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Supporting Information

A Luminescent Zr-Based Metal-Organic Framework for Sensing/Capture of Nitrobenzene and High-Pressure Separation of CH_4/C_2H_6

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Experimental Section

All reagents and solvents for synthesis were used as received from commercial suppliers without further purification. All gases used in experiments were provided by Beijing AP BAIF Gas Industry Co. Ltd. (Beijing, China). The purity of He, H_2, CH_4, N_2 and CO_2 is higher than 99.99 % and that of C_2H_6 is higher than 99.9 %. The composition of the gas mixture used in experiments was 57.61 % of CH_4, and 42.39 % of C_2H_6.

Powder X-ray diffraction patterns (PXRD) were recorded on a Rigaku Dmax / 2400 X-ray diffractometer operating at 40 kV and 100 mA, using Cu-Kα radiation. Thermogravimetric analysis (TGA) was carried out using a Q600SDT TGA–DTA–DSC thermal analyzer from room temperature to 800 °C with a heating rate of 5 °C min^{-1} in a flowing nitrogen atmosphere. Gas sorption data were collected by a QUANTACHROME AUTOSORB-IQ gas adsorption analyzer. The PL spectra were recorded on a Hitachi F7000 fluorescence spectrophotometer at room temperature. The photomultiplier tube (PMT) voltage was 600 V, the scan speed was 240 nm / min and the slit width of excitation and emission was 2.5 nm. ^1H (^{13}C) NMR measurements were conducted on Bruker AV 400 NMR Spectrometer at ambient temperature unless specifically mentioned (**Figure S4-9**).

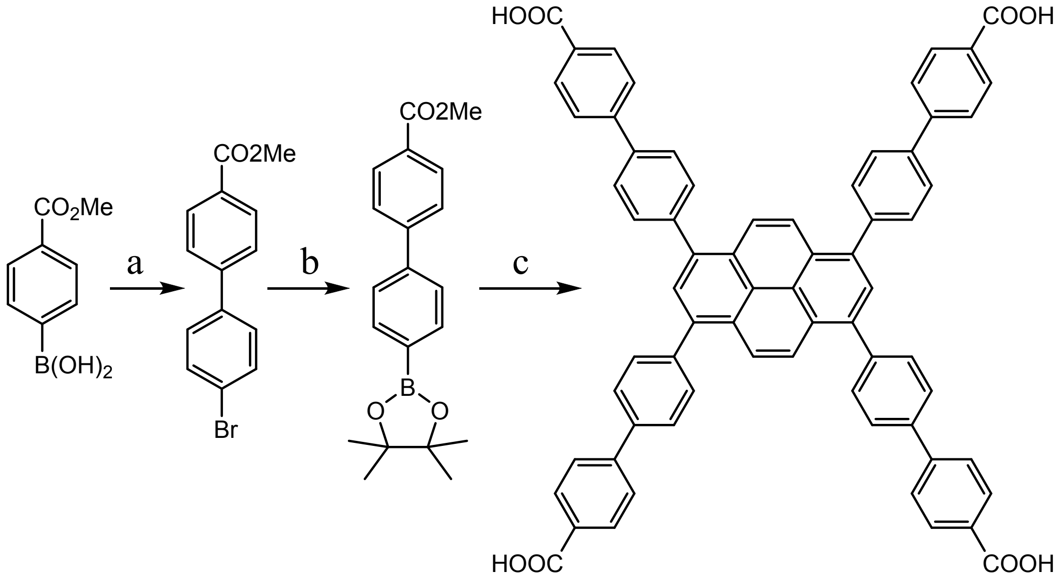
Synthesis of 1,3,6,8-tetra(4-carboxylbiphenyl)pyrene: As shown in scheme S1, a mixture of 1-bromo-4-iodobenzene(5.94 g, 21 mmol), 4-(methoxycarbonyl)phenylboronic acid (3.60 g, 20 mmol), K_2CO_3 (6.90 g, 65 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.5 mmol%) in anhydrous 1,4-dioxane (60 mL) was stirred under argon for 24 h at 80 °C. Afterthat the mixture was cooled to room temperature and filtered subsequently to remove insoluble salts which were washed further with EtOAc. The filtrate was concentrated *in vacuo* and the residue was washed three times with hexane and left to dry in air without further purification. Yield: 61.62 %.[S1] ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12-8.07(m, 2H, Ph*H*CO_2CH_3), 7.81-7.78 (m, 2H, Ph*H*CO_2CH_3), 7.63-7.60 (m, 2H, BrPh*H*), 7.37-7.34 (m, 2H, BrPh*H*), 3.94 (s, 3H, CO_2CH_3) (Figure S4). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.84, 144.44, 139.50, 138.06, 130.23, 129.33, 129.05, 126.81, 94.16, 52.19.

A mixture of methyl (4'-bromobiphenyl)-4-carboxylate (3.58 g, 12.3 mmol), bis(pinacolato)diboron (3.436 g, 13.5 mmol), KOAc (3.62 g, 36.9 mmol) and $(Ph_3P)_2PdCl_2$ (0.216 g, 2.5 mmol%) in anhydrous 1,4-dioxane (60 mL) was stirred under argon for 24 h at 90 °C. Afterward the mixture were cooled to room temperature and filtered subsequently to remove insoluble salts which were washed further with EtOAc. The filtrate was concentrated *in vacuo* and the residue was recrystallized from hot hexanes (30 mL). Yield: 65.95 %.[S1] ^1H NMR (400 MHz, $CDCl_3$) δ（ppm) 8.11 (dd, 2H, Ph$H$$CO_2CH_3$), 7.96 (d, 2H, BPh$H$), 7.68 (dd, 2H, Ph$H$$CO_2CH_3$), 7.63 (d, 2H, BPh$H$), 3.94 (s, 3H, CO_2CH_3), 1.37 (s, 12H, $(CH_3)_2CC(CH_3)_2$) (Figure S5). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.97, 145.44, 142.59, 135.37, 130.10, 129.15, 127.16, 126.57, 83.94, 52.15, 24.89.

A mixture of 1,3,6,8-tetrabromopyrene (0.84 g, 1.62 mmol), methyl 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-carboxylate (2.74 g, 8.11 mmol), K_2CO_3(1.79 g, 12.98 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.5 mmol%) in anhydrous 1,4-dioxane (30mL) was stirred under argon for 72 h at 85 °C. The reaction mixture was poured into ice water containing concentrated hydrochloric acid (3:1). The organic phase was extracted with chloroform and dried over anhydrous Na_2SO_4, the solvent was taken away under reduced pressure. The residue was recrystallized with hot toluene, yield: 68.25 %.[S3] ^1H NMR (400 MHz, $CDCl_3$) δ（ppm) 8.29 (s, 4H, Pyrene$H$), 8.17 (d, 8H, Biph$H$), 8.11 (s, 2H, Hpyrene), 7.84-7.78 (m, 24H, Biph$H$), 7.27-7.17 (m, CH_3PhH),[S2]3.97 (s, 12H, CO_2CH_3), 2.36 (S, PhCH_3) [S2] (Figure S6).

A solution of NaOH (6 g) in H_2O (10 mL) was added to a suspension of 1,3,6,8-tetra[(4-methoxycarbonyl)biphenyl]pyrene (1 g) in THF/dioxane/H_2O (100 mL, ratio: 5/2/2) and the resulting biphasic solution was stirred under reflux at 85 °C for 36 h. The solvent was removed under vacuum, and then H_2O was added to the residue. The yellow clear solution was acidified with concentrated

HCl until pH < 2, the resulting yellow solid was collected by filtration, washed with water and MeOH in turn, and then dried under vacuum.[S3] Taking into account of the poor solubility and characterization of the ligand, ^{1}H (^{13}C) NMR and ^{1}H-^{1}H COSY measurements were conducted at 40 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.96 (s, 4H, BiphenylCOO*H*), 8.17 (s, 4H, 4, 5, 9 and 10-Pyrene*H*), 8.05 (d, 8H, J = 8 Hz, 3', and 5'-Biphenyl*H*), 8.00 (s, 2H, 2 and 7-Pyrene*H*), 7.84 (d, 16H, J = 8 Hz, 3, 5, 2' and 6'-Biphenyl*H*), 7.69 (d, 8H, J = 8 Hz, 2, and 6-Biphenyl*H*) (Figure S4-5). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 167.51, 144.17, 140.35, 138.68, 131.59, 130.50, 130.36, 127.99, 127.60, 127.24, 127.10, 126.00, 125.70 (Figure S6).



Scheme S1 Synthesis of the ligand H_4TCBPPy. Reagents and conditions: a) K_2CO_3, 1-bromo-4-iodobenzene, $Pd(PPh_3)_4$, 1,4-dioxane, 80 °C. b) bis(pinacolato)diboron, KOAc, $(PPh_3)_2PdCl_2$, 1,4-dioxane, 90 °C. c) 1,3,6,8-tetrabromopyrene, K_2CO_3, $Pd(PPh_3)_4$, 1,4-dioxane, 85 °C; NaOH, THF/dioxane/H_2O, 85 °C.

Synthesis of $Zr_6O_4(OH)_4(TCBPPy)_3$, LMOF-1. H_4TCBPPy (23.67 mg, 0.024 mmol), $ZrCl_4$ (56 mg, 0.024 mmol) in 10 mL of DMF were ultrasonically dissolved in a 25 mL vial. After the addition of acetic acid (2 mL), the vial was capped and heated at 90 °C for 48 h before being cooled to room temperature slowly. Yellow cubic single crystals were obtained and washed by DMF, Zr (IV)-based yield of 62.78 %.

Table S1 Crystal structure data and structure refinement for **LMOF-1**.

Identification code	**LMOF-1**
Empirical formula	$C_{34}H_{19}O_{5.34}Zr$
Formula weight	604.15
Temperature/K	180(2)
Crystal system	cubic
Space group	*P*m-3m
a, *b*, *c*/Å	24.2929(4)
α, β, γ/°	90°
Volume/Å^3	14336.2(4)
Z	6
P_{calc} mg/mm^3	0.420
μ/mm^{-1}	0.127
F(000)	1834.0
Crystal size/mm^3	0.10 0.09 0.06
2Θ range for data collection	6.89° to 50.05°
Index ranges	
Reflections collected	10984
Independent reflections	3067
Data/restraints/parameters	2865/15/46
Goodness-of-fit on F2	0.966
Final R indexes [I>=4σ (I)]	R_1=0.0917, wR_2=0.2731
Final R indexes [all data]	R_1=0.1183, wR_2=0.3822

Activaion of LMOF-1. Prior to the sorption measurement, the as-synthesized sample LMOF-1 was immersed in DMF for around two days, during which DMF was refreshed several times. Then the sample was further dried under vacuum at 100 °C overnight followed by an “outgas” function of the adsorption instrument at 150 °C for 5 h. As discussed above, the activated sample LMOF-1a still has good crystallinity after the removal of solvent molecules.

Fluorescence measurement. All samples were measured in solid phases. The as-synthesized sample **LMOF-1** was evacuated at 150 °C under vacuum overnight to give the activated sample **LMOF-1a**. The samples used in Figure S4 were prepared by introducing 10.0 mg of **LMOF-1a** crystals/powders into 10 mL of DMF, toluene benzene, acetone, ethanol, cyclohexane and nitrobenzene, respectively, kept in the ultrasonic bath for 5 mins, in air for 3 d standing, then filtered under vacuum to remove the solvents. Similarly, the samples in Figure 3 were prepared by introducing 10.0 mg of **LMOF-1a** into 20 mL of cyclohexane with the different content of NB (2, 10, 20, 100, 200 and 1000 μL).

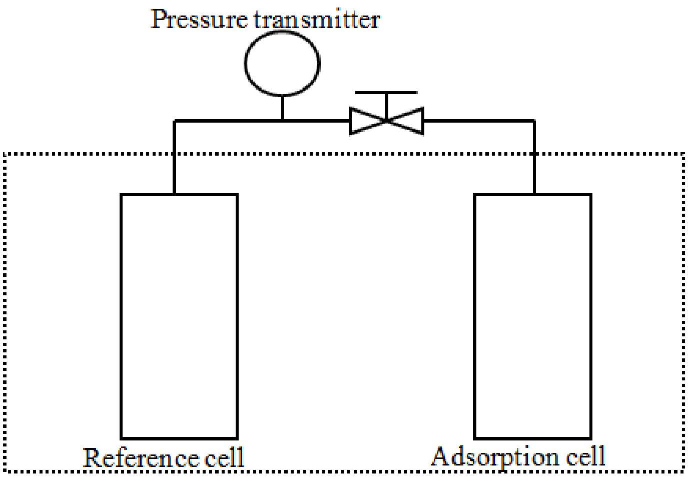
MD simulation. The models of LMOF-1a were used for simulation. The unit cells of frameworks adopted in this simulation were 2 × 2 × 2 with periodic boundary. The frameworks were treated as rigid with frozen atoms during simulation. A total of 2 × 107 steps were used; the first half moves were used for equilibration, and the remaining steps were used for calculating the ensemble averages. The potential parameter values for frameworks and gas molecules were from the COMPASS force field. Monte Carlo (MC) simulations in the grand canonical ensemble were used to calculte the adsorptive desity field of NB with fixed loading.

Gas sorption properties. The as-synthesized sample **LMOF-1** was immersed in DMF for two days, during which the solvent was refreshed several times. The sample after solvent exchange was further dried under vacuum at 150 °C for 5 h before the measurement. The N_2 sorption isotherms were acquired in the pressure rage of P/P_0 from 0.01 to 0.99 at 77 K in a liquid nitrogen bath. The gas sorption experiments of CO_2, CH_4, H_2, C_2H_6 and N_2 were conducted at 273 K or 298 K in a glycol-water bath.

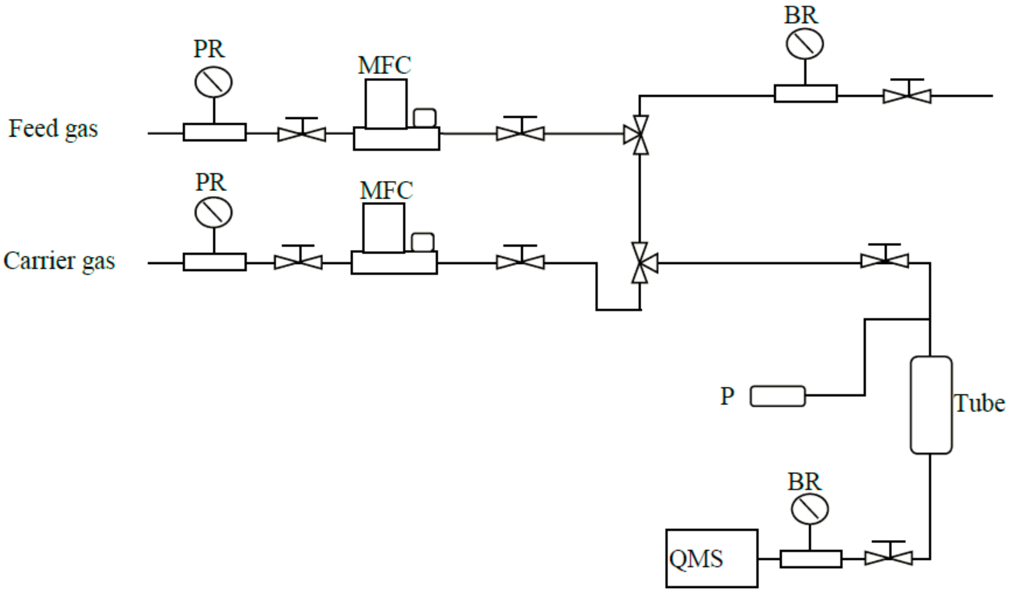
High pressure adsorption. The adsorption equilibrium data were measured on a volumetric setup shown schematically in Scheme S2. There are two cells, a reference cell and an adsorption cell. Both cells were kept in a thermostat, whose temperature was 298 K and constant within ±0.1 K. A pressure transmitter model PAA-23/8465.1-200 manufactured by Keller Druckmesstechnik, Switzerland was used to measure its pressure. The deviation from linearity in the whole range of 20 MPa was within 0.05 %.

Experiments were carried out on a setup shown in Scheme S3. The fine powder sample (0.183 g) was packed in a tube of length 10 mm and inner diameter 4 mm. Two mass flow controllers (Type SY-9312 of precision ±1 %) were used to control the flow rate of 40 ml/min. A backpressure regulator was used to control adsorption pressure and a pressure transducer (Type SY-9411 of accuracy ±0.1 %) was used to detect the pressure. The zero point of transducers was adjusted automatically to compensate for the fluctuation of room temperature.

Composition of the effluent stream was analyzed by a Quadruple mass spectrograph (Stanford Research Systems, Inc. USA) & gas chromatography (GC). All parts were connected by stainless steel capillary tubes of inner diameter 2 mm and wall thickness 0.5 mm.



Scheme S2 Schematic structure of setup for high pressure adsorption.



Scheme S3 Schematic structure of setup for breakthrough curve.

Table S2 selectivity of CH_4/C_2H_6.

Pressure（MPa）	Temperature（K)	n_{CH4} (mmol g^{-1})	n_{C2H6} (mmol g^{-1})	Selectivity
2.0	298	0.79	14.74	25.45

References:

S1 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O' Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science,* 2012, **336**, 1018.

S2 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, **29**, 2176.

S3 K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119.

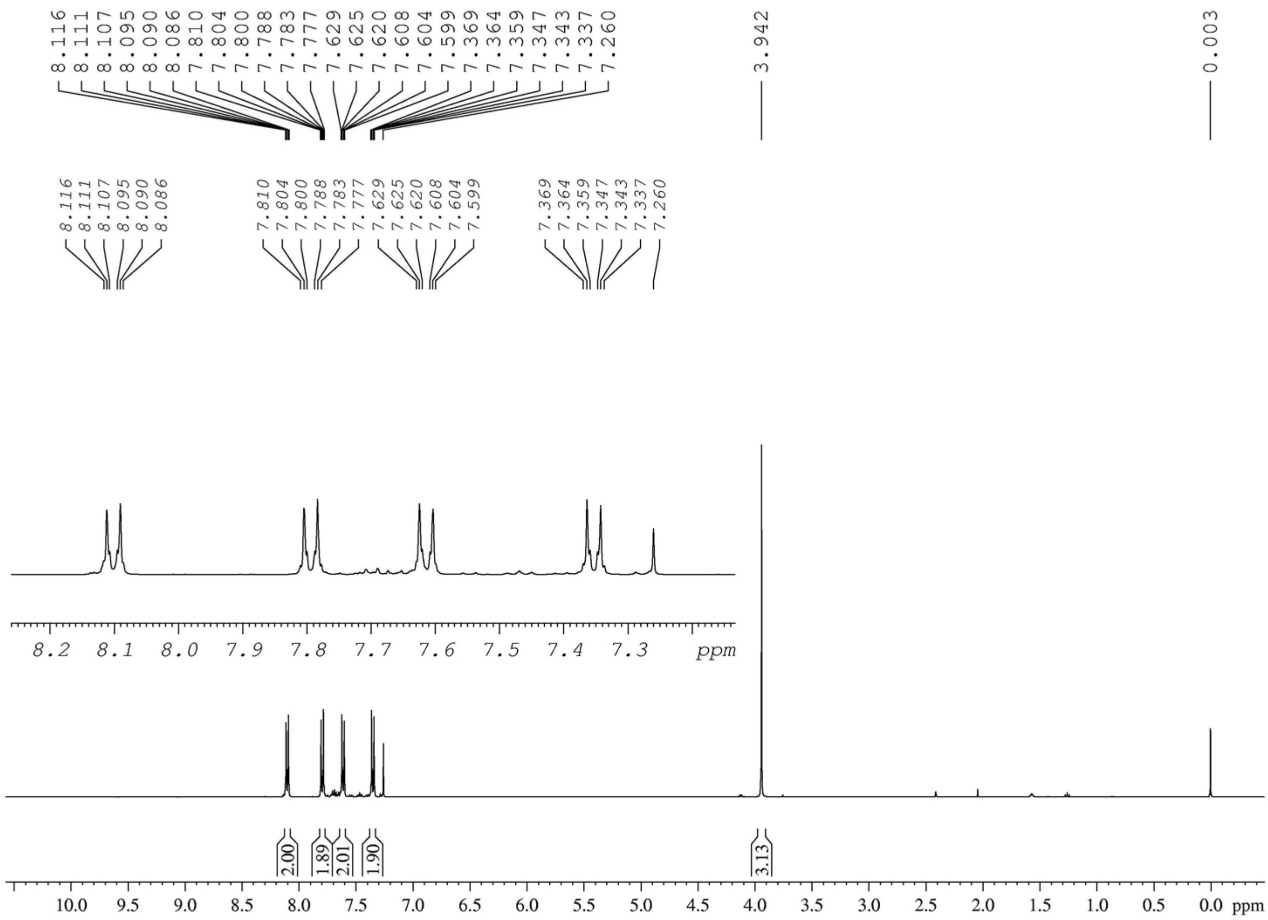


Figure S1 ^{1}H NMR spectrum of methyl (4'-bromobiphenyl)-4-carboxylate in $CDCl_3$.

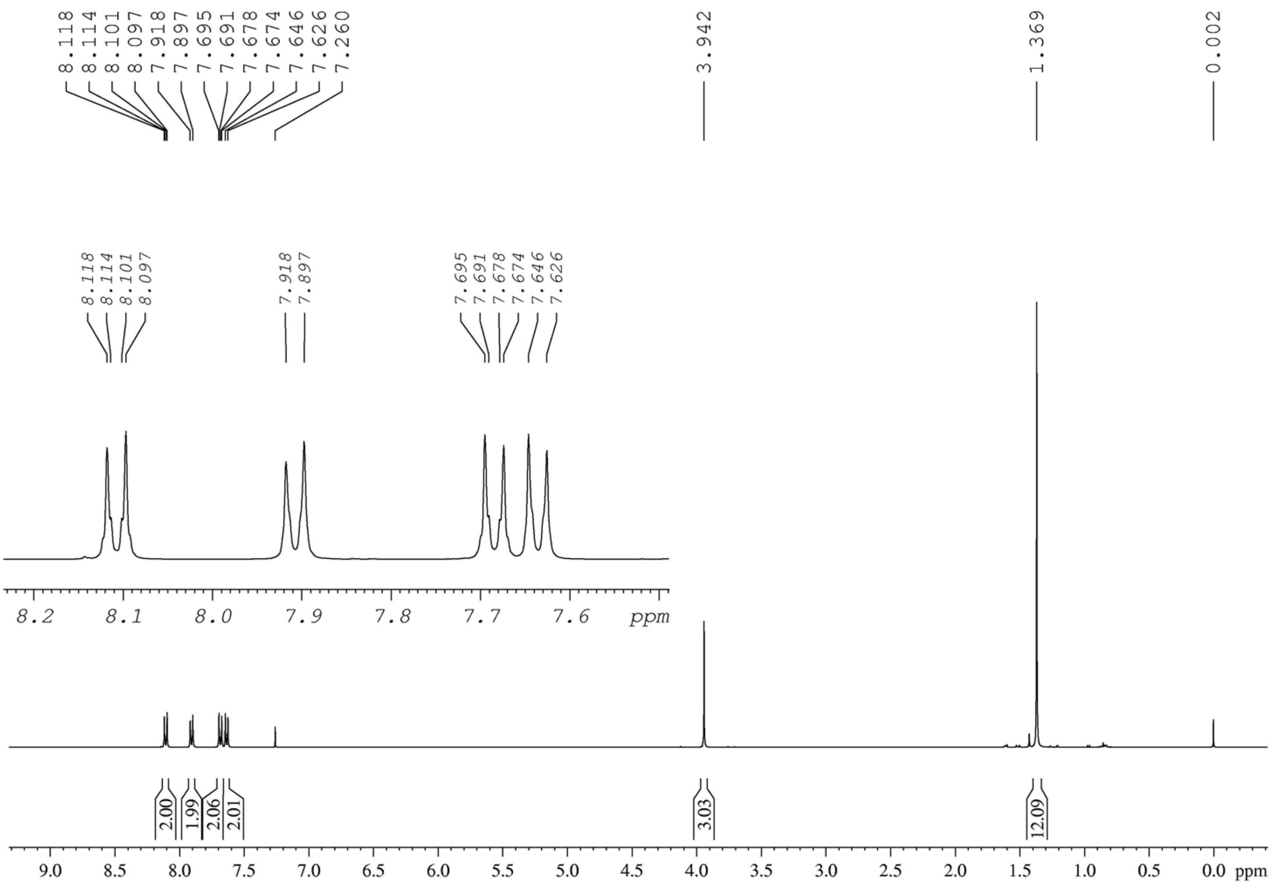


Figure S2 ^{1}H NMR spectrum of methyl **4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-carboxylate** in $CDCl_3$.

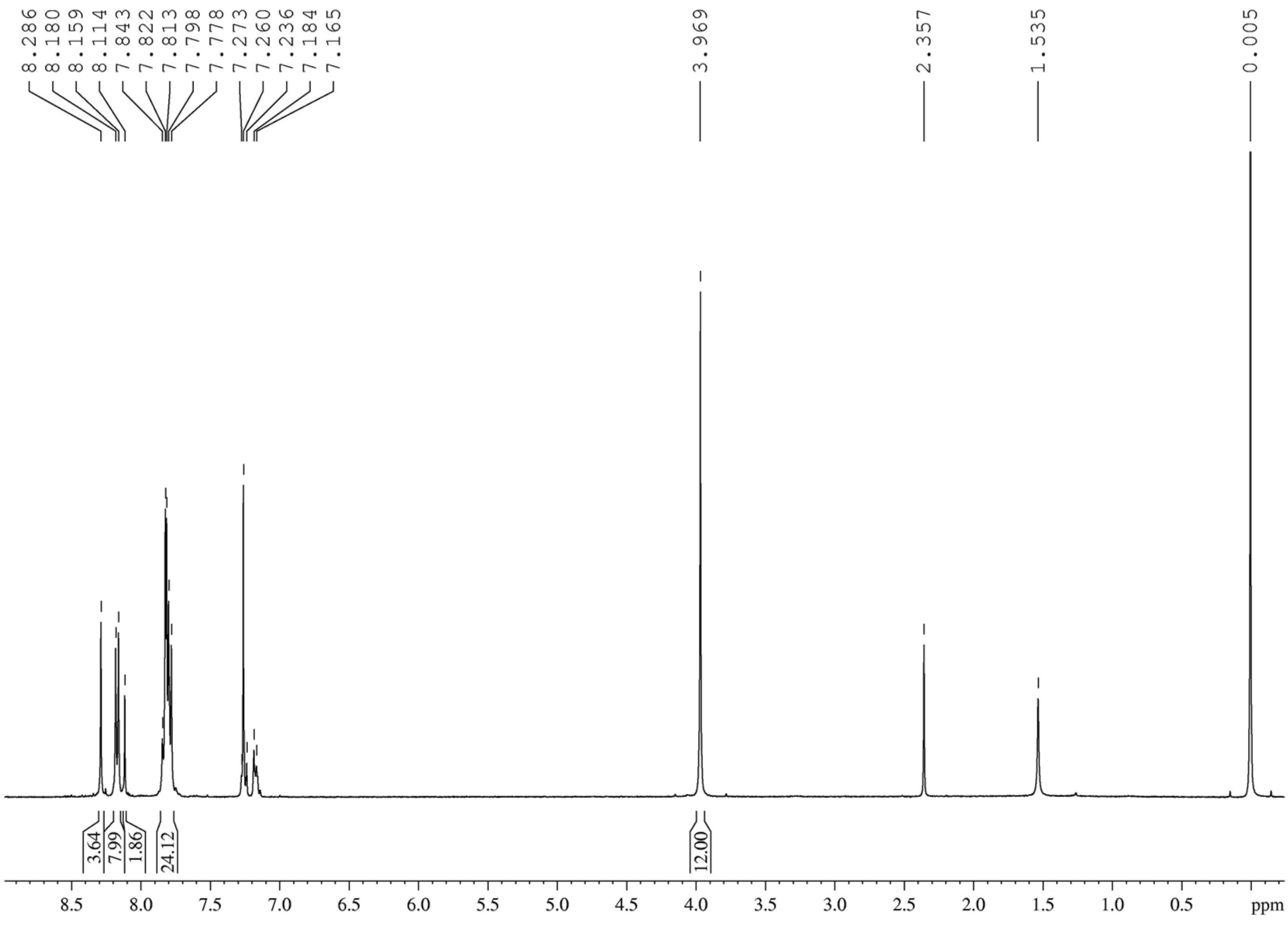


Figure S3 ^{1}H NMR spectrum of **1,3,6,8-tetra(4-methoxycarbonylbiphenyl)pyrene** in $CDCl_3$.

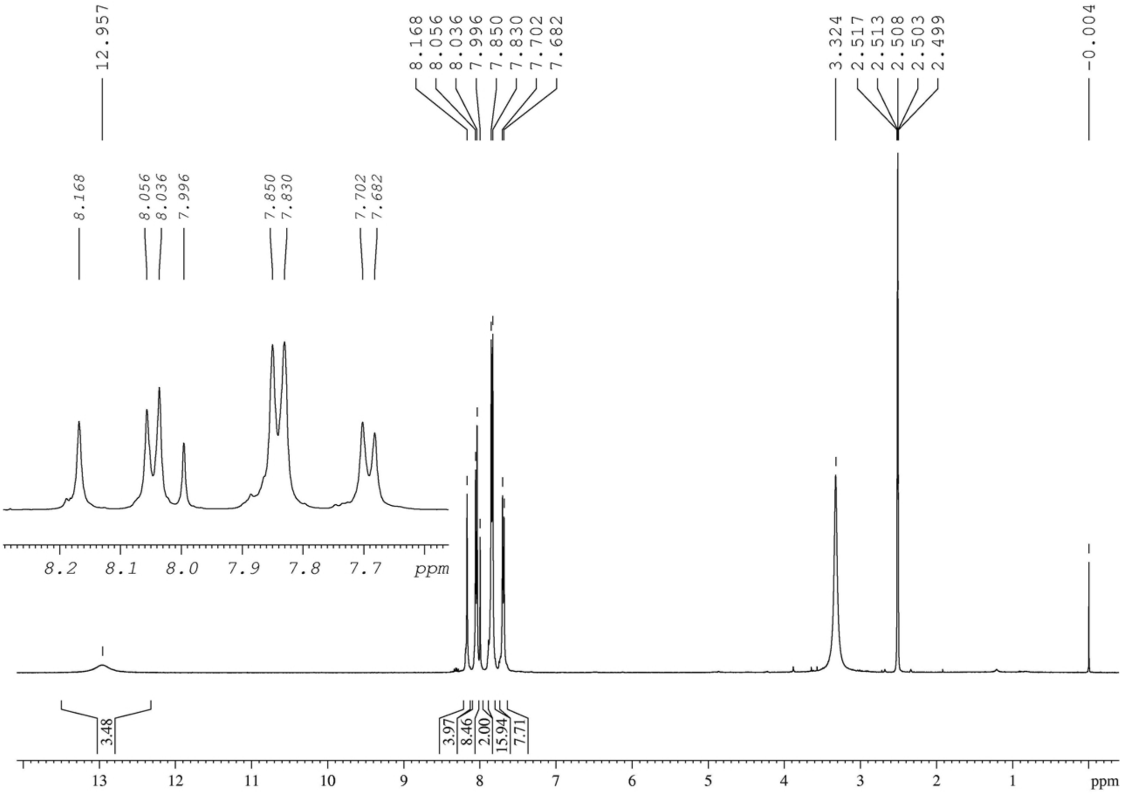


Figure S4 ^{1}H NMR spectrum of **1,3,6,8-tetra(4-carboxylbiphenyl)pyrene** in DMSO-d$_6$ at 40 °C.

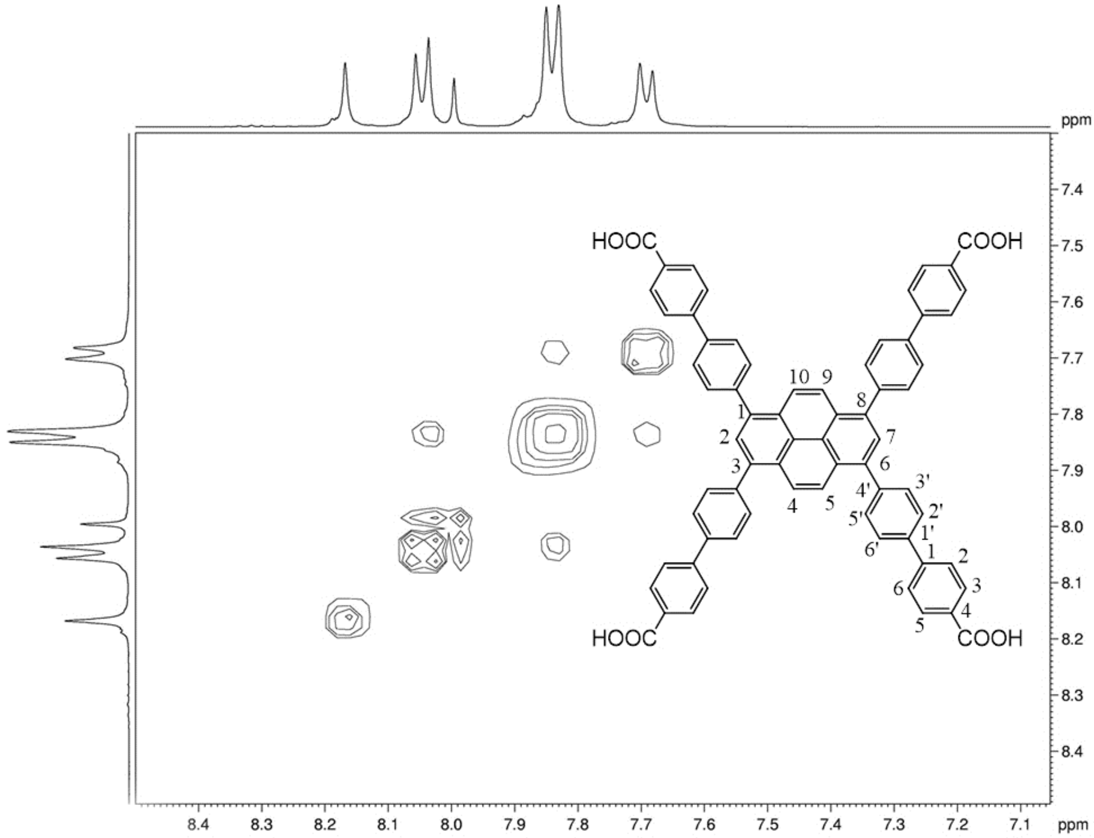


Figure S5 ^{1}H-^{1}H COSY of **1,3,6,8-tetra(4-carboxylbiphenyl)pyrene** in DMSO-d_6 at 40 °C.

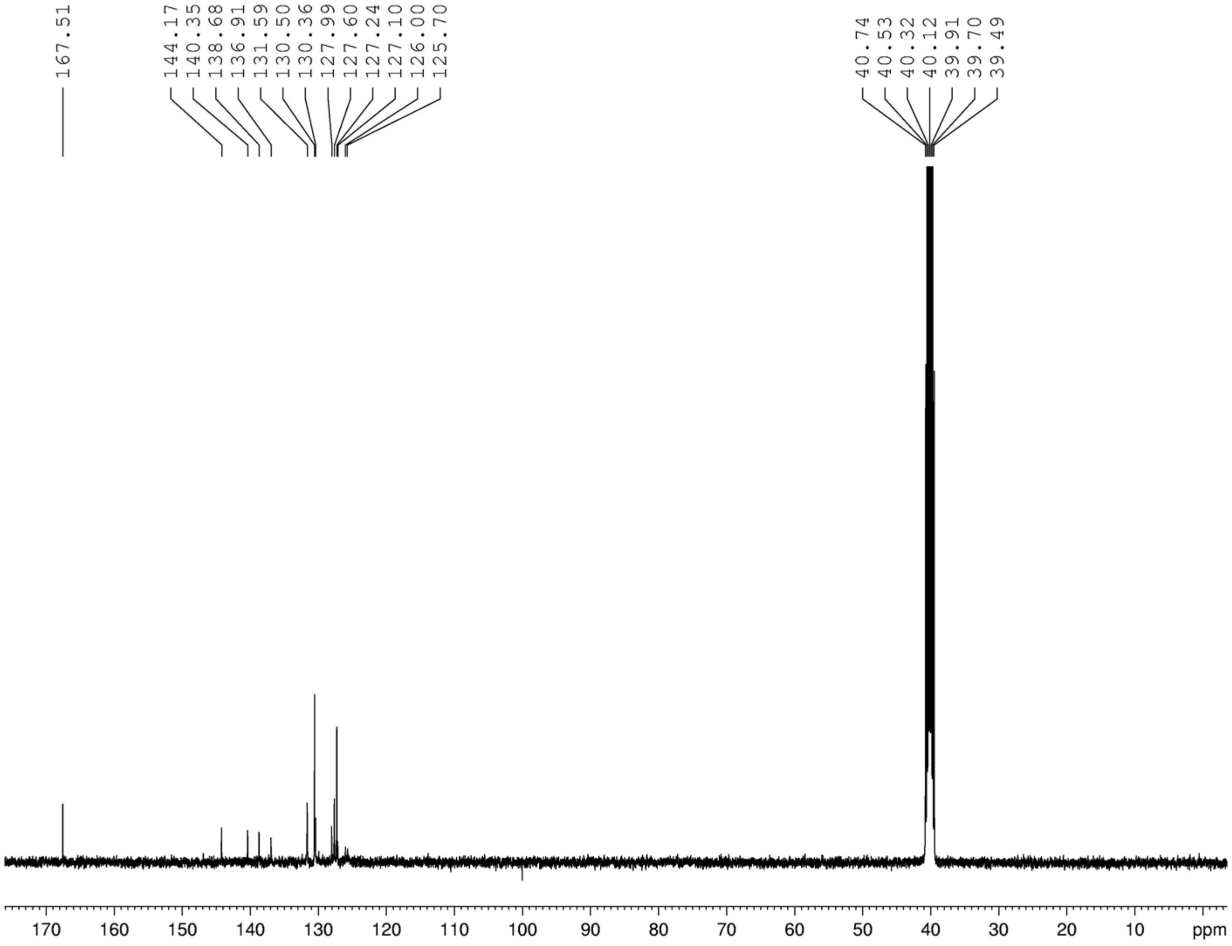


Figure S6 ^{13}C NMR spectrum of **1,3,6,8-tetra(4-carboxylbiphenyl)pyrene** in DMSO-d_6 at 40 °C.

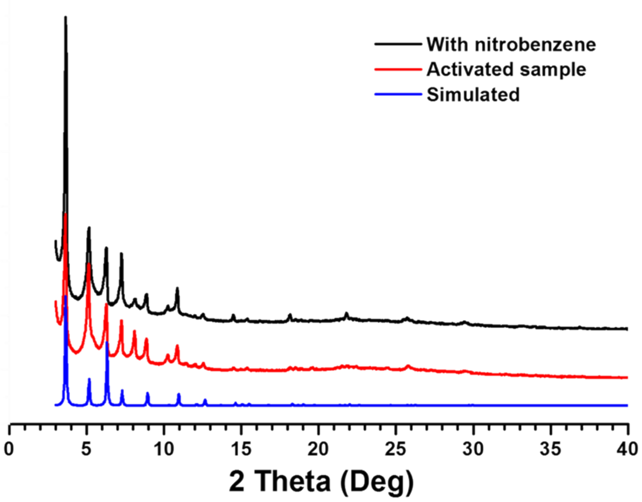


Figure S7 PXRD patterns of **1**. Blue: simulated, red: activated samples, and black: after nitrobenzene treatment.

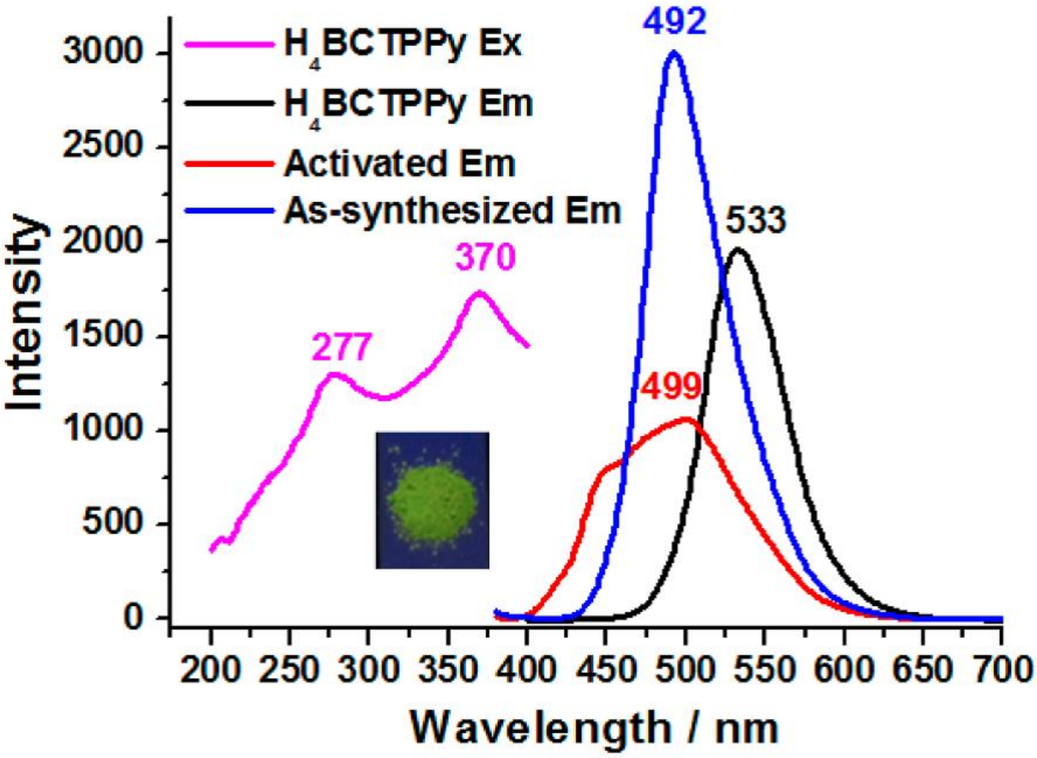


Figure S8 Excitation spectrum (magenta) of ligand H_4TCBPPy and Emission spectra of H_4TCBPPy (black), **LMOF-1** (blue) and **LMOF-1a** (red) (Excited at 370 nm). Inset: photograph of H_4TCBPPy powders under the UV lamp (365 nm).

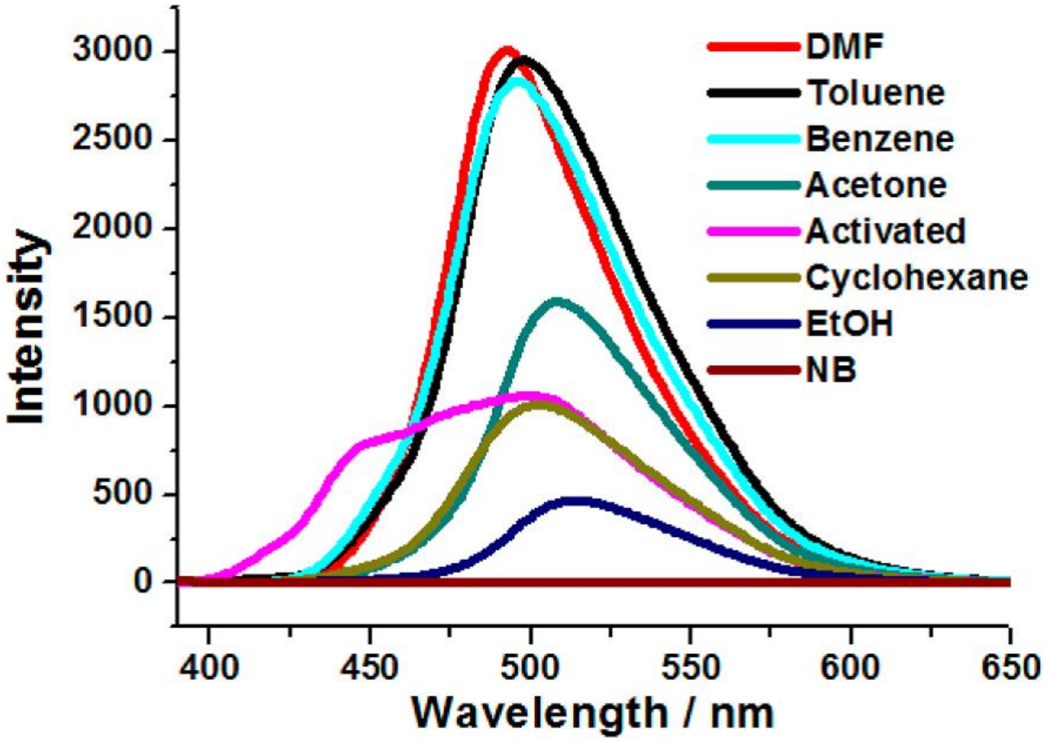


Figure S9 Solid-state PL spectra of **LMOF-1a** soaked with different solvents under λ_{ex} = 370 nm and room temperature.

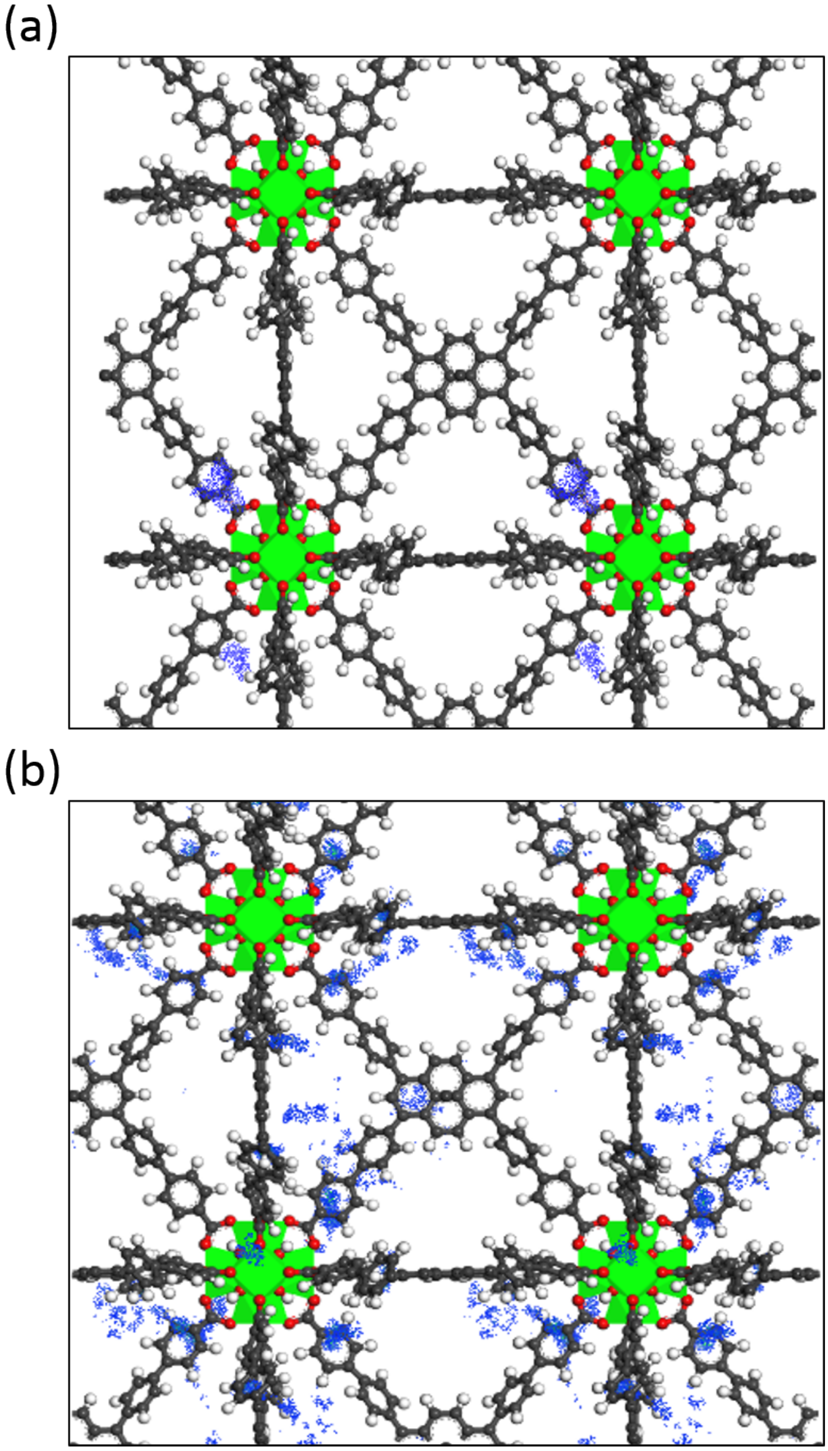


Figure S10 Adsorptive desity field (a) 1 NB per cell, (b) 50 NB per cell.