ARTICLE

Supporting Information

Multi-Stimuli-Responsive Luminescent MCM48 Hybrid for Advanced Anti-Counterfeiting Applications

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Chemicals

Cetyl bromide (CTAB) (Sigma aldrich, 98%), F127 (Pluronic®F-127) (Sigma aldrich), absolute ethanol (EtOH) (Merck, 99.9% PA), 29% ammonium hydroxide solution Sigma Aldrich, 98%), aminopropyl 3-(triethoxysilane) (APTES) and 3-Isocyanatopropyl 3-(Triethoxysilane) (TESPIC) (Sigma Aldrich, 95%), trimesic acid) (Sigma Aldrich, 95%), Dicyclohexylcarbodiimide (DCC) (Sigma Aldric, 99%), 4-dimethylaminopyridine (DMPA) (Sigma Aldrich, 99%), dimethylformamide (DMF) 1.21 mmol), (Sigma aldrich, 95%), Toluene, 4,4,4-trifluoro-1-phenyl-1,3-butadione (BTFA) and Ethylene glycol (Dynamic) (masterprint), Europium oxide (Sigma Aldric, 99%).

Synthesis of hybrid materials

The europium-complexes grafted onto mesoporous silica MCM-48 (SiO_2) were synthesized in four steps procedure following the experimental approach described by Li et al. [21] and Fujiwara, [22] respectively for grafting of trimesic and chelidamic acids. We starting by synthesizing the SiO_2 through modified Stöber method.[20] Then, were performed reaction of SiO_2 and H_2DAMIC with the coupling agent TESPC, respectively for H_2BTC-SiO_2 and H_2DAMIC-SiO_2. Next, trimesic and TESPIC-H_2DAMIC was covalently linked to silica, resulting in the H_2BTC-SiO_2 and H_2DAMIC-SiO_2 materials. Finally, the trivalent europium ions (Eu^{3+}) were coordinated to the benzene-carboxylic (H_2BTC-SiO_2) and pyridine-carboxylic (H_2DAMIC-SiO_2) chelating groups, using europium nitrate aqueous solutions resulting in the luminescent hybrids Eu$(H_2O)_n$BTC-SiO_2 and Eu$(H_2O)_n$DAMIC-SiO_2.

Synthesis of MCM48 mesoporous silica

MCM48 was synthesized according methodology adapted from Kin, Chung et al.[1] In that approach 0.5g of cetyltrimethylammonium bromide (CTAB) was stirred with 2.05g of Pluronic®F Diluted in 96 mL of distilled water, 43 mL of absolute ethanol (ETOH) and 11 mL of 29% ammonium hydroxide solution. After complete dissolution of the reagents, 2 mL of Tetraethyl Orthosilicate (TEOS) was added and stirred for about 5 minutes, until the solution became whitish. The mixture was allowed to stand for 24 hours at room termperature for condensation of the silica. Subsequently, the sample was centrifuged using 6000 rpm for 40 min and washed 4 times with distilled water. A white precipitate was obtained and it was held at 70 °C for 24 hours, and then calcined at 550 °C in air for 4 hours to remove the organic phase.

Eu$(H_2O)_n$BTC-SiO_2 hybrid

Firstly, functionalization of MCM48 was performed with the coupling silane aminopropyl 3-(triethoxysilane) (APTES). This synthesis was adapted from the methodology of Saindulo Gangi and collaborators.[2] In that approach 100 mg of MCM48 were suspended in 10 mL of toluene, then 3 mL of APTES were added dropwise. The mixture was refluxed for 24 h at 120 °C. Subsequently, the suspension was precipitated by centrifugation at 6000 rpm, washed several times with toluene and dried at 60 ° C for 6 hours. Finally, a white solid was obtained and called as H_2N-SiO_2. Afterward, 280 mg of the synthesized H_2N-SiO_2 was dispersed in 28 mL of DMF, then 260 mg (1.23 mmol) of H_3BTC, 260 mg (1.26 mmol) Dicyclohexylcarbodiimide (DCC) and 15.3 mg (0.1 mmol) 4-dimethylaminopyridine (DMPA) was following added. This mixture was refluxed under nitrogen atmosphere and heating (100 °C) for 36 hours. Subsequently, the system was centrifuged at 6000 rpm and the precipitate washed in DMF, water and absolute ethanol in the ratio of 1:1:4, respectively. Finally, the powder was washed with acetone. The solid, light brown,

corresponding to the $H_2BTC\text{-}SiO_2$ hybrid, was dried at 60 ° C under vacuum for 5 hours. The last step was the coordination of Eu^{3+} ions with chelating groups of the $H_2BTC\text{-}SiO_2$ material. To do this, europium nitrate (0.1, 0.2, and 0.3 mmol) was solubilized in 3 ml of distilled water using a borosilicate microwave reactor (10 ml). Then, 50 mg of $H_2BTC\text{-}SiO_2$ was dispersed in this solutions and heated at 140 ° C in a microwave (100 W) for 20 minutes.[3] At the end, the samples were centrifuged and washed with water 5 times and drying in vacuum oven at 60 ° C for 5h.

$Eu(H_2O)_nDAMIC\text{-}SiO_2$ hybrid

The synthetic approach for graft H_2DAMIC to SiO_2 is somewhat different from used for the H_3BTC. Here we have used the protocol developed by Fujiwara et al with some modifications.[2] Firstly, 0.222 g (1.21 mmol) of H_2DAMIC, 0.300 g (1.21 mmol) of 3-(triethoxysilyl) propylisocyanate (TESPIC) and 1.5 mL of DMF was stirred and refluxed at 120 °C for 24 h. Then, 0.5 mL of dry toluene suspension and M mg of SiO_2 were added to this system and refluxed for a further 24 h. Afterward, the $H_2DAMIC\text{-}SiO_2$ was collected by centrifugation (6000 rpm) and washed 3 times with 1:1 DMF/toluene to give a white solid, in which was dried at 70 °C under vacuum for 5 hours. The complexation step with Eu^{3+} ions was carried out from europium nitrate dissolution in 3 ml of distilled water using a borosilicate microwave reactor with a capacity of 10 ml. Then, 50 mg of $H_2DAMIC\text{-}SiO_2$ was dispersed in this solutions and heated at 140 ° C in a microwave (100 W) for 20 minutes.[4] Finilly, the $Eu(H_2O)nDAMIC\text{-}SiO_2$ hybrid was collected by centrifuged and washed with water 5 times and drying in vacuum oven at 60 ° C for 5h.

Amount of Eu^{3+} loaded

The quantifications of the Eu^{3+} loaded in the hybrids (**Table S2**) were carried out via complexometric titration with ethylene diamine tetraacetic acid (EDTA) 0.01 $mol.L^{-1}$. After complexation step and centrifugation, 1mL of the supernatants and 0.5 mL of the orange xylenol indicator were mixed. Next, the titration was performed using EDTA solution up to the sample color change from red-violet to yellowish (equivalence point).

Booth hybrids showed amount saturation of Eu^{3+} ions equal to ca. 0.01 mmol on each 50 mg of material. This indicates that $Eu(H_2O)_nBTC\text{-}SiO_2$ hybrid shows a smaller concentration of chelating agent once that the stoichiometric proportion Eu^{3+}/quelating are 1:1 for $Eu(H_2O)_nDAMIC\text{-}SiO_2$ and 2:1 for $Eu(H_2O)_nBTC\text{-}SiO_2$.

Table S1. Amount of Eu^{3+} in 50 mg of the SiO_2.

Hybrid	Amount of Eu^{3+} (mmol)
$Eu(H_2O)_nBTC\text{-}MCM48$	0.02
	0.10
	0.09
$Eu(H_2O)_nDAMIC\text{-}MCM48$	0.04
	0.12
	0.11

Anticouterfeit ink preparation

The anticouterfeiting inks were obtined by dispersion of 3.0 mg of $Eu(H_2O)_nBTC\text{-}SiO_2$ and $Eu(H_2O)_nDAMIC\text{-}SiO_2$ in 10 mL of a mixture of monoethyleneglycol/ethanol, 93:7, using ultrasound probe for 30 min (180 W, 40 KHz). Than, the homogeneous dispersion was introduced into a cartridges and the optimized printer parameters were set according to **Table S4**.

In vitro assay

Cell Culture

3T3 fibroblast were cultured in Dulbecco's Modified Eagle Medium (DMEM) containing 10% fetal bovine serum (FBS), L-glutamine (2 mM) and gentamicin (40 μg/mL) in a humidified incubator in atmosphere with 5% CO_2 at 37°C.

Human lung epithelial cells (A549), a cell line, were cultured in RPMI-1640 supplemented with 10% SBF, L-glutamine (2 mM) and 40 μg/mL gentamicin. For treatments, the cells were cultured in serum-free medium.

Cell viability Assay

The effect of MCM48, BTFA, NH_2-MCM48, H_2BTC-SiO_2, Eu(H_2O)$_n$BTC-SiO_2, H_2DAMIC-SiO_2, Eu(H_2O)$_n$DAMIC-SiO_2, Eu(BTFA)$_3$BTC-SiO_2, Eu(BTFA)$_3$DAMIC-SiO_2 and TTA on A549 and 3T3 cell viability was performed by MTT assay (MOSMANN, 1983).[5]

Briefly, the cells were seeded in a 96-well plate (A549 1 x 10^4 or 3T3 7 x 10^3 cells/well) overnight and treated with different concentration of the samples (3, 30, 100 or 300 μg/mL) for 24 hours.

After the incubation with the treatment, 22.5 μL of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphe-nyltetrazolium bromide) (Sigma-Aldrich – EUA) (5 mg/mL in PBS) was added to each well for 3 hours. Then, the supernatant was discarded and 150 μL of DMSO was added to each well to solubilize the formed formazan crystals. The absorbance of each well was recorded using a microplate spectrophotometer and the optical density (OD) was measured at 540 nm. The percentage of viability cell was calculated through this formula: (OD treated cells/OD non-treated cells) X100.

Equipment

The Fourier Transform Infrared Analysis were performed in a Perkin Elmer device, model Spectrum 400, in the region of 4000-400 cm^{-1} with UATR accessory (Universal sampling accessory with pressure arm). The spectra had a resolution of 2 cm^{-1} to 32 accumulations. The measurements were carried out at room temperature in the Fuel Laboratory (LAC), in the Department of Chemical Engineering (DEQ), UFPE. Porosimetry was performed in the Micromeritics Model ASAP 2420. The equipped has 12 independent sample treatment stations and 6 analysis stations operating simultaneously.

The XRD, The measurements were performed on a Rigaku diffractometer, model RINT 2000 / PC, which uses Cu K rad radiation. The diffraction patterns for the angular range 2θ = 1 ° -9 ° to obtain the MCM48 standards, in continuous scan module with step of 0,01 °, with a speed of 1 min with a counting time of 1 second. The scanning electron microscopy (SEM) was obtained TESCAN MIRA's 4th generation with FEG Schottky electron emission source combines SEM imaging and live elemental composition analysis. To perform SEM and elemental analysis, the powder samples were caped with a gold film. The samples was previously coated with gold film by sputtering coater. To preform EDS and FTIR analysis of Eu(BTFA)3L-SiO2 hybrids, after soaking hydrated samples in BTFA solution and then, the samples were dispersed in ethanol under stirring for 30 min. Next, the powder was collected by centrifugation. This wash procedure was performed for three times. After drying in ambient conditions, the samples were analyzed. The thermogravimetric-TGA analysis was obtained in the equipment manufactured by Shimadzu model DTG-60H with the analysis parameters in the range of 10 ° C per minute in nitrogen atmosphere. Emission and excitation and lifetime spectra were performed in a Horiba Jobin Yvon, Fluorolog-3 ISA spectrofluorimeter. The values for lifetime are determined by fitting the luminescence decay curve to the function $I = I_0 e^{-(t/\tau)} + b$.

Quantum Yield (Q_{Ln}^{Ln}) calculation

The intrinsic emission quantum yield (Q_{Ln}^{Ln}) of the $^5D_0$ emitting level is defined by the ratio between the radiative emission and total decay rates (radiative and non-radiative) for this particular energy level, according to follows equation. [4]

$$Q_{Eu}^{Eu} = \frac{A_{rad}}{A_{rad} + A_{nrad}}$$

The total decay rate (A_{rad} + A_{nrad}) is related to the deactivation process of the $^5D_0$ level, mainly by multiphoton relaxation, which is determined by the experimental lifetime values as follows:

$$\frac{1}{A_{rad} + A_{nrad}} = \frac{1}{A_{Total}} = \frac{1}{\tau}$$

In these equations, A_{rad} and A_{nrad} are the radiative and non-radiative spontaneous emission coefficients of $^5D_0 \rightarrow {}^7F_J$ transitions (J = 1, 2 and 4) of the Eu^{3+} ion. A_{rad} coefficient values were determined by $A_{rad} = \sum A_{0\rightarrow J}$ where $A_{0\text{-}J}$ are the spontaneous emission coefficients of $^5D_0 \rightarrow {}^7F_J$ transitions (J = 1, 2 and 4) of the Eu^{3+} ion. $A_{0\rightarrow J}$ are determined by

$$A_{0\to J} = A_{0\to 1}\left(\frac{S_{0\to J}}{S_{0\to 1}}\right)$$

Where $S_{0\text{-}J}$ are the integrated areas under the emission curves. The spontaneous emission coefficient $A_{0\to 1}$ of the $^5D_0 \rightarrow {}^5F_1$ transition is mostly ruled by the magnetic dipole mechanism and depends only on the refractive index of the material. Therefore, this transition is taken as a reference.[4]

FTIR Discussion

The success of graft reaction steps were monitored through FTIR spectroscopy (**Figure S1**). FT-IR spectrum for unmodified SiO_2 showed characteristic band at 1052 and 792 cm^{-1} assigned to the Si–O–Si and Si-O stretching vibrations, respectively (Black lines of Figure S1a). Also, the broadband in the region between 3,000 and 3,700 cm^{-1} corresponds to the stretching of the O-H bond of the silane hydroxyl groups and water molecules adsorbed on the mesoporous materials.[6] The functionalization of surface of the SiO_2 with amine groups on the surface was confirmed by additional peaks at 1560 and in the region of 3377-3120 cm^{-1} assigned to the NH_2 scissoring and stretching of the N-H bond (blue line of Figure S1a).[7] Moreover, characteristic peaks of the C-H stretching of the methylene groups of the TESPIC coupling agent in the range of 3023-2760 cm^{-1} are further evidence of the successful functionalization. After reaction with H_3BTC, the FTIR spectrum (green line of Figure S1a) showed new bands at ca. 1560 and 1660 cm^{-1} related to C=O of acid and amide groups indicating that chelating ligand has been successfully grafted onto NH_2-SO_2. Also, a small band assigned to N-H stretching of the secondary amide group is observed at 3275 cm^{-1}. These results unambiguously confirmed the mechanism displayed in the Scheme 1a. The coordination of the metal ions Eu^{3+} is evidenced by the shift of the -40 cm^{-1} in the energy of signal of the $\nu_{as}(COO^-)$ regarding $\nu_s(C=O)$ signal of protonated H_2BTC-SiO_2. In addition, the energy of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are typical of the chelate bidentate mode of the carboxylic group of the BTC.[5,6,7] On the other hand, after consecutive reactions between TESPIC, H_2DAMIC and SiO_2, in that order, in the FTIR of the resulting material H_2DAMIC-SiO_2 (Figure S1b) the disappearing of the N=C=O stretch vibration peak at 2,270 cm^{-1} for TESPIC and the emergence of N-H stretching of secondary amide group at 3,300 cm^{-1} indicates that H_2DAMIC has been grafted on to TESPIC. [8,9] In addition, the Si–C stretching vibration located at ca. 1,211 cm^{-1}, and the stretching vibration band of Si–O at 1,052 cm^{-1} reveal the existence of the siloxane bonds. As well as for Eu(H_2O)nBTC-SiO_2, the coordination of the metal ions Eu^{3+} is evidenced by the shift of energy of $\nu_{as}(COO^-)$ of the 81 cm^{-1} regarding $\nu_s(C=O)$ signal of protonated H_2DAMIC-SiO_2 hybrid. In addition, the energy of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is typical for the chelate tridentate mode of the carboxylic group of the DAMIC.[8]

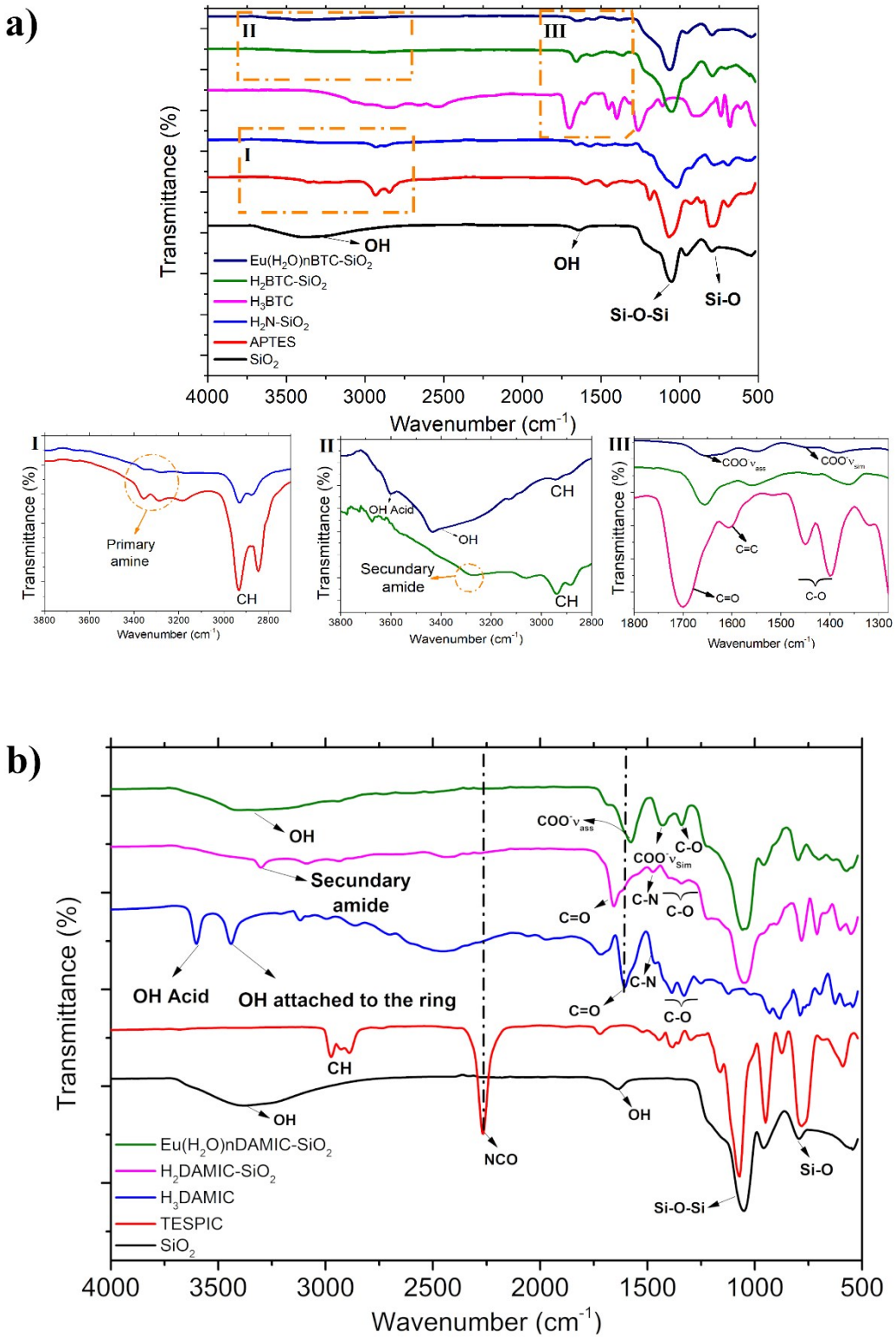


Figure S1: FTIR spectra of (a) SiO_2, APTES, H3BTC, H_2N-SiO_2, H_2BTC-SiO_2, Eu(H_2O)nBTC-SiO_2 and (b) SiO_2, TESPIC, H_2DAMIC, H_2DAMIC-SiO_2, Eu(H_2O)nDAMIC-SiO_2.

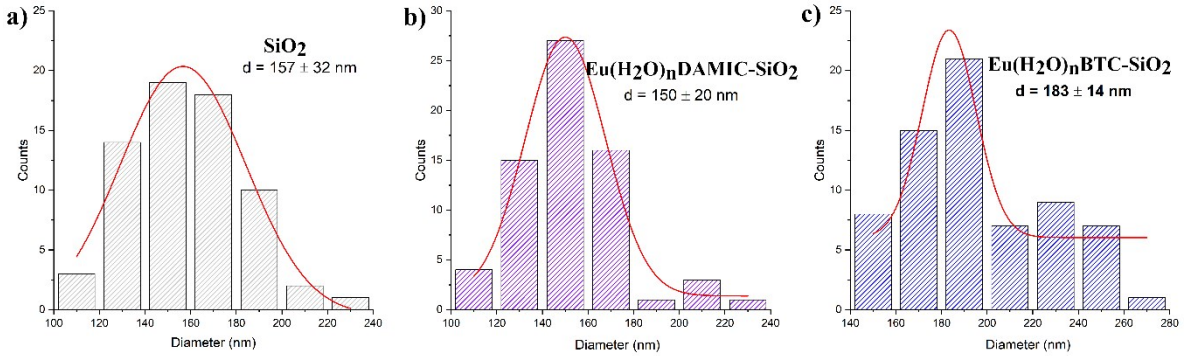


Figure S2: Particle distribution hystogram of MCM48, Eu(H_2O)nBTC-SiO_2 and Eu(H_2O)nDAMIC-SiO_2.

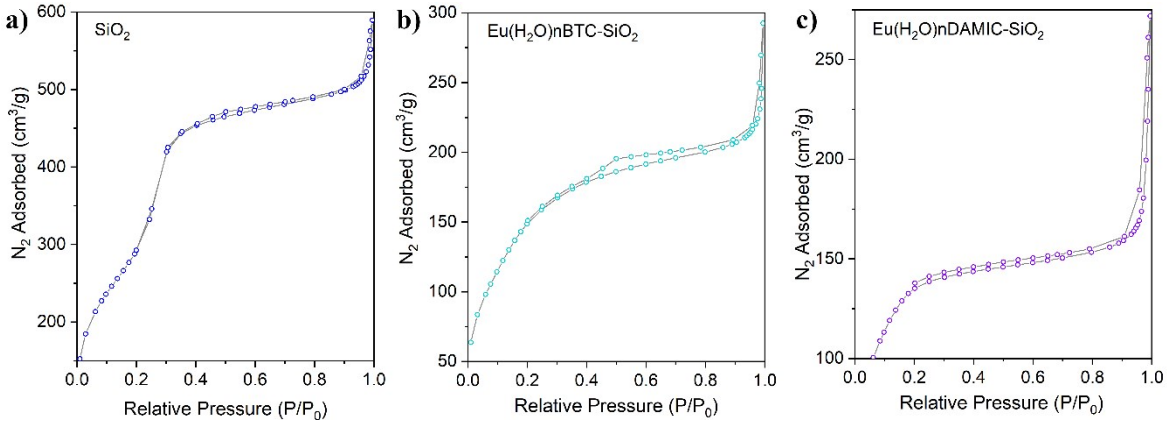


Figure S3. Nitrogen adsorption–desorption isotherms for MCM48 and hybrids Eu(H_2O)$_n$BTC-SiO_2 and Eu(H_2O)$_n$DAMIC-SiO_2.

Table S2. Porosiometry of MCM48 and hybrids EuBTC-MCM48 and EuDAMIC-MCM48.

Materials	Surface area m^2/g	Pore volume cm^3/g
MCM48	1,070.6	0.973
Eu(H_2O)nBTC-SiO_2	578.8	0.386
Eu(H_2O)nDAMIC-SiO_2.	499.5	0.388

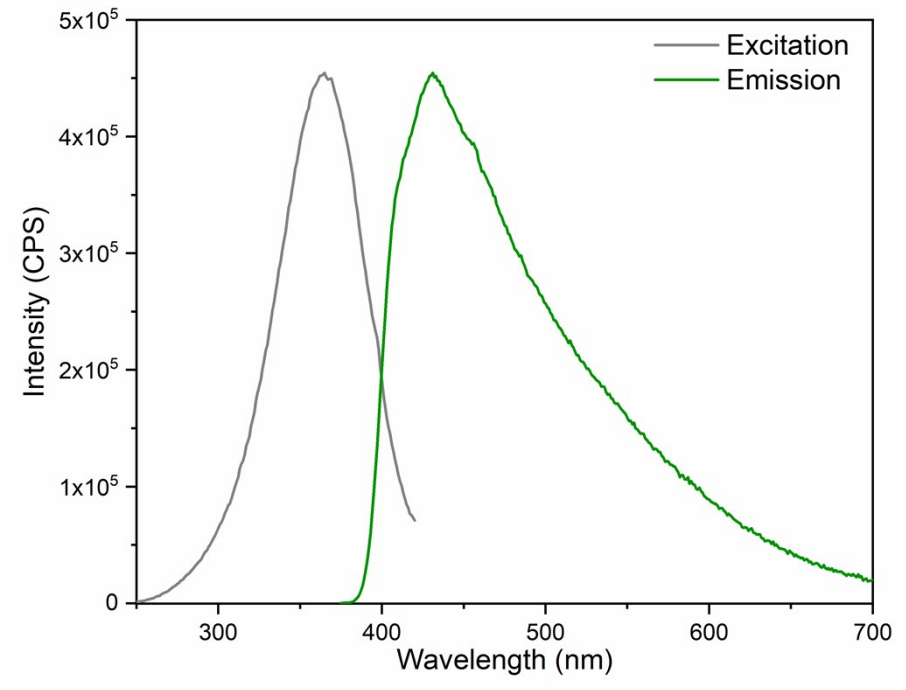


Figure S4. Excitation (λ_{Em} = 437 nm) and emission (λ_{Ex} = 362 nm) spectra of the SiO_2.

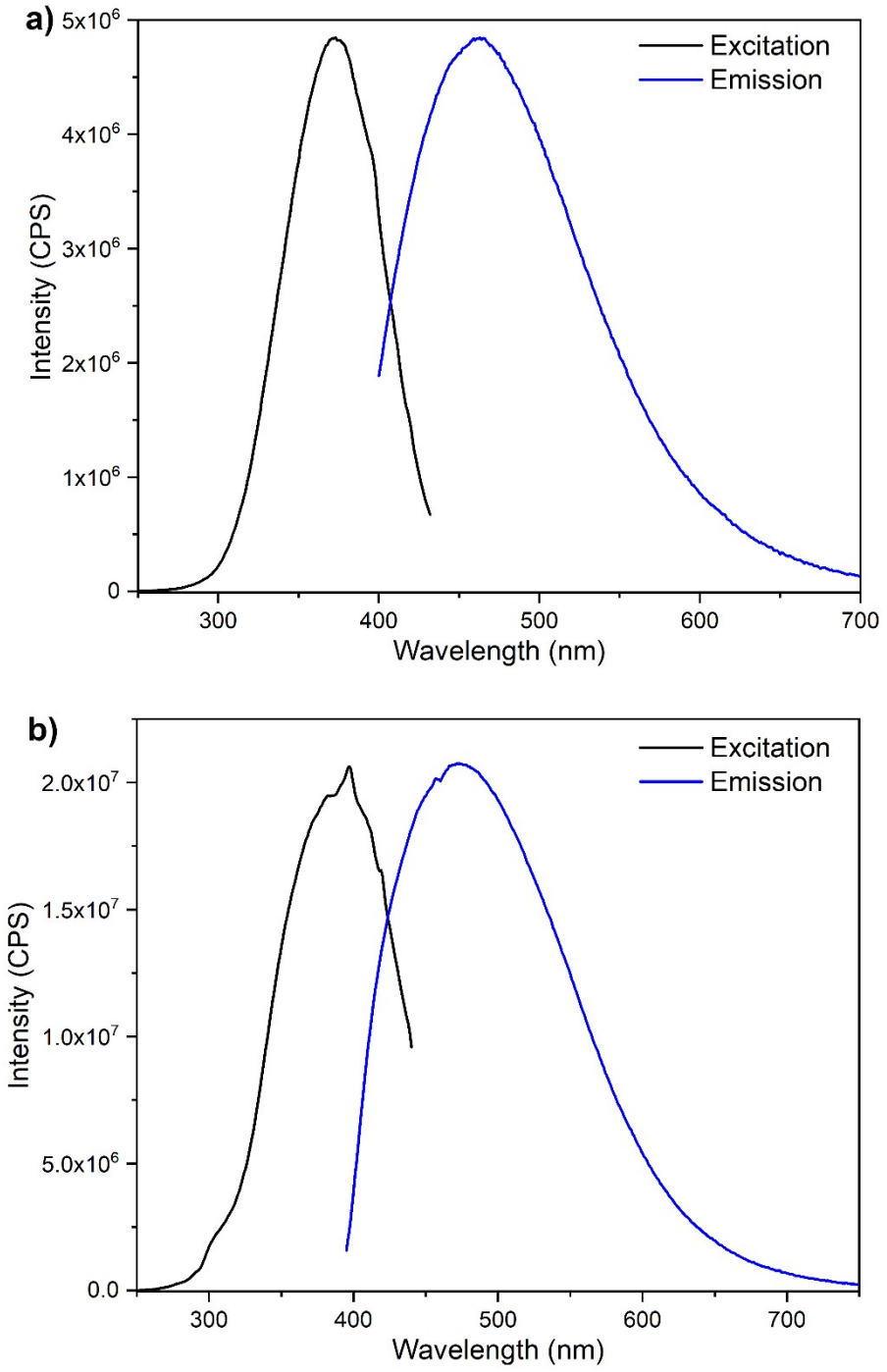


Figure S5. Excitation and emission spectra of the (a) H_2DAMIC-SiO_2 (λ_{Em} = 442 nm λ_{Ex} = 375 nm) and (b) H_3BTC-SiO_2 (λ_{Em} = 470 nm λ_{Ex} = 382 nm).

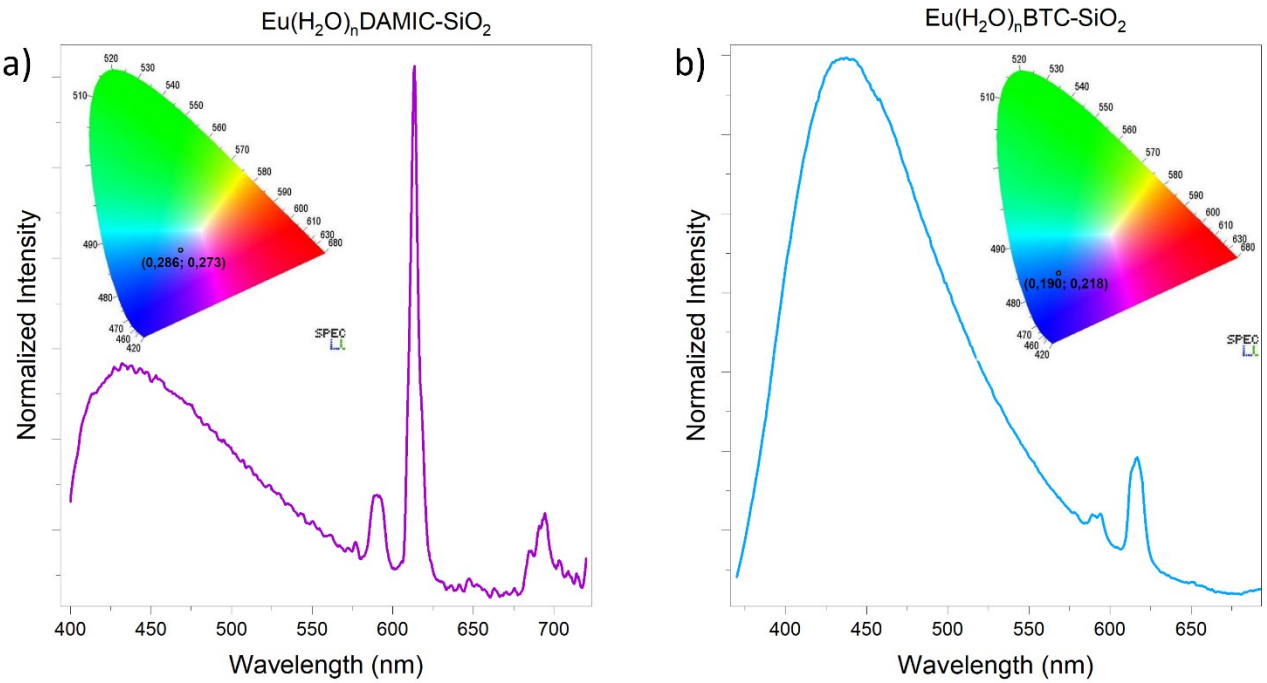


Figure S6. Emission spectra (λ_{Ex} = 365 nm) and corresponding chromaticity diagram of (a) $Eu(H_2O)_nDAMIC\text{-}SiO_2$ b) $Eu(H_2O)_nBTC\text{-}SiO_2$.

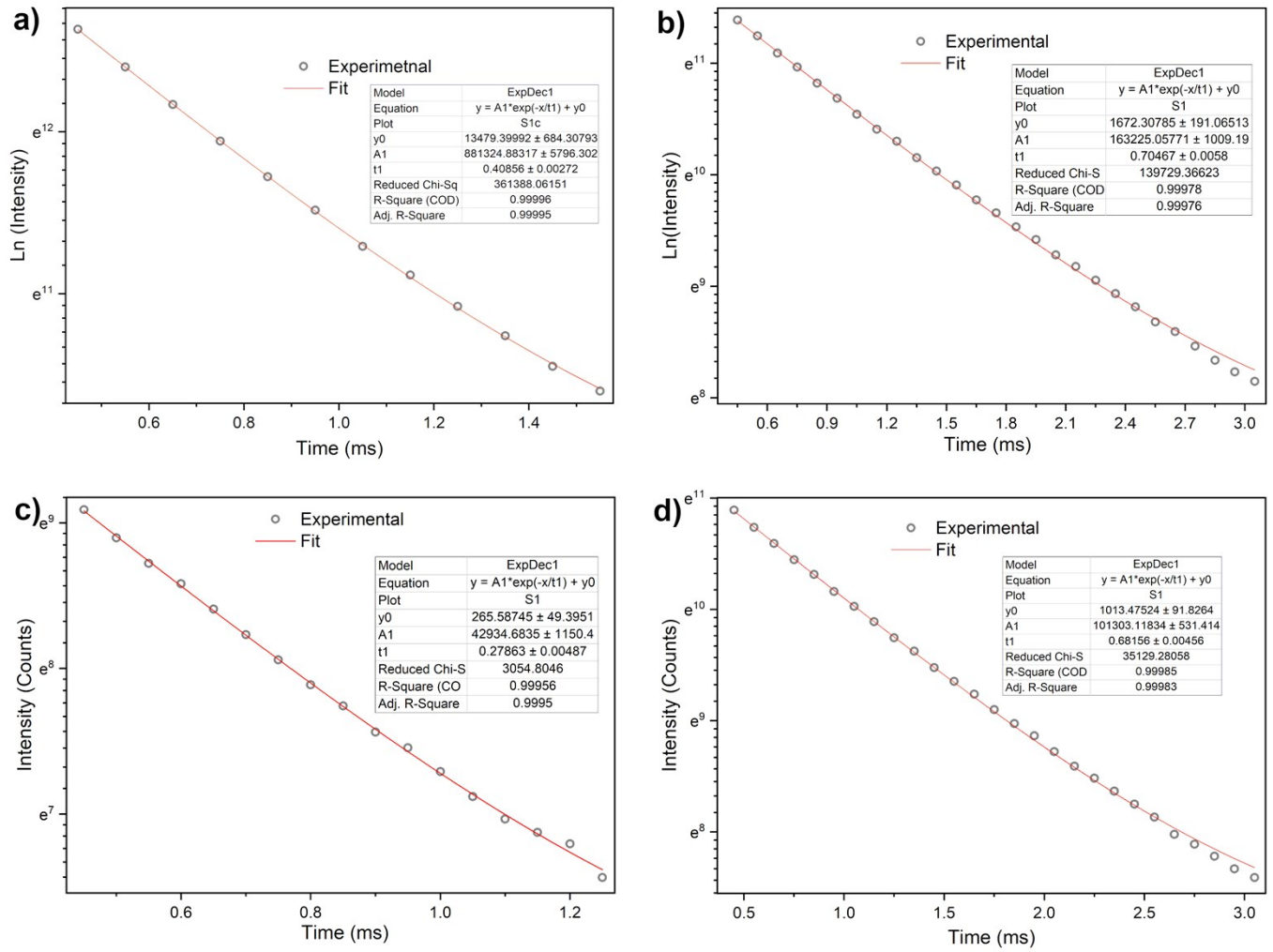


Figure S7. Luminescence decay curves of the (a) $Eu(H_2O)_nDAMIC\text{-}SiO_2$ (λ_{Ex} = 312 nm λ_{Em} = 618 nm), b) $Eu(BTFA)_3DAMIC\text{-}SiO_2$ (λ_{Ex} = 355 nm λ_{Em} = 612 nm), c)$Eu(H_2O)_nBTC\text{-}SiO_2$ (λ_{Ex} = 292 nm λ_{Em} = 616 nm) and d) $Eu(BTFA)_3DAMIC\text{-}SiO_2$ (λ_{Ex} = 370 nm λ_{Em} = 611 nm).

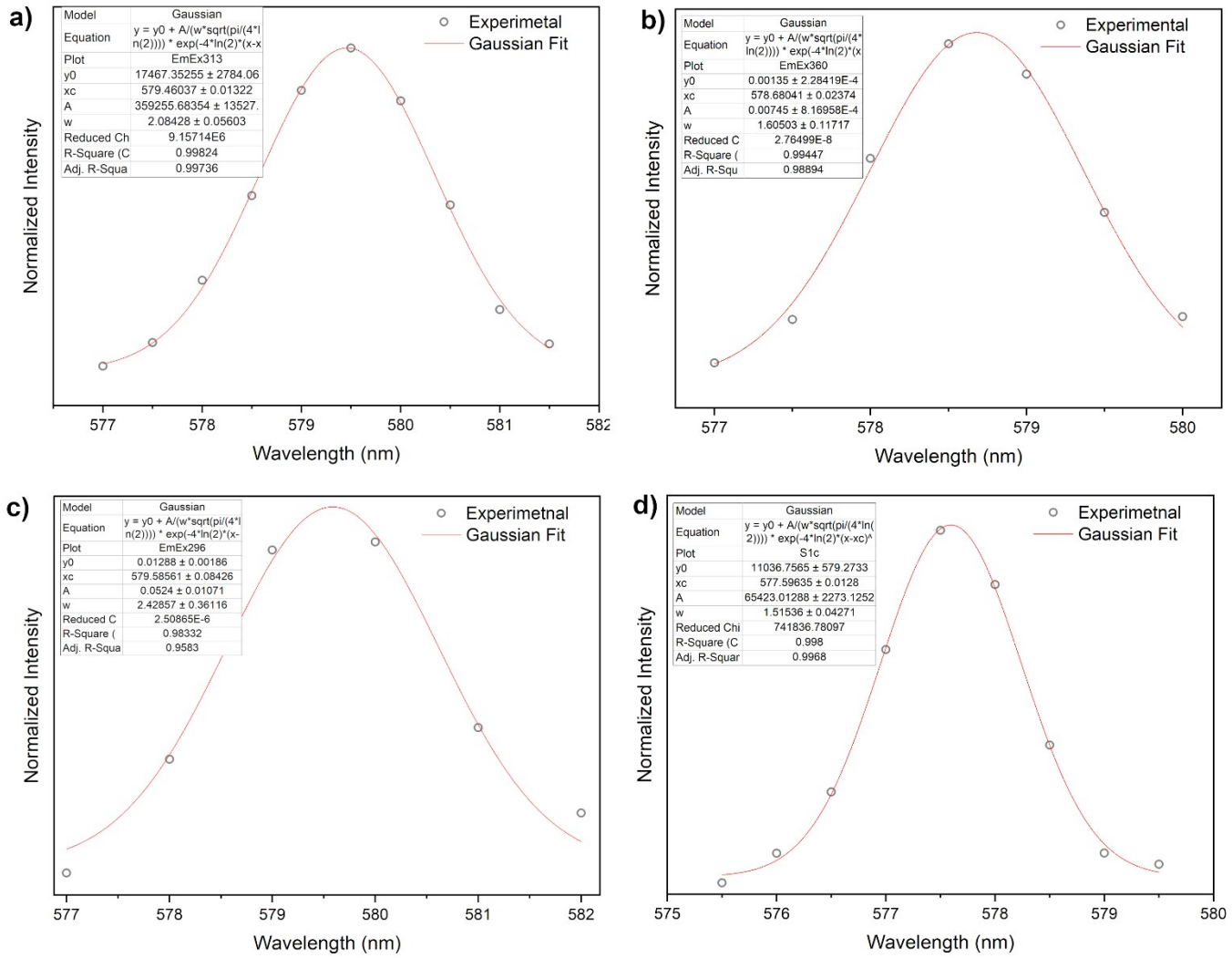


Figure S8. Emission spectra and Gaussian fit of the $^5D_0 \rightarrow {}^7F_0$ of the (a) $Eu(H_2O)_nDAMIC\text{-}SiO_2$, b) $Eu(BTFA)_3DAMIC\text{-}SiO_2$, c)$Eu(H_2O)_nBTC\text{-}SiO_2$ and d) $Eu(BTFA)_3DAMIC\text{-}SiO_2$.

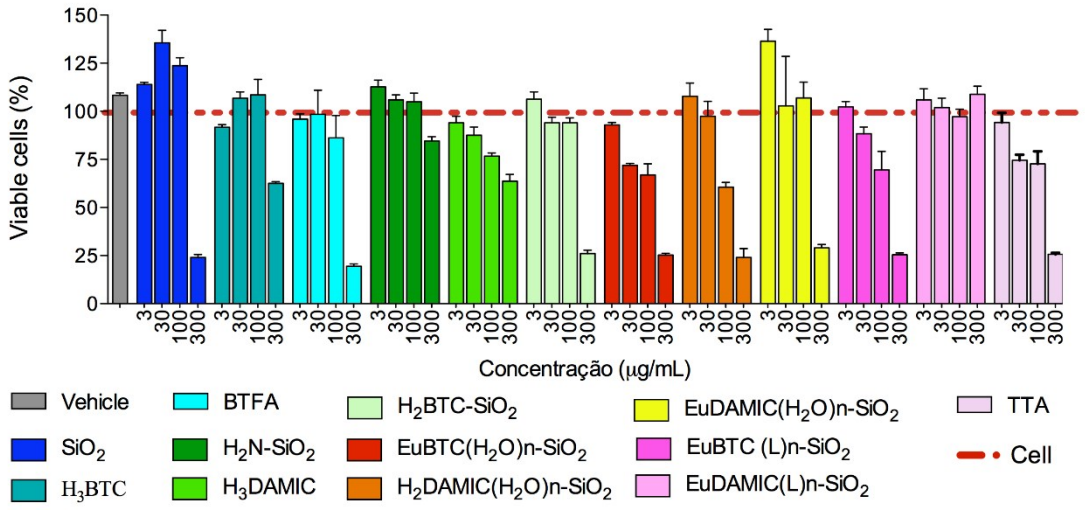


Figure S9. Effects on 3T3 cell viability (24 hours). The bars represent the mean ± SEM. The dashed line represents the control group (treated with DMEM). The group vehicle represent the treatment with ethanol 0.001%. Data were expressed as % viable cells compared to the control group. One-way ANOVA followed by the Newman-Keuls post-test, ** p <0.01 and *** p <0.001 (Control vs. treatment).

Table S3. Integrated intensity, $R[I(^5D_0 \rightarrow ^7F_2)]/[I(^5D_0 \rightarrow ^7F_1)]$, ratio of the powders of the hybrids

Material	$R[I(^5D_0 \rightarrow ^7F_2)]/[I(^5D_0 \rightarrow ^7F_1)]$
$Eu(H_2O)_nBTC\text{-}SiO_2$	5.5
$Eu(BTFA)_3BTC\text{-}SiO_2$	12.5
$Eu(H_2O)_nDAMIC\text{-}SiO_2$	5.1
$Eu(BTFA)_3DAMIC\text{-}SiO_2$	16.8

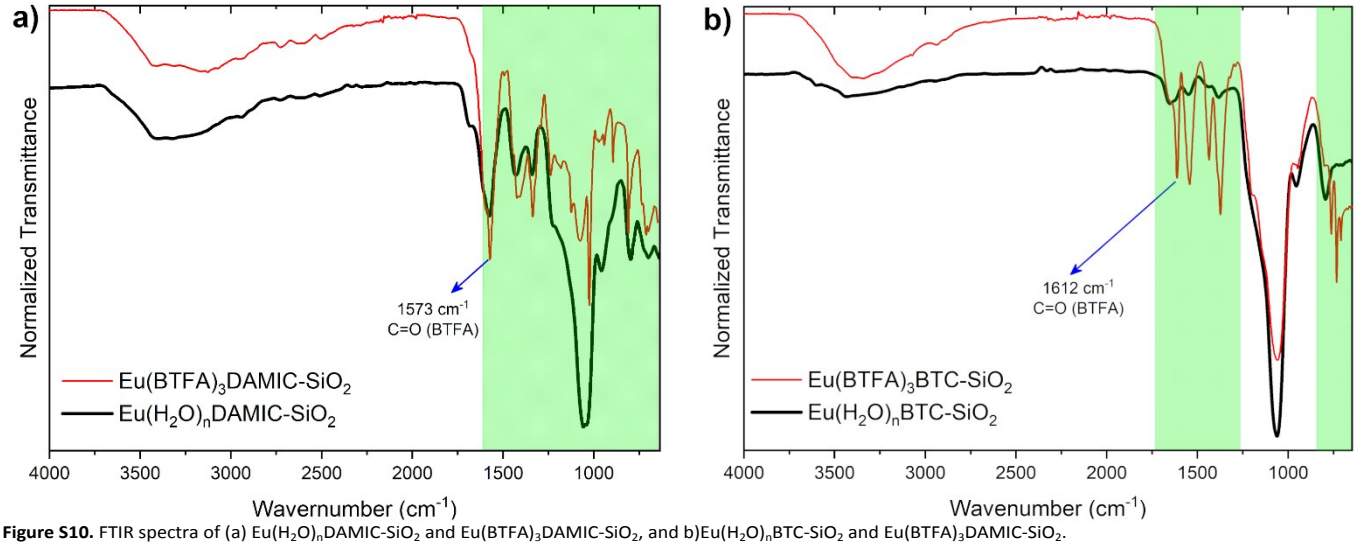


Figure S10. FTIR spectra of (a) $Eu(H_2O)_nDAMIC\text{-}SiO_2$ and $Eu(BTFA)_3DAMIC\text{-}SiO_2$, and b)$Eu(H_2O)_nBTC\text{-}SiO_2$ and $Eu(BTFA)_3DAMIC\text{-}SiO_2$.

Table S4. Elemental quantitative analysis with the mass percentage obtained by EDS for the $Eu(BTFA)_3L\text{-}SiO_2$ hybrids, L = BTC or DAMIC.

Material		Eu (%)	F (%)
$Eu(BTFA)_3BTC\text{-}SiO_2$	Experimental	7.6	28.4
	Calculated	72.7	27.3
$Eu(BTFA)_3DAMIC\text{-}SiO_2$	Experimental	70.6	29.4
	Calculated	72.7	27.3

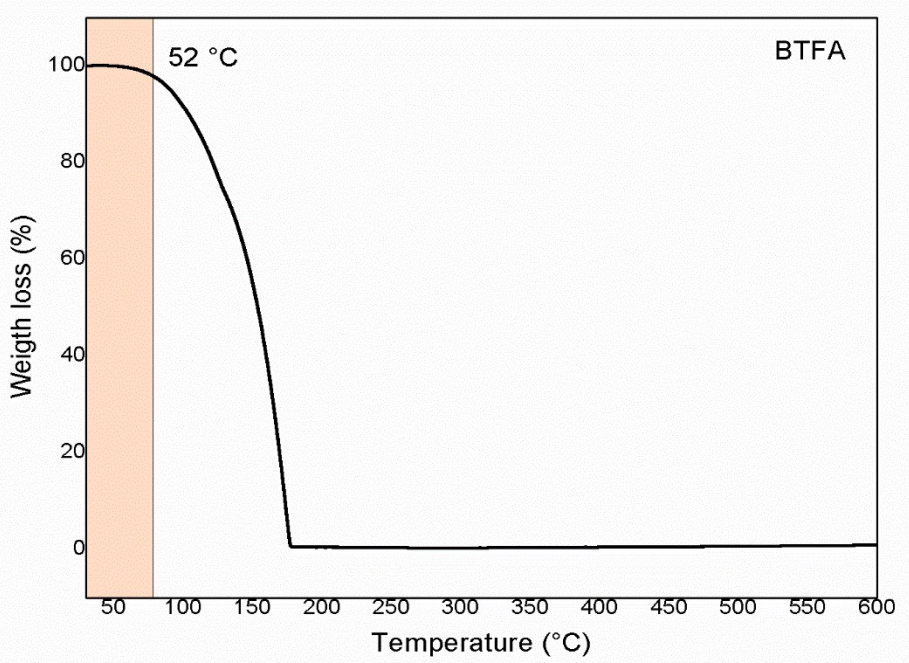


Figure S11. BTFA thermogravimetric analysis

Table S4. Parameters used in the print and cleaning cartridges for the compounds EuBTC-MCM48 and EuDAMIC-MCM48

Parameters	EuBTC-MCM48 andEuDAMIC-MCM48
DDP [V]	15
Fmax [kHz]	20
Cartridge temperature [ºC]	30°C
Cleaning Cycles (sipt-sipt)	Purge.3 secs after 25 bands
Plate temperature [ºC]	28
Waiting time between subsequent layers (> 10 layers) [s]	90 second per deposition
Waiting time between subsequent layers (> 20 layers) [s]	120 second per deposition

Table S5. Parameters for control algorithms

Control phase	Level	Slope	Duration
DDP constant	3.584 µs	9.472 µs	26.816 µs
Fluid ejection	5.056 µs	20.416 µs	26.816 µs

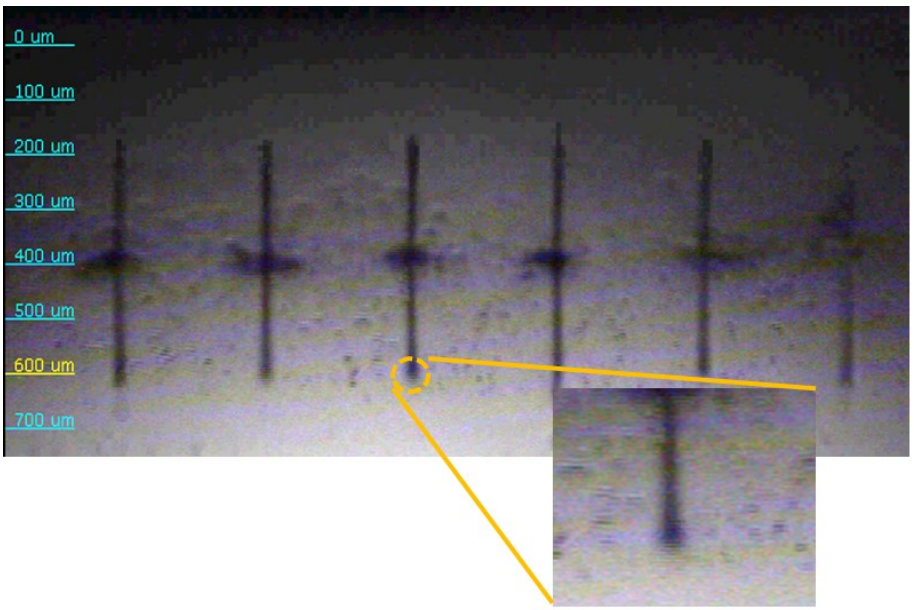
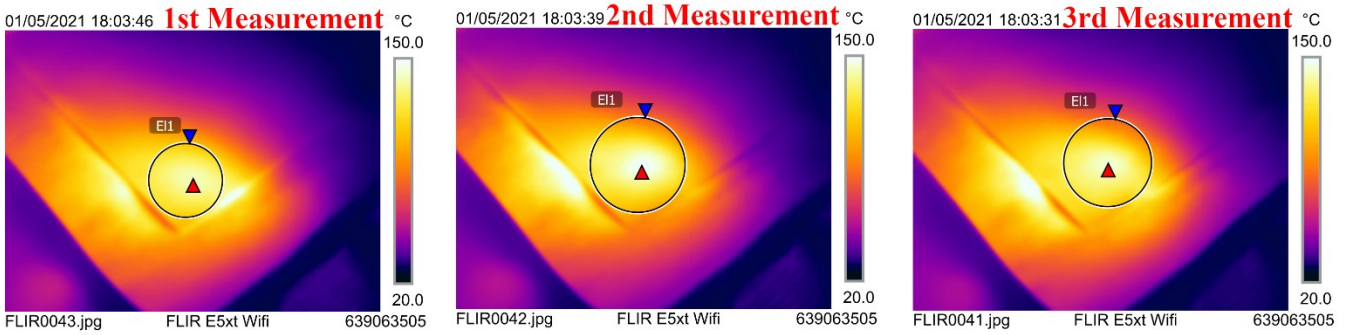


Figure S12. Image taken by the Fiducial Camera tool of security ink being ejected under a DoD printhead.



Measurements

EI1	Max	141.8 °C
	Min	114.5 °C
	Average	132.2 °C

Parameters

Emissivity	0.7
Refl. temp.	22 °C

Measurements

EI1	Max	149.7 °C
	Min	93.6 °C
	Average	129.4 °C

Parameters

Emissivity	0.7
Refl. temp.	22 °C

Measurements

EI1	Max	144.6 °C
	Min	90.9 °C
	Average	127.8 °C

Parameters

Emissivity	0.7
Refl. temp.	22 °C

Figure S13. Thermal images of a sample of printed label heated during luminescence quenching experiment.

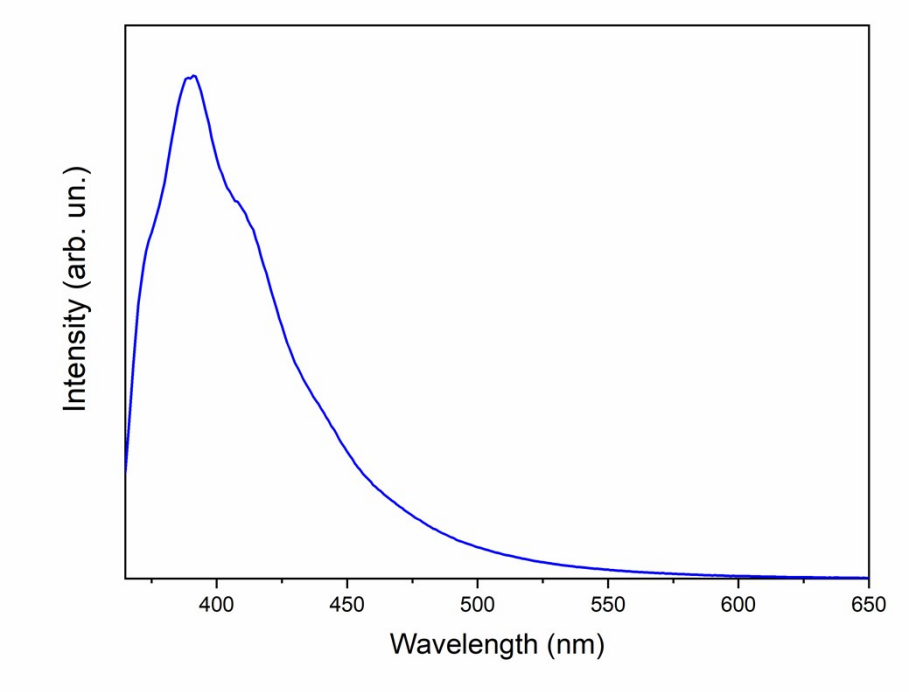


Figure S14. Emission spectra (λ_{Ex} = 342 nm) of the BOP.

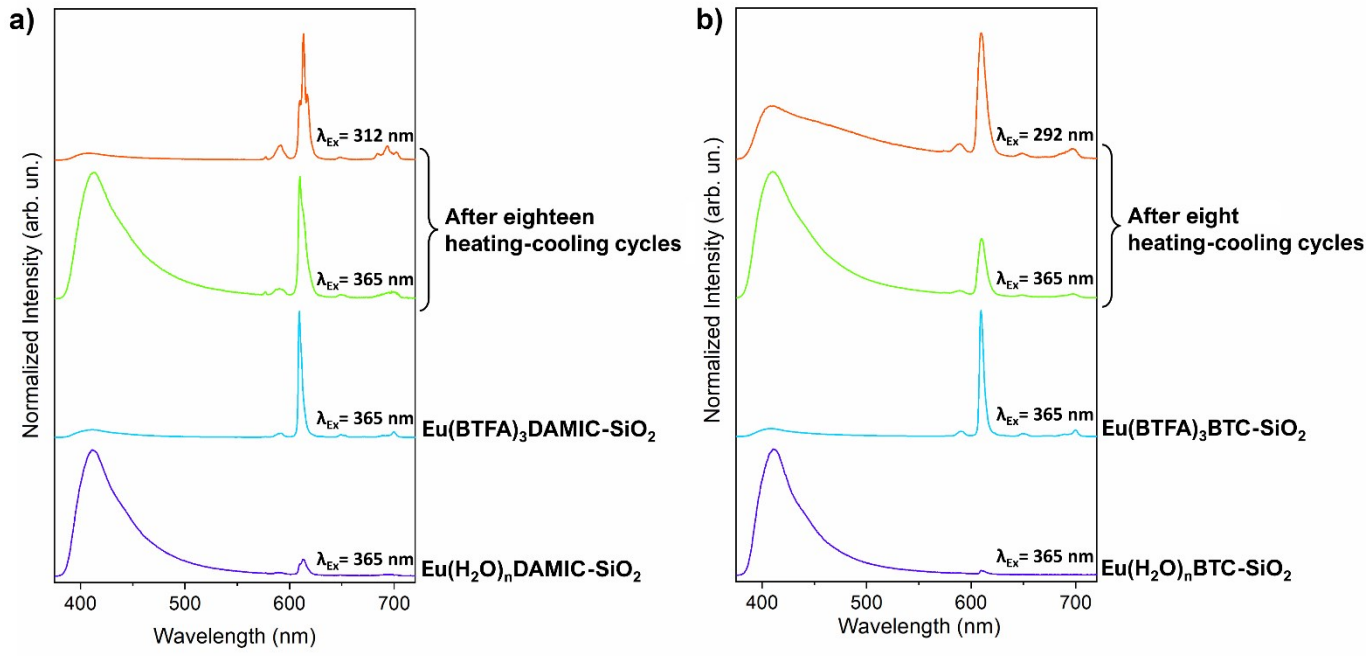


Figure S15. Emission spectra of the a) UFPE and b) BSTR labels before, after soak with BTFA and after heating cycles.

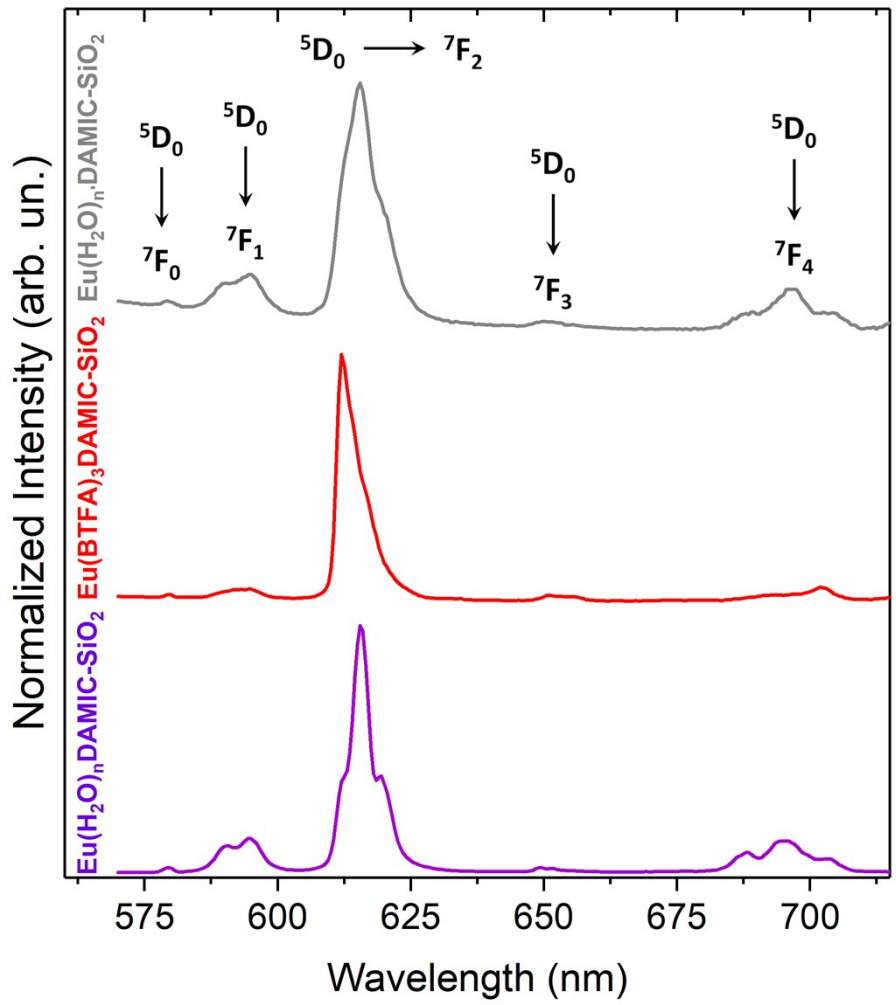


Figure S16. Emission spectra (λ_{Ex} = 365 nm) of Eu(L)DAMIC-SiO_2 as-printed (purple line), after soak with BTFA (red line) and after heating (gray line).

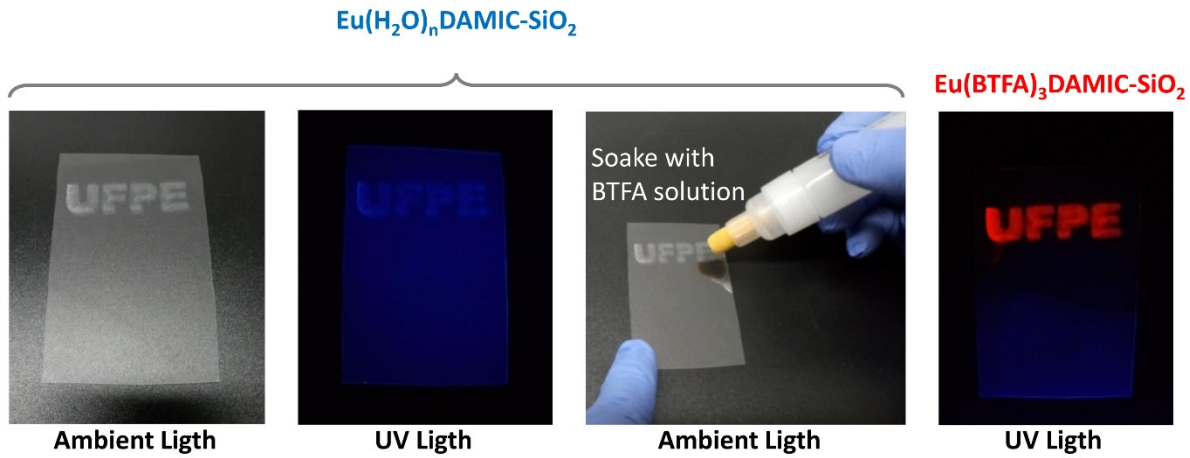


Figure S17. Procedure of bright red luminescence ON of the printed security label "UFPE" and its luminescence with a UV light with wavelength of 365 nm.

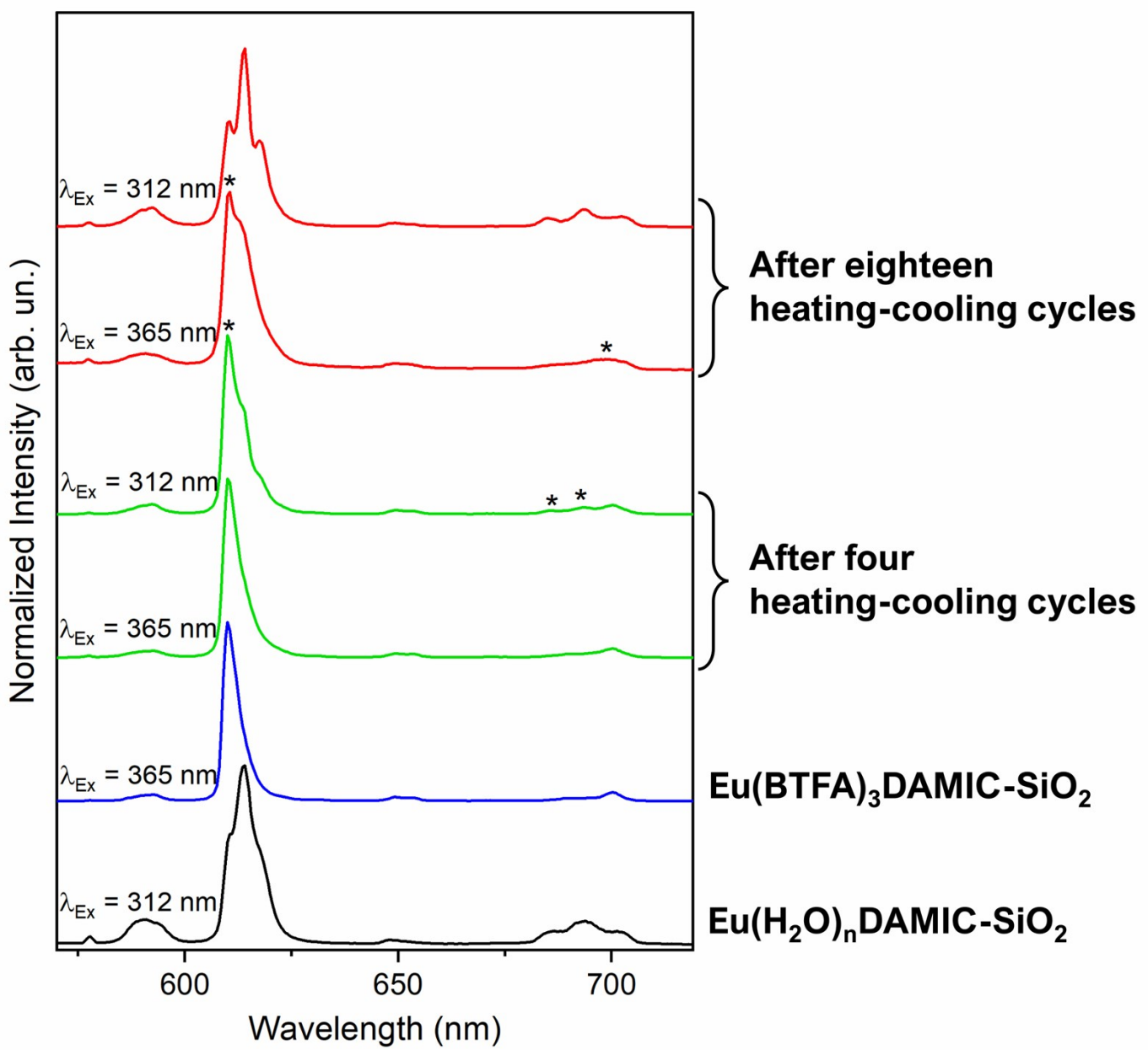


Figure S18. Emission spectra of the UFPE label before, after soak with BTFA and after heating cycles.

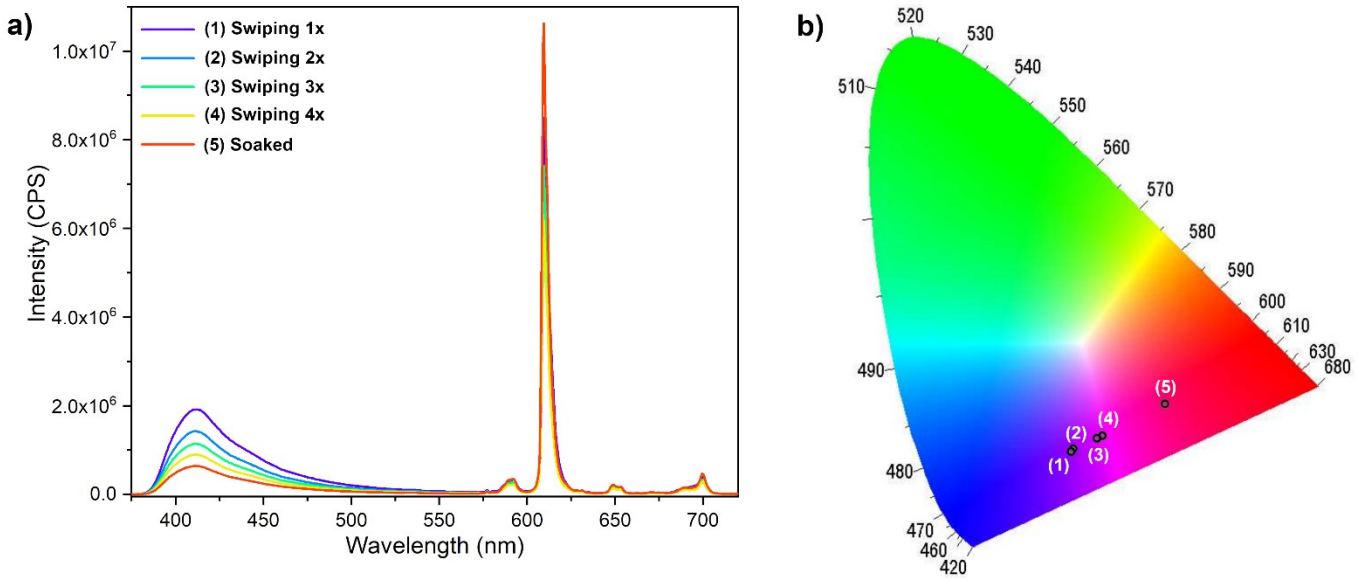


Figure S19. Emission spectra of the UFPE label before and after successive addition of the BTFA solution with the marker pen.

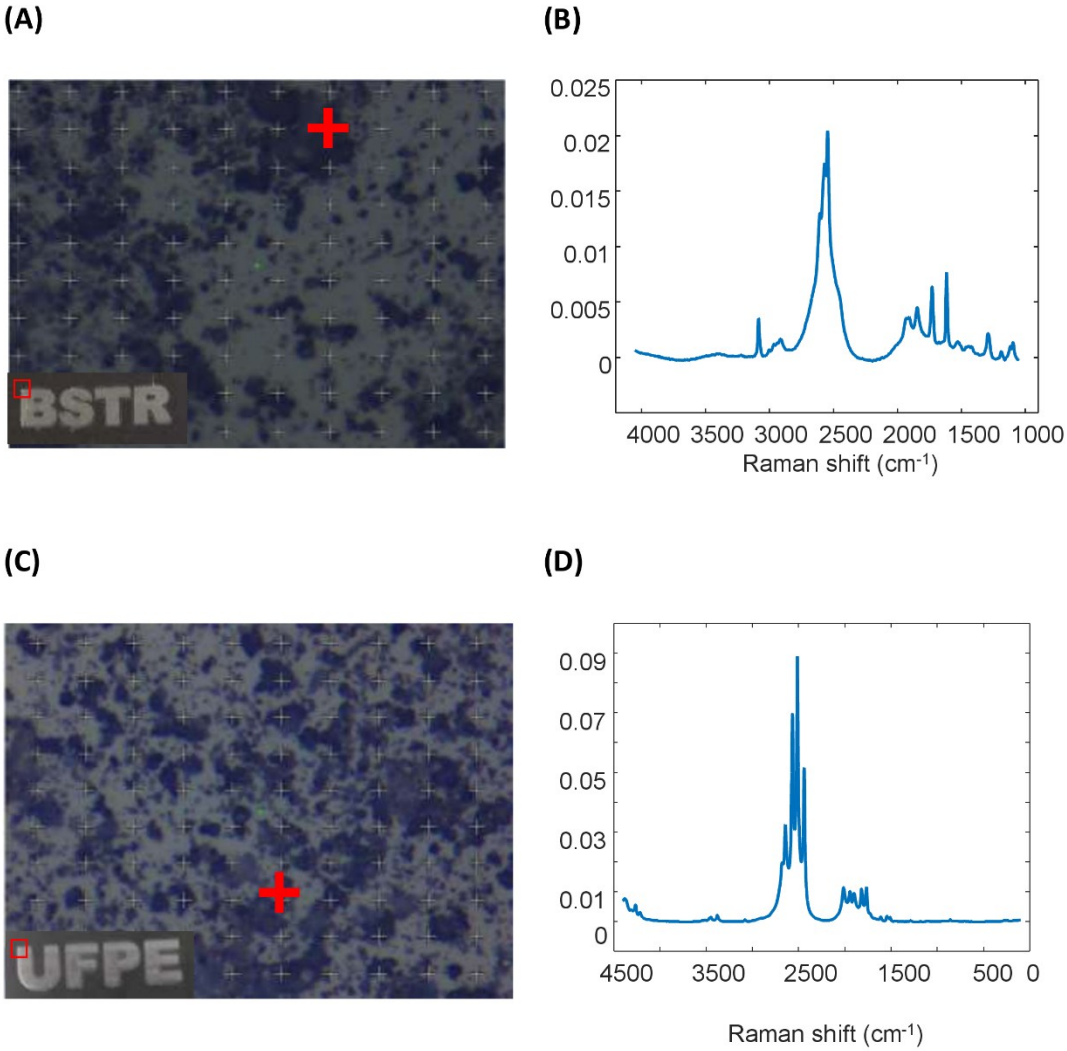


Figure S20. Images of (a) EuDAMIC-MCM48 and (c) EuBTC-MCM48 using magnification of 50x and the respective Raman spectra acquired (c) and (d) using the 532 nm laser.

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