Supplementary Information

Understanding the interactions between the bis(trifluoromethylsulfonyl)imide anion and absorbed CO$_2$ using X-ray diffraction analysis of a soft crystal surrogate

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Supplementary Methods

1. Methods

**Elemental analysis:** Elemental analysis was measured in Global Facility Center, Hokkaido University, using MICRO CORDER JM10 (J-Science Lab), CE440 (Exeter Analytical), and DX-500 (Dionex).

**Fourier Transform Infrared (FT-IR) spectrum:** FT-IR spectrum was measured by using a Nicolet iS10 FT-IR (Thermo Scientific) at room temperature.

**Thermogravimetric (TG) analysis:** TG curve was measured by using a ThermoPlus2/TG-DTA8129 (Rigaku Corp.) from room temperature to 773 K under nitrogen flow of 100 mL/min and at a heating rate of 10 K/min.

**Powder X-ray diffraction (PXRD) analysis:** Powder X-ray diffraction analysis was measured by using a RINT-Ultima III diffractometer (Rigaku Corp.) with Cu-Kα radiation (\( \lambda = 1.5418 \, \text{Å} \)).
### 2. Crystal Structures

**Supplementary Table 1.** Crystallographic data of \( \text{I} \) and \( \text{I} \cdot 2\text{CO}_2 \).

| Chemical Formula | \([\text{Cu(NTf}_2]_2(\text{bpp})_2]\) | \([\text{Cu(NTf}_2]_2(\text{bpp})_2\cdot 2\text{CO}_2]\) |
|------------------|--------------------------------|----------------------------------|
| Formula          | \( \text{C}_{28}\text{H}_{28}\text{CuF}_6\text{N}_7\text{O}_4\text{S}_2 \) | \( \text{C}_{30}\text{H}_{28}\text{CuF}_6\text{N}_9\text{O}_8\text{S}_2 \) |
| Formula weight   | 1020.36                         | 1108.38                          |
| Crystal system   | Monoclinic                       | Monoclinic                       |
| Space group      | \( P2/n \)                       | \( C2/c \)                       |
| Temperature / K  | 173                              | 173                              |
| \( a / \AA \)    | 9.7230(9)                        | 20.5810(6)                       |
| \( b / \AA \)    | 12.1946(10)                      | 12.3407(2)                       |
| \( c / \AA \)    | 17.1072(14)                      | 18.9377(6)                       |
| \( \alpha / ^\circ \) | 90                              | 90                              |
| \( \beta / ^\circ \) | 96.176(3)                       | 114.545(4)                       |
| \( \gamma / ^\circ \) | 90                              | 90                              |
| \( V / \AA^3 \)  | 2016.6(3)                        | 4375.2(2)                        |
| \( Z \)          | 2                                | 4                               |
| GOF on \( F^2 \) | 1.102                            | 1.280                            |
| \( R_1 [I > 2\sigma(I)] \) | 0.0579                          | 0.0823                           |
| \( R_w [I > 2\sigma(I)] \) | 0.1530                          | 0.2665                           |

\( aR_1 = \frac{\sum ||F_o| - |F_c||}{\Sigma |F_o|}, \ bR_w = \frac{[(\sum w(|F_o|^2 - |F_c|^2)^2)/\Sigma w(F_o^2)^2]^{1/2}}{.} \)
Supplementary Table 2. Crystallographic data of 2.

| 2          |                  |
|------------|------------------|
| Chemical Formula               | [Cu(NMes$_2$)$_2$(bpp)$_2$] |
| Formula                | C$_{30}$H$_{40}$CuN$_6$O$_8$S$_4$ |
| Formula weight            | 804.46            |
| Crystal system            | Monoclinic        |
| Space group               | $P2_1/c$          |
| Temperature / K           | 293               |
| $a$ / Å                  | 9.7086(8)         |
| $b$ / Å                  | 17.8811(11)       |
| $c$ / Å                  | 11.4903(7)        |
| $\alpha$ / °             | 90                |
| $\beta$ / °              | 109.910(8)        |
| $\gamma$ / °             | 90                |
| $V$ / Å$^3$              | 1875.5(2)         |
| $Z$                      | 2                 |
| GOF on $F^2$             | 1.282             |
| $R_1 [I > 2\sigma(I)]^a$ | 0.1282            |
| $R_w [I > 2\sigma(I)]^b$ | 0.2712            |

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $^bR_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2]^{1/2}$. 
Supplementary Figure 1. Conformation of NTf$_2^-$ anions in (a) 1 and (b) 1·2CO$_2$. The CF$_3$ parts in 1 are disordered over two sites with occupancies of 0.66 and 0.34.
Supplementary Figure 2. One-dimensional structure of (a) 1 and (b) 1·2CO₂ viewed along the $a$ and $c$ axes, respectively. The hydrogen atoms are omitted for clarity.
Supplementary Figure 3. Packing structures of (a) 1 and (b) 1·2CO₂ viewed along the b and c axes, respectively. The hydrogen atoms and CO₂ molecules are omitted for clarity.
Supplementary Figure 4. View of the interchain interactions of (a) 1 and (b) 1·2CO₂. The CF₃ parts in 1 are disordered over two sites with occupancies of 0.66 and 0.34. In 1, there are two kinds of weak interactions; one is observed between the NTf₂⁻ fluorine atom and the bpp methylene hydrogen atom with F₁⋯H₁₁B = 2.54(2) Å, F₁⋯C₁₁ = 3.37(2) Å, and F₁⋯H₁₁B-C₁₁ = 140.9(5) °, F₁A⋯H₁₁B = 2.43(2) Å, F₁A⋯C₁₁ = 3.24(3) Å, and F₁A⋯H₁₁B-C₁₁ = 139.1(7) °. The other is between the NTf₂⁻ oxygen atom and the bpp pyridine hydrogen atom with O₃⋯H₅ = 2.362(4) Å, O₃⋯C₅ = 3.188(5) Å, and O₃⋯H₅-C₅ = 145.0(2) °. In 1·2CO₂, one kind of interchain interaction is found between the NTf₂⁻ oxygen atom and the bpp pyridine hydrogen atom with O₃⋯H₁₀ = 2.575(3) Å, O₃⋯C₁₀ = 3.359(5) Å, and O₃⋯H₁₀-C₁₀ = 142.3(2) °.
**Supplementary Figure 5.** Arrangement of NTf$_2^-$ anions in (a) 1 and (b) 1·2CO$_2$ viewed along the $a$ and $c$ axes, respectively. The hydrogen atoms are omitted for clarity.
Supplementary Figure 6. Views of the crystal structure of 2. (a) Coordination environment around the Cu center and (b) 1D chain structure.
3. Thermogravimetric Analysis

**Supplementary Figure 7.** TG curve of 1. There is no weight loss until ca. 570 K, implying the thermal stability of 1.
4. Fourier Transform Infrared Spectroscopy

Supplementary Figure 8. FT-IR spectrum of 1. The bands at 1317 and 1354 cm\(^{-1}\) can be assigned to the asymmetric vibration bands of the NTf\(_2^-\) sulfonyl group, while the band at 1132 cm\(^{-1}\) can be assigned to the symmetric vibration band of the NTf\(_2^-\) sulfonyl group. The band at 1173 cm\(^{-1}\) can be assigned to the vibration band of the NTf\(_2^-\) trifluoromethyl group.
5. Absorption/Desorption Isotherms

Supplementary Figure 9. Adsorption (closed symbols)/desorption (open symbols) isotherms of 1 for N₂ (blue reversed triangle) and Ar (green triangle) at 195 K.
Supplementary Figure 10. Gas absorption (closed symbols)/desorption (open symbols) isotherms of 2 for N\textsubscript{2} (blue reversed triangle) and Ar (green triangle) at 195 K.
Supplementary Figure 11. CO$_2$ absorption (closed symbols)/desorption (open symbols) isotherms of 1 at 243 K (black square), 258 K (red circle), and 273 K (blue rhombus).
Supplementary Figure 12. Plot of $\ln P_{th}$ ($P_{th}$ = the threshold pressures) against $T^{-1}$. From the CO$_2$ absorption isotherms at different temperatures (Figure S8), remarkable $P_{th}$ are determined and they are regarded as the equilibrium pressures for the CO$_2$ absorption reaction. Therefore, the enthalpy of CO$_2$ absorption can be calculated using the following Clausius-Clapeyron equation,

$$
\frac{Q_{st}}{R} = \frac{d \ln P_{th}}{dT^{-1}}
$$

where $R$ and $Q_{st}$ represent the gas constant and the enthalpy of absorption, respectively. The plot of $\ln P_{th}$ versus $T^{-1}$ yields the straight line, whose slope affords the $Q_{st} = -29.1$ kJ mol$^{-1}$. 

6. Theoretical Calculation

**Supplementary Figure 13.** Definition of the NTf$_2^-$ dihedral angle for relax scan calculation.
Supplementary Figure 14. Optimized structures of 1 (left) and 1·2CO₂ (right). The upper and bottom right figures show the optimized structures with the disordered CO₂ molecules A and B, respectively. The binding energies, $E_b$, were calculated from these optimized structures to be $-31.3 \text{ kJ}\cdot\text{mol}^{-1}$ for both disordered CO₂ molecules.
**Supplementary Table 3.** Atomic charges obtained from the Bader analysis for NTf$_2^-$ anions in the model structure with CO$_2$ constructed from the CO$_2$-absorbed phase (1·2CO$_2$). The atom numbering figures are shown in the bottom. Atomic charges in the similar model without CO$_2$ constructed from the desolvated phase (I) are shown in parentheses.

| NTf$_2^-$ in the model |  |  |
|------------------------|---|---|
| F1: -0.607 (-0.608)    | F2: -0.605 (-0.618) | F3: -0.598 (-0.603) |
| F4: -0.610 (-0.600)    | F5: -0.611 (-0.608) | F6: -0.616 (-0.584) |
| O3: -1.260 (-1.261)    | O4: -1.267 (-1.281) | O5: -1.264 (-1.278) |
| O6: -1.260 (-1.285)    | S1: +2.992 (+3.027) | S2: +3.014 (+3.053) |
| N1: -1.538 (-1.577)    | C2: +1.670 (+1.645) | C3: +1.645 (+1.600) |
| F1’: -0.602 (-0.603)   | F2’: -0.612 (-0.618) | F3’: -0.601 (-0.608) |
| F4’: -0.610 (-0.608)   | F5’: -0.603 (-0.584) | F6’: -0.615 (-0.600) |
| O3’: -1.274 (-1.281)   | O4’: -1.252 (-1.261) | O5’: -1.271 (-1.278) |
| O6’: -1.291 (-1.285)   | S1’: +2.970 (+3.027) | S2’: +3.004 (+3.053) |
| N1’: -1.518 (-1.577)   | C2’: +1.657 (+1.645) | C3’: +1.664 (+1.600) |
Supplementary Figure 15. Model structure used for the energy decomposition analysis with the natural orbitals from chemical valence theory (EDA-NOCV). The values indicate the distances (Å) between neighboring atoms.

Supplementary Table 4. Energetic components of interaction energy (in kJ mol$^{-1}$) in the framework•••CO$_2$ model structure used for the EDA-NOCV analysis.

|      |       |
|------|-------|
| $E_{\text{pauli}}$ | 31.1  |
| $E_{\text{elst}}$  | -25.0 |
| $E_{\text{orb}}$   | -13.3 |
| $E_{\text{disp}}$  | -28.7 |
| $E_{\text{int}}$*$ | -35.9 |

*a $E_{\text{int}}$ is a summation of $E_{\text{pauli}}$, $E_{\text{elst}}$, $E_{\text{orb}}$, and $E_{\text{disp}}$. 