PXRD pattern for single-crystal data of MOF-253 (black) and recorded PXRD patterns of MOF-253 (dark violet), nMOF-253 (pale violet), surfactants (blue) and educts (black).

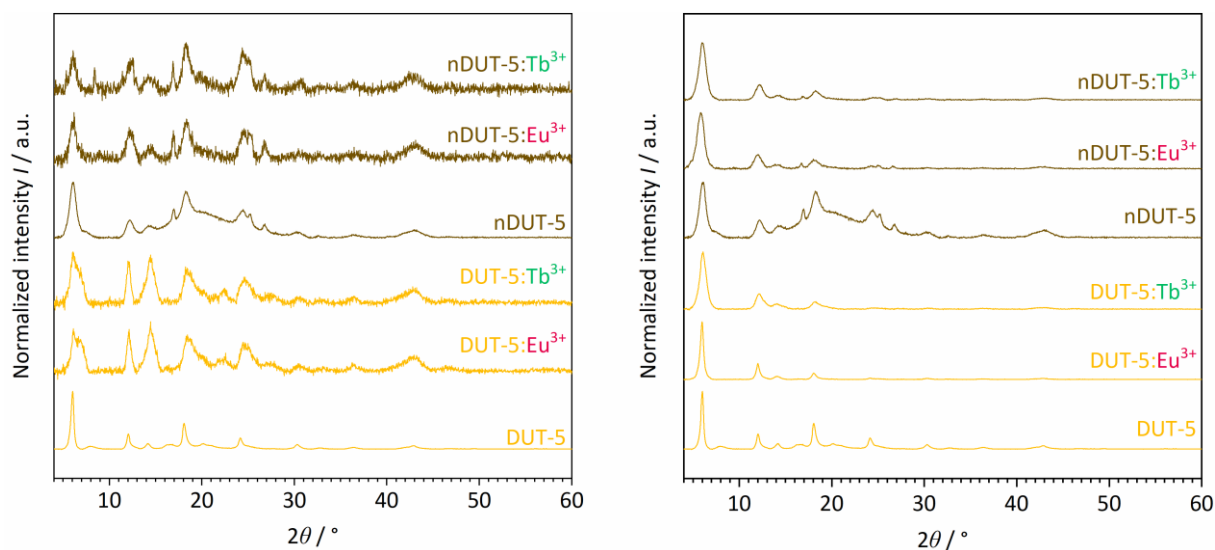
PXRD patterns of post-synthetic modified DUT-5:Ln³⁺ and nDUT-5:Ln³⁺ with Ln³⁺= Eu³⁺, Tb³⁺

Figure SI 7 Powder diffractograms of post-synthetic modified DUT-5:Ln³⁺ (pale yellow) and nDUT-5:Ln³⁺ (dark yellow) with Ln³⁺= Eu³⁺, Tb³⁺ in EtOH (left) and MeCN (right).

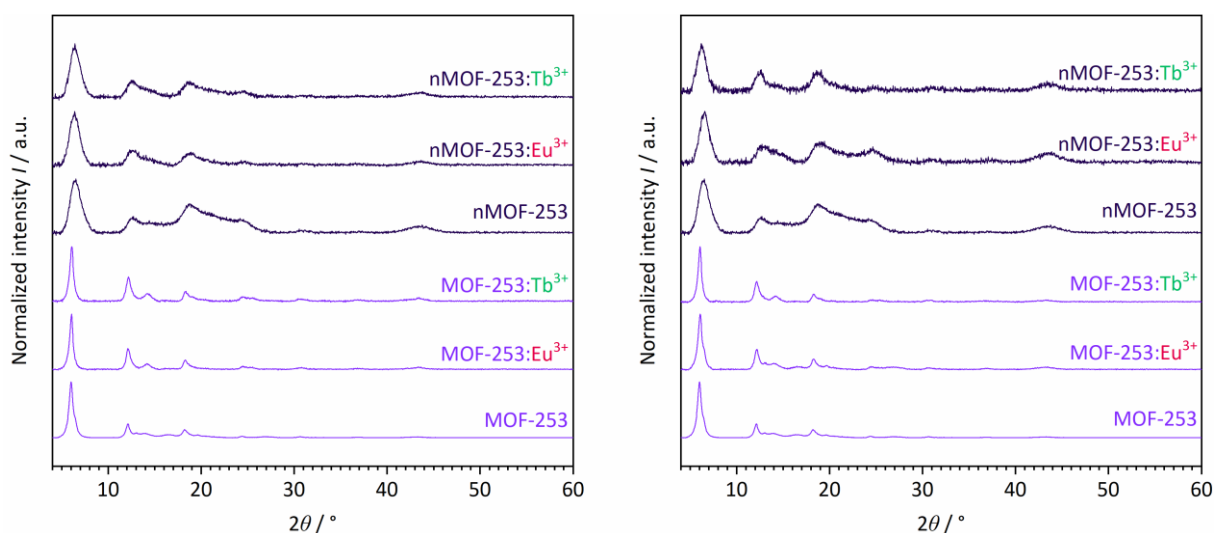
PXRD patterns of post-synthetic modified MOF-253:Ln³⁺ and nMOF-253:Ln³⁺ with Ln³⁺= Eu³⁺, Tb³⁺

Figure SI 8 Powder diffractograms of post-synthetic modified MOF-253:Ln³⁺ (pale violet) and nMOF-253:Ln³⁺ (dark violet) with Ln³⁺= Eu³⁺, Tb³⁺ in EtOH (left) and MeCN (right).

Oxidation products of DUT-5, nDUT-5, MOF-253 and nMOF-253 ($=\text{Al}_2\text{O}_3$) as well as Tb^{3+} -bdc and nTb^{3+} -bdc ($=\text{Tb}_4\text{O}_7$)

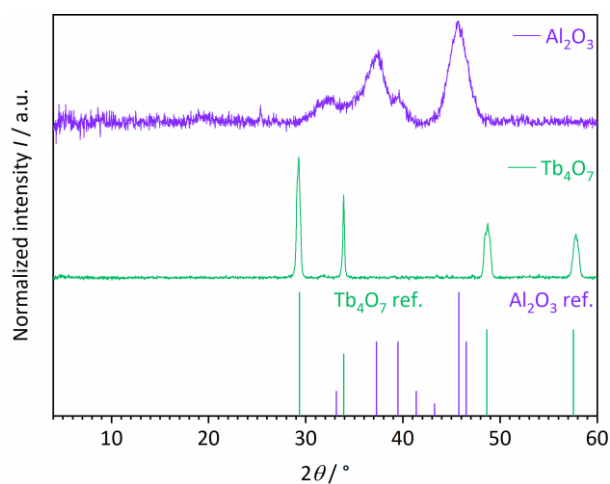


Figure SI 9 Powder diffractograms of the investigated oxidation products of DUT-5, nDUT-5, MOF-253 and nMOF-253 ($=\text{Al}_2\text{O}_3$, violet) as well as Tb^{3+} -bdc and nTb^{3+} -bdc ($=\text{Tb}_4\text{O}_7$, green) and corresponding reference (ref.) angles in 2θ for Al_2O_3 (JCPDS 00-047-1308) and Tb_4O_7 (JCPDS 00-013-0387).

Scanning Electron Microscopy and Dynamic Light Scattering

SEM images and DLS results of Eu^{3+} -bdc, Tb^{3+} -bdc, DUT-5 and MOF-253

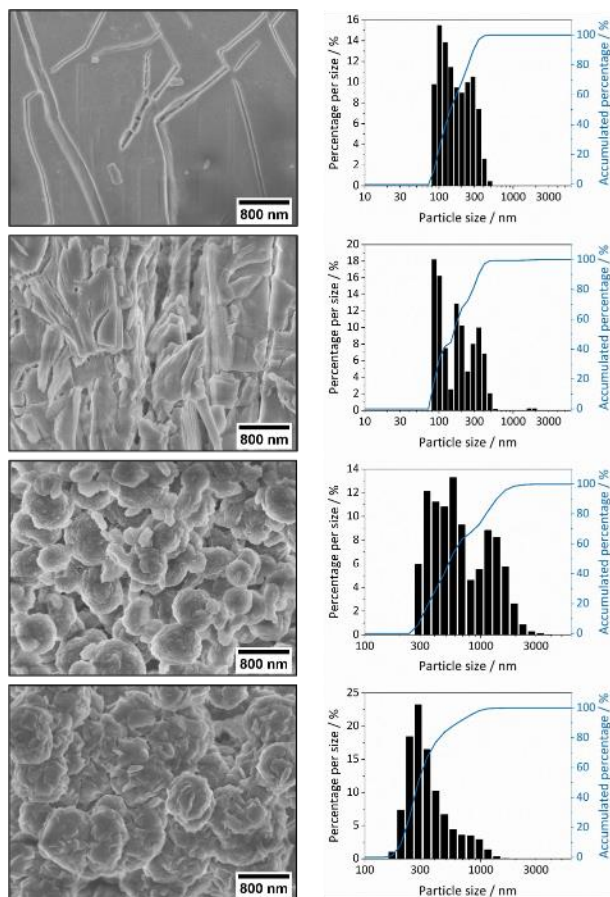
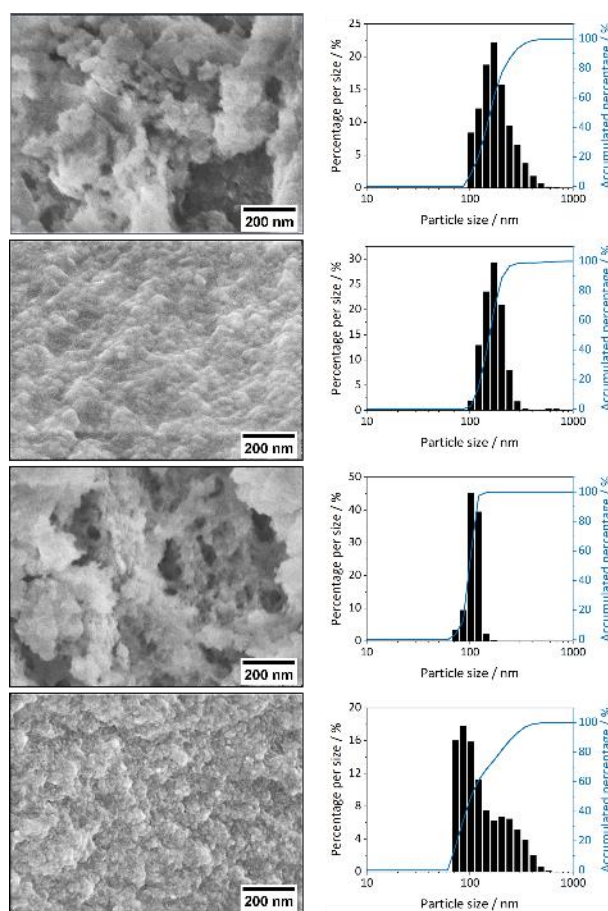
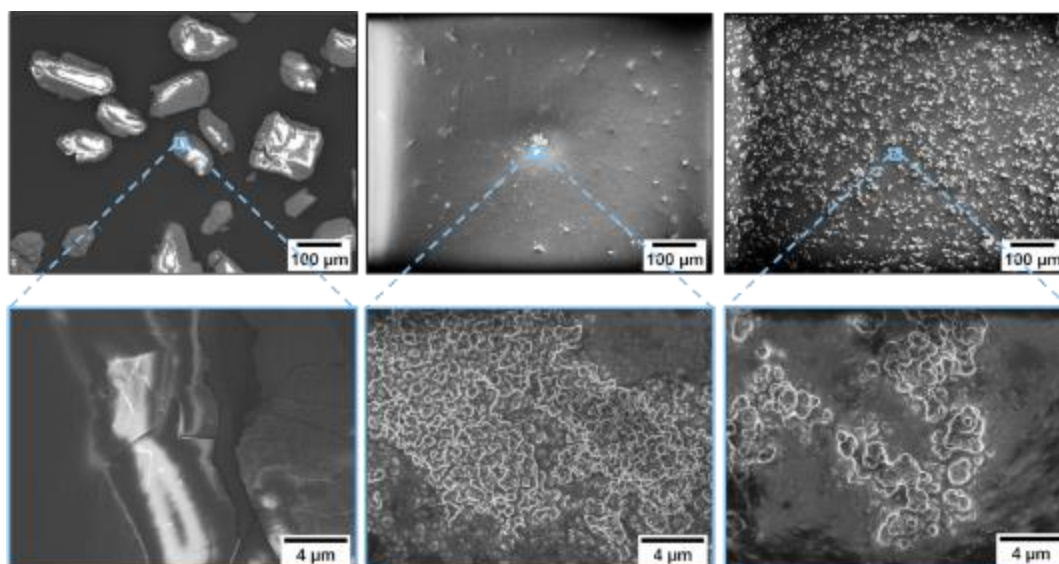


Figure SI 10 SEM images (25k magnification, left) and particle size distributions (right) of Eu^{3+} -bdc, Tb^{3+} -bdc, DUT-5 and MOF-253 (top to bottom).

SEM images and DLS results of nDUT-5:Ln³⁺ and nMOF-253:Ln³⁺ with Ln³⁺= Eu³⁺, Tb³⁺Figure SI 11 SEM images (100k magnification, left) and particle size distributions (right) of nDUT-5:Eu³⁺, nDUT-5:Tb³⁺, nMOF-253:Eu³⁺ and nMOF-253:Tb³⁺ (top to bottom).SEM images of Eu³⁺-bdc, DUT-5:Eu³⁺ and MOF-253:Eu³⁺Figure SI 12 SEM images (150 magnification, top) with blue enlarged sectors (5k magnification, bottom) of Eu³⁺-bdc (left), DUT-5:Eu³⁺ (mid) and MOF-253:Eu³⁺ (right).

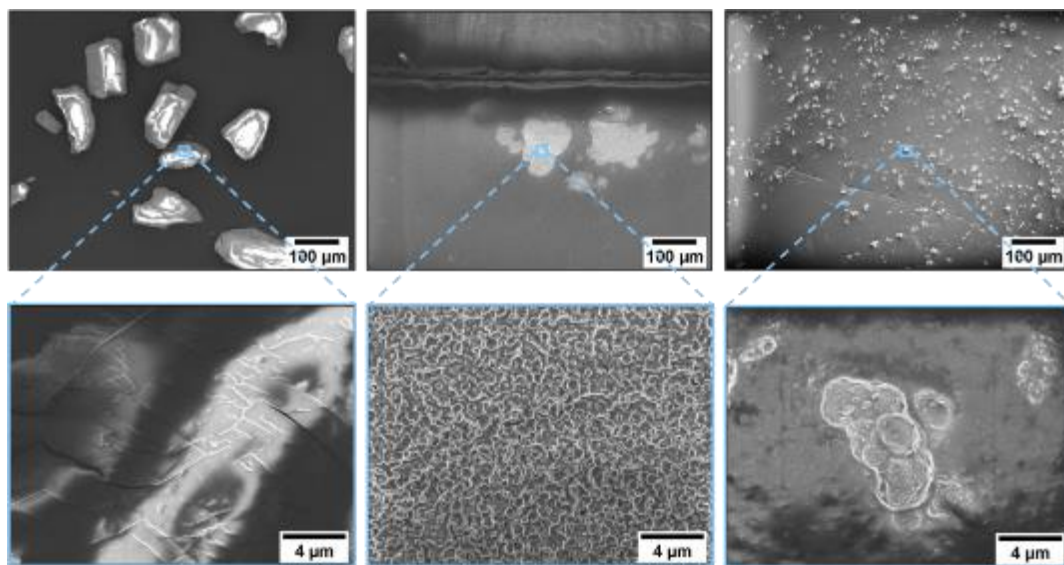
SEM images of Tb^{3+} -bdc, DUT-5: Tb^{3+} and MOF-253: Tb^{3+} 

Figure SI 13 SEM images (150 magnification, top) and blue enlarged sectors (5k magnification, bottom) of Tb^{3+} bdc (left), DUT 5: Tb^{3+} (mid) and MOF 253: Tb^{3+} (right).

Differential Thermal Analysis/Thermogravimetric-Mass Spectrometry

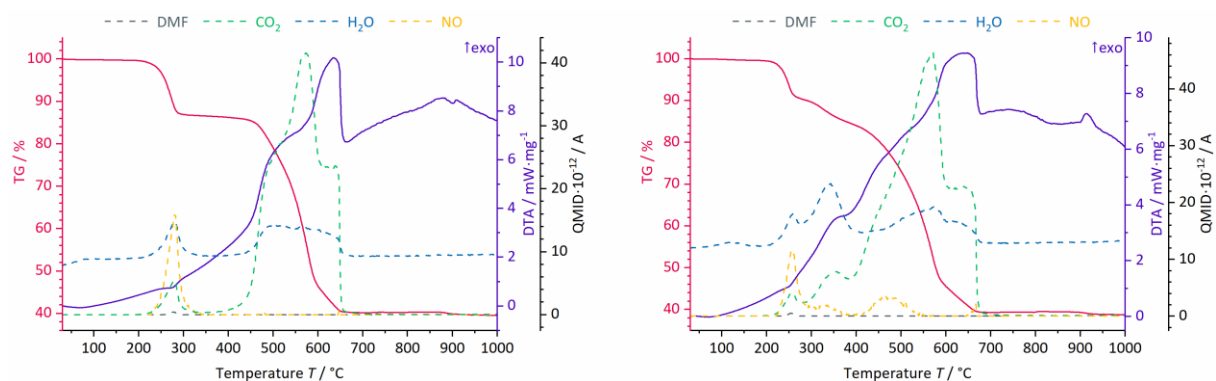
 Tb^{3+} -bdc and nTb^{3+} -bdc

Figure SI 14 DTA/TG-MS results of Tb^{3+} -bdc (left) and nTb^{3+} -bdc (right) for a constant stream of synthetic air as working gas. NO signal (yellow) is given in QMGID-10⁻¹² A for a more detailed insight.

DUT-5 and nDUT-5

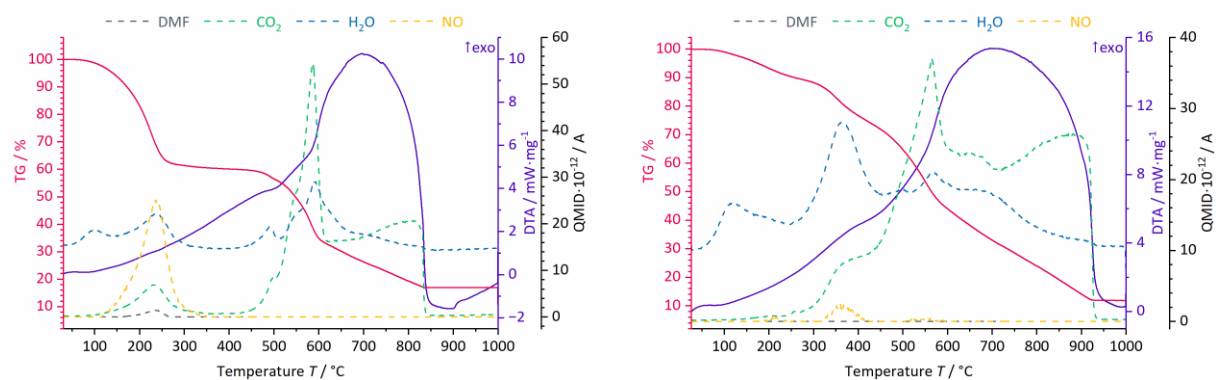


Figure SI 15 DTA/TG-MS results of DUT-5 (left) and nDUT-5 (right) for a constant stream of synthetic air as working gas. NO signal (yellow) is given in QMGID-10⁻¹² A for a more detailed insight.

MOF-253 and nMOF-253

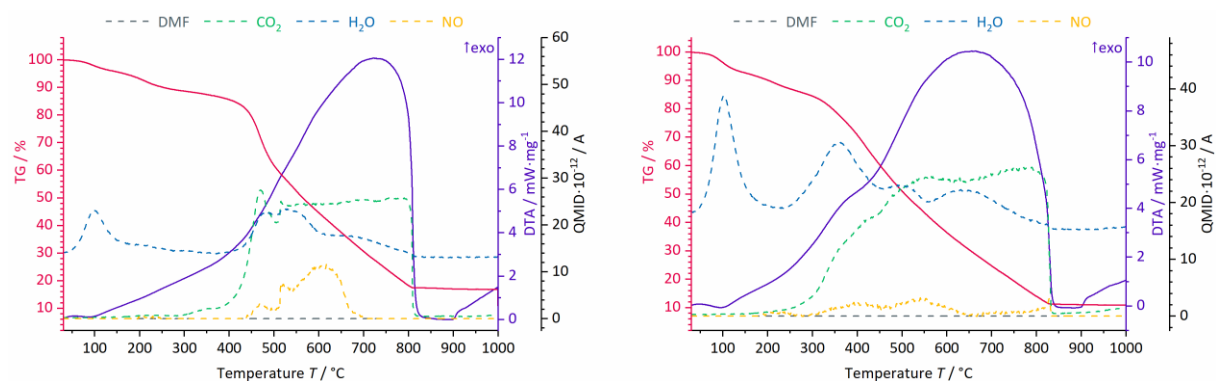


Figure SI 16 DTA/TG-MS results of MOF-253 (left) and nMOF-253 (right) for a constant stream of synthetic air as working gas. NO signal (yellow) is given in QMGID-10⁻¹² A for a more detailed insight.

UV-Vis-Diffuse Reflectance Spectroscopy

Eu^{3+} -bdc and nEu^{3+} -bdc

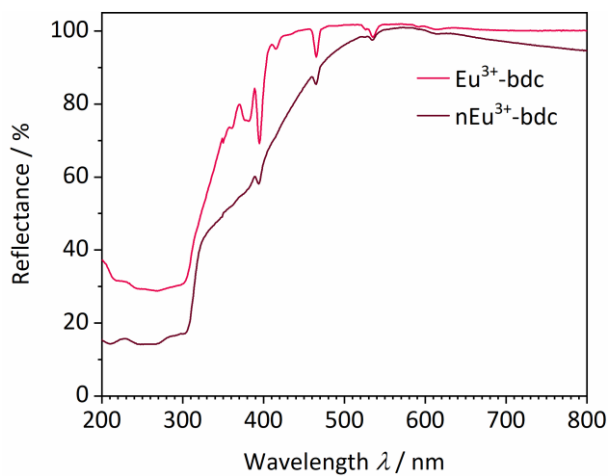


Figure SI 17 UV-Vis diffuse reflectance spectra of Eu^{3+} -bdc (pale red) and nEu^{3+} -bdc (dark red).

Tb^{3+} -bdc and nTb^{3+} -bdc

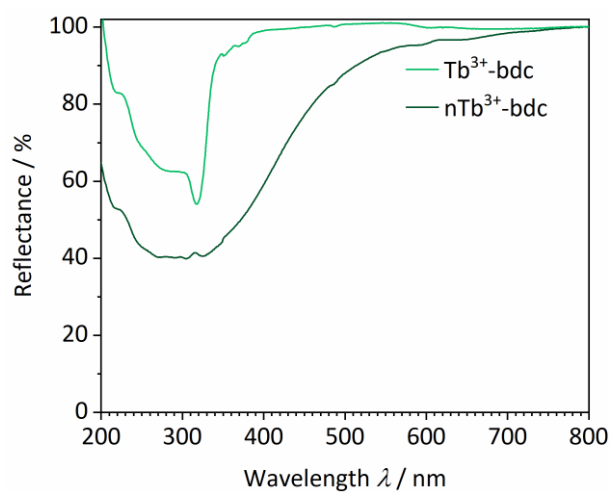


Figure SI 18 UV-Vis diffuse reflectance spectra of Tb^{3+} -bdc (pale green) and nTb^{3+} -bdc (dark green).

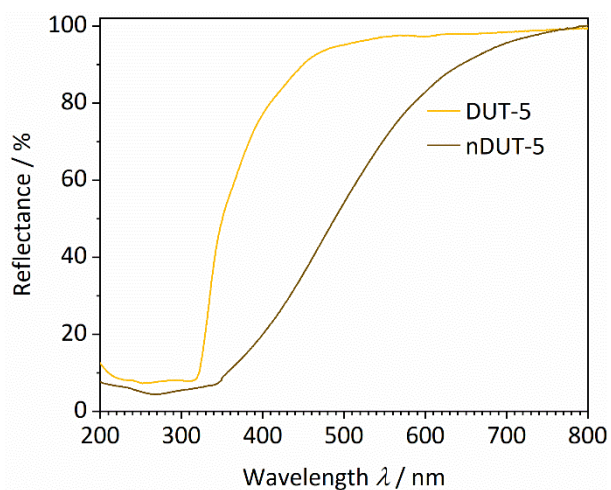
DUT-5 and nDUT-5

Figure SI 19 UV-Vis diffuse reflectance spectra of DUT-5 (pale yellow) and nDUT-5 (dark yellow).

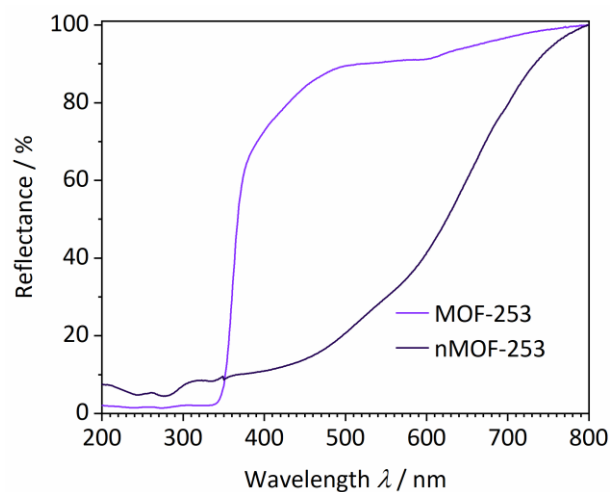
MOF-253 and nMOF-253

Figure SI 20 UV-Vis diffuse reflectance spectra of MOF-253 (pale violet) and nMOF-253 (dark violet).

Photoluminescence Spectra

DUT-5:Tb³⁺ and nDUT-5:Tb³⁺

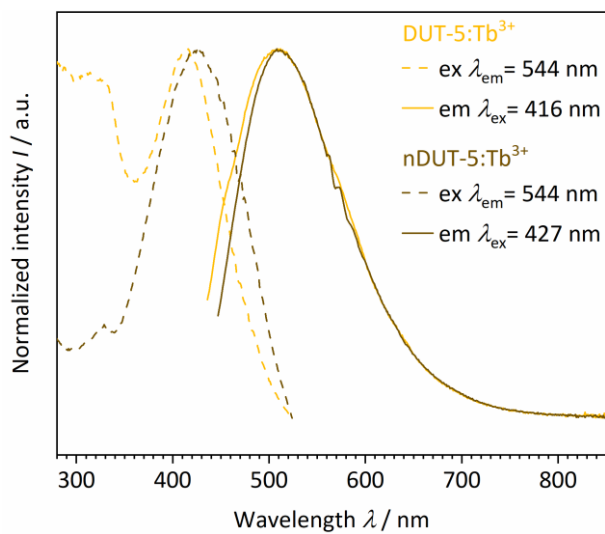


Figure SI 21 Excitation and emission photoluminescence spectra of DUT-5:Tb³⁺ (pale yellow) and nDUT-5:Tb³⁺ (dark yellow).

MOF-253:Tb³⁺ and nMOF-253:Tb³⁺

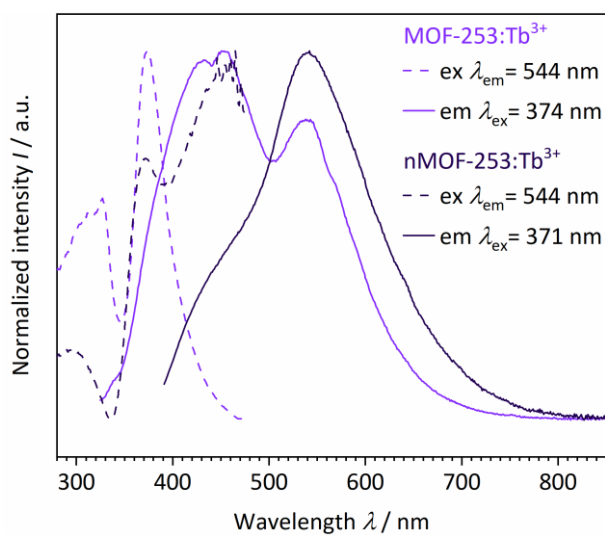


Figure SI 22 Excitation and emission photoluminescence spectra of MOF-253:Tb³⁺ (pale violet) and nMOF-253:Tb³⁺ (dark violet).

Triplet State Determinations

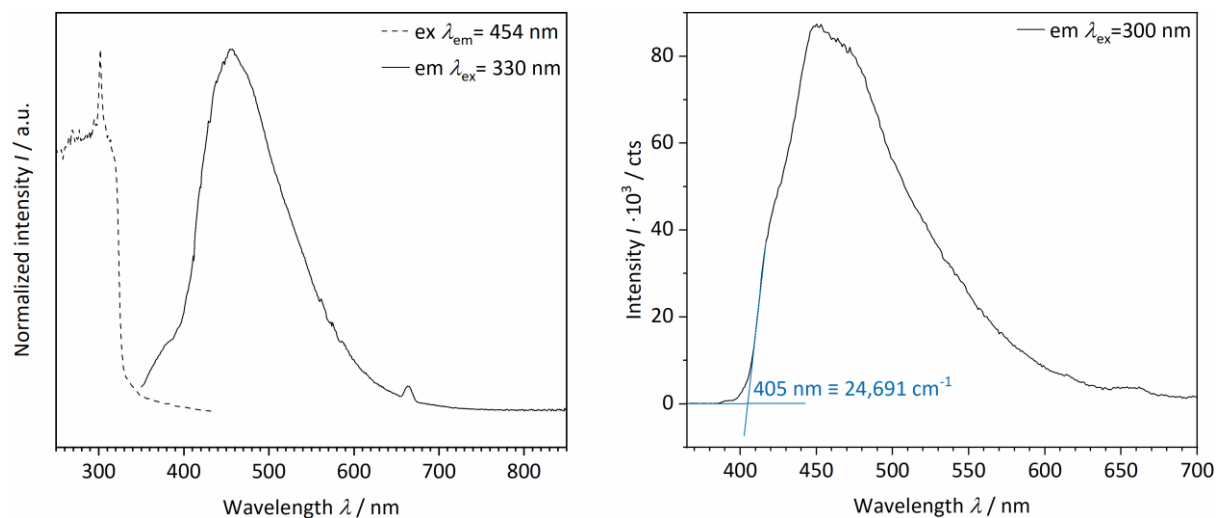
Gd³⁺-bdc

Figure SI 23 Photoluminescence spectra (left) and triplet state phosphorescence spectrum (right) of Gd³⁺-bdc. Recording delay time: 0.2 ms, sample window time: 2 ms, and counts per flash: 30.

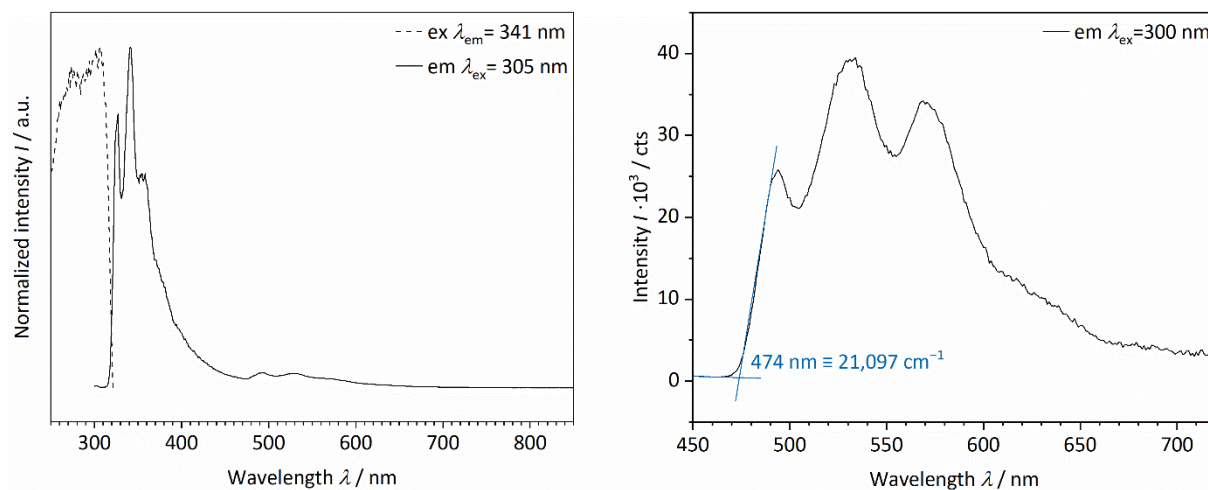
DUT-5:Gd³⁺

Figure SI 24 Photoluminescence spectra (left) and triplet state phosphorescence spectrum (right) of DUT-5:Gd³⁺. Recording delay time: 0.1 ms, sample window time: 1 ms, and counts per flash: 50.

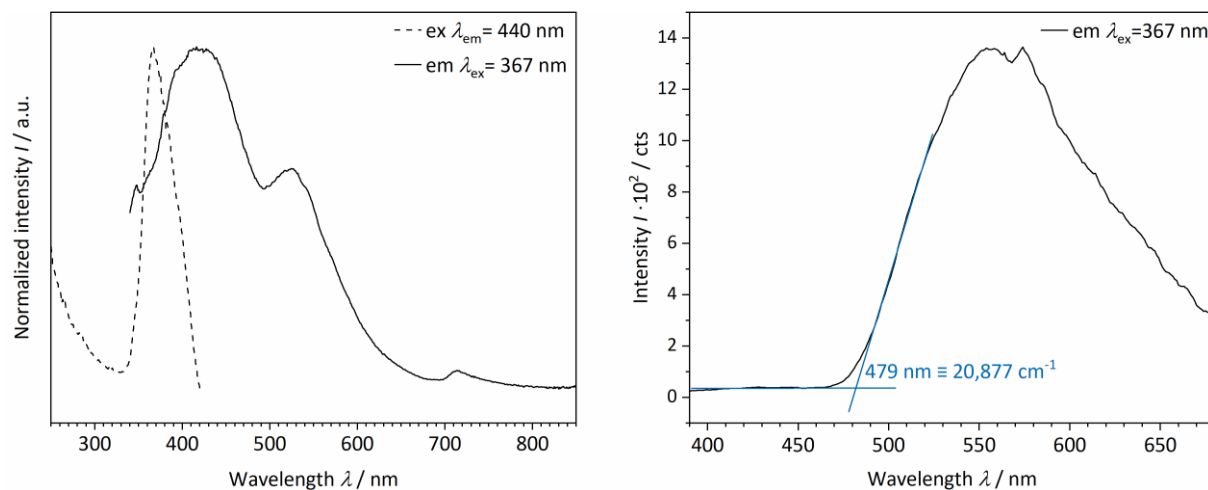
MOF-253:Gd³⁺

Figure SI 25 Photoluminescence spectra (left) and triplet state phosphorescence spectrum (right) of MOF-253:Gd³⁺. Recording delay time: 0.1 ms, sample window time: 0.5 ms, and counts per flash: 50.

Luminescence Decay Measurements

Eu³⁺-bdc and nEu³⁺-bdc

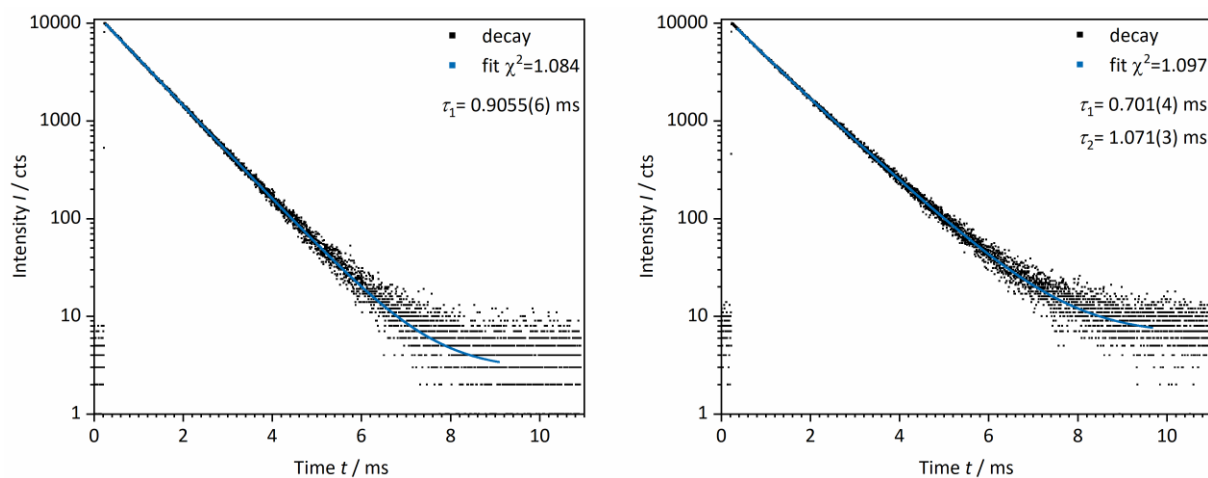


Figure SI 26 Luminescence decay measurement of Eu³⁺-bdc (left, $\lambda_{\text{ex}}=288$ nm, $\lambda_{\text{em}}=614$ nm) and nEu³⁺-bdc (right, $\lambda_{\text{ex}}=296$ nm, $\lambda_{\text{em}}=614$ nm).

Tb³⁺-bdc and nTb³⁺-bdc

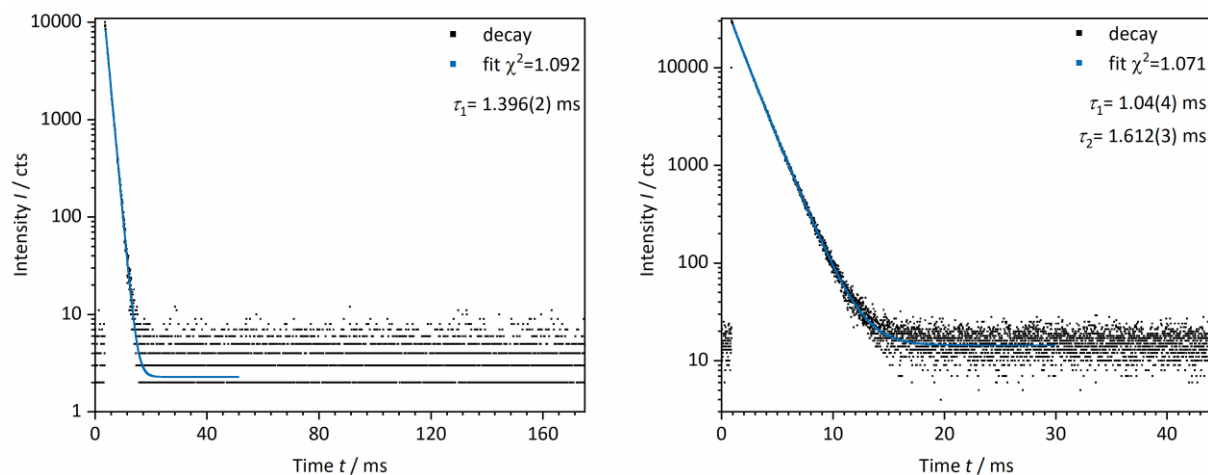


Figure SI 27 Luminescence decay measurement of Tb³⁺-bdc (left, $\lambda_{\text{ex}}=300$ nm, $\lambda_{\text{em}}=544$ nm) and nTb³⁺-bdc (right, $\lambda_{\text{ex}}=286$ nm, $\lambda_{\text{em}}=543$ nm).

DUT-5 and nDUT-5

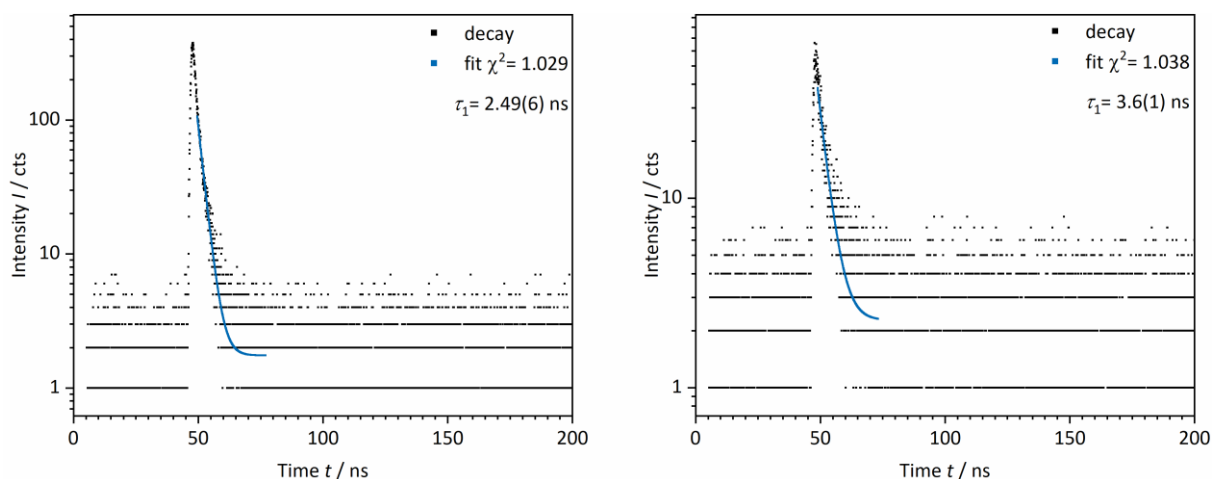


Figure SI 28 Luminescence decay measurement of DUT-5 (left, $\lambda_{\text{ex}}=287$ nm, $\lambda_{\text{em}}=378$ nm) and nDUT-5 (right, $\lambda_{\text{ex}}=287$ nm, $\lambda_{\text{em}}=378$ nm).

MOF-253 and nMOF-253

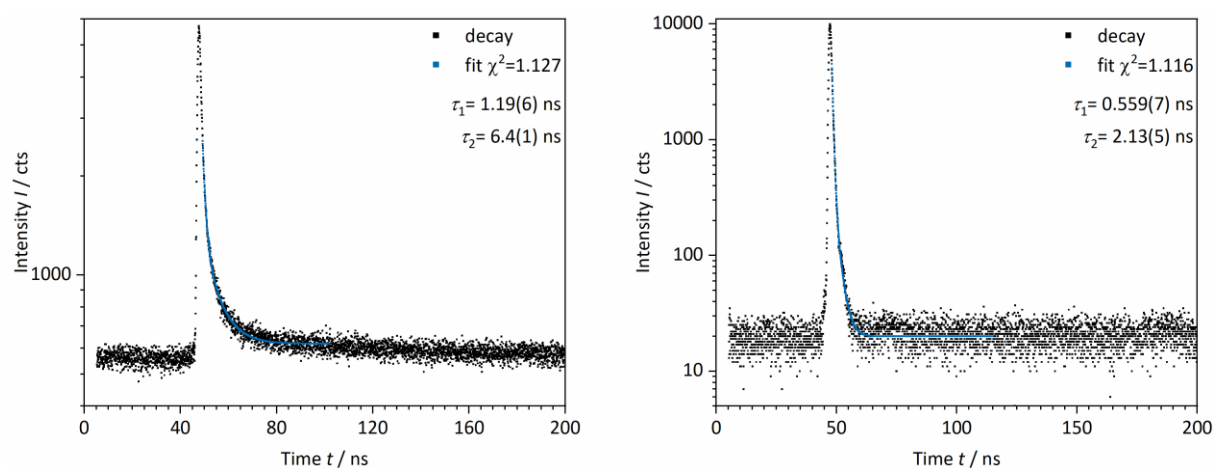


Figure SI 29 Luminescence decay measurement of MOF-253 (left, $\lambda_{\text{ex}}=287$ nm, $\lambda_{\text{em}}=536$ nm) and nMOF-253 (right, $\lambda_{\text{ex}}=287$ nm, $\lambda_{\text{em}}=536$ nm).

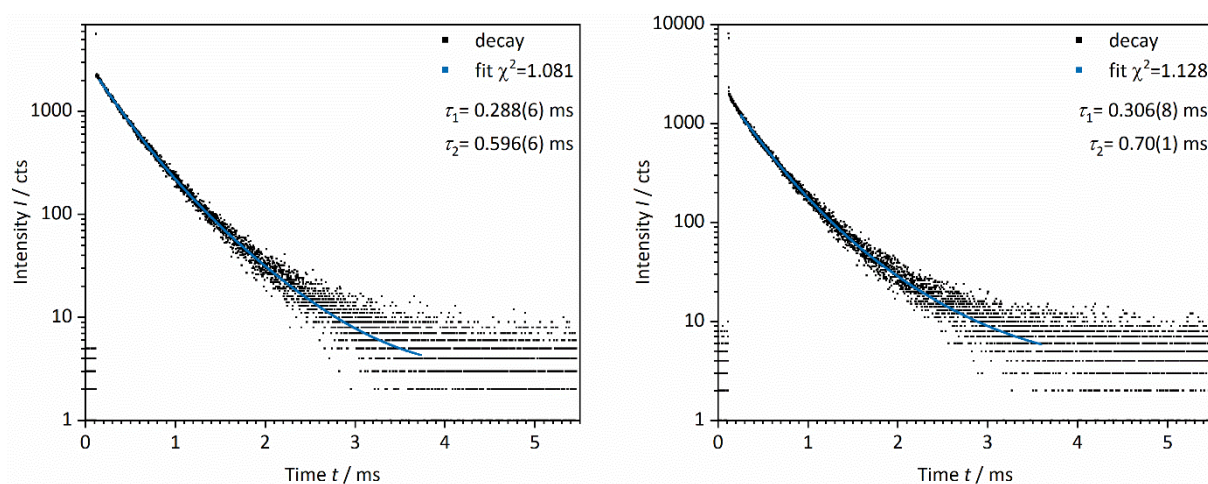
DUT-5:Eu³⁺ and nDUT-5:Eu³⁺

Figure SI 30 Luminescence decay measurement of DUT-5:Eu³⁺ (left, $\lambda_{\text{ex}}=298$ nm, $\lambda_{\text{em}}=616$ nm) and nDUT-5:Eu³⁺ (right, $\lambda_{\text{ex}}=295$ nm, $\lambda_{\text{em}}=616$ nm).

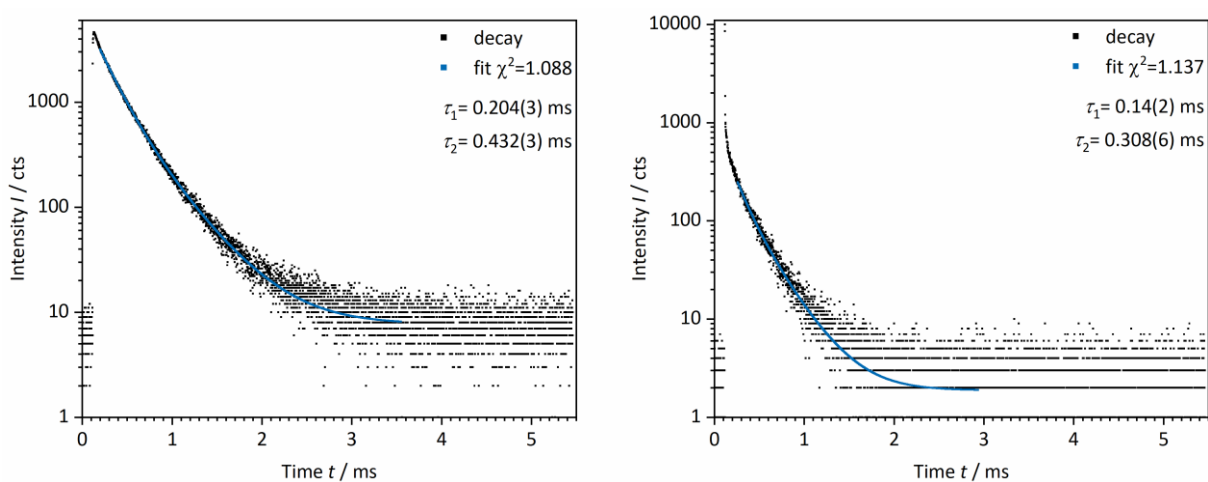
MOF-253:Eu³⁺ and nMOF-253:Eu³⁺

Figure SI 31 Luminescence decay measurement of MOF-253:Eu³⁺ (left, $\lambda_{\text{ex}}=327$ nm, $\lambda_{\text{em}}=617$ nm) and nMOF-253:Eu³⁺ (right, $\lambda_{\text{ex}}=310$ nm, $\lambda_{\text{em}}=616$ nm).

External Calibration of Microwave Plasma - Atomic Emission Spectroscopy Measurements

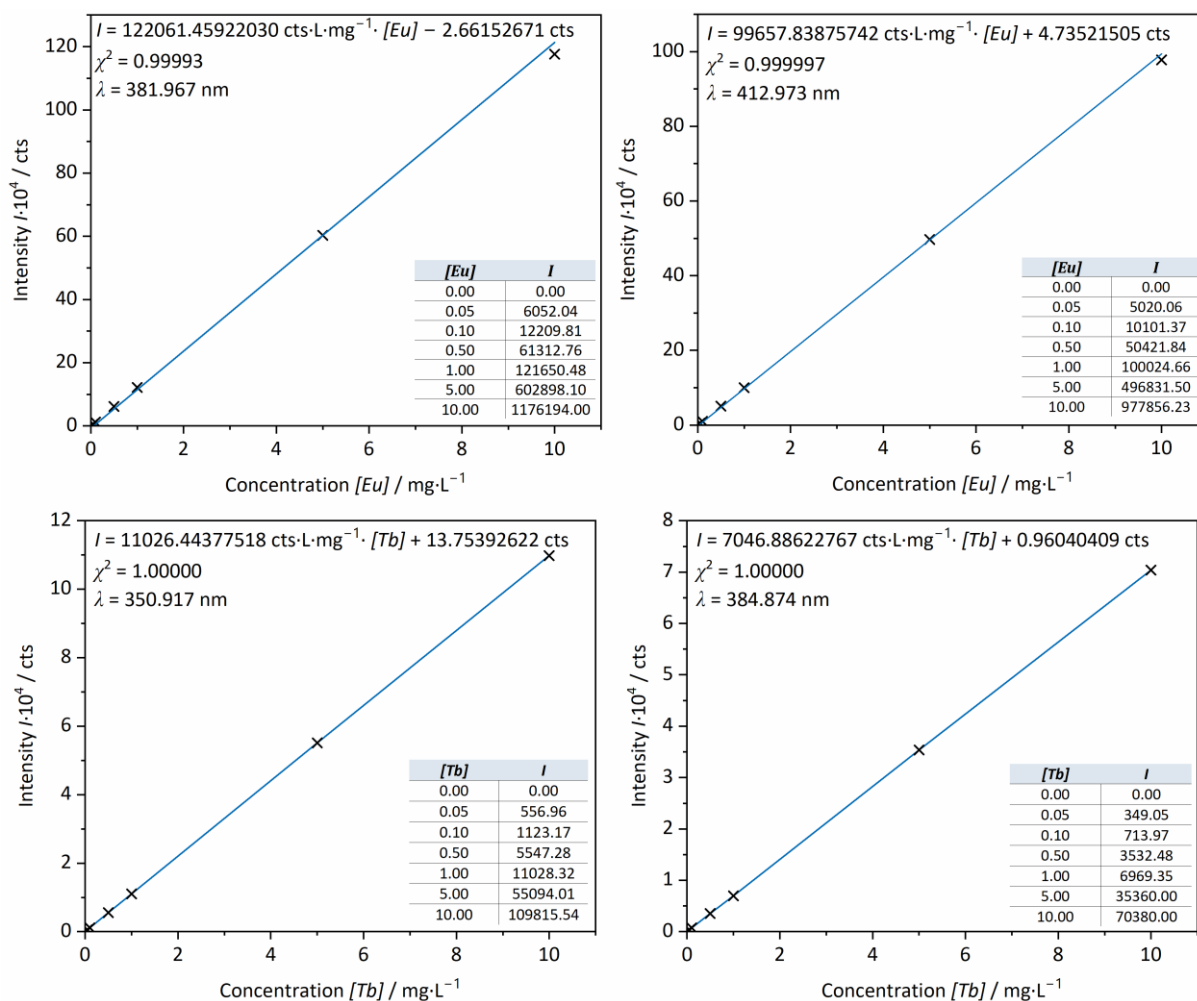


Figure SI 32 External calibration of microwave plasma - atomic emission spectroscopy for characteristic Eu (top) and Tb (bottom) emission lines. The table insets show the data points marked in the graph. Fitting parameters of the blue linear fit are also given at the top of the graph.

Investigated MOFs exposed to Vis-light and UV-light

Figure SI33 is also available as video download.

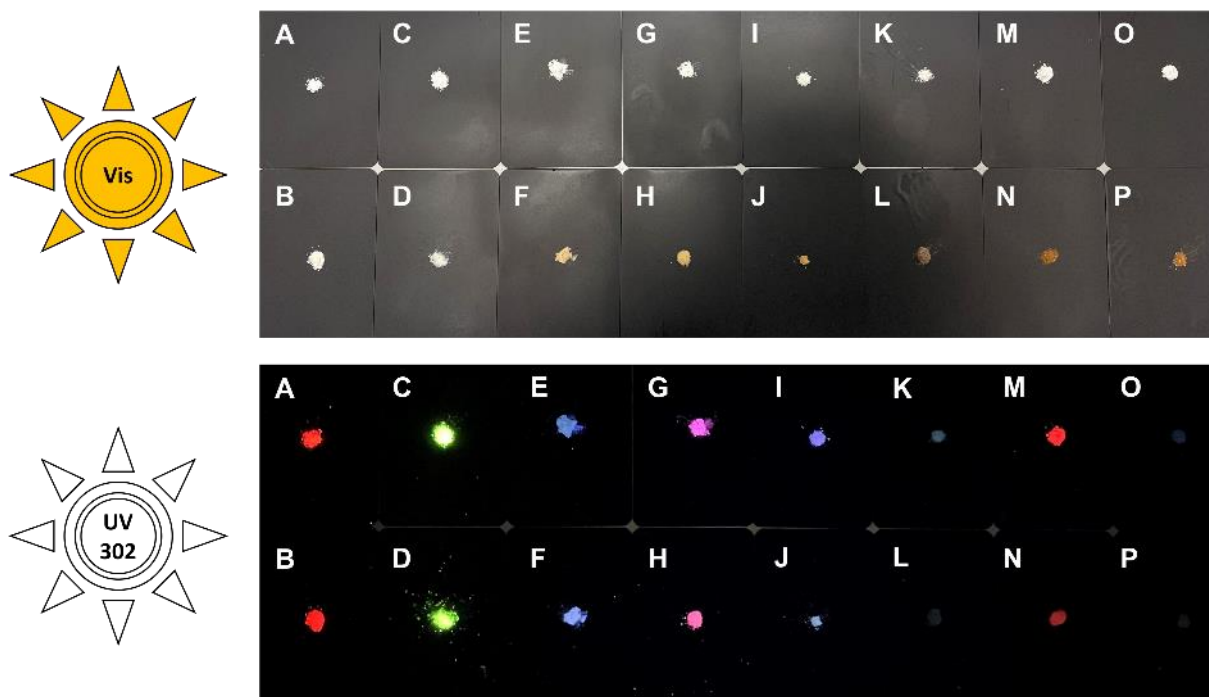


Figure SI 33 Photographs of powders of investigated bulk MOFs and nMOFs exposed to Vis-light (top) and UV-light (302 nm, bottom). A= Eu^{3+} -bdc, B= nEu^{3+} -bdc, C= Tb^{3+} -bdc, D= nTb^{3+} -bdc, E= DUT-5, F= nDUT-5, G= DUT-5: Eu^{3+} , H= nDUT-5: Eu^{3+} , I= DUT-5: Tb^{3+} , J= nDUT-5: Tb^{3+} , K= MOF-253, L= nMOF-253, M= MOF-253: Eu^{3+} , N= nMOF-253: Eu^{3+} , O= MOF-253: Tb^{3+} , P= nMOF-253: Tb^{3+} .

References

- 1 X. Guo, G. Zhu, F. Sun, Z. Li, X. Zhao, X. Li, H. Wang and S. Qiu, *Inorg. Chem.*, 2006, **45**, 2581–2587.
- 2 I. Senkovska, F. Hoffmann, M. Fröba, J. Getzschmann, W. Böhlmann and S. Kaskel, *Microporous Mesoporous Mater.*, 2009, **122**, 93–98.
- 3 E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382–14384.