Encapsulation of redox polysulphides via chemical interaction with nitrogen atoms in the organic linkers of metal-organic framework nanocrystals

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Lithium polysulphides generated during discharge in the cathode of a lithium-sulphur redox cell are important, but their dissolution into the electrolyte from the cathode during each redox cycle leads to a shortened cycle life. Herein, we use in situ spectroelectrochemical measurements to demonstrate that sp2 nitrogen atoms in the organic linkers of nanocrystalline metal-organic framework-867 (nMOF-867) are able to encapsulate lithium polysulphides inside the microcages of nMOF-867, thus helping to prevent their dissolution into the electrolyte during discharge/charge cycles. This encapsulation mechanism of lithiated/delithiated polysulphides was further confirmed by observations of shifted FTIR spectra for the C=N and C-N bonds, the XPS spectra for the Li-N bonds from nMOF-867, and a visualization method, demonstrating that nMOF-867 prevents lithium polysulphides from being dissolved in the electrolyte. Indeed, a cathode fabricated using nMOF-867 exhibited excellent capacity retention over a long cycle life of 500 discharge/charge cycles, with a capacity loss of approximately 0.027% per cycle from a discharge capacity of 788 mAh/g at a high current rate of 835 mA/g.

The most critical challenge in energy storage is the development of high-performance energy storage devices that combine a stable cycle life with a high energy density1–6. The lithium-sulphur (Li-S) redox cell, which has a high theoretical energy density, may be a good system that can overcome this challenge7,8. In addition, sulphur is safe, inexpensive and abundant on Earth9,10. Unfortunately, the high-order polysulphides formed by reactions between cyclic octasulphur (S8) and lithium ions during the discharge reactions are soluble in most organic electrolyte solutions11,12, thus leading to quickly fading capacities during discharge/charge redox cycles. Moreover, the lithium polysulphides can move to the lithium anode electrode and form insoluble Li2S2 and/or Li2S species on its surface13,14. Furthermore, the lithium polysulphides can diffuse back and forth between the cathode and anode electrodes, in a phenomenon known as the shuttle effect, thus decreasing the cycle life of Li-S redox cells15,16. Therefore, a new paradigm structure or mechanism that can effectively prevent the dissolution of polysulphides to provide excellent capacity retention over long discharge/charge redox cycles would represent a major breakthrough in the realization of high-performance energy storage.

In principle, the functional heteroatoms embedded in the organic linkers in metal-organic frameworks (MOFs)17–19 can be used to create specific interactions with the lithium polysulphides20,21. Therefore, we hypothesized that the sp2 nitrogen in the linkers of the microcages of nanosized MOF-86722 (Zr6O4(OH)4(BPYDC)6, nMOF-867).
BPYDC = 2,2′-bipyridine-5,5′-dicarboxylate, abbreviated as nMOF-867) could be combined with the lithium polysulphides to prevent their dissolution into the electrolyte, as shown in Fig. 1. This combination would allow full redox reactions with sulphur over an extended cycle life. For comparison, we also prepared another nanosized MOF with no sp² nitrogens in its organic linker (Zr₆O₄(OH)₄(BPDC)₆, BPDC = 4,4′-biphenyldicarboxylate, termed nUiO-67) but with the same crystal structure as nMOF-867. We found that the high-order polysulphides from the lithiation of the S₈ species could be encapsulated inside the microcages of nMOF-867, thus preventing lithium polysulphide dissolution and extending the cycle life. To confirm the self-encapsulation of polysulphides in the microcages, we used a combination of experimental characterizations including in situ spectroelectrochemical measurements, FTIR spectroscopy to identify C=N and C-N bonds, XPS spectroscopy to determine the existence of Li-N bond orbitals during discharge, and a visualization method. This is the first direct demonstration confirming the mechanism and interaction of lithium polysulphide with functional heteroatoms in the organic linkers of MOFs.

Results and Discussion

nMOF-867 was prepared by dissolving zirconium chloride (ZrCl₄) and HₓBPYDC in N,N-dimethylformamide (DMF) in a 20 mL glass vial at room temperature. The sp² nitrogen in BPYDC exists as a heteroatom replacing the =CH₂ group in the aromatic ring. Then, acetic acid and triethylamine (TEA) were added to the stock solution, which was sonicated for 20 min. The glass vial was placed into an oven at 85 °C for 12 hrs to grow the nanocrystalline MOFs. For nUiO-67, a HₓBPDC organic linker was used in place of HₓBPYDC in nMOF-867, and all of the other ingredients as well as the heating process were the same as those used for nMOF-867 (Figure S1). The products were washed with DMF several times and immersed in methanol for three days. Next, the products were activated in a vacuum oven at 100 °C for 24 hrs. Then, the activated nMOFs were mixed with high-purity sulphur in a mortar in an Ar-filled glove box, and the mixtures were placed in a sealed vessel. The vessel was heated to 155 °C for 12 hrs in a tubular quartz furnace with flowing Ar. The viscosity of sulphur was lowest at 155 °C, and the molten sulphur was found to be infused into the microcages of nMOFs. The sulphur-infiltrated nMOF-867 and nUiO-67 (abbreviated as nMOF-867/S and nUiO-67/S, respectively) were maintained in an Ar-filled glove box to avoid moisture uptake from the atmosphere.

The structures were characterized by powder X-ray diffraction (PXRD), nitrogen gas adsorption isotherm measurements, scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDS) and thermal gravimetric analysis (TGA). The PXRD patterns for nMOF-867 and nUiO-67 contained sharp diffraction peaks at defined positions that were in agreement with simulated patterns, indicating that the samples possessed high crystallinity, and their underlying crystal...
structures were the same (Fig. 2a). The type I nitrogen gas adsorption isotherm (Fig. 2b) indicated that the permanent porosity and high BET surface areas (2250 m²/g for nMOF-867 and 2256 m²/g for nUiO-67) provided sufficient space for retaining the sulphur. The octahedral morphologies of nMOF-867 and nUiO-67 that were ca. 500 nm in diameter were also determined through SEM measurements (Figure S2). Notably, the fabrication of nMOF-867 and nUiO-67 particles that are homogeneous in size and morphology can eliminate the issues related to the transport properties of sulphur, lithium ions, and electrons26.

Before the infiltration of sulphur into the nMOFs, nMOF-867 and nUiO-67 were mixed with sulphur without a heating process. The measured PXRD patterns, which are shown in Figures S3 and S4, contained the main peak for pure sulphur at approximately 23° as well as the sharp peaks for nMOFs. In addition, the PXRD patterns after the heating process at 155 °C (Fig. 2a) demonstrated that nMOF-867/S and nUiO-67/S retained their crystal structures. However, the main peak for pure sulphur (indicated as the red triangle in the PXRD patterns shown in Fig. 2a) disappeared after the heating process because the sulphur particles were well absorbed into the microcages of the nMOF-867 and nUiO-67 particles27. In addition, after sulphur infiltration, the specific surface areas of nMOF-867/S and nUiO-67/S substantially decreased to 147 and 150 m²/g, respectively (Fig. 2b). In combination with the PXRD patterns, this evidence indicates that these surface area reductions did not result from structural collapse but were due to the infiltration of sulphur into the microcages of nMOF-867 and nUiO-67. The SEM images shown in Fig. 2c,e further indicated that both the crystal size and shape of nMOF-867/S and nUiO-67/S were well maintained after sulphur infiltration. Moreover, the STEM and EDS mapping (Fig. 2d,f) of nMOF-867/S and nUiO-67/S indicated that sulphur had infiltrated into both MOFs after the heating process. The nitrogen signal was detected only in nMOF-867/S because its organic linkers (BPYDC) contain sp² nitrogen atoms. Moreover, the TGA measurements (Figures S5 and S6) of nMOF-867 and nUiO-67 demonstrated their identically high thermal stability up to 400 °C.

![Figure 2](https://www.nature.com/scientificreports/)
We also explored the electrochemical performance of the Li-S redox system with nMOFs/S. First, the nMOFs/S was mixed with conductive super P and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP), which resulted in the formation of a viscous slurry that was coated on aluminium foil and dried under vacuum at 60 °C for 24 hrs. Next, 2032-type cells were assembled with lithium foil as the counter electrode in an Ar-filled glove box. The electrolyte consisted of 1 M lithium bis(trifluoromethanesulphonyl) imide (LiTFSI) in N-methyl-N-butylpyrrolidinium bis(trifluoromethane sulphonyl)imide (PYR14TFSI)/1, 2-dimethoxyethane/1,3-dioxolane (2:1:1 by volume) with LiNO₃ (1 wt%) as an additive to help passivate the surface of the lithium anode and prevent the shuttle effect.  

The typical discharge/charge profiles of the nMOF-867/S composites are shown in Fig. 3a. Initially, a constant current of 167 mA/g, corresponding to 0.1 C, was used to study discharge/charge behaviours for nMOF-867 over 500 cycles at a constant current of 835 mA/g.
a voltage range of 1.7 to 2.8 V. Two plateaus were observed at approximately 2.3 and 2.1 V in the discharge process. The plateau at approximately 2.3 V was related to the reduction of S₄ to long-chain lithium polysulphides (Li₂S₄, 4 ≤ n ≤ 8), and the plateau at approximately 2.1 V corresponded to the formation of short-chain lithium polysulphides, such as Li₂S₂ and Li₂S₃. The initial discharge capacity of nMOF-867/S was 1121 mAh/g. For nUiO-67/S, the initial discharge behaviour and capacity (1115 mAh/g at 167 mAh/g) were very similar to those of nMOF-867/S (Fig. 3b). Figure S7 also shows the first few discharge/charge profiles of nMOFs/S, in which the profiles for the 4th to 8th cycles were similar to those of the 1st and 2nd cycles. This result indicated that the N atoms covalently bound to C atoms in the organic linkers of the nanocrystalline MOFs formed secondary interactions with lithium polysulphides. In addition, nMOF-867/S (Fig. 3c) exhibited capacities of 906, 824 and 790 mAh/g for the 10th, 50th and 100th discharge capacities, respectively, at a high current rate of 835 mA/g. However, nUiO-67/S (Fig. 3d) exhibited capacities of 811, 704 and 600 mA/h/g, respectively. Even after a long cycle life with more than 500 discharge/charge cycles, nMOF-867/S exhibited stable capacity retention with an average capacity loss of approximately 0.027% per cycle. Furthermore, our calculation for the number of N involved in nMOF-867 indicated that each nitrogen would form secondary interactions with multiple Li₂S species when S₄ was completely converted to 8 LiS₂.

The nitrogen forms a strong covalent bond to carbon in the organic linkers (BPYDC, chemical formula = C₉H₈N₂O₄) of the MOF. Indeed, the results in Fig. 3c.e indicated that the electrochemical behaviour of MOF-867 was very stable over long cycles, thus implying that the BPYDC linkers in nMOF-867 were not destroyed but maintained the sp² nitrogen in their aromatic rings over repeated discharge/charge cycles. Notably, excellent performance with a specific energy density of ~1700 Wh/g over 500 cycles at a high current rate of 835 mA/g was observed. Moreover, the capacity retention behaviours of nMOF-867 were maintained at high areal loadings of active materials up to 5 mg/cm² (Figure S8). nMOF-867 with sp² nitrogen atoms in its organic linkers provided stable capacity retention along with an excellent coulombic efficiency over a long discharge/charge cycle life for Li-S batteries. Therefore, the simple introduction of heterogeneous atoms into the organic linkers in the microcages of MOFs leads to stable energy performance with a high capacity retention over a long cycle life.

Additionally, we tested another set of Zn-based IRMOF-10s (Zn₆(OH)(BPDC), and Zn₆(OH)(BPYDC)), which were separately prepared with BPDC, which has no sp² nitrogen, and BPYDC, which has sp² nitrogen in its linker²₂,²₃. The measured electrochemical performance (Figure S9) indicated that the capacity retention for the IRMOF-10 with the sp² nitrogen (i.e., 64%) was much higher than for the IRMOF-10 with no sp² nitrogen (i.e., 27%). These results confirmed that the sp² nitrogen in the linker of the MOF structure enhanced the capacity retention over repeated discharge/charge cycles. Therefore, these results demonstrate that the simple introduction of heterogeneous atoms into the organic linkers in the microcages of MOFs can lead to excellent energy storage performance, thus opening a new route for providing an excellent solution for current energy storage issues.

We further investigated the discharge/charge behaviour by using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), and these results provided detailed information regarding the chemical binding of sp² nitrogen atoms with polysulphides. Moreover, a visual verification method was used to directly observe the interactions between sp² nitrogen atoms and polysulphides in the electrolyte. In addition, spectroelectrochemical measurements were performed with in situ observation of the chemical interactions during the discharge/charge processes. To identify the interaction, we prepared a polysulphide species (Li₂S₄), which was synthesized by mixing stoichiometric amounts of Li₂S and sulphur in tetraethylene glycol dimethyl ether (TEGDME)²⁴. Then, nMOF-867 and nUiO-67 were directly mixed with the polysulphide (Li₂S₄) solution. Finally, the products were washed with methanol to remove excess polysulphide molecules, and this was followed by drying in a vacuum oven at 60 °C for 24 hrs.

The FTIR spectra of nMOF-867 and nMOF-867/Li₂S₄ are shown in Figure S10, and partial ranges of the spectra are shown in Fig. 4a,b. The double bond stretching of C = C (1591 cm⁻¹), the asymmetric and symmetric stretching modes of the carboxylate (-COO⁻, 1473 and 1410 cm⁻¹), and the single bond stretching of C-O (1245 cm⁻¹) and C-C (1163 cm⁻¹) (Figure S11) indicated that the spectra of both samples did not change after interaction with Li₂S₄. However, Fig. 4a,b show that the peaks related to atomic nitrogen (N sp² orbitals) shifted from 1537 to 1541 cm⁻¹ for the C = N double bonds and 1364 to 1367 cm⁻¹ for the C-N single bond because the polysulphides undergo chemical interactions with the sp² nitrogen atoms, which shift its stretching frequency. Moreover, to obtain more detail on the chemical binding of the nitrogen sp² orbitals during lithiation, we also determined the XPS spectra (Fig. 4c,d) of pristine nMOF-867 and nMOF-867/Li₂S₄. The XPS spectrum of nMOF-867 in the absence of Li₂S₄ (Fig. 4c) was fitted to a single peak that corresponded to a Zr-O binding energy of 53.7 eV.²⁵ After chemical binding of nMOF-867 with Li₂S₄, the XPS spectra were deconvoluted into three peaks corresponding to Zr-O (53.7 eV), Li-N (55.6 eV) and Li-S (54.6 eV). Figure 4d,²⁵ which indicate that the lone pair of electrons in the sp² nitrogen orbitals interacted with the Li in Li₂S₄.

Additionally, we developed a visualization method by mixing nMOF-867 and nUiO-67 with a 0.1 M Li₂S₄ TEGDME solution for up to 240 min. Because Li₂S₄ in solution is yellow, we were able to visualize the migration of Li₂S₄ by following the colour change. The photos show the colour changes of the Li₂S₄ solution after mixing with both MOFs at regular intervals of 0 min, 120 min and 240 min. The results in Fig. 4e indicate that the Li₂S₄ solution became transparent as Li₂S₄ was captured by MOF-867, and the nUiO-67 in the Li₂S₄ solution maintained its yellow colour even after 240 min (Figure S12a). These results were quantified through UV-Vis spectroscopic analysis of the Li₂S₄ solution after sedimentation of nMOFs every 30 min. The results demonstrated that the Li₂S₄ solutions that were mixed with both nMOFs initially exhibited high absorbance intensities in the wavelength range of 400 to 500 nm. As time progressed, the absorbance of the Li₂S₄ solutions mixed with nMOF-867 decreased substantially as the Li₂S₄ was encapsulated into nMOF-867 (Fig. 4f). However, the effect observed for nUiO-67 was much smaller (Figure S12b). These results imply that the sp² nitrogen atoms in the organic linkers of nMOF-867 can encapsulate Li₂S₄ via chemical interactions, which prevent the dissolution of polysulphide into the electrolyte. Moreover, we performed additional experiments (Figure S13) to provide additional insight into
the colour change. Initially, only nMOF-867 was placed in the TEGDME solvent in the absence of lithium polysulphides and stirred for 240 min. No colour change was observed after stirring for 240 min. Next, another glass vial was prepared containing only 0.1 M Li₂S₄ (lithium polysulphides) in the TEGDME solution. The initial colour of Li₂S₄ was yellow, and this colour was maintained after stirring for 240 min. These results provide clear evidence that the colour change was due to chemical interactions between sp² nitrogens and lithium polysulphides and not to photooxidation.

In addition, an in situ spectroelectrochemical method using a UV-visible instrument (DH-2000, Ocean Optics) linked to a potentiostat (SP-300, Bio-Logic) was developed. The cell system (Fig. 5a) was equipped with Li metal as the counter/reference electrode, and nMOFs/sulphur was deposited on Au-coated quartz plates as the working electrode. The Au-coated quartz plates were irradiated with UV and visible light to record the cyclic voltammetry (CV) data. We used quartz plates that barely absorb UV light and coated them with a thin film of Au to improve the conductivity. The UV-visible spectra of nMOF-867/S and nUiO-67/S were obtained at different voltage points on their CV profiles (Figures S14 and S15). Absorption peaks in the UV-Vis region (Fig. 5) were observed in both nMOF-867/S and nUiO-67/S during the discharge and charge cycles. The absorption intensities of nMOF-867/S (Fig. 5b) increased during the discharge reactions and returned to their original intensities during the charge reactions (Fig. 5c). The absorption intensities of nUiO-67/S remained unchanged (Fig. 5d,e). From these results along with those from the FTIR, XPS, and visualization verification analyses, we conclude that

Figure 4. Investigation of the chemical interaction between the nitrogen atoms and the polysulphides. (a,b) FTIR spectra of pristine nMOF-867 and nMOF-867 with Li₂S₄. (c) XPS spectrum of pristine nMOF-867. (d) XPS spectrum of nMOF-867/Li₂S₄. (e) Photos show the colour changes of nMOF-867/Li₂S₄ over 240 min. (f) Absorbance intensity of UV-visible spectra for nMOF-867/Li₂S₄ every 30 min.
polysulphides are generated and encapsulated in the microcages of nMOF-867, which exhibited an in situ change in the UV-Vis absorption intensity due to light scattering from the polysulphides during the discharge/charge cycles\(^3\_8, 39\). In addition, nUiO-67 exhibited no change in its UV-Vis absorption because the generated polysulphides were easily dissolved in the electrolyte.

### Methods

#### Synthesis of nMOF-867 and nUiO-67.

For nMOF-867, zirconium chloride and acetic acid were dissolved in DMF. Simultaneously, BPYDC and triethylamine were dissolved in DMF. The solutions containing metal ions and organic linkers were combined in glass vials, which were tightly sealed and placed into an oven for 12 hrs. The white product was washed three times with DMF using a centrifuge and sonication. After the washing process, nMOF-867 was immersed in methanol for three days, with refreshing of the methanol. Finally, nMOF-867 was activated by removing the solvent in a vacuum oven. For nUiO-67, all of the procedures were the same as those used for nMOF-867 except that the organic linkers were exchanged with BPCD, and the reaction time was 6 hrs.

#### Cathode preparation using nMOF/sulphur composites.

The dried nMOF-867 or nUiO-67 was mixed with sulphur in a mortar. The mixtures were deposited into a sealed vessel that was placed into a quartz tubular furnace and heated to 155 °C for 12 hrs under an Ar flow. For the viscous slurry, nMOF-867/S (or nUiO-67/S) was mixed with carbon black (Super P) and polyvinylidene fluoride binder in N\(_2\)-methyl-2-pyrrolidine. The well-mixed slurry was cast on aluminium foil using a doctor blade and dried in a vacuum oven at 60 °C for 12 hrs. The entire sample preparation including mixing of the powders were conducted in an Ar-filled glove box with a low humidity below 1 ppm.

#### Electrochemical measurements.

1 M lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in N-methyl-N-butylpyrrolidinium bis(trifluoromethane sulphonymide)imide (PYR14TFSI)/1, 2-dimethoxyethane/1,3-dioxolane (2:1:1 by volume) with LiNO\(_3\) (1 wt%) was used as the electrolyte. The electrochemical measurements were carried out using 2032-tyte coin cells, and lithium foil was used as the counter/reference electrode. Polypropylene membranes (Celgard Inc.) were used as separators. Galvanostatic discharge/charge tests were performed by cycling between 1.7 and 2.8 V at 167 mA/g and 835 mA/g using an electrochemical redox cycler (WBS3000, Wonatech). Moreover, the capacity retention behaviours of nMOF-867 were investigated by varying the loading amount of the active materials from 3.6 to 5 mg/cm\(^2\) (Figure S8).
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Author Contributions

J.H.P., K.M.C. and J.K.K planned the project, and J.H.P. and S.R.S. fabricated the nanocrystalline MOFs. J.H.P. and K.M.C. characterized the nMOF and nMOF/S structures. J.H.P. and M.-K.S. measured the electrochemical...
properties. J.H.P., D.K.L. and B.C.M. carried out the FTIR, XPS and in situ spectroelectrochemical measurements. J.K.K. wrote the manuscript with J.H.P. and all of the authors reviewed the manuscript.

Additional Information
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