Supporting Information

Mechanochemically Synthesized Schiff-base Engineered 2D Mixed-Linker MOF for CO$_2$ Capture and Cationic Dyes Removal

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Experimental Section

Materials and General Methods

All reagents and solvents were purchased from commercial sources and were used as received without any purification. Distilled water was used for synthetic manipulations. (E)-N'-(pyridin-4-ylmethylene)isonicotinohydrazide (**L**) was synthesized according to our previous report.[S1] FTIR spectra were recorded on a Thermo Nicolet 6700 spectrophotometer using KBr pellet method. TG analysis was performed on Mettler Toledo thermal analyzer under nitrogen environment with a heating rate at 10 °C/min. Powder X-ray diffraction (PXRD) data were collected using a Bruker, D2 phaser bench top diffractometer. Single crystal structures were determined using Bruker D8 QUEST diffractometer. Liquid and solid-state UV–vis spectra were recorded using a Shimadzu UV-visible Spectrophotometer (UV-1800) and Shimadzu UV-visible-NIR Spectrometer (DMP-2800) respectively with $BaSO_4$ as a reference for solid state measurements. Field Emission-Scanning Electron Microscopy (FE-SEM) micrographs were recorded using a JEOL JSM-7100F instrument employing a 15-kV accelerating voltage. The gas adsorption-desorption data was measured on a Micromeritics, 3 Flex instrument. Dynamic Light Scattering (DLS) measurements were recorded using Malvern Zetasizer Nano-S90 at room temperature.

Synthesis and General Characterizations:

Preparation of Stock Ligand Solution used for ADES-7 crystallization: 5-OH-H_2**IPA** (5-hydroxyisophthalic acid) (2.5 mmol) and KOH (5 mmol) were dissolved in 20 mL of H_2O to form a clear solution. N-donor linker (E)-N'-(pyridin-4-ylmethylene)isonicotinohydrazide (**L**) (1.25 mmol) was separately solubilized in 20 mL of MeOH. A stock ligand solution was prepared by mixing the

individual linker solution with constant stirring for 15 min and further diluted to 70 mL with a MeOH/H$_2$O (1:1) mixture.

Crystallization of {[Cd(5OH-IP)(L)]·(CH$_3$OH)}$_n$ (ADES-7D) (Diffusion Method): In a narrow test tube, a 3-mL aqueous metal solution (Cd(ClO$_4$)$_2$·xH$_2$O; 1 mmol in 15 mL of water) was placed followed by 8 mL solution of MeOH/H$_2$O (1:1/v:v). The 3-mL ligand solution was then carefully layered upon the MeOH/H$_2$O layer and the test tube was sealed and left for crystallization. The colorless crystals of X-ray diffraction quality appeared within one week. (Yield ∼74%). FTIR (cm^{-1}, KBr): 3377 (br), 3203 (br), 3064 (w), 2845 (w), 1675 (s), 1612 (m), 1560 (s), 1384 (m), 1293 (s), 1222 (s), 1145 (s), 1102 (m), 1068 (s), 1011 (s), 978 (s), 940 (s), 889 (m), 852 (m), 811 (m), 782 (s), 732 (s), 696 (s), 536 (m), 453 (m).

Bulk powder synthesis of ADES-7C by conventional (reflux) method: Bulk powder of ADES-**7C** was synthesized by refluxing a mixture of Cd(NO$_3$)$_2$·4H$_2$O (1.2 mmol), **5OH**-H$_2$**IPA** (1 mmol), KOH (2.2 mmol), and **L** (1 mmol) in 40 mL of H$_2$O:MeOH (1:1/v:v) for 6h. The obtained precipitates were filtered and thoroughly washed with methanol/water (1/1) followed by acetone. The material was allowed to dry at ambient temperature (yield ∼85%). FTIR (cm^{-1}, KBr): 3305 (br), 3205 (br), 3060 (w), 2843 (m), 1677 (s), 1611 (m), 1564 (m), 1386 (m), 1294 (s), 1222 (s), 1146 (s), 1101 (m), 1071 (s), 1014 (s), 980 (s), 944 (s), 895 (w), 853 (w), 806 (m), 784 (s), 728 (s), 696 (s), 538 (s), 454 (m).

Bulk powder synthesis of ADES-7M by mechanochemical (grinding) method: ADES-**7M** were synthesized in bulk *via* manually grinding, a mixture of 1 mmol of Cd(OAc)$_2$·2H$_2$O, 1 mmol of **5OH**-H$_2$**IPA**, and 1 mmol of **L** in a mortar and pestle for 25 min. The resulting solids were washed with methanol/water (1/1, 5 mL) followed by acetone (5 mL) to remove any unreacted starting

material and then dried at ambient temperature, which has been used for dye removal studies.

(yield ~90%). FTIR (cm^{-1}, KBr): 3355 (br), 3200 (br), 3059 (w), 2841 (m), 1674 (s), 1614 (m), 1566

(m), 1385 (m), 1296 (s), 1221 (s), 1146 (s), 1101 (m), 1071 (s), 1014 (s), 980 (s), 943 (s), 891 (w),

854 (m), 806 (m), 783 (s), 729 (s), 695 (s), 538 (s), 454 (m).

Adsorption of the organic dyes by ADES-7: Malachite green (MG), rhodamine B (RhB), methyl

violet (MV), methylene blue (MB), methyl orange (MO), and bromocresol green (BCG) were used

in the adsorption experiment having 5×10^{-5} M aqueous solution of organic dyes. The 100 mg of

MOF material (ADES-**7C** or **7M**) was added to 10-mL of the dye solution and stirred continuously

for 3h under dark conditions. The adsorbed dye solution was then obtained by centrifuging the

adsorbent. The concentration of the resulting dye solution was monitored by UV-vis

spectroscopy.

The amount of dye adsorbed after 3h, was calculated by following equation considering initial

and equilibrium concentration of dye solutions.[S2]

$$q_e = (C_i - C_e)V \times MW/m \qquad \textbf{(Equation S1)}$$

Where, C_i-initial concentration of dyes (moles/L), C_e-equilibrium concentration of dyes (moles/L),

V-volume of the solution (L), MW-molecular weight of dye and m-mass of the adsorbent (g).

The following equation was used to find dyes removal percentage (η):[S2]

$$\eta = (C_i - C_e)/C_i \times 100\% \qquad \textbf{(Equation S2)}$$

Where, C_i-initial concentration of dyes (moles/L) and C_e-equilibrium concentration of dyes

(moles/L).

To investigate the adsorption capacity of ADES-**7M** in mixture of dyes, 10 mL aqueous solution of

MO+MG, MO+RhB, MO+MV, MO+MB, BCG+MG, BCG+RhB, BCG+MV, and BCG+MB (1:1, v/v)

were stirred with 100 mg ADES-**7M** for 3h. The concentration of adsorbed dye solution was monitored by UV-vis spectroscopy.

Dye separation through chromatographic column filled with ADES-7M: Each individual separation used a 5×10^{-5} M aqueous solution of the organic dyes MG, RhB, MV, MB, MO and BCG. A 15-cm (length) and 0.5-cm (diameter) chromatographic column was filled up to 5-cm with ADES-**7M** aqueous slurry, and dye aqueous solutions were allowed to pass through the column at room temperature. UV-Vis spectra were used to investigate the concentrations of the discharge solutions in order to determine the separation capability of ADES-**7M**.

Dye desorption ability of ADES-7M: To investigate the dye desorption ability of ADES-**7M**, 20 mg dye-adsorbed materials ADES-**7M**@MG, ADES-**7M**@RhB, ADES-**7M**@MV, and ADES-**7M**@MB were placed in a glass cuvette with 1-mL of MeOH. Individual cuvettes were placed in a spectrophotometer and UV-vis spectra were recorded at regular intervals for a total period of 360 minutes.

Kinetic study of RhB removal

Effects of *p*H: To investigate the influence of *p*H on adsorption process on the surface of ADES-**7M**, we took one cationic dye (RhB). A set of adsorption tests were done in the *p*H scale ranging from 2 to 11 with the adsorbent under ambient temperature. The *p*H of the mixture was adjusted by the addition of 0.1 N NaOH and 0.1 N HCl solutions. The 100 mg of ADES-**7M** was added to 10 mL of the dye solution having *p*H range of 2-11 and stirred continuously for 3h under dark conditions. The concentration of the resulting dye solution was monitored by UV-vis spectroscopy.

Adsorption of dye at different time: In order to evaluate the kinetic mechanism that controls the adsorption process of RhB by ADES-**7M**, time-dependent adsorption capacity was obtained. RhB was used in the adsorption experiment having 5×10^{-5} M aqueous solution of organic dye. 100 mg of ADES-**7M** was added to 10 mL of the dye solution and stirred continuously for 3h under dark conditions. Small portions of samples for analyses were taken from the reaction suspension at specified reaction times (20, 40, 60, 80, 100, 120, 140, 160, and 180 min) and immediately centrifuged it to remove the particles which were further analyzed by monitoring the absorbance using UV-vis spectrophotometer.

Temperature tendency on dye adsorption: The impact of temperature on the adsorption capacity of dye (RhB) was considered by performing the experiment at three varying temperatures *i.e.*, 25°C, 35°C, and 45°C. A set of adsorption tests were done in the temperature range 25°C, 35°C, and 45°C with the adsorbent under ambient temperature. 100 mg of ADES-**7M** was added to 10 mL of the dye solution under different temperatures. The concentration of the resulting dye solution was monitored by UV-vis spectroscopy.

Adsorption Kinetic Models: Pseudo second- order (**equation S3**) and Pseudo second- order (**equation S4**) kinetic model is used to express the mechanism of RhB adsorption on ADES-**7M**.[S3]

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \hspace{4cm} \textbf{(Equation S3)}$$

$$\frac{t}{q^t} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{1}{(q_e)} \cdot t \hspace{4cm} \textbf{(Equation S4)}$$

where k_1 (min^{-1}) and k_2 (mg·g^{-1}·min^{-1}) are the rate constants of adsorption, q_t (mg·g^{-1}) is the adsorption capacity at time t (min), and q_e (mg·g^{-1}) is the maximum adsorption capacity at equilibrium.

Adsorption Isotherms Models: Adsorption isotherms obtained through fitting of experimental data (RhB conc. range = 2.00 x 10^{-5} to 1.40 x 10^{-4} M) with Langmuir, and Freundlich model is presented in the **equation S3** and **S4**, respectively.[S4-S5]

$$\frac{1}{q^e} = \frac{1}{(q_{max})} + \frac{1}{(q_{max} K_L)} C_e \qquad \textbf{(Equation S5)}$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad \textbf{(Equation S6)}$$

where q_e (mg·g^{-1}) is the equilibrium adsorption capacity, c_e (mg L^{-1}) is the equilibrium concentration of adsorbate; q_{max} represents the maximum adsorption capacity and K_L is the adsorption constant related to the adsorption energy and affinity of binding sites, K_F is a Freundlich constant indicative of the adsorption capacity of the adsorbent, n is the heterogeneity factor related to the capacity and intensity of adsorption.

Stability Study:[S6-S7] For stability testing of ADES-**7**, 20 mg of MOF powder was dispersed in the respective media and monitored over selected time. The MOF powder was then recovered, washed, dried, and subjected to PXRD and FTIR analysis. Most of the stability testing samples showed negligible changes in weight; any slight changes were attributed to work-up loss. Representative data for the room temperature stability test is provided below.

Cycle	1	2	3
Initial weight	20.0 mg	20.0 mg	20.0 mg
Recovered sample weight	19.8 mg	19.8 mg	19.9 mg

X-ray Crystallography: For **ADES-7**, crystals suitable for X-ray crystallography were obtained by layering of the metal salts and ligand precursors mentioned in the experimental section. The crystal data were collected on a Bruker D8 Quest diffractometer, with CMOS detector in shutter

less mode. The crystals were cooled to low temperature using an Oxford Cryostream liquid nitrogen cryostat. The instrument was equipped with a graphite monochromatized MoK$_\alpha$ X-ray source (λ = 0.71073 Å), with Triumph™ X-ray source optics. Data collection and initial indexing and cell refinement were handled using APEX II software.[S8] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[S9] The data were corrected for absorption using the SADABS program.[S10] Decay of reflection intensity was monitored by analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically, structure solution and refinement were performed with SHELXTL.[S11] The 'Calc Void/Solv' calculation from PLATON analysis indicates that ADES-**7** possesses an estimated solvent-accessible void volume of 21% of the entire framework.[S12] In the structure of ADES-**7**, the calculated Potential Solvent Area Vol 234.8 Å^3 per Unit Cell Vol 1122.9 Å^3 features voids making upto ca 21% of the unit-cell volume, which is very tiny to accommodate only small solvent molecule. CCDC number 2241084 corresponds to **ADES-7** reported in this manuscript and this data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Table S1. Crystal Data and Refinement Parameters for **ADES-7**.

Identification code	ADES-7
Chemical formula	$CdC_{20}H_{14}N_4O_6$
Formula weight (g/mol)	518.75
Crystal Color	Yellow
Crystal Size (mm)	0.04 x 0.15 x 0.22
Temperature (K)	158(2)
Crystal System	Triclinic
Space Group	$P\bar{1}$
a($\mathring{A}$)	9.259(3)
b($\mathring{A}$)	10.309(4)
c($\mathring{A}$)	12.640(4)
α($^\circ$)	104.788(10)
β($^\circ$)	92.695(11)
γ($^\circ$)	104.240(10)°
Z	2
V($\mathring{A}^3$)	1122.9(6)
Density (g/cm^3)	1.534
μ(mm^{-1})	1.014
F(000)	516
Reflections Collected	28595
Independent Reflections	6116
R_{int}	0.0718
Number of parameters	297
GOF on F^2	1.060
Final R_1/wR_2 (I ≥2σ(I)	0.0514/0.1042
Weighted R_1/wR_2 (all data)	0.0823/0.1195
CCDC number	2241084
$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$	
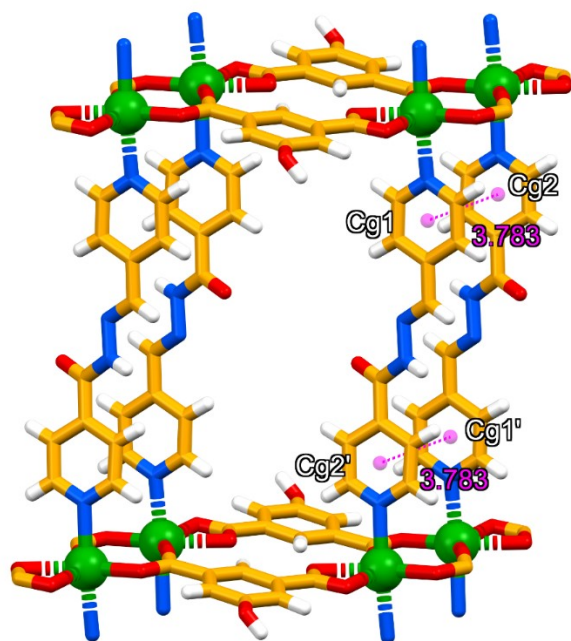
Figure S1. The π···π stacking interactions observed in ADES-**7**.
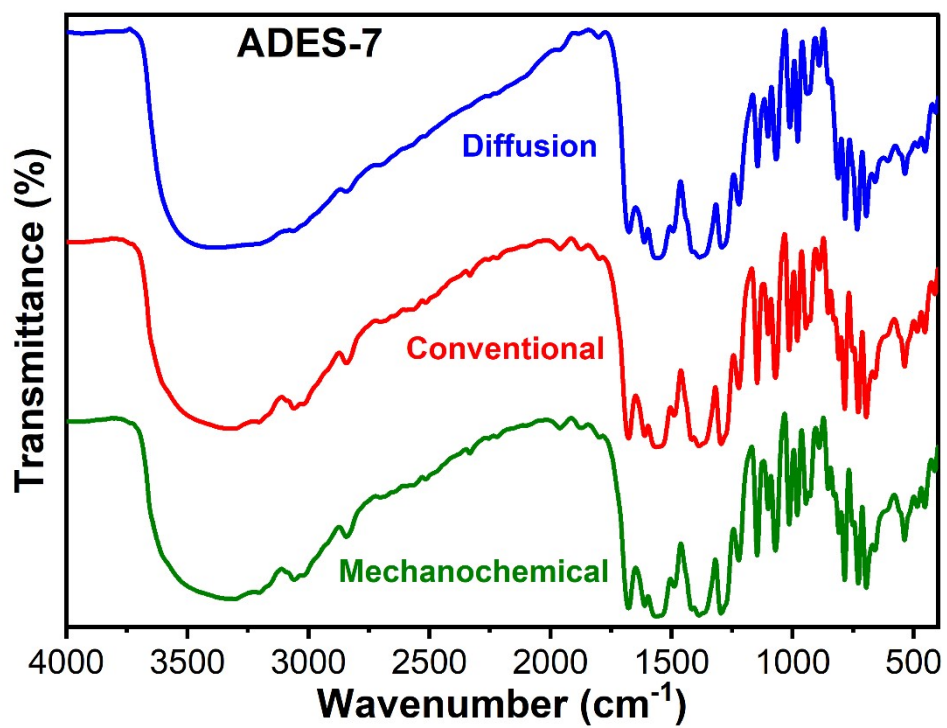
Figure S2. FTIR spectra of ADES-**7** (synthesized by diffusion, conventional and mechanochemical method) recorded by dispersing in KBr pellet.
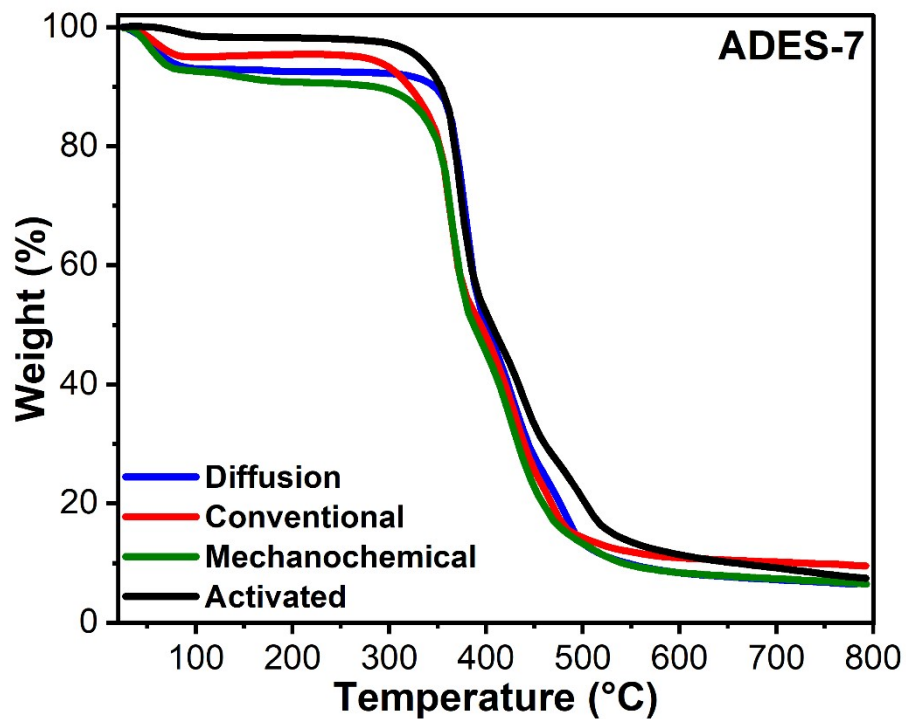
Figure S3. TGA plot for the ADES-**7** (synthesized by diffusion, conventional and mechanochemical method as well as activated).
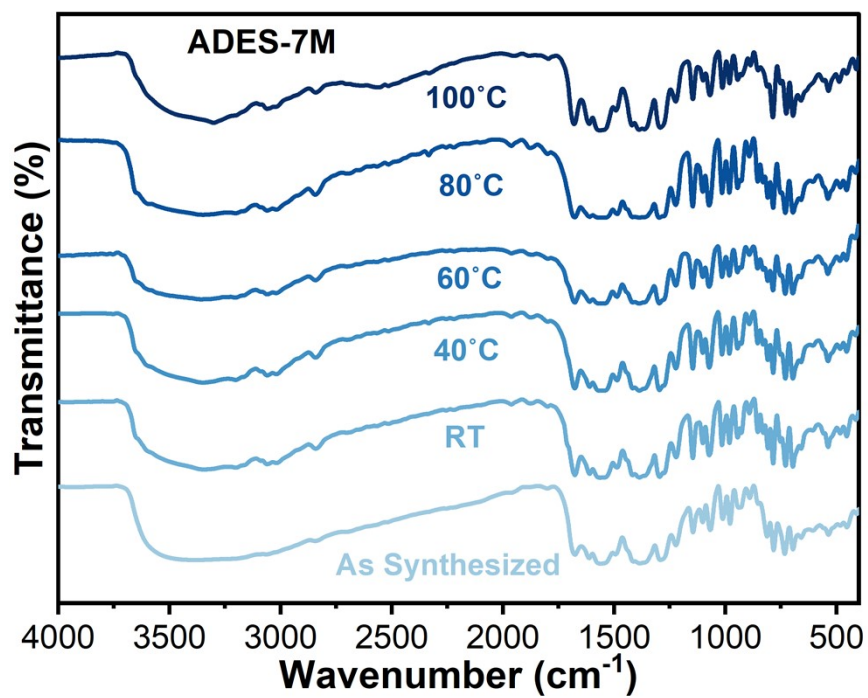

Figure S4. FTIR spectra of ADES-**7M** (dispersed in water at RT and refluxed at different temperatures for 24 h) recorded by dispersing in KBr pellet.
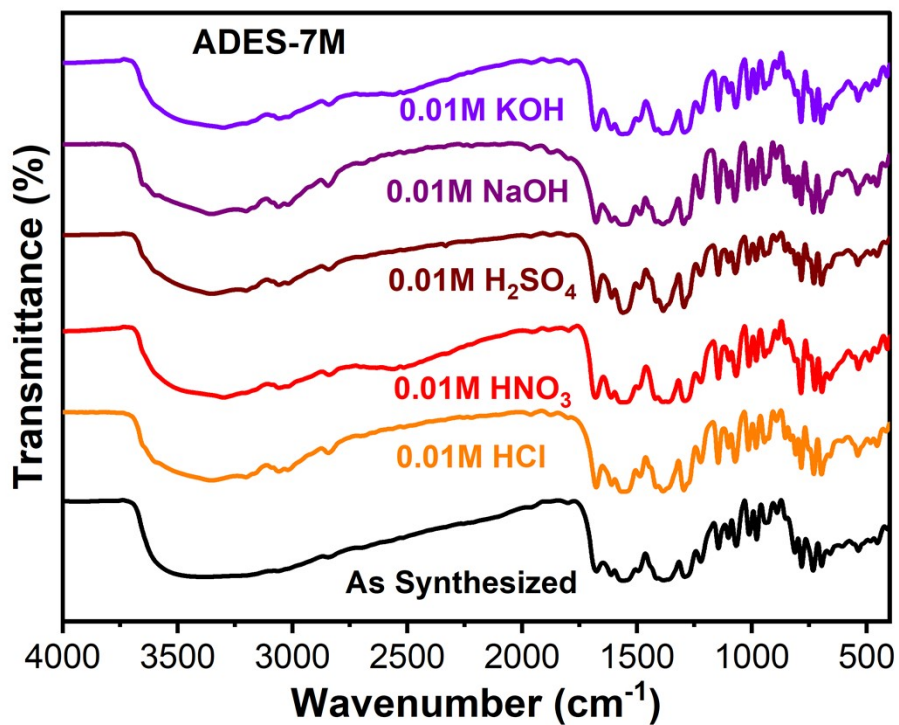
Figure S5. FTIR spectra of ADES-**7M** (dispersed in aqueous acidic and basic media for 24 h) recorded by dispersing in KBr pellet.
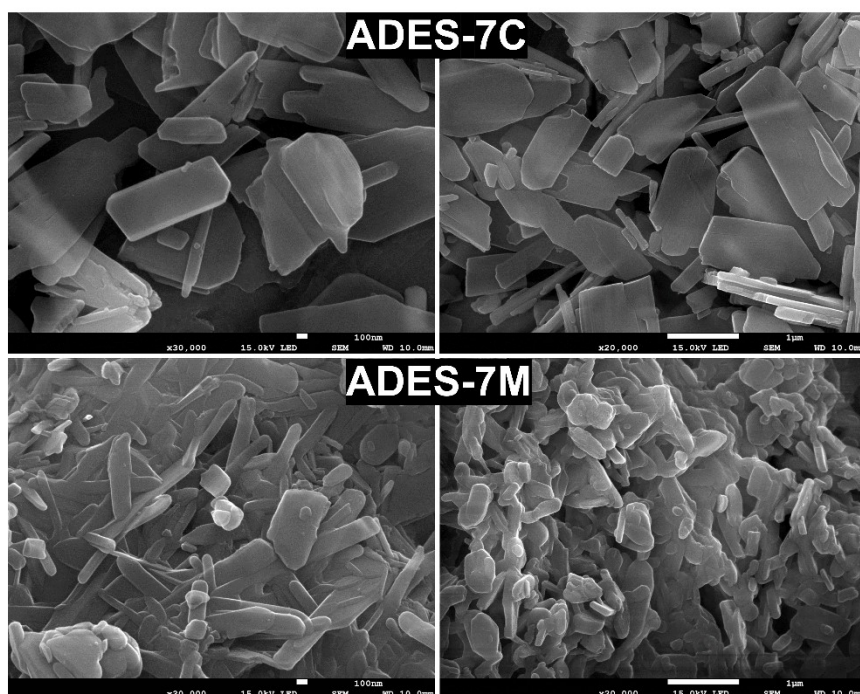
Figure S6. FE-SEM images of ADES-**7C** and ADES-**7M**.
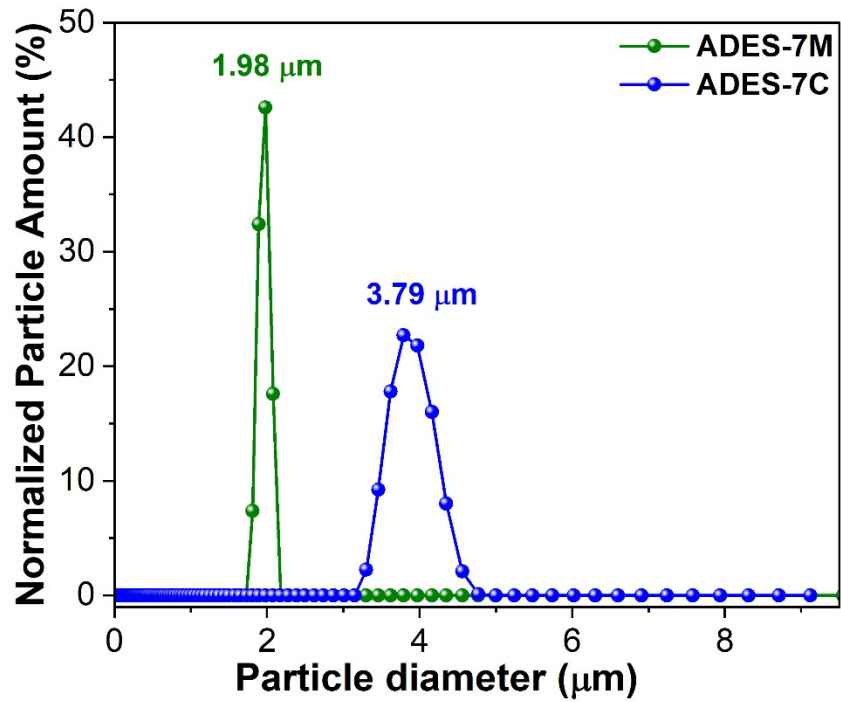
Figure S7. DLS measurement for ADES-**7M** and ADES-**7C** at RT.
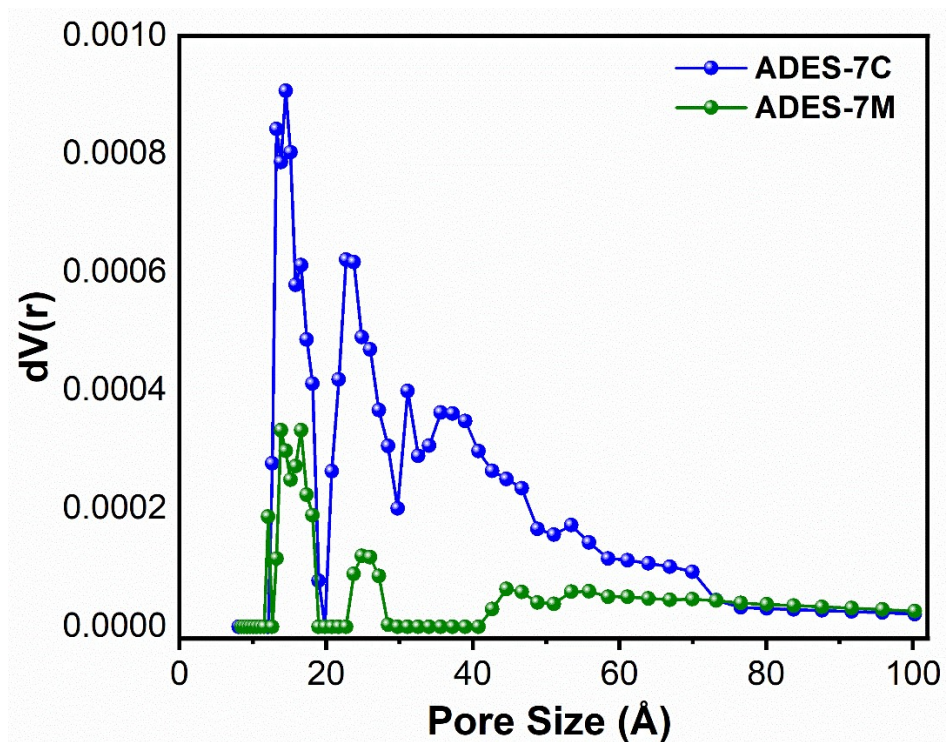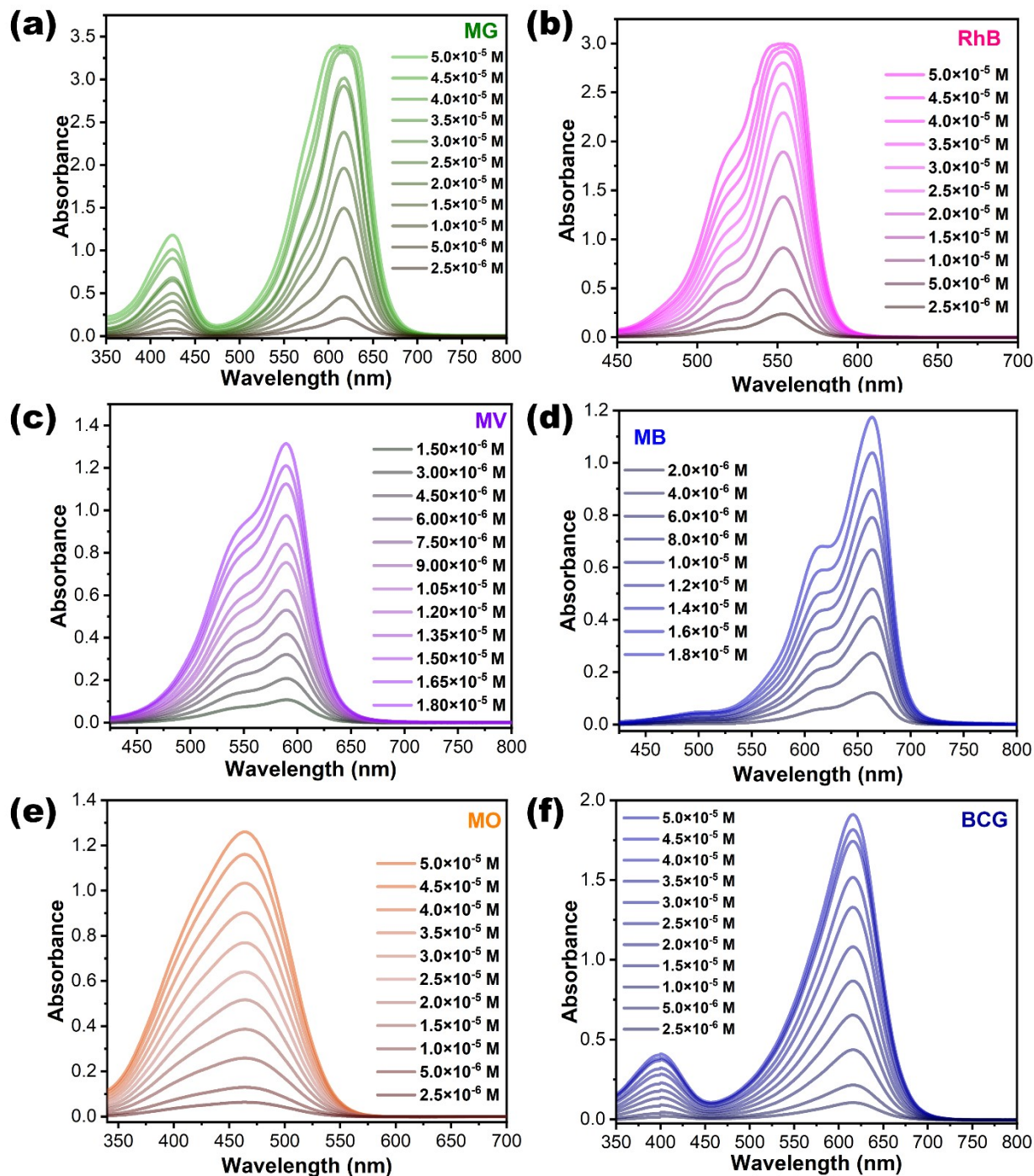

Figure S8. Pore size distribution plot for ADES-**7M** and ADES-**7C**.

Figure S9. (a-f) UV-vis calibration plots of standard organic dyes MG, RhB, MV, MB, MO and BCG.
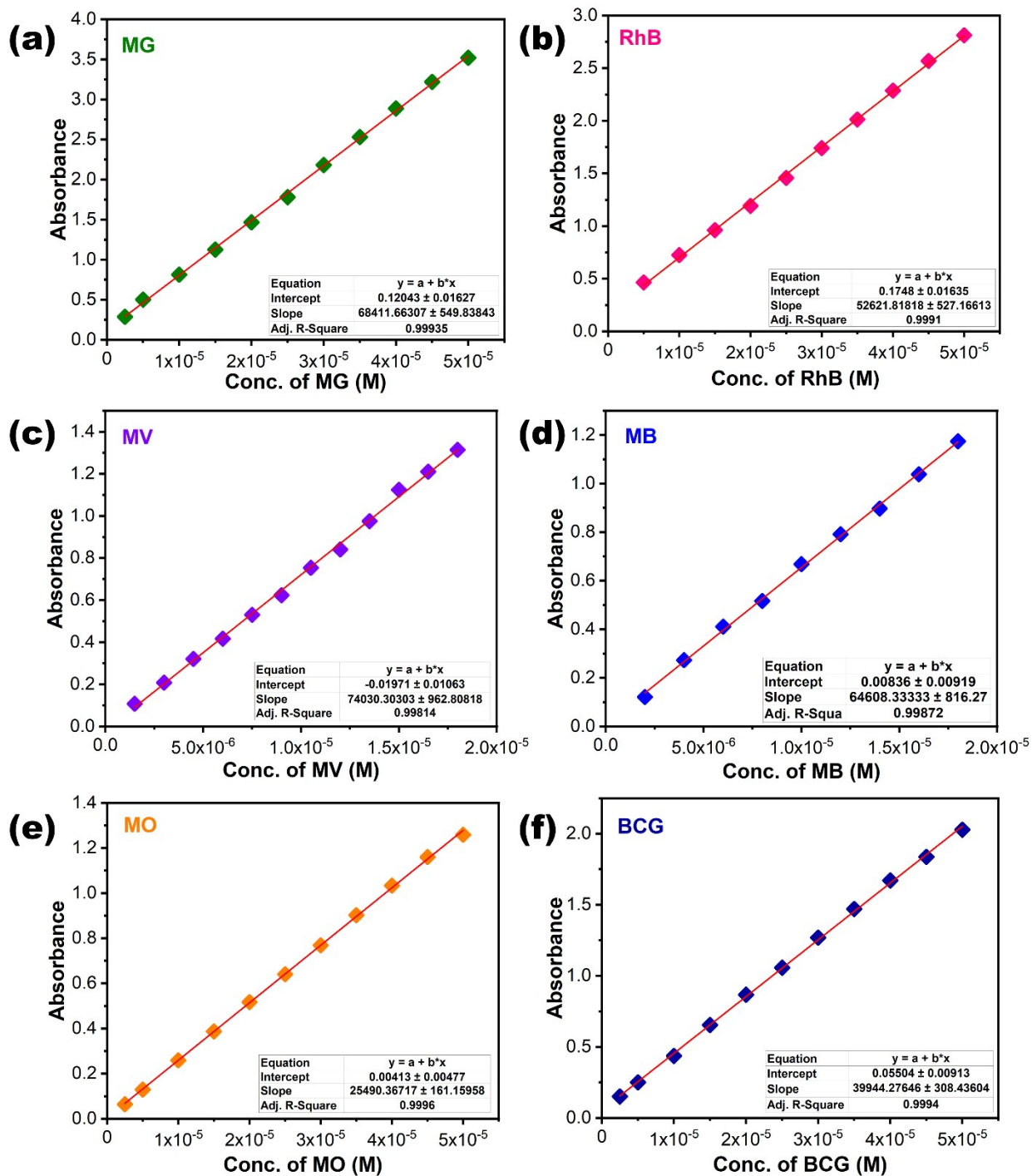
Figure S10. (a-f) UV-Vis absorbance vs concentration (calibration) plots of standard organic dyes MG, RhB, MV, MB, MO and BCG.
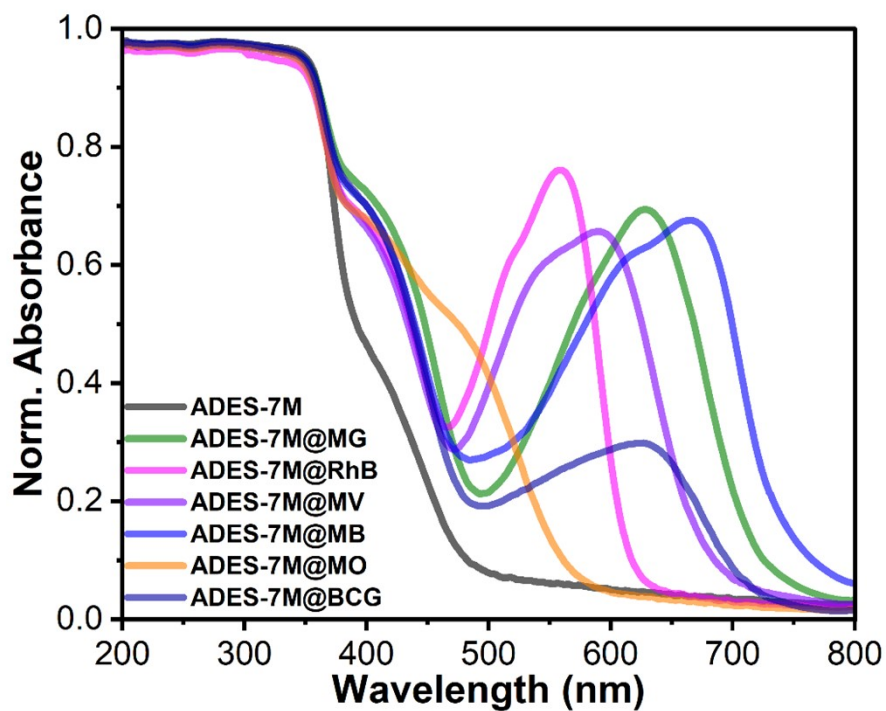
Figure S11. Solid state UV-vis spectra of ADES-**7M** and ADES-**7M**@Dye materials confirming the adsorbents characteristic bands at particular wavelengths after adsorption of organic dyes.
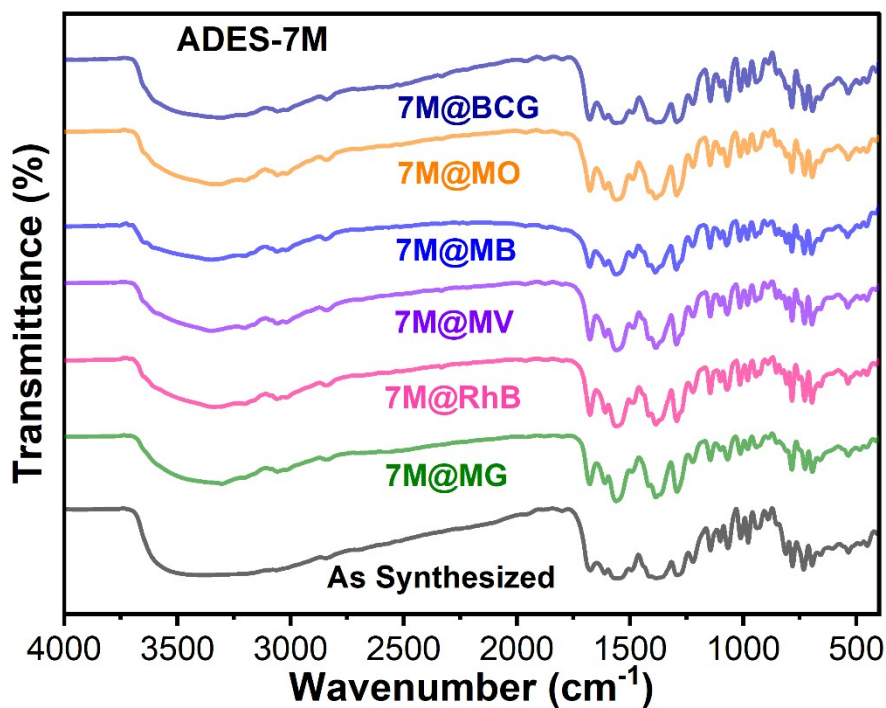

Figure S12. FTIR spectra of ADES-**7M** and ADES-**7M**@Dye materials confirming the retainment of characteristic bands after adsorption of organic dyes.
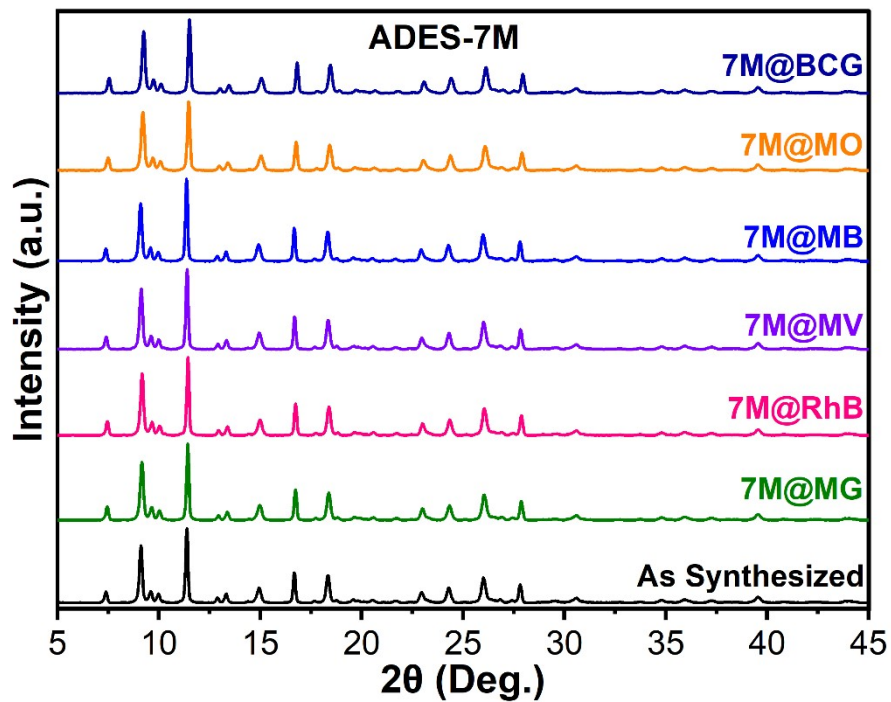
Figure S13. PXRD patterns of ADES-**7M** and ADES-**7M**@Dye materials confirming the phase stability of MOF after adsorption of organic dyes.
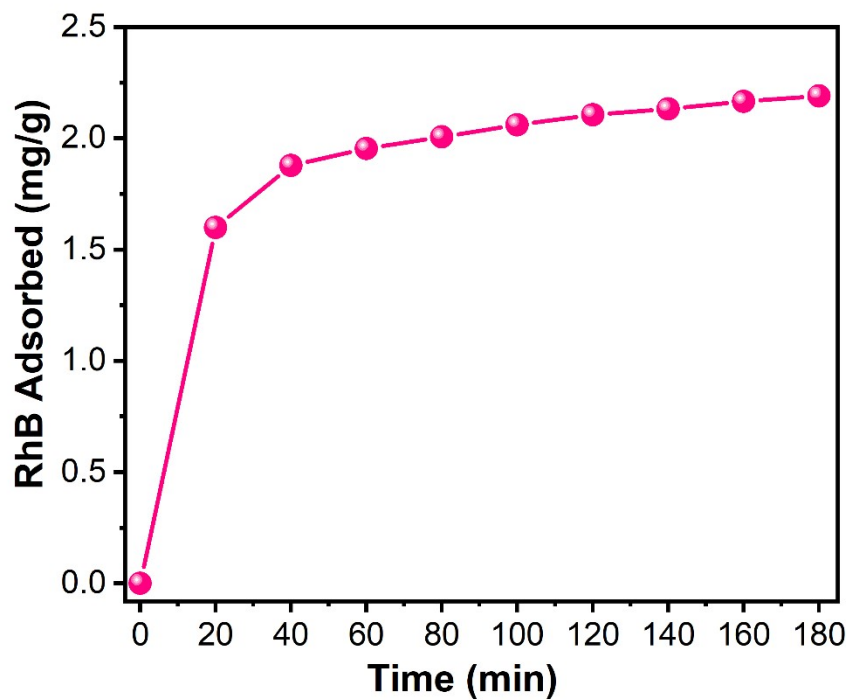

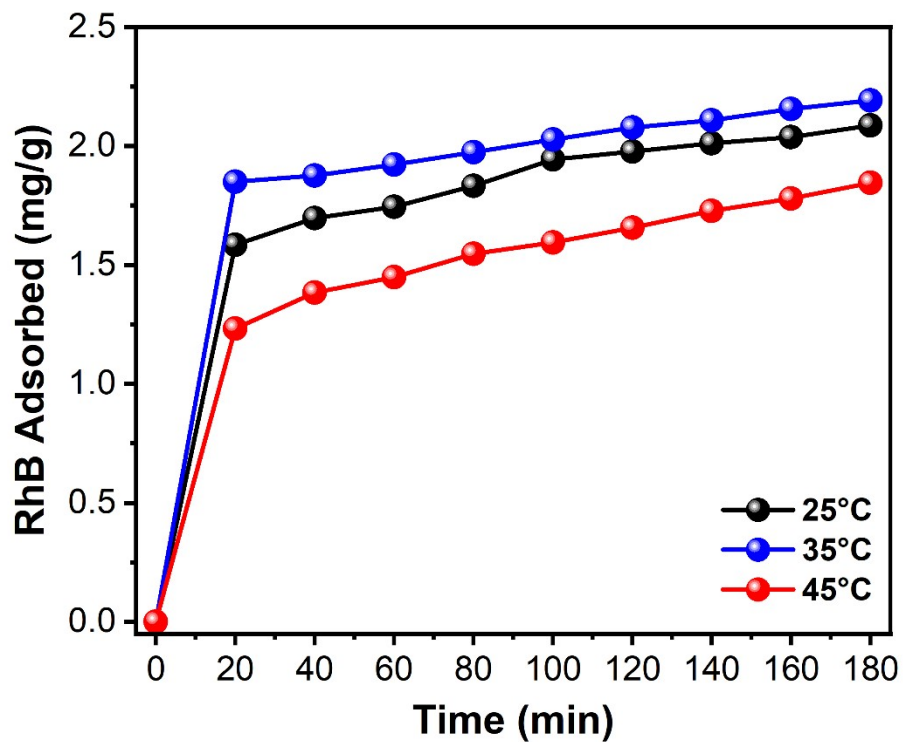**Figure S14.** Time dependent RhB adsorption capacity by ADES-**7M**.

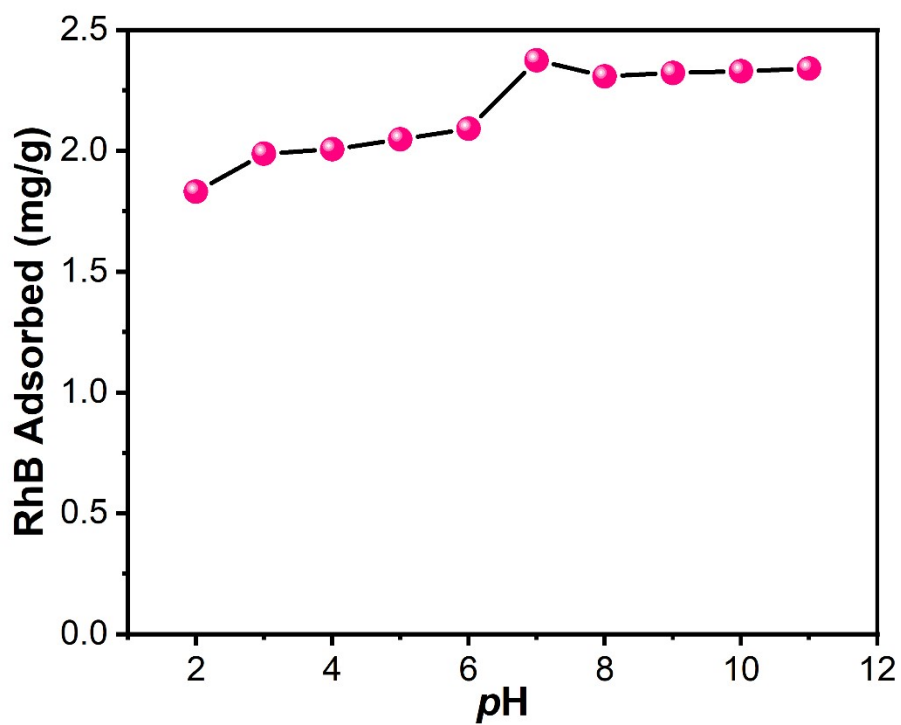**Figure S15.** Temperature dependent RhB adsorption capacity by ADES-**7M**.

Figure S16. *p*H dependent RhB adsorption capacity by ADES-**7M**.

(a)

$$\frac{1}{q_e} = \left(\frac{1}{q_{max}}\right) + \left(\frac{1}{q_{max}\,K_L}\right) C_e$$

Intercept	0.13743
Slope	0.02487
Adj. R-Sq.	0.95901
q_{max}	7.276
K_L	5.526

1/q_e (y-axis), 1/C_e (x-axis)

(b)

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$$

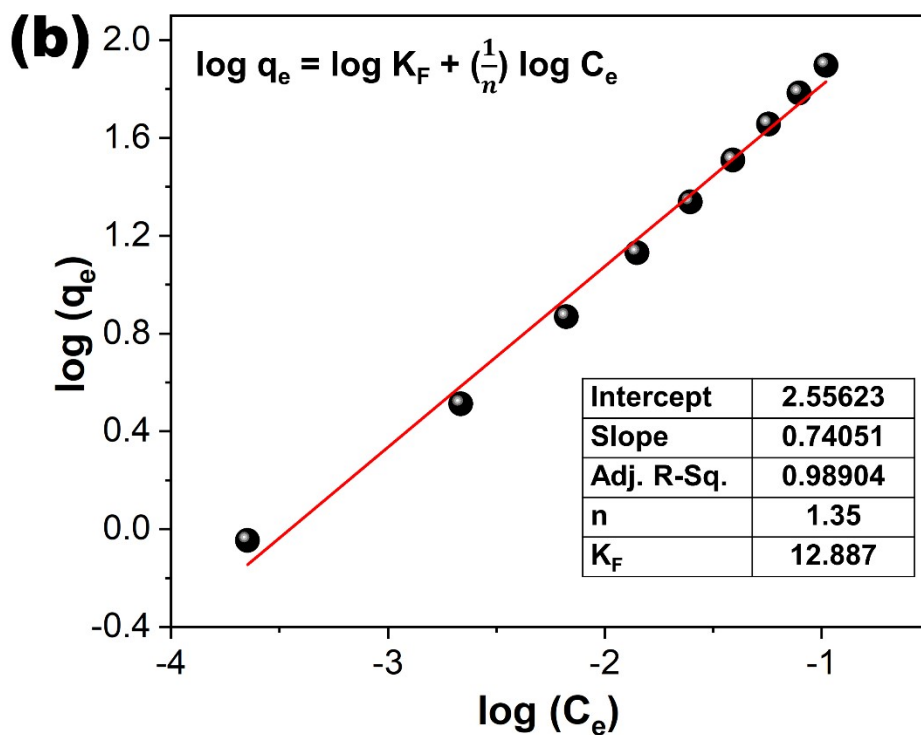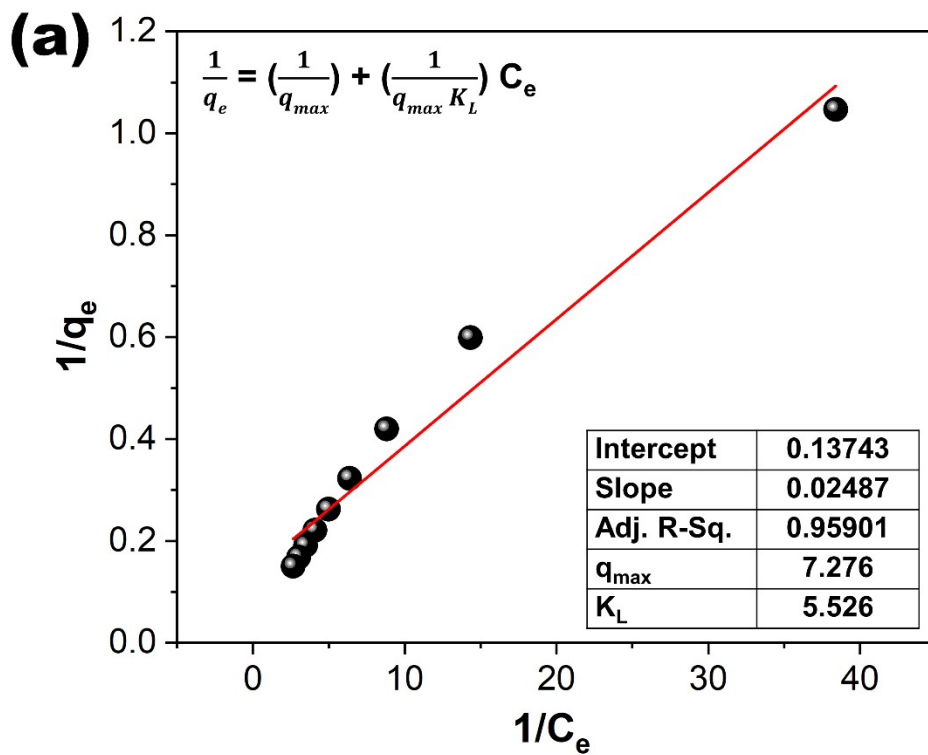| Intercept	2.55623
Slope	0.74051
Adj. R-Sq.	0.98904
n	1.35
K_F	12.887

log (q_e) (y-axis), log (C_e) (x-axis)

Figure S17. Langmuir (a) and Freundlich (b) isotherm fitting for RhB adsorption by ADES-**7M** (time = 180 min; conc. range = 2.00×10^{-5} to 1.40×10^{-4} M).
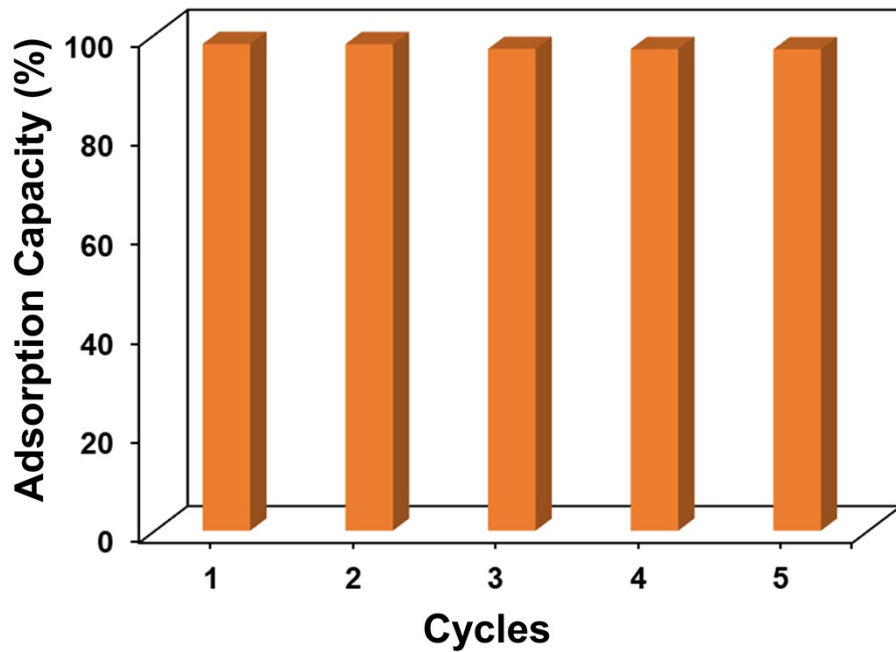
Figure S18. Recyclability test for RhB adsorption by ADES-**7M** at room temperature.
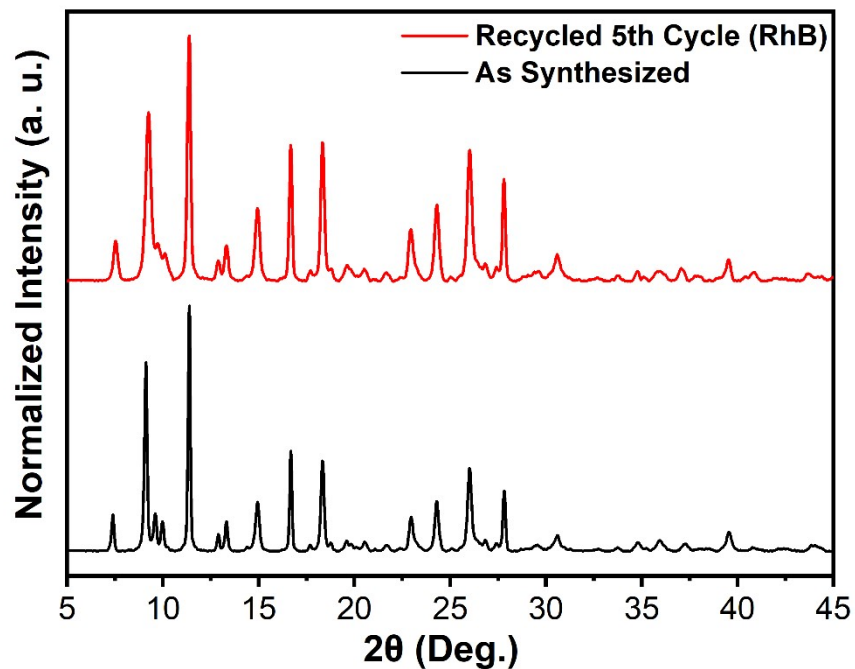

Figure S19. PXRD patterns of ADES-**7M** as synthesized and recycled after 5th cycle (RhB) confirming the phase stability of MOF after adsorption of dyes.

Table S2. Selected bond lengths and bond angles for **ADES-7**.

ADES-7			
Cd01-O1	2.250(3)	Cd01-O2	2.258(4)
Cd01-N1	2.325(3)	Cd01-N4	2.352(4)
Cd01-O5	2.367(3)	Cd01-O4	2.387(3)
Cd01-C8	2.722(4)	O1-C1	1.265(5)
O2-C1	1.234(6)	O3-C4	1.356(5)
O5-C8	1.250(5)	O4-C8	1.266(5)
O1-Cd01-O2	127.54(13)	O1-Cd01-N1	90.67(13)
O2-Cd01-N1	88.40(15)	O1-Cd01-N4	87.58(13)
O2-Cd01-N4	89.46(15)	N1-Cd01-N4	175.60(14)
O1-Cd01-O5	143.82(12)	O2-Cd01-O5	88.61(13)
N1-Cd01-O5	88.86(13)	N4-Cd01-O5	94.94(13)
O1-Cd01-O4	89.28(12)	O2-Cd01-O4	142.73(13)
N1-Cd01-O4	97.77(13)	N4-Cd01-O4	86.26(13)
O5-Cd01-O4	55.03(11)	O1-Cd01-C8	116.70(13)
O2-Cd01-C8	115.73(14)	N1-Cd01-C8	92.84(13)
N4-Cd01-C8	91.56(13)	O5-Cd01-C8	27.33(12)
O4-Cd01-C8	27.73(12)	C1-O1-Cd01	110.8(3)
C1-O2-Cd01	165.9(4)	C8-O5-Cd01	92.3(3)
C8-O4-Cd01	91.0(3)	C13-N1-Cd01	121.3(3)
C9-N1-Cd01	120.7(3)	C19-N4-Cd01	123.2(3)
C18-N4-Cd01	119.4(3)	O5-C8-O4	121.5(4)
O2-C1-O1	122.8(4)	O4-C8-Cd01	61.3(2)
O5-C8-Cd01	60.3(2)	C6-C8-Cd01	176.8(3)

Table S3. Details of hydrogen bonding interactions observed in **ADES-7**.

D-H···A	d(H···A) (Å)	d(D···A) (Å)	∠D-H···A (°)
ADES-7			
N2-H2C···O4[1]	1.96(6)	2.840(6)	176(7)
O3-H3C···O6[2]	2.02	2.799(6)	154
O3-H3C···N3[2]	2.54	3.182(6)	135
C7-H7···O5[3]	2.56(4)	3.542(6)	167(3)
C12-H12···O4[1]	2.43	3.248(6)	144
C17-H17···O3[4]	2.54	3.484(7)	172
C19-H19···O1[5]	2.57	3.195(7)	124
Symmetry code: 1. 1-x,1-y,1-z 2. x,1+y,1+z 3. -x,1-y,1-z 4. x,-1+y,-1+z 5. 1+x,y,-1+z			

References:

S1. B. Parmar, Y. Rachuri, K. K. Bisht and E. Suresh, Syntheses and Structural Analyses of New 3D Isostructural Zn(II) and Cd(II) Luminescent MOFs and their Application Towards Detection of Nitroaromatics in Aqueous Media, *ChemistrySelect*, 2016, **1**, 6308–6315.

S2. Y. Rachuri, S. Subhagan, B. Parmar, K. K. Bisht and E. Suresh, Selective and reversible adsorption of cationic dyes by mixed ligand Zn(ii) coordination polymers synthesized by reactant ratio modulation, *Dalton Trans.*, 2018, **47**, 898–908.

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