

Supporting Information

Carbon dot based superhydrophobic modification of covalent organic framework for oil-in-water emulsion separation

Experimental section

Materials

Citric acid diammonium salt and 1,2-Dibromoethane were purchased from Sigma-Aldrich. Phenol, hexamethylenetetramine, trifluoroacetic acid (TFA), 4-aminobenzonitrile, and triflic acid were procured from Spectrochem chemicals. 2-hydroxybenzene-1,3,5-tricarbaldehyde (TFP) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline (TAPT)) were synthesized using the previously reported procedure by Zhao¹ and Bhaumik² group respectively. All the other solvents/reagents and buffers were obtained from Sisco Research Laboratories. Chemicals are used as received.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded using a PerkinElmer Spectrum 400 FTIR spectrophotometer. The experiment was performed in both KBr and ATR modes.

Solid and liquid state nuclear magnetic resonance (NMR) spectroscopy

Solid state NMR spectra were recorded on JEOL 500 MHz NMR spectrometer. Solution phase NMR were recorded on Bruker 400 MHz NMR spectrometer. Carbon and proton chemical shifts are expressed in ppm (δ scale). The ¹H and ¹³C NMR of the TFP and TAPT were recorded in DMSO-d₆ solvent. The proton NMR of separated water from the oil/water emulsion was recorded in D₂O.

Scanning electron microscopy (SEM)

SEM images were obtained using a Carl Zeiss ultra plus Field Emission Scanning Electron Microscope (FE-SEM). Prior to analysis, the samples were sputter-coated with gold. 15 kV voltage was applied while performing elemental analyses using an EDX detector.

Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM, Model: JEM-F200). TEM analysis was done after the drop-casting of a diluted sample on a carbon-coated copper TEM grid.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed by using a SDT Q600 (TA Instruments) analyzer in the temperature range of 30–700 °C, under a nitrogen atmosphere and at a heating rate of 10°C/min.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns were recorded on Empyrean Malvern PANalytical diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 2°/min.

Nitrogen adsorption-desorption isotherm measurements

Surface area of the samples were measured using Quantochrome Autosorb instrument (Quantachrome, USA) with extra-high purity gases (99.999%). Prior to surface area analysis, the samples were activated by heating them at 120 °C for 12h. The resulting samples were subjected to gas adsorption measurements (P/P_0 range from 0 to 1 atm) at 77 K. The Brunauer-Emmett-Teller (BET) model was utilized to calculate the specific surface areas. The pore size distributions were derived from the sorption curves by using the non-local density functional theory.

UV-visible absorption spectra

UV-visible absorption spectra of as-obtained materials were measured on a Shimadzu UV-2550 UV-vis spectrometer. The samples were scanned in the entire UV-Vis range.

Steady-state fluorescence spectra

Steady-state fluorescence spectra were done on a Fluoromax-400 spectrofluorometer (Horiba, Japan), by dissolving the CD in ethyl acetate solvent.

Zeta potential

The Zeta potential of the samples was analyzed by Anton Paar (Litesizer 500) instrument, by dispersing the sample in ethanol.

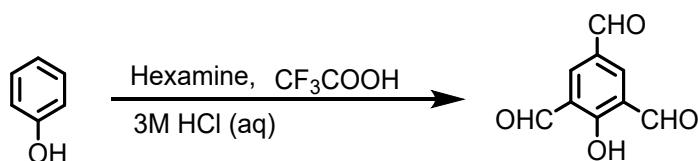
Water contact angle measurements

The water contact angle measurements were carried out in CA Goniometer Ramé-Hart instrument, Model 250 and the contact angle were measured using DROP image Advance CA, and ImageJ software.

Preparation of Carbon Dot

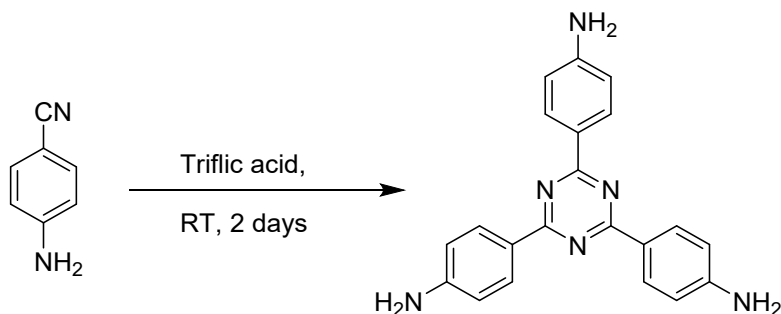
CD was synthesized by using Citric acid diammonium salt and 1,2-Dibromoethane by hydrothermal method, briefly 100 mg of citric acid and 1ml of 1,2-Dibromoethane (98%) were mixed in 4ml water. The reaction mixture was stirred then transferred to a Teflon-lined autoclave (25ml), and heated at 200 °C for 5 h. The autoclave was allowed to cool to room temperature and the black immiscible solid was collected and diluted to 10 ml with ethyl acetate and centrifuged for 10 min, at 10,000 rpm to settle down the large particle and collect the supernatant. Then the resultant solution was filtered through a 0.2 μm syringe filter to remove large aggregates. The sample was then purified through solvent extraction using two immiscible solvents, water and ethyl acetate to eliminate the hydrophilic particles present in hydrophobic CD.

Synthesis of 2-hydroxybenzene-1,3,5-tricarbaldehyde (TFP) ¹



A mixture of phenol (1 g, 10.6 mmol) and hexamethylenetetramine (3.23 g, 23.04 mmol) were dissolved in 15 mL trifluoroacetic acid (TFA) under an argon atmosphere. The reaction mixture was refluxed at 130 °C for 16 h, and then heated to 150 °C for additional 3h. Subsequently, the reaction mixture was cooled to 100 °C and treated with 20 ml, 3M HCl. After the addition of HCl, we observed the formation of a yellow precipitate within 5 minutes. Reaction was heated for additional 30 min at 100 °C. The crude products thus obtained were filtered and washed with ethanol until the filtrate was clear. The desired product was obtained as a powder after drying in oven at 60 °C for several hours. The ¹H and ¹³C NMR of the TFP are shown Fig. S8 and S9 respectively. The ¹H and ¹³C NMR of the TFP are shown Fig. S8 and Fig. S9 respectively. ¹H NMR (DMSO-d₆, 400 MHz): δ 10.32 (s, 2H), 10.01 (s, 2H) and 8.53 (s, 2H). ¹³C NMR (DMSO-d₆ 100 MHz) δ 191.71, 190.84, 166.00, 137.35, 128.28, 124.16; FT-IR (ATR): carbonyl bands = 1686 and 1665 cm⁻¹.; aldehydic -CH_{stretching} = 2884 cm⁻¹. ; colour - yellow; yield - 55%.

Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline (TAPT) ²



A 50 mL round bottom flask was placed on an ice bath in which 4-aminobenzonitrile (2 gm) was placed. 2 mL of triflic acid was added to the flask drop-wise and the solution obtained was stirred for 48h at room temperature. The reaction mixture was poured into 200 mL of ice cold water and neutralized with 2 (M) NaOH solution. With the gradual addition of NaOH solution, a clear deep yellow colour appeared. After neutralization, a deep yellow precipitate was formed. The precipitate was collected by filtration, washed with a copious amount water and dried in vacuum to obtain the desired pure compound. The ¹H and ¹³C NMR of the TAPT are shown Fig. S10 and Fig. S11 respectively. ¹H NMR (DMSO-d₆, 400 MHz): δ 8.35 to 8.37 (d J = 8 Hz, 6H), 6.69 to 6.71 (d J = 8 Hz, 6H), 5.92 (6H). ¹³C NMR (DMSO-d₆, 100 MHz) δ 170.04, 153.45, 130.61, 123.39, 113.57).; FT-IR (ATR): triazine ring= 1503 cm⁻¹ and 1360 cm⁻¹, N-H_{stretching}=3456 cm⁻¹, 3327 cm⁻¹ and 3206 cm⁻¹. colour– orange; yield - 49%.

Synthesis of COF1.^{3,4} In a typical synthetic procedure two C₃-symmetry based monomers 2-hydroxy-1,3,5-benzenetricarbaldehyde (TFP) and 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline (TAPT) were chosen to condense solvothermally, where a pyrex tube was charged with TFP (0.1 mmol) and TAPT (0.1mmol). Then mesitylene (2.5 ml) and dioxane (2.5 ml) along with 6M 0.5 mL acetic acid were added to the mixture. After that, the tube was sonicated for 15 minutes and flash-frozen in liquid N₂ and degassed by three consecutive freeze-pump-thaw cycles. Prior to keeping in 120 °C oven it was flame sealed under vacuum. After 72 h the sealed tube was taken out to obtain deep red-colour material. Finally, it was collected and washed with copious amount of different organic solvents and dried at 120 °C for 6 hours and used for analyses. Colour-dark red brown, yield- 86%.; Solid state ¹³C CP-MAS NMR (500 MHz) δ 116-140 (aromatic carbons),

151 and 169 (sp² carbon and triazine ring carbons), 156 (imine carbon).; FT-IR (ATR):1623 cm⁻¹ (C=N, imine stretching). 1482 cm⁻¹ (C=C, stretching). 1323 cm⁻¹ (C-N, stretching).

Preparation of CD@COF1 composite

An appropriate weight ratio of COF1 to CDs (w/w% - 4, 8, 12, 16, 20wt % CD, with respect to COF1) was mixed with ethyl acetate. The suspension was ultrasonicated for 30min and vacuum dry at 60 °C until all the solvent was evaporated. The 16 wt% CD@COF1 composite was used for various characterizations.

Measurement of hydrophobicity – Hydrophobicity of the CD, COF1 and CD@COF1 were primarily tested by placing the water droplet on their surface and taking the digital images. Pristine COF1 absorb the water droplet due to its hydrophilic nature whereas pristine CD and CD@COF1 showed significant hydrophobicity as observed from the digital images. Further, the water contact angle measurements were carried out on the CD, COF1 and CD@COF1 surface by using CA Goniometer (Ramé-Hart instrument, Model 250). The superhydrophobicity of CD@COF1 was also studied with real samples like water from sea, river and water with manipulated pH (acidic water (pH 1), and alkaline water (pH 12)).

Separation of the oil/water emulsion.

In the current oil/water separation process, oil (10 ml) was mixed with distilled water (500 ml) and sonicated for about 60 sec. Once the emulsions were prepared, 25 mg of synthesized CD@COF1 was added to a 5 ml of turbid o/w emulsion and then it was manually agitated for a minute. For control, 25mg CD, COF1 and CD+COF1 physical mixture (4mg+21mg, this is the same composition to form 25mg, 16w/w% CD@COF1) were used to find the oil adsorption capacity. Thereafter, oil-absorbed CD@COF1 was separated using a metal mesh (average dimension ~ 50 μm) to obtain clean water. Here the clean water pass through the metal mesh and selectively oil-absorbed aggregated CD@COF1 remained on top of the metal mesh. Then the separated aqueous phase was characterized through visual inspection, and proton NMR study.

The oil-absorption capacity was estimated by using the following formula:

$$\text{Absorption capacity (\%)} = \frac{W1 - W0}{W0} \times 100$$

Where, W0 and W1 are the weights of CD, COF1, CD@COF1 before and after oil absorption.

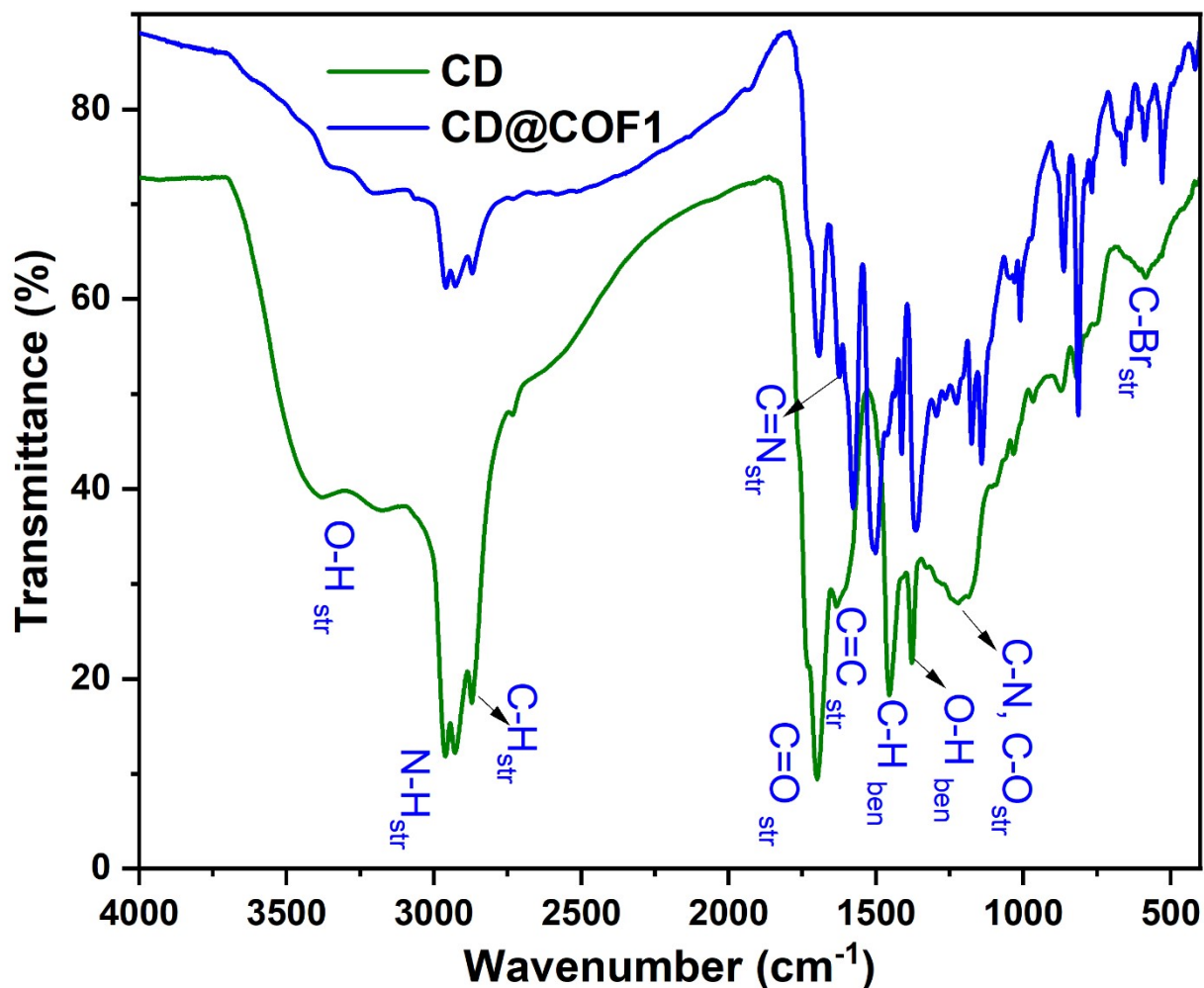


Figure S1. FT-IR spectra of the CD and CD@COF1.

For CD:1734 cm^{-1} (C=O, stretching frequency of carboxylic acid). 1700 cm^{-1} (C=O, stretching frequency of ketones). 1629 cm^{-1} (C=C, stretching frequency of graphene layers present in core). 1452 cm^{-1} (C-H, bending). 1377 cm^{-1} (O-H, bending). 1260-1100 cm^{-1} (C-N, C-O, stretching), 2872 cm^{-1} (C-H stretching). 3405 cm^{-1} (-O-H, symmetric stretching). 586 cm^{-1} (C-Br stretching). **For CD@COF1:**1623 cm^{-1} (C=N, imine stretching). 1482 cm^{-1} (C=C, stretching). 1323 cm^{-1} (C-N, stretching).

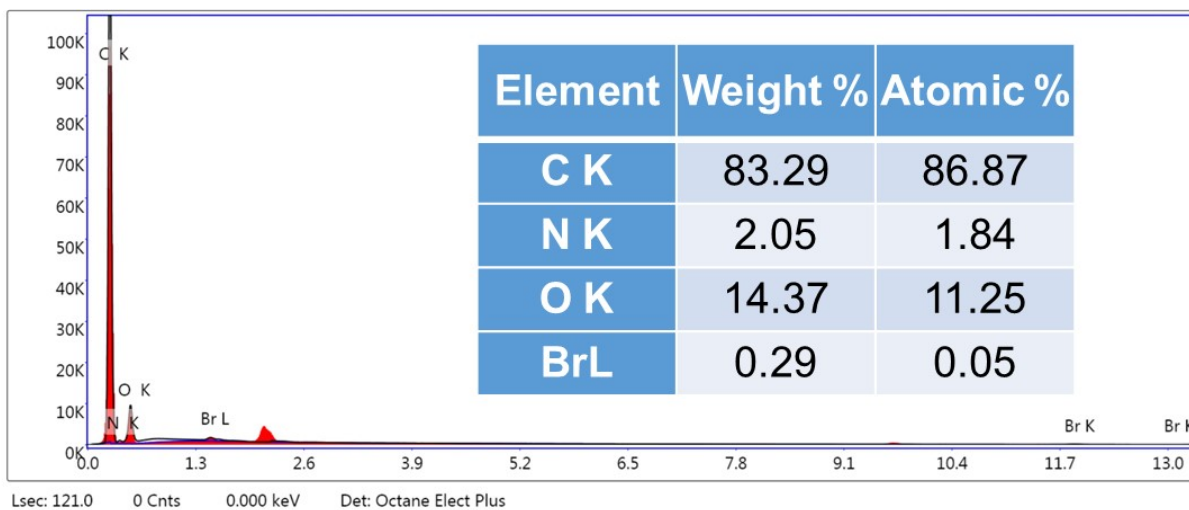
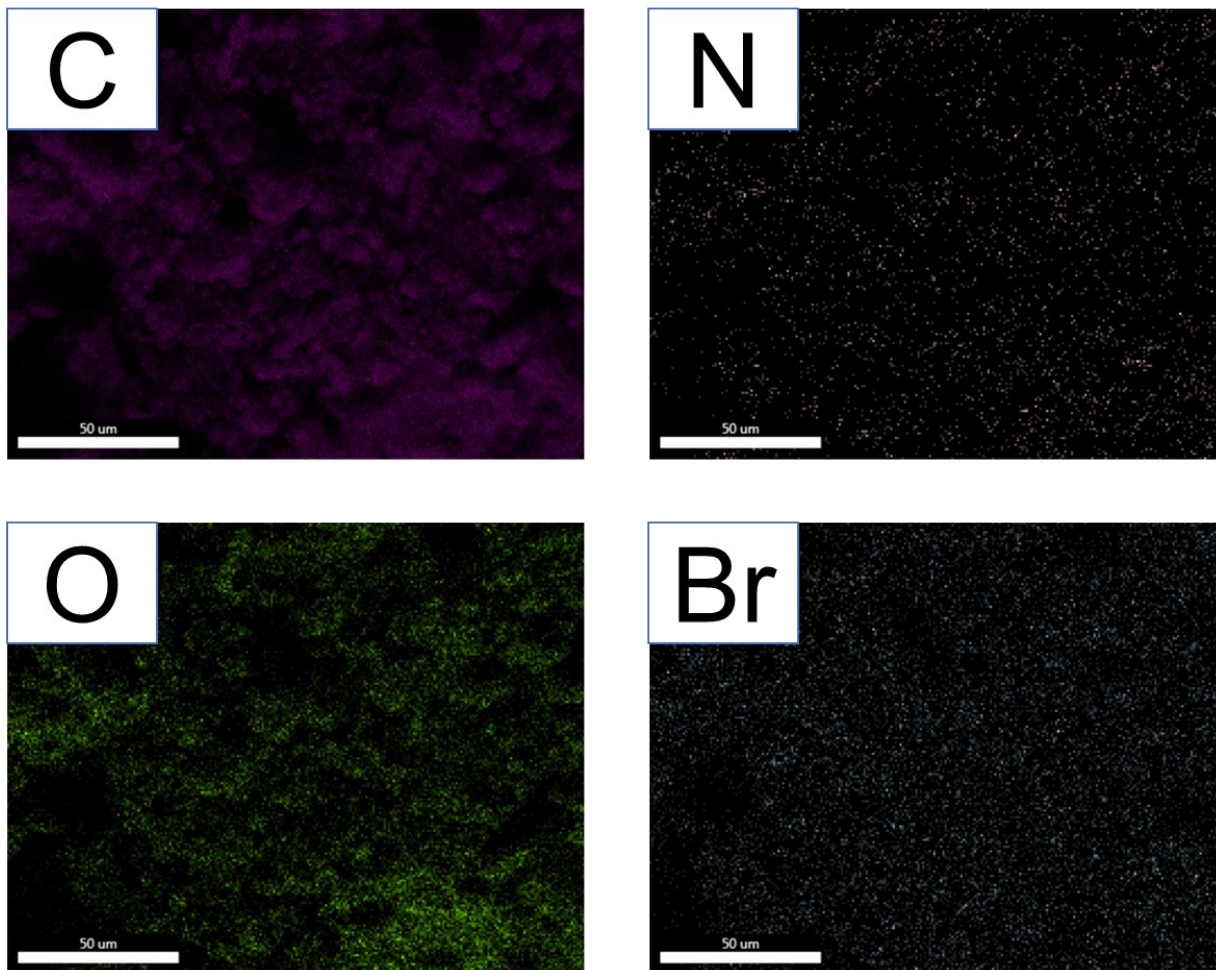


Figure S2. Elemental mapping and EDS analysis of CD showing the presence of C, O, N and Br.

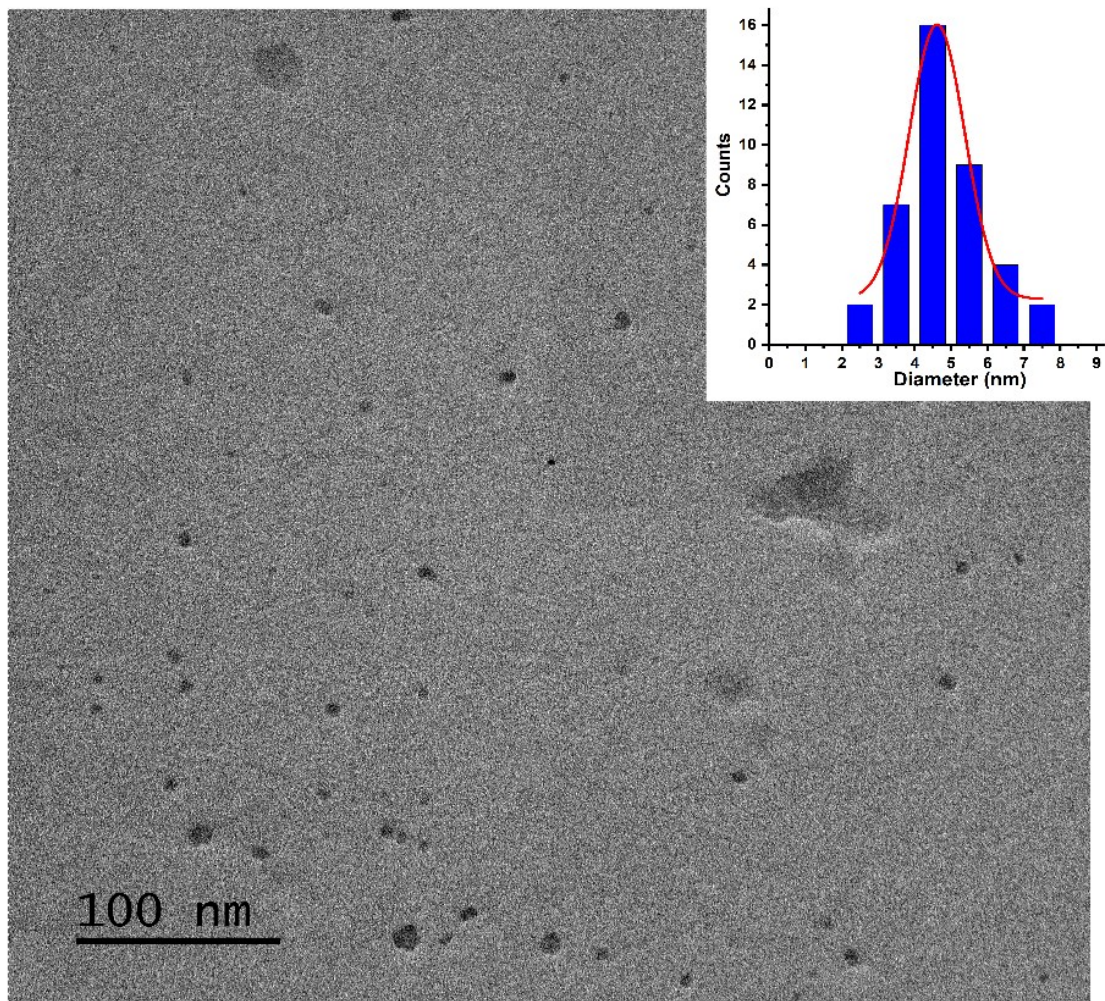


Figure S3. TEM image of the CD (inset-size distribution).

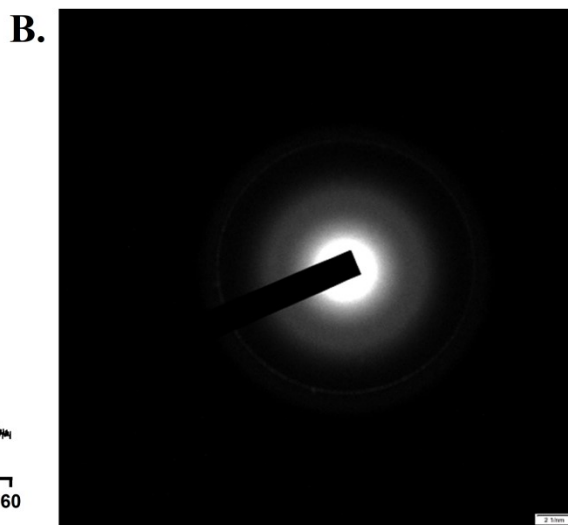
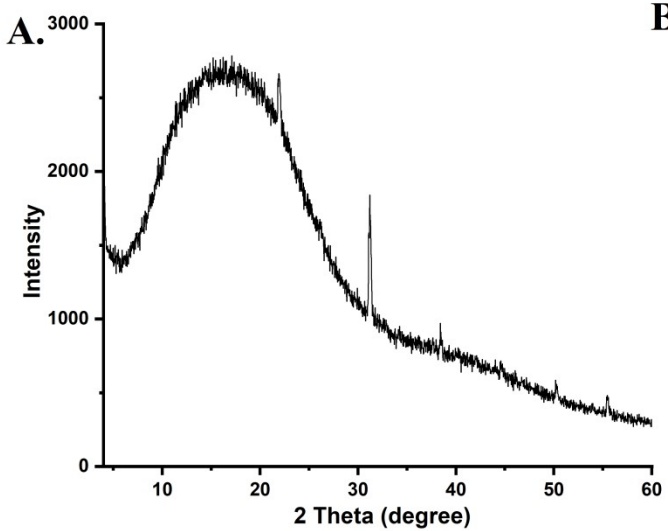


Figure S4. A. Powder-XRD and B. SAED pattern of the CD.

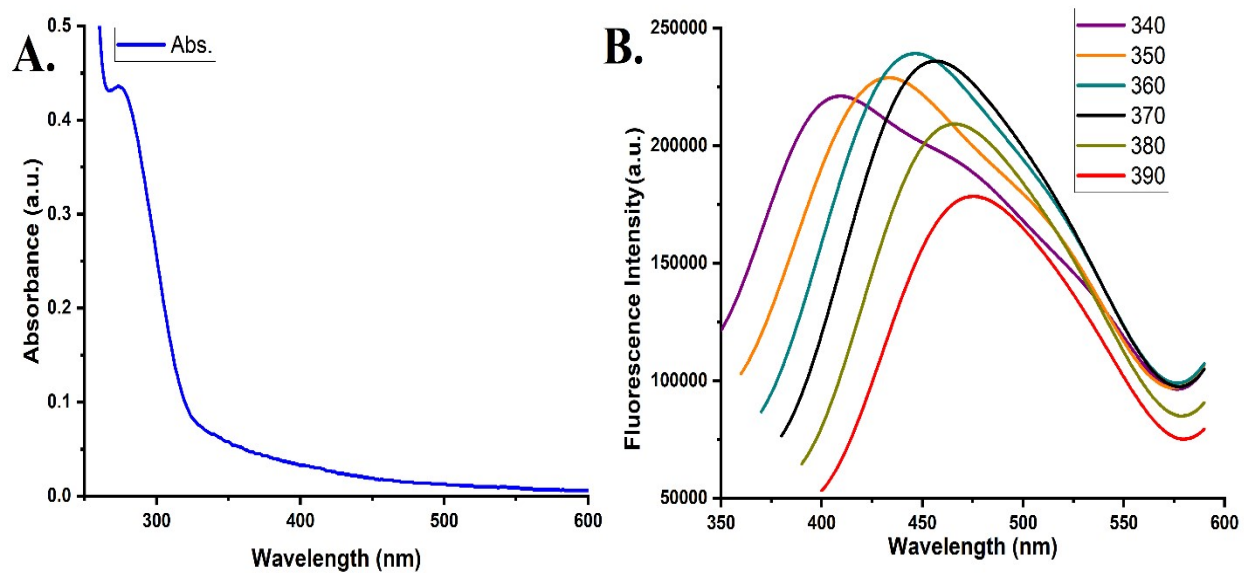


Figure S5. A. UV-Vis spectrum and B. Fluorescence spectra of the CD.



Figure S6. The contact angle of water on CD surface.

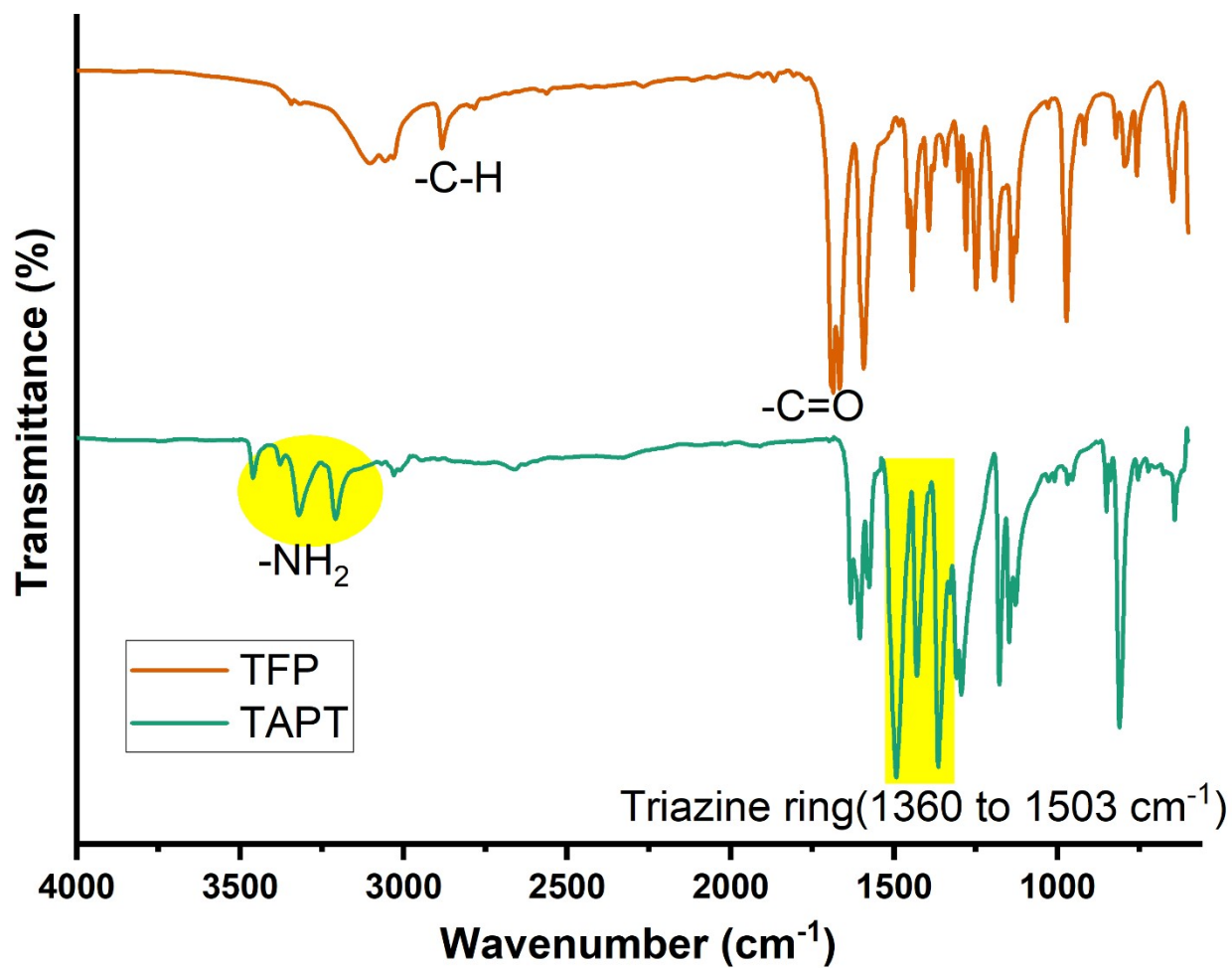


Figure S7. FT-IR spectra of TFP and TAPT.

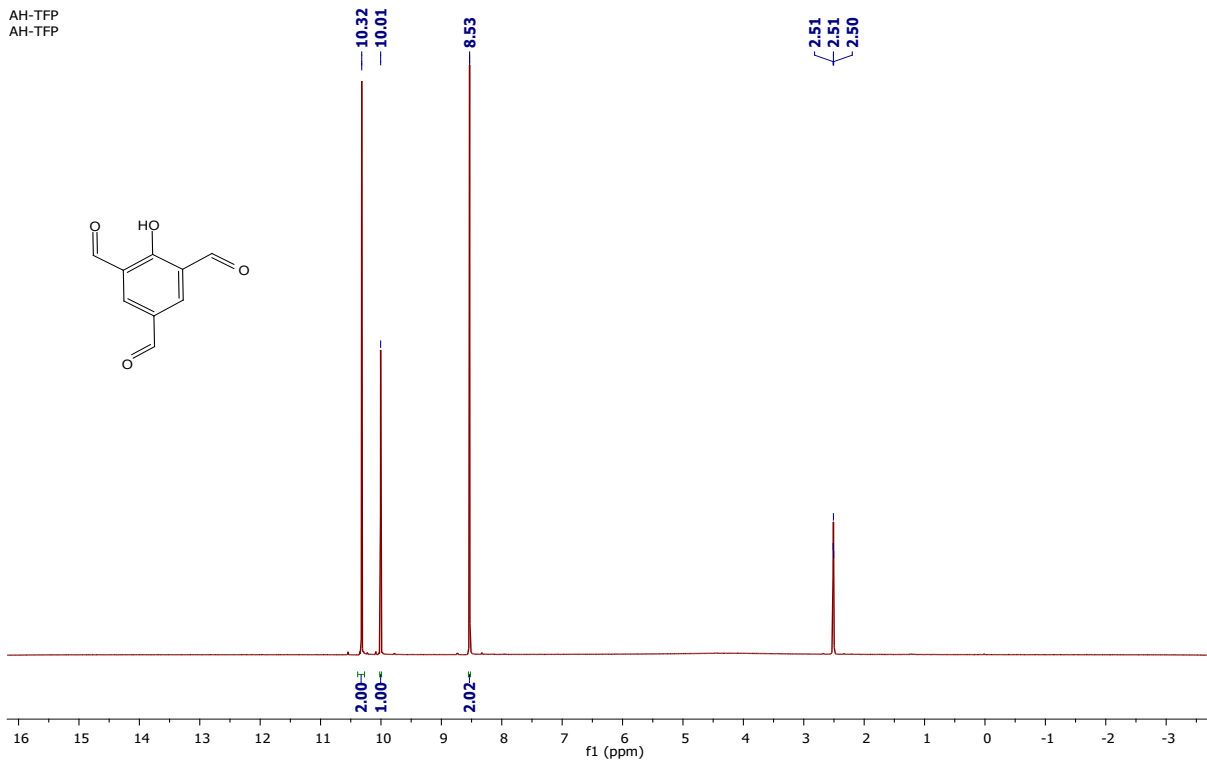


Figure S8. ^1H NMR spectrum of 2-hydroxy-1,3,5-benzenetricarbaldehyde (TFP).

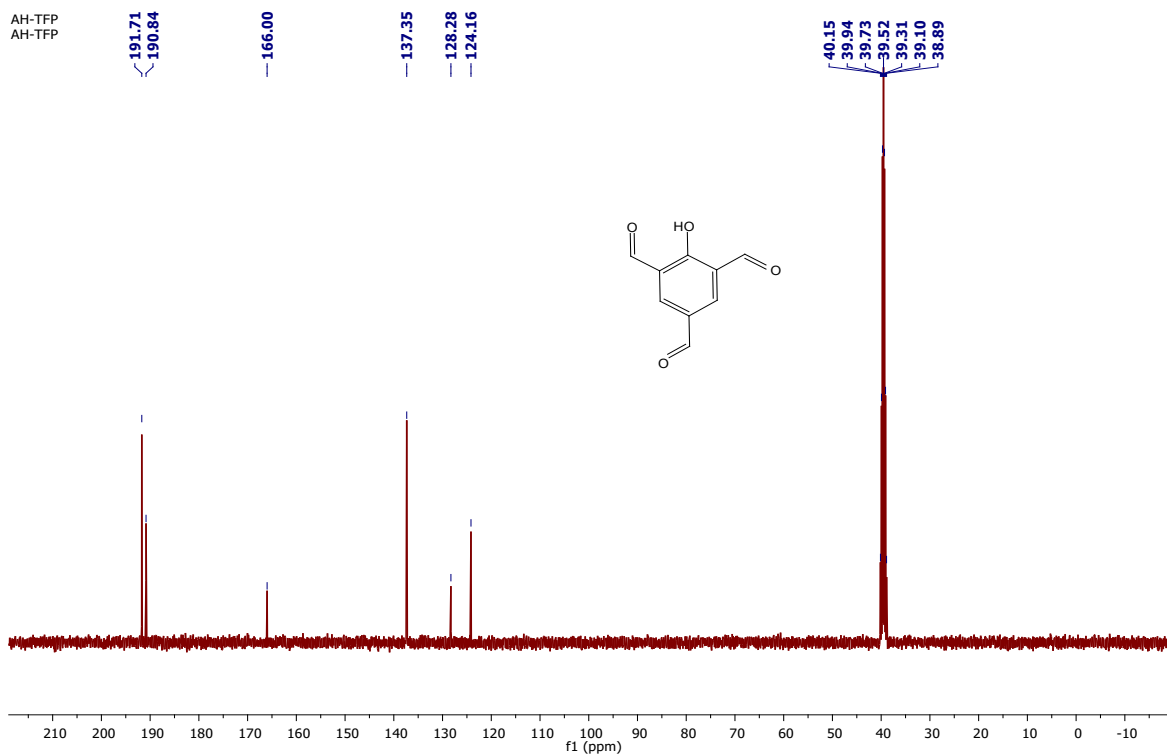


Figure S9. ^{13}C NMR spectrum of 2-hydroxy-1,3,5-benzenetricarbaldehyde (TFP).

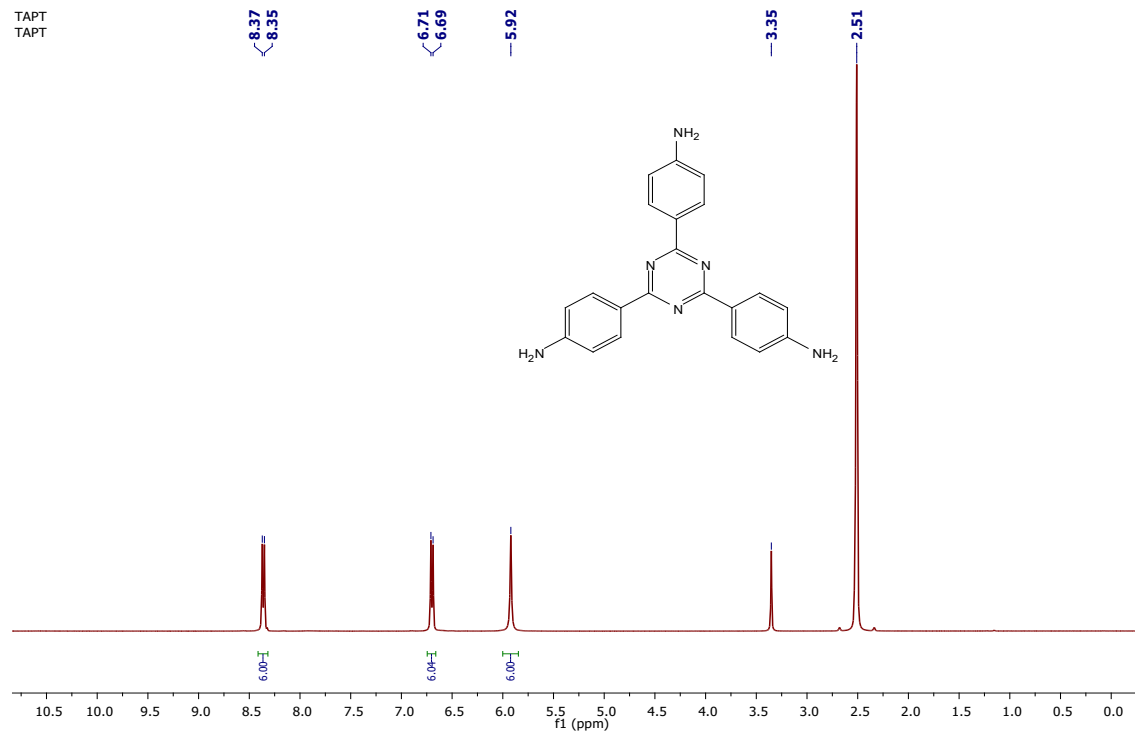


Figure S10. ^1H NMR spectrum of 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline (TAPT).

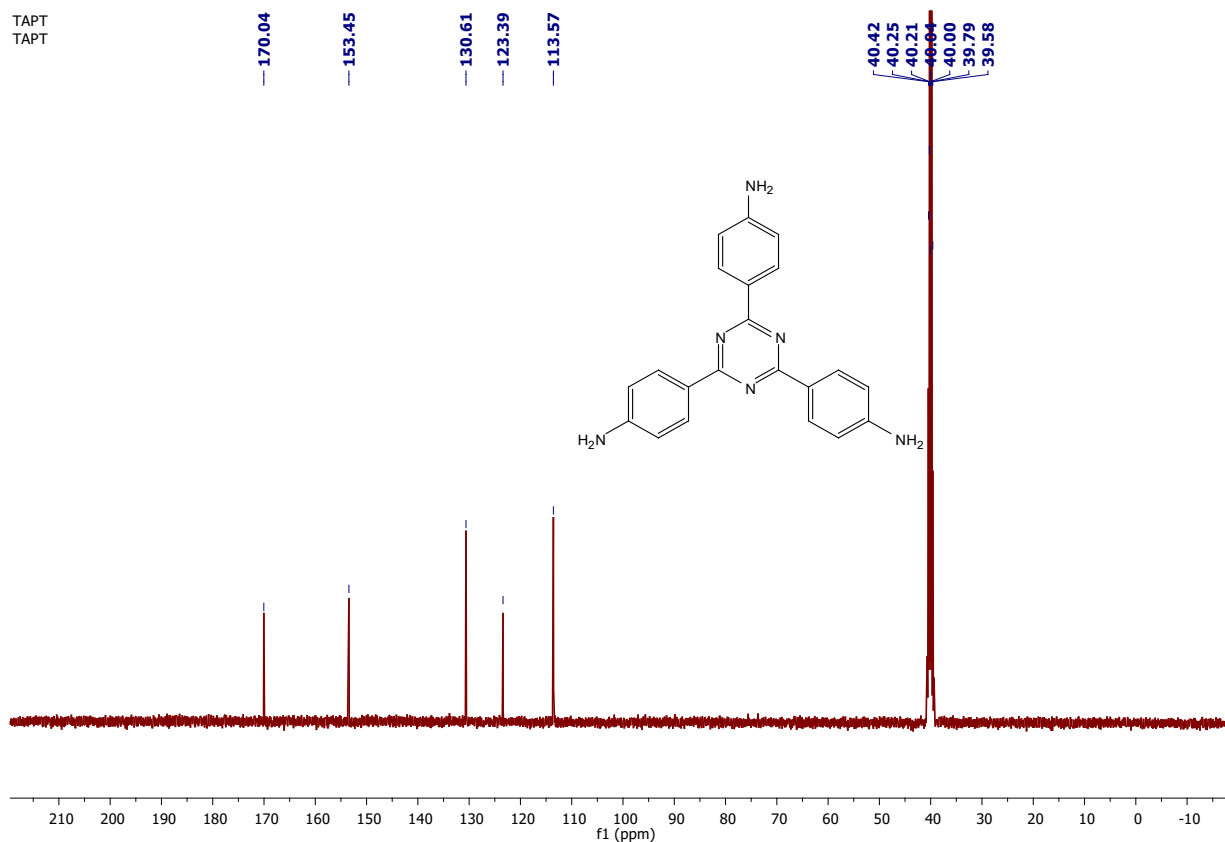


Figure S11. ^{13}C NMR spectrum of 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline (TAPT).

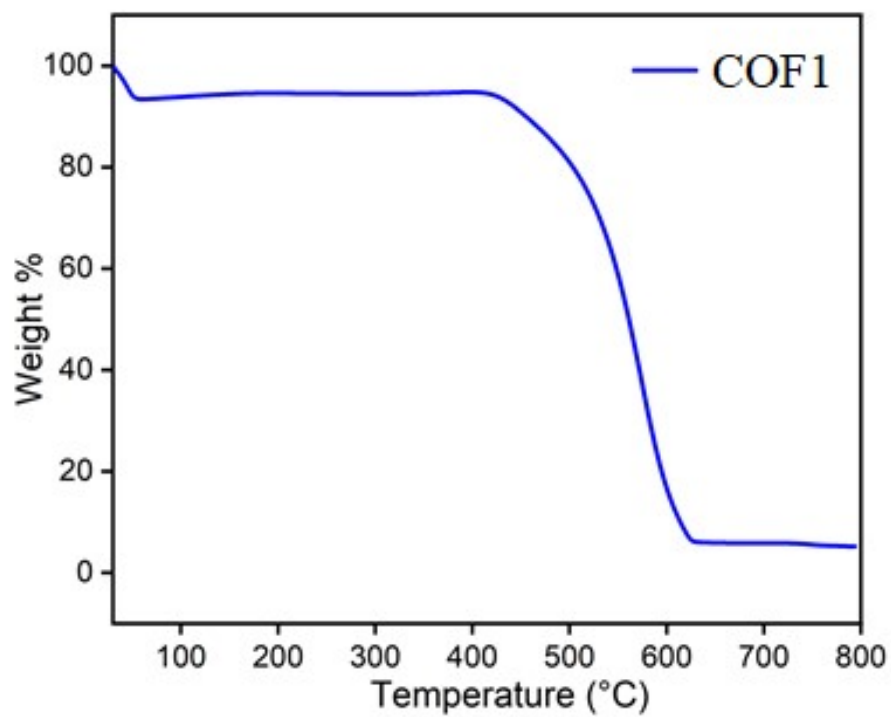


Figure S12. Thermogravimetric analysis of COF1.

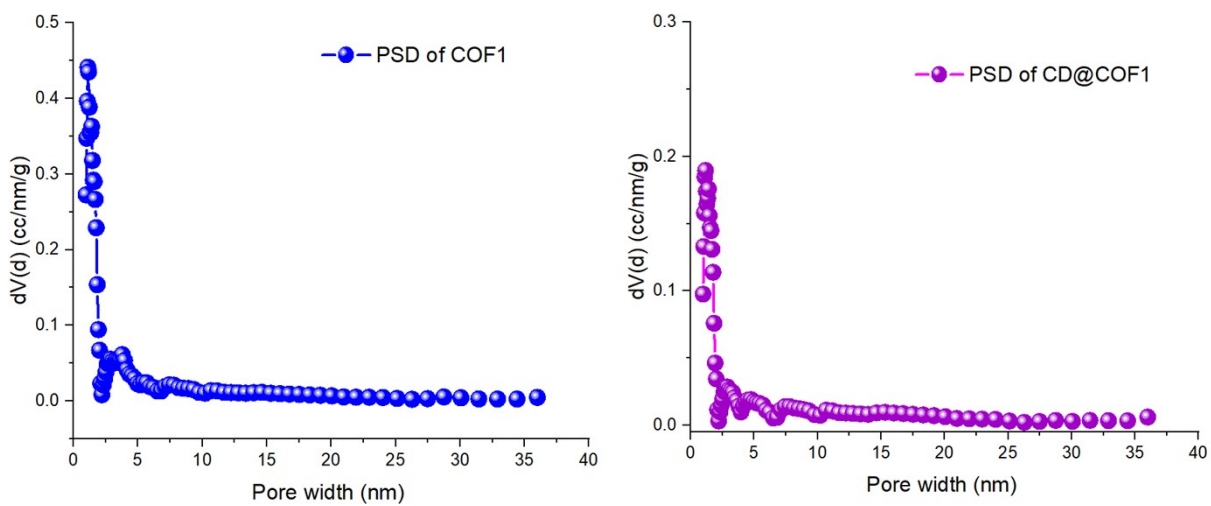


Figure S13. Pore size distribution of COF1 and CD@COF1.

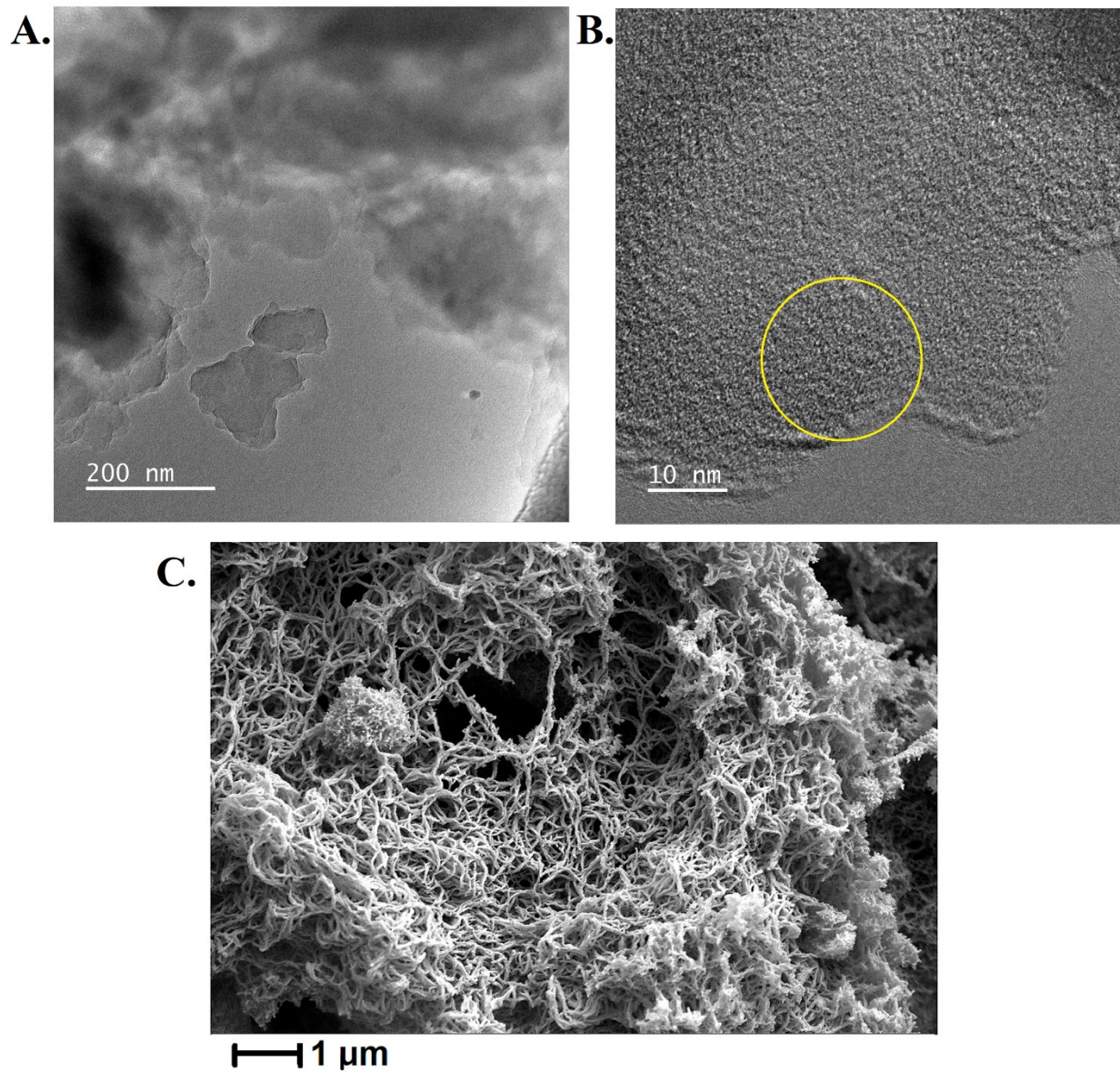


Figure S14. A. TEM, B. HR-TEM image of COF1. C. SEM image of COF1.

Under HR-TEM, ribbon like structure was observed that form few-layer thick stacked plates similar to FESEM findings. Lattice fringes due to interlayer d-spacing of COF1 was observed in HR-TEM.

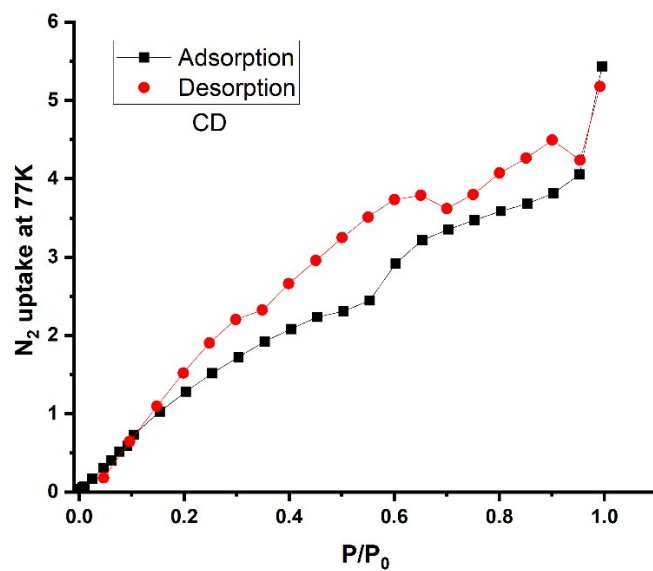


Figure S15. Nitrogen adsorption and desorption isotherms for the CD.

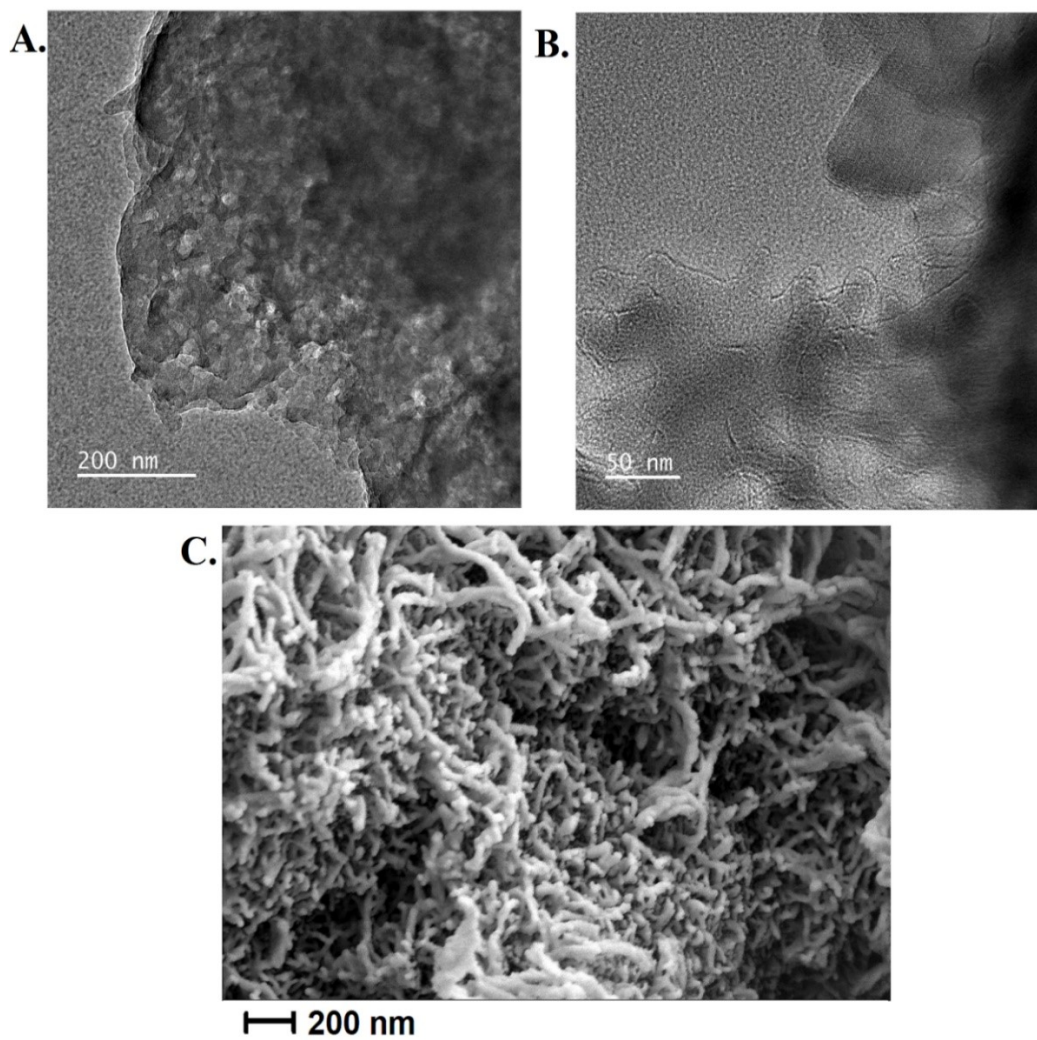


Figure S16. A. TEM, B. HR-TEM image of CD@COF1. C. SEM image of CD@COF1.

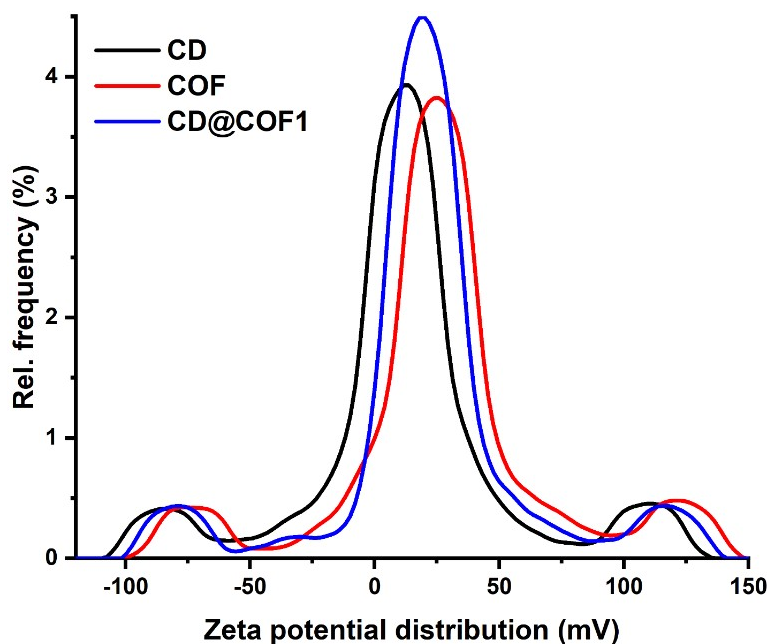


Figure S17. Zeta potential analysis of the CD, COF1 and CD@COF1.

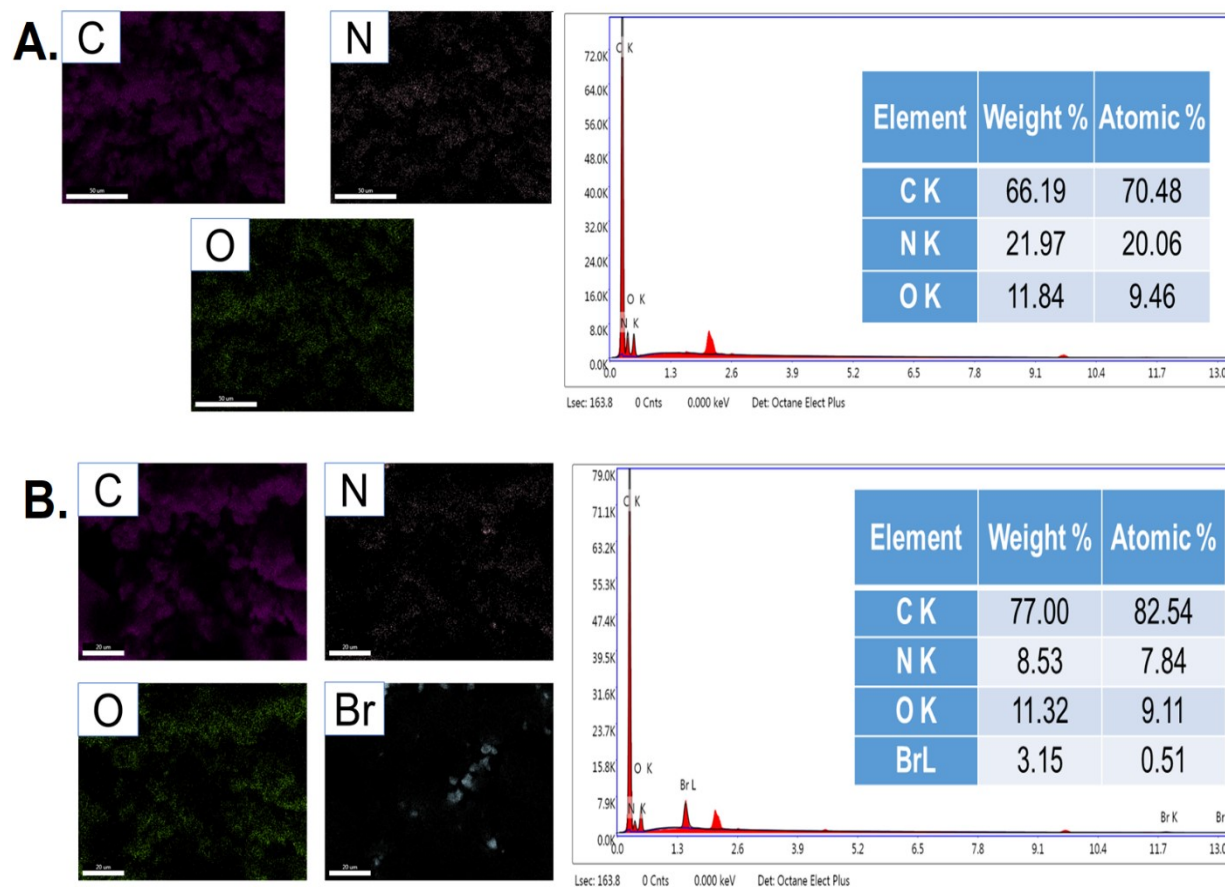


Figure S18. Elemental mapping and EDS analysis of **A.** COF1 and **B.** CD@COF1 showing the presence of C, O, N and C, O, N, Br respectively.

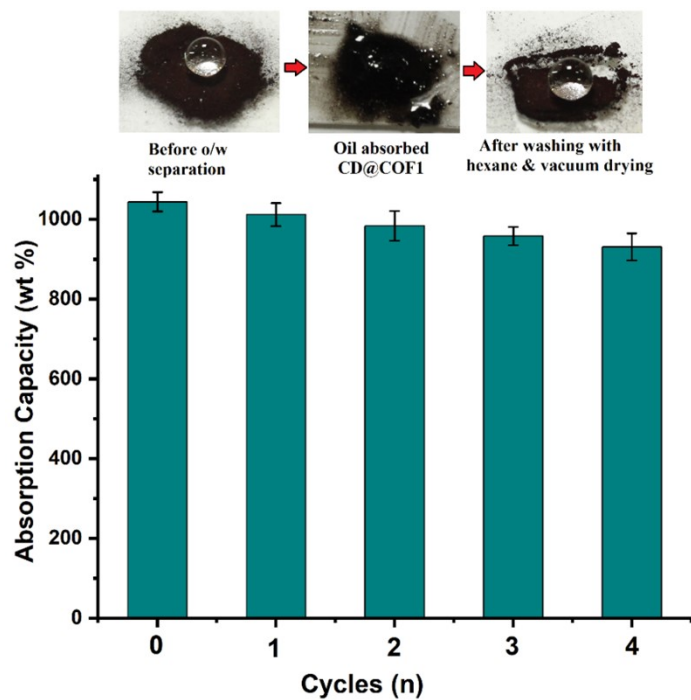


Figure S19. Reusability of synthesized CD@COF1 material after oil absorption.

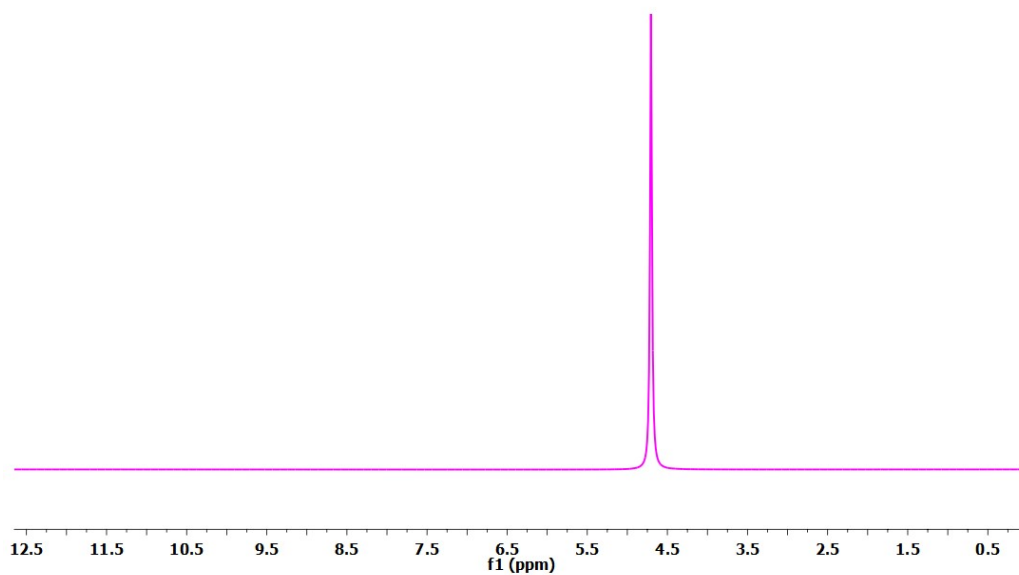


Figure S20. Proton NMR of separated water from the oil/water emulsion.

1. *J. Am. Chem. Soc.* 2020, **142**, 4862–4871
2. *Chem. Commun.*, 2018, **54**, 11475–11478
3. *Angew. Chemie Int. Ed.*, 2022, **61**, e202210507

4. *Adv. Energy Mater.*, 2021, **11**, 2003626.