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Supporting Information

Pore size dependent cation adsorption in a nanoporous polymer film derived from a plastic columnar phase

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Materials and Instrumentation

The chemicals used were commercial products purchased from Acros, Sigma-Aldrich, Alfa Aesar, Merck or Biosolve and used without further purification.

FT-IR spectra were recorded at room temperature on a Perkin Elmer Spectrum Two spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory.

NMR spectra were recorded at room temperature on a Bruker, FT-NMR spectrometer AVANCE III HD-NanoBay (400 MHz, Bruker UltraSchield magnet, BBFO Probehead, BOSS1 shim assembly) in $CDCl_3$. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS, 0 ppm) an internal standard. Coupling constants are reported as J-values in Hz.

Column or flash chromatography was carried out using silica gel (0.035-0.070 mm, ca. 6 nm pore diameter).

MALDI-TOF-MS spectra were obtained on a PerSeptive Biosystems Voyager-DE PRO spectrometer, with α-cyano-4-hydroxycinnamic acid (CHCA) as matrix.

Polarized optical microscopy (POM) was performed with a Jeneval microscope equipped with crossed polarizers, a Linkam THMS 600 heating stage, and a Polaroid DMC le CCD camera.

Differential Scanning calorimetry (DSC) measurements were performed in hermetic T-zero aluminium sample pans using a TA Instruments Q2000 – 1037 DSC instrument equipped with a RCS90 cooling accessory. Transition temperatures and enthalpies were typically determined from the first cooling and first heating run using Universal Analysis 2000 software (TA Instruments, USA), with heating and cooling rates of 10 K min^{-1}.

XRD profiles were recorded on a Ganesha lab instrument equipped with a Genix-Cu ultra-low divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of $1x10^8$ photons s^{-1}. Diffraction patterns were collected using a Pilatus 300K silicon pixel detector with 487 x 619 pixels of 172 μm^2 placed at a sample to detector distance of 91 mm. Temperature was controlled with a Linkam HFSX350 heating stage and cooling unit. Measurements were performed on bulk samples sealed in 1.0 mm diameter glass capillaries, 0.01-mm-wall thickness (Hilgenberg).

UV/Vis absorption experiments were performed using a Cary 300 UV/Vis spectrophotometer equipped with peltier temperature controller. All experiments were performed in 10x10 mm quartz cuvets at 20 ^{o}C.

Solid state ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 MHz solid state spectrometer with 4 mm MAS probe.

Height profiles of thin polymer films were measured in a Vecco Dektak Profilometer.

Detailed experimental conditions:

Fabrication of nanoporous polymer thin films of [S]-COOH and [S]-COONa

10 mg of MeTB•GBA$_3$ or TB•GBA$_3$ complex in 0.3 mL 8:2 $CHCl_3$/MeOH (v/v) and 0.2 mg of Grubbs' catalyst, second generation in 30 µL $CHCl_3$ were mixed together in a 10 mL round-bottom flask and the solution was allowed to evaporate at 150 mbar pressure in a rotavap vacuum system while rotating the flask (rotational molding). The flask was then placed in a vacuum oven at 100 ^{o}C for 12 h. After successful polymerization of the above mentioned complexes, the polymer films were immersed in DMSO and shaken gently at room temperature for 2 days. After that DMSO was removed and the polymer films were washed with excess of methanol followed by washing with distilled water. The porous polymer films, [S]-COOH obtained from both MeTB•GBA$_3$ and TB•GBA$_3$ complexes, was dried before characterization. The –COOH groups of [S]-COOH in the pore surface were converted to –COONa groups ([S]-COONa) by treating with 10 mM aqueous solution of NaOH for 10-12 min. The reaction of NaOH with –COOH groups of [S]-COOH was monitored by FT-IR spectroscopy and was found to complete within ≈10 minutes of reaction time.

Fabrication of nanoporous polymer thin films of [B]-COONa and [B]-Pore-COOH

A piece of polymer or [S]-COOH (10 mg) was immersed in 6 mL of 1 M NaOH solution in EtOH:H_2O (23:1 v/v) and kept for 12 h at 45 °C without agitation. The resultant polymer film was washed with excess of methanol followed by distilled water, which afforded porous polymer film of [B]-COONa. The –COONa groups in [B]-COONa was converted to –COOH groups by reacting with EtOH:HCl (11:1 v/v) solution for 10-12 min. It is important to mention that [S]-COOH, [S]-COONa and [B]-COOH, [B]-COONa were prepared from MeTB•GBA$_3$ complex and used for different studies. However, formation of these porous polymers and their characterization were also further verified by preparing them from TB•GBA$_3$ complex.

Comparison of the amount of MB adsorbed in the pores of the porous polymers of [S]-COONa and [B]-COONa

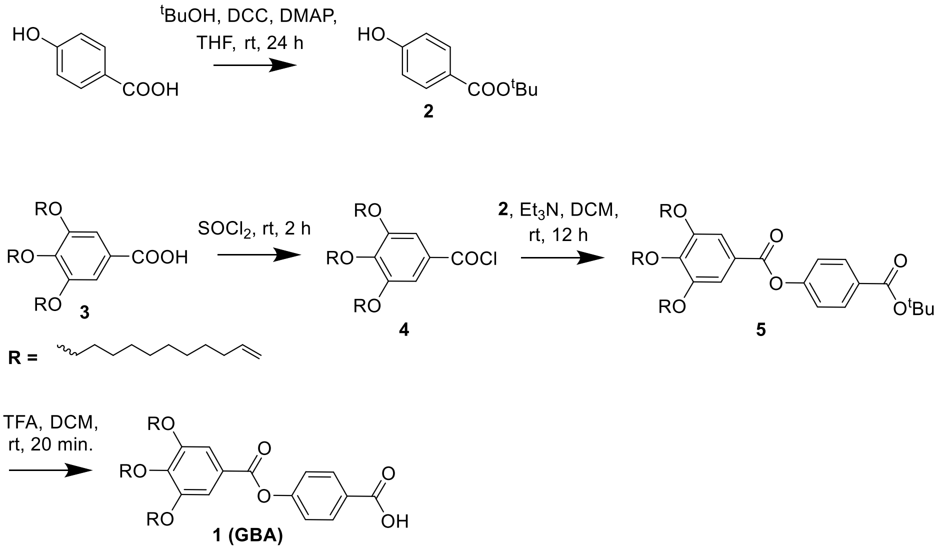
Molecular weights of each disc of [S]-COONa and [B]-COONa are 2181 and 1821 respectively. Accordingly 0.24 mg [S]-COONa and 0.2 mg of [B]-COONa were used for dye adsorption study in order to keep the number of –COONa groups same in both porous polymers. **For [B]-COONa:** Molar extinction coefficient (ε) of MB is 95000 cm^{-1} M^{-1}. Initial and final absorbance of the MB solution after adsorption experiment were 0.607 and 0.224 respectively. Therefore the concentration of MB before and after adsorption were 0.607/95000 M (or 6.4×10^{-6} M) and 0.224/95000 M (or 2.3×10^{-6} M) respectively as derived from the Lambert-Beer equation. From the above data, the number of MB molecules adsorbed in the big pores of [B]-COONa was calculated as ($N \times 6.05 \times 10^{-9}$) (where N is Avogadro's number). **For [S]-COONa:** Initial and final absorbance of the MB solution after adsorption experiment were 0.607 and 0.521 respectively. Therefore the concentration of MB before and after adsorption were 0.607/95000 M (or 6.4×10^{-6} M) and 0.521/95000 M (or 5.5×10^{-6} M) respectively as derived from the Lambert-Beer equation. From the above data, the number of MB molecules adsorbed in the small pores of [S]-COONa was calculated as ($N \times 1.36 \times 10^{-9}$) (where N is the Avogrado's number). This indicates that [B]-COONa adsorbs MB ~ $\{(N \times 6.05 \times 10^{-9})/(N \times 1.36 \times 10^{-9})\}$ or 4.5 times more than [S]-COONa although the intial rate of adsorption is almost similar for both porous polymers.

Estimation pore size from molecular van der Waals volumes

The van der Waals volumes (V_{vdW}) of the templates and the additionally removed material were calculated according to equation 4 from the paper of Zhao *et al.*[S1] The suggested corrections to further improve the results to fit with either the Tran or TSAR calculations had no major implications. The used molecular formulas for the different pores are given in Table 1. The pore diameter was estimated by calculating the diameter of a disk with a volume equal to the V_{vdW} of the removed material. For the disk height, the observed interdisk distance was used, which was set to 0.35 nm. The small pores had a diameter of ≈1.1 nm, the big pores were calculated to be ≈1.6 nm.

Supporting Information

Synthetic scheme:



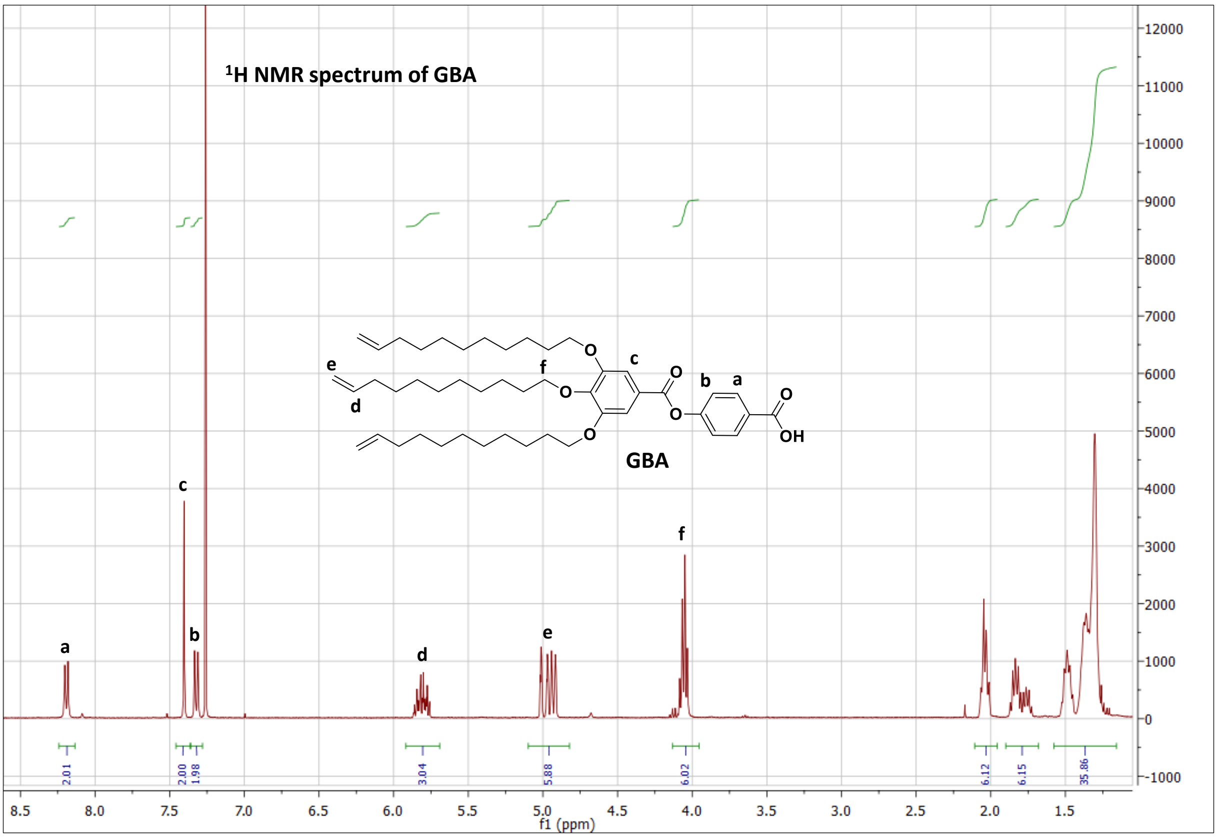
Synthetic procedures: Synthesis of compound **2**, **3** and template TB, MeTB were performed following reported procedures.[S2,S3,S4]

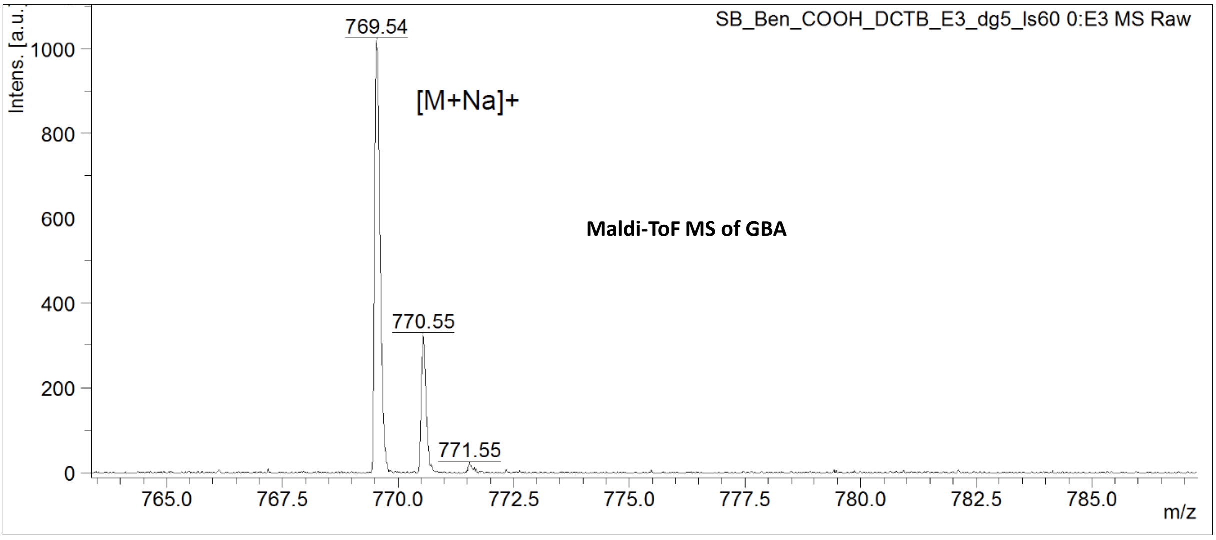
Synthesis of compound 1 (GBA): The compound **3** (3.24 g, 5.17 mmol) was reacted with $SOCl_2$ (5 mL) for 2 h at room temperature. Excess $SOCl_2$ was evaporated using high vacuum pump for approximately 45 minute to prepare compound **4**. A mixture of compound **4** (5.17 mmol) and compound **2** (1.1 g, 5.66 mmol) in 30 mL of dry DCM was subjected to Et_3N (1.43 mL, 10.3 mmol) at 0 °C. The reaction was continued for 12 h at room temperature. After completion of the reaction, the crude product was purified by silica column chromatography using hexane/EtOAc (1→4% v/v). Compound **5** was obtained as a viscous liquid in 90% yield. [^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.26-1.50 (m, 36 H), 1.61 (s, 9H), 1.72-1.86 (m, 6H), 2.01-2.06 (m, 6H), 4.03-4.08 (m, 6H), 4.91-5.02 (dd, 6H, *J* = 12 Hz and 16 Hz, 3 x CH_2=CH), 5.76-5.86 (ddt, 3H, *J* = 7, 10 and 17 Hz, 3 x CH2=C*H*-CH_2), 7.23-7.25 (d, *J* = 8 Hz, 2H, aromatic CH), 7.4 (s, 2H, gallate aromatic C*H*), 8.05-8.07 (d, *J* = 8 Hz, 2H, aromatic CH). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.07, 28.21, 28.95, 28.98, 29.15, 29.20, 29.29, 29.37, 29.45, 29.54, 29.56, 29.66, 30.34, 33.81, 69.29, 73.59, 81.22, 108.64, 114.12, 121.62, 123.50, 129.62, 130.99, 139.19, 143.20, 152.99, 154.32, 164.59, 165.03; ATR FT-IR (Neat, cm^{-1}): 3076, 2924, 2854, 1738, 1715, 1641, 1586, 1503, 1466, 1430, 1335, 1289, 1185, 1156, 1115, 1017, 992, 908, 851, 752, 722, 689].

To a solution of compound **5** (0.7 g) in 2 mL of dry DCM, 2 mL of TFA was added and the reaction was continued at room temperature for ~20 min. The reaction was quenched by adding saturated $NaHCO_3$ solution. The crude product was extracted with $CHCl_3$ (30 mL), in which 10 mL of H_2O was added. The pH of the water layer was adjusted to 2 before extracting the $CHCl_3$ layer. The crude product was purified by silica column chromatography using $CHCl_3$/MeOH (1→5% v/v). Compound **1** (**GBA**) was obtained as a white solid in 95% yield. ^{1}H

NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 1.26-1.51 (m, 36 H), 1.73-1.87 (m, 6H), 2.01-2.07 (m, 6H), 4.03-4.08 (m, 6H), 4.91-5.02 (dd, 6H, *J* = 12 Hz and 16 Hz, 3 x C*H*$_2$=CH), 5.76-5.87 (ddt, 3H, *J* = 7, 10 and 17 Hz, 3 x CH2=C*H*-CH$_2$), 7.31-7.33 (d, *J* = 8 Hz, 2H, aromatic CH), 7.4 (s, 2H, gallate aromatic C*H*), 8.18-8.20 (d, *J* = 8 Hz, 2H, aromatic CH). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ = 26.07, 28.95, 28.98, 29.15, 29.20, 29.29, 29.37, 29.46, 29.54, 29.57, 29.66, 30.34, 33.81, 33.84, 69.31, 73.61, 108.67, 114.13, 122.03, 123.31, 126.76, 131.91, 139.19, 143.31, 153.01, 155.44, 164.46, 170.44. ATR FT-IR (Neat, cm^{-1}): 3076, 2921, 2850, 1735, 1691, 1640, 1587, 1503, 1465, 1429, 1339, 1198, 1127, 1088, 992, 908, 856, 748, 727, 633, 546; Maldi-Tof MS: *m/z* calculated for $C_{47}H_{70}O_7$ (M+Na)$^+$: 769.51, found: 769.54.

Supporting Information





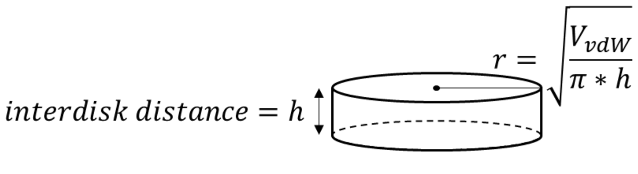
Supporting Information

Table S1. Principal spacing of monomer complexes MeTB•GBA$_3$ and TB•GBA$_3$, polymers and porous polymers derived from XRD data.

Materials	**Pricipal spacing in materials derived from MeTB as template/ nm**	**Pricipal spacing in materials derived from TB as template/ nm**
Monomer complex	3.93	3.98
Polymer	3.91	3.73
[S]-COOH	3.74	3.58
[S]-COONa	3.67	3.75
[B]-COOH	2.95	3.07
[B]-COONa	3.07	2.96

Table S2. Calculation of van der Waals Volumes and estimated pore diameters of the porous polymer thin films. Diameters along the short axis of the cationic dyes were also included in the table which were calculated as shown in figure S11.

Template that was removed	**Formula**	**V_{vdW} / Å^3**	**Diameter of the pore / nm**
TB	$C_{27}H_{18}N_6$	338.8	1.11
TB & Benzoic acid	$C_{48}H_{36}N_6O_6$	660.7	1.55
MeTB	$C_{30}H_{24}N_6$	389.4	1.19
MeTB & Benzoic acid	$C_{51}H_{42}N_6O_6$	712.8	1.61
Cationic dyes	**Formula**	**Diameter along the short axis / nm**	
MB	$C_{28}H_{31}N_2O_3Cl$	0.6	
R6G	$C_{16}H_{18}ClN_3S$	0.8	
AB8G	$C_{56}H_{68}Cl_4CuN_{16}S_4$	1.4	



Schematic representation of pore size calculation when assuming the template is a perfect disk.

Supporting Information

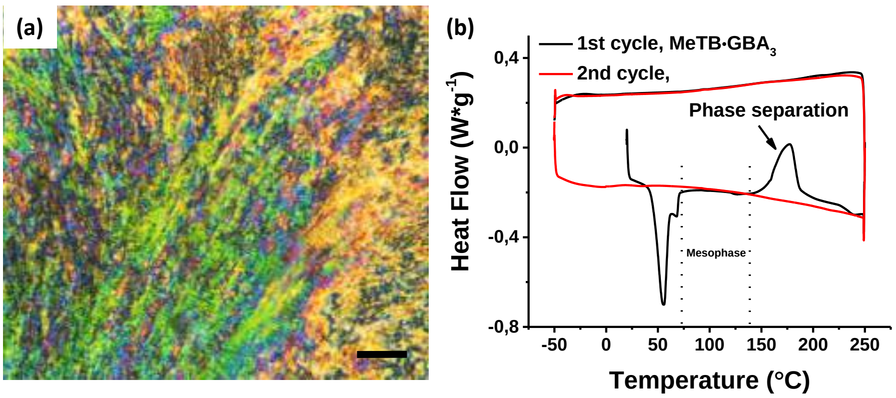


Figure S1. (a) Plastic columnar mesophase of the hydrogen-bonded MeTB•GBA$_3$ complex observed by POM at 100 °C (scale bar represents 100 µm). (b) DSC curves of MeTB•GBA$_3$ complex obtained at 10 °C/min.

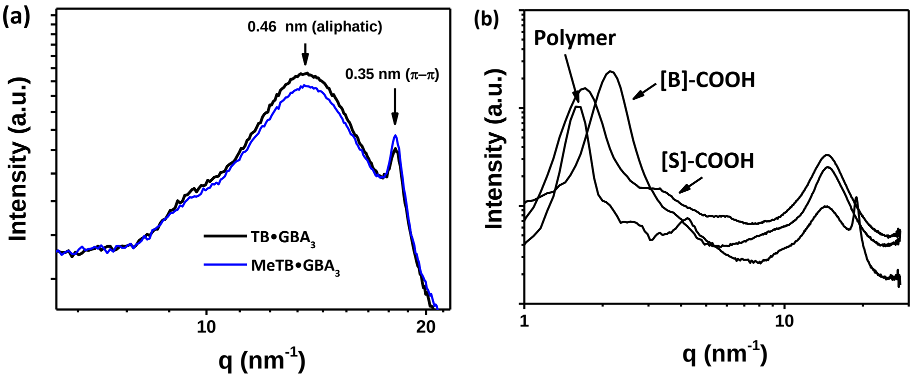


Figure S2. (a) Wide angle XRD data of the mesophases showing two peaks at 0.46 nm and 0.35 nm for both complexes at 100 °C. (b) XRD patterns of the thin films of polymer, [S]-COOH and [B]-COOH derived from MeTB•GBA$_3$ complex.

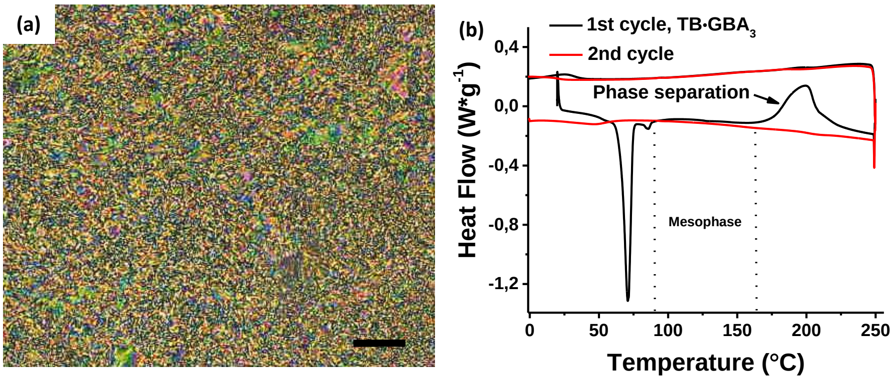
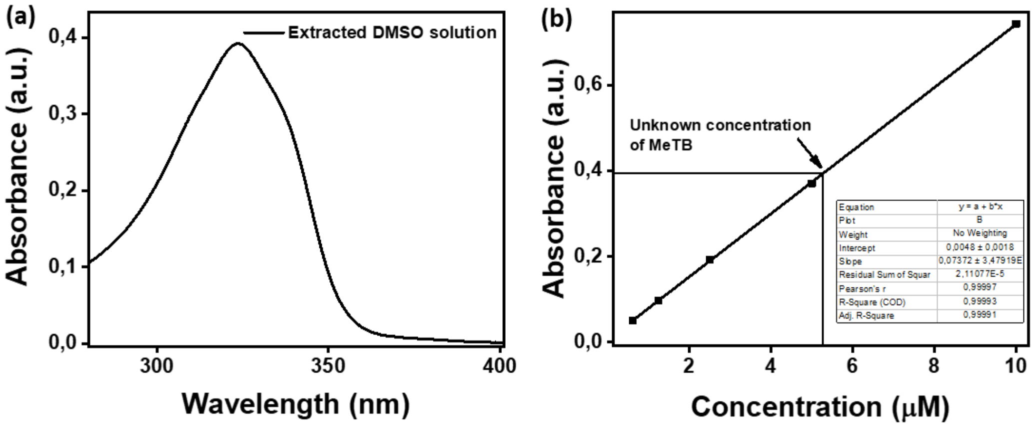


Figure S3. (a) Plastic columnar mesophase of the hydrogen-bonded TB•GBA$_3$ complex observed by polarized optical microscopy (POM) at 100 °C (scale bar represents 100 µm). (b) DSC curves of TB•GBA$_3$ complex obtained at 10 °C/min.



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0,0048 ± 0,0018
Slope	0,07372 ± 3,47919E
Residual Sum of Squar	2,11077E-5
Pearson's r	0,99997
R-Square (COD)	0,99993
Adj. R-Square	0,99991

Figure S4. (a) UV/Vis absorption spectrum of the extracted DMSO solution (DMSO has UV/Vis cut-off wavelength of 268 nm). A polymer film derived from MeTB•GBA$_3$ complex (0.32 mg) was immersed in 1.5 mL DMSO for template, MeTB removal. The solution was diluted 15 times for UV/Vis measurement. (b) The unknown concentration of MeTB in the diluted, extracted solution was determined to be ~5.3 μM from a calibration curve of known concentrations, which indicated ~96% removal of MeTB from the polymer.

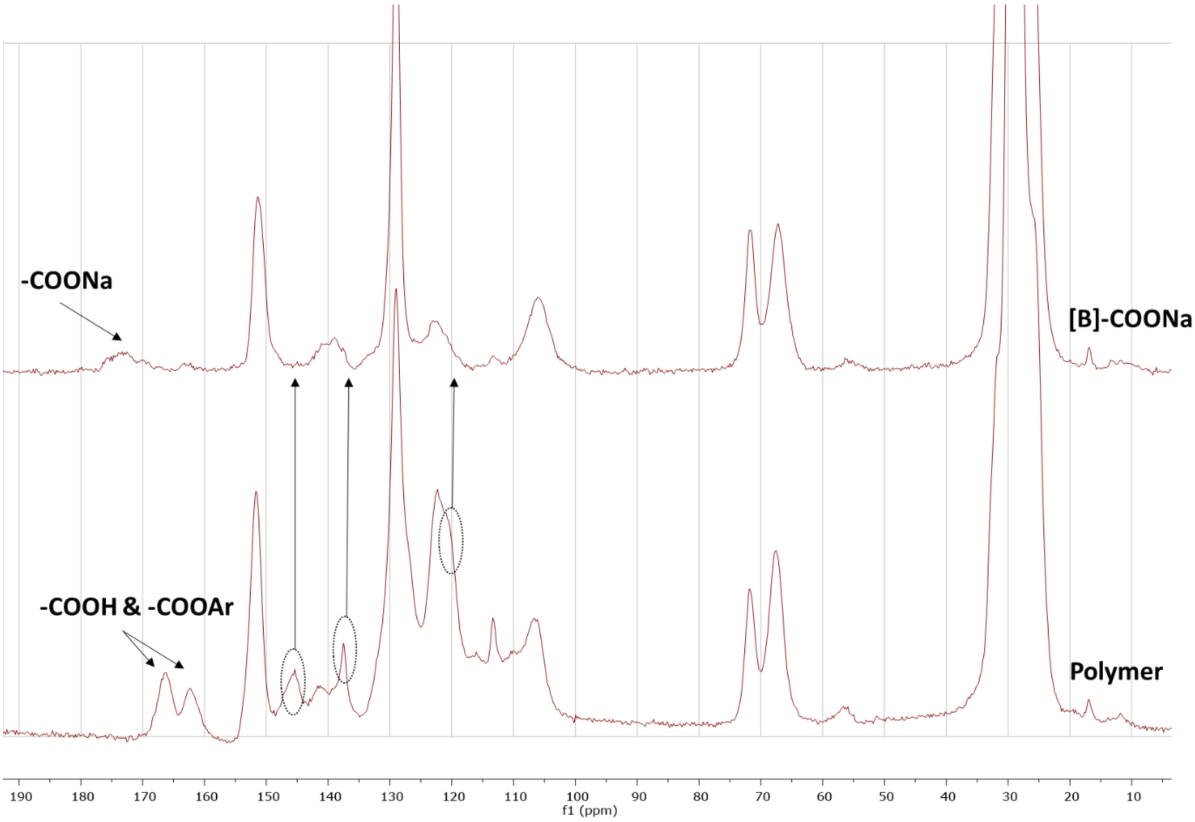


Figure S5. Solid state ^{13}C NMR spectra of the native polymer derived from TB•GBA$_3$ complex and the porous polymer [B]-COONa. The analysis of the spectra clearly showed two broad peaks at 160-170 ppm range that corresponds to the C-atoms in the ester and carboxylic group of GBA in the polymer derived from TB•GBA$_3$ complex. However, in the porous polymer, [B]-COONa, a new broad peak in the range of 170-177 ppm appeared in exchange of the two peaks at 160-170 ppm range observed in the native polymer, which confirms hydrolysis of the ester linkage of GBA in the polymer during the fabrication of [B]-COONa. In addition, the peak population in the range of 100-150 ppm was significantly reduced in the porous polymer relative to the native polymer. This result clearly indicate removal of template TB and the benzoic acid moiety of GBA during hydrolysis step. It is important to mention that, the ^{13}C NMR signals from the C-atoms of protonated TB are known to appear between 100-150 ppm.[S5]

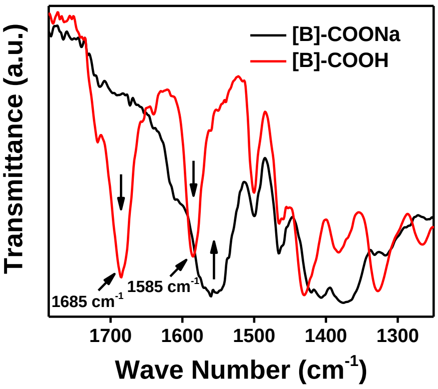


Figure S6. Comparison of FT-IR spectra of the porous polymer [B]-COOH lined with –COOH groups in the pore with [B]-COONa lined with –COONa surface groups.

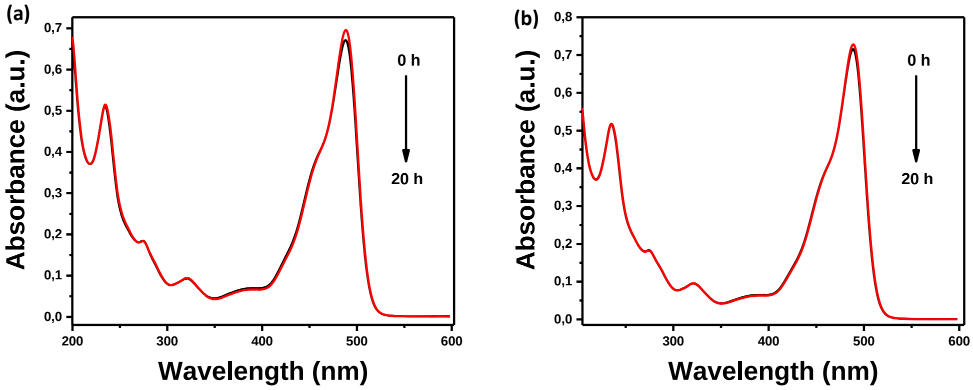


Figure S7. UV/Vis absorption spectra demonstrating negligible adsorption of SF (6 µM) after 20 h by (a) [S]-COONa and (b) [B]-COONa porous polymer films respectively.

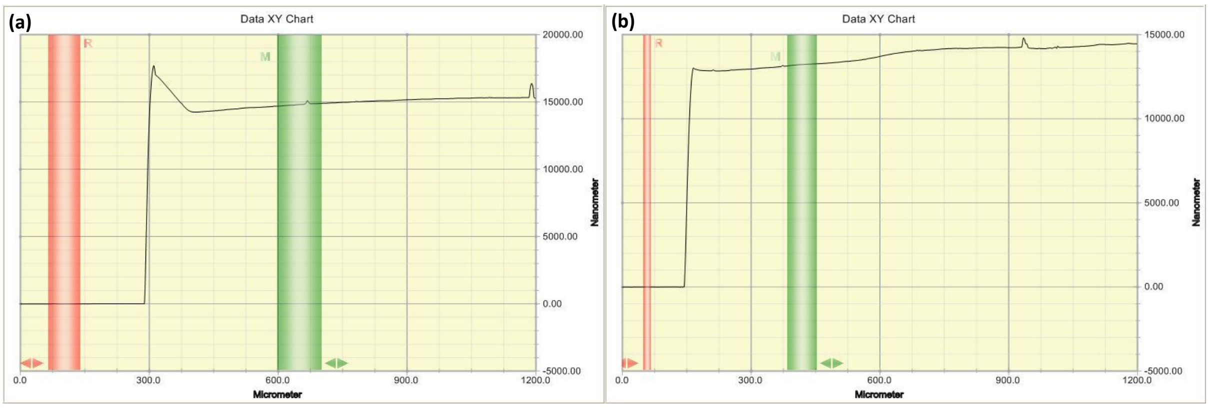


Figure S8. (a,b) Height profiles of [S]-COOH, [S]-COONa and [B]-COOH, [B]-COONa thin films utilized for dye and alkali metal ions adsorption studies respectively.

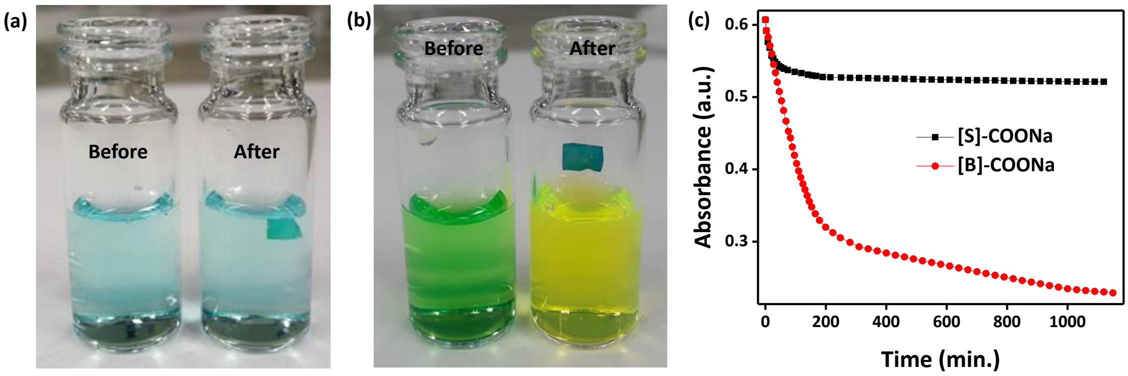


Figure S9. (a) The color of the MB solutions and the porous polymer thin film did not change appreciably after adsorption of MB dye from solution by [S]-COONa for 20 h. (b) [MB (6.4 µM) + SF (6 µM)] solution before and after adsorption by [B]-COONa porous film. The [B]-COONa porous film turned deep blue after adsorption. (c) Absorbance at 665 nm versus time showing rate and relative amount of adsorption of MB by [S]-COONa and [B]-COONa.

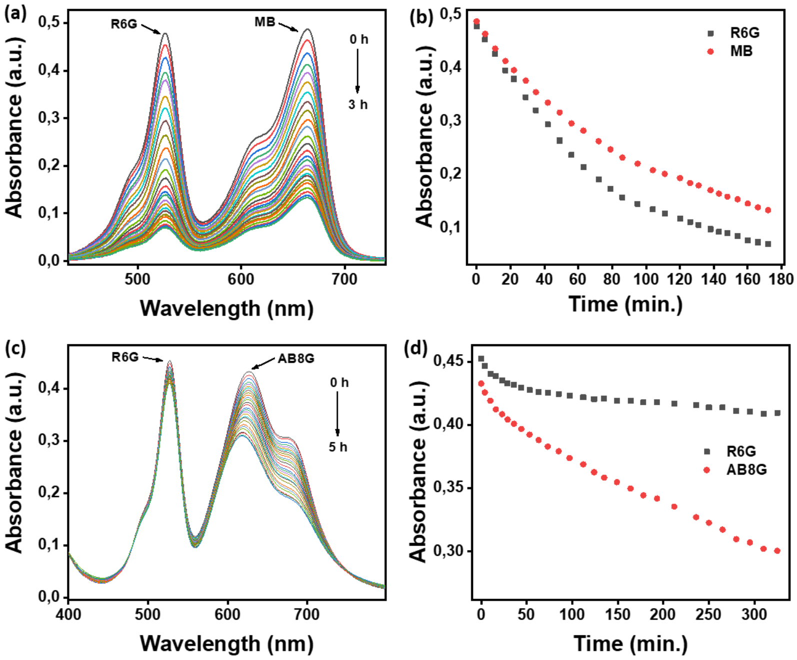


Figure S10. Monitoring simultaneous adsorption of the cationic dyes (a) MB (5.2 µM) + R6G (4.1 µM) and (c) AB8G (3.6 µM) + R6G (3.9 µM) by anionic [B]-COONa porous films (0.35 mg and 0.3 mg respectively) in aq. medium using UV/Vis absorption spectroscopy**.** Plot b and d showed the decrease in absorbance of the dyes at their absorption maximum versus time.

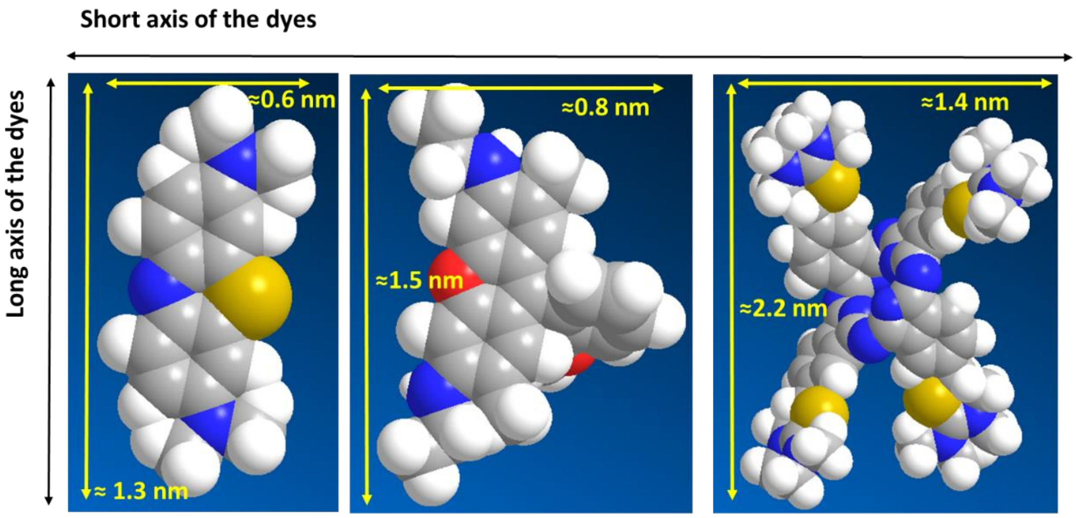


Figure S11. Space filling molecular structures of the MB, R6G and AB8G respectively derived from the Chem3D software. Anisotropic shape of the dyes are shown by using lengths along the short and long axis respectively. Chloride counter anions in the dye molecules were not considered for calculation of the short and long axis diameters in the dye molecules as only the cationic counter part of the dyes adsorbed in the pores. We believe that the dye enters in the pores along the long axis during adsorption. Therefore only the short axis length is considered as a measure of their variable sizes.

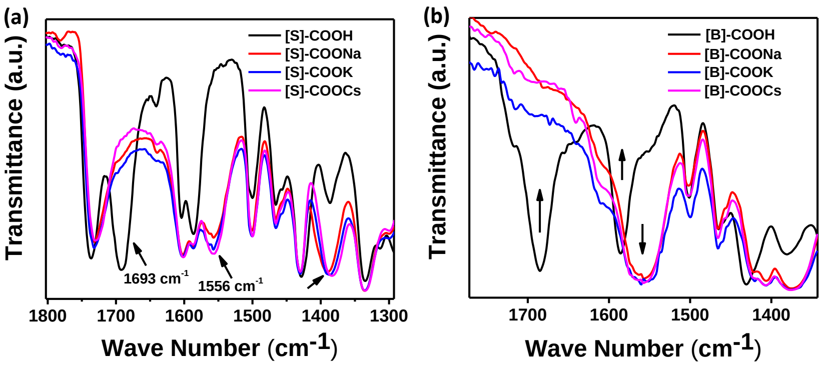


Figure S12. (a,b) FT-IR spectra of [S]-COOH, [B]-COOH porous polymer films and their sodium, potassium and cesium carboxylate salts after exposure to 10 mM aqueous solutions of the corresponding hydroxides for 10 minutes**.**

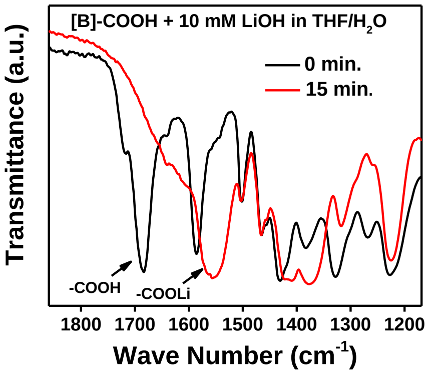


Figure S13. FT-IR spectra showing quantitative formation of [B]-COOLi from [B]-COOH porous polymer film in THF/H_2O (1:1 v/v) within 15 min.

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(S1) Y. H. Zhao, M. H. Abraham and A. M. Zissimos, *J. Org. Chem.*, **2003**, *68*, 7368–7373.

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(S4) G. M. Bögels, J. A. M. Lugger, O. J. G. M. Goor and R. Sijbesma, *Adv. Funct. Mater., **2016**, 26*, 8023-8030.

(S5) X. Feng, K. Kawabata, G. Kaufman, M. Elimelech and C. O. Osuji, *ACS Nano*, 2017, **11**, 3911–3921.