Electronic Supplementary Information (ESI)

For

Tetrazole-based infinite coordination polymer for encapsulation of TiO_2 and its potential application for fabrication of ZnO@TiO_2 core-shell structures

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Characterization

The elemental analysis was performed with a Heraeus CHN-O- rapid analyzer. Infrared (IR) spectra were performed on a Perkin–Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus between 35 and 600 ˚C in a static atmosphere of nitrogen. X-ray powder diffraction (XRD) measurements were performed using a X'pert diffractometer manufactured by Philips with monochromatized CuKa radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with a gold coating. Transmission electron microscopy (TEM) images were obtained with a Hitachi H-9500 apparatus. NMR data were collected by a BRUKER DRX500 AVANCE. An ultrasonic bath (Tecna 6; 50– 60 Hz and 0.138 kW) was used for the ultrasonic irradiation. PL spectra were measured by means of a spectrofluorimeter manufactured by Cary eclipseFL0912M014. Dynamic light scattering measurements of particle sizes were determined by means of a Zetasizer Nano equipment.

1. Synthesis details and characterization of the ligand btb

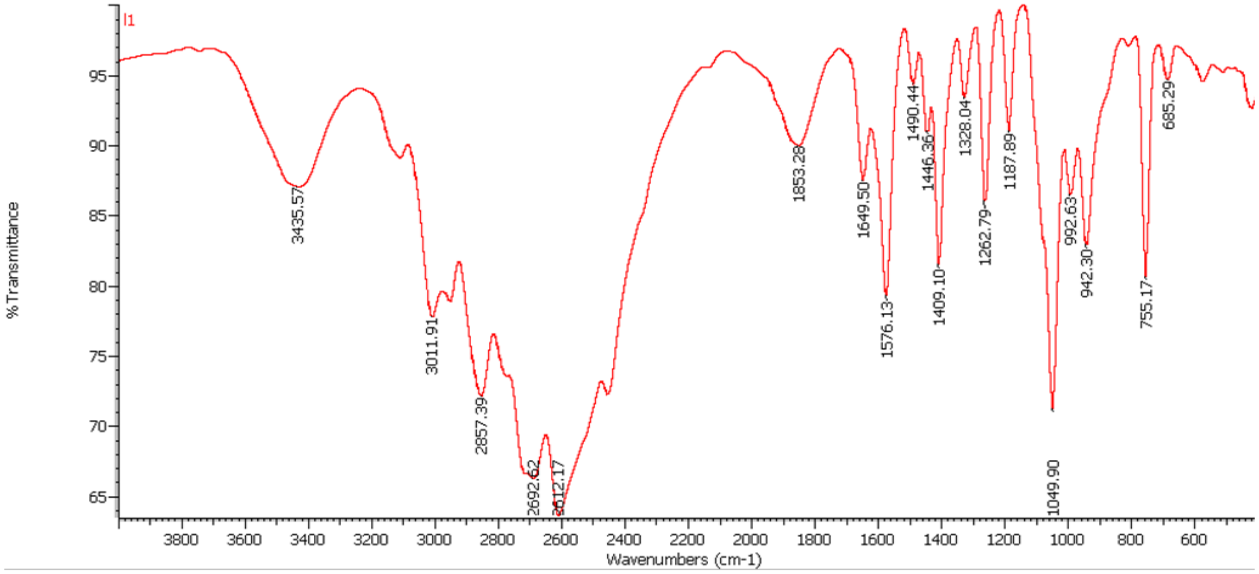
Synthesis of btb. To a 250 mL round-bottomed flask was added the nitrile (20 mmol), sodium azide (60 mmol), zinc bromide (20 mmol), and 40 mL of water. The reaction mixture was refluxed for 48 h at 270˚C; vigorous stirring is essential. After cooling to room temperature, HCl (3 N, 30 mL) were added, and vigorous stirring was continued until the aqueous layer had a pH of 1. 200 mL of 0.25 N NaOH was added, and the mixture stirred for 30 min, until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid washed with 20 mL of 1 N NaOH. To the filtrate was added 40 mL of 3 N HCl with vigorous stirring causing the tetrazole to precipitate. The tetrazole was filtered and washed with HCl and dried in a drying oven to furnish the tetrazole as a white or slightly colored powder. The product had the following data: mp 269-270 °C.

^{1}H NMR (d -DMSO): 7.27 (t, 1H), 7.25 (b, 1H), 7.24 (b, 1H), 7.17 (m, 3H), 4.2 (s, 4H),

^{13}C NMR: 173, 155, 136.5, 129.16, 127.9, 29.60.

Anal. Calcd. for btb: C, 49.57; H, 4.13; N, 46.28. Found: C, 49.12; H, 4.04; N, 43.86.

Figure S1. IR spectra of btb



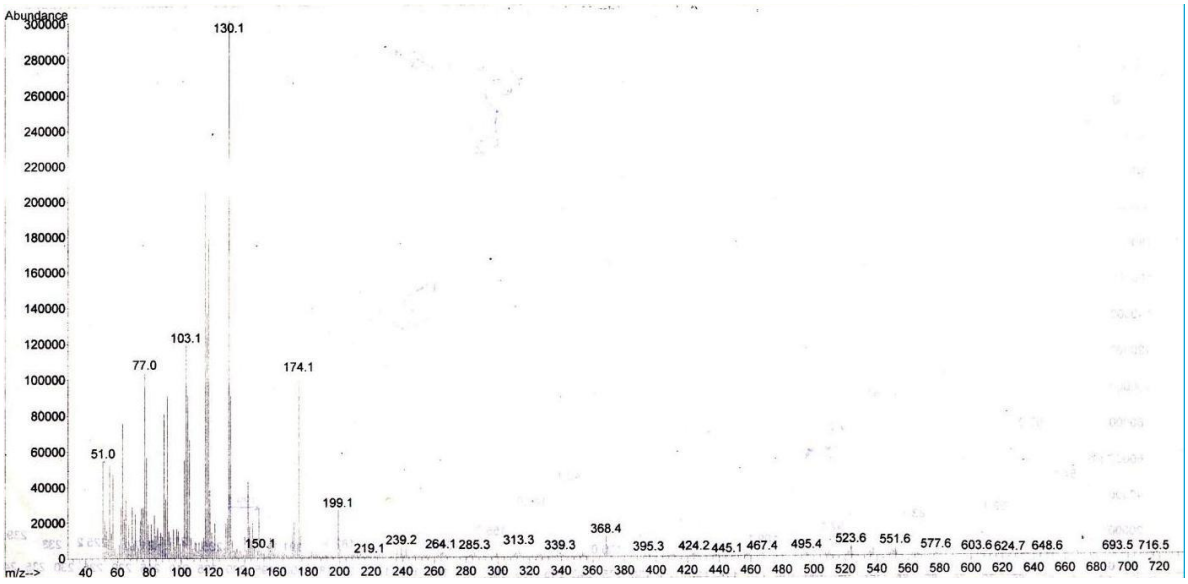


Figure S2. Mass data of the ligand, btb

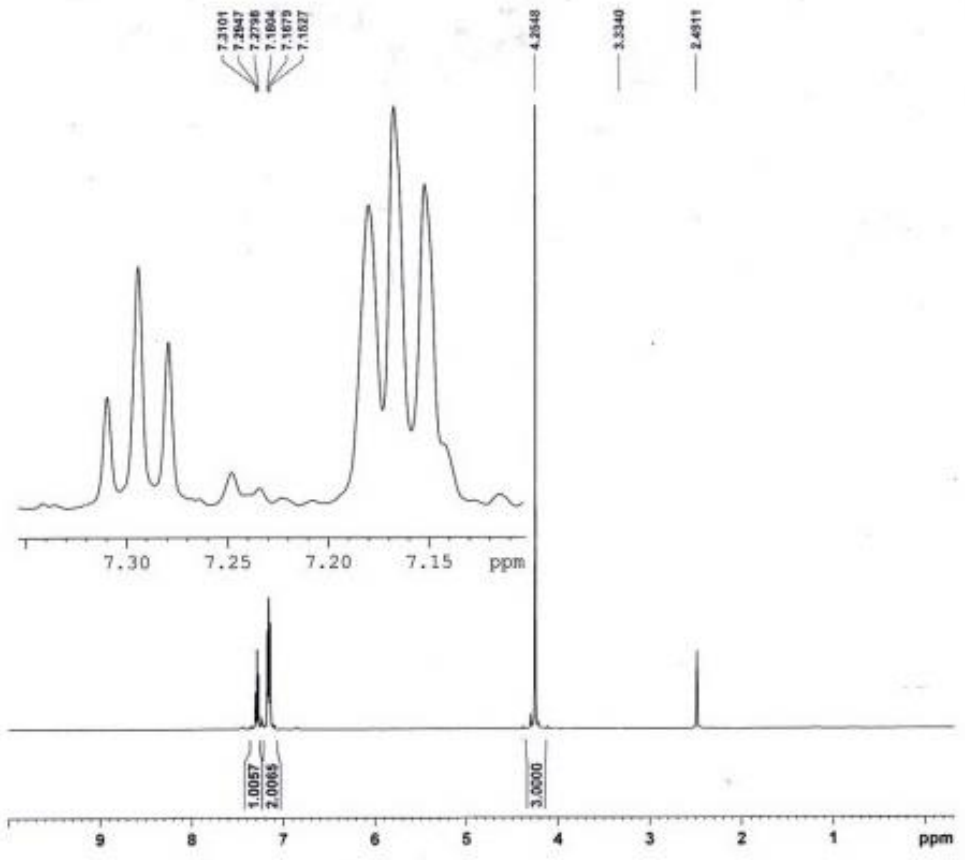


Figure S3. ^{1}H NMR spectra of the ligand, btb, (the peak in 2.5 ppm, is for solvent DMSO)

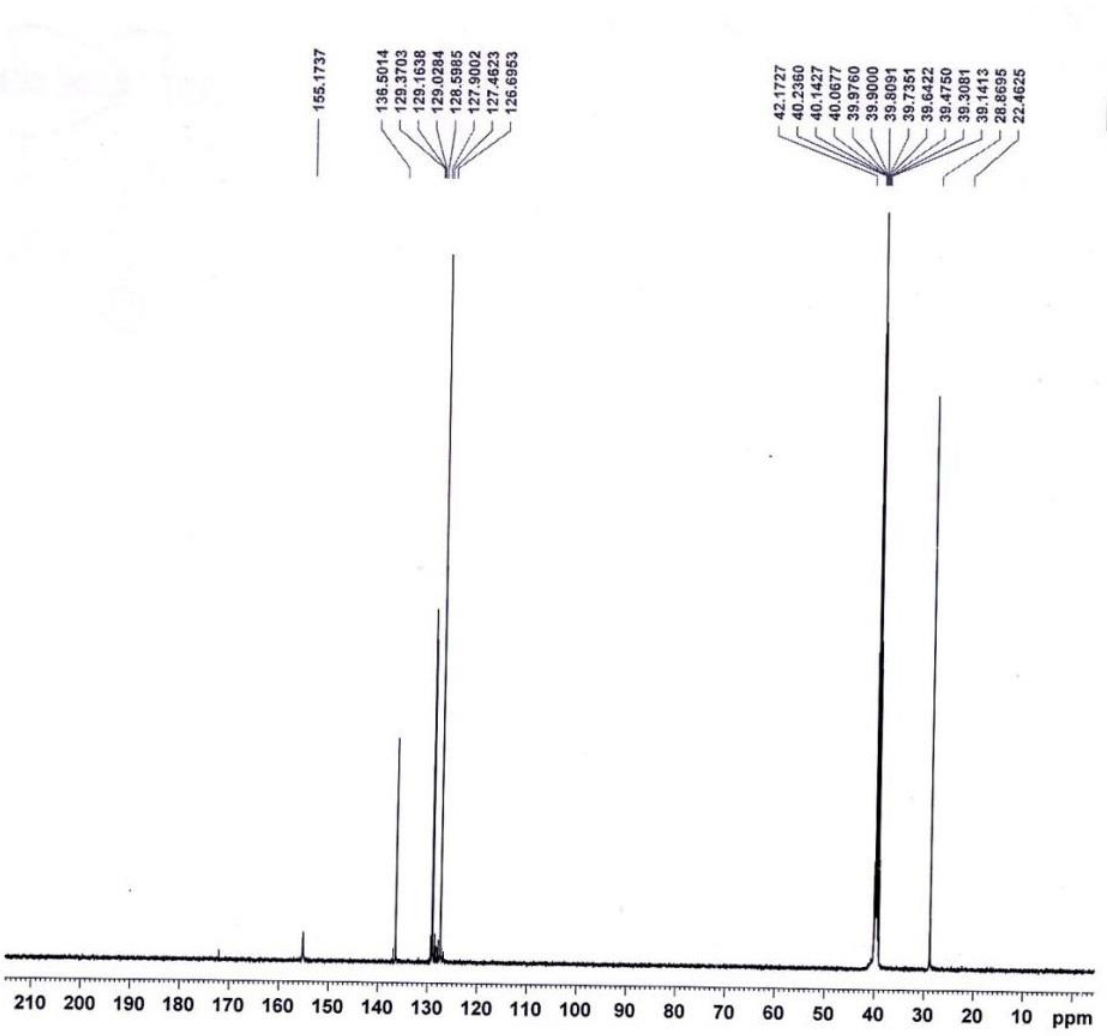


Figure S4. ^{13}C NMR spectra of the ligand, btb

2. Synthesis details of TiO_2 linked RB in hollow Zn(btb) spheres (RB/TiO_2@Zn(btb)

In a typical experiment, a mixture of btb (242 mg, 1 mmol) in DMF (40 ml), Rodamine B (20 μl, 200 ppm) and TiO_2 (1-3 mg, Degussa P25) was prepared. The mixture was homogenized by sonication and stirred for specific times (30 min-12 h) at room temperature. After overnight stirring, a methanolic solution (10 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (296 mg, 1 mmol) was added, to generate the nano-micro spheres encapsulate TiO_2 containing-dye nanoparticles. The resulting encapsulated metal-organic systems in all these cases were purified by centrifugation and washed three times with DMF, and redispersed in DMF to obtain the corresponding colloidal solutions was named **RB/TiO_2@Zn(btb)**. The product had the following data: mp >300 °C. Anal. Calcd. for H Zn(btb): C, 39.34; H, 2.62; N, 36.74. Found: C, 38.65; H, 2.97; N, 31.30.

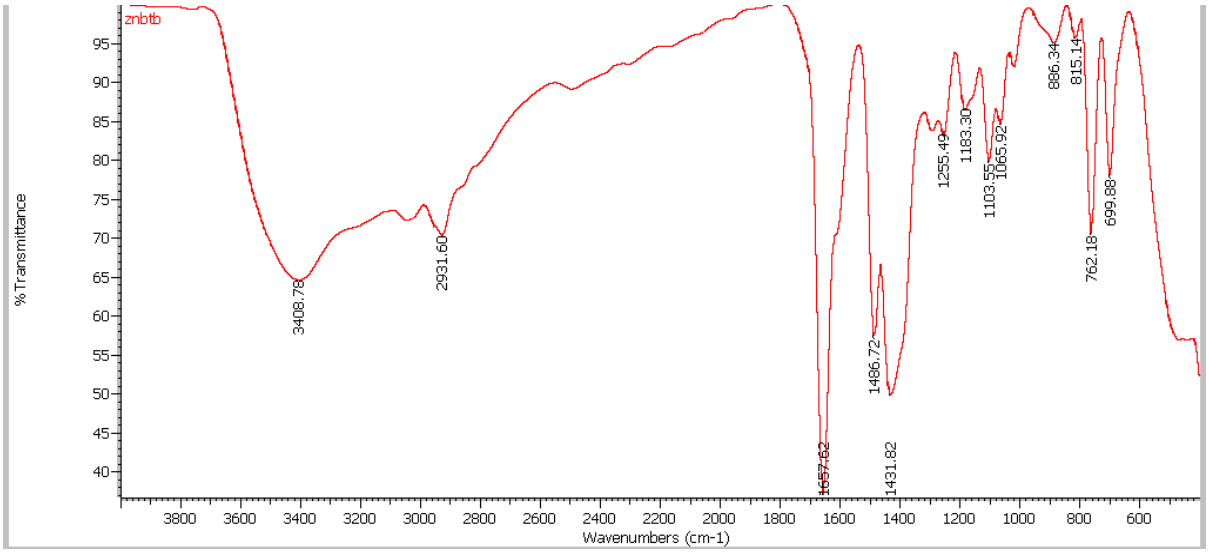


Figure S5. IR spectrum of **Zn(btb)**

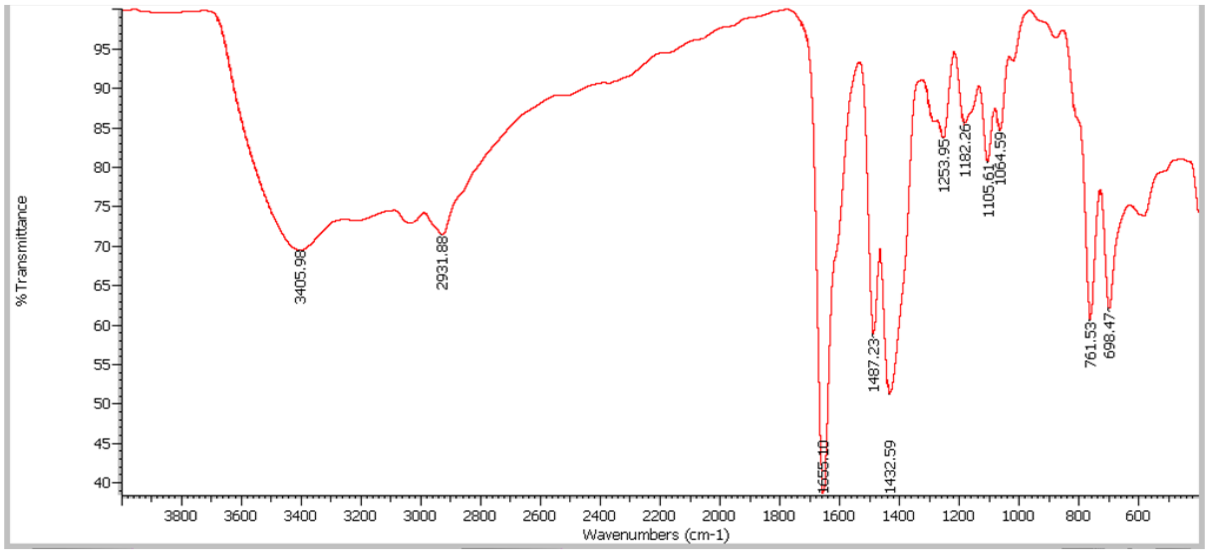


Figure S6. IR spectrum of **RB/TiO_2@Zn(btb)**

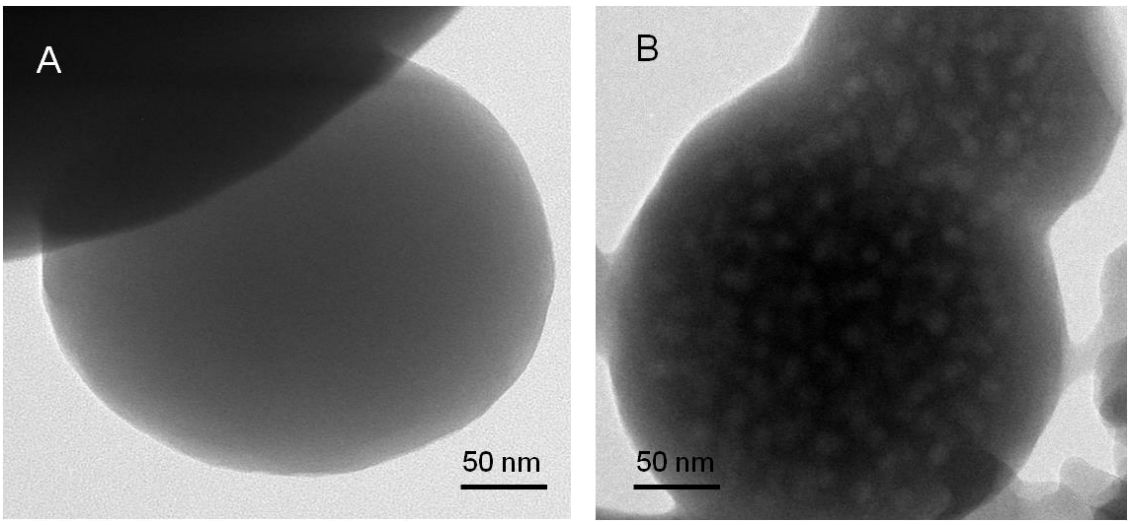


Figure S7. HRTEM images of (a) the bare Zn(btb) spheres, (b) RB/TiO_2 encapsulated within the spherical Zn(btb), RB/TiO_2@Zn(btb).

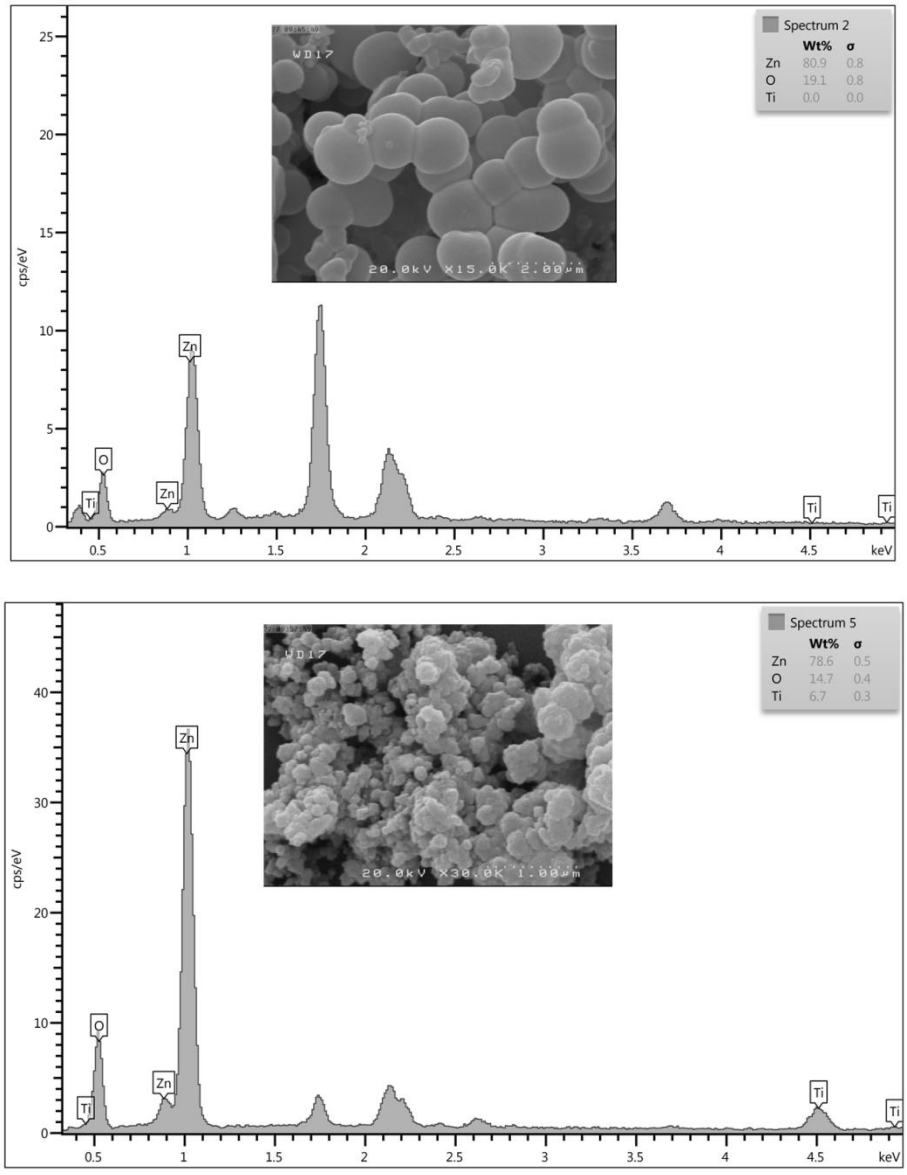


Figure S8. EDX analysis (of SEM images) of RB/TiO_2@Zn(btb) (up), and calcined RB/TiO_2@Zn(btb) spheres at 400 ºC, 3h (down): The zero content of Ti species in EDX of RB/TiO_2@Zn(btb) indicates entrance of titania species within the Zn(btb) spheres that slightly coming out of the polymeric spheres after calcination at 400 ºC.