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Selective Organosulfur Removal by a Heterometallic MOF: Synthesis and Thermodynamically-Controlled Phase Transition

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Supporting Information

ABSTRACT: Selective removal of heterocyclic organosulfur compounds from fuels can relieve increasingly serious environmental problems (e. g. gas exhaust contaminants triggering the formation of acid rain that can damage fragile ecological systems). Toward this end, we designed and synthesized novel MOF-based sorbent materials with distinct hard and soft metal building units, specifically

$\{[\text{Yb}_6\text{Cu}_{12}(\text{OH})_4(\text{PyC})_{12}(\text{H}_2\text{O})_{36}]\cdot(\text{NO}_3)_{14}\cdot x\text{S}\}_n$ (QUST-81) and

$\{[\text{Yb}_4\text{O}(\text{H}_2\text{O})_4\text{Cu}_8(\text{OH})_{8/3}(\text{PyC})_8(\text{HCOO})_4]\cdot(\text{NO}_3)_{10/3}\cdot x\text{S}\}_n$ (QUST-82), where H_2PyC = 4-Pyrazolecarboxylic acid. Exploiting the hard/soft duality, we show the more stable QUST-82 can selectively remove organosulfur in the presence of competing nitrogen-containing contaminate. In addition, we uncovered a thermodynamically-controlled single-crystal-to-single-crystal (SC-SC) phase transition from QUST-81 to QUST-82, and, in turn, probed mechanistic features *via* XRD, ICP-AES and *ab initio* molecular dynamics (AIMD) simulations.

Gasoline and diesel contain significant levels of heterocyclic organosulfur compounds, such as dibenzothiophene (DBT) and benzothiophene (BT). Such contaminants lead to serious environmental and health issues; namely, exhaust gases SO_x, eventually contribute to the formation of acid rain and harmful particulate matter. To address such

problems, fuel producers are required to reduce sulfur level to less than 10 ppmw S.¹⁻³ Current methods rely on catalytic hydrodesulphurization (HDS)—a high-cost, high-temperature/pressure catalytic process that consumes a great deal of hydrogen.⁴⁻⁶ A promising alternative method of sulfur mitigation is based on the adsorptive removal of organosulfur compounds, a difficult prospect considering the complicated mixture of contaminants in fuels.⁷⁻¹¹

In this context, metal-organic frameworks (MOFs), a class of crystalline porous materials¹²⁻¹⁴ composed of metal building units connected by organic linkers *via* strong coordination bonds, have emerged for broad potential applications in adsorption and separation.^{15,16} Particularly, MOF structures offer significant advantages over traditional porous materials, such as mesoporous silica and activated carbon. Potential of MOFs for adsorptive desulfurization has been recognized by Matzger and coworkers^{17,18} and carried forward by a number of other scientists and engineers.¹⁹ The resulting research showed: i) nitrogen-containing heterocycle compounds, such as (substituted) indoles or carbazoles, are known to compete for the same adsorption sites as sulfur derivatives;^{20,21} ii) MOFs with open metal sites (OMSs) are found to be more efficient for the adsorption of organosulfur or nitrogen compounds, possibly due to sulfur/nitrogen...metal interactions;²² and iii) hard bases (nitrogen containing aromatics) preferentially interact with hard Lewis acid sites (*i.e.* Fe³⁺, Cr³⁺ or Al³⁺), and softer organosulfur compounds prefer to interact with soft Lewis acid sites (*i.e.* Cu²⁺, Zn²⁺,

Co²⁺ or Ni²⁺)—in accordance with Pearson's hard–soft acid–base (HSAB) theory.²³

To date, only homo-MOFs (Fe³⁺, Cr³⁺, Al³⁺, Cu²⁺, Zn²⁺, Co²⁺ or Ni²⁺) have been employed in desulfurization or denitrogenation applications.¹⁹ The hard Lewis acidic MIL-100 and MIL-101 (Fe³⁺, Cr³⁺ or Al³⁺), for instance, demonstrate excellent selectivity for nitrogen contaminants over organosulfur compounds from simulated fuel feeds.²³ In contrast, the softer Lewis acidic HKUST-1 and CPO-27 (Ni²⁺ or Co²⁺) demonstrate acceptable adsorption of organosulfur compounds; however, competitive adsorption of nitrogen compounds has been shown to decrease desulfurization efficacy.²³ Therefore, the rational design and synthesis of specific heterometallic MOFs, in which both distinct hard- and soft-metal building units are periodically segregated among a crystallographic net,^{24–38} would be an ideal alternative to selectively remove sulfur aromatics in the presence of competing nitrogen compounds.

molecular dynamics (AIMD) simulations. To our knowledge, we are the first to describe such a phase transition in a heterometallic MOF. In addition, the air-stable QUST-82 exhibits great promise for the absorptive removal of prototypical organosulfur compounds, such as DBT and BT, as well as a nitrogen-containing contaminate, indole (IND). Furthermore, QUST-82 continued to selectively prefer organosulfur in a mixture containing competing nitrogen compounds. We hypothesize the selective removal of organosulfur even in the presence of competing nitrogen heterocycles to the dual hard/soft Lewis acid nature in QUST-82.

Solvothermal reactions of 4-Pyrazolecarboxylic acid (H₂PyC), Yb(NO₃)₃·5H₂O and Cu(NO₃)₂·2.5H₂O in a mixture of DMF/DMA/NMP at 100 °C yielded greenish blue single crystals of QUST-81. SCXRD analysis done at the Advanced Light Source (ALS) reveals that the MOF crystallizes in the cubic space group *Fm*-3*m* and has a three-dimensional (3D) network possessing interconnected nanotubular

Figure 1. X-ray crystal structure of QUST-81, showing (a) distinct heterometallic SBUs, (b) cages (c) 3D framework with *pcu* topology. Crystal structure of QUST-82, highlighting structural differences and similarities between QUST-81 and QUST-82 in the (d) cage-metalloligand, (e) SBUs, (f) cages, and (g) *pcu* topology. Atom colors: Yb = green; Cu = light blue; O = red; C = black; N = dark blue. Parts of coordinated water molecules are omitted for clarity.

To this end, herein we report a novel heterometallic MOF, QUST-81 (where QUST = Qingdao University of Science and Technology), having the formula $\{[\text{Yb}_6\text{Cu}_{12}(\text{OH})_4(\text{PyC})_{12}(\text{H}_2\text{O})_{36}] \cdot (\text{NO}_3)_{14} \cdot x\text{S}\}_n$ (where S = unassigned free solvent molecules). Surprisingly, QUST-81 could be transformed into a new MOF, QUST-82 with the formula $\{[\text{Yb}_4\text{O}(\text{H}_2\text{O})_4\text{Cu}_8(\text{OH})_{8/3}(\text{PyC})_8(\text{HCOO})_4] \cdot (\text{NO}_3)_{10/3} \cdot x\text{S}\}_n$, in a single-crystal-to-single-crystal (SC-SC) manner by heating single crystals of QUST-81 in the reaction mixture of origin at an increased temperature (120 °C). Importantly, both MOFs possess identical channel sizes and topological nets, however structural changes can be observed in the metal nodes *via* single-crystal X-ray diffraction (SCXRD). We further probed mechanistic features of the thermodynamically-controlled SC-SC phase transition *via* inductively coupled plasma atomic emission spectroscopy (ICP-AES) and *ab initio*

channels with a pore size of 18 Å. The network is constructed from two distinct and periodic secondary building units (SBUs) (Figure 1a): the classic triangular $\text{Cu}_3(\text{OH})(\text{PyC})_3$ SBU (composed of Cu²⁺ and N atoms of the pyrazolate), and a paddle-wheel $\text{Yb}_2(\text{COO})_4(\text{H}_2\text{O})_8$ SBU (generated from Yb³⁺ and COO[−] from PyC^{2−}). The rare earth-based paddle-wheel SBU is uncommon in MOFs, however, it was first observed in a photo luminescent europium organic framework.³⁹ As a consequence of the assembly process, QUST-81 possesses two kinds of cages (Figure 1b): Cage I, an octahedral cage of diameter 13 Å composed of four triangular $\text{Cu}_3(\text{OH})(\text{PyC})_3$ and six paddle-wheel $\text{Yb}_2(\text{COO})_4$ units. The Cage II is 23 Å in diameter residing in the body center of four Cage I, decorated with eight $\text{Cu}_3(\text{OH})(\text{PyC})_3$ and twelve $\text{Yb}_2(\text{COO})_4$ SBUs. The topology of QUST-81 is *pcu*, in which Cage I and paddle-wheel $\text{Yb}_2(\text{COO})_4$ SBU are respectively recognized as 6- and 2-coordinated nodes (Figures 1c and S1).⁴⁰ The

solvent-accessible volume in QUST-81 is estimated to be 79.9% after removing all of disordered guest solvent molecules and NO_3^- .⁴¹

Figure 2. (a) SEM images of QUST-81-SC, QUST-82-SC and QUST-82-P (SC = single crystal and P = powder). (b) The process of SC-SC phase transition between QUST-81 and QUST-82.

The as-synthesized QUST-81 gradually lost its crystallinity under solvent-free conditions, as confirmed by powder X-ray diffraction (PXRD). However, a new, stable crystalline phase (herein, QUST-82) formed when the single crystals of QUST-81 were reheated at an increased temperature of 120 °C in the original reaction solution (Figure S2a). During this process, we observe neither dissolution nor recrystallization of the single crystals. Scanning electron microscopy (SEM) further confirmed similarities in the size and shape of single-crystals of QUST-81 and QUST-82 (Figure 2a), indicating a possible SC-SC transformation. Further evidence for the SC-SC process comes from the observation that *single crystals* of QUST-82—suitable for SCXRD—could only be obtained through single crystals of QUST-81. *Bulk-powder* of QUST-82, however, can be directly synthesized by similar reaction conditions as QUST-81, a notable difference being a 20 °C increases in the reaction temperature (Figure 2b).

Interestingly, the dark green crystals of QUST-81 turned colorless during the process before turned back to green crystals, suggesting that Cu^{2+} in QUST-81 was first reduced to Cu^+ , and then oxidized back to Cu^{2+} upon exposure to ambient air when QUST-82-SC was isolated (Figure S4).²⁷ Notably, we observed colorless intermediates both in the SC-SC transformation and direct synthesis. PXRD indicated that the structural features of the colorless intermediates are similar to those of QUST-82 (Figure S2a).

To elucidate mechanistic features of the phase transition, single crystals of QUST-81 were heated at 120 °C for 12 h in a fresh mixture of DMF/DMA/NMP and also in a solvent-free condition (Figure 2b). PXRD showed that both resulting products displayed similarities to QUST-81 (Figure S2b), suggesting that the excess of Yb^{3+} in the original reaction solution plays a key role in the formation of QUST-82. Indeed, when we examined the change in Yb^{3+} in the original solution *via* ICP-AES, we noticed a decrease in the concentration of Yb^{3+} from 325.2 to 236.8 ppm, possibly suggesting a change in the Yb^{3+} -based SBU

of QUST-81 occurring in the transformation. This was further confirmed by SCXRD.

SCXRD analysis revealed that the SC-SC transformation, in this case, involved the breaking and formation of new coordination bonds, resulting in changes to the coordination environment of the SBUs in QUST-82. The triangular SBU $\text{Cu}_3(\text{OH})(\text{PyC})_3$ remained intact, however, the coordinated water molecules on the Cu ions were substituted by HCOO^- , generated from the decomposition of DMF,⁴² to form a novel cage-based metalloligand $[\text{Cu}_3(\text{OH})(\text{PyC})_3]_8(\text{HCOO})_{12}$ (Figure 1d). Also, the 8-coordinated Yb^{3+} in QUST-81 changed to 6-coordinated, resulting in a remarkable structural rearrangement from the original paddle-wheel $\text{Yb}_2(\text{COO})_4(\text{H}_2\text{O})_8$ to a squared $\text{Yb}_4\text{O}(\text{COO})_8(\text{H}_2\text{O})_4$ SBU. Despite several reports, by us and others, on SC-SC transformations by external stimuli,^{27,43-49} this is the first example of a heterometallic MOF in which both distinct metal-containing building units underwent remarkable transformations that are unambiguously characterized by SCXRD.

Furthermore, *ab initio* molecular dynamics (AIMD) simulations performed at 60 and 120 °C revealed that the possible mechanism for a temperature induced phase transition between the paddle-wheel $\text{Yb}_2(\text{COO})_4(\text{H}_2\text{O})_8$ SBU and the squared $\text{Yb}_4\text{O}(\text{COO})_8(\text{H}_2\text{O})_4$ SBU is related to the elongation of the $[\text{Yb}-\text{O}]$ bonds upon heating. As shown in Figure 3, the average bond length for $[\text{Yb}-\text{O}]_A$ bonds is equal to 2.08 Å at 60 °C. These bonds are shorter than those of type B bonds, $[\text{Yb}-\text{O}]_B = 2.15$ Å. The resultant higher strength of type A bonds suggest that only limited substitution of these bonds by carboxyls is energetically favorable, making the paddle-wheel SBU more stable at 60 °C. In contrast, at 120 °C the relative stability of type A and B bonds is reversed. The bonds in the paddle-wheel SBU stretch and the average length of type A bonds becomes 2.29 Å, while type B bonds stretch only to 2.21 Å. This reversed stability of Yb-O bonds favors a higher level of O substitution with COO^- . Furthermore, this substitution along with the formation of a squared $\text{Yb}_4\text{O}(\text{COO})_8(\text{H}_2\text{O})_4$ SBU facilitates Yb-O bond contraction and stabilization. The corresponding bond lengths in the squared SBU are equal to 2.16 and 2.09 Å for $[\text{Yb}-\text{O}]_A$ and $[\text{Yb}-\text{O}]_B$, respectively.

In addition to the changes to the SBUs, X-ray diffraction analysis revealed that QUST-82, which crystallizes in the cubic space group $Pm\bar{3}m$, also contains two distinct cages: octahedral cage I with 15 Å in diameter defined by six $\text{Yb}_4\text{O}(\text{COO})_8(\text{H}_2\text{O})_4$ and one $[\text{Cu}_3(\text{OH})(\text{PyC})_3]_8(\text{HCOO})_{12}$. Cage II is similar in terms of shape and chemical composition to that in QUST-81, but slightly larger in size (25 vs 23 Å) (Figure 1f). Compared with QUST-81 (79.9%), the solvent-accessible volume in QUST-82 decreased to 71.9%, possibly due to the structural rearrangement.⁴¹ As a consequence of the assembly process, QUST-82 also possesses **pcu** topology with an approximate pore size of 18 Å (Figures 1g and S1).⁴⁰ Oriented towards the channel centers or locate on the surface of the pores are both the hard Yb^{3+} and soft Cu^{2+} metal sites. The location of these sites suggests an increased probability that a foreign

guest can interact with either a hard or a soft metal site for possible adsorption and separation applications.

Figure 3. Simulated mechanism of the temperature induced phase transition between the paddle-wheel $\text{Yb}_2(\text{COO})_4(\text{H}_2\text{O})_8$ and squared $\text{Yb}_4\text{O}(\text{COO})_8(\text{H}_2\text{O})_4$ SBUs. Yb-O bond length analysis indicates that the paddle-wheel SBU has higher stability at 60 °C and the squared one has higher stability at 120 °C.

To assess the permanent porosity of QUST-82, N_2 adsorption experiments at 77 K were run after activation. The N_2 adsorption isotherms of QUST-82 showed characteristic type-I behavior with BET and Langmuir surface area of 2148 and 2733 m^2/g , as well as a pore volume of 0.964 $\text{cm}^3 \text{g}^{-1}$, respectively (Figure S5 and Table S3). Furthermore, QUST-82's structure remains intact after N_2 adsorption, as confirmed by PXRD (Figure S2c). The permanent porosity, stability, pore size, and accessibility of both hard/soft metal sites inspired us to use this MOF as an adsorbent for desulfurization and denitrogenation applications.

To do so, we first measured single-component adsorption isotherms for S-containing DBT and BT, as well as for N-containing IND in isooctane by UV/Vis spectra at a variety of concentrations (Table S2). QUST-82 exhibits excellent capacities at high concentrations (1500 ppmw S for DBT and BT, or 46 mM for IND, Figures S7-9 and Table S2) with, DBT capacity of 262 ($\text{g DBT kg}^{-1} \text{ MOF}$); BT capacity of 116 ($\text{g BT kg}^{-1} \text{ MOF}$); and IND capacity of 219.4 ($\text{g IND kg}^{-1} \text{ MOF}$), respectively. For comparison with classic MOFs, QUST-82 shows higher adsorption capacity for DBT ($\text{g DBT kg}^{-1} \text{ MOF}$, 1500 ppmw S) than MOF-177 (≈ 92),¹⁷ CPO-27 (Ni) (158), MOF-5 (≈ 161),¹⁷ $\text{Cu}_3(\text{NAPANA})$ (187)⁵⁰ and MOF-505 (225),¹⁷ similar to that of HKUST-1 (259),¹⁷ and only lower than UMCM-150 (478).¹⁷ For BT ($\text{g BT kg}^{-1} \text{ MOF}$, 1500 ppmw S), QUST-82 displays higher adsorption capacity than MOF-177 (≈ 37),¹⁷ MOF-5 (≈ 51)¹⁷ and HKUST-1 (105),¹⁷ similar to $\text{Cu}_3(\text{NAPANA})$ (117),⁵⁰ and lower than UMCM-150 (169)¹⁷ and MOF-505 (215).¹⁷ For IND ($\text{g IND kg}^{-1} \text{ MOF}$, 46 mM), we found that QUST-82 exhibits higher adsorption capacity (219.4) than the

observed HKUST-1 (206.4) and CPO-27 (Ni) (105.5) in this work.

Typically, the differences in the adsorption capacities listed here are attributed to the correlations between OMS, surface area and pore volume among the related MOFs (Table S3). However, the saturation has not been reached for all the three isotherms, suggesting that QUST-82 has the potential for even greater adsorption (Figure S10). Clearly, the adsorption amount of DBT at equilibrium at any investigated concentrations is higher than those recorded for BT (Figure S10). We attributed the lower BT adsorption to a combination of interactions between OMS (coordination) and electron-rich organosulfur compounds, π - π interactions between conjugated organosulfur compounds and aromatic ligand used in this work.^{22,23,51} In addition, the N_2 adsorption isotherms at 77 K of DBT@QUST-82, BT@QUST-82, and IND@QUST-82 showed decreases in the BET surface area and pore volume as a result of DBT, BT or IND uptake (Figure S5 and Table S4), suggesting that QUST-82 pores are accommodating the DBT, BT or IND guests.

Next, we investigated the reversibility of QUST-82, our results indicate full regeneration is feasible via the exchange of organosulfur and nitrogen compounds with a polar solvent such as ethanol, as confirmed by UV/Vis and N_2 adsorption studies. The UV/Vis spectra show that DBT, BT and IND molecules trapped in QUST-82 can be completely released within 48 h (Figure S13). The BET surface-area and pore-volume values of as-synthesized and regenerated QUST-82 are very similar (Figure S5 and Table S4). PXRD demonstrated that regenerated QUST-82 maintains its original structural characteristics after one run of the regeneration measurement (Figure S2c). After being used for adsorptive desulfurization (900 ppmw S for DBT or BT) or denitrogenation (28 mM for IND) for a second run, the regenerated QUST-82 retained its adsorption capabilities (Table S2). Thus, we concluded that QUST-82 has potential as a cost-effective adsorbent for the removal of organosulfur and nitrogen compounds.

Figure 4. UV/Vis spectra of isooctane solution to check the adsorption capacity of QUST-82 for DBT in pure or mixed systems.

Motivated by the coexistence of hard and soft Lewis acid sites in QUST-82, its excellent stability, and high single-component capacity for desulfurization and denitrogenation, we further investigated the process of using QUST-82 to selectively remove organosulfur contaminants (DBT) from isooctane in the presence of competing

nitrogen compounds (IND) at equivalent concentrations for the first time (Figure 4). In this case, HKUST-1 and CPO-27 (Ni) were selected, both of which can adsorb both organosulfur and nitrogen compounds, for comparison (Figure S12). It was found that, QUST-82, HKUST-1 and CPO-27 (Ni) could respectively adsorb 92%, 87% and 51% (DBT/IND at 1500 ppmw S/46 mM) or 87%, 45%, and 18% (DBT/IND at 300 ppmw S/9 mM) of the amount of DBT adsorbed from pure DBT (1500 or 300 ppmw S), with corresponding DBT uptake capacities of 241, 196 and 80 (g DBT kg⁻¹ MOF, DBT/IND at 1500 ppmw S/46 mM) and 69.5, 34.8 and 12.3 (g DBT kg⁻¹ MOF, DBT/IND at 300 ppmw S/9 mM) (Note: the concentrations of DBT at 1500 or 300 ppmw S are equal to those of IND at 46 or 9 mM, respectively) (Figure 5 and Table S5). Comparing the adsorption behaviors in pure and mixed systems of the three MOFs, the adsorption amount of DBT changes little in QUST-82, both at high or low concentrations. In contrast, a sharp decrease is observed at low concentration in HKUST-1, however, in CPO-27 (Ni), we found both much sharper decreases at both high or low concentrations (Figure 5). Altogether, the results indicate that the dual hard and soft Lewis acid nature in QUST-82 contribute to its strongly selective adsorption capacity for DBT in the presence of competing IND, regardless of their relative concentrations.

Figure 5. Columnar illustration showing the efficiency for selective removal of DBT using QUST-82, HKUST-1 and CPO-27 (Ni) in mixed systems with (a) DBT/IND = 1500 ppmw S/46 mM or (b) DBT/IND = 300 ppmw S/9 mM (Note: in pure systems with (a) DBT = 1500 ppmw S or (b) DBT = 300 ppmw S).

Furthermore, we examined the adsorption capacity of QUST-82 for IND from the mixture of DBT and IND (1500 ppmw S/46 mM) (Figure S14). QUST-82 could only adsorb 113.5 g IND/kg⁻¹ MOF, which is 51.7% of the amount of IND adsorbed from pure IND at 46 mM. This dramatic decrease suggests that both Yb and Cu ions can interact with pure IND, whereas in the presence of DBT, IND has to preferentially bind with Yb³⁺ due to the stronger coordination between Cu²⁺ and S in DBT. We also attempted to determine the adsorption capacity of BT from the mixture of BT/IND, but this failed because the characteristic absorption bands of BT and IND merged into one broad band, making them indistinguishable. Nevertheless, QUST-82 may be a potential candidate for the selective removal of organosulfur contaminants in the presence of competing nitrogen compounds.

In summary, the work described herein demonstrates that the thermodynamically-controlled, heterometallic MOF QUST-82 obtained via

SC-SC transformation. Surprisingly, even though the bond breaking and formation of new coordination bonds induced structural rearrangements occurring in the process, both MOFs were identical in terms of pore size and topology. QUST-82 is an excellent adsorbent suitable for the removal of both organosulfur and nitrogen compounds in isooctane. In addition, compared with HKUST-1 and CPO-27 (Ni), QUST-82 maintained relatively high adsorption capacity for DBT from a mixture of DBT and IND. These results demonstrate the potential for new porous materials predicted to selectively remove organosulfur contaminants in the presence of competing nitrogen compounds. The discoveries in this work represent the beginning of possibly extensive exploration of a unique synthesis approach and potential applications of stable heterometallic MOFs. Continued research into the practical uses of functional heterometallic MOFs is underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and additional data (PDF)

Crystallographic data for QUST-81 CCDC 1835704 (CIF)

Crystallographic data for QUST-82 CCDC 1827059 (CIF)

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Notes

The authors declare no competing financial interests.

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