

Supporting Information

Stable and Efficient Rare-Earth free Phosphors based on an Mg(II) Metal-Organic Framework for Hybrid Light-Emitting Diodes

Youssef Atoini,^{a,*} [§] Luca M. Cavinato,^{a,§} Jean-Louis Schmitt,^b Daniel Van Opdenbosch,^c Rubén D. Costa ^{a,*}

*a. Chair of Biogenic Functional Materials,
Technical University of Munich,
Schulgasse, 22, Straubing 94315, Germany.
E-mail: y.atoini@tum.de, ruben.costa@tum.de*

*b. Laboratoire de Chimie Supramoléculaire
Institut de Science et d'Ingénierie Supramoléculaires
8, allée Gaspard Monge, 67000 Strasbourg, France.*

*c. Chair for Biogenic Polymers
Technical University of Munich,
Schulgasse, 16, Straubing 94315, Germany.*

[§]. These authors equally contributed to the paper

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Materials and methods

All the chemicals were purchased from Sigma Aldrich, Tokyo Chemicals Industry, or Fluorochem without any further purification. The solvents were dried from a solvent purification system MB SPS-800/7 from MBraun, using argon as inert gas and a double column solvent filtration system. Deuterated solvents were bought from Eurisotop or Sigma Aldrich and used without any further purification.

Nuclear magnetic resonance (NMR) spectra were recorded from a JEOL 400 MHz Year Hold Super Conducting Magnet (400JYH, JEOL, Tokyo, Japan). Each spectrum was calibrated according to the residual peak of the solvent as internal standard.

Liquid-chromatography coupled with high-resolution mass spectrometry (HPLC-HRMS) was performed in positive mode using a Thermo Fisher Ultimate3000 with Scientific Vanquish Flex UHPLC and a Thermo Fisher Orbitrap (Exactive Plus with Extend Mass Range: Source HESI II). The detector was a Vanquish PDA Detector (VF-XX, detection ≤ 5 ppm). Direct injection high-resolution mass spectrometry was used using as eluant HPLC grade acetonitrile.

Powder X-ray diffraction (PXRD) data used in this work were obtained from a Miniflex diffractometer (Rigaku, Tokyo, Japan) with a copper source (1.54Å) and a silicon strip detector (D/teX Ultra, Rigaku), a goniometer radius of 150 mm; both Soller slits at 2.5°; a divergence slit fixed at 0.625°; an anti-scatter screen; and a $k\beta$ filter of 0.06 mm nickel foil. The powder was placed on a zero-background silicon wafer sample holder (cut 911) and the measurement was performed between 2θ values between 3° and 40° at room temperature using a step size of 0.5°/min. Scanning electron microscopy (SEM) images were recorded using a DSM 940A (Zeiss, Germany). The sample holders were mounted by sticking a double-sided adhesive tape on an aluminium stub at the bottom, and a glass disk plate on the top. The sample was prepared by drop-casting a suspension of the material in ethanol on the glass plate and left at ambient conditions until the complete evaporation of ethanol. The samples were then sputter-coated with gold. SEM images were obtained using 25 keV electron energy, using the secondary electron detector.

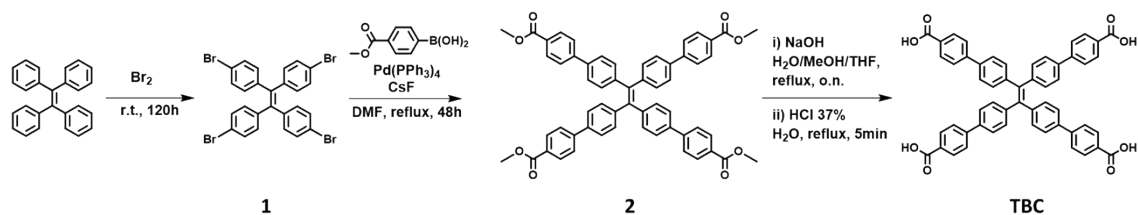
Nitrogen adsorption–desorption curves were recorded from samples degassed overnight at 80 °C, and corrected for the corresponding blank measurements (Surfer Nano, Thermo Fisher, Waltham, USA). From these, the specific surfaces of the materials were determined by the method of Brunauer, Emmett, and Teller (BET) from the relative pressure range $0.05 < P/P_0 < 0.999$.^{s1, s2} Pore size distributions were recorded in the range $1 \text{ nm} < d < 20 \text{ nm}$ and were obtained by the method of Broekhoff and de Boer,^{s3} based on the theory of Barrett, Joyner, and Halenda.^{s4}

Thermogravimetric analyses were carried out with a PT1600 analyser (Linseis, Germany) under ambient atmosphere (TGA, PT1600 Linseis, Selb, Germany) and a heating rate of $15 \text{ K}\cdot\text{min}^{-1}$. For this purpose, the TG detector was mounted. The measurement was related to the original sample mass, established at 100%.

Solid-state emission and excitation spectra were recorded with an FS5 spectrofluorometer, (Edinburgh Instruments) and a Xe lamp as a light source. The powder samples were inserted into a quartz tube, and the latter was placed into a quartz cuvette. The measurements were performed using the cuvette holder (SC-05 sample chamber). Regarding films into polymeric matrixes samples, they were performed in the same way, but the films were directly placed in a quartz cuvette.

Solid state excited-state lifetime data were recorded using the same spectrofluorometer and the same sample holder. The light source employed for exciting the sample is a pulsed LED EPLED at 375 nm. Photoluminescence quantum yields were determined using a Hamamatsu Quantaurus C11347 absolute photoluminescence quantum yield spectrometer and exciting the samples between 300 and 400 nm.

Synthesis and characterisation



Scheme S1. Synthetic route of TBC

Synthesis of 1,1,2,2-tetrakis(4-bromophenyl)ethene (**1**)

Caution: bromine is a toxic and a corrosive chemical. It has to be handled with extreme care.

The synthesis procedure for **1** is modified according to a previous work.⁵⁵ Tetraphenylethene (2.5 g, 7.5 mmol, 1.0 eq.) was placed in a glass petri dish in a desiccator. Bromine (3 mL, 58.5 mmol, 7.8 eq.) was placed in another glass petri dish, side by side to the first petri dish, in the same desiccator. The latter was closed for 120 h at r.t., and was quickly opened from time to time to release the over pressure. The resulting dark brown solid was collected, washed several times with ethanol and recrystallized in methanol in order to obtain **1** as an off-white powder (4.8 g, 7.4 mmol, 99%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.25 (d, 8H, *J* = 8.7 Hz), 6.84 (d, 8H, *J* = 8.7 Hz). ¹³C NMR (100 MHz, CDCl₃): 141.7, 139.8, 132.8, 131.2, 121.1. HRMS (ESI⁺): *m/z* calcd. for C₂₆H₁₆Br₄: 647.7941, found: 647.7938 (*z*=1).

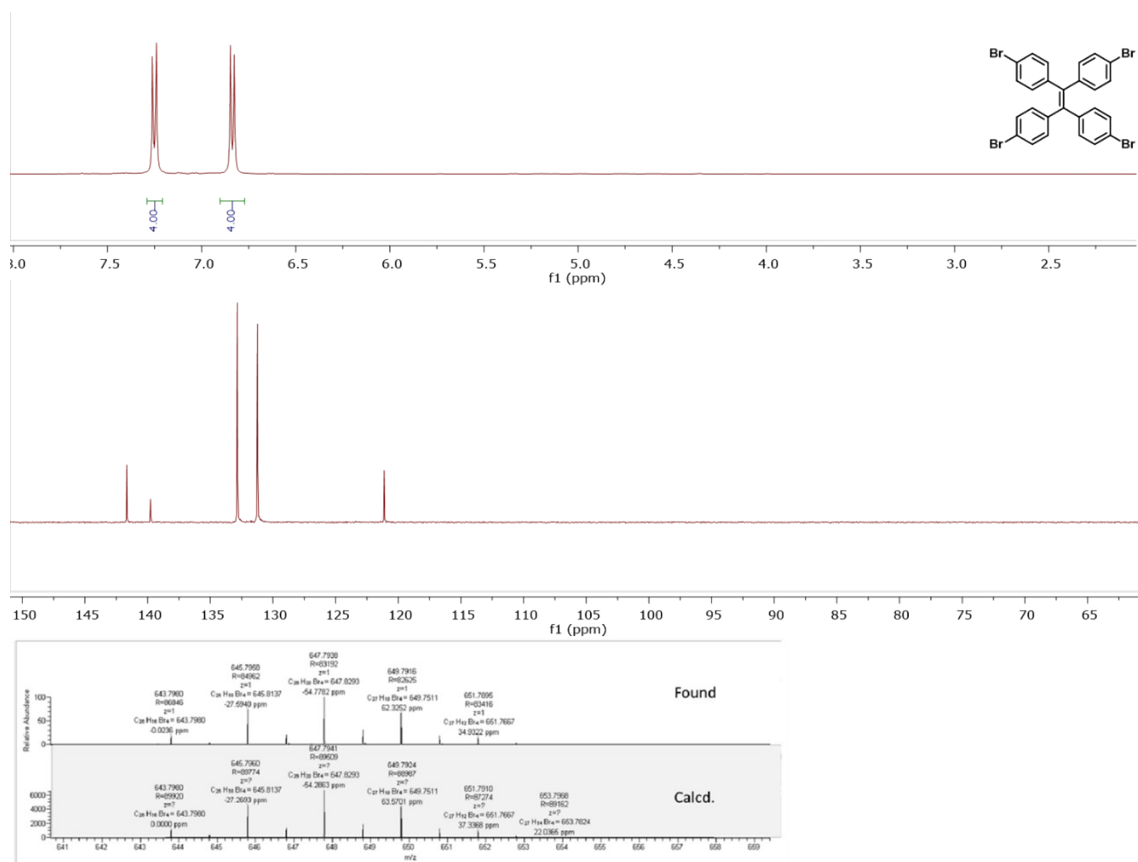


Figure S1. Top: ¹H NMR spectrum of **1**; middle: ¹³C NMR spectrum of **1**; bottom: HR-MS spectrum of **1**.

Synthesis of tetramethyl 4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylate) (**2**)

The synthesis procedure for **2** is modified according to a previous work.⁵⁵ 1,1,2,2-tetrakis(4-bromophenyl)ethene **1** (1 g, 1.4 mmol, 1 eq.), 4-methoxycarbonylphenylboronic acid (1.025 g, 8.14 mmol, 6 eq.), palladium (II) acetate (104.1 mg, 0.46 mmol, 0.33 eq.), and potassium carbonate (1.31 g, 9.48 mmol, 7 eq.) were mixed together in dry dimethylformamide (DMF, 100 mL). The reaction medium was heated at 150 °C for 48 h under nitrogen atmosphere. The reaction mixture was afterwards cooled down to r.t., and the solvent was removed under vacuum and extracted with dichloromethane (DCM, 3 times 60 mL). The organic layer was collected, washed with water, dried with anhydrous magnesium sulphate, and DCM was evaporated under reduced pressure. The crude product was purified by column chromatography (stationary phase: silica; mobile phase: DCM 94 : 6 methanol) (802 mg, 0.92 mmol, 66%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.05 (d, 8H, J= 8.2 Hz), 7.62 (d, 8H, J= 8.2 Hz), 7.43 (d, 8H, J= 8.2 Hz), 7.19 (d, 8H, J= 8.2 Hz), 3.91 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): 167.1, 145.0, 143.5, 140.7, 138.2, 132.1, 130.2, 129.0, 128.6, 126.8, 126.7, 52.2. HRMS (ESI⁺): m/z calcd. for C₄₈H₄₄O₈: 868.3031, found: 868.3024 (z=1).

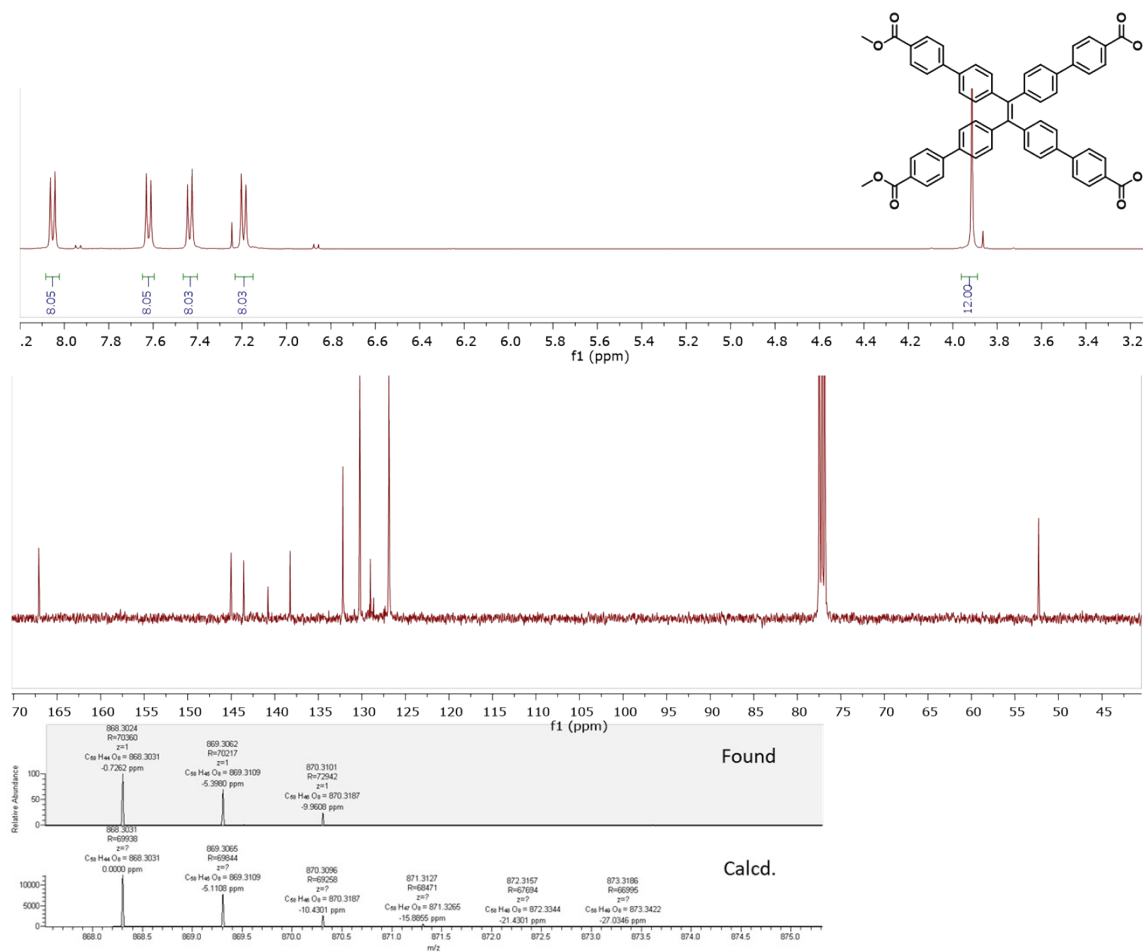


Figure S2. Top: ¹H NMR spectrum of **2**; middle: ¹³C NMR spectrum of **2**; bottom: HR-MS spectrum of **2**.

Synthesis of **TBC**

Compound **2** (1 g, 1.15 mmol, 1 eq) and sodium hydroxide (1 g, 25 mmol, 21.7 eq) were added into a mixture of tetrahydrofuran (40 mL), methanol (40 mL), and water (40 mL). The mixture was heated at 65°C overnight. After cooling down the reaction medium to room temperature, all the solvent was removed under reduced pressure, and the solid was dissolved in water (30 mL), and acidified with a 2 M HCl solution, until complete precipitation. The obtained precipitate was filtered, washed with water (3x 50 mL) and dried under vacuum. yield a yellow precipitate, which was filtered, washed with water, and dried under vacuum, to yield the final product as a yellow powder (924.7 mg, 1.137 mmol, 99%). ¹H NMR (400 MHz, d₁₀-THF): δ (ppm) 7.29 (d, 8H, J= 8.3 Hz), 6.96, (d, 8H, J= 8.3 Hz), 6.81 (d, 8H, J= 8.3 Hz), 6.50 (d, 8H, J= 8.3 Hz). ¹³C NMR (100 MHz, d₁₀-THF): δ (ppm) 165.7, 143.6, 142.9, 140.0, 137.5, 131.3, 129.3, 129.0, 125.7, 125.6. HRMS (ESI⁺): m/z calcd. for C₄₈H₄₄O₈: 813.2483, found: 813.2467 (z=1).

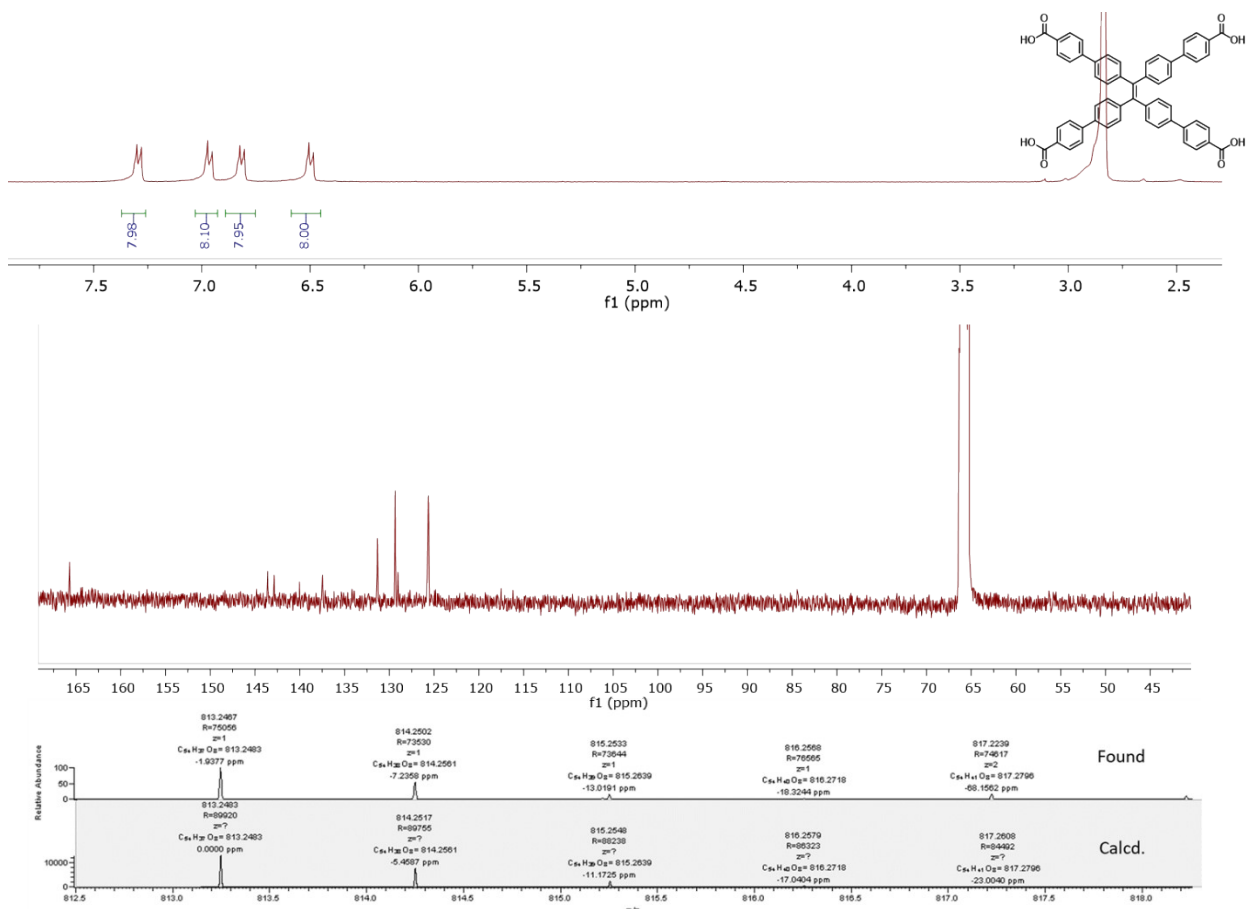


Figure S3. Top: ¹H NMR spectrum of **TBC**; **middle:** ¹³C NMR spectrum of **TBC**; **bottom:** HR-MS spectrum of **TBC**.

Synthesis of **Mg-TBC MOF**

In a pressure tube, **anhydrous** MgCl₂ (300 mg, 3.1 mmol, 17.5 eq) **TBC** (150 mg, 0.18 mmol, 1 eq), acetic acid (5 mL, 0.087 mmol, 0.44 eq) and dimethylformamide (DMF, 50 mL) were mixed together. The tube was sonicated for 2 min, and was heated at 150°C for 48 h. The crystalline yellow crystalline powder was purified by a Soxhlet extraction in ethanol for 24 h. The powder was dried under vacuum in order to obtain the final material (88 mg).

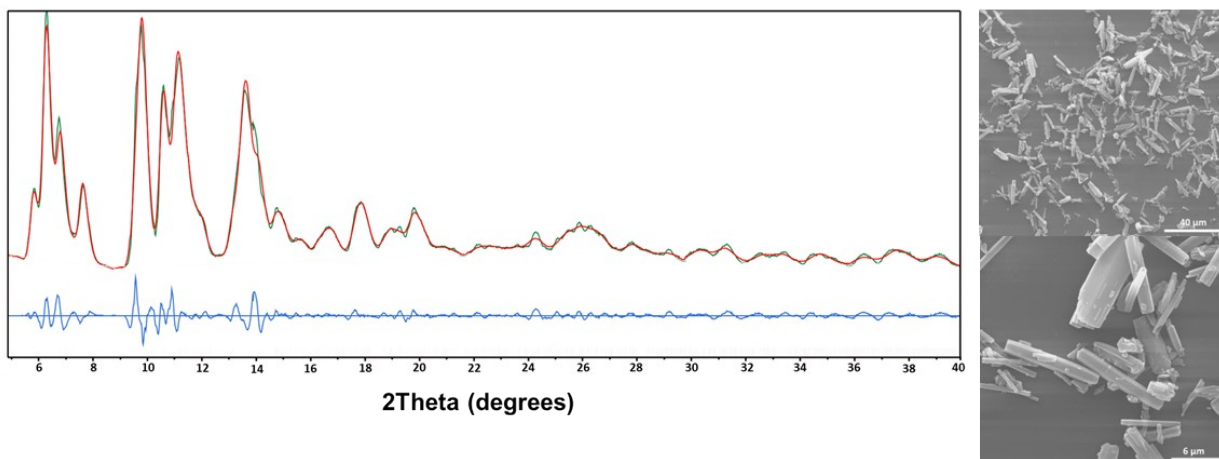


Figure S4. Left: PXRD pattern of **Mg-TBC MOF**; (green: measured data, red: calculated data, blue: difference between the calculated and measured data), right: SEM micrographs of **Mg-TBC MOF** (top: scale bar= 40 μm; bottom: scale bar= 6 μm).

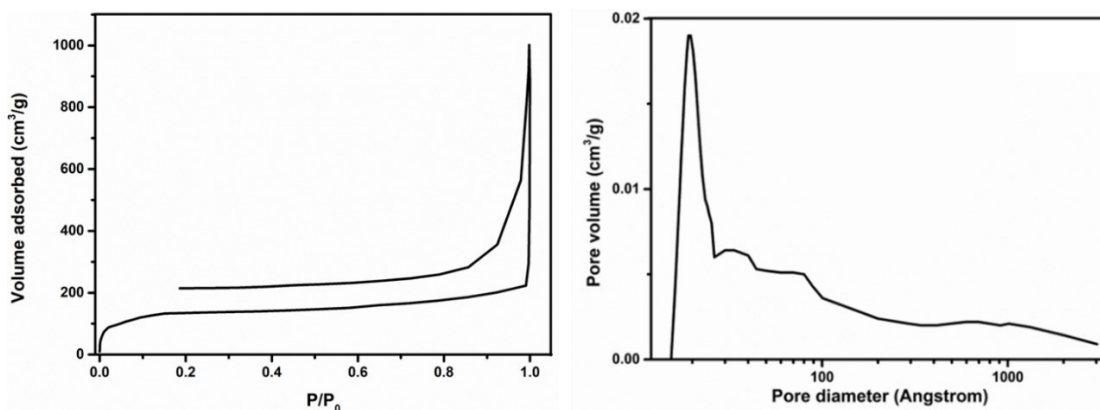


Figure S5. Left: volume adsorbed vs. relative pressure plot of **Mg-TBC MOF**, right: Pore size distribution of **Mg-TBC MOF**.

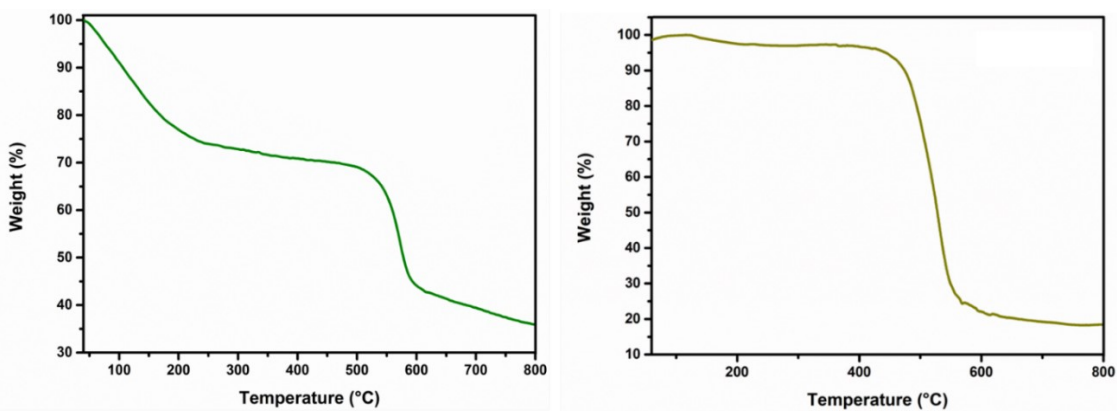


Figure S6. Left: TGA diagram of **Mg-TBC MOF**, right: TGA diagram of **TBC**.

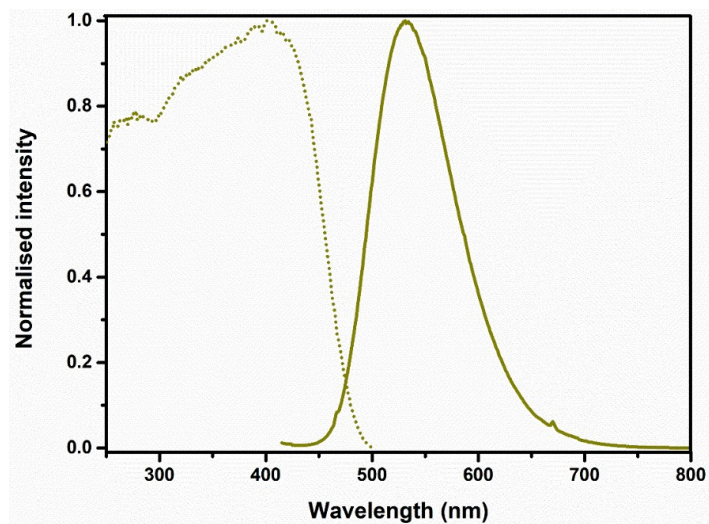


Figure S7. Excitation (dotted line, $\lambda_{Em}=540$ nm) and emission (full line, $\lambda_{Exc}=370$ nm) of TBC.

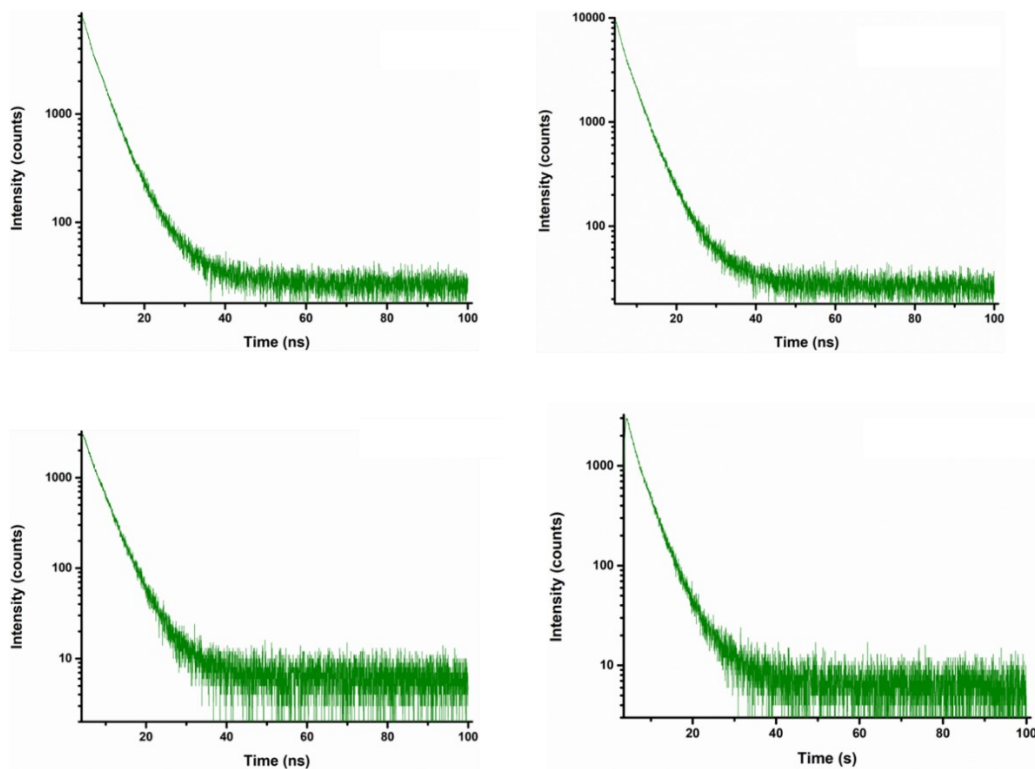


Figure S8. τ decay plots. Top left: TBC; top right: Mg-TBC MOF; bottom left: Mg-TBC MOF@PS; bottom right: Mg-TBC MOF@PS.

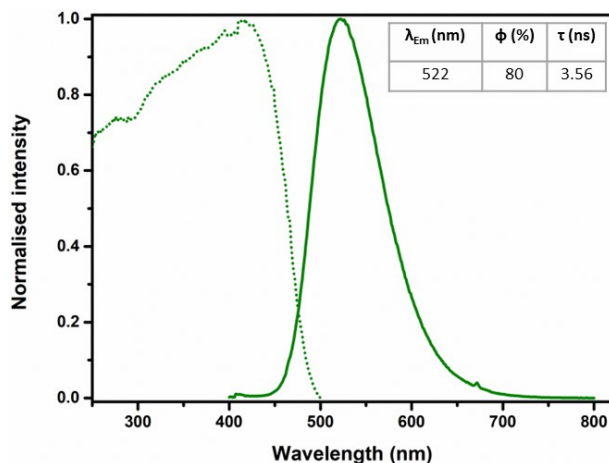


Figure S9. Excitation (dotted line, λ_{Em} = 520 nm) and emission (full line, λ_{Exc} = 370 nm) spectra of **Mg-TBC MOF** after solvent removal; inset: luminescence properties of the sample.

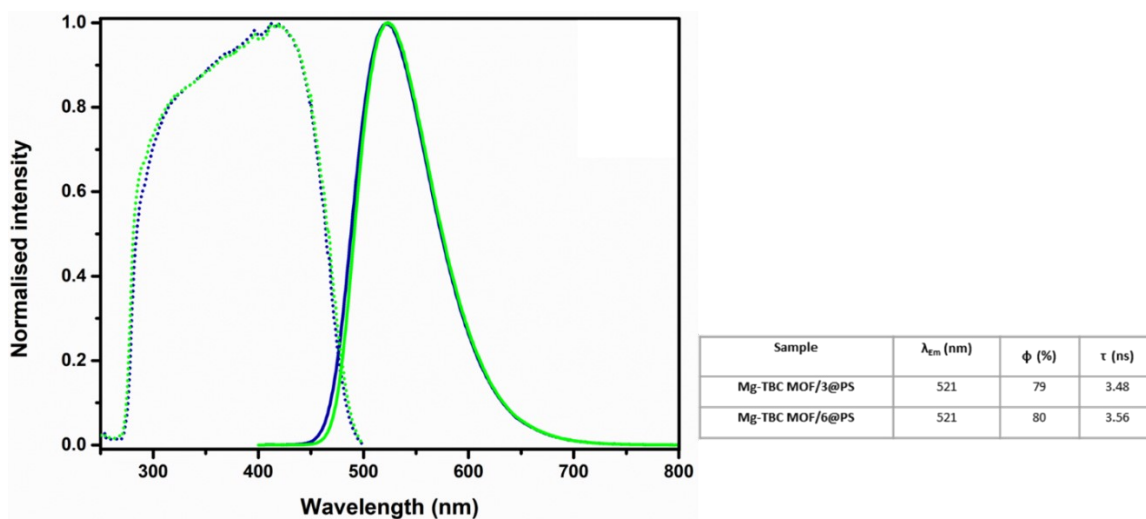


Figure S10. Left: excitation (dotted line, λ_{Em} = 520 nm) and emission (full line, λ_{Exc} = 370 nm) spectra of **Mg-TBC MOF/3@PS** (blue line) and **Mg-TBC MOF/6@PS** (green line); right: luminescence properties of both samples.

Coating & HLEDs preparation

The photon down-converting coatings were prepared and optimized as followed. A 200 mg·mL⁻¹ polystyrene (PS, average Mw=350000 g/mol) solution in toluene was made by mixing 4 g of PS in 20 mL toluene, prior to heating at 80°C and stirring for 2 h. 6 mg of **Mg-TBC MOF**, was put in a vial and 900 μ L of the PS solution was poured in the vial. The resulting suspension was heated at 80°C and stirred at 300 rpm for 10 minutes. The final suspension was allowed to cool down to r.t., and 300 μ L of it were put in a well-shaped Teflon mould. The suspension was left to dry for 48h at r.t., and the resulting dry, dome-shaped coating was recovered. The thickness of the coating was measured using a Helios-Preisser electronic outside micrometre.

The HLEDs fabrication was performed as followed: the prepared coatings were placed according to either an on-chip (zero distance to the emitting chip) or a remote (2 cm distance to the emitting chip) configuration on a 380 nm LED (HotRed 1 W). Luminous efficiency was determined at different applied currents (10-200 mA), while device stability was monitored at constant 200 or 20 mA under ambient conditions. The employed power source was a Keithley 2231-A-30-3. The electro-luminescence spectra were recorded by an Avantes 2048L spectrometer (300 VA grating, 200 μ m slit, CCD detector) coupled with an AvaSphere 30-Irrad integrated sphere. The temperature of the photon down-converting coatings under operation condition was monitored using a thermographic camera FLIR ETS320. The

stability of the air-free coatings was performed the same way, but in a glove box, using as inert gas grade 5 nitrogen (99.999% purity).

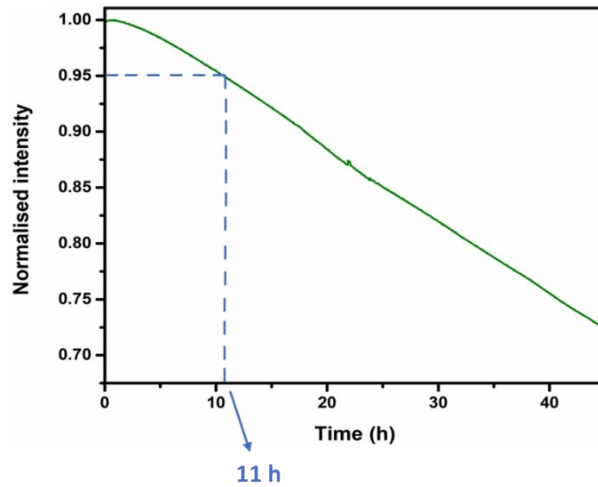


Figure S11. Emission intensity over time of the **Mg-TBC MOF**-based HLED in an on-chip configuration at 200 mA under nitrogen atmosphere.

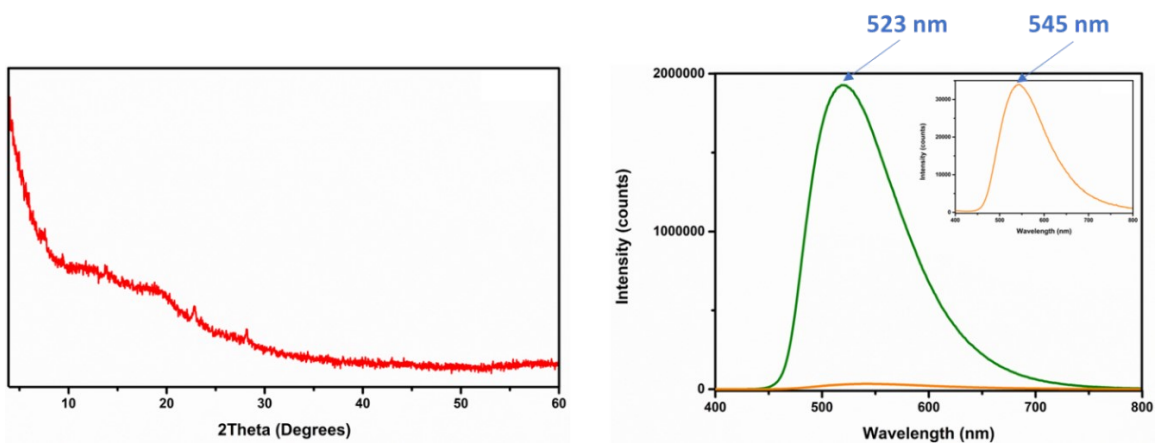


Figure S12. Left: PXRD pattern; and right: emission of spectra of the fresh (green line) and of the *post-mortem* (orange line) **Mg-TBC MOF** sample in its powder state. Inset: zoom of the *post-mortem* sample.

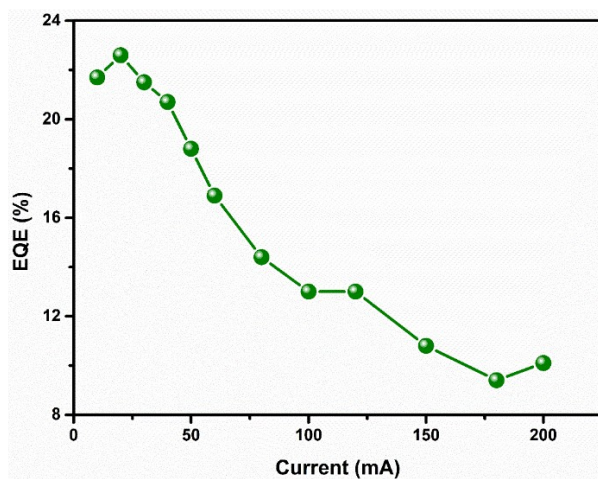


Figure S13. EQE vs. applied current, from 10 mA to 200 mA.

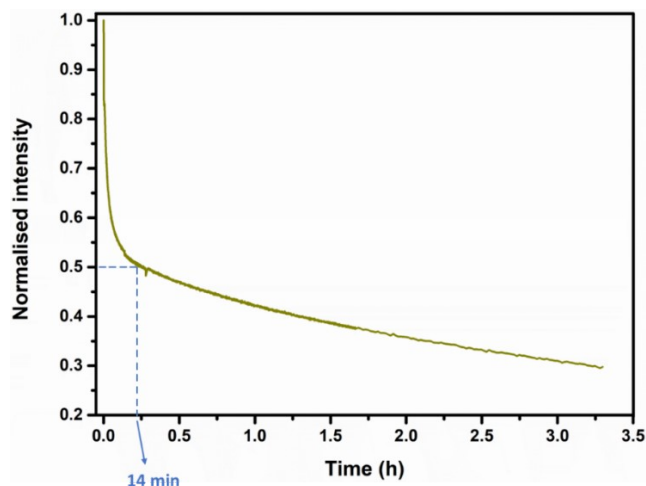


Figure S14. Emission intensity over time of the TBC-based HLED in an on-chip configuration at 200 mA.

Table S1. Emission properties of LMOFs reported in the literature.

LMOF	λ_{Em} (nm)	ϕ	Ref.
MOF-BTBMBA	501	42.5%	S6
Cd- H ₆ TATPT MOF	425	15%	S7
ZJU 28 (In)	445	n. d.	S8
Zn-2-MOF (Zn)	482	53%	S9
NENU-524 (Zn)	445	7%	S10
NENU-521 (Zn)	450	11%	S11
PCN-921	447	94%	S12
MOF74-Eu	616	82%	S13
MOF74-Tb	546	91%	S13
MOF74-Sm	600	4%	S13
MOF74-Dy	484/577	18%	S13

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