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A Metal–Organic Framework Based on a Nickel Bis(dithiolene) Connector: Synthesis, Crystal Structure, and Application as an Electrochemical Glucose Sensor

Yan Zhou, Qin Hu, Fei Yu, Guang-Ying Ran, Hai-Ying Wang, Nicholas D. Shepherd, Deanna M. D'Alessandro, Mohamedally Kurmoo, and Jing-Lin Zuo*



ABSTRACT: Functionalizing the redox-active tetrathiafulvalene (TTF) core with groups capable of coordination to metals provides new perspectives on the modulation of architectures and electronic properties of organic—inorganic hybrid materials. With a view to extending this concept, we have now synthesized nickel bis(dithiolene-dibenzoic acid), $[Ni(C_2S_2(C_6H_4COOH)_2)_2]$, which can be considered as the inorganic analogue of the organic tetrathiafulvalene-tetrabenzoic acid (H_4TTFTB). Likewise, $[Ni(C_2S_2(C_6H_4COOH)_2)_2]$ is a redox-active linker for new functional metal—organic frameworks, as demonstrated here with the synthesis of $[Mn_2{Ni(C_2S_2(C_6H_4COO)_2)_2}(H_2O)_2] \cdot 2DMF$, (1, DMF = *N*,*N*-dimethylformamide). 1 is isomorphic to the reported $[Mn_2(TTFTB)(H_2O)_2]$ (2) but is a better electrochemical glucose sensor due to the multiple oxidation—reduction states of the $[NiS_4]$ core, which allow glucose to be oxidized to glucolactone by the high oxidation state $[NiS_4]$ center. As a non-enzymatic glucose sensor, 1 on Cu foam (CF), 1-CF, was synthesized by a one-step hydrothermal method and exhibited an excellent electrochemical performance. The fabricated 1-CF electrode offers a high sensitivity of 27.9 A M⁻¹ cm⁻², with a wide linear detection range from 2.0 × 10⁻⁶ to 2.0 × 10⁻³ M, a low detection limit of 1.0×10^{-7} M (signal/noise = 3), and satisfactory stability and reproducibility.

Metal–organic frameworks (MOFs) are a class of materials composed of organic linkers and metal or cluster nodes.¹ In recent years, MOFs have been extensively explored in the fields of magnetism,² gas storage³ and separation,³ drug delivery,⁴ catalysis,⁵ clinical diagnosis,⁶ chemical sensors,⁷ and analysis,⁸ because of their advantageous physical and chemical properties, such as their three-dimensional (3D) highcrystallinity structure, high specific surface area, and multiple porosities. Among known MOFs, those with redox activity are alluring, because they can add a new functional dimension in fields such as electrochemistry and optics.⁹ Tetrathiafulvalene (TTF, $C_6H_4S_4$) is a redox-active, sulfur-rich conjugated core that can undergo two reversible and easily accessible redox processes and can act as an effective linker to construct novel functional materials.¹⁰ Recently, several redox-active compounds based on tetrathiafulvalene-tetrabenzoate (TTFTB) have been studied¹¹⁻¹³ and widely used in the fields of catalysis,¹⁴ electronics,¹⁵ proton/electron conductors,^{16,17} and redox-controlled adsorption.^{18,19}

Nickel bis(dithiolene) complexes can be seen as inorganic analogues of the corresponding TTF-type donors where the metal replaces the central C==C bond.²⁰ Like TTF and its derivatives, they also have rich redox behavior and favorable solid-state interactions.²¹ Metal-bis(dithiolene) complexes are attracting increasing interest; for example, Mo-bis(dithiolene) complexes have been well studied as analogues of the active site in dimethyl sulfoxide reductase (DMSOR).²² Nickel bis-(dithiolene) complexes have been employed for their special characteristics in magnetism,²³ electron conductors,^{24–26} nearinfrared (NIR) dyes,²⁷ and nonlinear-optical materials,²⁸ because of the mixing of organic and metal orbitals and unique redox properties.^{29,30} They exist in several clearly defined oxidation states which are connected through reversible redox steps and are often ideal for electronic and spectroscopic applications.³¹ Introducing inorganic ligand analogs into MOFs, in place of purely organic ligands, endows frameworks with a range of additional multifunctional properties.

Recently, electrochemical sensors have attracted great attention due to advantages including their simple operation, rapid response, and sensitivity, especially for glucose detection.³² The blood glucose level in the human body is an important index to measure metabolic ability and clinical diagnosis of diabetes.³³ Therefore, the accurate measurement of blood glucose is of great significance.³⁴ To date, commercial glucose sensors are mainly based on glucose oxidase-assisted electro-oxidation. Despite the high sensitivity and selectivity, such sensors suffer from high cost, low reproducibility, complex and tedious enzyme immobilization process, and degradation of activity, limiting their large-scale applications. To avoid such issues, much effort has been directed toward designing and

Received: August 21, 2020



exploiting non-enzymatic sensors based on direct electrocatalysis of electrode materials.³⁵ Nevertheless, there are still some obstacles for the application of MOFs in the field of electrochemical sensors for non-enzymatic glucose detection, such as the small detection range, lower sensitivity, and poor stability.³⁶ Based on the above-mentioned obstacles of the MOF-based electrode materials, it is extremely important to develop highly active MOFs with good stability for glucose detection.

Herein, nickel bis(dithiolene-dibenzoic acid), $[Ni(C_2S_2-(C_6H_4COOH)_2)_2]$, as the inorganic analogue of H_4TTFTB , is successfully synthesized as a new building block (Schemes 1 and

Scheme 1. Structures of $[\rm Ni(C_2S_2(C_6H_4COOH)_2)_2]$ and $\rm H_4TTFTB$



S1). It is a redox-active, versatile, and important linker for new functional MOFs. As an example, a new 3D MOF, $[Mn_2{Ni-(C_2S_2(C_6H_4COO)_2)_2}(H_2O)_2]\cdot 2DMF$ (1, DMF = *N*,*N*-dime-thylformamide), has been constructed, which shows a better electrochemical activity for glucose sensing than $[Mn_2(TTFTB)(H_2O)_2]$ (2). Because the nickel bis(dithiolene) compounds have several reversible and stable oxidation states, glucose can be oxidized to glucolactone by the highly oxidizing nickel. The high sensitivity, wide detection range, and low detection limit underlie the performance of 1 as a good electrochemical sensor for glucose.

Single-crystal X-ray diffraction showed that 1 is isostructural to 2^{15} crystallizing in space group $P6_1$ (Table S1 and Figure S3). The asymmetric unit consists of two Mn(II), a ligand $[Ni(C_2S_2(C_6H_4COO)_2)_2]^{4-}$, and two coordinated water molecules. In 1, two crystallographically independent framework Mn(II) centers (Mn1, Mn2) exhibit distorted polyhedral coordination geometries coordinated by linker carboxylates and oxygen atoms of coordinated water. The five-coordinated Mn1 was coordinated with a chelating carboxyl group of $[Ni(C_2S_2 (C_6H_4COO)_2)_2]^{4-}$ and three oxygen atoms from another three carboxylate ligands. The six-coordinated Mn2 was completed by four oxygen atoms from four nickel dithiolene ligands and two oxygen atoms from coordinated water (Figure S4). In 1, a rhombic 1D channel of 12.2 \times 12.4 Å² extends along the *c* direction (Figure 1a). The linkers form helical stacks along the *b*axis, and the Ni…Ni distance is 3.797 Å (Figure 1b). The pronounced stacking of nickel bis(dithiolene) often leads to anisotropic optical and electronic properties.^{37,38} The solid-state diffuse reflectance of $[Ni(C_2S_2(C_6H_4COOH)_2)_2]$ and 1 shown in Figure S5 reveals bands in the NIR region which are consistent with $\pi - \pi^*$ transitions associated with the bis-(dithiolene) connector.³⁹ Hence, we sought to further quantify the stacking geometries in the MOF (Figure S6), and each nickel dithiolene core is nearly planar.

Materials coated on copper foam (CF), 1-CF and 2-CF, were obtained by a one-step hydrothermal method. The X-ray powder diffraction patterns show that the structures of the materials match well with those simulated from the crystal data of 1, 2, and bare CF (Figures S7 and S8), indicating that the loaded 1 and 2 on the CF have the same structures as the crystal samples. Scanning electron microscope (SEM) images of bare



Figure 1. Crystal structure of 1 viewed along the c-axis, showing rhombic pores (a), and along the b-axis, showing helical stacking of nickel dithiolene cores (b). H atoms are omitted for clarity.

CF (Figure S9a) and 1-CF indicate that the entire surface of CF is completely covered by nanorods, as shown in Figures 2 and S9b. The corresponding elemental mapping analysis further demonstrates their uniform distribution throughout 1-CF. Figures S10b and S11 show that the bare CF is uniformly covered with nanorods of 2.

The electrochemical sensor activity of a **1-CF** electrode for glucose oxidation was investigated using a standard threeelectrode system in a 0.1 M NaOH aqueous solution with a scan rate of 50 mV s⁻¹. Figure 3a shows the cyclic voltammograms (CVs) of **1-CF** and bare **CF** in the absence and presence of 1.0×10^{-3} M glucose with an applied potential range of 0-1.0 V. Bare **CF** is active for glucose electro-oxidation, but the responses toward glucose are quite weak (Figure S12). However, **1-CF** exhibited cathodic and anodic peaks at around 0.42 and 0.67 V,



Figure 2. Crystal picture of **1** (a), SEM image of **1-CF** (b), and EDX elemental mapping images of **1-CF** (c).



Figure 3. CV curves of bare CF and 1-CF in 0.1 M NaOH with and without 1.0×10^{-3} M glucose (scan rate: 50 mV s⁻¹) (a). CV curves for 1-CF in 1.0×10^{-3} M glucose at scan rates from 20 to 200 mV s⁻¹ (from inner to outer) (b). The corresponding plots of anodic current density vs the square root of scan rate. The error bars indicate the standard deviations of three measurements (c). Amperometric responses of the 1-CF electrode at different potentials (from 0.50 to 0.65 V) with continuous addition of 1.0×10^{-3} M glucose in 0.1 M NaOH (d).

respectively. The addition of 1 mM glucose resulted in a rise in anodic peak current density, which showed the electro-oxidation

activity for glucose oxidation. The reaction mechanism for the oxidation of glucose at 1-CF can be described as follows:

 $[NiS_4]^0 + glucose \rightarrow [NiS_4]^- + glucolactone$

Figure 3b shows the CVs for 1-CF at different scan rates with 1.0×10^{-3} M glucose. With an increase in the scan rate, the currents also rise and the potentials of the redox peaks shift to a more negative or positive position. This phenomenon is mainly due to the fact that the increasing scan rate also causes the internal diffusion resistance within 1-CF to increase.⁴⁰ However, the observation of a good linear relationship between the peak current densities and the square root of the scan rate implies a reversible and diffusion-controlled electrochemical process for glucose oxidation on the 1-CF electrode (Figure 3c).⁴¹ Furthermore, even at the high scan rate of 200 mV s⁻¹, the shape of the CV curve does not significantly distort, implying fast electron transport. To achieve the optimum applied potential, the amperometric current response of 1-CF with continuous addition of 1.0 \times 10⁻³ M glucose around the peak potential (from 0.50 to 0.65 V) was measured. The current response increases with increased working potential and reaches a maximal value at 0.65 V (Figure 3d). Thus, 0.65 V was chosen as the optimum potential in the following experiments.

The CVs of **1-CF** with different concentrations of glucose suggest that the current density of the anode increases with increasing concentration from 0 to 6 mM (Figure 4a). Selectivity



Figure 4. 1-CF in 0.1 M NaOH with the presence of varied glucose concentrations: 0, 1, 2, 3, 4, 5, and 6 mM at a scan rate of 50 mV s⁻¹ (a). Amperometric response of **1-CF** electrode toward the addition of glucose with various interfering species in 0.1 M NaOH (b). Amperometric response of **1-CF** with successive addition of glucose in 0.1 M NaOH (inset: the current response of electrode toward the addition of glucose from 2 to 40 μ M) (c). The corresponding calibration curve of **1-CF** electrode to successive additions of glucose at 0.65 V in 0.1 M NaOH (d).

is a major factor to assess the performance of the electrode for non-enzymatic glucose detection. In an anti-interference test, it is clear that there was a significant current response after the addition of glucose, whereas no significant current response was observed with the addition of a series of interferents, which indicates that 1-CF possesses selectivity toward common interfering species in human blood (Figure 4b). Figure 4c represents a typical current—time plot of the 1-CF electrode with consecutive step changes in the glucose concentration. The

inset in Figure 4c shows the low magnification of glucose concentration from 2.0×10^{-6} to 4.0×10^{-5} M. The calibration curve shows a linear range of 2.0×10^{-6} – 2.0×10^{-3} M, with a high sensitivity of 27.9 A M^{-1} cm⁻² and a low detection limit of 1.0×10^{-7} M at the signal-to-noise ratio of 3 (Figure 4d). The 1-CF sensor has an insignificant variation about the catalytic current toward glucose after 400 cycles (Figure S13), and with testing every 7 days over 1 month, the electrode maintained 96.4% of its initial current density (Figure S14), indicating its stability. The reproducibility of this sensor was examined by measuring the current response of glucose oxidation for 10 1-CF electrodes. The relative standard deviation (RSD) of anode peak current densities is only 2.7%, suggesting good reproducibility (Figure S15). The recognition performance is rare in MOF materials and is attributed to the redox-active core [NiS₄] and the good stability of the framework following the electrochemical measurements.

CV (red lines) and SQW (blue lines) voltammograms for the solid samples of $[Ni(C_2S_2(C_6H_4COOH)_2)_2]$ and 1 (Figure S16) indicate the highly electroactive nature of the metalloligand. To investigate the electrochemically active center of 1, a comparative experiment with the isostructural 2 was conducted. As shown in Figure S17, 1 is active but 2 is not, demonstrating the advantages of introducing the redox-active $[NiS_4]$ core in the ligand. A comparison of the analytical performance for 1-CF with other non-enzymatic glucose sensors in alkaline media (Table S4) shows that 1 serves as a superior sensor for non-enzymatic glucose detection. It exhibits high catalytic activity, stability, selectivity, and reproducibility for glucose electro-oxidation.

In conclusion, we successfully synthesized a neutral nickel bis(dithiolene) as a new type of connector, $[Ni(C_2S_2-(C_6H_4COOH)_2)_2]$, to form new redox-active 3D MOFs. As the inorganic analogue of TTFTB, $[Ni(C_2S_2(C_6H_4COO)_2)_2]^4$ stands out thus far in preparing functional MOFs with several defined reversible redox states and a wide range of spectral absorption, suggesting that $[Mn_2{Ni(C_2S_2(C_6H_4COO)_2)_2}-(H_2O)_2]\cdot 2DMF$ is a highly effective material in the fields of electrochemistry and optics. It behaves as a highly sensitive sensor for glucose with a wide detection range and low detection limit, exhibiting the importance of introducing the redox-active $[NiS_4]$ core. This may offer a new opportunity to design and develop non-noble-metal-based redox-active MOFs for electrochemical applications, and further research will be presented in our following studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c09009.

Synthesis procedures of the $[Ni(C_2S_2(C_6H_4COOH)_2)_2]$; characterization and additional analysis of 1, including Scheme S1, Figures S1–S25, and Tables S1–S5 (PDF) Crystal data of 1 (also deposited at Cambridge Crystallographic Data Centre, CCDC 2009308) (CIF)

AUTHOR INFORMATION

Corresponding Author

Jing-Lin Zuo – State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China; orcid.org/0000-0003-1219-8926; Email: zuojl@nju.edu.cn

Authors

pubs.acs.org/JACS

- Yan Zhou State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China
- **Qin Hu** College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, P. R. China
- Fei Yu State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China
- Guang-Ying Ran College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, P. R. China
- Hai-Ying Wang College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610066, P. R. China
- Nicholas D. Shepherd School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia
- Deanna M. D'Alessandro School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia
- Mohamedally Kurmoo Institut de Chimie de Strasbourg, CNRS-UMR7177, Université de Strasbourg, 67008 Strasbourg, France; © orcid.org/0000-0002-5205-8410

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c09009

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program (No. 2018YFA0306004), the National Natural Science Foundation of China (Nos. 21875099, 21631006, and 21801127), and the Australian Research Council (FT170100283). M.K. was funded by the CNRS of France.

REFERENCES

(1) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal– Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 673–674.

(2) Kurmoo, M. Magnetic Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1353–1379.

(3) Millward, A. R.; Yaghi, O. M. Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* **2005**, *127* (51), 17998–17999.

(4) Suresh, K.; Matzger, A. J. Enhanced Drug Delivery by Dissolution of Amorphous Drug Encapsulated in a Water Unstable Metal-Organic Framework (MOF). *Angew. Chem., Int. Ed.* **2019**, *58* (47), 16790–16794.

(5) García-García, P.; Müller, M.; Corma, A. MOF Catalysis in Relation to Their Homogeneous Counterparts and Conventional Solid Catalysts. *Chem. Sci.* **2014**, *5* (8), 2979–3007.

(6) Ning, Y.; Liu, Y. W.; Yang, Z. S.; Yao, Y.; Kang, L.; Sessler, J. L.; Zhang, J. L. Split and Use: Structural Isomers for Diagnosis and Therapy. J. Am. Chem. Soc. 2020, 142 (14), 6761–6768.

(7) Ko, M.; Mendecki, L.; Eagleton, A. M.; Durbin, C. G.; Stolz, R. M.; Meng, Z.; Mirica, K. A. Employing Conductive Metal-Organic Frameworks for Voltammetric Detection of Neurochemicals. *J. Am. Chem. Soc.* **2020**, *142* (27), 11717–11733.

(8) Liu, C.-S.; Li, J.; Pang, H. Metal-Organic Framework-Based Materials as an Emerging Platform for Advanced Electrochemical Sensing. *Coord. Chem. Rev.* **2020**, *410*, 213222–213260.

(9) Hua, C.; Doheny, P. W.; Ding, B.; Chan, B.; Yu, M.; Kepert, C. J.; D'Alessandro, D. M. Through-Space Intervalence Charge Transfer as a Mechanism for Charge Delocalization in Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140* (21), 6622–6630.

(10) Wang, H.-Y.; Cui, L.; Xie, J.-Z.; Leong, C. F.; D'Alessandro, D. M.; Zuo, J.-L. Functional Coordination Polymers Based on Redox-Active Tetrathiafulvalene and Its Derivatives. *Coord. Chem. Rev.* **2017**, 345, 342–361.

(11) Narayan, T. C.; Miyakai, T.; Seki, S.; Dinca, M. High Charge Mobility in a Tetrathiafulvalene-Based Microporous Metal-Organic Framework. J. Am. Chem. Soc. **2012**, *134* (31), 12932–12935.

(12) Su, J.; Yuan, S.; Wang, H. Y.; Huang, L.; Ge, J. Y.; Joseph, E.; Qin, J.; Cagin, T.; Zuo, J. L.; Zhou, H. C. Redox-Switchable Breathing Behavior in Tetrathiafulvalene-Based Metal-Organic Frameworks. *Nat. Commun.* **2017**, *8* (1), 2008–2016.

(13) Su, J.; Yuan, S.; Wang, T.; Lollar, C. T.; Zuo, J.-L.; Zhang, J.; Zhou, H.-C. Zirconium Metal–Organic Frameworks Incorporating Tetrathiafulvalene Linkers: Robust and Redox-Active Matrices for In Situ Confinement of Metal Nanoparticles. *Chem. Sci.* **2020**, *11* (7), 1918–1925.

(14) Souto, M.; Santiago-Portillo, A.; Palomino, M.; Vitorica-Yrezabal, I. J.; Vieira, B. J. C.; Waerenborgh, J. C.; Valencia, S.; Navalon, S.; Rey, F.; Garcia, H.; Minguez Espallargas, G. A Highly Stable and Hierarchical Tetrathiafulvalene-Based Metal-Organic Framework with Improved Performance as a Solid Catalyst. *Chem. Sci.* **2018**, 9 (9), 2413–2418.

(15) Park, S. S.; Hontz, E. R.; Sun, L.; Hendon, C. H.; Walsh, A.; Van Voorhis, T.; Dinca, M. Cation-Dependent Intrinsic Electrical Conductivity in Isostructural Tetrathiafulvalene-Based Microporous Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2015**, *137* (5), 1774–1777.

(16) Sun, L.; Campbell, M. G.; Dinca, M. Electrically Conductive Porous Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2016**, 55 (11), 3566–3579.

(17) Xie, L. S.; Skorupskii, G.; Dinca, M. Electrically Conductive Metal-Organic Frameworks. *Chem. Rev.* **2020**, *120* (16), 8536–8580.

(18) Pointillart, F.; le Guennic, B.; Cador, O.; Maury, O.; Ouahab, L. Lanthanide Ion and Tetrathiafulvalene-Based Ligand as a "Magic" Couple Toward Luminescence, Single Molecule Magnets, and Magnetostructural Correlations. *Acc. Chem. Res.* **2015**, *48* (11), 2834–2842.

(19) Souto, M.; Romero, J.; Calbo, J.; Vitorica-Yrezabal, I. J.; Zafra, J. L.; Casado, J.; Orti, E.; Walsh, A.; Minguez Espallargas, G. Breathing-Dependent Redox Activity in a Tetrathiafulvalene-Based Metal-Organic Framework. *J. Am. Chem. Soc.* **2018**, *140* (33), 10562–10569.

(20) Rabaça, S.; Cerdeira, A. C.; Neves, A. I. S.; Dias, S. I. G.; Mézière, C.; Santos, I. C.; Pereira, L. C. J.; Fourmigué, M.; Henriques, R. T.; Almeida, M. Complexes Based on Asymmetrically Substituted Pyridine–Dithiolene Ligands [M(4-pedt)2] (M=Au, Cu, Ni; 4pedt=1-(pyridin-4-yl)-ethylene-1,2-dithiolate): Synthesis. *Polyhedron* **2009**, 28 (6), 1069–1078.

(21) Mebrouk, K.; Kaddour, W.; Auban-Senzier, P.; Pasquier, C.; Jeannin, O.; Camerel, F.; Fourmigue, M. Molecular Alloys of Neutral Gold/Nickel Dithiolene Complexes in Single-Component Semiconductors. *Inorg. Chem.* **2015**, *54* (15), 7454–7460.

(22) McNaughton, R. L.; Lim, B. S.; Knottenbelt, S. Z.; Holm, R. H.; Kirk, M. L. Spectroscopic and Electronic Structure Studies of Symmetrized Models for Reduced Members of the Dimethylsulfoxide Reductase Enzyme Family. *J. Am. Chem. Soc.* **2008**, *130* (14), 4628– 4636.

(23) Fukuroi, K.; Takahashi, K.; Mochida, T.; Sakurai, T.; Ohta, H.; Yamamoto, T.; Einaga, Y.; Mori, H. Synergistic Spin Transition Between Spin Crossover and Spin-Peierls-Like Singlet Formation in the Halogen-Bonded Molecular Hybrid System: [Fe(Iqsal)₂][Ni(dmit)₂]-CH₃CN·H₂O. *Angew. Chem., Int. Ed.* **2014**, *53* (7), 1983–1986.

(24) Dalgleish, S.; Yoshikawa, H.; Matsushita, M. M.; Awaga, K.; Robertson, N. Electrodeposition as a Superior Route to a Thin Film Molecular Semiconductor. *Chem. Sci.* **2011**, *2* (2), 316–320. (25) Bousseau, M.; Valade, L.; Legros, J. P.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. Highly Conducting Charge-Transfer Compounds of Tetrathiafulvalene and Transition Metal-"dmit" Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 1908–1916.

(26) Tanaka, H.; Okano, Y.; Kobayashi, H.; Suzuki, W.; Kobayashi, A. A Three-Dimensional Synthetic Metallic Crystal Composed of Single-Component Molecules. *Science* **2001**, *291*, 285–287.

(27) Dalgleish, S.; Robertson, N. A Stable Near IR Switchable Electrochromic Polymer Based on an Indole-Substituted Nickel Dithiolene. *Chem. Commun.* **2009**, *39*, 5826–5828.

(28) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R.A.; Underhill, A.E. Molecular Metals and Superconductors Derived from Metal Complexes of 1,3-Dithiol-2-Thione-4,5-Dithiolate (Dmit). *Coord. Chem. Rev.* **1991**, *110* (1), 115–160.

(29) Aubrey, M. L.; Kapelewski, M. T.; Melville, J. F.; Oktawiec, J.; Presti, D.; Gagliardi, L.; Long, J. R. Chemiresistive Detection of Gaseous Hydrocarbons and Interrogation of Charge Transport in $Cu[Ni(2,3-pyrazinedithiolate)_2]$ by Gas Adsorption. J. Am. Chem. Soc. **2019**, 141 (12), 5005-5013.

(30) Kim, H.; Kobayashi, A.; Sasaki, Y.; Kato, R.; Kobayashi, H. Crystal Structure and Molecular Structure of Neutral Nickel Bis(5,6-dihydro-1,4-dithiolate), Ni(dddt)₂. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 579–581.

(31) Fogeron, T.; Retailleau, P.; Gomez-Mingot, M.; Li, Y.; Fontecave, M. Nickel Complexes Based on Molybdopterin-Like Dithiolenes: Catalysts for CO_2 Electroreduction. *Organometallics* **2019**, 38 (6), 1344–1350.

(32) Sameenoi, Y.; Koehler, K.; Shapiro, J.; Boonsong, K.; Sun, Y.; Collett, J., Jr.; Volckens, J.; Henry, C. S. Microfluidic Electrochemical Sensor for On-Line Monitoring of Aerosol Oxidative Activity. *J. Am. Chem. Soc.* **2012**, *134* (25), 10562–10568.

(33) He, L.; Ni, Q.; Mu, J.; Fan, W.; Liu, L.; Wang, Z.; Li, L.; Tang, W.; Liu, Y.; Cheng, Y.; Tang, L.; Yang, Z.; Liu, Y.; Zou, J.; Yang, W.; Jacobson, O.; Zhang, F.; Huang, P.; Chen, X. Solvent-Assisted Self-Assembly of a Metal-Organic Framework Based Biocatalyst for Cascade Reaction Driven Photodynamic Therapy. *J. Am. Chem. Soc.* **2020**, *142* (14), 6822–6832.

(34) Fischer, A.; Lilienthal, S.; Vazquez-Gonzalez, M.; Fadeev, M.; Sohn, Y. S.; Nechushtai, R.; Willner, I. Triggered Release of Loads from Microcapsule-in-Microcapsule Hydrogel Microcarriers: En-Route to an "Artificial Pancreas". J. Am. Chem. Soc. **2020**, 142 (9), 4223–4234.

(35) Burke, A. M.; Gorodetsky, A. A. Electrochemical Sensors: Taking Charge of Detection. *Nat. Chem.* **2012**, *4* (8), 595–597.

(36) Al-Zoubi, T.; Zhou, Y.; Yin, X.; Janicek, B.; Sun, C.; Schulz, C. E.; Zhang, X.; Gewirth, A. A.; Huang, P.; Zelenay, P.; Yang, H. Preparation of Nonprecious Metal Electrocatalysts for the Reduction of Oxygen Using a Low-Temperature Sacrificial Metal. *J. Am. Chem. Soc.* **2020**, *142* (12), 5477–5481.

(37) Amb, C. M.; Heth, C. L.; Evenson, S. J.; Pokhodnya, K. I.; Rasmussen, S. C. Thiophene-Fused Nickel Dithiolenes: A Synthetic Scaffold for Highly Delocalized π -Electron Systems. *Inorg. Chem.* **2016**, 55 (21), 10978–10989.

(38) Li, W.-H.; Deng, W.-H.; Wang, G.-E; Xu, G. Conductive MOFs. *Energy Chem.* **2020**, *2* (2), 100029–100091.

(39) Xie, L. S.; Park, S. S.; Chmielewski, M.I J.; Liu, H.; Kharod, R. A.; Yang, L.; Campbell, M. G.; Dinca, M. Isoreticular Linker Substitution in Conductive Metal-Organic Frameworks with Through-Space Transport Pathways. *Angew. Chem., Int. Ed.* **2020**, *59* (44), 19623–19626.

(40) Li, L.; Xu, J.; Lei, J.; Zhang, J.; McLarnon, F.; Wei, Z.; Li, N.; Pan, F. A One-Step, Cost-Effective Green Method to in Situ Fabricate $Ni(OH)_2$ Hexagonal Platelets on Ni Foam as Binder-Free Supercapacitor Electrode Materials. J. Mater. Chem. A **2015**, 3 (5), 1953–1960.

(41) Dong, X.; Wang, X.; Wang, L.; Song, H.; Zhang, H.; Huang, W.; Chen, P. 3D Graphene Foam as a Monolithic and Macroporous Carbon Electrode for Electrochemical Sensing. *ACS Appl. Mater. Interfaces* **2012**, *4* (6), 3129–3133.