Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Embedding lanthanide-functionalized polymers into hollow mesoporous silica spheres: a ship-in-a-bottle approach to luminescent hybrid materials

Ning Yuan,[a] Yucang Liang,*[,a] Egil Severin Erichsen[b] and Reiner Anwander*[,a]

[a] Institute of Inorganic Chemistry, Eberhard Karls University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

[b] Laboratory for Electron Microscopy, University of Bergen, Allégaten 41, 5007 Bergen, Norway

Chemicals

Cetyltrimethylammonium bromide (CTAB, Sigma), tetraethyl orthosilicate (TEOS, Aldrich), ammonium hydroxide (25%, Fluka), azobisisobutyronitrile (AIBN, Merck Schuchardt), terbium(III) chloride hydrated (Alfa), europium(III) chloride hydrated (Alfa) and 1,10-phenanthroline (Phen, Alfa-Aesar) were used as received. 4-Vinylpyridine (4VP, Acros Organics) was freshly distilled before use. Absolute ethanol over molecular sieves was used for the polymer synthesis. Pure water was used for the preparation of hollow mesoporous silica spheres.

Characterization

Powder X-ray diffraction patterns were obtained using a Bruker D8 ADVANCE instrument in the step/scan mode (step width = 0.00825; accumulation time = 2 s per step; range (2θ) = 0.50-10.00°) using monochromatic Cu Kα (λ = 1.540562 Å). IR spectra were recorded on a NICOLET 6700 FTIR spectrometer using a DRIFT chamber with KBr/sample mixtures. The collected data were converted using the Kubelka-Munk refinement. Nitrogen physisorption was carried out on an ASAP 2020 volumetric adsorption apparatus (Micromeritics) at 77.4 K [$a_m(N_2, 77\ K) = 0.162\ nm^2$). All samples underwent an outgassing step of 4 h, 10^{-3} Torr and at 383 K prior to measurement. The specific surface areas of the samples were obtained using the BET method. Pore size distributions were determined *via* the *Barrett-Joyner-Halenda* (BJH) method using the Kelvin equation to calculate the mean pore diameter. The excitation and emission spectra were recorded in Hellma® fluorescence quartz cuvette in ethanol at room temperature on a Varian Cary Eclipse Fluorescence Spectrophotometer. Scanning electron microscopy (SEM) were conducted on a JEOL JSM-5900LV microscope operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) observations were obtained using a JEOL JEM2010 operated at 160 kV. ^{13}C CP MAS NMR spectrum was recorded at room temperature with a Bruker 200 MHz Ultrashield Plus instrument (4.7 T) equipped with CP magic-angle-spinning hardware and using ZrO_2 rotors with a diameter of 4 mm and ^{13}C chemical shifts were referenced to Glycine (^{13}C: 50.288 ppm). UV/Vis spectra were measured with a Lambda 35 spectrophotometer from PerkinElmer. Elemental analyses were performed on an Elementar Vario MICRO cube instrument. Lanthanide contents were measured *via* inductively coupled plasma mass spectrometry (ICP-MS) method by WESSLING GmbH. Thermogravimetric and differential thermal analysis were carried out using a Netzsch STA 449F3 instrument with a quartz crucible at a heating rate of 2 K/min under $Ar/O_2/Ar$ atmosphere.

Synthesis Procedures

Synthesis of hollow mesoporous silica spheres (HMSS)

The host mesoporous hollow spherical silica was synthesized according to a recent publication applying slight modifications.[1] Ammonia hydroxide (25%) solution was added to an ethanol aqueous solution of cetyltrimethylammonium bromide (CTAB), and then the solution was heated to 35 °C, followed by rapid addition of 5 ml tetraethyl orthosilicate (TEOS) under vigorous stirring. The molar ratio of the reactants was 1.00 TEOS : 0.0922 CTAB : 2.96 NH_3 : 115 EtOH : 621 H_2O. After stirring at 35 °C for 24 h, the silica was

recovered by centrifugation and then washed with ethanol and water. The obtained as-synthesized silica was dispersed into 800 ml H_2O. After incubation at 70 ^oC for 15 h, the product was filtered and washed with ethanol and water. The surfactant-free hollow silica product was obtained by calcination at 540 ^oC for 4 h.

Synthesis of P4VP@HMSS

In a 50 ml Schlenk tube were added pre-degassed hollow silica host (900 mg) and azobisisobutyronitrile (AIBN) (246 mg, 1.5 mmol). Then freshly distilled 4-vinylpyridine (4VP) (16 ml, 150 mmol) and dry ethanol (15 ml) were injected under argon atmosphere. After stirring overnight at ambient temperature, the suspension was heated up to 65 ^oC and allowed to react for 3 h. The polymer containing silica was collected by centrifugation and washed with ample ethanol to completely remove the untrapped polymer. The molar to volume ratio between 4-vinylpyridine monomer and ethanol used here is 10 mmol/ml. This obtained product was dried under vacuum and denoted as P4VP@HMSS. When the concentration of monomer in ethanol was increased to 20 mmol/ml and 100 mmol/ml, the obtained products were denoted as P4VP@HMSS-1 and P4VP@HMSS-2, respectively.

Synthesis of Phen-Tb-P4VP@HMSS

The obtained fine powder of P4VP@HMSS (300 mg) was dispersed in 20 ml ethanol, followed by the addition of a 10 ml ethanol solution containing excessive amount of hydrated terbium(III) chloride (194 mg, 0.5 mmol). The suspension was stirred at ambient temperature for 24 h, and then the product was collected by centrifugation and washed with ample ethanol to remove the free Tb(III) ions. Then, this product was dispersed in 20 ml ethanol again, and 1,10-phenanthroline (94 mg, 0.5 mmol) in 10 ml ethanol was added to the suspension. After reaction at ambient temperature for 24 h, the product was recovered by centrifugation and washed with ample ethanol to remove any free Phen ligand. This product was denoted as Phen-Tb-P4VP@HMSS.

Synthesis of Phen-Eu-P4VP@HMSS

The Eu(III) hybrid was obtained following the similar procedure, but using hydrated europium(III) chloride (190 mg, 0.5 mmol) instead of hydrated terbium(III) chloride.

[1] Z. Teng, X. Su, Y. Zheng, J. Sun, G. Chen, C. Tian, J. Wang, H. Li, Y. Zhao, G. Lu, *Chem. Mater.* **2013**, *25*, 98.

Table S1 Structural parameters of hollow mesoporous silica spheres (HMSS), P4VP@HMSS, Phen-Tb-P4VP@ HMSS, and Phen-Eu-P4VP@HMSS.

Samples	d_{100} (nm)	a_0 (nm)	d (nm)	w (nm)	S_{BET} (m^2/g)	V (cm^3/g)
HMSS	3.39	3.92	2.30	1.62	988	0.72
P4VP@HMSS	3.69	4.26	1.90	2.36	987	0.50
Phen-Tb-P4VP@HMSS	3.75	4.33	1.90	2.43	894	0.44
Phen-Eu-P4VP@HMSS	3.74	4.32	1.90	2.42	883	0.47

d_{100}: (100) spacing; a_0: cell parameter; d: pore diameter; w: wall thickness; S_{BET}: surface area; V: pore volume.

Table S2 CHN elemental analyses and lanthanide contents *via* the ICP-MS method of P4VP@HMSS, P4VP@HMSS-1, P4VP@HMSS-2, Phen-Tb-P4VP@ HMSS, and Phen-Eu-P4VP@HMSS (*wt*%).

Samples	C	N	H	Tb	Eu
P4VP@HMSS	14.02	2.10	1.47	/	/
P4VP@HMSS-1	23.34	3.71	2.36	/	/
P4VP@HMSS-2	29.40	4.82	3.32	/	/
Phen-Tb-P4VP@HMSS	8.84	1.46	1.39	1.6	/
Phen-Eu-P4VP@HMSS	8.27	1.27	1.57	/	1.1

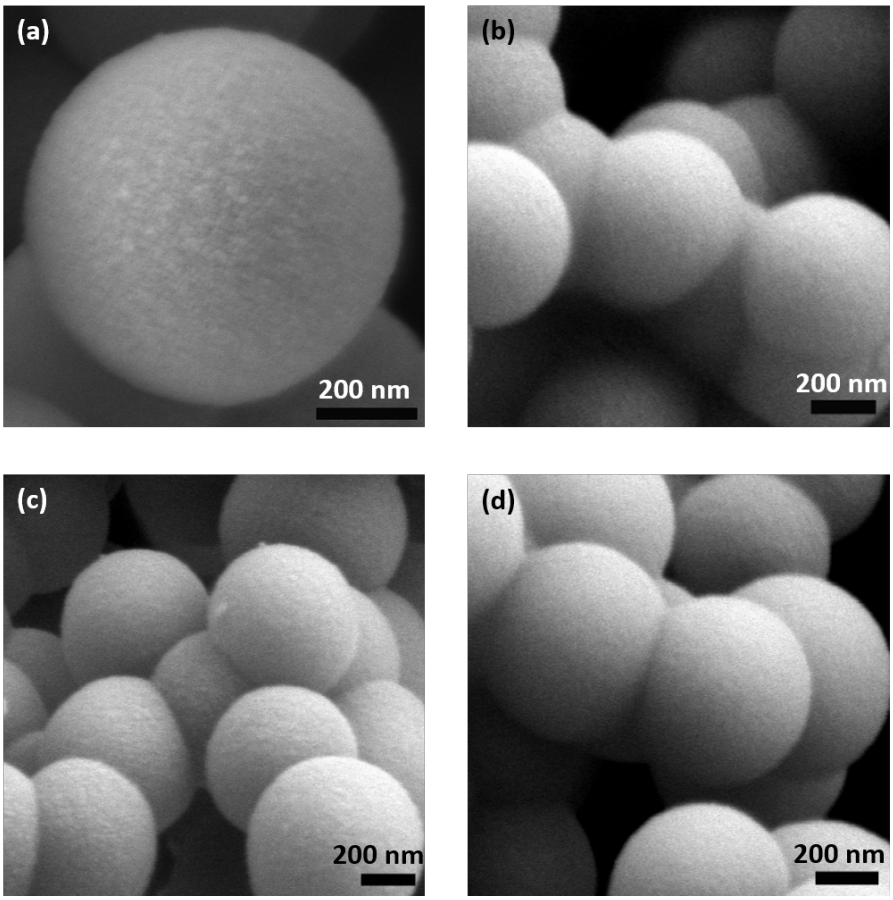


Figure S1 SEM images of (a) hollow mesoporous silica spheres (HMSS), (b) P4VP@HMSS, (c) Phen-Tb-P4VP@HMSS and (d) Phen-Eu-P4VP@HMSS.

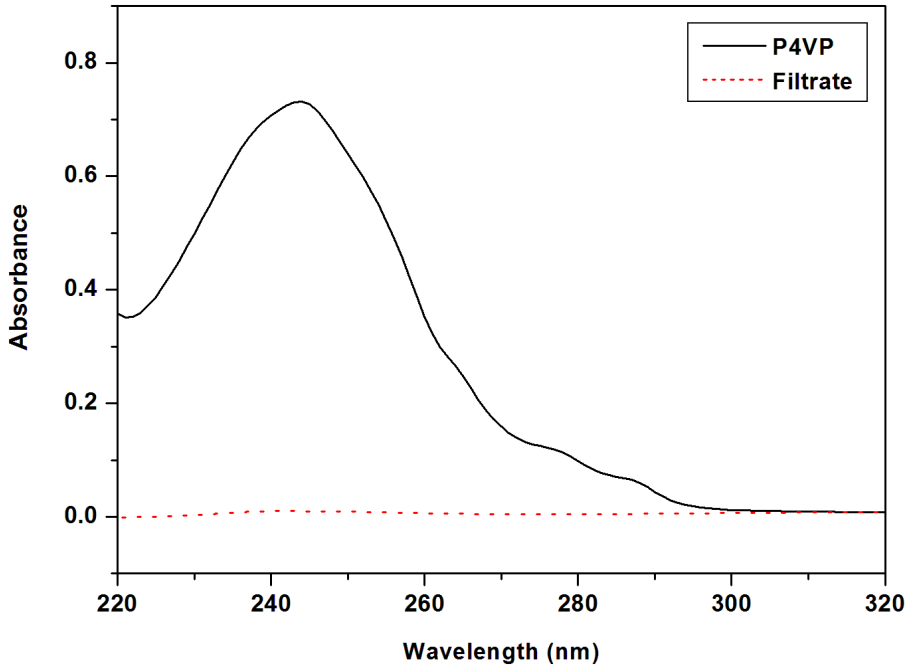


Figure S2 UV absorption spectra of P4VP (black solid line) and the filtrate (red dash line).

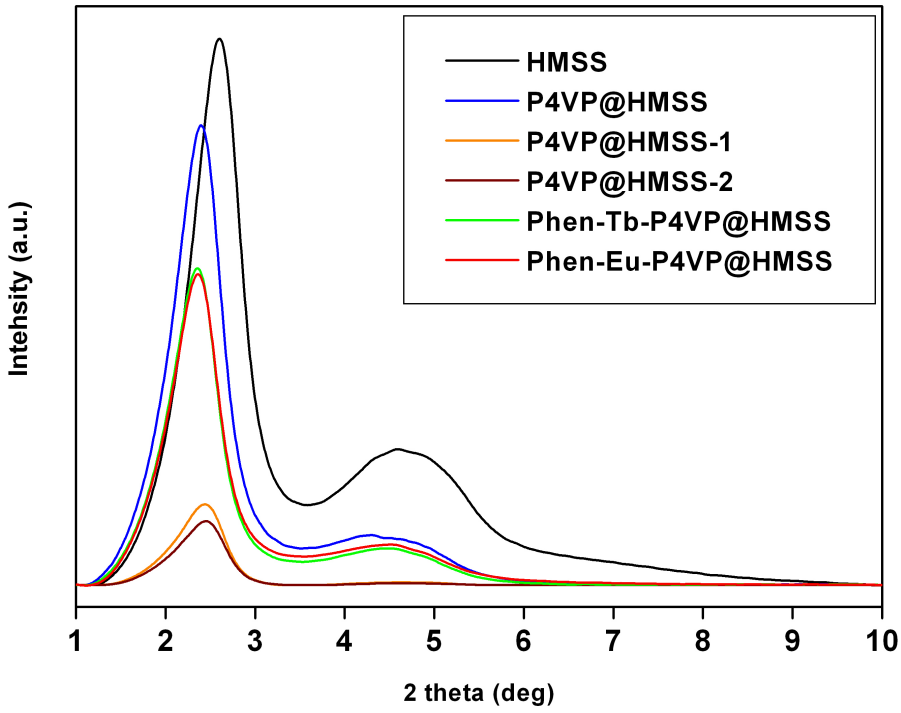
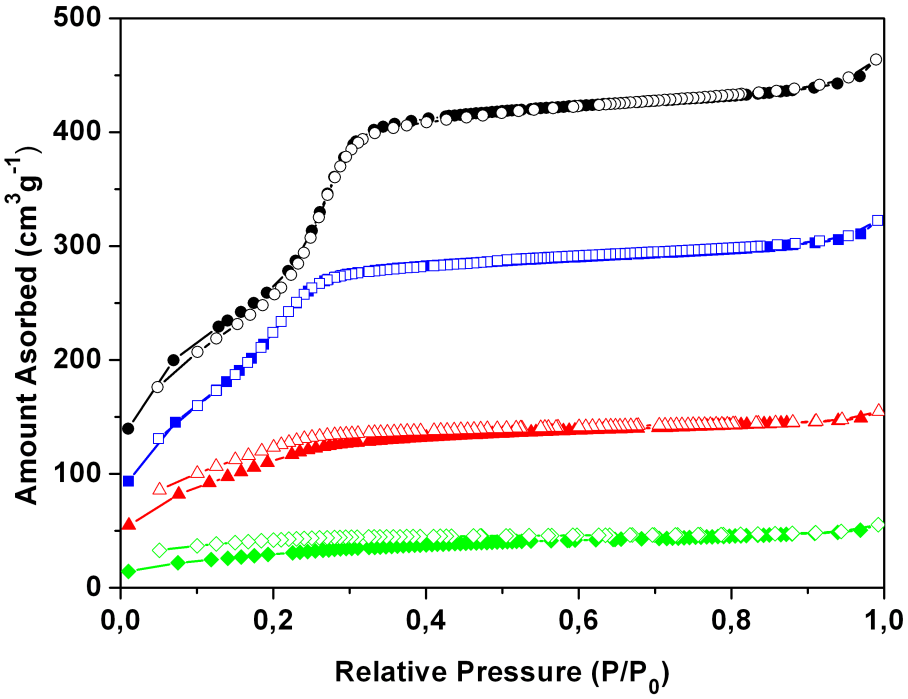
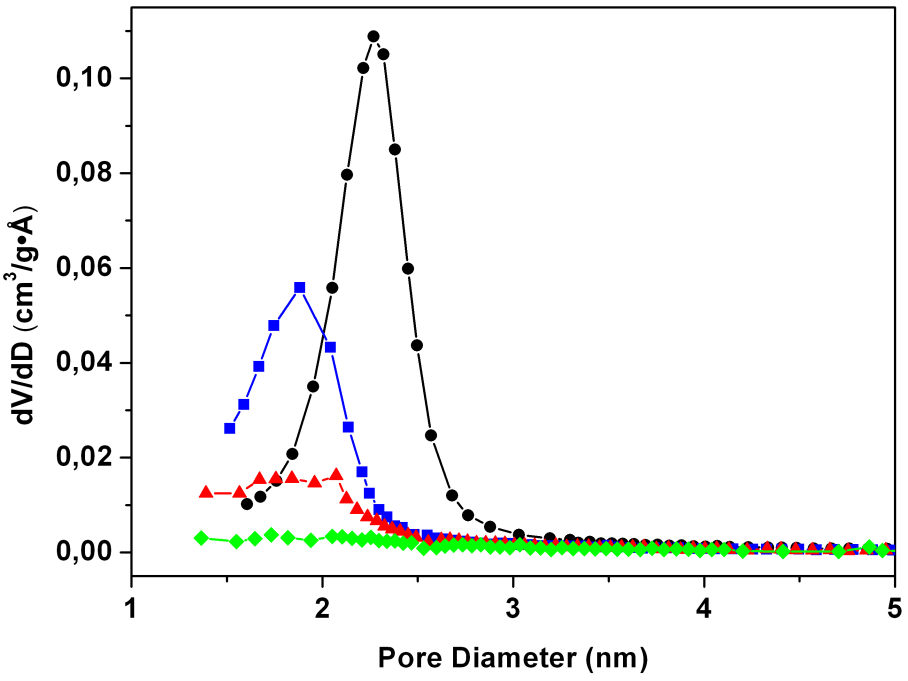


Figure S3 Small angle PXRD patterns of hollow silica mesoporous spheres (HMSS) (black), P4VP@HMSS (blue), Phen-Tb-P4VP@HMSS (green), Phen-Eu-P4VP@HMSS (red) P4VP@HMSS-1 (orange) and P4VP@HMSS-2 (violet).

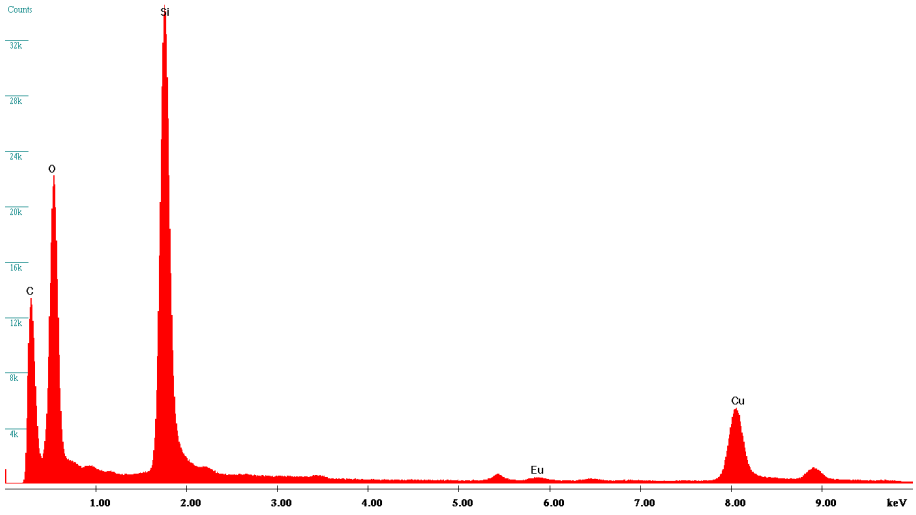


(a)

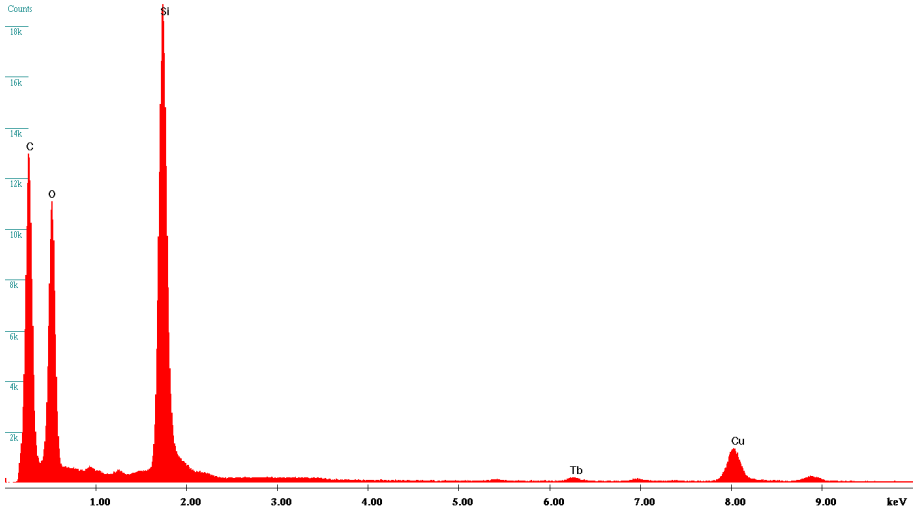


(b)

Figure S4 (a) Nitrogen adsorption-desorption isotherms (b) and pore size distribution curves of parent HMSS (black), P4VP@HMSS (blue), P4VP@HMSS-1 (red) and P4VP@HMSS-2 (green).

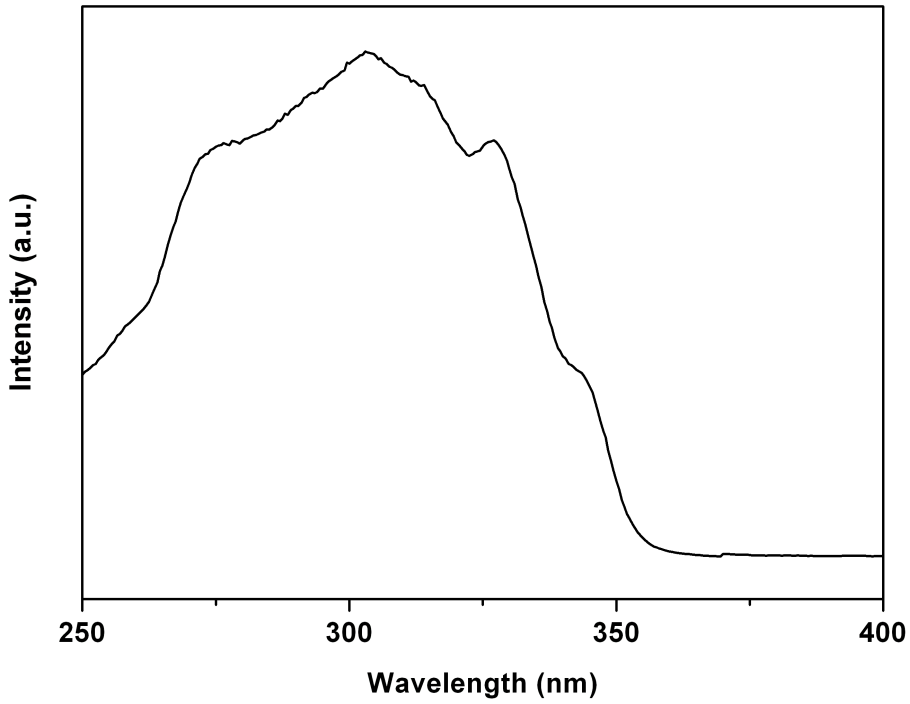


(a)

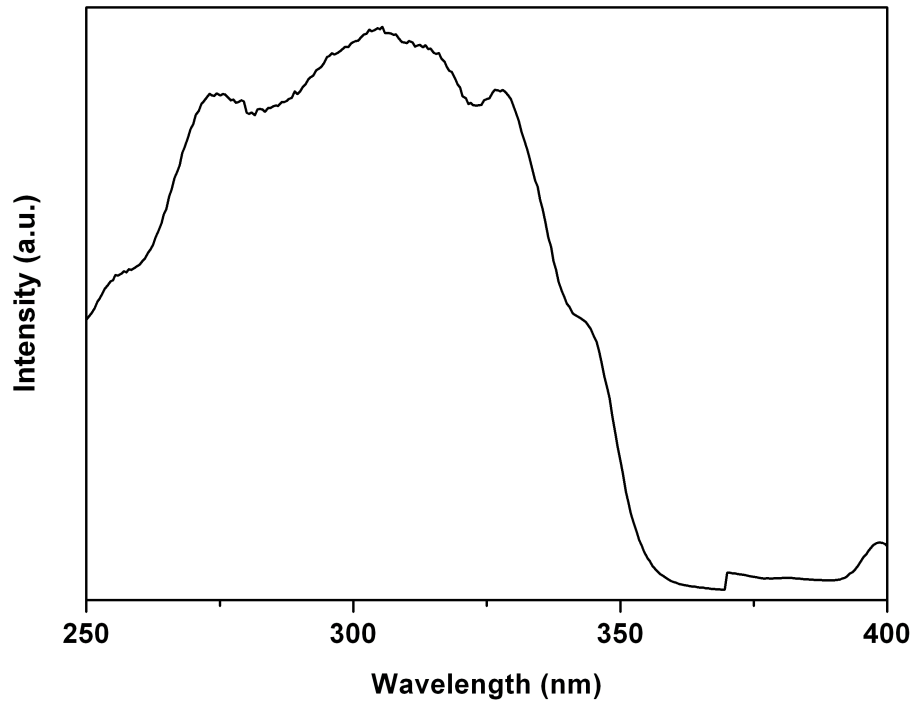


(b)

Figure S5 Energy-dispersive X-ray (EDX) spectra of Phen-Ln-P4VP@HMSS (Ln = Eu, Tb).



(a)



(b)

Figure S6 Excitation spectra of (a) Phen-Eu-P4VP@HMSS and (b) Phen-Tb-P4VP@HMSS.

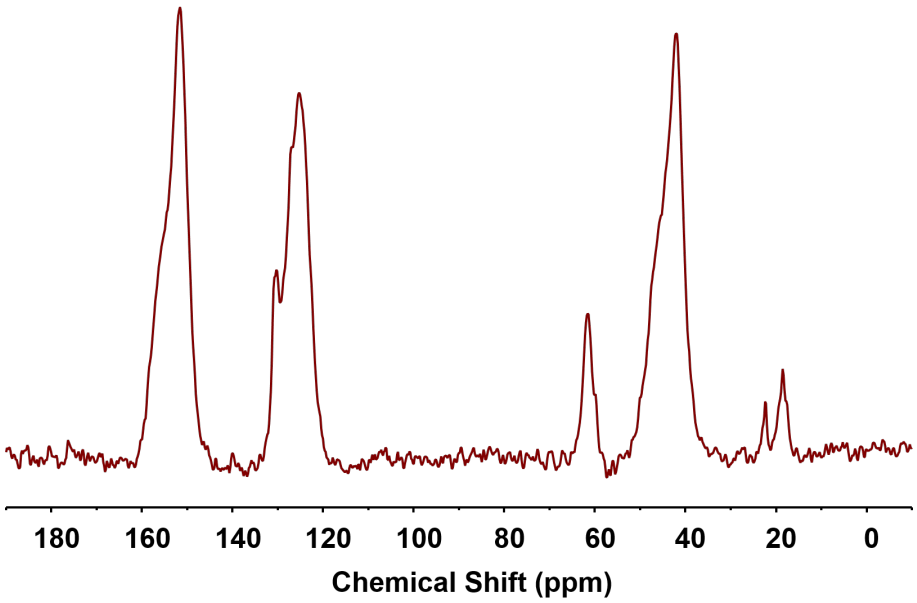


Figure S7 Solid-state ^{13}C MAS NMR spectrum of P4VP@HMSS.

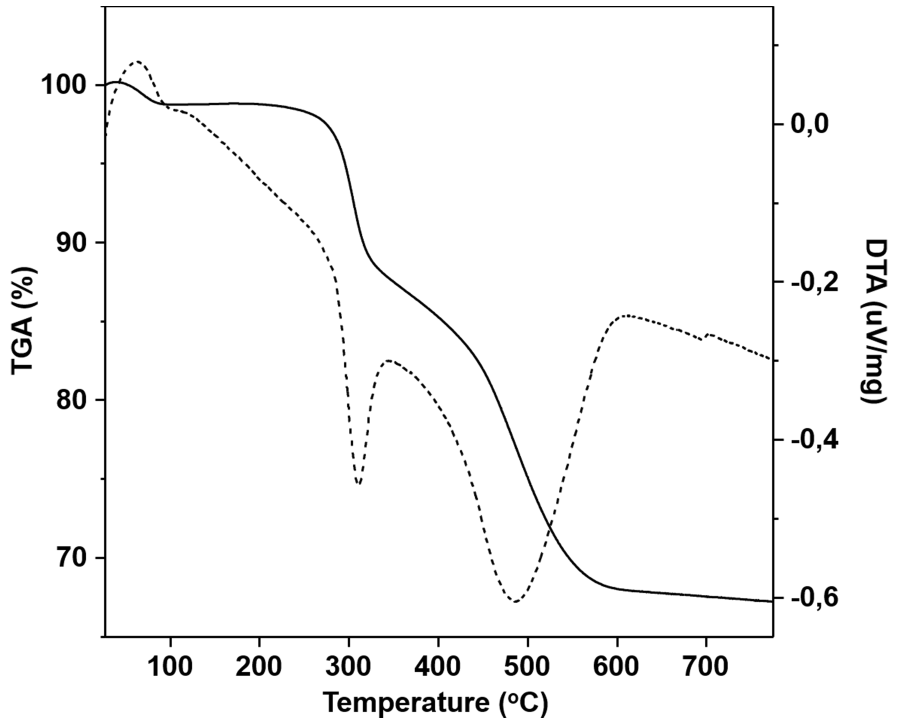


Figure S8 Thermogravimetric analysis (TGA, solid line) and differential thermal analysis (DTA, dashed line) curves of Phen-Tb-P4VP@HMSS.