Electronic Supplementary Information (ESI)

For

Fabrication of Novel Multi-Morphological Tetrazole-Based Infinite Coordination Polymers; Transformation Studies and Their Calcination to Mineral Zinc Oxide Nano- and Microarchitectures

Zahra Sharifzadeh, Sedigheh Abedi, and Ali Morsali*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran.

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Fig. S18 Fluorescence optical microscope images of FITC@H Zn(btb) and Rhodamine B@H Zn(btb) spheres collected at: (i) FITC@H Zn(btb): $\lambda_{\text{exc.}} = 359$ - 371 nm and $\lambda_{\text{em.}} > 397$ nm (left) and $\lambda_{\text{exc.}} = 450$ - 490 nm and $\lambda_{\text{em.}} > 515$ nm (right); (ii) Rhodamine B@H Zn(btb): $\lambda_{\text{exc.}} = 359$ - 371 nm and $\lambda_{\text{em.}} > 397$ nm (left) and $\lambda_{\text{exc.}} = 540$ - 552 nm and $\lambda_{\text{em.}} > 590$ nm (right).

Fig. S19 PXRD pattern of crystalline ZnO

Fig. S20 PXRD patterns of crystalline ZnO prepared after cacination of (a) C Zn(btb), (b) P Zn(btb), (c) R Zn(btb), and (d) S Zn(btb)

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Fig. S22 PXRD pattern of QD@H Zn(btb) after calcinations at 450 °C for 3 h.
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

Scheme S1. Synthesis route of 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.
**Preparation of coral-like, C Zn(btb):** It was prepared by adding dropwise a solution of btb (0.01 M) in DMF (50 ml) into methanolic solution (50 ml) of Zn(NO$_3$)$_2$.6H$_2$O (0.02 M) under ultrasound irradiation for 60 min. Particle products were isolated and subsequently washed with DMF and methanol via centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh DMF.

IR for **C Zn(btb)** (KBr pellet, cm$^{-1}$): 596 (w), 694 (w), 762 (m), 1103 (m), 1282 (w), 1427 (m) 1655 (s) 2800 (m), 2900 (m), and 3434 (m). Anal. Calcd. for C Zn(btb): C,39.34; H, 2.62; N, 36.74. Found: C, 38.03; H, 2.97; N, 34.30.

**Preparation of sphere, P Zn(btb):** A precursor solution was prepared by mixing btb (0.01 M) in DMF (5 ml) and Zn (NO$_3$)$_2$.6H$_2$O (0.02 M) in methanol (5 ml). The resulting mixture was placed in an oil bath (140 °C) and refluxed for 72 h. The spheres **P Zn(btb)** generated in this time were isolated by cooling the reaction mixture to room temperature. Particle products were isolated and subsequently washed with DMF and methanol via centrifugation-redispersion cycles. Each successive supernatant was decanted and replaced with fresh DMF.

IR for **P Zn(btb)** (KBr pellet, cm$^{-1}$): 699 (w), 762 (m), 1103 (m), 1266 (w), 1431 (m),1487 (m), 1657 (s), 2800 (m), 2900 (m), and 3408 (m). Anal. Calcd. for P Zn(btb): C, 39.34; H, 2.62; N, 36.74. Found: C, 37.95; H, 3; N, 35.43.

**Preparation of rod-like, R Zn(btb):** A precursor solution was prepared by mixing btb (0.2 M) in DMF (1 ml) and Zn (NO$_3$)$_2$.6H$_2$O (0.044 M) in distilled water (9 ml). The resulting mixture under stirring was placed in an oil bath (140 °C) and refluxed for 72 h. The rods **R Zn(btb)** generated in this time were isolated by cooling the reaction mixture to room temperature. Particle
products were isolated and subsequently washed with DMF via centrifugation redispersion cycles. Each successive supernatant was decanted and replaced with fresh DMF.

IR for R Zn(btb) (KBr pellet, cm\(^{-1}\)): 697 (w), 761 (m), 1099 (m), 1261 (w), 1435 (m), 1487 (m), 1657 (s), 2800 (m), 2925 (m), and 3437 (s). Anal. Calcd. for R Zn(btb): C, 39.34; H, 2.62; N, 36.74. Found: C, 37.95; H, 3.17; N, 34.38.

**Preparation of spheres, S Zn(btb):** A certain amount of btb (0.2 M) in DMF (1 ml) was added into 9 mL aqueous solution of Zn (NO\(_3\))\(_2\).6H\(_2\)O (0.044 M) under stirring for 30 min. The obtained homogeneous solution was then transferred into a 50 ml Teflon-lined autoclave, then heated to 140 °C in 12 h, and maintained at this temperature for 24 h. The reactor was cooled to room temperature naturally. The resultant product was collected and washed several times with DMF, and then dried in air.

IR for S Zn(btb) (KBr pellet, cm\(^{-1}\)): 695 (w), 761 (m), 1105 (m), 1263 (w), 1426 (m), 1483 (m), 1613 (s), 1657 (s), 2800 (m), 2925 (m), and 3436 (s). Anal. Calcd. for S Zn(btb): C, 17.81; H, 3; N, 16.07. Found: C, 18.45; H, 3.6; N, 16.84.

**Preparation of zinc oxide sphere, rod and coral-shape:** C Zn(btb), P Zn(btb), R Zn(btb) and S Zn(btb) individually were placed in a furnace and calcined at 450 °C in air. After 3 h holding at 450 °C, the generated ZnO was cooled to room temperature.
Figure S1. IR spectra of btb

IR (cm$^{-1}$) selected bands: 681 (w), 756 (w), 1056 (m), 1189 (w), 1261 (w), 1410 (w), 1579 (w), 1650 (w), 1860 (w), 2608 (s), 2708 (s), 2860 (m), 3059 (m) and 3447 (w).
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
Figure S5. IR spectra of C Zn(btb), P Zn(btb), S Zn(btb) and R Zn(btb)
Fig. S6 TGA curves of (a) C Zn(btb), (b) P Zn(btb), (c) R Zn(btb), and (d) S Zn(btb)
**Fig. S7** Emission spectra of (a) C Zn(btb), (b) P Zn(btb), (c) R Zn(btb), and (d) S Zn(btb)
Fig. S8 XRD spectra of (a) C Zn(btb), (b) P Zn(btb), (c) R Zn(btb), and (d) S Zn(btb)
Fig. S9 FE-SEM images of the obtained coral-like particles as $\text{C Zn(btb)}$
Fig. S10 FE-SEM images of the obtained spherical particles as P Zn(btb)
Fig. S11 FE-SEM images of the obtained rod-like particles as $\text{R Zn(btb)}$
Fig. S12 FE-SEM image of the obtained sphere particles as $\text{S Zn(btb)}$
**Fig. S13** FE-SEM images of the sphere particles $S \text{ Zn(btb)}$, obtained from $R \text{ Zn(bt)}$ to $S \text{ Zn(btb)}$ transformation.
2. Synthesis details of bare H Zn(btb) spheres

Metal-organic H Zn(btb) spheres was prepared by addition of an methanolic solution (5 ml) of Zn(NO$_3$)$_2$·6H$_2$O (148 mg, 0.5 mmol) to a solution of btb (121 mg, 0.5 mmol) in N,N dimethyl formamide (DMF) (25 ml) under vigorous stirring at room temperature. For the nanospheres to reach their final stable size, 10 minutes after precipitation, DMF was added to the reaction mixture. The resulting spheres were then purified by centrifugation and washed several times with DMF, and ultimately redispersed in DMF. H Zn(btb) spheres with different average sizes were prepared using the same synthetic methodology and just by simply modifying the concentration of both Zn(NO$_3$)$_2$·6H$_2$O and Btb ligand. 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.
FigS14. Infrared Spectrum of $\text{H Zn(btb)}$ spheres

IR (cm$^{-1}$) selected bands: 593 (w), 689 (w), 760 (m), 1103 (m), 1260 (w), 1430 (m), 1652 (s), 2800 (m), 2900 (m) and 3430 (m).
3. Synthesis details of encapsulation in H Zn(btb) spheres

For Iron oxide nanoparticles@Zn(btb) spheres synthesis to a solution of btb (121 mg, 0.5 mmol) in DMF(25 ml), an amount of iron oxide nanoparticles was added, to obtain a final solution of 4.5.10-4 M. Next, this mixture was homogenized by sonication and a methanolic solution (5 mL) of Zn(NO3)2·6H2O (148 mg, 0.5 mmol) was added, to generate the nanospheres that encapsulate the magnetic nanoparticles. For QD@Zn(btb) spheres synthesis to a solution of btb (121 mg, 0.5 mmol) in DMF(25 ml), an amount of QDs (4·10-8 M) was added. Next a methanolic solution (5 mL) of Zn(NO3)2·6H2O (148 mg, 0.5 mmol) under vigorous stirring at room temperature was added. For Dyes@Zn(btb) spheres synthesis to a solution of btb (121 mg, 0.5 mmol) in DMF(25 ml), an amount of luminiscent dye (3.3·10-5 M) was added. Next a methanolic solution (5 mL) of Zn(NO3)2·6H2O (148 mg, 0.5 mmol) under vigorous stirring at room temperature was added. For QDs&iron oxide nanoparticles@Zn(btb) spheres synthesis to a solution of btb (121 mg, 0.5 mmol) in DMF(25 ml), an amount of iron oxide nanoparticles (4.5·10-4 M) and QDs (4·10-8 M) was added. Next, this mixture was homogenized by sonication and a methanolic solution (5 mL) of Zn(NO3)2·6H2O (148 mg, 0.5 mmol) was added, to generate the nanospheres that encapsulate the magnetic nanoparticles and QDs. 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.
Fig. S15 EDX spectrum of Fe@H Zn(btb) spheres (The peaks marked by a star symbol correspond to the silica).
Fig. S16 EDX spectrum performed on QDs@H Zn(btb) spheres, showing the presence of zinc, cadmium, telluride and sulphur (The peaks marked by a star symbol correspond to the silica).
Fig. S17 Fluorescence emission spectra of (a) FITC@H Zn(btb) (collected at $\lambda_{\text{exc.}} = 490$ and 350 nm), (b) QDs@H Zn(btb) spheres (collected at $\lambda_{\text{exc.}} = 470$ and 350 nm) and (c) Rhodamine B@H Zn(btb) (collected at $\lambda_{\text{exc.}} = 510$ and 350 nm).
FITC@ H Zn(btb)

Rhodamine B@ H Zn(btb)

**Fig. S18** Fluorescence optical microscope images of FITC@ H Zn(btb) and Rhodamine B@ H Zn(btb) spheres collected at: (i) FITC@H Zn(btb): $\lambda_{\text{exc.}} = 359 - 371$ nm and $\lambda_{\text{em}} > 397$ nm (left) and $\lambda_{\text{exc.}} = 450 - 490$ nm and $\lambda_{\text{em}} > 515$ nm (right); (ii) Rhodamine B@ H Zn(btb) : $\lambda_{\text{exc.}} = 359 - 371$ nm and $\lambda_{\text{em}} > 397$ nm (left) and $\lambda_{\text{exc.}} = 540 - 552$ nm and $\lambda_{\text{em}} > 590$ nm (right). The blue fluorescence in left images mainly arises from H Zn(btb) spheres, whereas the green (FITC) and red (Rhodamine B) fluorescence in right images stems from the encapsulated fluorophores.
*Fig. S19* PXRD pattern of crystalline ZnO.
Fig. S20 PXRD patterns of crystalline ZnO prepared after cacination of (a) C Zn(btb), (b) P Zn(btb), (c) R Zn(btb), and (d) S Zn(btb)
Fig. S21 PXRD pattern of Fe@H Zn(btb) after calcinations at 450 °C for 3 h.
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