Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information

Construction of bi-functional inorganic-organic hybrid nanocomposite

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Experimental

Materials: All the chemicals were obtained from Aldrich chemical Co. and used without further purification.

Physical Measurement: XRD patterns of the synthesized composites in different step were recorded in Bruker D8 Discover instrument using Cu-K_α radiation. FTIR Spectra of the nano-composites were acquired on Bruker IFS 66v/S instrument in the range of 4000-400 cm^{-1}. Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer was used for the UV-Vis spectra measurements of the composites in the wavelength range of 190-800 nm. PL spectra were taken with Perkin-Elmer model LS 55 luminescence spectrometer.

FESEM observation: FESEM observations were carried out in FEI NOVA NANOSEM 600 instrument. We dispersed small amount of the sample in ethanol and sonicated for half an hour and one drop of the sample was taken on aluminum stub and dried in the open atmosphere and then FESEM images were taken.

TEM observation: TEM observation of the synthesized composites was carried out in JOEL JEM-3010 electron microscope under 3K Volt accelerating voltage. Sample for the TEM observation was prepared by dispersion in water and one drop of it was put on a carbon coated copper grid. The excess of the solution was removed using a filter paper. The grid was kept in a desiccator for drying.

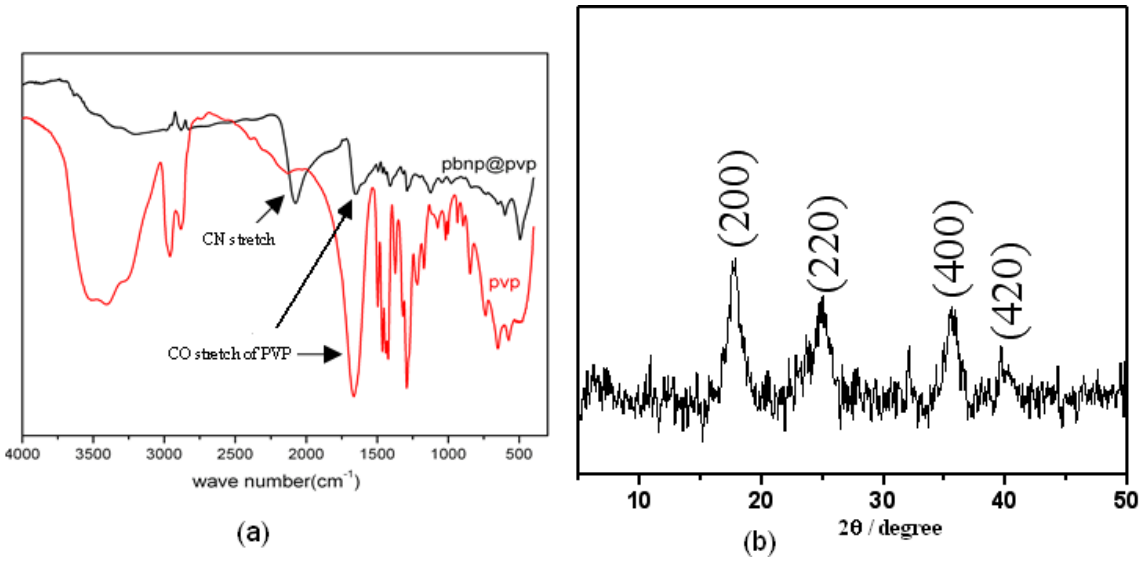
Synthesis of PB@PVP: The *Prussian blue* nanoparticle precursor was prepared by the method described by Kitagawa *et.al*.[12] According to reported procedure 0.033 gm (0.1 mmol) $K_3[Fe(CN)_6]$ and 0.10 gm (0.05 mmol) of $FeCl_2.4H_2O$ and 0.222 gm (2 mmol) of polyvinylpyrrolidone (PVP) was

taken as precursors. $FeCl_2.4H_2O$ and PVP was taken in 8 mL water solution and vigorously stirred for 5 minutes for complete dissolve of the PVP. To the above clear solution an aqueous solution (2 mL) of $K_3[Fe(CN)_6]$ was added drop wise. The resulting reaction mixture immediately turned as blue color indicating the formation of *Prussian blue*. The solution was vigorously stirred to ensure the monodisperse formation of the PB nanoparticles and continued for two days. The resultant nanoparticles were separated as a solid form by adding acetone (1: 2.5 ratio) drop wise with constant stirring to the reaction mixture. The solid was separated out by centrifuge and washed with pure acetone for three times and dried in vacuum for two days The resultant solid was characterized as PVP protected PB nanocomposite and used further for coating with the SiO_2.

Synthesis of PB@SiO_2: PVP protected PB NPs (1 mg) was dispersed in absolute ethanol by sonication and stirred for 10 min. and then 1.3 mL tetraethylorthoslicate (TEOS) was added drop wise and stirred well. Ethanolic solution of concentrated ammonia (10 mL) was added drop wise to the above solution and stirred for 12 h. The resultant solution was centrifuged and the solid product was washed three-four times with water so that uncoated PB nanoparticles could be removed. The solid was again washed with ethanol thoroughly and dried in vacuum for two days. This product was characterized as silica coated PB@SiO_2 nanocomposite and used for further study.

Fabrication of PB@SiO_2@BTC and PB@SiO_2@BTC@Ln: In order to attach the benzenetricarboxylic acid (BTC) on silica coated nanocomposite for fabricating hybrid inorganic-organic PB@SiO_2@BTC nanocomposite, 20 mg PB@SiO_2 was dispersed in 20 mL water. Then aqueous solution (30 mL) of BTC (0.15 g) was added drop wise to the PB@SiO_2 solution and then resulting reaction mixture was vigorously stirred for 48 h. The reaction mixture was centrifuged and characterized as hybrid nanocomposite, PB@SiO_2@BTC where BTC molecules are covalently linked with the silica.

In order to link Tb(III) / Sm(III) ions with the BTC on the surface of the hybrid nanocomposite, corresponding $Ln(NO_3)_3$ solution was added to the aqueous solution containing dispersed PB@SiO_2@BTC nanocomposite. Then the resultant solution was stirred for one day and the isolated solid was characterized as a hybrid bi-functional nanocomposite, PB@SiO_2@BTC@Tb/Sm.



Characterization of PVP protected PB NPs: (a) FTIR spectra of PVP (red) and PVP protected PB (black); (b) PXRD pattern of PVP protected PB NPs.

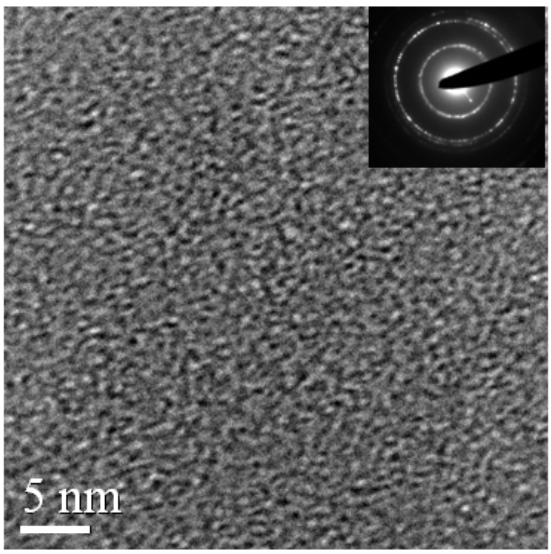


Fig. S1: TEM image of the PVP coated PB nanoparticles (inset image showing the polycrystalline nature of the particles)

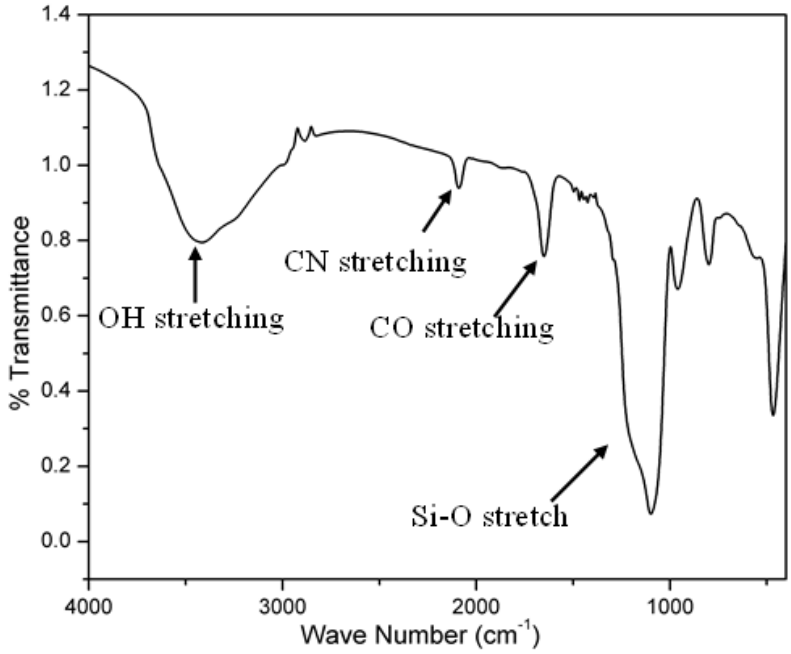


Fig. S2: FTIR spectrum of PB@SiO_2.

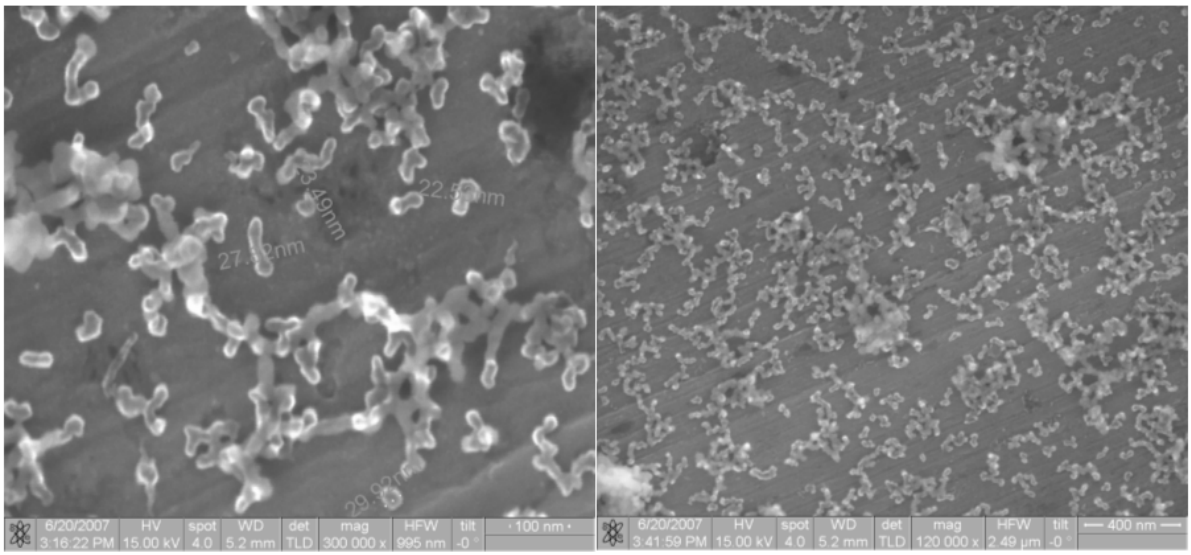


Fig. S3: FESEM images of PB@SiO_2 nanocomposite.

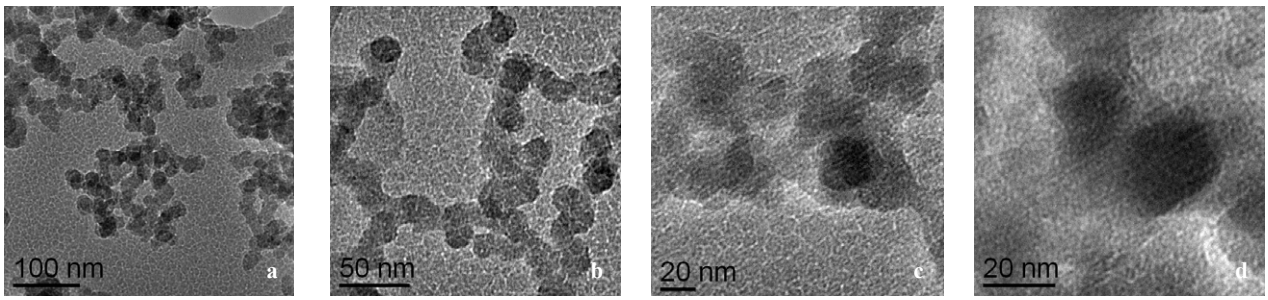


Fig. S4: High resolution TEM images of PB@SiO_2 in different resolution.

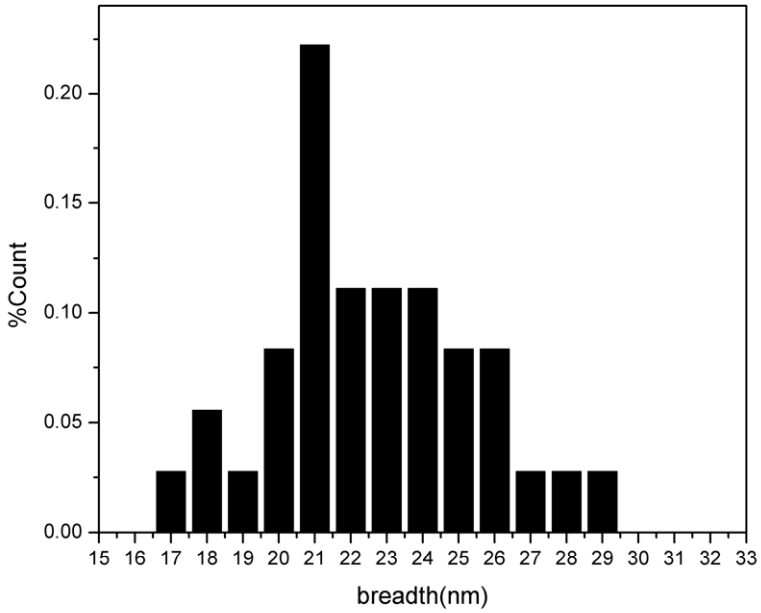


Fig. S5: Histogram of the distribution of breadth of PB@SiO_2 nanocomposite.

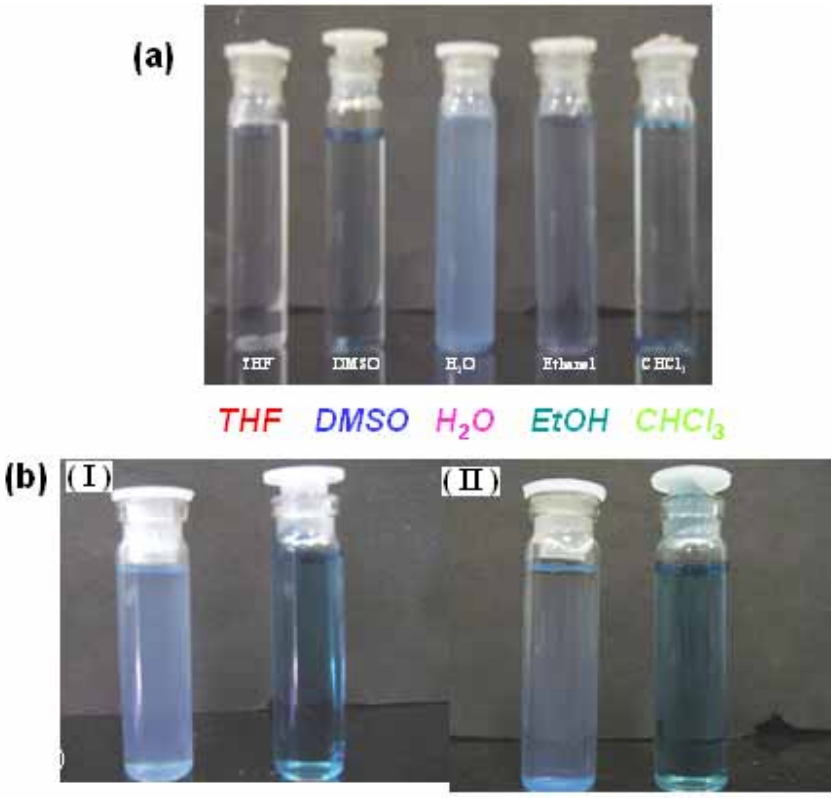


Fig. S6: (a) Dispersion of PB@SiO_2 in different solvents.

(b) Dispersion of PB@SiO_2 (left) and PB@PVP (right) in water: (I) at just dispersed condition and (II) after 4 days.

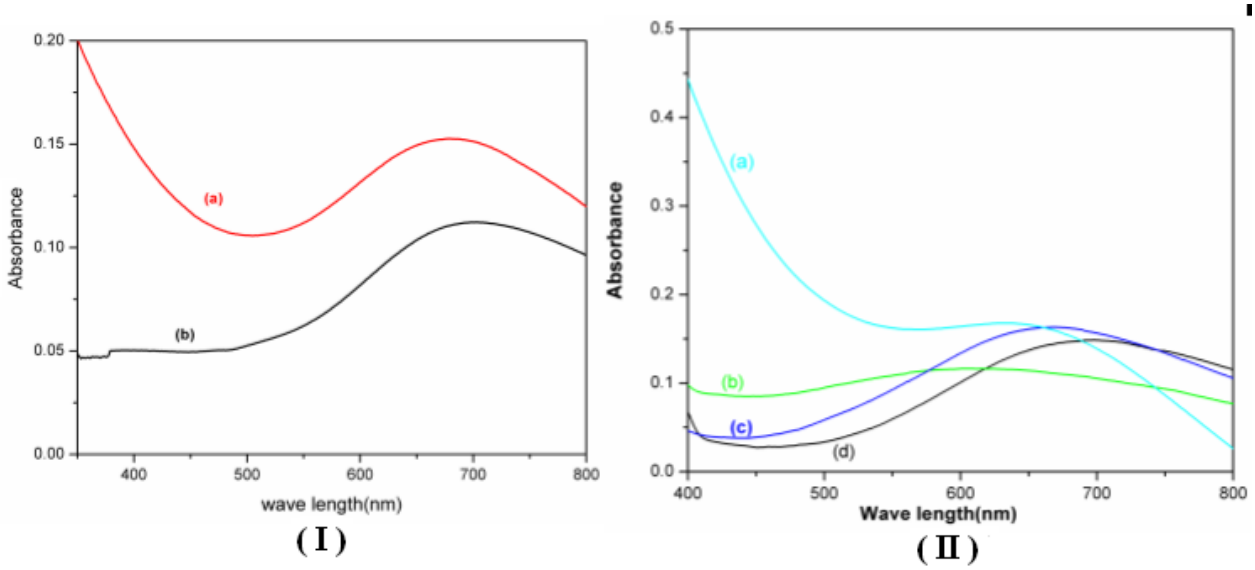


Fig. S7: (I) UV-Vis spectra of (a) PB@SiO_2 and (b) PVP protected PB NPs; (II) UV-Vis spectra PB@SiO_2 in different solvents. (a) H_2O (b) THF (c) DMSO and (d) $CHCl_3$.

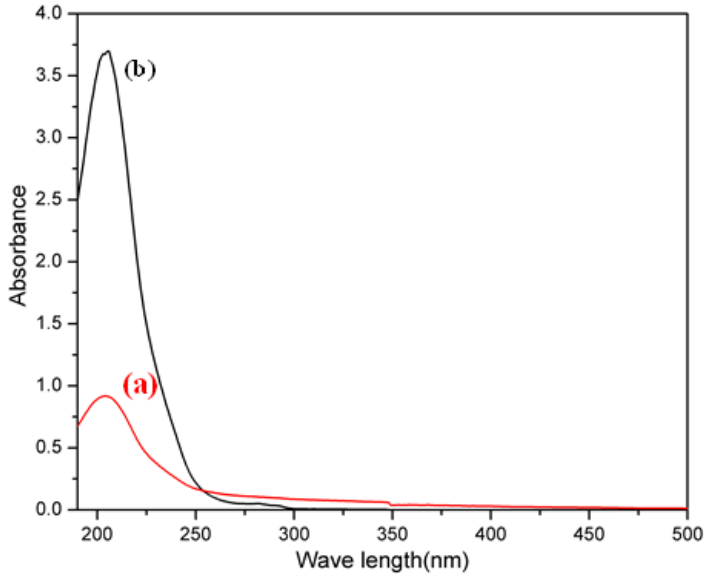


Fig. S8: UV-Vis spectra: (a) PB@SiO_2@BTC and (b) free benzene tricarboxylate.

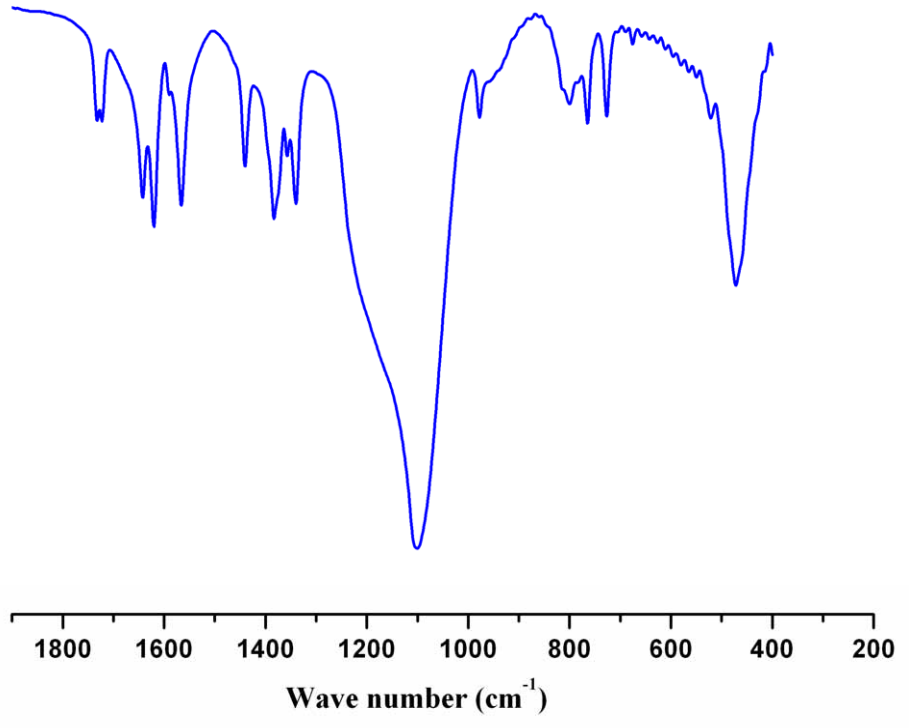


Fig. S9: FTIR spectra of PB@SiO_2@BTC.

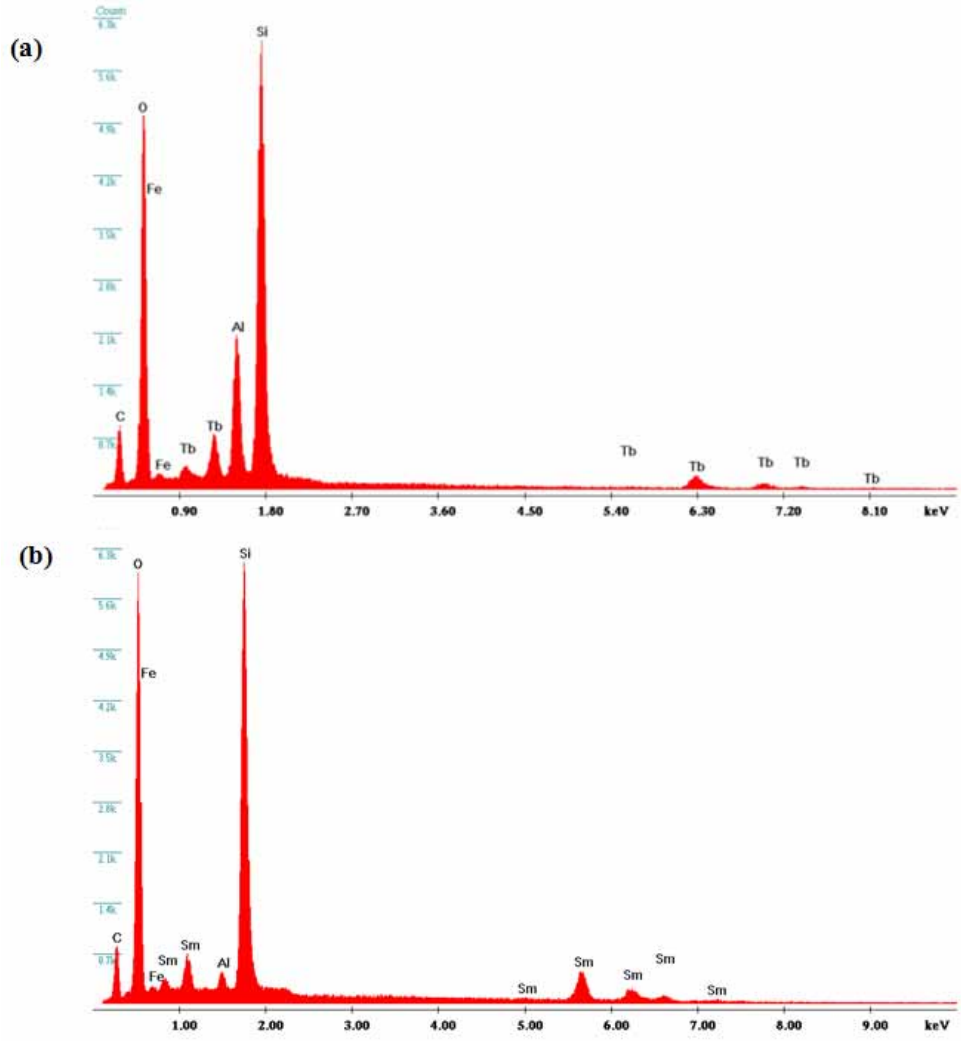


Fig. S10: EDX analysis of the hybrid nanocomposite (a) PB@SiO_2@BTC@Tb and (b) PB@SiO_2@BTC@Sm

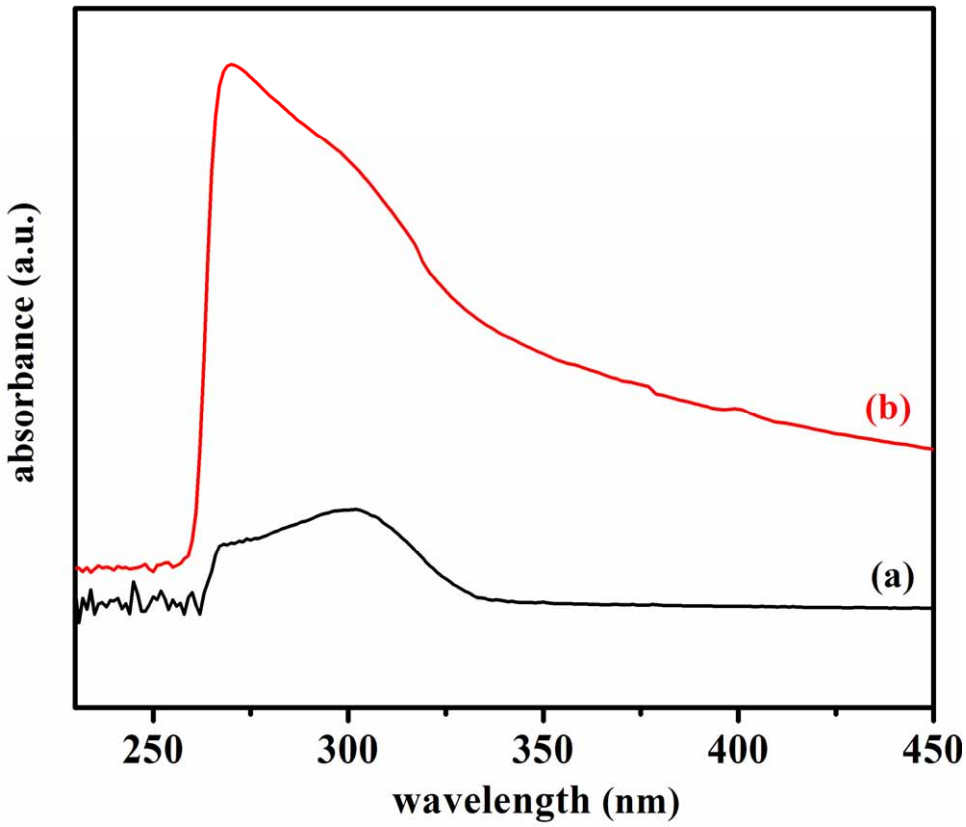


Fig. S11: UV-Vis spectra: PB@SiO_2@BTC@Tb and (b) PB@SiO_2@BTC@Sm.

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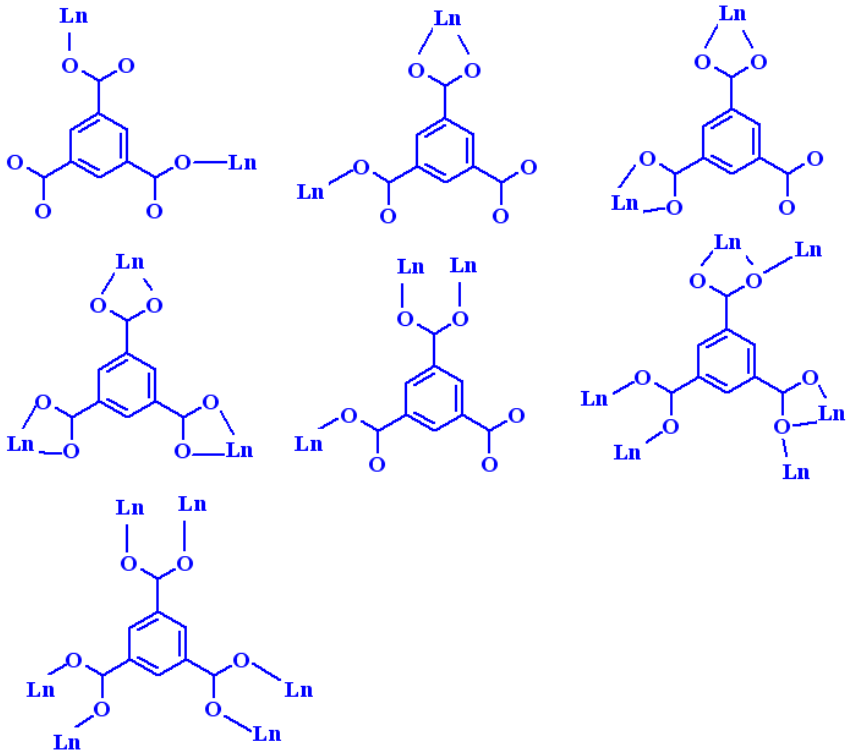

Scheme S1: The probable binding mode BTC linker with the Ln(III) ions.