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A Water-Stable Twofold Interpenetrating Microporous MOF for Selective CO₂ Adsorption and Separation

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S Supporting Information

ABSTRACT: Self-assembly of bent dicarboxylate linker 4,4'-sulfonyldibenzoic acid (H₂SDB) and flexible N,N-donor spacer 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L) with $Co(NO_3)_2 \cdot 6H_2O$ forms a twofold interpenetrated $\{[Co_2(SDB)_2(L)] \cdot (H_2O)_4 \cdot (DMF)\}_{n}$ (IITKGP-6) network via solvothermal synthesis with sql(2,6L1) topology, which is characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, elemental analysis, powder X-ray diffraction (XRD), and single-crystal XRD. The framework is microporous with a solvent-accessible volume of 25.5% and forms a one-dimensional channel along $\begin{bmatrix} 1-1 & 0 \end{bmatrix}$ direction with the dimensions of $\sim 3.4 \times 5.0$ Å². As the stability of metal–organic frameworks (MOFs) in the presence of water is a topic of significant importance while considering them for practical applications, this framework reveals its high stability toward water.



The desolvated framework shows modest uptake of CO2 (50.6 and 37.4 cm³ g⁻¹ at 273 and 295 K under 1 bar pressure, respectively), with high selectivity over N_2 and CH_4 . Ideal adsorbed solution theory calculations show that the selectivity values of CO_2/N_2 (15:85) are 51.3 at 273 K and 42.8 at 295 K, whereas CO_2/CH_4 (50:50) selectivity values are 36 at 273 K and 5.1 at 295 K under 100 kPa. The high CO₂ separation selectivity over N₂ and CH₄ along with its water stability makes this MOF a potential candidate for CO₂ separation from flue gas mixture and landfill gas mixture as well.

INTRODUCTION

The benefits in simple construction and structural investigations of metal-organic frameworks (MOFs) have manifestly decreased during the past several years; however, research interest in extending MOF applications¹ is rapidly increasing in diverse fields such as gas storage, ^{1b,2} gas separation, ^{1b,3} proton conduction,⁴ drug delivery,⁵ catalysis,⁶ sensing,⁷ photoluminescence,⁸ and many others⁹ due to their permanent porosity, flexible pore surface, fine-tuning pore size, and extra-high surface areas. While considering new porous materials including MOFs for practical applications, in particular, adsorption-based gas separation and purification systems, the stability of an adsorbent in humid environments is a serious issue that must be taken into account with the obvious high adsorption loadings and selectivities for the target gas molecule, as water is omnipresent in various industrial streams. For example, water is a major component of flue gas $(CO_2/N_2 = 15/85)$ of coal-fired power plants and must not be ignored while examining the potential of adsorbent materials for CO₂ capture and separation from flue gas stream. Purification of landfill gas $(CO_2/CH_4 =$ 50/50) also needs to deal with varying amount of water content during separation process by adsorbent materials. Obviously, hydrostability of the MOF-based adsorbent will be a serious issue for successful implementation in carbon capture technology, as the material may degrade over time because of lack of stability in the presence of water. Although much has been studied on porous MOFs for their above-mentioned diverse applications, less focus has been made to investigate

those materials for their stability in water.¹⁰ Sadly, many reported MOFs are water-unstable except for some examples of imidazolate-based zeolitic imidazolate frameworks (ZIFs), Materials of Institut Lavoisier based on the trivalent metal ions, zirconium(IV)-based MOFs, and a few more. 10c In general, MOFs ligated with N-coordination exhibit better stability toward water, as the basicity of those ligands are higher than their carboxylate counterparts.¹¹ While comparing the traditional hydrophobic adsorbents such as activated carbons and zeolites to their MOF counterparts, the easily hydrolyzable nature of metal-carboxylate bonds along with high susceptibility of coordinatively unsaturated metal nodes toward water are the main deterrents of MOF materials for successful implementations in practical applications.^{10a}

Several factors such as adsorption energy of CO2, the framework polarity, and shape/size of the pores determine the aforementioned selectivities.¹² Additionally, the separation selectivity can be controlled by modifying the network structures thorough immobilization of different polar functionality onto the pore surface.¹³ Hence, the introduction of polar parts like open metal sites or direct incorporation of polar functionality on the framework backbone is a very useful practice to improve adsorption selectivity for CO₂ with a large quadrupole moment.¹² For example, existence of a polar group like H₂O onto the pore surface of an MOF can have significant

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impact on CO_2 adsorption and separation properties as demonstrated by Chen et al.¹⁴ Additionally, by taking advantage of Lewis acidic nature of CO_2 itself, the selectivity for CO_2 adsorption can also be enhanced by judicious selection of N-rich spacers such as hydrazine derivatives of N,N donor spacers for enhanced interactions with CO_2 . Keeping those facts in mind, we designed our MOF bearing a $-SO_2$ polar functionality on a V-shaped organic linker and N-rich sites on a linear spacer for enhanced interactions of CO_2 molecules with excellent separation selectivity toward CO_2/N_2 and CO_2/CH_4 .

To this end, we report a water-stable twofold interpenetrating MOF, { $[Co_2(SDB)_2(L)] \cdot (H_2O)_4 \cdot (DMF)$ } (IITKGP-6, IITKGP stands for Indian Institute of Technology Kharagpur), constructed by 4,4'-sulfonyldibenzoic acid (H₂SDB), flexible N,N-donor linear spacer 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L) and Co(NO₃)₂·6H₂O. This framework has polar functionality exposed toward the channel along $\begin{bmatrix} 1-1 & 0 \end{bmatrix}$ direction and unbound N-sites on the spacer. Gas sorption analysis of the desolvated IITKGP-6a shows modest uptake of CO_2 (50.6 and 37.4 cm³ g⁻¹ at 273 and 295 K, respectively) under 1 bar pressure with good selectivity over N₂ and CH₄. IAST calculations based on dual-site Langmuir-Freundlich fittings of single component isotherms indicate that the selectivity values of CO_2/N_2 (15:85) are 51.3 at 273 K and 42.8 at 295 K and that the selectivity values of CO_2/CH_4 (50:50) are 36 at 273 K and 5.1 at 295 K under 100 kPa, which makes this MOF a potential contender for separation of flue gas and purification of landfill gas mixture.

EXPERIMENTAL SECTION

Materials. $Co(NO_3)_2$ · $6H_2O$ (Merck India), pyridine-4-carboxaldehyde (Alfa Aesar), 4,4'-sulfonyldibenzoic acid (H₂SDB; Sigma-Aldrich), hydrazine hydrate (Merck), and organic solvents (dimethylformamide (DMF), chloroform) were used without additional purification.

Synthesis of 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L). This ligand was synthesized according to a literature report.¹⁵ To a 30 mL dry ethanol solution of pyridine-4-carboxaldehyde (3.79 mL, 40 mmol), hydrazine hydrate (0.97 mL, 20 mmol) was added dropwise and was allowed to stir for 24 h under nitrogen. The yellow product that appeared as precipitate was filtered, washed with hexane/ethanol (1:1, 20 mL), and treated under vacuum. Yield: 90%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.70 (d, 4H), 8.50 (s, 2H), 7.64 (d, 4H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 123.84, 142.29, 152.32, 162.13. Mass (matrix-assisted laser desorption/ionization time of flight (MALDI-TOF)): *m/z* 211.495 (M+1). Fourier transform infrared (FT-IR; KBr, cm⁻¹): 1624.8(s), 1590.8(m), 1553.5(m), 1414(s), 1339.5(w), 1308.5(s), 1237.2(s), 1209.3(w), 1082.2(s), 973(s), 955.01(s), 877.5(s), 815.5(s), 744.19(s), 716.28(s), 679.1(s), 508.53(s).

Physical Measurements. Elemental analyses (C, H, N, S) were performed on an Elementar, Vario Micro Cube elemental analyzer.

FT-IR spectra (KBr pellets) were recorded on a PerkinElmer RX1 spectrophotometer. Powder X-ray diffraction (PXRD) data were collected (Cu K α radiation of 1.5418 Å) on a Bruker D8 Advance diffactometer. Thermogravimetric analysis (TGA) was executed with a TG 209 F3 Tarsus (Netzsch), and the sample was heated from room temperature to 800 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}$ min $^{-1}$ rate under N_2 gas flow. $^1\text{H}\text{,}~^{13}\text{C}$ NMR spectrum was recorded using a Bruker Avance II 400 spectrometer. Mass spectrum was obtained using a Bruker MALDI-TOF/TOF spectrometer. Gas sorption experiments were performed using a Micromeritics 3-Flex Surface Characterization Analyzer (with micropore ports) at different temperatures. All the guest solvents in the framework were exchanged with dry chloroform at least 10 times within 3 d, and the framework was evacuated at 373 K for 12 h until an outgas rate of 5 μ mHg min⁻¹ was achieved. The measurement temperatures for sorption isotherms at 273 and 295 K were maintained with an ice-water bath and water bath, respectively.

Single Crystal X-ray Diffraction. The cell parameters and refinement data are collected in Table S1 (Supporting Information). Particular bond lengths and angles are listed in Table S2. A suitable size single crystal protected with mineral oil was mounted on a fiber glass tip and cemented using epoxy resin. Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) is used for data collection at 298 K. The structure was solved by direct method (SIR97),¹⁶ and the data were refined using full-matrix least-squares technique on F^2 (WINGX, v2014.1) and SHELXL-2014.¹⁷ Riding model was used to place all H atoms in calculated positions with fixed isotropic displacement parameters. Highly disordered solvent molecules could not be modeled with certainty, and thus, SQUEEZE/PLATON¹⁸ is used to generate a new set of F^2 (*hkl*) values without solvent contributions, which was used for further refinements of the structure. CCDC 1569337 contains the full crystallographic data with embedded hkl, res, and SQUEEZE files.

RESULTS AND DISCUSSION

The reaction of bent dicarboxylate linker 4,4'-sulfonyldibenzoic acid (H₂SDB) and flexible N,N-donor spacer 1,4-bis(4pyridyl)-2,3-diaza-1,3-butadiene (L) with $Co(NO_3)_2 \cdot 6H_2O$ under solvothermal condition gave reddish crystal of IITKGP-6. The molecular formula was established as $\{[Co_2(SDB)_2(L)] \cdot (H_2O)_4 \cdot (DMF)\}_n$ by the combination of elemental analysis, TGA, and single-crystal XRD. The result of single-crystal X-ray analysis revealed that it crystallizes in a triclinic crystal system, with a space group of $P\overline{1}$, and the asymmetric unit contains two Co(II) ions, one L spacer, and two SDB²⁻ linkers. The coordination geometry around the dinuclear Co(II) units with a Co-Co separation distance of 2.81 Å is depicted in Figure 1a. The Co(II) ions display distorted square-pyramidal geometries by coordination of four oxygen atoms [Co-O = 2.003(4)-2.086(4) Å] from four linkers and a nitrogen atom [Co-N = 2.033(5)-2.053(5) Å]of the L spacer. The framework is composed of paddle-wheel $\{Co_2(COO)_4\}$ secondary building units that are bridged by both the ligands to form a layer structure. While considering the central sulfur atoms of the SDB²⁻ ligands as two-connected nodes and the paddle wheel unit as six-connected nodes, the framework can be evaluated as a 2,6-connected two-dimensional (2D) net with sql(2,6L1) topology with point symbol: $\{(4^2.6^8.8.10^4)(4)_2\}$ (Figure 1b).¹⁹ The linkers L with length of 17.99 Å connect the looped chains of rhombic grids (8.63 \times 8.65 Å) leading to the formation of a twofold interpenetrating parallel network as represented in Figure1c. Total potential solvent-accessible volume is 604 Å³ (25.5%) per unit cell volume of 2371.1 Å³ as estimated by PLATON.¹⁸ Despite interpenetration, IITKGP-6 shows lozenge-shaped channels of approximate size of 3.4×5.0 Å² (considering van der Waals



Figure 1. (a) View of paddle-wheel unit and surrounding environment in **IITKGP-6**. (b) An illustration of a layer with the *sql*(2,6*L1*) topology. (c) A schematic representation of twofold interpenetrated network. (d) Packing diagram showing pore surfaces decorated with $-SO_2$ functionality along $[1-1 \ 0]$ direction.

radii) along $[1-1 \ 0]$ direction as depicted in Figure 1d, which are filled by solvent molecules. Moreover, five intermolecular C-H…O contacts among the components are accountable for stabilizing the whole framework (Table S3, Supporting Information).

The phase purity of the bulk material was established by PXRD study, which revealed a good agreement with the corresponding simulated patterns obtained from single-crystal data (Figure S1, Supporting Information). The TGA showed ~14.3% weight loss until 200 °C, which is ascribed to the release of lattice solvent molecules (four water molecules and one DMF molecule; Figure S4, Supporting Information). No weight loss from 200 to 375 °C could be seen before degradation of the framework indicating its good thermal stability. To assess the water stability, IITKGP-6 was immerged in water for 48 h, filtered, and dried. The PXRD pattern of the dried sample after soaking in water reveals exact similarity with

as-synthesized pattern (Figure S3, Supporting Information) confirming its water stability. Recently, effect of catenation/ interpenetration on the water stability of MOFs was demonstrated by Walton et al.²⁰ Thus, absence of coordinatively unsaturated metal centers, which is mostly responsible for framework degradation,¹⁰ presence of N coodinations¹¹ to the paddle-wheel {Co₂(COO)₄} structural building unit (SBU) and interpenetrating nature,²⁰ possibly makes this MOF a water-stable material.

To evaluate the permanent porosity, the as-synthesized sample was immersed in dry chloroform for 3 d to remove the high-boiling guest solvents. PXRD showed good agreement among the simulated pattern, the as-synthesized pattern, the chloroform-exchanged pattern, and the activated pattern indicating retention of the porous structure after solvent exchange and successive elimination of exchanged solvent molecules from the channels (Figure S2, Supporting Information). Approximately 70 mg of exchanged sample was activated at 100 °C for 12 h for the adsorption study. The N₂ sorption isotherm of activated sample (IITKGP-6a) displays an uptake of 83.4 cm³ g⁻¹ at 1 bar pressure with steep increase in adsorption amounts under low relative pressure $(P/P_0 < 0.01)$ as depicted in Figure S5 (Supporting Information). The Brunauer-Emmett-Teller (BET) surface area was estimated to be 279 m² g⁻¹ from the low-pressure adsorption region with pore volume of 0.12 cm³ g⁻¹ (Figure S6, Supporting Information). Moreover, the N₂ sorption isotherm of watertreated and dried sample displays an uptake of 76 cm³ g^{-1} at 1 bar and 77 K (Figure S7, Supporting Information) exhibiting negligible loss in BET surface area compared to the pristine sample (254 vs 279 $m^2 g^{-1}$) and thus unambiguously establishing the water stability of IITKGP-6. The hydrogen sorption isotherm indicates an uptake of 0.76 wt % at 77 K/1 bar (Figure S8, Supporting Information).

We further investigated the sorption behaviors of IITKGP-6a for CO₂, CH₄, and N₂ to test its CO₂/CH₄ and CO₂/N₂ separation selectivity at ambient conditions. Single-component gas sorption isotherms performed at 273 and 295 K are presented in Figure 2a,b, respectively. CO₂ uptake values at 273 and 295 K/1 bar are 50.6 cm³ g⁻¹ (9.9 wt %) and 37.4 cm³ g⁻¹ (7.3 wt %), respectively. It is of particular interest that the



Figure 2. CO_2 , CH_4 , and N_2 sorption isotherms of IITKGP-6a (a) at 273 K and (b) at 295 K (CO_2 : red, CH_4 : blue, N_2 : magenta, solid and open symbols represent adsorption and desorption, respectively).



Figure 3. Loading amounts in mixed gas phase and separation selectivities at 273 K (a, b) and 295 K (c, d) predicted by IAST for CO_2/CH_4 (50:50) and CO_2/N_2 (15:85).

present CO₂ uptake capacities are similar to the uptake amounts of well-known MOFs such as SIFSIX-2-Cu, [Cu- $(bcppm)H_2O]$, $[Zn_2(BME-bdc)_2(bipy)]_w$ and activated carbon^{21,22c,25d} but higher than familiar MOFs, to name a few such as ZIFs-25, -71, -93, -95, -97, and -100, IRMOF-3, and MOF- $177.^{22}$ Interestingly, it adsorbed high amounts of CO₂ at 0.5 bar $(1.66 \text{ mmol } \text{g}^{-1} \text{ at } 273 \text{ K and } 1.08 \text{ mmol } \text{g}^{-1} \text{ at } 295 \text{ K})$, which is the partial pressure of CO₂ in landfill gas mixture. Therefore, steep uptakes in the low-pressure regions indicate a high CO₂ affinity toward the polar pore surfaces. On the one hand, in addition to well-established quadrupole-quadrupole interactions among CO₂ molecules and presence of high density of N atoms for Lewis base-Lewis acid interactions, plausible dipole-quadrupole interactions of CO2 gas molecules with the polar pore surface decorated with $-SO_2$ groups that are exposed toward the channels (Figure 1d) may also correspond to the present uptake capacity.^{12–14} On the other hand, it takes up much lower amount of CH_4 (13.8 cm³ g⁻¹, 0.98 wt % at 273 K; 9.2 cm³ g⁻¹, 0.66 wt % at 295 K) and N₂ (6.2 cm³ g⁻¹, 0.78 wt % at 273 K; 4.1 cm³ g⁻¹, 0.52 wt % at 295 K) under 1 bar pressure.

To evaluate quantitative binding strengths of CO_2 , CH_4 , and N_2 gas molecules with the framework, the coverage-dependent adsorption enthalpies were calculated from their adsorption isotherms at 273 and 295 K by using Clausius–Clapeyron equation (Figure S9, Supporting Information). The enthalpies at zero loading are 23, 18.4, and 5.1 kJ mol⁻¹ for CO_2 , CH_4 , and

N₂, respectively, indicating the gas affinity in the decreasing order of CO₂ > CH₄ > N₂. The enthalpy value of CO₂ is comparable to the values for MIL-53-Al (20.1 kJ mol⁻¹), PCN-88 (27 kJ mol⁻¹), MOF-5 (17 kJ mol⁻¹), and NOTT-140 (25 kJ mol⁻¹). The fairly constant enthalpy values specify homogeneity of CO₂ binding sites over the entire loading range within the pores. On the one hand, the higher CO₂ affinity may be attributed to the strong interactions of CO₂ with the $-SO_2$ groups and the confined channel structure. On the other hand, the high difference in polarizability between CH₄ and N₂ could be the reason for stronger interaction of CH₄ with the pore surface and thus result in comparatively better uptake than N₂.

We further studied the potential of IITKGP-6a for gas separations. The mixture selectivities at two different temperatures (273 and 295 K) were calculated based on ideal adsorbed solution theory (IAST) developed by Myers and Prausnitz for mixed CO_2/CH_4 (50:50, landfill gas composition), and CO_2/N_2 (15:85, flue gas composition) with pressures up to 100 kPa.²³ Pure-component adsorption data at particular temperatures are taken as inputs to the IAST calculation, whereas the output predicts mixture adsorption equilibrium over a desired pressure range. The precision of the IAST calculations for loading approximation of gas components present in binary mixtures in a diverse range of MOFs and zeolites are well-recognized in comparison with the Configurational-Biast Monte Carlo (CBMC) simulations for calculation

of mixture adsorption studies.²⁴ The results of IAST calculations have shown that, under 100 kPa, the selectivity for CO₂/N₂ mixture is 51.3 at 273 K and 42.8 at 295 K; the selectivity for CO₂/CH₄ mixture is 36 at 273 K and 5.1 at 295 K (Figure 3a-d). All of these four values are significantly higher than those of many well-known MOFs: PCN-88 (CO₂/N₂: 18/ 296 K, CO₂/CH₄: 5/296 K), PCN-61 (CO₂/N₂: 15/298 K), ZJNU-44a (CO₂/N₂: 15/296 K), UTSA-34a (CO₂/CH₄: 5.1/ 296 K), SIFSIX-2-Cu (CO₂/N₂: 13.7/298 K), Cu₂₄(TPBTM)₈ (CO₂/N₂: 22/298 K), PMOF-3a (CO₂/N₂: 29.2/273 K and 23.4/296 K, CO₂/CH₄: 8/273 K and 5.1/296 K), MOF-177 (CO₂/N₂: 3.6/296 K), Cu-BTTri (CO₂/N₂: 21/298 K), en-Cu-BTTri (CO₂/N₂: 25/298 K), JUC-141 (CO₂/N₂: 21.6/273 K and 27.6/298 K, CO₂/CH₄: 4.2/273 K), NOTT-202a (CO₂/ N₂: 26.7/273 K and 4.3/293 K, CO₂/CH₄: 2.9/273 K and 1.4/ 293 K), many ZIF materials (ZIF-68, CO₂/N₂: 18.7/298 K, CO₂/CH₄: 5/298 K; ZIF-69, CO₂/N₂: 19.9/298 K, CO₂/CH₄: 5.1/298 K) and benchmark zeolite MFI (CO_2/N_2 : 11.2/296 K, CO_2/CH_4 : 2.5/296 K).^{14,25} Both CO_2/N_2 and CO_2/CH_4 selectivity at different pressures and temperatures with the type of selectivity calculations (IAST, Henry Law, isotherm slopes) based on literature survey is tabulated in Table S5 (Supporting Information). It needs to be pointed out that IITKGP-6a has the modest CO₂ uptake capacity but displays a higher CO_2/N_2 and CO_2/CH_4 selectivity, underlying the uniqueness of this new water-stable interpenetrating MOF for carbon dioxide capture and separation from flue gas as well as landfill gas mixture.

Besides gas separation selectivity, capacity consideration of adsorbed amount of the desired gas in mixed gas phase is important to assess the capability of a given adsorbent material in a pressure-swing adsorption (PSA) unit. The loading capacity of CO_2 in the mixed gas phase at equilibrium $(CO_2/$ N_2 : 15/85 and CO_2/CH_4 : 50/50) within the porous framework at 273 K (Figure 3a,b) and 295 K (Figure 3c,d) was calculated up to 100 kPa pressure. At this pressure, we note that maximum CO_2 loadings from binary CO_2/N_2 mixture are 0.7 and 0.33 mmol g^{-1} at 273 and 295 K, respectively. The loading value of 0.33 mmol g^{-1} at 296 K is higher than MOF-177 (0.16 mmol g^{-1} at 295 K/100 kPa) and zeolite MFI (0.26 mmol g^{-1} at 295 K/100 kPa).¹⁴ For the case of binary CO₂/CH₄ gas mixture these values are 1.54 and 0.77 mmol g^{-1} at 273 and 295 K, respectively, which is comparable to Zn₄O(FMA)₃ (0.89 mmol g^{-1} at 296 K/2 bar) and zeolite MFI (1.07 mmol g^{-1} at 296 K/ 2 bar).¹⁴

CONCLUSION

To conclude, a new water-stable twofold interpenetrating microporous MOF with sql (2,6L1) topology, assembled from a V-shaped carboxylic acid linker with $-SO_2$ functionality and a N-rich N,N-donor spacer, has been synthesized. The incorporation of polar functional group in corroborating with Lewis basic N-sites may have significant effect on CO₂ adsorption with the help of enhanced interactions with those multiple functional sites. Gas adsorption studies demonstrate its potential toward high separation selectivity for CO₂ over N₂ and CH₄ under the conditions relevant to flue gas and landfill gas separation. High separation values supporting with high loadings in mixed gas phase were achieved. Given the fact that poor stability of porous MOFs in water are of real concern, the development of water-stable porous MOFs with introduction of multiple functional sites into a single framework to produce a synergistic effect to expand the interaction with CO_2 to those functional groups in combination with adjusting the pore size should be appealing from the practical application point of view for carbon dioxide separation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02136.

Crystallographic data, PXRD, TGA, IAST calculation details, related plots, and tabulated data of IAST selectivity (PDF)

Accession Codes

CCDC 1569337 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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