Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Spray Drying for Making Covalent Chemistry II: Synthesis of Covalent−Organic Framework Superstructures and related Composites

Luis Garzón-Tovar,[a] Ceren Avci-Camur,[a] David Rodríguez-San-Miguel,[b] Inhar Imaz,[a] Félix Zamora*[b,c] and Daniel Maspoch*[a,d]

[a]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[b]Departamento de Química Inorgánica and Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Madrid, 28049, Spain

[c]Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanociencia), Cantoblanco, 28049, Madrid, Spain

[d]ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

Section S1: Materials, methods and synthetic procedures

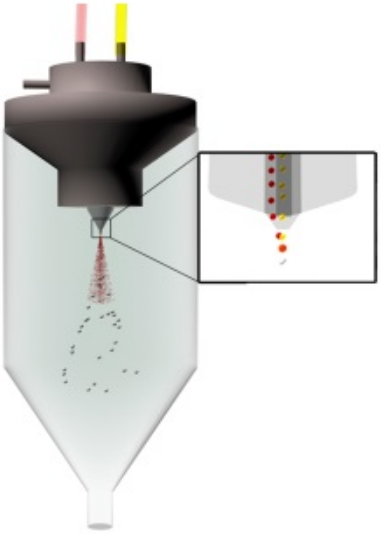
1. Materials and methods

1,3,5-benzenetricalbaldehyde, *p*-phenylenediamine, terephthalaldehyde, 1,4-dioxane, acetic acid and mesitylene were purchased from Sigma Aldrich. 1,3,5-tris-(4-aminophenyl)benzene was obtained from TCI. THF, DMSO, acetone and toluene were obtained from Fisher Chemical. All the reagents were used without further purification. Deionised water was obtained with a Milli-Q® system (18.2 MΩ·cm).

X-ray powder diffraction (XRPD) patterns were collected on an X'Pert PRO MPDP analytical diffractometer (Panalytical) at 45 kV, 40 mA using CuKα radiation (λ = 1.5419 Å). Nitrogen adsorption and desorption measurements were done at 77 K using an Autosorb-IQ-AG analyser (Quantachrome Instruments). Field-Emission Scanning Electron Microscopy (FESEM) images were collected on a FEI Magellan 400L scanning electron microscope at an acceleration voltage of 2.0 KV, using aluminium as support. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) and HR-TEM images were collected on a Transmission Electron Microscope (TEM; FEI Tecnai G2 F20) at 200 KV. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27FTIR spectrometer equipped with a Golden Gate diamond attenuated total reflection (ATR) cell, in transmittance mode at room temperature. Fluorescence emission spectra were recorded on a Carey Eclipse Fluorescence Spectrophotometer at an excitation wavelength of 525 nm. ICP-MS measurements were performed using an Agilent 7500 after aqua regia digestion. ^{13}C {^{1}H} cross-polarization (CP-MAS) experiments were performed at room temperature on a Bruker Avance III 9.4T spectrometer equipped with a double channel 4.0 mm MAS probe. Sample spinning was set to 12 kHz in all experiments. Thermogravimetric analysis (TGA) was performed on a Pyris 8000 Thermo Gravimetric Analyzer at a heating rate of 10 ^{o}C·min^{-1} from 30 ^{o}C to 700 ^{o}C under nitrogen. Magnetic hysteresis loop at 10 K was measured with a Quantum Design MPMS XL SQUID Magnetometer.

2. General description of the multi-fluid nozzle used in the spray-drying process

Three fluid nozzle

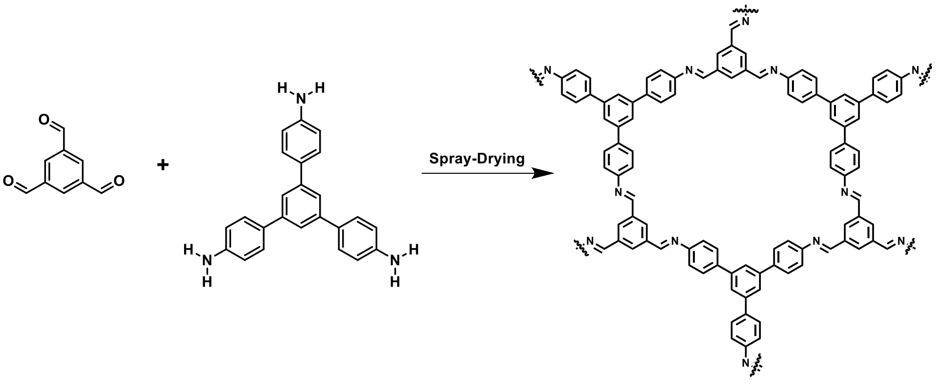


Scheme S1. Schematic representation of the three fluid-nozzle.

In the 3-fluid mode, the solutions that contain the COF precursors are pumped individually through the two separate inner channels of the nozzle while the drying gas flows through the third channel. Thus, the two solutions only come in contact at the nozzle tip, where the three channels meet. This three-fluid mode allows spraying incompatible or reactive precursors avoiding the fast precipitation before the process.

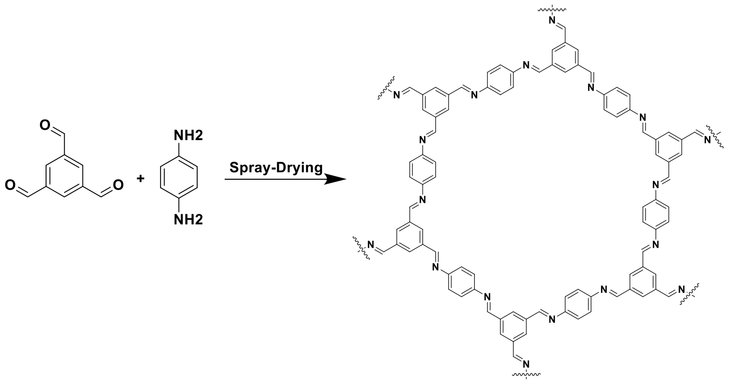
3. Synthetic procedures

Spray-drying synthesis of COF-TAPB-BTCA



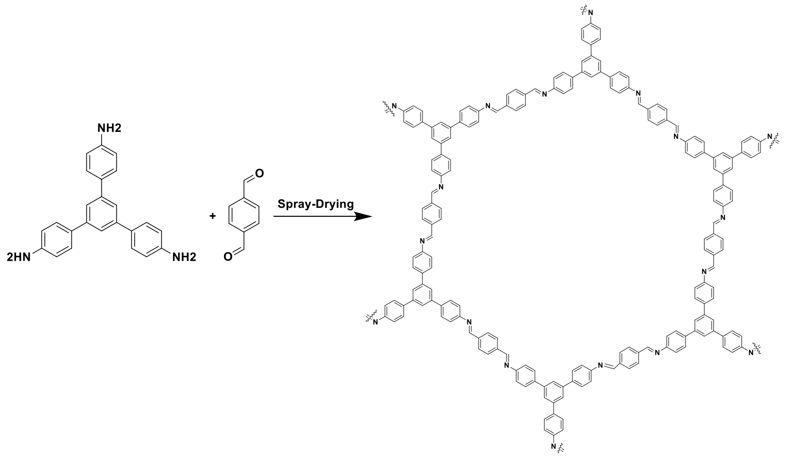
A solution of 136.5 mg of 1,3,5-benzenetricalbaldehyde (BTCA) in 30 mL of a mixture of DMSO and acetic acid (9:1 v/v) and a solution of 281.2 mg of 1,3,5-tris-(4-aminophenyl)benzene (TAPB) in 30 mL of DMSO were independently atomized using a three-fluid nozzle at a feed rate of 3.0 mL·min^{-1}, a flow rate of 336 mL·min^{-1} and an inlet temperature of 200 °C, using a B-290 Mini Spray Dryer (BÜCHI Labortechnique). A yellow powder was collected after 10 min. The resulting solid was then dispersed in 20 mL of THF and precipitated by centrifugation at 9000 rpm for 4 min. This process was repeated three times. The final product was washed three times with acetone and centrifuged again at 9000 rpm and dried for 48 h at room temperature.

Spray-drying synthesis of COF-LZU1



A solution of 165 mg of BTCA in 6 mL of a mixture of 1,4-dioxane and acetic acid (2:1 v/v) and a solution of 162 mg of *p*-phenylenediamine in 6 mL of 1,4-dioxane were independently atomized using a two fluid nozzle in T-mode at a feed rate of 3.0 mL·min^{-1}, a flow rate of 336 mL·min^{-1} and an inlet temperature of 150 °C, using a B-290 Mini Spray Dryer (BÜCHI Labortechnique). A yellow powder was collected after 2 min. The resulting solid was then dispersed in 20 mL of THF and precipitated by centrifugation at 9000 rpm for 4 min. This process was repeated three times. The final product was washed three times with acetone and centrifuged again at 9000 rpm and dried for 48 h at room temperature.

Spray-drying synthesis of COF-PDA-TAPB



A solution of 92.3 mg of terephthalaldehyde in 21.5 mL of a mixture of 1,4-dioxane, mesitylene water and acetic acid (1.9:0.37:0.66:1 v/v) and a solution of 162.1 mg of 1,3,5-tris-(4-aminophenyl)benzene in 21.5 mL of a mixture of 1,4-dioxane and mesitylene (9.8:1 v/v) were independently atomized using a three-fluid nozzle at a feed rate of 3.0 mL·min^{-1}, a flow rate of 336 mL·min^{-1} and an inlet temperature of 150 °C, using a B-290 Mini Spray Dryer (BÜCHI Labortechnique). A yellow powder was collected after 7 min. The resulting solid was then dispersed in 20 mL of toluene and precipitated by centrifugation at 9000 rpm for 4 min. This process was repeated three times. The final product was washed three times with acetone and centrifuged again at 9000 rpm and dried for 48 h at room temperature.

Spray-drying synthesis of Dye@COF-TAPB-BTCA

A solution of 67.3 mg of BTCA in 15 mL of a mixture of DMSO and acetic acid (9:1 v/v) and a solution of 143.4 mg of TAPB and 20 mg of rose bengal in 15 mL of DMSO were independently atomized using a three-fluid nozzle at a feed rate of 3.0 mL·min^{-1}, a flow rate of 336 mL·min^{-1} and an inlet temperature of 200 °C, using a B-290 Mini Spray Dryer (BÜCHI Labortechnique). A pink powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of THF and precipitated by centrifugation at 9000 rpm for 4 min. This process was repeated six times. The final product was washed three times with acetone and centrifuged again at 9000 rpm and dried for 48 h at room temperature.

Spray-drying synthesis of F_3O_4@COF-TAPB-BTCA

0.6 mL of Fe_3O_4 6.3 mmol·L^{-1} in DMF was added to a solution of 286.3 mg of TAPB in 30 mL of DMSO. The resulting mixture and a solution of 136.9 mg of BTCA in 30 mL of a mixture of DMSO and acetic acid (9:1 v/v) were independently atomized using a three-fluid nozzle at a feed rate of 3.0 mL·min^{-1}, a flow rate of 336 mL·min^{-1} and an inlet temperature of 200 °C, using a B-290 Mini Spray Dryer (BÜCHI Labortechnique). A brown powder was collected after 10 min. The resulting solid was then dispersed in 20 mL of THF and precipitated by centrifugation at 9000 rpm for 4 min. This process was repeated three times. The final product was washed three times with acetone and centrifuged again at 9000 rpm and dried for 48 h at room temperature.

Amorphous to crystalline transformation process

The amorphous to crystalline transformation was performed following a previously reported method.[1] 80 mg of COF was dispersed in a mixture of 1,4-dioxane and mesitylene (9:1 v/v). Then, 1.75 mL of water and 2.6 mL of acetic acid were to the dispersion at room temperature and stirring for 5 min. The resulting mixture was heated at 80 °C under stirring for 8 days. The obtained solid was collected by centrifugation at 9000 rpm for 4 min, washed three times with 10 mL of toluene and dried at 60 °C overnight. All washed samples were degassed at 150 °C for 12 h under vacuum prior to the N_2 sorption measurement at 77 K.

References

1. B. J. Smith, A. C. Overholts, N. Hwang and W. R. Dichtel, *Chem. Commun.*, 2016, **52**, 3690-3693.

SECTION II: Supplementary Figures

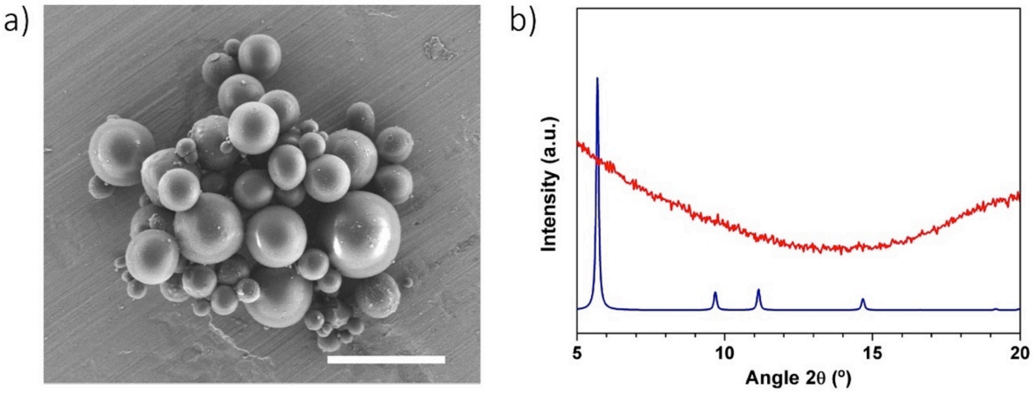


Figure S1. a) FESEM image of the amorphous **COF-TAPB-BTCA**. b) XRPD patterns of the amorphous COF-TAPB-BTCA (red) compared to the simulated powder pattern for **COF-TAPB-BTCA** (blue). Scale bar: 5 µm.

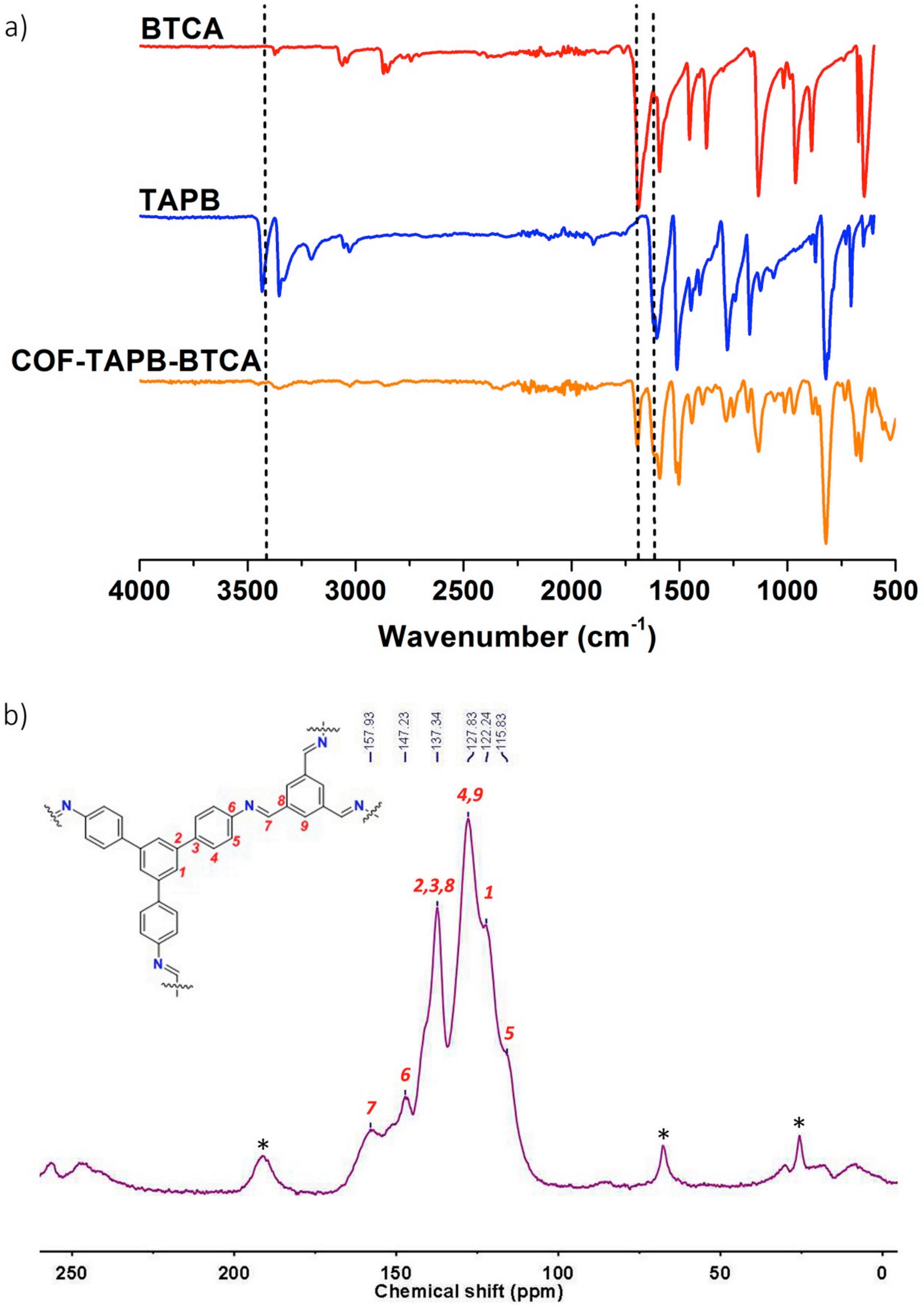


Figure S2. a) FT-IR spectra of BTCA (red) and TAPB (blue) and amorphous **COF-TAPB-BTCA** (orange), highlighting the imine C=N vibrational bands and the disappearance of the N-H stretching bands. b) ^{13}C MAS-NMR spectrum of amorphous **COF-TAPB-BTCA**. The peaks corresponding to the CH_2 groups of the residual THF and terminal aldehyde groups in the amorphous **COF-TAPB-BTCA** are highlighted with asterisks.

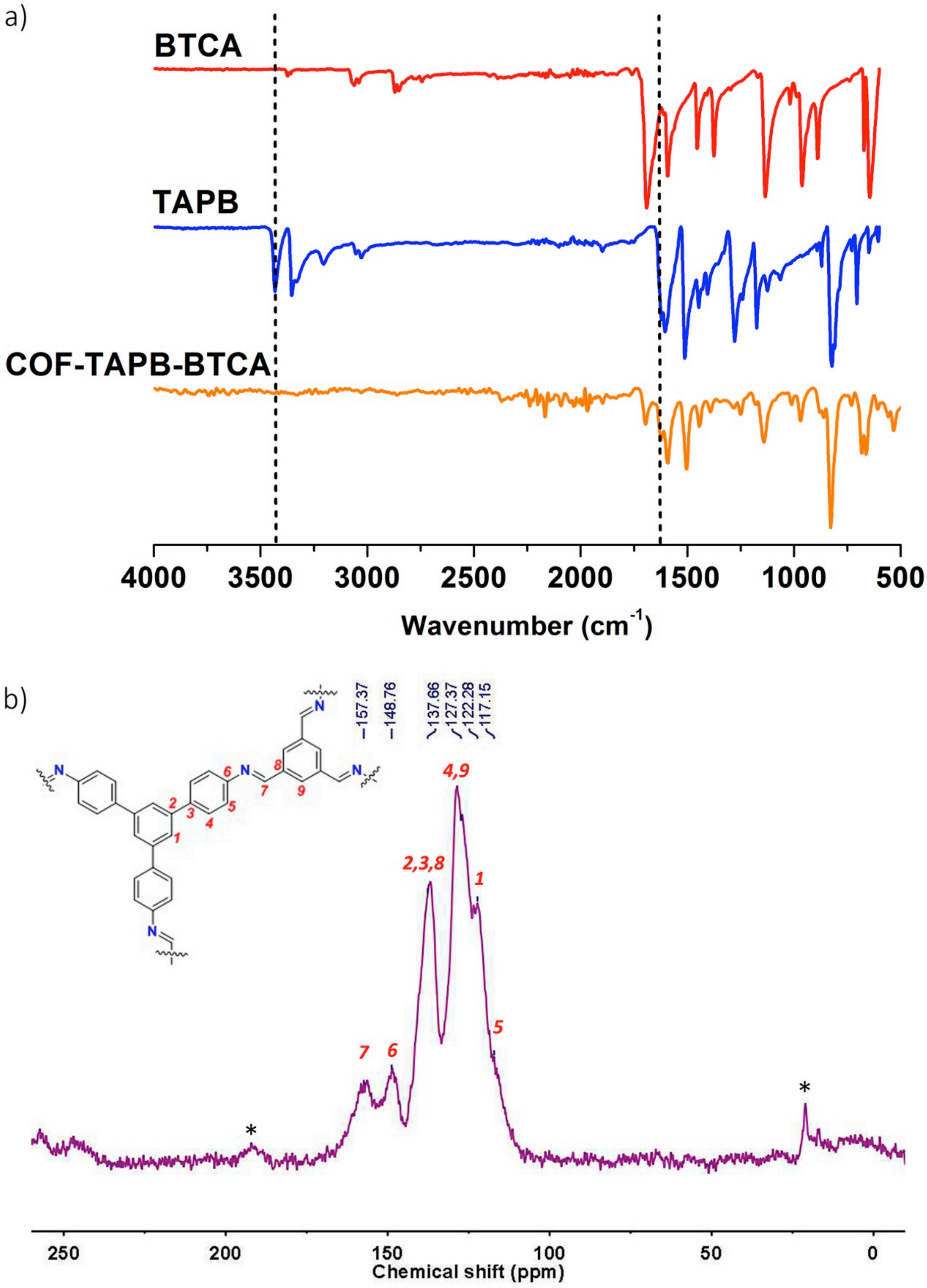


Figure S3. a) FT-IR spectra of BTCA (red) and TAPB (blue) and crystalline **COF-TAPB-BTCA** (orange), highlighting the imine C=N vibrational bands and the disappearance of N-H stretching bands. b) ^{13}C MAS-NMR spectrum of crystalline **COF-TAPB-BTCA**. The peaks corresponding to the CH_3 groups of the residual toluene and terminal aldehyde groups in the crystalline **COF-TAPB-BTCA** are highlighted with asterisks.

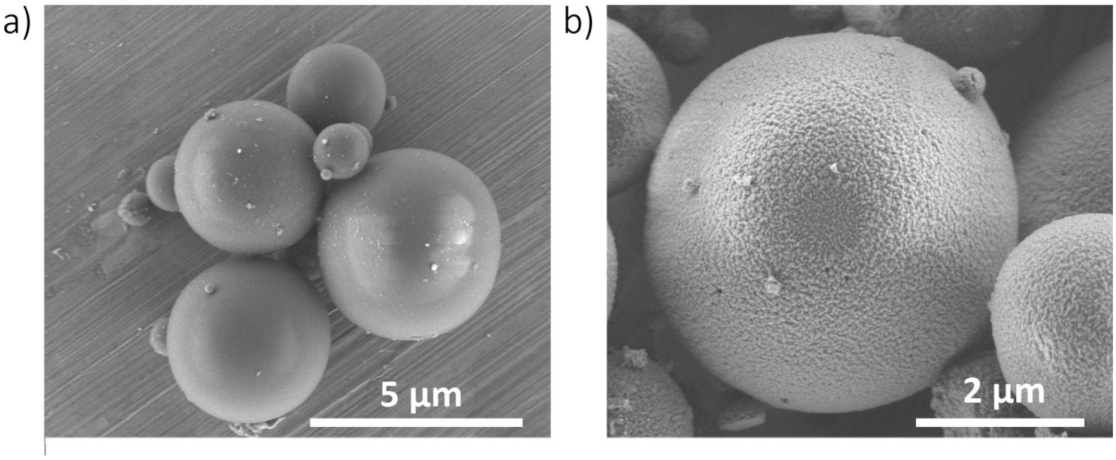


Figure S4. FESEM images of a) the smooth amorphous **COF-TAPB-BTCA** superstructures compared with the b) rough crystalline **COF-TAPB-BTCA** superstructures.

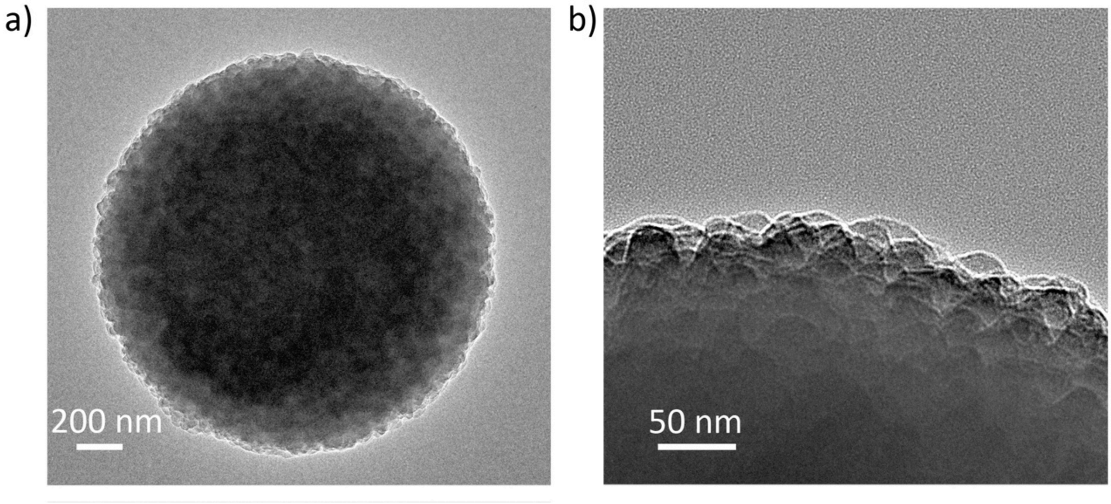


Figure S5.HRTEM images of a) crystalline **COF-TAPB-BTCA** superstructure, and b) a zoom image of its surface revealing the presence of COF nanocrystals.

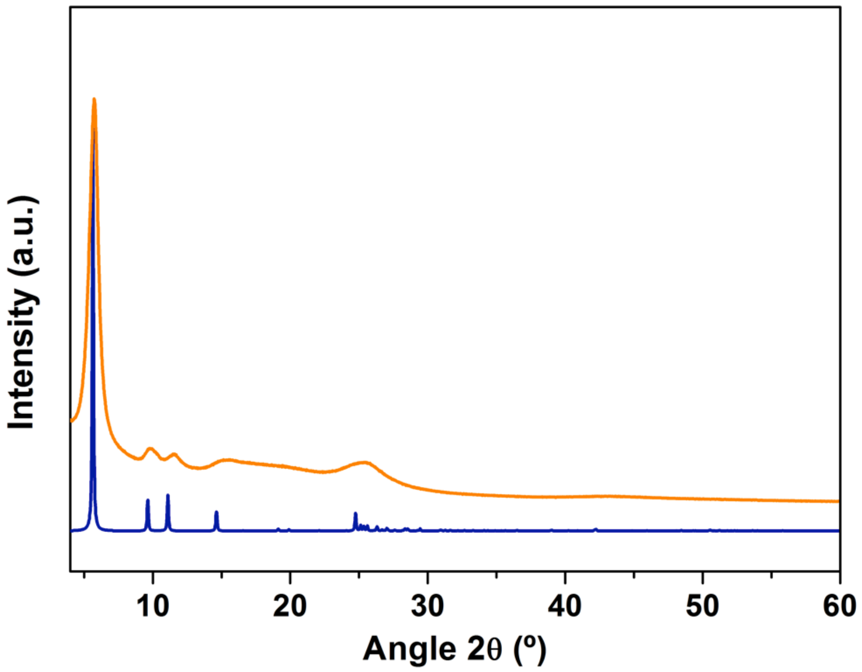


Figure S6. XRPD diffractogram of **COF-TAPB-BTCA** (orange), compared with the simulated powder pattern (blue).

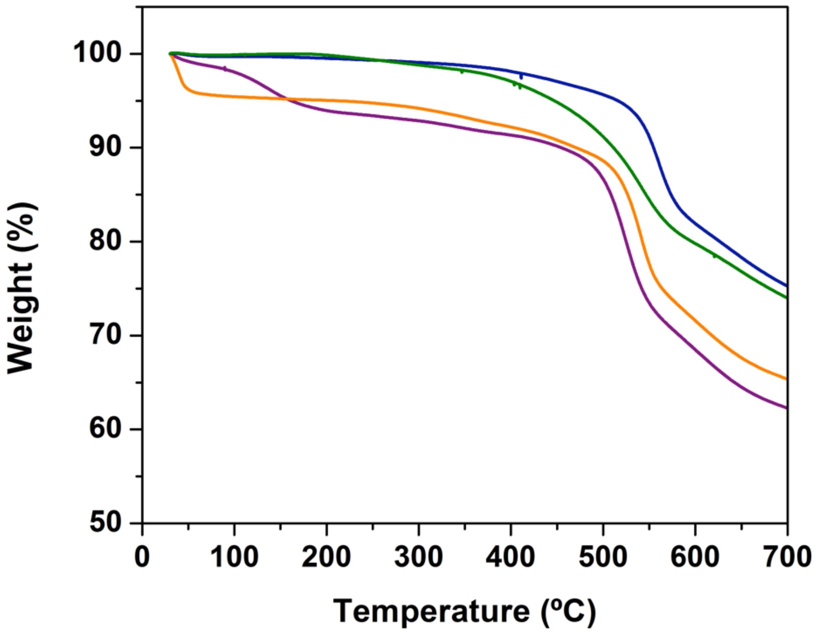


Figure S7. TGA of the as-synthesized amorphous (purple) and crystalline (orange) COF-TAPB-BTCA compared with the amorphous (green) and crystalline (blue) samples after they have been degassed at 150 °C for 12 h under vacuum

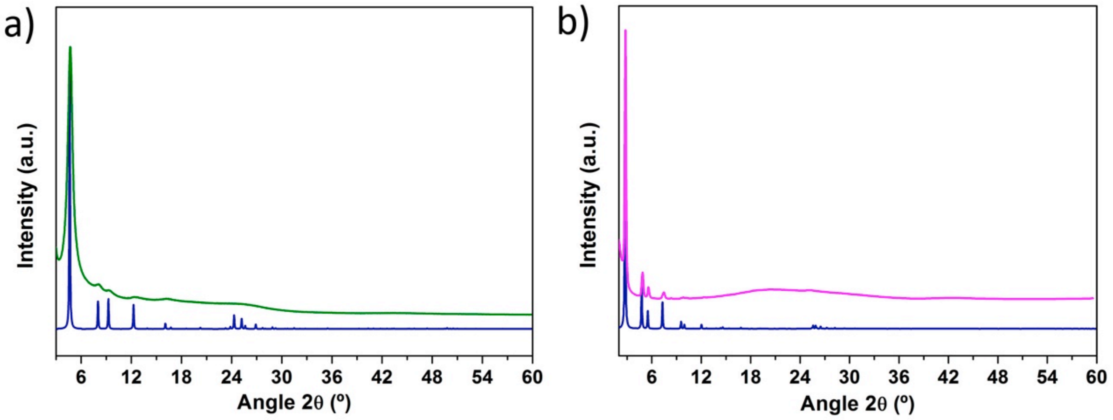


Figure S8. a) XRPD diffractogram of the obtained **COF-LZU1** (green) compared with simulated powder pattern (blue). b) XRPD diffractogram of the obtained **COF-TAPB-PDA** (pink) compared with simulated powder pattern (blue)

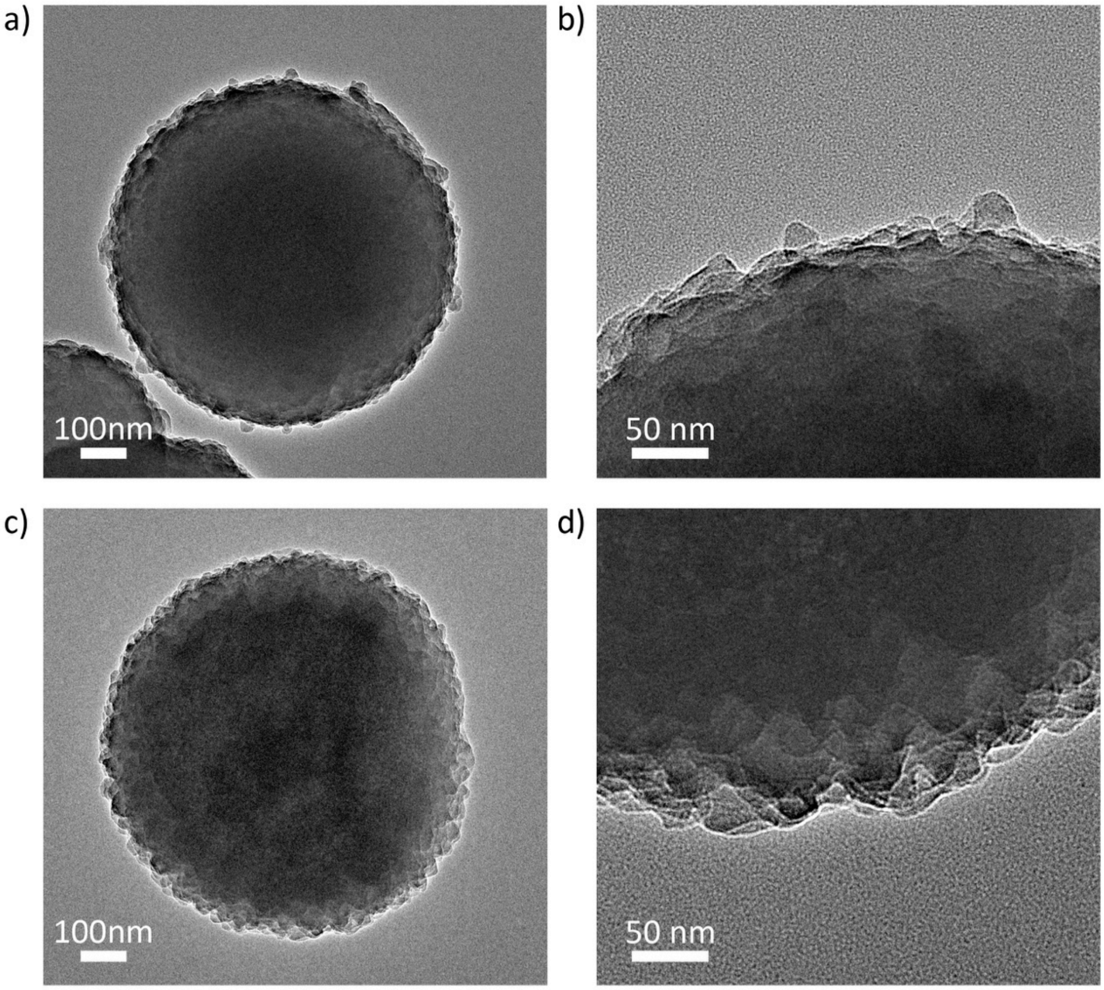


Figure S9. HRTEM images of a-b) crystalline **COF-LZU1** superstructure and c-d) crystalline **COF-TAPB-PDA** superstructure.

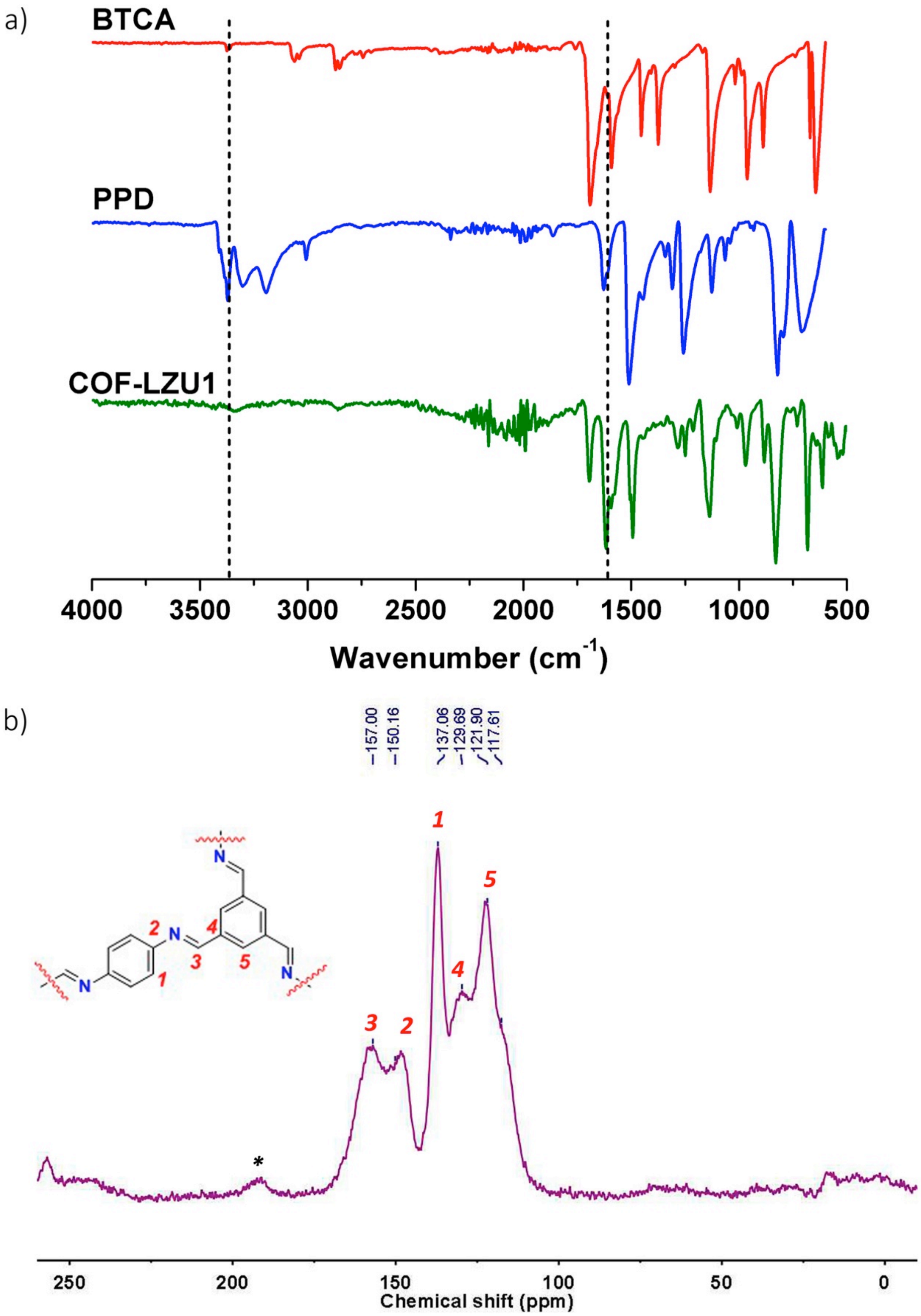


Figure S10. a) FT-IR spectra of BTCA (red) and PDA (blue) and crystalline **COF-LZU1** (green), highlighting the imine C=N vibrational bands and the disappearance of the N-H stretching bands. b) ^{13}C MAS-NMR spectrum of crystalline **COF-LZU1**. The peak corresponding to the terminal aldehyde groups in the crystalline **COF-LZU1** are highlighted with asterisk.

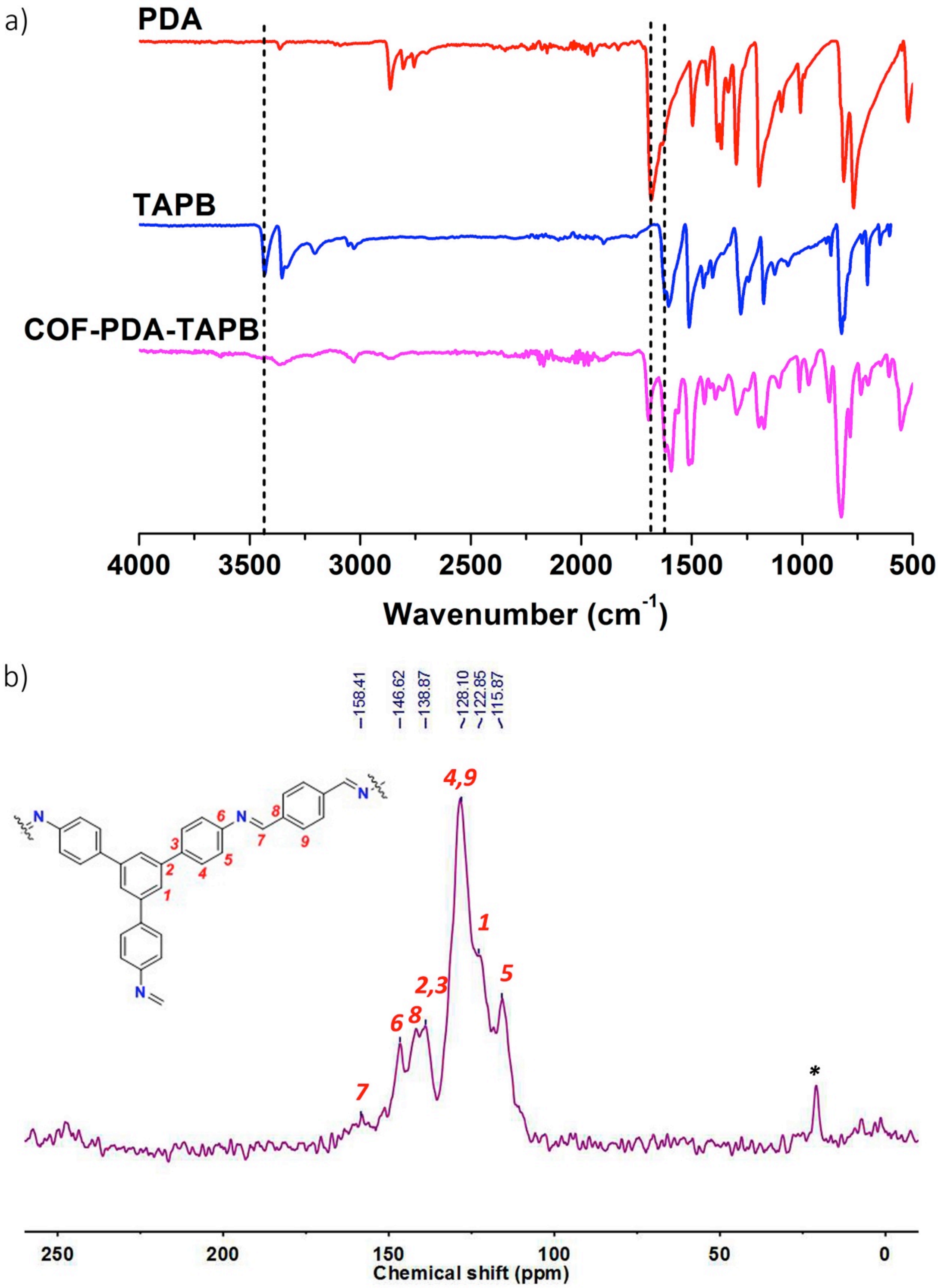


Figure S11. a) FT-IR spectra of BTCA (red) and PDA (blue) and crystalline **COF-PDA-TAPB** (green), highlighting the imine C=N vibrational bands and the disappearance of the N-H stretching bands. b) ^{13}C MAS-NMR spectrum of crystalline **COF-PDA-TAPB**. The peak corresponding to the CH_3 groups of the residual toluene is highlighted with asterisk.

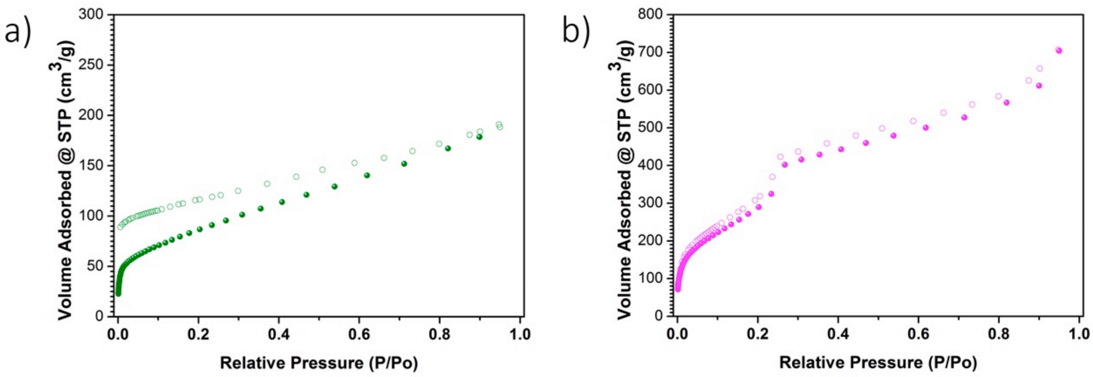


Figure S12. N_2 adsorption isotherms of a) **COF-LZU1** and b) **COF-TAPB-PDA**.

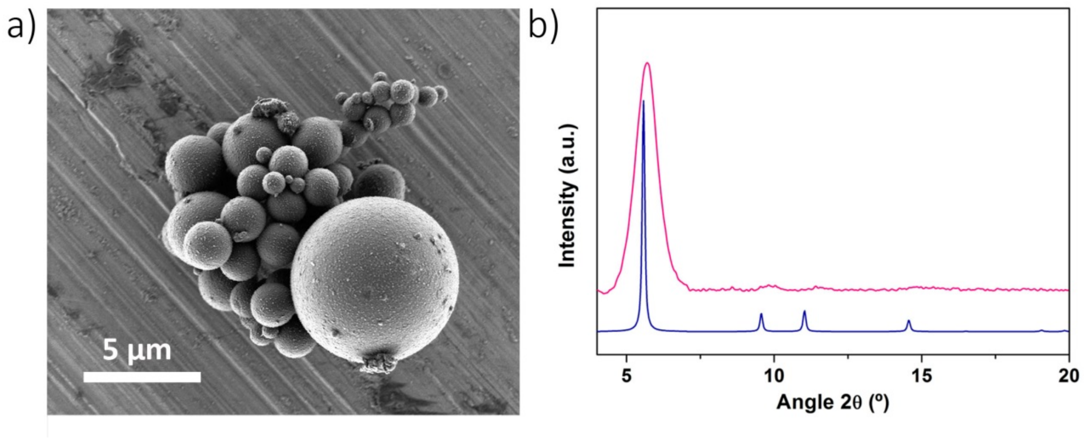


Figure S13. a) FESEM image showing the microspherical **Dye@COF-TAPB-BTCA** superstructures. b) XRPD diffractogram of the obtained composite (pink) compared with the simulated powder pattern of **COF-TAPB-BTCA** (blue).

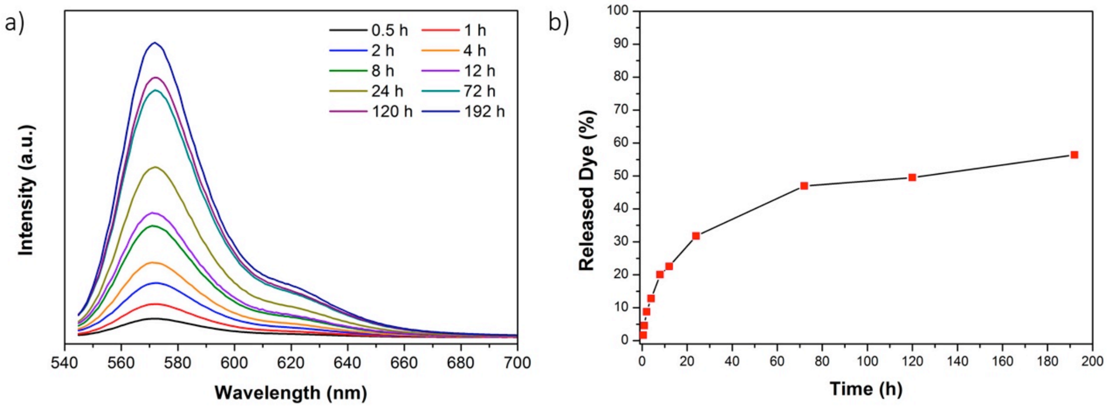


Figure S14. a) Fluorescence emission spectra of **Dye@COF-TAPB-BTCA** (collected at λ_{exc} = 525 nm) at different periods of incubation. b) Rose Bengal release from the **Dye@COF-TAPB-BTCA** composite.

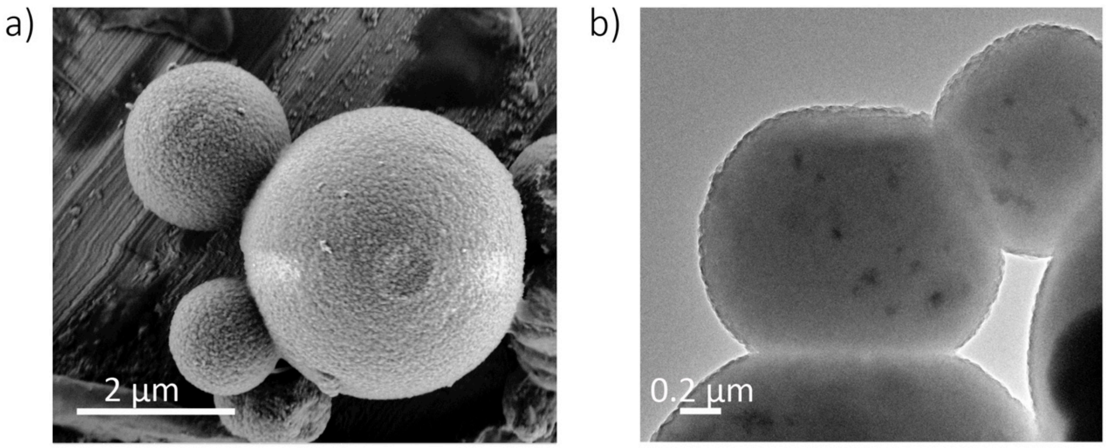


Figure S15. a) FESEM and b) HRTEM images showing the microspherical **Fe_3O_4@COF-TAPB-BTCA** composite.

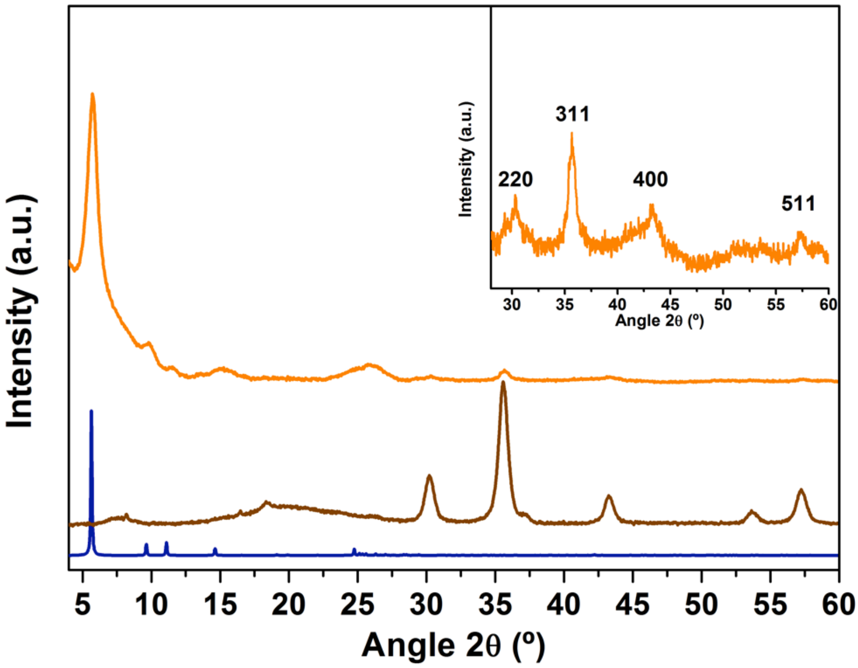


Figure S16. XRPD diffractogram of **Fe_3O_4@COF-TAPB-BTCA** (orange) compared with the experimental powder pattern of Fe_3O_4 nanoparticles (brown) and the simulated XRPD diffractogram of **COF-TAPB-BTCA** (blue). The inset shows the XRPD pattern of the composite in the range of 2θ from 25º to 60º, highlighting the peaks of the cubic structure of the Fe_3O_4 NPs (JCPDS Card No. 19-629).

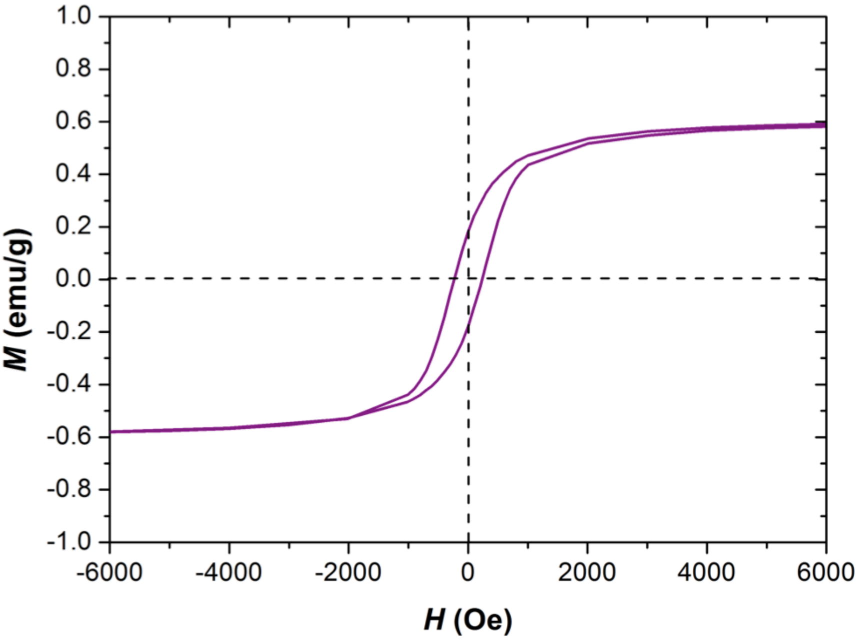


Figure S17. Magnetic hysteresis loop of **Fe_3O_4@COF-TAPB-BTCA** measured at 10 K (M_{sat} = 0.6 emu·g^{-1}).