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Supporting Information

A \( \pi \)-electron Deficient Diaminotriazine Functionalized MOF For Selective Sorption of Benzene Over Cyclohexane

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**Figure S1:** General conformations of planar aromatic Benzene (Bz) (left) and non-planar aliphatic Cyclohexane (Cy) (right).

**Figure S2:** Electrostatic potential surface for the ligand (LH) representative of the electron density map.
Table S1. Physical Properties of C₆ adsorptive species.

| Dimensions of Adsorptive molecules (Å) | Boiling and Freezing Points | Conformers |
|---------------------------------------|----------------------------|------------|
| (each atom surrounded by a van der Waals sphere) | B.P. | F.P. | Type(s) |
| x | y | z | MIN-1 | MIN-2 |            |
| Bz | 6.628 | 7.337 | 3.277 | 3.277 | 6.628 | 353.3 K | 278.7 K | Planar |
| Cy | 7.168 | 6.580 | 4.982 | 4.982 | 6.580 | 353.9 K | 279.6 K | Non-planar: Boat and Chair |

MIN-1: Size of the adsorptive in the minimum dimension.

MIN-2: Second minimum dimension for molecular orientations that enable a molecule to enter the channel.

Table S2. Dual-site Langmuir-Freundlich parameters for aromatic hydrocarbons at 298 K in DAT-MOF-1.

| | Site A | Site B |
|----------------|--------|--------|
| | qᵢ,A,sat | bᵢ,A | νᵢ,A | qᵢ,B,sat | bᵢ,B | νᵢ,B |
| | mol kg⁻¹ | Pa⁻νᵢ | dimensionless | mol kg⁻¹ | Pa⁻νᵢ | dimensionless |
| Bz | 0.85 | 3.1×10⁻² | 0.7 | 3 | 3.7×10⁻¹⁶ | 3.6 |
| Cy | 0.5 | 9.55×10⁻⁵ | 0.8 | 0.5 | 2.01×10⁻²⁵ | 6 |
**Experimental Section:**

**Materials:** All the reagents and solvents were commercially available and used without further purification.

**Synthesis of Ligand (LH):** 4-cyano benzoic acid (5g, 33.98 mmol) and dicyanamide (4.1619 g, 49.49 mmol) were added to a stirring solution of potassium hydroxide (2.772, 49.5 mmol) in 2- methoxy ethanol (100 ml) in a round bottomed flask. Resulting mixture was refluxed at 423K for 30 h. This mixture was subsequently cooled down to room temperature. The solution was neutralized using dilute HCl until the pH of reaction mixture was ~7 to get white precipitate. Then the resulting solution was filtered off, dried under vacuum to get white powder. The compound was characterized using $^1$H NMR, $^{13}$C NMR and HRMS. $^1$H NMR (400 MHz, DMSO-d$_6$): δ 8.3 (td, $J = 1.6$, 8.8 Hz, 2H); 8.0 (td, $J = 2.0$, 8.8 Hz, 2H), 6.8 (S, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 169.4, 167.4, 167.1, 141.0, 133.1, 129.2, 127.7; HRMS (ESI): Calc. for C$_{10}$H$_{10}$N$_5$O$_2$ [M+H]$^+$: 232.083; Found: 232.083.

![Diagram of ligand synthesis](image)

**Figure S3:** Ligand (LH) synthesis protocol.
Figure S4: HRMS of ligand (LH).

Figure S5: $^1$H NMR of ligand (LH).
Synthesis of DAT-MOF-1a: Single crystals of DAT-MOF-1a were synthesized by reacting Cu(NO$_3$)$_2$.3H$_2$O (0.012 g, 0.05 mmol), LH (0.0231 g, 0.1 mmol) in DMF (2 mL) and MeOH (1mL) in a 5 ml screw-capped vial. The vial was heated to 90 °C for 48h under autogenous pressure and then cooled to RT over 12 h. The green block shaped single crystals of DAT-MOF-1a were obtained with ~50% yield. Anal. found (elemental analysis) for DAT-MOF-1a (%): C, 46.92; H, 5.23; N, 22.88.

Physical measurements: Powder X-ray diffraction (PXRD) patterns were measured on Bruker D8 Advanced X-Ray diffractometer at room temperature using Cu-Kα radiation ($\lambda=1.5406$ Å) with a scan speed of 0.5° min$^{-1}$ and a step size of 0.01° in 2theta. Thermogravimetric analysis was recorded on Perkin-Elmer STA 6000, TGA analyser under N$_2$ atmosphere with heating rate of 10° C/min. The IR-spectra were recorded on a Thermoscientific–Nicolet-6700 FT-IR spectrometer. FT-IR spectra were recorded on NICOLET 6700 FT-IR Spectrophotometer using KBr Pellets.
Figure S7: Synthetic scheme of DAT-MOF-1a.

X-ray Structural Studies: Single-crystal X-ray data of DAT-MOF-1a was collected at 150 K on a Bruker KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal was on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The data integration and reduction were processed with SAINT\textsuperscript{S1} software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL\textsuperscript{S2} and was refined on \( F^2 \) by full-matrix least-squares technique using the SHELXL-97\textsuperscript{S3} program package within the WINGX\textsuperscript{S4} programme. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The structures were examined using the Adsym subroutine of PLATON\textsuperscript{S5} to assure that no additional symmetry could be applied to the models.
**Electron density plot for Ligand (LH):** Electrostatic potential surface calculation was performed with the Gaussian09 Rev D program suite using Density functional theory (DFT) with Becke’s three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d,p) basis set.

**Low-Pressure Gas and Solvent Sorption Measurements.** Low-pressure solvent (Benzene and Cyclohexane) sorption measurements were performed using BelAqua (Bel Japan). Low pressure gas adsorption measurements were performed using BelSorpmax (Bel Japan). All the gases used were of 99.999% purity. As-synthesized crystals of compound DAT-MOF-1a were exchanged thrice each day over a period of five days with fresh batches of lower-boiling solvent acetone, before heating it under vacuum to end up with guest-free crystalline phase DAT-MOF-1.

![IR spectra of DAT-MOF-1a and the monocarboxylic acid ligand (LH)](image)

**Figure S8:** IR spectra of DAT-MOF-1a and the monocarboxylic acid ligand (LH), wherein the labelled peaks refer to the presence of N,N,-dimethyl formamide (DMF) molecules within DAT-MOF-1a, present in addition to the coordinated monocarboxylate dianinotriazine linker L. a: N-H stretching (also in DMF); b: C-O stretching (also in DMF); c: C-H stretching (also in DMF); d: C-N stretching (DMF); e: C-H rocking (in DMF, –CH₃).
Figure S9: Asymmetric unit of DAT-MOF-1a (Color code: Carbon: grey, oxygen: red, nitrogen: blue, copper: deep green).

Figure S10: Coordination environment around the metal centre of DAT-MOF-1a (Color code: Carbon: grey, oxygen: red, nitrogen: blue, copper: green).
Figure S11: Perspective view of overall packing of DAT-MOF-1a along $a$ axis (free guests have been omitted for clarity) (Color code; Carbon: grey, oxygen: red, nitrogen: blue, copper: green).

Figure S12: Perspective view of a single pore of DAT-MOF-1a along $a$ axis (free guests have been omitted for clarity) (Color code; Carbon: grey, oxygen: red, nitrogen: blue, copper: green).
**Figure S13:** Single 2D net of DAT-MOF-1a $a$ axis (Color code; Carbon: grey, oxygen: pale orange, nitrogen: blue, copper: dark yellow).

**Figure S14:** Pore surface of DAT-MOF-1a along $a$ axis (Color code; Carbon: grey, oxygen: pale orange, nitrogen: blue, copper: green polyhedral).
**Figure S15:** Overall packing along $b$ axis of DAT-MOF-1a (free guests have been omitted for clarity) (Color code; Carbon: grey, oxygen: pale orange, nitrogen: blue, copper: green ball).

**Figure S16:** Overall packing along $b$ axis of DAT-MOF-1a (free guests have been omitted for clarity) (Color code; Carbon: grey, oxygen: pale orange, nitrogen: blue, copper: green ball).
Figure S17: TGA plot of as-made and desolvated phases of DAT-MOF-1a.
**Figure S18:** PXRD patterns of simulated, as-made and desolvated phases of DAT-MOF-1a.
**Figure S19**: PXRD patterns for the Bz and Cy-vapor exposed phases of DAT-MOF-1, when compared together with the simulated and as-made patterns for DAT-MOF-1a.
Figure S20: Low-temperature gas adsorption isotherms for DAT-MOF-1.
Figure S21: Room temperature CO\textsubscript{2} adsorption isotherms for DAT-MOF-1.
Figure S22: Benzene and Cyclohexane sorption isotherms for the desolvated phase DAT-MOF-1 recorded at 298K and 1atm.
Figure S23: $^{13}$C NMR spectra for Bz and Cy vapor-exposed phases of compound DAT-MOF-1, as compared to the desolvated phase itself. Vapor of each of these two solvents were exposed for 48h to the phase DAT-MOF-1 before digesting in DCI/DMSO-$d_6$. a) Extended $^{13}$C NMR view showing no Cy peak at the characteristic cyclohexane region ($\delta = 27$ ppm); while b) zoomed $^{13}$C NMR view presenting Bz peaks for the Bz and Bz/Cy (1:1) vapor exposed phases observed at Bz characteristic region ($\delta = 128.3$ ppm).
Table S3. Crystal data and structure refinement for DAT-MOF-1a.

| Property                        | Value                                                                 |
|---------------------------------|----------------------------------------------------------------------|
| Identification code             | DAT-MOF-1a                                                           |
| Empirical formula               | C_{20}H_{16}CuN_{10}O_{4}                                           |
| Formula weight                  | 523.97                                                              |
| Temperature                     | 100(2) K                                                            |
| Wavelength                      | 0.71073 Å                                                           |
| Crystal system                  | Orthorhombic                                                        |
| Space group                     | P b n b                                                              |
| Unit cell dimensions            |                                                                      |
| \(a\)                           | 17.7157(6) Å                                                       \(\alpha= 90^\circ\). |
| \(b\)                           | 22.1231(8) Å                                                       \(\beta= 90^\circ\). |
| \(c\)                           | 25.3814(9) Å                                                       \(\gamma= 90^\circ\). |
| Volume                          | 9947.6(6) Å                                                        |
| \(Z\)                           | 8                                                                  |
| Density (calculated)            | 0.700 Mg/m³                                                         |
| Absorption coefficient          | 0.462 mm\(^{-1}\)                                                  |
| F(000)                          | 2136                                                               |
| Crystal size                    | 0.15 x 0.11 x 0.10 mm\(^3\)                                        |
| Theta range for data collection | 1.40 to 25.41\(^\circ\)                                            |
| Index ranges                    | -21\(\leq\)h\(\leq\)21, -23\(\leq\)k\(\leq\)26, -30\(\leq\)l\(\leq\)30 |
| Reflections collected           | 163610                                                             |
| Independent reflections         | 9132 [R(int) = 0.0919]                                              |
| Completeness to theta = 25.41\(^\circ\) | 99.4 %                                                              |
| Absorption correction           | Semi-empirical from equivalents                                    |
| Max. and min. transmission      | 0.9552 and 0.9339                                                   |
| Refinement method               | Full-matrix least-squares on F\(^2\)                               |
| Data / restraints / parameters   | 9132 / 0 / 316                                                      |
| Goodness-of-fit on F\(^2\)      | 0.963                                                               |
| Final R indices [I>2\sigma(I)]  | R\(_1\) = 0.0656, wR\(_2\) = 0.1540                                 |
| R indices (all data)            | R\(_1\) = 0.0814, wR\(_2\) = 0.1646                                 |
| Largest diff. peak and hole     | 1.273 and -0.315 e.Å\(^{-3}\)                                      |
Table S4. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 x 10^3$) for DAT-MOF-1a. $U(eq)$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x     | y     | z     | U(eq) |
|-------|-------|-------|-------|-------|
| Cu(01)| 9438(1)| 362(1)| 144(1)| 34(1) |
| O(4)  | 10190(1)| 994(1)| 35(1) | 42(1) |
| O(2)  | 8845(1)| -396(1)| 189(1)| 33(1) |
| O(1)  | 9855(1)| 210(1)| 847(1)| 39(1) |
| O(3)  | 9201(1)| 408(1)| -615(1)| 40(1) |
| N(7)  | 8561(1)| 980(1)| 424(1)| 25(1) |
| N(9)  | 7650(1)| 481(1)| -47(1)| 34(1) |
| N(6)  | 8291(1)| 1992(1)| 694(1)| 32(1) |
| N(8)  | 7436(1)| 1469(1)| 127(1)| 29(1) |
| N(2)  | 11406(2)| -536(1)| 4180(1)| 44(1) |
| C(18) | 7681(2)| 1961(1)| 387(1)| 28(1) |
| N(10) | 9310(1)| 1482(1)| 1017(1)| 43(1) |
| N(3)  | 11490(2)| -914(1)| 3294(1)| 48(1) |
| C(19) | 8709(2)| 1489(1)| 706(1)| 29(1) |
| C(13) | 7094(2)| 3603(1)| 341(1)| 33(1) |
| C(20) | 7881(1)| 979(1)| 174(1)| 25(1) |
| C(16) | 6480(2)| 2469(1)| 142(1)| 39(1) |
| N(4)  | 11972(2)| -1430(1)| 3986(1)| 53(1) |
| C(14) | 7524(2)| 3090(1)| 411(1)| 38(1) |
| C(1)  | 10405(2)| -132(1)| 946(1)| 34(1) |
| C(15) | 7228(2)| 2512(1)| 309(1)| 30(1) |
| C(7)  | 11223(2)| -551(1)| 1662(1)| 43(1) |
| N(1)  | 10886(2)| 27(2)| 3459(1)| 59(1) |
| C(12) | 6350(2)| 3552(1)| 166(1)| 33(1) |
| C(2)  | 10620(2)| -205(2)| 1514(1)| 42(1) |
| C(8)  | 11114(2)| -411(2)| 3151(1)| 51(1) |
| C(11) | 5866(2)| 4104(1)| 104(1)| 29(1) |
| C(9)  | 11036(2)| -47(2)| 3983(1)| 53(1) |
| C(10) | 11612(2)| -948(1)| 3814(1)| 41(1) |
| C(6)  | 11399(2)| -624(2)| 2200(1)| 44(1) |
| C(17) | 6048(2)| 2985(1)| 57(1)| 37(1) |
| C(3)  | 10173(2)| 66(2)| 1897(1)| 71(1) |
| N(5)  | 10832(2)| 371(2)| 4316(1)| 72(1) |
|   |   |   |   |   |
|---|---|---|---|---|
| C(5) | 10955(2) | -351(2) | 2572(1) | 53(1) |
| C(4) | 10340(2) | 10(2) | 2423(2) | 70(1) |
| Bond Lengths (Å) | Bond Angles (°) |
|------------------|-----------------|
| Cu(01)-O(4)      | 1.9522(19)      |
| Cu(01)-O(1)      | 1.9585(19)      |
| Cu(01)-O(3)      | 1.975(2)        |
| Cu(01)-O(2)      | 1.9824(18)      |
| Cu(01)-N(7)      | 2.190(2)        |
| Cu(01)-Cu(01)#1  | 2.6563(7)       |
| O(4)-C(11)#2     | 1.267(3)        |
| O(2)-C(11)#3     | 1.238(3)        |
| O(1)-C(1)        | 1.258(3)        |
| O(3)-C(1)#1      | 1.252(4)        |
| N(7)-C(19)       | 1.358(3)        |
| N(7)-C(20)       | 1.362(3)        |
| N(9)-C(20)       | 1.303(3)        |
| N(6)-C(18)       | 1.332(3)        |
| N(6)-C(19)       | 1.338(3)        |
| N(8)-C(20)       | 1.345(3)        |
| N(8)-C(18)       | 1.345(3)        |
| N(2)-C(10)       | 1.351(4)        |
| N(2)-C(9)        | 1.359(4)        |
| C(18)-C(15)      | 1.472(3)        |
| N(10)-C(19)      | 1.325(4)        |
| N(3)-C(10)       | 1.340(4)        |
| N(3)-C(8)        | 1.346(4)        |
| C(13)-C(14)      | 1.378(4)        |
| C(13)-C(12)      | 1.395(4)        |
| C(16)-C(17)      | 1.391(4)        |
| C(16)-C(15)      | 1.395(4)        |
| N(4)-C(10)       | 1.316(4)        |
| C(14)-C(15)      | 1.407(4)        |
| C(1)-O(3)#1      | 1.252(4)        |
| C(1)-C(2)        | 1.500(4)        |
| C(7)-C(2)        | 1.367(4)        |
| C(7)-C(6)        | 1.409(5)        |
| N(1)-C(8)        | 1.310(5)        |
| N(1)-C(9)        | 1.367(5)        |
| C(12)-C(17)      | 1.392(4)        |
C(12)-C(11)  1.501(3)
C(2)-C(3)  1.390(5)
C(8)-C(5)  1.502(4)
C(11)-O(2)#4  1.238(3)
C(11)-O(4)#5  1.267(3)
C(9)-N(5)  1.305(5)
C(6)-C(5)  1.369(5)
C(3)-C(4)  1.372(5)
C(5)-C(4)  1.404(5)

O(4)-Cu(01)-O(1)  89.72(10)
O(4)-Cu(01)-O(3)  88.21(10)
O(1)-Cu(01)-O(3)  167.78(9)
O(4)-Cu(01)-O(2)  167.58(8)
O(1)-Cu(01)-O(2)  90.14(9)
O(3)-Cu(01)-O(2)  89.30(9)
O(4)-Cu(01)-N(7)  94.72(8)
O(1)-Cu(01)-N(7)  94.53(8)
O(3)-Cu(01)-N(7)  97.64(8)
O(2)-Cu(01)-N(7)  97.67(8)

O(4)-Cu(01)-Cu(01)#1  83.18(6)
O(1)-Cu(01)-Cu(01)#1  82.25(6)
O(3)-Cu(01)-Cu(01)#1  85.54(6)
O(2)-Cu(01)-Cu(01)#1  84.49(6)
N(7)-Cu(01)-Cu(01)#1  176.15(6)
C(11)#2-O(4)-Cu(01)  124.18(16)
C(11)#3-O(2)-Cu(01)  121.74(17)
C(1)-O(1)-Cu(01)  125.23(19)
C(1)#1-O(3)-Cu(01)  120.64(17)
C(19)-N(7)-C(20)  114.7(2)
C(19)-N(7)-Cu(01)  123.44(17)
C(20)-N(7)-Cu(01)  118.36(16)
C(18)-N(6)-C(19)  114.8(2)
C(20)-N(8)-C(18)  114.8(2)
C(10)-N(2)-C(9)  114.6(3)
N(6)-C(18)-N(8)  126.2(2)
N(6)-C(18)-C(15)  118.6(2)
N(8)-C(18)-C(15)  115.3(2)
C(10)-N(3)-C(8)  113.1(3)
N(10)-C(19)-N(6)  117.9(2)
N(10)-C(19)-N(7)  117.3(2)
N(6)-C(19)-N(7)  124.7(2)
C(14)-C(13)-C(12)  119.7(2)
N(9)-C(20)-N(8)  117.4(2)
N(9)-C(20)-N(7)  118.7(2)
N(8)-C(20)-N(7)  123.9(2)
C(17)-C(16)-C(15)  120.9(3)
C(13)-C(14)-C(15)  121.3(3)
O(3)#1-C(1)-O(1)  126.3(3)
O(3)#1-C(1)-C(2)  116.8(2)
O(1)-C(1)-C(2)  117.0(3)
C(16)-C(15)-C(14)  118.2(2)
C(16)-C(15)-C(18)  120.2(2)
C(14)-C(15)-C(18)  121.6(2)
C(2)-C(7)-C(6)  120.2(3)
C(8)-N(1)-C(9)  115.6(3)
C(17)-C(12)-C(13)  120.0(2)
C(17)-C(12)-C(11)  119.5(2)
C(13)-C(12)-C(11)  120.5(2)
C(7)-C(2)-C(3)  119.6(3)
C(7)-C(2)-C(1)  121.5(3)
C(3)-C(2)-C(1)  118.8(3)
N(1)-C(8)-N(3)  127.1(3)
N(1)-C(8)-C(5)  117.5(3)
N(3)-C(8)-C(5)  115.4(3)
O(2)#4-C(11)-O(4)#5  126.3(2)
O(2)#4-C(11)-C(12)  118.2(2)
O(4)#5-C(11)-C(12)  115.5(2)
N(5)-C(9)-N(2)  117.5(3)
N(5)-C(9)-N(1)  119.4(3)
N(2)-C(9)-N(1)  123.1(3)
N(4)-C(10)-N(3)  116.8(3)
N(4)-C(10)-N(2)  116.7(3)
N(3)-C(10)-N(2)  126.5(3)
C(5)-C(6)-C(7)  119.4(3)
C(16)-C(17)-C(12)  119.8(3)
| Bond                        | Angle (°) (ESD) |
|-----------------------------|-----------------|
| C(4)-C(3)-C(2)              | 121.3(3)        |
| C(6)-C(5)-C(4)              | 120.7(3)        |
| C(6)-C(5)-C(8)              | 122.0(3)        |
| C(4)-C(5)-C(8)              | 117.3(3)        |
| C(3)-C(4)-C(5)              | 118.7(3)        |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z  
#2 x+1/2,-y+1/2,-z  
#3 -x+3/2,y-1/2,z  
#4 -x+3/2,y+1/2,z  
#5 x-1/2,-y+1/2,-z
Table S6. Anisotropic displacement parameters (Å²x 10³) for DAT-MOF-1a. The anisotropic displacement factor exponent takes the form: -2\pi²[ h²a²U_{11} + ... + 2hka*b*U_{12} ]

|        | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|--------|--------|--------|--------|--------|--------|--------|
| Cu(01) | 33(1)  | 23(1)  | 47(1)  | 2(1)   | -5(1)  | -2(1)  |
| O(4)   | 27(1)  | 18(1)  | 81(2)  | -6(1)  | 12(1)  | -7(1)  |
| O(2)   | 24(1)  | 17(1)  | 59(1)  | -2(1)  | -1(1)  | -1(1)  |
| O(1)   | 47(1)  | 36(1)  | 33(1)  | -2(1)  | -16(1) | 18(1)  |
| O(3)   | 39(1)  | 46(1)  | 34(1)  | 7(1)   | -11(1) | 16(1)  |
| N(7)   | 25(1)  | 12(1)  | 39(1)  | -3(1)  | -10(1) | 2(1)   |
| N(9)   | 30(1)  | 17(1)  | 55(2)  | -10(1) | -18(1) | 11(1)  |
| N(6)   | 29(1)  | 21(1)  | 46(1)  | -7(1)  | -12(1) | 7(1)   |
| N(8)   | 31(1)  | 15(1)  | 41(1)  | -9(1)  | -6(1)  | 3(1)   |
| N(2)   | 45(2)  | 44(2)  | 43(2)  | 8(1)   | -16(1) | -7(1)  |
| C(18)  | 28(1)  | 19(1)  | 38(2)  | -5(1)  | -5(1)  | 1(1)   |
| N(10)  | 41(1)  | 28(1)  | 60(2)  | -16(1) | -25(1) | 13(1)  |
| N(3)   | 57(2)  | 44(2)  | 43(2)  | 2(1)   | -19(1) | 6(1)   |
| C(19)  | 23(1)  | 25(1)  | 40(2)  | -2(1)  | -6(1)  | -2(1)  |
| C(13)  | 25(1)  | 18(1)  | 57(2)  | 2(1)   | -10(1) | -3(1)  |
| C(20)  | 20(1)  | 23(1)  | 32(1)  | 2(1)   | -6(1)  | 5(1)   |
| C(16)  | 31(2)  | 17(1)  | 68(2)  | -10(1) | -7(1)  | 3(1)   |
| N(4)   | 82(2)  | 39(2)  | 39(2)  | 3(1)   | -21(2) | 5(2)   |
| C(14)  | 25(1)  | 20(1)  | 69(2)  | -10(1) | -12(1) | 1(1)   |
| C(1)   | 37(2)  | 24(1)  | 40(2)  | 1(1)   | -10(1) | 7(1)   |
| C(15)  | 31(1)  | 18(1)  | 40(2)  | -4(1)  | -9(1)  | 7(1)   |
| C(7)   | 46(2)  | 38(2)  | 45(2)  | -2(1)  | -4(2)  | 7(1)   |
| N(1)   | 27(1)  | 58(2)  | 44(2)  | 0(2)   | -20(1) | 28(2)  |
| C(12)  | 27(1)  | 56(2)  | 56(2)  | -1(1)  | 0(1)   | 5(1)   |
| C(2)   | 39(2)  | 42(2)  | 44(2)  | 6(1)   | -11(1) | 9(1)   |
| C(8)   | 62(2)  | 57(2)  | 35(2)  | 0(2)   | -12(2) | 19(2)  |
| C(11)  | 24(1)  | 45(2)  | 45(2)  | -1(1)  | 2(1)   | 2(1)   |
| C(9)   | 45(2)  | 68(2)  | 47(2)  | 3(2)   | -6(2)  | 13(2)  |
| C(10)  | 42(2)  | 36(2)  | 46(2)  | 1(1)   | -16(1) | -5(1)  |
| C(6)   | 44(2)  | 45(2)  | 43(2)  | 4(1)   | -9(1)  | 10(2)  |
| C(17)  | 25(1)  | 24(1)  | 61(2)  | -8(1)  | -12(1) | 5(1)   |
| C(3)   | 68(3)  | 104(3) | 43(2)  | -16(2) | -16(2) | 57(3)  |
| N(5)   | 76(2)  | 95(3)  | 44(2)  | 6(2)   | -14(2) | 39(2)  |
|       |     |     |     |     |     |     |
|-------|-----|-----|-----|-----|-----|-----|
| C(5)  | 61(2)| 64(2)| 34(2)| 5(2) | -14(2)| 15(2) |
| C(4)  | 65(2)| 101(3)| 45(2)| -6(2)| -11(2)| 45(2) |

Notation

\( b_A \) dual-Langmuir-Freundlich constant for species \( i \) at adsorption site A, \( \text{Pa}^{\nu} \)

\( b_B \) dual-Langmuir-Freundlich constant for species \( i \) at adsorption site B, \( \text{Pa}^{\nu} \)

\( c_i \) molar concentration of species \( i \) in fluid mixture, \( \text{mol m}^{-3} \)

\( c_{i0} \) molar concentration of species \( i \) in fluid mixture at inlet to adsorber, \( \text{mol m}^{-3} \)

\( L \) length of packed bed adsorber, m

\( n \) number of species in the mixture, dimensionless

\( p_i \) partial pressure of species \( i \) in mixture, Pa

\( p_t \) total system pressure, Pa

\( q_i \) component molar loading of species \( i \), \( \text{mol kg}^{-1} \)

\( q_{i, \text{sat}} \) molar loading of species \( i \) at saturation, \( \text{mol kg}^{-1} \)

\( q_t \) total molar loading in mixture, \( \text{mol kg}^{-1} \)

\( q_{\text{sat}, A} \) saturation loading of site A, \( \text{mol kg}^{-1} \)

\( q_{\text{sat}, B} \) saturation loading of site B, \( \text{mol kg}^{-1} \)

\( t \) time, s

\( T \) absolute temperature, K

\( u \) superficial gas velocity in packed bed, \( \text{m s}^{-1} \)

\( v \) interstitial gas velocity in packed bed, \( \text{m s}^{-1} \)

Greek letters

\( \varepsilon \) voidage of packed bed, dimensionless

\( \nu \) exponent in dual-Langmuir-Freundlich isotherm, dimensionless

\( \theta_i \) fractional occupancy within the pores, dimensionless

\( \rho \) framework density, \( \text{kg m}^{-3} \)

\( \tau \) time, dimensionless
\textit{Subscripts}

\begin{itemize}
\item[i] referring to component $i$
\item[A] referring to site A
\item[B] referring to site B
\item[t] referring to total mixture
\end{itemize}
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