Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

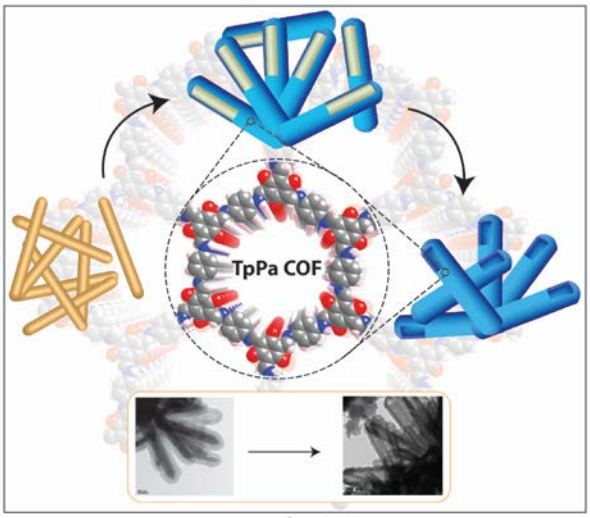
Hollow Tubular Porous Covalent Organic Framework (COF) Nanostructures

*Pradip Pachfule,[a] Sharath Kandmabeth,[a,b] Arijit Mallick,[a,b] Rahul Banerjee[a,b]**

[a]Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr.HomiBhabha Road, Pune 411008, India.

[b]Academy of Scientific and Innovative Research (AcSIR), New Delhi 110 025, India.

E-mail: r.banerjee@ncl.res.in; Tel: +912025903205



Contents List

Section S1. Experimental procedures, materials and methods:

All the reagents and solvents used for the synthesis of **TpPa** and **ZnO@TpPa** were commercially available and used as received. The $Zn(NO_3)_2.6H_2O$ used for the synthesis of ZnO-nanords was purchased from Sigma Aldrich. Paraphenylenediamine used for COF synthesis were purchased from TCI Chemicals.

FT-IR, PXRD, SEM, EDAX, TEM, TGA and NMR analyses:

Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR (Golden Gate). Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu $K\alpha$ radiation (l = 1.5406 Å), with a scan speed of 1° min^{-1} and a step size of 0.02° in 2θ. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D. Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV was used to get SEM images. Microscopy analyses were performed using a LEICA Stereoscan 440 scanning electron microscope (SEM) equipped with Phoenix energy dispersive analysis of X-ray (EDAX). To investigate the microstructure and morphology of the ZnO-nanorods, **ZnO@TpPa** and hollow **TpPa** nanostructures, we used the FEI (model Tecnai F30) high resolution transmission electron microscope (HRTEM) equipped with field emission source operating at 300 KeV to image the materials loaded on carbon-coated copper TEM grids. The nonmaterials were dispersed in *i*PrOH and drop casted on the TEM grids. NMR data were taken on Bruker 200 and 400 MHz NMR spectrometers.

N_2 adsorption isotherms and pore size distribution measurements:

Autosorb-iQ automatic volumetric instrument has been used for low pressure volumetric N_2 gas adsorption measurements involved in this work, performed at 77 K maintained by a liquid nitrogen bath, with pressures ranging from 0 to 760 Torr. Ultra high-purity N_2 was obtained by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the system. For the gas adsorption studies of **TpPa**, **ZnO@TpPa** and hollow **TpPa** nanostructures the solvent exchanged samples were dried under a dynamic vacuum (<10^{-3} Torr) at room temperature (RT) overnight followed by heating at 100 °C for 12 h and 120 °C for 12 h under a dynamic vacuum. The completely dried samples (50 mg) were loaded for gas adsorption study in the sample cells. The as synthesized sample of **TpPa**, **ZnO@TpPa** and hollow **TpPa** nanostructures were used for the N_2 adsorption isotherm studies and pore sized distributions plots were calculated using Quenched Solid Density Functional Theory (QSDFT) and Density Functional Theory (DFT) methods using the nitrogen adsorption isotherms obtained at 77 K and 1 atm pressure.

Section S2. Synthesis and characterization of TpPa:

Synthesis of TpPa:

The synthesis of **TpPa** was performed according to the literature reported our recent communication.[1] Specifically, a pyrex tube (o.d. × i.d. = 10 × 8 mm^2 and length 18 cm) was charged with triformylphloroglucinol (**Tp**) (63 mg, 0.3 mmol), paraphenylenediamine (**Pa**) (48 mg, 0.45 mmol), mesitylene (1.5 mL), dioxane (1.5 mL), and aqueous acetic acid (0.5 mL, 3 M solution). The mixture was sonicated for 10 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. A red colored precipitate formed was collected by centrifugation or filtration and washed with anhydrous acetone. The powder collected was then solvent exchanged with anhydrous acetone 5-6 times and then dried at 180 °C under vacuum for 24 h to give the product as a deep red colored powder in 80% isolated yield (89 mg).

IR (powder, cm^{-1}): 1592 (w), 1578 (s), 1454 (s), 1251 (s), 1087 (m), 995 (s), 832 (s)

Elemental analysis. For $C_{80}O_{12}N_{13}H_{48}$

Calculated: **C**, 69.5; **H**, 3.47; **N**, 13.87

Found: **C**, 68.2; **H**, 3.97; **N**, 13.20

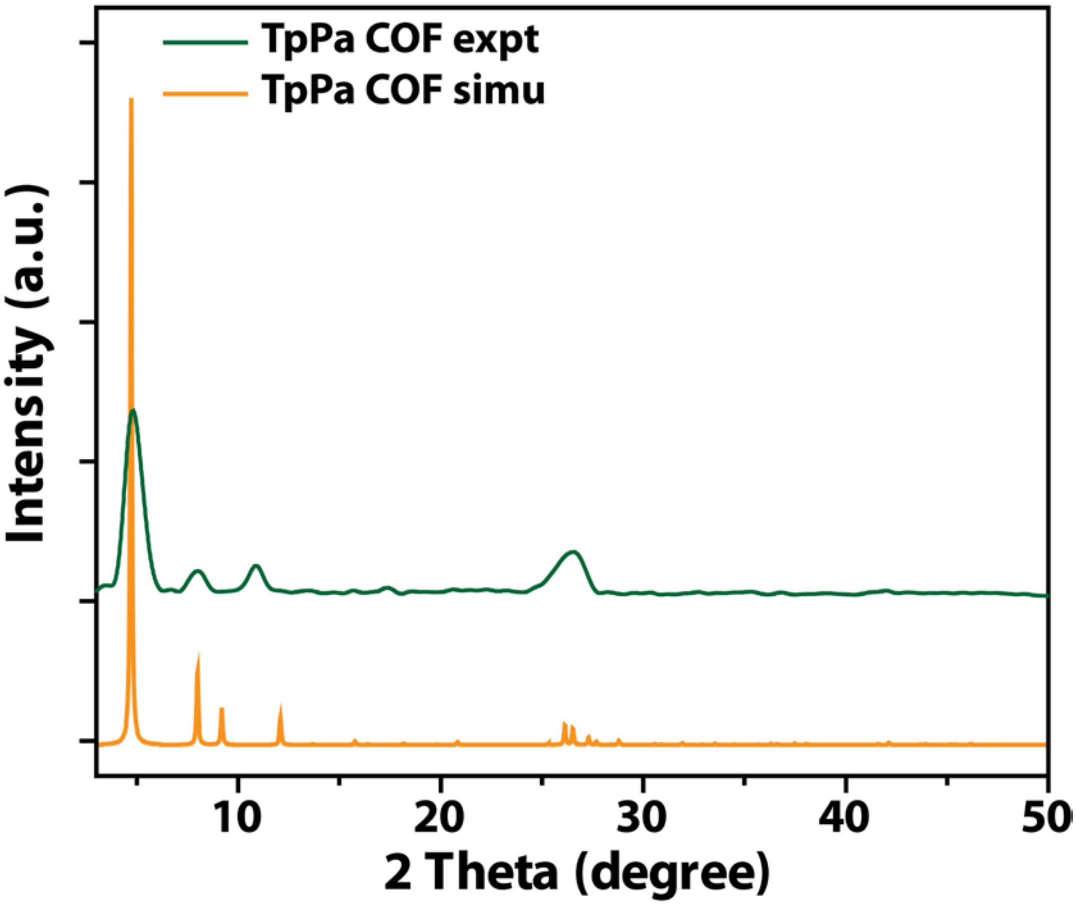


Figure S1. *PXRD pattern observed for* ***TpPa*** *and its comparison with the corresponding simulated pattern, showing peak to peak match with the bulk material.*

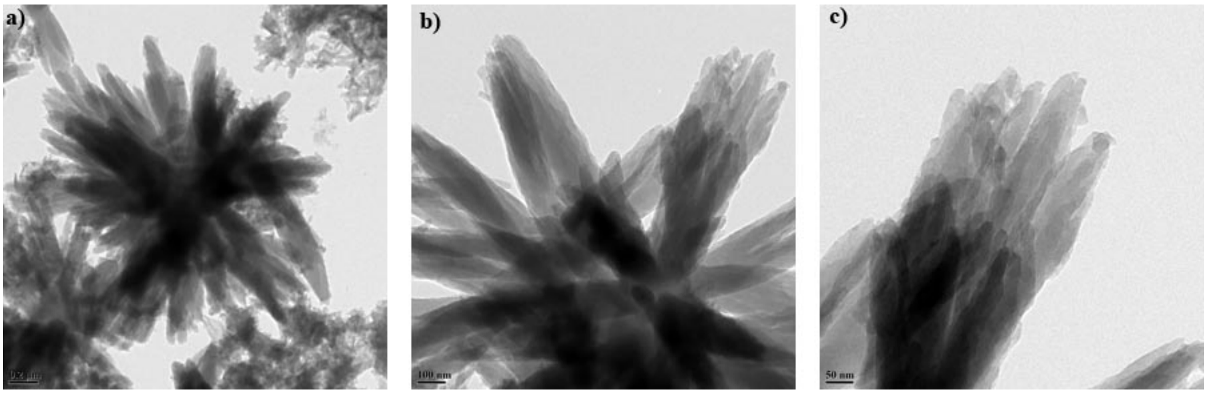


Figure S2. *TEM images of* ***TpPa****. a) TEM image of* ***TpPa*** *showing flower like morphology of COF. b) and c) High resolution TEM image of* ***TpPa*** *showing sheets like structures arranged in lamellar fashion.*

Section S3. Synthesis and characterization of ZnO-nanords:

The solution of alkaline-zinc was prepared by dissolving 14.87 g of zinc nitrate [$Zn(NO_3)_2.6H_2O$] and 40.00 g of NaOH in deionized water to form a 100.0 mL solution ([Zn^{2+}]) 0.50 M, [OH^{-}]) 10.00 M; molar ratio of Zn^{2+}:OH^{-}) 1:20). 3 mL of the above solution was then mixed with 0.0–5.0 mL of deionized water and 25.0 mL of pure alcohol (C_2H_5OH), followed by adding 5.0 mL of ethylenediamine ($C_2H_4(NH_2)_2$, EDA; molar ratio of Zn^{2+}: EDA) ca. 1:50 to 1:60. Before being transferred to a Teflon-lined autoclave, the solution mixture was pretreated under an ultrasonic water bath for 30 min. The hydrothermal syntheses were conducted at 180 °C for 24 h in an electric oven. After the reactions, white crystalline products (ZnO-nanorods) were separated by centrifugation and purified by washings with deionized water. The obtained ZnO-nanorods were characterized with scanning electron microscopy and XRD analyses.

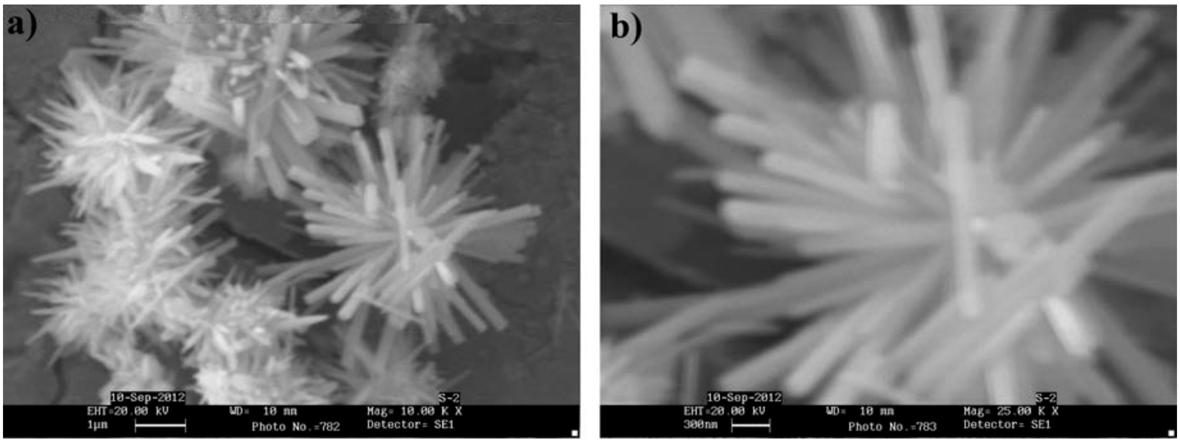


Figure S3. *SEM image of the ZnO-nanorods synthesized showing follower like morphology at: a) Low magnification, and b) High Resolution.*

Section S4. Synthesis and characterization of ZnO@TpPa:

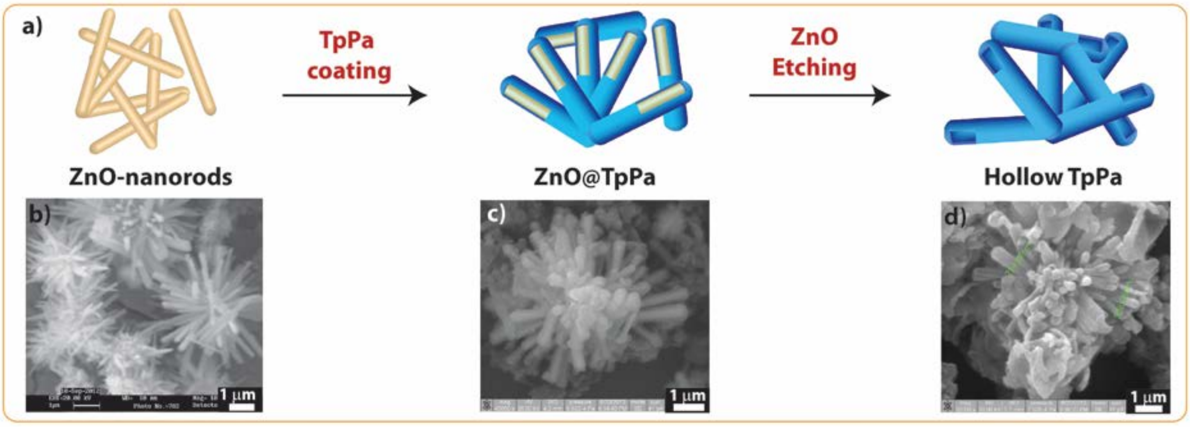


Figure S4. *The process of synthesis of hollow **TpPa** nanostructures from ZnO-nanorods and **TpPa**-COF. a) Transformation of ZnO-nanorods to hollow **TpPa** structures. SEM images of b) ZnO-nanorods, c) **ZnO@TpPa** and d) Hollow **TpPa** nanostructures.*

The synthesis of **ZnO@TpPa** was performed by modifying the synthesis procedure for **TpPa** COF synthesis. Specifically, a pyrex tube (o.d. × i.d. = 10 × 8 mm^2 and length 18 cm) was charged with triformylphloroglucinol (**Tp**) (63 mg, 0.3 mmol), paraphenylenediamine (**Pa**) (48 mg, 0.45 mmol), mesitylene (1.5 mL), dioxane (1.5 mL), and aqueous acetic acid (3 M, 50 µL). The acetic acid solution was added after the addition of all the reactants and solvents as the ZnO gets dissolved in excess acid. The mixture was sonicated for 10 minutes in order to get a homogenous dispersion. After sonication for 10 min, addition of 30 mg as synthesized ZnO-nanorods was performed and mixture was further sonicated for 60 min in order to achieve the dispersion of ZnO-nanorods. The critical steps involves the addition of catalytic amount of acetic acid (3 M, 50 µL), as excess acid consumes the ZnO-nanorods. Similarly, dispersion and quantitative addition of ZnO-nanorods (30 mg) into the reaction mixture is also important for the selective loading of **TpPa** COF on ZnO-nanorods. The tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. A red colored precipitate formed was collected by centrifugation or filtration and washed with anhydrous acetone. The powder collected was then solvent exchanged with anhydrous acetone 5-6 times and then dried at 180 °C under vacuum for 24 h to give the product as a deep red colored powder of hollow TpPa nanostructures in quantitative yield (95 mg).

IR (powder, cm^{-1}): 1591 (w), 1574 (s), 1453 (s), 1248 (s), 1085 (m), 990 (s), 837 (s)

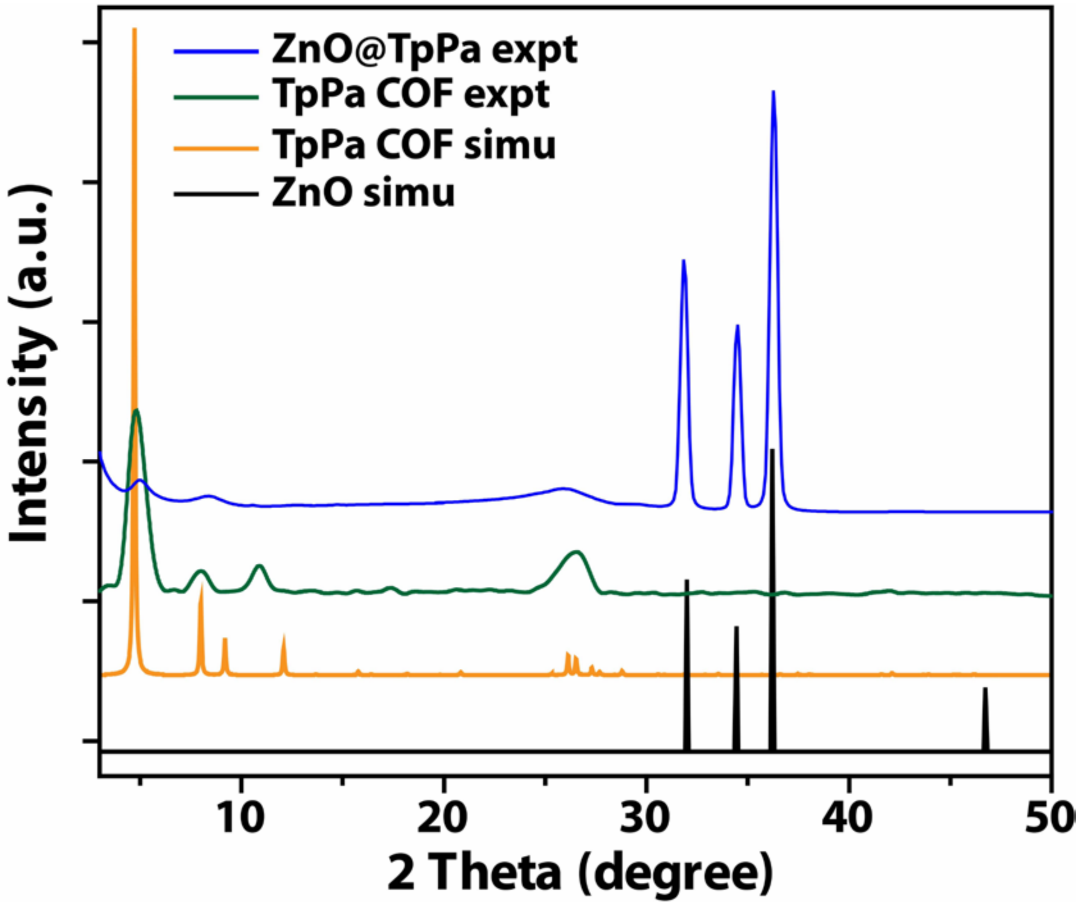


Figure S5. *PXRD pattern of* ***ZnO@TpPa*** *and its comparison with the corresponding simulated XRD patterns of ZnO-nanorods (JCPDS 89-1397) and* ***TpPa****-COF, and experimental PXRD patterns of* ***TpPa****-COF, showing peak to peak match.*

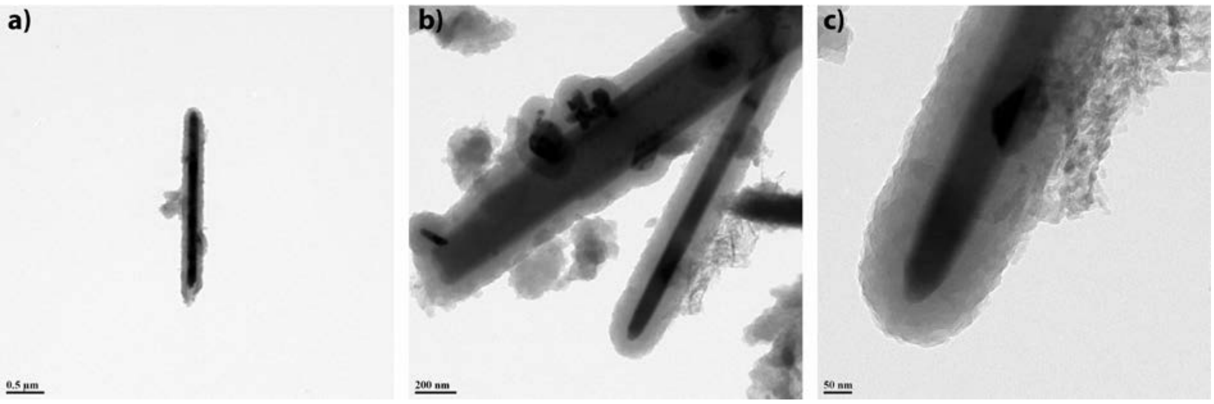
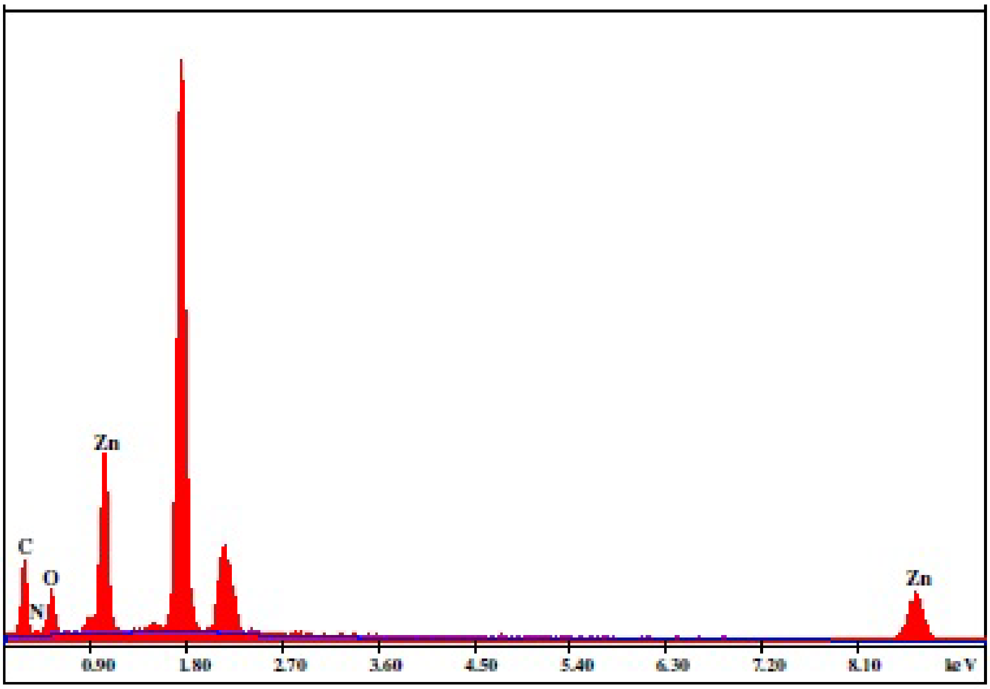
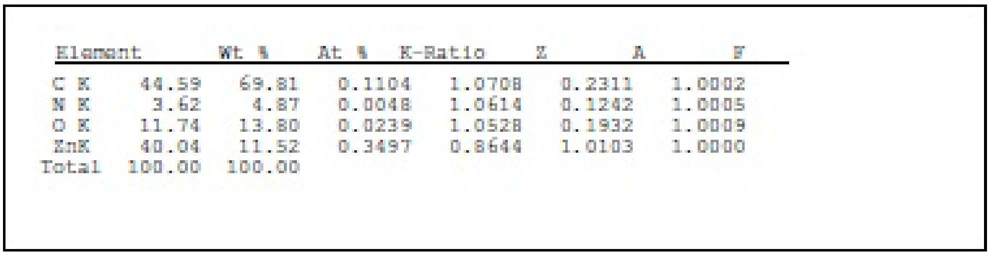


Figure S6. *TEM images of* ***ZnO@TpPa****. a) TEM image of* ***ZnO@TpPa*** *showing capsule like morphology, where ZnO-nanorods get encapsulated in* ***TpPa*** *COF shell. b) TEM image of* ***ZnO@TpPa*** *at low magnification showing the loading of TpPa on the surface of ZnO-nanorods. c) High resolution TEM image of* ***ZnO@TpPa*** *showing capsular morphology and uniform loading of* ***TpPa*** *on the surface of ZnO-nanorods.*





Element	Wt %	At %	K-Ratio	Z	A	F
C K	44.59	69.81	0.1104	1.0708	0.2311	1.0002
N K	3.62	4.87	0.0048	1.0614	0.1242	1.0005
O K	11.74	13.80	0.0239	1.0528	0.1932	1.0009
ZnK	40.04	11.52	0.3497	0.8644	1.0103	1.0000
Total	100.00	100.00				

Figure S7. *EDAX analyses of the as synthesized* ***ZnO@TpPa*** *showing the presence of 40% Zn showing the presence of ZnO-nanorods as core.*

Section S5. Synthesis and characterization of hollow TpPa nanostructures:

The as ZnO-nanorods synthesized by reported procedure are easily soluble in dilute acid solution.[2] On the other hand, the as synthesized **TpPa**-COF is highly stable into aqueous acid solution for long time.[3] Hence, in order to achieve the selective removal of ZnO-nanorods from **ZnO@TpPa**, we have treated this material with aqueous HCl solution. The as synthesized **ZnO@TpPa** (100 mg) was suspended into the 10 ml aq. HCl solution (1N) and stirred for 1 h. After 1 h, the material was kept undisturbed into room temperature for 24 hrs. The materials was separated by purification and washed with water (3 x 10 ml) and dried at 100 °C in vacuum oven for 12 h. The obtained pure and hollow **TpPa** nanostructures were collected after vacuum evacuation and characterized by PXRD, gas adsorption, ^{13}C NMR, SEM and TEM analyses.

IR (powder, cm^{-1}): 1590 (w), 1576 (s), 1453 (s), 1251 (s), 1087 (m), 991 (s), 835 (s)

Elemental analysis. For $C_{80}O_{12}N_{13}H_{48}$

Calculated: **C**, 69.5; **H**, 3.47; **N**, 13.87

Found: **C**, 67.8; **H**, 4.12; **N**, 12.96

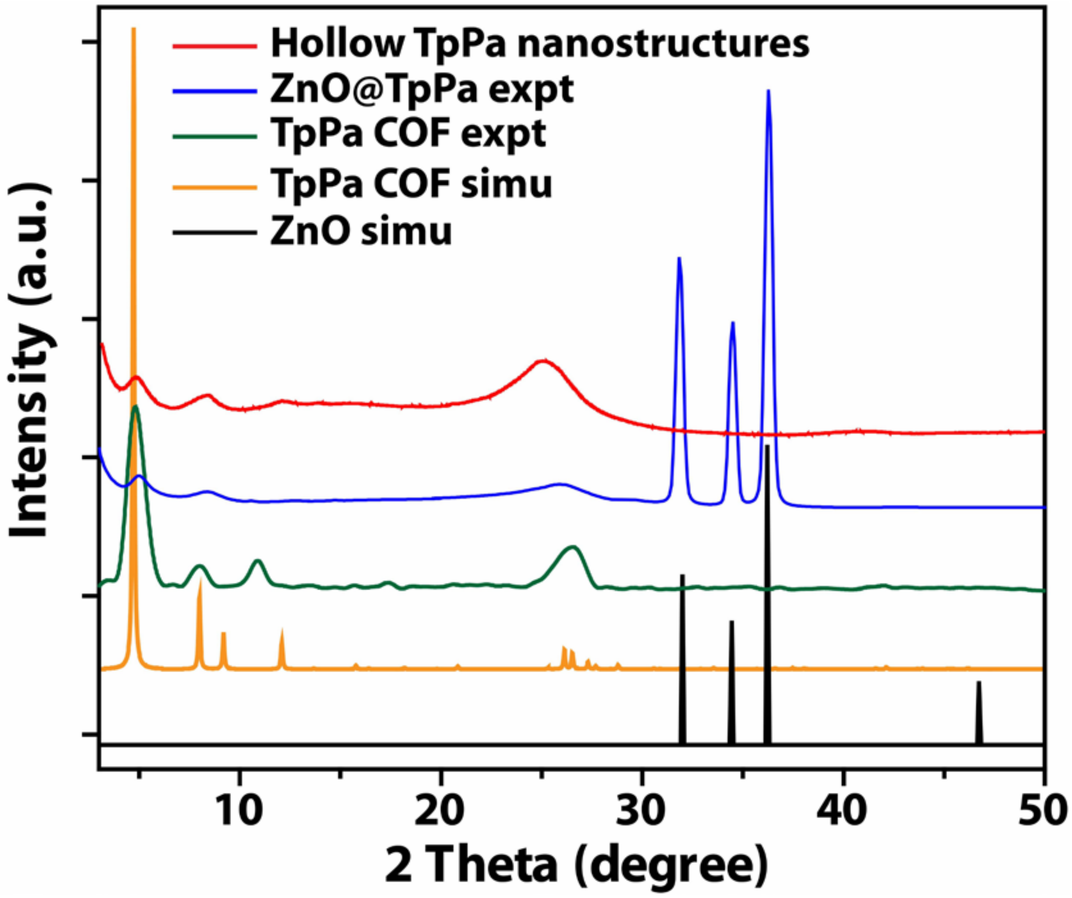


Figure S8. *PXRD pattern of hollow* ***TpPa*** *nanostructures and its comparison with the corresponding simulated XRD patterns of ZnO-nanorods (JCPDS 89-1397) and* ***TpPa****-COF, and experimental PXRD patterns of* ***TpPa****-COF, showing peak to peak match.*

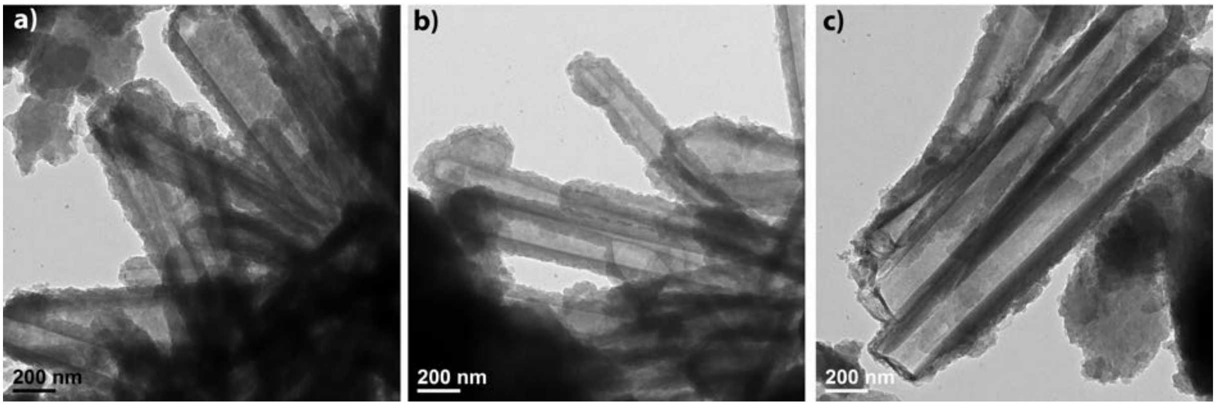
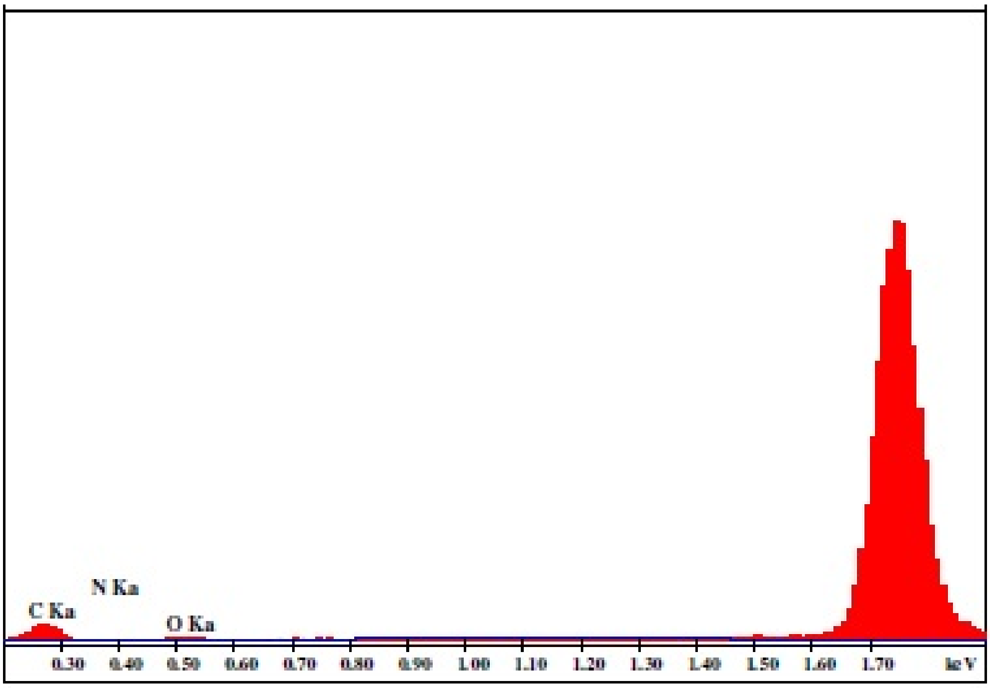
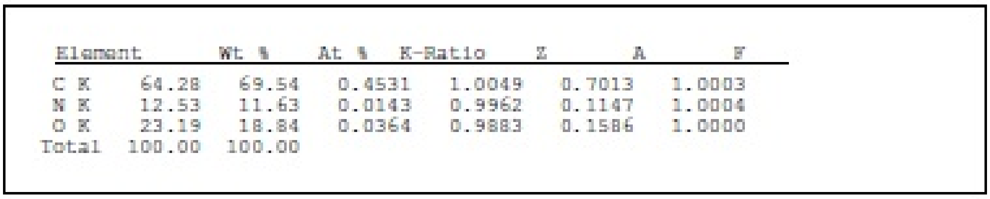


Figure S9. *TEM images of hollow* ***TpPa*** *nanostructures. a) TEM image of hollow* ***TpPa*** *nanostructures showing maintained capsule like morphology after acid washing, where ZnO-nanorods from* ***ZnO@TpPa*** *clearly visible. b) TEM image of hollow* ***TpPa*** *nanostructures at low magnification showing complete removal of ZnO. c) High resolution TEM image of hollow* ***TpPa*** *nanostructures showing tubular morphology and uniform* ***TpPa*** *shell.*





Element	Wt %	At %	K-Ratio	Z	A	F
C K	64.28	69.54	0.4531	1.0049	0.7013	1.0003
N K	12.53	11.63	0.0143	0.9962	0.1147	1.0004
O K	23.19	18.84	0.0364	0.9883	0.1586	1.0000
Total	100.00	100.00				

Figure S10. *EDAX analyses of the as synthesized hollow* ***TpPa*** *nanostructures showing the absence of Zn confirming the complete removal of ZnO-nanorods from core.*

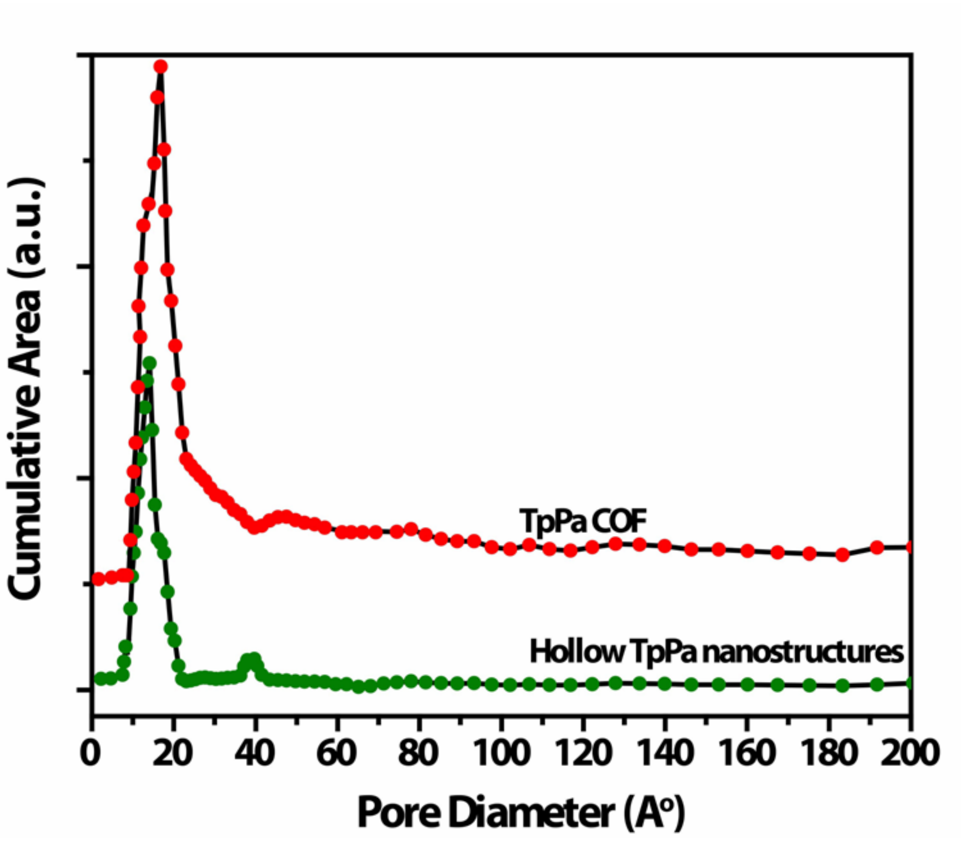


Figure S11. *Pore size distribution for hollow **TpPa** nanostructures and **TpPa** calculated using Density Functional Theory (DFT) method. The maintained pore size distribution for hollow **TpPa** nanostructures and **TpPa** is probably due to the very large size voids encapsulated within the **TpPa** core, as these voids are too large for the adsorption of tiny* N_2 *gas molecules.*

Section S6. The process of removal of ZnO-nanorods from ZnO@TpPa:

The process of removal of ZnO-nanorods from the core of **ZnO@TpPa** is very important for the synthesis of hollow TpPa nanostructures. In order to confirm the minimum time required for the removal of ZnO from these **ZnO@TpPa** structures, we have followed this procedure using TEM and EDAX analyses. These analyses confirm that for the complete removal of ZnO from **ZnO@TpPa**, minimum 24 h time span is needed.

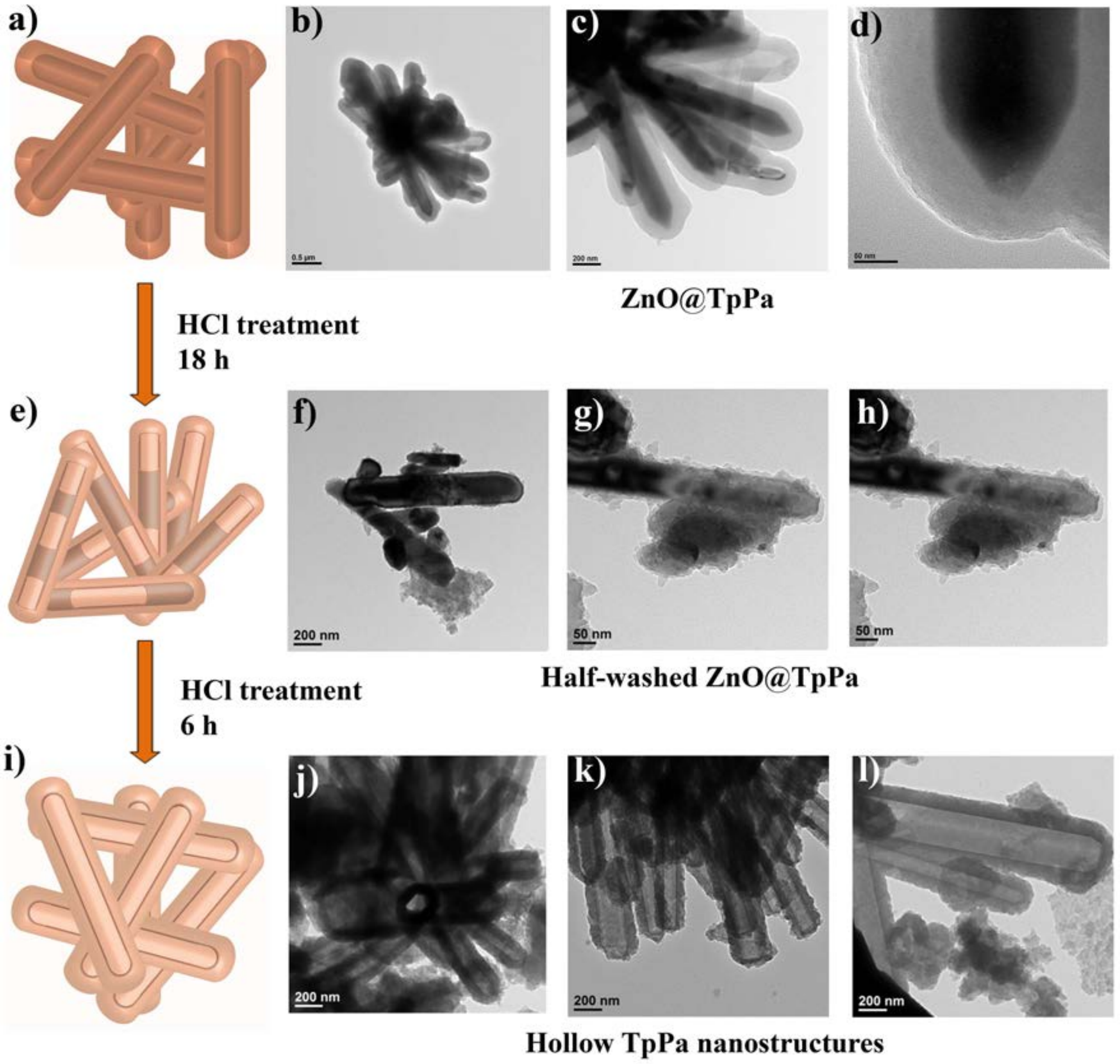
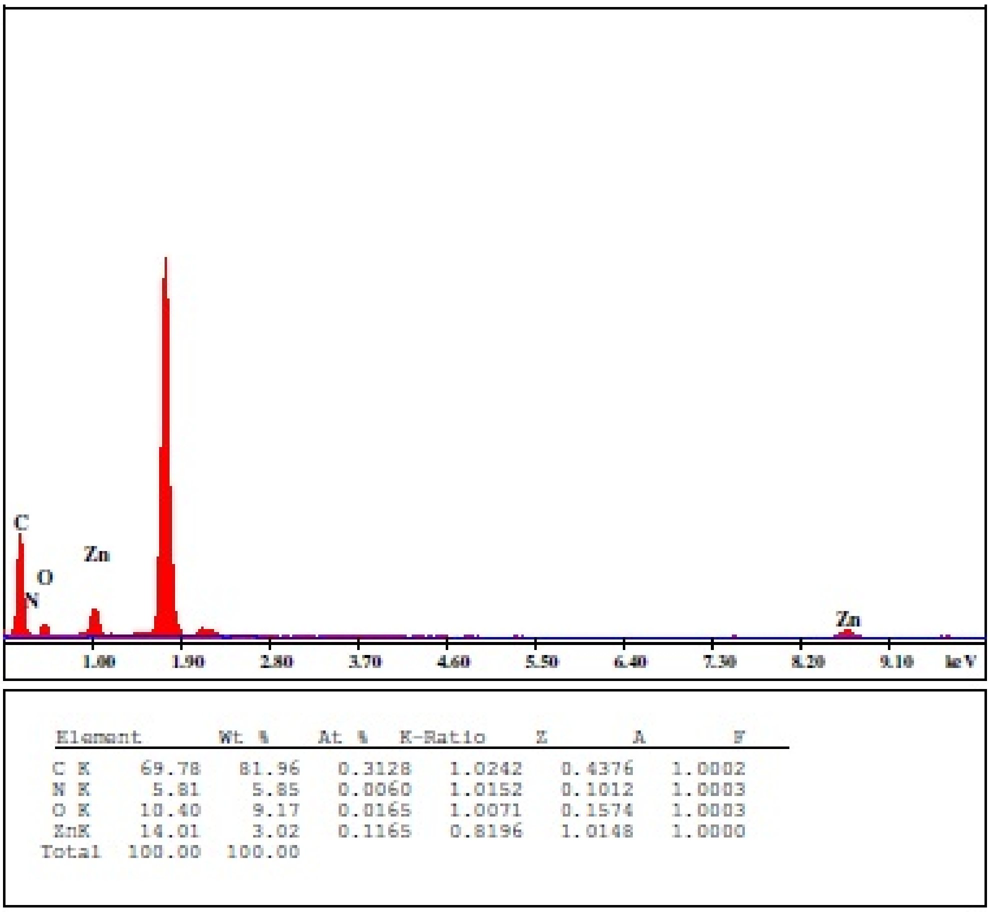


Figure S12. *The process of synthesis of hollow* ***TpPa*** *nanostructures from ZnO-nanorods and* ***TpPa****-COF followed by TEM analyses. a) Morphological model of* ***ZnO@TpPa****. b), c) and d) TEM images of* ***ZnO@TpPa*** *before HCl treatment. e) Morphological model of half washed* ***ZnO@TpPa*** *after washing for 18 h with 1N HCl. f), g) and h) TEM images of half washed* ***ZnO@TpPa****. i) Morphological model of hollow* ***TpPa*** *nanostructures. j), k) and l) TEM images of hollow* ***TpPa*** *nanostructures after HCl treatment for 24 h.*



Element	Wt %	At %	K-Ratio	Z	A	F
C K	69.78	81.96	0.3128	1.0242	0.4376	1.0002
N K	5.81	5.85	0.0060	1.0152	0.1012	1.0003
O K	10.40	9.17	0.0165	1.0071	0.1574	1.0003
ZnK	14.01	3.02	0.1165	0.8196	1.0148	1.0000
Total	100.00	100.00				

Figure S13. *EDAX analyses of* ***ZnO@TpPa*** *after washing with 1N HCl for 18 h showing the presence of 14% Zn confirming the incomplete removal of ZnO.*

Section S7. Pawley refinement results for XRD analyses of hollow TpPa nanostructures:

The Pawley refinements were performed in order to compare and validate the experimental XRD data of hollow **TpPa** nanostructures with simulated XRD data of **TpPa** COF in eclipsed as well as staggered conformation. We have modelled the eclipsed structure of **TpPa** COF in $P6/m$ space group with the unit cell parameter a = b = 22.5 Å, c = 3.40 Å and $\alpha = \beta = 90°$, $\gamma = 120°$. The Pawley refinement performed using the Materials Studio showcases good agreement between simulated and experimental PXRD patterns considering the eclipsed stacking (R-pattern factor (Rp) = 6.25%, R-weighted-profile factor (Rwp) = 4.16%).

We have further modelled the staggered structure of **TpPa** COF in $P6_3/m$ space group with the unit cell parameter a = b = 22.5 Å, c = 6.80 Å and $\alpha = \beta = 90°$, $\gamma = 120°$ (ESI, Fig. S13c). However, the simulated PXRD pattern for the staggered conformation has poor matching (Rp = 17.56%, Rwp = 16.07%) with the experimental PXRD pattern of hollow **TpPa** nanostructures (ESI, Fig. S13c). From these Pawley refinements between experimental and simulated XRD data of hollow **TpPa** nanostructures and **TpPa** COF, we have verified the crystallization of hollow **TpPa** nanostructures in eclipsed pattern.

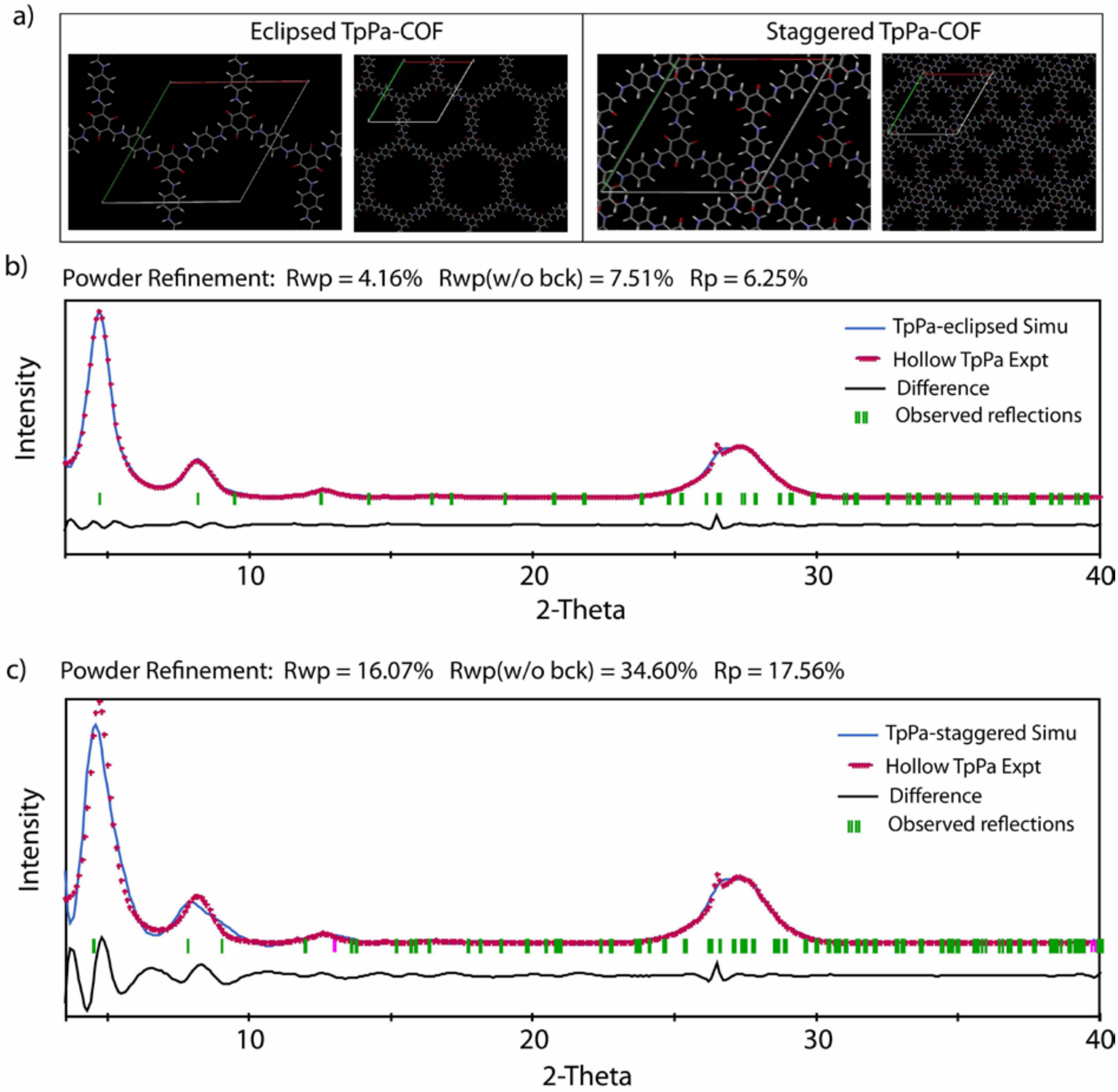


Figure S14. *The unit cell structure, crystal lattice packing arrangements and Pawley refinement results. a) Unit cell and crystal lattice packing structures for* ***TpPa*** *COF in eclipsed and staggered models. b) Experimental (blue) compared with refined (red) PXRD profiles of* ***TpPa*** *COF with an eclipsed arrangement; difference plot is given in (black). c) Experimental (blue) compared with refined (red) PXRD profiles of* ***TpPa*** *COF with a staggered arrangement; difference plot is given in (black).*

Section S8. References

1. S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524.

2. B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2003, **125**, 4430.

3. P. Pachfule, S. Kandambeth, D. D. Díaz and R. Banerjee, *Chem. Commun.*, 2014, **50**, 3169.