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Nanostructured Metal-Organic Conjugated Coordination Polymers with Ligand Tailoring for Superior Rechargeable Energy Storage

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Dedicated to Professor Yunqi Liu, Professor Yongfang Li, Professor Yuliang Li on occasion of their 70th birthdays!

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Abstract: Conjugated coordination polymers have become an emerging category of redox-active materials. Although recent studies heavily focus on the tailoring of metal centers in the complexes to achieve stable electrochemical performance, the effect on different substitutions of the bridging bonds has rarely been studied yet. Herein we present an innovative tailoring strategy toward the enhancement of the capacity storage and the stability of metal-organic conjugated coordination polymers. Two nanostructured d- π conjugated compounds, Ni[C₆H₂(NH)₄]_n (**Ni-NH**) and Ni[C₆H₂(NH)₂S₂]_n (**Ni-S**), have been evaluated and

demonstrated to exhibit hybrid electrochemical processes. Particularly, **Ni-S** delivers a high reversible capacity of 1164 mAh g⁻¹, an ultra-long stability up to 1500 cycles and a fully recharge ability in 67 sec. Our tailoring strategy would provide a guideline to design future effective conjugated coordination polymer-based electrodes.

With the ever-increasing demand in the fields of electronic devices, smart vehicles and grid-scale storage systems, the development of advanced electrochemical cells requires not only high specific capacity but also fast charging ability as well as long cycle life.^[1] Although lithium-ion batteries (LIBs) currently dominate the rechargeable battery market, the conventional lithiation mechanism purely based on diffusion-controlled process limits the pursuit of high energy storage, particularly at harsh current density conditions.^[2] To achieve next-generation of promising energy storage systems, rational design of hybrid electrode materials that integrate the capacitor-like non-faradaic effect with the battery-like faradaic behavior is of great interest.^[3-4] Meanwhile, the combination of both characteristics requires the electrode architecture that can rapidly deliver sufficient charges in a short given time period. In this respect, nanostructured redox-active materials with large surface areas and multi-redox activities are the most potential candidates.^[5-12]

One class of redox-active materials that offers high electronic conductivity and tunable electrochemical property is the d- π conjugated coordination compounds.^[13-17] Among them, metallically-conductive two-dimensional (2D) frameworks have gained considerable efforts as effective materials for field-effect transistors,^[18] supercapacitors^[19-21] and batteries.^[22-23] Nevertheless, their one-dimensional (1D) alternatives,^[24-26] which possess similar repeating units and redox properties are keeping unexplored for electrochemical cells. Such linear conjugated coordination polymers, which are often obtained through the coordination of d⁸ metal ions and conjugated tetradentate ligands, are able to provide good chemical stability due

to their strong intermolecular interactions.^[13-14] Moreover, their energy storage capability can be further stimulated through nanoengineering approaches.

From the perspective of molecular design, here we present an innovative strategy to attain high performance conjugated coordination polymers. Prior to the fabrication of electrodes, nanostructured **Ni-NH** and **Ni-S** were prepared in the first place. Differing from literature methods on precise control of the metal centers (M = Ni, Co, Cu, etc.),^[20, 22] we focus on the alteration of the bridging bonds in organic ligands (Figure 1a). By keeping the metal center remain unchanged, our initiative motivation is to improve the energy storage stability by substituting the bridging bond in metal-coordination complex. Inspired by the good redox ability of diamino- and dithiolene- based metal coordination compounds,^[17, 19-20, 22-23, 27-30] we hypothesize that two π -d conjugated coordination polymers: $\text{Ni}[\text{C}_6\text{H}_2(\text{NH})_4]_n$ (denoted as **Ni-NH**) and its derivative $\text{Ni}[\text{C}_6\text{H}_2(\text{NH})_2\text{S}_2]_n$ (denoted as **Ni-S**), could be feasible candidates for this comparison (Figure 1b). As a unique category of redox-active polymers, such d- π conjugated coordination polymers were recognized to possess multi-redox abilities through the co-existence of metal and ligand redox activities (Figure 1c).^[22-23, 31-36] Furthermore, other than common oxygen- and nitrogen- bonded organic compounds, sulfur-bonded compounds stand out due to the possible intermolecular S...S reactions, which could lead to the enhanced conductivity and stability of the electrodes.^[14, 37-39] To the best of our knowledge, conjugated coordination polymers have been rarely explored as active anode materials with high energy storage performance. Additionally, the effect of different bridging bonds in conjugated coordination polymers has not been investigated on energy storage devices yet.

Hence, we propose this study to gain insight into the outcome of this tailoring strategy. Nanostructured **Ni-NH** and **Ni-S** were evaluated through the construction of hybrid electrochemical cells using lithium metals as the counter electrodes (Figure 1d). By the substitution of S atoms with NH bonds in the organic ligand, nanostructured **Ni-S** delivered a

greatly improved electrochemical stability and energy storage. Ultra-fast rate stability was also achieved by **Ni-S** with one complete charge of only 67 sec. More importantly, a high capacity of 285 mAh g⁻¹ was retained after 1500 cycles. On the contrary, **Ni-NH** showed continuous deterioration with a moderate capacity retention of 157 mAh g⁻¹ after 1000 cycles. Further kinetic studies confirmed that the high energy storage of **Ni-S** was contributed by both the diffusion and pseudocapacitive processes. Our strategy would provide a guideline to design redox-active energy storage materials toward high capacity, fast charging and long cycle life.

Ni-NH and **Ni-S** were synthesized according to the previously reported procedures.^[24, 40] The chemical structure differences of pristine **Ni-NH** and **Ni-S** were identified by Fourier-transform infrared spectroscopy (FTIR) (Figure S1). Typical chemical bonds are observed from the spectra of both **Ni-NH** and **Ni-S**, for example, the N-H stretching vibration at the frequency of about 3270 cm⁻¹, the stretching vibration of the aromatic ring from 1390 to 1470 cm⁻¹, and the C-N stretching vibration at 1034 cm⁻¹.^[23-25] To be differentiated that, the strong peaks at 1034 and 846 cm⁻¹, which are ascribed to the C-S bond,^[39, 41-42] could only be observed from **Ni-S**. To further confirm the element compositions, energy dispersive X-ray spectroscopy (EDS) elemental mappings of pristine **Ni-NH** and **Ni-S** were carried out (Figure 2a & b). At low magnifications, pristine **Ni-NH** and **Ni-S** were observed to be irregular blocks with the diameters of several micrometers. Essential elements including nickel (Ni), carbon (C) and nitrogen (N) were recognized from both compounds. Moreover, these elements are evenly distributed, suggesting the homogeneity of both materials. The compositional differences between **Ni-NH** and **Ni-S** could be obviously observed from the elemental mappings. On the contrary to **Ni-NH** which does not contain any sulphur (S) atom (Figure 2a), **Ni-S** clearly shows the existence of a sufficient amount of S atoms (Figure 2b). These results are in well accordance with the chemical structures of **Ni-NH** and **Ni-S**, respectively.

Field-emission scanning electron microscopy (FESEM) was conducted to realize the morphologies of **Ni-NH** and **Ni-S**. After grinding both compounds with a pestle, they were found to form nano- to micro-sized fragments (Figure 2c & f). To be noted that, **Ni-NH** exhibits block-like aggregates, while **Ni-S** was observed to be well-distributed flower-like porous structures (Figure 2f). To check the porosity and surface area of **Ni-S**, nitrogen (N_2) adsorption-desorption experiments on the basis of Brunauer–Emmett–Teller (BET) method were conducted. **Ni-S** shows a BET surface area of $36.77 \text{ m}^2 \text{ g}^{-1}$ from the isotherm linear plot (Figure S2). The corresponding pore size distribution is presented (Figure S3), an adsorption average pore width of 20.5 nm could be observed from **Ni-S**. Although the values could not compete with those from the metal-organic frameworks (MOFs) with high surface areas and low pore widths,^[19-20, 22] **Ni-S** still shows certain degree of porosity. The difference in morphologies between **Ni-NH** and **Ni-S** could be probably caused by the slight variation in synthetic conditions with respect to the selection of solvents and concentration of solutions during the preparations of two compounds.^[24, 40] In the following process, by adequate dispersion of both compounds in N-Methyl-2-pyrrolidone (NMP) (refer to the experimental section in the supporting information), **Ni-NH** and **Ni-S** nanostructures were obtained with the diameters ranging from dozens to several hundred nanometers (Figure 2d & g). Particularly, from the transmission electron microscopy (TEM) images, single **Ni-NH** and **Ni-S** particle exhibits the morphology with 60-100 nm in diameter (inset of Figure 2d & g). By further adding multi-wall carbon nanotubes (MWCNTs) and binders, **Ni-NH** and **Ni-S** electrodes were obtained to be fully covered with MWCNTs, forming a visible conductive network between the active materials and MWCNTs (Figure 2e & h). This highly interconnected structure could endow the active materials with a feasible electrochemical activity, which is a pre-requisite for good kinetics of the cells.^[5]

Detailed electrochemical evaluations were conducted on both **Ni-NH** and **Ni-S** electrodes in the voltage range of 3.0-0.005 V (versus Li^+/Li). At a current density of 0.1 A g^{-1} , **Ni-NH**

delivered an initial capacity of 1655 mAh g⁻¹ with a high reversible capacity of 1195 mAh g⁻¹ (the 2nd charge process) (Figure 3a). Although the average Coulombic efficiency (CE) of **Ni-NH** could be maintained at 98.44% (Figure 3b), the cycling stability was unstable. This could be attributed to the permanent destruction of the compound at the Ni-NH coordination upon deep reduction.^[22] Thereafter, **Ni-NH** exhibited continuous capacity deterioration, and a low capacity of 272 mAh g⁻¹ was delivered after 180 cycles. The rate stability of **Ni-NH** was investigated at different current densities (Figure 3c). **Ni-NH** delivered the capacities of 1206, 802, 644, 507, 406, 321, 230, 158 and 84 mAh g⁻¹ at 0.1, 0.3, 0.5, 0.8, 1.2, 1.8, 3, 5 and 10 A g⁻¹, respectively. When the current density was reset back to 0.1 A g⁻¹, **Ni-NH** showed an obvious decrease trend in capacity. As for **Ni-S**, it delivered an initial capacity of 1734 mAh g⁻¹ with a high reversible capacity of 1164 mAh g⁻¹ (Figure 3d). This reversible storage capacity is comparable to that of **Ni-NH**. To be highlighted that, owing to the stronger bonding at the Ni-S coordination, **Ni-S** exhibited a remarkably improved cycling stability as compared to **Ni-NH**. It could retain a stable and high capacity of 705 mAh g⁻¹ even after 180 cycles, with an improved average CE of 99.01% (Figure 3e). Other than CE, energy efficiency is another critical parameter to assess the suitability of redox-active electrode materials (particularly those materials with distinct charge/discharge plateaus) for practical usage.^[43-44] As shown in Figure S4, **Ni-S** presents an average energy efficiency of 40.5%, which is higher than 35.5% of **Ni-NH**. Both energy efficiency values of **Ni-NH** and **Ni-S** are comparable to or even higher than those literature reported anode materials.^[43] The rate stability of **Ni-S** was also improved as compared with that of **Ni-NH** (Figure 3f). **Ni-S** delivered the capacities of 1192, 753, 618, 536, 478, 425, 360 and 292 mAh g⁻¹ at the current densities of 0.1, 0.3, 0.5, 0.8, 1.2, 1.8, 3, and 5 A g⁻¹, respectively. Even at an extremely high current density of 10 A g⁻¹ (corresponding to a complete charge of only 67 sec as shown in Figure S5), **Ni-S** could still provide a capacity of 185 mAh g⁻¹. Moreover, the cycling process of **Ni-S** was still stable when the current density was reset back to 0.1 A g⁻¹. As demonstrated

by this excellent rate stability, **Ni-S** is a promising material to be used as a quick charging electrode material.

Long-term cycling was introduced to further assess the electrochemical stability of **Ni-NH** and **Ni-S** (Figure 3g). After an activation process of 10 cycles at a small current density of 0.1 A g⁻¹, both compounds were then cycled at 3 A g⁻¹. Under such a high current density, **Ni-NH** displayed a slight decay in capacity; a moderate capacity of 157 mAh g⁻¹ was maintained after 1000 cycles, corresponding to a capacity retention of 61.8% as compared to the 11th cycle. Additionally, the average CE of **Ni-NH** was 99.84%. As for **Ni-S**, it showed a surprisingly extraordinary long-term stability with an upward trend in the capacity. To be highlighted that, after 1500 cycles of continuous testing, **Ni-S** could still be stabilized at a high capacity of 285 mAh g⁻¹. The average CE was as high as 99.87%. From the comparison results of the two compounds, it is easy to conclude that the coordination of **Ni-S** provides better electrochemical stability than that of **Ni-NH**.

Such competitive rate and long-term stability of **Ni-S** is superior to most of the previously reported coordination polymers.^[45] The performance comparison of **Ni-S** and **Ni-NH** with representative nanostructured redox-active materials, either organic or inorganic, is further illustrated in Figure 4a. Among those anodes reported with high capacity storage, for example, the 2D conductive coordination polymer frameworks with similar chemical structures (Co-HAB and Ni-HAB)^[22] as well as the typical redox-active metal-oxides (Co₃O₄ and α -Fe₂O₃),^[46-47] **Ni-S** demonstrates higher values both at low and high current densities. The outstanding electrochemical performance of **Ni-S** can also be realized from the specific energy and specific power values, which are calculated based on the loading of the active material in the range of 3.0-0.005 V versus Li/Li⁺ (Figure 4b). In agreement with the good cycling and rate performance, **Ni-S** can reach high gravimetric energy and power density values up to 811 Wh kg⁻¹ and 10097 W kg⁻¹, respectively. Whereas, the maximum values delivered by Ni-NH were lower at about 685 Wh kg⁻¹ and 4643 W kg⁻¹, respectively. Even

compared with the values provided by batteries, pseudocapacitors, and supercapacitors, the energy and power density values delivered by **Ni-S** and **Ni-NH** are still competitive.^[48-50]

Electrochemical impedance spectroscopy (EIS) analyses were conducted to evaluate the kinetics of **Ni-NH** and **Ni-S** (Figure 4c). From the Nyquist plots, the semi-circles in the high frequency range (region 1) correspond to the charge-transfer resistances at the electrolyte-electrode interfaces of both compounds. A slightly lower impedance of 151 Ω could be observed from **Ni-S**, indicating a faster kinetic reaction at the electrolyte-electrode interface of **Ni-S** as compared with that of **Ni-NH** (171 Ω). The diagonal lines in the middle frequency range (region 2) correspond to the Warburg resistances as a result of the adsorption of charges at specific sites of both compounds. **Ni-S** possesses a lower resistance than **Ni-NH**, indicating a stronger adsorption at the sites of **Ni-S** as compared with **Ni-NH**. These positive results further confirmed the better rate capability and higher power density of **Ni-S** as compared with **Ni-NH**.^[51] The tail (oblique line) in the low frequency range (region 3) corresponds to the resistances caused by the diffusion of charges along or in-between the surfaces of both compounds. Interestingly, **Ni-NH** shows a slightly faster surface diffusion since there is a clock-wise deviation of the line from **Ni-NH** to **Ni-S**.

To understand the redox mechanisms of both compounds for Li^+ storage, cyclic voltammetry (CV) measurements were conducted (Figure 4d). Both **Ni-S** and **Ni-NH** display two distinct couples of well redox peaks, confirming the two-step electron transfer process as explained by Figure 1c. In detail, the first two pairs of redox peaks centered at 1.60/2.31 and 0.57/1.33 V are known as the reduction/oxidation of the organic ligands from the neutral to negatively charged dianionic state.^[22, 27, 30] While, the second pair of redox peaks started at relatively lower potentials of 0.63/1.37 and 0.26/1.07 V could be possibly attributed to the redox change of the metal centers.^[23, 33-35] Therefore, a total uptake of four lithium-ions could be achieved on **Ni-NH** and **Ni-S** per unit formula. Moreover, the locations of the peaks are in well agreement with the behaviors of the charge-discharge profiles of **Ni-NH** and **Ni-S**.

Since **Ni-S** exhibited superior rechargeable energy storage performance, quantitative analysis on the charge storage behavior of **Ni-S** was conducted by CV measurements at various scan rates (0.2-4.0 mV s⁻¹) (Figure S6). In fact, the theoretical capacity ($C_{th/Ni-S}$) of **Ni-S** can be derived to be 472 mAh g⁻¹ based on the proposed four-electron reaction (refer to the supporting information for the calculation). Apparently, **Ni-S** delivered much higher practical capacity ($C_{p/Ni-S}$) than $C_{th/Ni-S}$ in this study. As such, the capacity gap between $C_{p/Ni-S}$ and $C_{th/Ni-S}$ clearly indicates that a large quantity of the capacity should come from other contributions apart from the battery-like diffusion process. To realize this capacity gap, scan-rate dependence of voltammetry currents was carried out on Ni-S. With the assumption that the current obeys the power law, the relationship between the peak current (i_p) and scan rate (v) can be expressed by the following equation^[2, 52-53]:

$$i_p = av^b$$

Where a and b are adjustable values. In particular, value b , which can be obtained from the slop of the plot of $\log(i)$ versus $\log v$, determines the type of electrochemical reaction of the cell; $b \approx 0.5$ indicates a battery-like diffusion-controlled (faradaic) characteristic, whereas $b \approx 1$ indicates a non-diffusion-controlled pseudocapacitive (non-faradaic) characteristic.^[2] The linear fit of Ni-S electrode is presented in Figure 4e, the b value for the peak of anodic currents is calculated to be 0.89, which is indicative of a capacitive-dominated hybrid electrochemical process.^[54-56] The separation of diffusion and pseudocapacitive contribution in Ni-S was quantified in detail by the following equation^[8, 55-57]:

$$i = k_1v + k_2v^{1/2}$$

Where k_1v represents the capacitive contribution, and $k_2v^{1/2}$ stands for the redox reaction limited by semi-infinite diffusion. By plotting $v^{1/2}$ versus $i/v^{1/2}$, k_1 and k_2 can be obtained from the slop and y-axis intercept of the plot, respectively (Figure S7). As a result, the proportion of capacitive contribution in **Ni-S** is calculated to be 63.8% out of the total

capacity, at a scan rate of 0.2 mV s^{-1} (Figure 4f). While, the proportion of diffusion contribution in **Ni-S** is calculated to be 36.2%, corresponding to a capacity of 421 mAh g^{-1} , which is close to the theoretical capacity of **Ni-S** from the redox reactions. Therefore, on the basis of this result, the extra capacity of **Ni-S** was verified to be originated from the capacitive contribution that predominantly occurred during the whole electrochemical processes. As expected, the capacitive contribution becomes gradually pronounced when scanning the electrode at higher rates ($0.6\text{-}4.0 \text{ mV s}^{-1}$) due to the rapid charging and discharging. All these results reveal the superiority of nanostructured d- π conjugated coordination polymers as high energy storage materials.

In conclusion, we have successfully proposed a novel tailoring strategy to develop electrochemically stable hybrid energy storage materials based on d- π conjugated coordination polymers. Our study has demonstrated the advantages of nanostructured d- π conjugated coordination polymers in achieving improved electrochemical performance. Apparently, after the substitution of S atoms with NH bonds in the organic ligand, nanostructured **Ni-S** delivered greatly improved electrochemical stability and energy storage ability. The superior performance of **Ni-S** outperforms all those previously reported demonstrations on conjugated coordination polymers. Further quantitative analyses have confirmed that the high energy storage of **Ni-S** was benefited from both the diffusion and pseudocapacitive processes. Given the tailorability of the bridging bonds in organic ligands, we believe that advanced electrode materials based on conjugated coordination polymers will be developed for next-generation of rechargeable energy storage devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, 4, 3243-3262.
- [2] P. Simon, Y. Gogotsi, B. Dunn, *Science* **2014**, 343, 1210-1211.
- [3] J. Ding, W. Hu, E. Paek, D. Mitlin, *Chem. Rev.* **2018**, 118, 6457-6498.
- [4] H. Wang, C. Zhu, D. Chao, Q. Yan, H. J. Fan, *Adv. Mater.* **2017**, 29, 1702093.
- [5] H. Sun, L. Mei, J. Liang, Z. Zhao, C. Lee, H. Fei, M. Ding, J. Lau, M. Li, C. Wang, *Science* **2017**, 356, 599-604.
- [6] M. Armand, J.-M. Tarascon, *Nature* **2008**, 451, 652.
- [7] J. Lu, Z. Chen, Z. Ma, F. Pan, L. A. Curtiss, K. Amine, *Nat. Nanotechnol.* **2016**, 11, 1031.
- [8] Z. Hu, S. Sayed, T. Jiang, X. Zhu, C. Lu, G. Wang, J. Sun, A. Rashid, C. Yan, L. Zhang, *Adv. Energy Mater.* **2018**, 8, 1802273.
- [9] J. Xie, P. Gu, Q. Zhang, *ACS Energy Lett.* **2017**, 2, 1985-1996.
- [10] J. Xie, C. e. Zhao, Z. q. Lin, P. y. Gu, Q. Zhang, *Chem. Asian J.* **2016**, 11, 1489-1511.
- [11] Z.-Q. Lin, J. Xie, B.-W. Zhang, J.-W. Li, J. Weng, R.-B. Song, X. Huang, H. Zhang, H. Li, Y. Liu, *Nano Energy* **2017**, 41, 117-127.
- [12] X. Zhan, Z. Chen, Q. Zhang, *J. Mater. Chem. A* **2017**, 5, 14463-14479.
- [13] C.-T. Chen, K. S. Suslick, *Coord. Chem. Rev.* **1993**, 128, 293-322.
- [14] G. Givaja, P. Amo-Ochoa, C. J. Gómez-García, F. Zamora, *Chem. Soc. Rev.* **2012**, 41, 115-147.

- [15] L. Sun, M. G. Campbell, M. Dincă, *Angew. Chem. Int. Ed.* **2016**, *55*, 3566-3579.
- [16] D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. I. Er, C. R. Wade, C. K. Brozek, A. n. Aspuru-Guzik, M. Dincă, *J. Am. Chem. Soc.* **2014**, *136*, 8859-8862.
- [17] T. Kambe, R. Sakamoto, T. Kusamoto, T. Pal, N. Fukui, K. Hoshiko, T. Shimojima, Z. Wang, T. Hirahara, K. Ishizaka, *J. Am. Chem. Soc.* **2014**, *136*, 14357-14360.
- [18] X. Huang, P. Sheng, Z. Tu, F. Zhang, J. Wang, H. Geng, Y. Zou, C.-a. Di, Y. Yi, Y. Sun, *Nat. Commun.* **2015**, *6*, 7408.
- [19] D. Sheberla, J. C. Bachman, J. S. Elias, C.-J. Sun, Y. Shao-Horn, M. Dincă, *Nat. Mater.* **2017**, *16*, 220.
- [20] D. Feng, T. Lei, M. R. Lukatskaya, J. Park, Z. Huang, M. Lee, L. Shaw, S. Chen, A. A. Yakovenko, A. Kulkarni, *Nat. Energy* **2018**, *3*, 30.
- [21] H. Wu, W. Zhang, S. Kandambeth, O. Shekhah, M. Eddaoudi, H. N. Alshareef, *Adv. Energy Mater.* **2019**, *9*, 1900482.
- [22] J. Park, M. Lee, D. Feng, Z. Huang, A. C. Hinckley, A. Yakovenko, X. Zou, Y. Cui, Z. Bao, *J. Am. Chem. Soc.* **2018**, *140*, 10315-10323.
- [23] K. Wada, K. Sakaushi, S. Sasaki, H. Nishihara, *Angew. Chem. Int. Ed.* **2018**, *57*, 8886-8890.
- [24] X. F. Cheng, E. B. Shi, X. Hou, J. Shu, J. H. He, H. Li, Q. F. Xu, N. J. Li, D. Y. Chen, J. M. Lu, *Adv. Electron. Mater.* **2017**, *3*, 1700107.
- [25] W. Hua, J. Xiu, F. Xiu, Z. Zhang, J. Liu, L. Lai, W. Huang, *RSC Adv.* **2018**, *8*, 30624-30628.
- [26] X. Hu, D. Yu, *RSC Adv.* **2012**, *2*, 6570-6575.
- [27] E. I. Stiefel, J. H. Waters, E. Billig, H. B. Gray, *J. Am. Chem. Soc.* **1965**, *87*, 3016-3017.
- [28] M. G. Miles, J. D. Wilson, *Inorg. Chem.* **1975**, *14*, 2357-2360.
- [29] G. S. Hall, R. Soderberg, *Inorg. Chem.* **1968**, *7*, 2300-2303.

- [30] A. L. Balch, R. Holm, *J. Am. Chem. Soc.* **1966**, 88, 5201-5209.
- [31] Z. Zhang, H. Yoshikawa, K. Awaga, *J. Am. Chem. Soc.* **2014**, 136, 16112-16115.
- [32] K. Jeong, J. M. Kim, S. H. Kim, G. Y. Jung, J. Yoo, S. H. Kim, S. K. Kwak, S. Y. Lee, *Adv. Funct. Mater.* **2019**, 1806937.
- [33] Z. Zhang, H. Yoshikawa, K. Awaga, *Chem. Mater.* **2016**, 28, 1298-1303.
- [34] S.-H. Kim, H. H. Lee, J.-M. Kim, S. Y. Hong, S.-Y. Lee, *Energy Storage Mater.* **2019**, 19, 130-136.
- [35] H. H. Lee, J. B. Lee, Y. Park, K. H. Park, M. S. Okyay, D.-S. Shin, S. Kim, J. Park, N. Park, B.-K. An, *ACS Appl. Mater. Interfaces* **2018**, 10, 22110-22118.
- [36] C. Wang, Y. Chen, M. Tang, Y. Wu, X. Su, X. Li, S. Xu, S. Zhuo, J. Ma, D. Yuan, *Angew. Chem. Int. Ed.* **2019**. DOI: 10.1002/ange.201908274
- [37] M. Kolek, F. Otteny, P. Schmidt, C. Mück-Lichtenfeld, C. Einholz, J. Becking, E. Schleicher, M. Winter, P. Bieker, B. Esser, *Energy Environ. Sci.* **2017**, 10, 2334-2341.
- [38] T. Ma, Q. Zhao, J. Wang, Z. Pan, J. Chen, *Angew. Chem. Int. Ed.* **2016**, 55, 6428-6432.
- [39] J. Xie, Z. Wang, Z. J. Xu, Q. Zhang, *Adv. Energy Mater.* **2018**, 8, 1703509.
- [40] X.-F. Cheng, J. Li, X. Hou, J. Zhou, J.-H. He, H. Li, Q.-F. Xu, N.-J. Li, D.-Y. Chen, J.-M. Lu, *Sci China Chem* **2019**, 62, 753-760.
- [41] K. Ray, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2005**, 44, 5345-5360.
- [42] T. Kambe, R. Sakamoto, K. Hoshiko, K. Takada, M. Miyachi, J.-H. Ryu, S. Sasaki, J. Kim, K. Nakazato, M. Takata, *J. Am. Chem. Soc.* **2013**, 135, 2462-2465.
- [45] Z. Wu, J. Xie, Z. J. Xu, S. Zhang, Q. Zhang, *J. Mater. Chem. A* **2019**, 7, 4259-4290.
- [46] D. Gu, W. Li, F. Wang, H. Bongard, B. Spliethoff, W. Schmidt, C. Weidenthaler, Y. Xia, D. Zhao, F. Schüth, *Angew. Chem. Int. Ed.* **2015**, 54, 7060-7064.
- [47] M.-S. Balogun, Z. Wu, Y. Luo, W. Qiu, X. Fan, B. Long, M. Huang, P. Liu, Y. Tong, *J. Power Sources* **2016**, 308, 7-17.
- [48] M. S. Whittingham, *MRS Bull.* **2008**, 33, 411-419.

- [49] A. Eftekhari, *Energy Storage Mater.* **2017**, 9, 47-69.
- [50] A. Eftekhari, *ACS Sustainable Chem. Eng.* **2017**, 5, 2799-2816.
- [51] A. Eftekhari, *ACS Sustainable Chem. Eng.* **2019**, 7, 3692-3701.
- [52] V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, *Nat. Mater.* **2013**, 12, 518.
- [53] J. Come, P.-L. Taberna, S. Hamelet, C. Masquelier, P. Simon, *J. Electrochem. Soc.* **2011**, 158, A1090-A1093.
- [54] C. Luo, R. Huang, R. Kevorkyants, M. Pavanello, H. He, C. Wang, *Nano Lett.* **2014**, 14, 1596-1602.
- [55] J. Park, C. W. Lee, J. H. Park, S. H. Joo, S. K. Kwak, S. Ahn, S. J. Kang, *Adv. Sci.* **2018**, 5, 1801365.
- [56] C. An, Y. Yuan, B. Zhang, L. Tang, B. Xiao, Z. He, J. Zheng, J. Lu, *Adv. Energy Mater.* **2019**, 9, 1900356.
- [57] T. C. Liu, W. Pell, B. Conway, S. Roberson, *J. Electrochem. Soc.* **1998**, 145, 1882-1888.

Figure 1. Schematic illustration of the design concept of a hybrid electrochemical cell based on nanostructured d- π conjugated coordination polymers. (a) Switching of the tailoring strategy from the metal control to the ligand alternation. (b) Chemical structures of **Ni-NH** and **Ni-S** compounds. (c) General mechanism of d- π conjugated coordination compounds on the basis of metal and organic ligand redox reactions. (d) Construction of an electrochemical cell based on d- π conjugated coordination polymer nanostructures and lithium metals.

Figure 2. Characterizations of **Ni-NH** and **Ni-S** compounds. EDS Elemental mappings of (a) pristine **Ni-NH** and (b) pristine **Ni-S**. FESEM images of (c) **Ni-NH** aggregates and (f) **Ni-S** aggregates. FESEM images of nanostructured (d) **Ni-NH** (inset TEM image shows the single particle of **Ni-NH**) and (g) **Ni-S** (inset TEM image shows the single particle of **Ni-S**). FESEM images of the prepared electrodes of (e) **Ni-NH** and (h) **Ni-S** with the addition of MWCNTs.

Figure 3. Comprehensive electrochemical investigations of nanostructured Ni-NH and Ni-S electrodes in the range of 3.0-0.005 V. Galvanostatic charge-discharge profiles (the 1st cycle) of (a) Ni-NH and (d) Ni-S anodes at 0.1 A g⁻¹. Cycling performance and corresponding CE of (b) Ni-NH and (e) Ni-S anodes at 0.1 A g⁻¹. Rate performance of (c) Ni-NH and (f) Ni-S anodes at various current densities (0.1-10 A g⁻¹). (g) Ultra-long cycling and corresponding CE of Ni-NH and Ni-S at 3 A g⁻¹ (after an activation process of 10 cycles at 0.1 A g⁻¹).

Figure 4. (a) Performance comparison of **Ni-NH** and **Ni-S** anodes with representative high energy storage nanostructured redox-active anodes. (b) Ragone plot on the performances of **Ni-S** and **Ni-NH** with state-of-the-art energy storage devices. (c) EIS analyses of **Ni-NH** and **Ni-S** fresh electrodes between 100 kHz and 100 mHz. (d) CV measurements of **Ni-NH** and **Ni-S** at the scan rate of 0.2 mV s⁻¹. (e) Linear fit of **Ni-S** from different CV scans (0.2-4.0 mV s⁻¹) to determine the b value according to the relationship $i_p = av^b$. (f) Capacitive and diffusion proportions of **Ni-S** at various scan rates from 0.2 to 4 mV s⁻¹.

An innovative tailoring strategy toward the enhancement of the capacity storage and stability of d- π metal-organic conjugated coordination polymers is proposed. The tailored compound **Ni-S** shows a high reversible capacity of 1164 mAh g⁻¹, an ultra-long stability up to 1500 cycles and a fully recharge ability of only 67 sec.

Keyword: lithium battery, conjugated coordination polymer, organic ligand, diffusion-controlled process, pseudocapacitive behavior

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Supporting Information

Nanostructured Metal-Organic Conjugated Coordination Polymers with Ligand Tailoring for Superior Rechargeable Energy Storage

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Experimental Section

Electrode Preparation: **Ni-NH** and **Ni-S** nanostructures were obtained through the grinding of pristine **Ni-NH** and **Ni-S** blocks followed by the thorough dispersion and sonication of them in N-Methyl-2-pyrrolidone (NMP) solvent for 30 mins. **Ni-NH** and **Ni-S** nanostructures were then washed with de-ionized water and ethanol for several times to remove away the residual NMP. After a drying process in vacuum oven, **Ni-NH** and **Ni-S** powders were obtained. The electrodes of **Ni-NH** and **Ni-S** nanostructures were prepared by mixing both compounds with multi-wall carbon nanotube (MWCNT) carbon additives and polyvinylidene fluoride (PVDF) polymer binders with a weight ratio of 7:2:1. The mixture powders were then ground with a pestle for 20 mins and further added with a few droplets of NMP solvent. Homogeneous electrode slurries of **Ni-NH** and **Ni-S** nanostructures were obtained after another 40 mins of grinding process at room temperature. After that, the slurries were uniformly pasted onto the battery grade copper foils and dried at 60 °C overnight in a vacuum atmosphere. Dried circular **Ni-NH** and **Ni-S** anodes with diameters of around 12 mm were punched to be used. The electrode loadings are between 0.44-0.92 mg, corresponding to an active material (either **Ni-NH** or **Ni-S**) of around 0.308-0.644 mg.

Characterization and Electrochemical Measurement: FTIR spectra were recorded on a PerkinElmer Spectrum Frontier FTIR spectrometer. EDS elemental mapping was collected by a Field Emission SEM (FESEM) JEOL/JSM-7600F at an accelerating voltage of 30 kV. SEM images were obtained by the same FESEM at the accelerating voltage of 5 kV. Nitrogen adsorption/desorption isotherm was measured at 77 K with a surface area and porosity analyzer (Micromeritics TriStar II 3020). Prior to the measurement, the dried sample was degassed under a vacuum atmosphere at the temperature of 80 °C for about 4 hours. Transmission electron microscopy (TEM) images were obtained by a thermionic TEM (JEM-2010UHR, JEOL) at the accelerating voltage of 200 kV. The fabricated cells were tested on a

NEWARE multichannel battery test system at room temperature with the galvanostatic charge and discharge in the ranges of 3.0-0.005 V. CV measurements were performed on an electrochemical analyzer (CH Instrument CHI604e) at various scan rates from 0.2 to 4.0 mV s⁻¹. EIS analysis was conducted by the same instrument between 100 kHz and 100 mHz.

Battery Fabrication: CR2032 coin-type electrochemical cell construction was applied in this study. The electrolyte solution used was 1 M lithium hexafluorophosphate (LiPF₆) in the mixture of ethylene carbonate and dimethyl carbonate (EC/DMC) solvent (1/1, v/v). Circular Celgard 2400 polymer membranes were prepared as the separators. Lithium foils were used as the counter electrodes. The cells were fabricated in a glovebox filled with pure argon gas wherein the oxygen and moisture levels were both maintained below 1 ppm. Before charging and discharging of the cells, an equilibration time of 12 h was applied for the electrolyte to thoroughly rinse the electrodes.

Theoretical capacity calculation

As for the redox process, Ni-S has a molecular weight (M_w) of 226.93 g mol⁻¹ per repeating unit. According to the theoretical calculation formula $C_{th} = \frac{n \times F}{M_w} = \frac{n \times 96485 \text{ (C mol}^{-1}\text{)}}{M_w \text{ (g mol}^{-1}\text{)}} = \frac{n \times 26801}{M_w} \text{ (mAh g}^{-1}\text{)}$ (n is the number of electrons involved into the reaction). As calculated, each electron or lithium-ion (when $n=1$) could contribute to a specific capacity of around 118 mAh g⁻¹ for Ni-S. Therefore, on the basis of the four-electron reaction, Ni-S possesses a theoretical redox specific capacity ($C_{th/Ni-S}$) of around 472 mAh g⁻¹.

Figure S1. FTIR spectra of pristine **Ni-NH** and **Ni-S** compounds. Typical characteristics of the bonds from both compounds are indicated.

Figure S2. Nitrogen adsorption-desorption isotherm linear plot of **Ni-S**.

Figure S3. Pore size distribution of Ni-S.

Figure S4. Energy efficiency values of **Ni-NH** and **Ni-S** anodes at 0.1 A g^{-1} .

Figure S5. Voltage versus time duration curves of **Ni-S** at an ultra-high current density of 10 A g⁻¹. Each complete charge or recharge process takes only a short period of ~67 sec.

Figure S6. CV measurements of **Ni-S** electrode at various scan rates from 0.2 to 4.0 mV s^{-1} . The locations of anodic peaks were selected as the peak currents (i_p).

Figure S7. Linear fit plot of **Ni-S** electrode to obtain the k_1 and k_2 values according the relationship $i = k_1 v + k_2 v^{1/2}$.