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### Permalink

<https://escholarship.org/uc/item/4m10c6k3>

### Journal

Angewandte Chemie International Edition, 65(15)

### ISSN

1433-7851

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### Publication Date

2026-04-06

### DOI

10.1002/anie.202525047

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Peer reviewed

# A Quinoidal Two-Dimensional Metal-Organic Framework for High-Performance Micro-Supercapacitors and Solid-State Lithium Batteries

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**Abstract:** Two-dimensional (2D) metal-organic frameworks (MOFs) integrating redox-active linkers enable dense charge sites and open ion pathways for microscale energy storage. We report a quinoidal dicarboxylate ligand, AQM-H<sub>2</sub>L, derived from *p*-azaquinodimethane, forming crystalline frameworks with Cu<sup>2+</sup> and Zn<sup>2+</sup> nodes. The Cu-based MOF (AQM-AQM-H<sub>2</sub>L-Cu) exhibits layered sheets (>14 Å spacing) constructed from dinuclear Cu-carboxylate units and conjugated AQM linkers, which narrow the bandgap and introduce Cu<sup>2+</sup>/Cu<sup>+</sup> pseudocapacitance. Exfoliated nanosheets (~5 nm) retain crystallinity and excellent processability. Integrated into graphene films, they deliver areal and volumetric capacitances of 29.6 mF cm<sup>-2</sup> and 18.1 F cm<sup>-3</sup>, achieving 2.6 mWh cm<sup>-3</sup> energy density at 160 mW cm<sup>-3</sup>. As ionic fillers (1 wt%) in PEO solid polymer electrolytes, the nanosheets markedly enhance LiFePO<sub>4</sub> cell performance, affording 169.8 mAh g<sup>-1</sup> at 0.2 C and 93% retention after 400 cycles. This work establishes quinoidal linkers as a compact and robust design motif for ionically active 2D frameworks toward high-performance miniature and solid-state energy devices.

## Introduction

Emerging classes of miniaturized electronics, wearable sensors, implantable diagnostics and distributed IoT nodes, require energy storage that is simultaneously compact, high-power, durable and mechanically adaptable. Micro-supercapacitors (MSCs) and solid-state lithium batteries represent two complementary solutions but are typically developed from different material paradigms: carbonaceous, highly conductive platforms for capacitive response,<sup>[1]</sup> and ionically conductive polymer/ceramic systems for solid electrolytes.<sup>[2]</sup> Bridging these orthogonal functionalities

within a single molecular platform would open pathways to multifunctional devices and simplified integration. Metal-organic frameworks (MOFs), with their modular organic linkers and coordination motifs, are attractive candidates for this unification because the organic ligand enables chemical tunability while metal nodes provide redox activity and structural diversity.<sup>[3]</sup> Yet conventional MOFs suffer from well-known limitations when applied to electrode and electrolyte functions: under-utilized capacity and sluggish kinetics, poor redox activity largely confined to metal nodes.

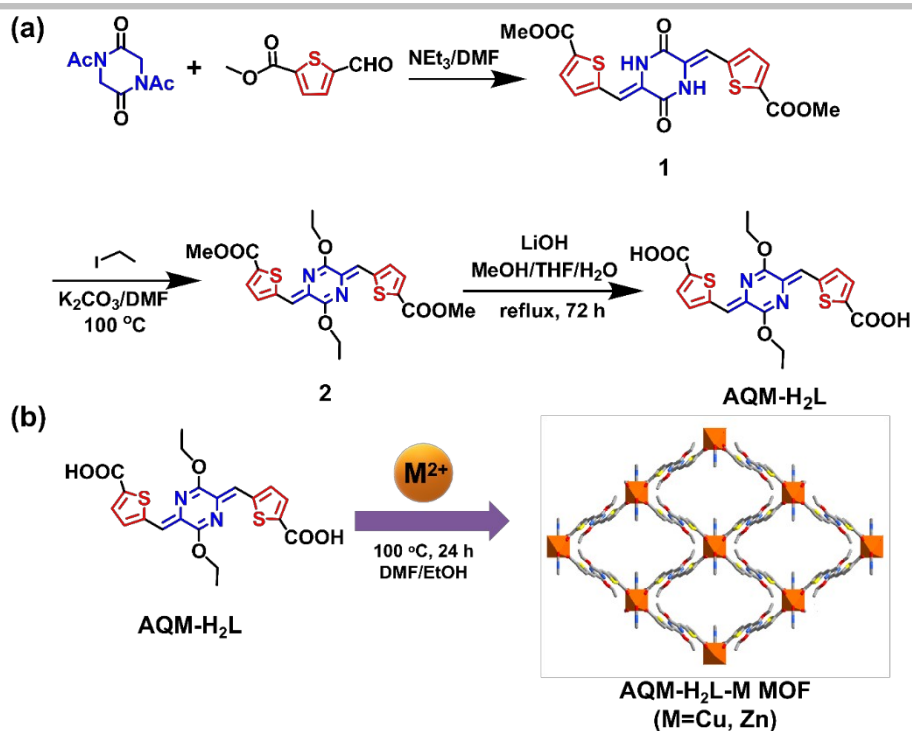
Two-dimensional (2D) MOFs built from conjugated or redox-active linkers alleviate these limitations by shortening charge and ion pathways and by introducing ligand-based redox functionality.<sup>[4]</sup> Among redox-active motifs, quinoidal scaffolds possess unique electronic adaptability due to resonance between closed-shell and open-shell forms, facilitating reversible multi-electron transfers and adjustable frontier orbital energies.<sup>[5]</sup> Despite these advantages, incorporation of quinoidal motifs into extended frameworks has been challenging owing to synthetic incompatibility, structural instability, and poor crystallinity of the resulting frameworks. Therefore, examples that deliver persistent structural order and robust redox activity at the framework level remain rare.

Herein we introduce 2D MOFs built on an azaquinodimethane-based dicarboxylate ligand (AQM-H<sub>2</sub>L) that combines chemical robustness, synthetic accessibility, and an electroactive quinoidal core. Coordination of AQM-H<sub>2</sub>L to divalent transition metal salts (Cu<sup>2+</sup>, Zn<sup>2+</sup>) produces crystalline, layered MOFs (AQM-H<sub>2</sub>L-Cu, AQM-H<sub>2</sub>L-Zn) with large interlayer spacing and dinuclear carboxylate secondary building units (SBUs). The quinoidal core narrows the molecular bandgap and places ligand frontier orbitals in energetic proximity to metal d-states, enabling efficient metal-ligand hybridization and dual charge storage pathways (ligand redox + metal redox). We show how interlayer proximity and exfoliation modulate band dispersion, surface reactivity and ion accessibility, factors that determine electrochemical performance. Using a combined suite of single-crystal X-ray diffraction (SCXRD), spectroscopy, Density Functional Theory (DFT) calculations, and device electrochemistry, we establish mechanistic connections between molecular design and device performance, and demonstrate that AQM-type quinoidal linkers constitute a generalizable design motif for multifunctional energy materials. Our work contributes two conceptual advances: (1) the demonstration that chemically robust quinoidal AQM units can be integrated into crystalline 2D MOFs while preserving redox accessibility and structural order, and (2) the identification of a proximity-tunable electronic/ionic design principle where interlayer orbital coupling and heteroatom-rich nanochannels are co-optimized to provide both electronic delocalization for pseudocapacitance and ionic pathways for solid electrolytes. These principles were validated experimentally in MSCs and PEO-based SPE batteries, which will inform the future design of electroactive quinoidal MOFs.

## Results and Discussion

### Design and crystallization of the quinoidal AQM-H<sub>2</sub>L ligand-based MOFs

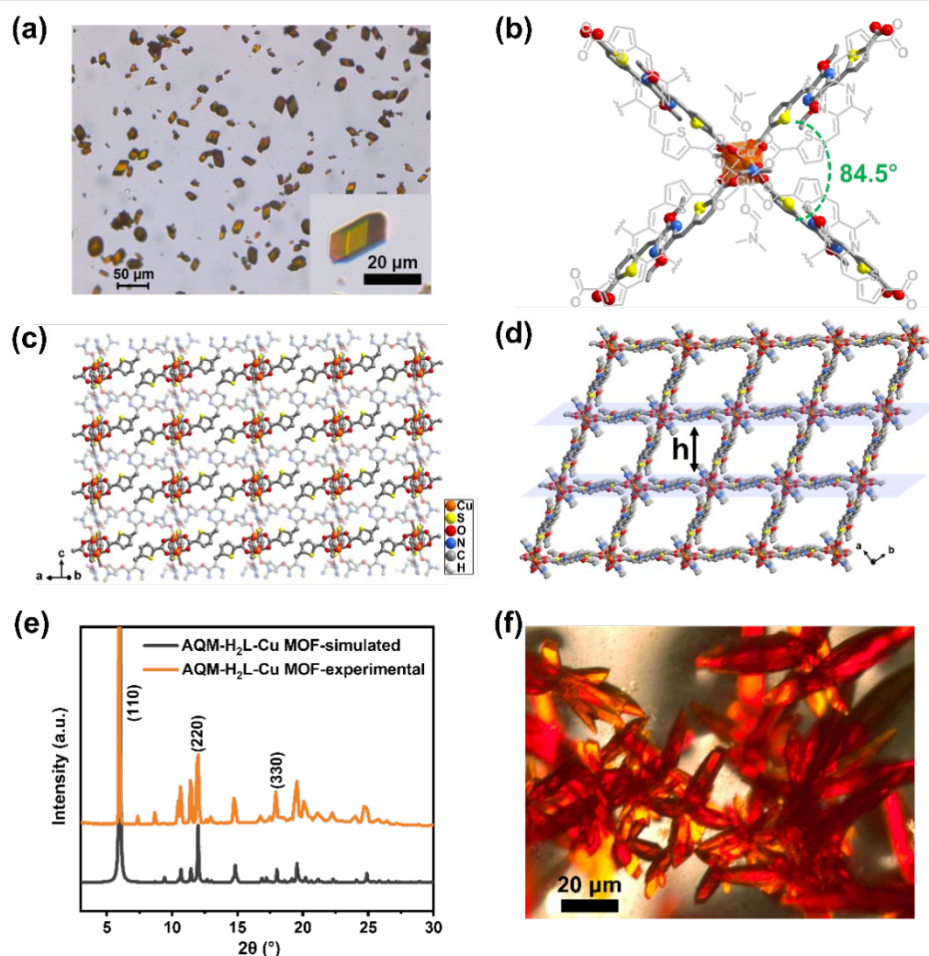
The quinoidal ligand AQM-H<sub>2</sub>L was synthesized via a three-step synthetic route (Figure 1a). A Knoevenagel condensation between 1,4-diacetyl-2,5-diketopiperazine and an ester-appended thienyl aldehyde yielded 2,5-bis(5-methoxycarbonylthiophen-2-ylidene)-3,6-diketopiperazine (1). Subsequent O-ethylation with iodoethane afforded a soluble intermediate that, after hydrolysis using LiOH, produced the dicarboxylic acid AQM-H<sub>2</sub>L featuring two coordinating termini. NMR and MALDI-TOF MS analyses confirmed the molecular purity and the preservation of the quinoidal backbone (Figures S1-S9).



**Figure 1.** Schematic of the synthesis of the AQM-H<sub>2</sub>L ligand and the formation of AQM-H<sub>2</sub>L-Cu MOF. (a) Synthetic route of the AQM-H<sub>2</sub>L ligand. (b) Schematic illustration of the formation of AQM-H<sub>2</sub>L-Cu MOF.

UV-vis spectroscopy of AQM-H<sub>2</sub>L in dilute DMF solution (Figure S10a) revealed a distinct  $\pi$ - $\pi^*$  transition at 460 nm and an absorption onset at 524 nm, corresponding to an optical bandgap of 2.37 eV, substantially narrower than that of typical aromatic MOF linkers.<sup>[6]</sup> Cyclic voltammetry (Figure S10b) showed irreversible redox waves with an onset reduction potential of -1.16 V (LUMO $\approx$ -3.64 eV) and oxidation onset of 0.57 V (HOMO $\approx$ -5.37 eV), defining an electrochemical bandgap of 1.73 eV. The irreversible character, common among AQM derivatives, reflects structural relaxation upon charge transfer.<sup>[7]</sup> Despite this, the narrow frontier orbital gap and accessible redox states underscore the strong electronic coupling intrinsic to the quinoidal scaffold, features essential for bandgap engineering and high-rate electrochemical activity.

Solvothermal coordination of AQM-H<sub>2</sub>L with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O or Zn(NO<sub>3</sub>)<sub>2</sub> (DMF/H<sub>2</sub>O 1:1 v/v, 100 °C, 24 h) produced prismatic single crystals (Figures 2a and 2f). SCXRD analysis (AQM-H<sub>2</sub>L-Cu: CCDC 2499051, monoclinic C2/m,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 91.984^\circ$ ,  $a = 16.999$ ,  $b = 24.768$ ,  $c = 10.078$ ; AQM-H<sub>2</sub>L-Zn: CCDC 2499057, monoclinic C2/m,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 92.358^\circ$ ,  $a = 17.518$ ,  $b = 24.858$ ,  $c = 10.145$ ) revealed layered frameworks built from dinuclear [M<sub>2</sub>(COO)<sub>4</sub>] (M = Cu, Zn) secondary building units linked by planar AQM ligands. S...N contacts within the thienyl-AQM backbone rigidify the 2D sheets and suppress rotational disorder,<sup>[8]</sup> while weak interlayer van der Waals forces confine crystal growth to two dimensions (Figures 2b-2f and Figure S11, Table S1-S4). The Cu and Zn analogues exhibit interlayer separations of 14.36 Å and 15.4 Å, respectively, sufficient to accommodate solvated ions or polymer segments.



**Figure 2.** Structural and morphological characterization of the MOFs. (a) Optical micrographs of prismatic single crystals of AQM-H<sub>2</sub>L-Cu MOF. (b) Local coordination environment of Cu<sup>2+</sup> with AQM-H<sub>2</sub>L, forming dinuclear Cu-carboxylate units. Single crystal structure of AQM-H<sub>2</sub>L-Cu MOF determined by SCXRD, viewed perpendicular to the 2D plane (c) and along the plane (d), showing a layered architecture with an interlayer spacing of ~14.36 Å. (e) Experimental powder XRD pattern of bulk AQM-H<sub>2</sub>L-Cu MOF (orange) compared with the simulated pattern (black) derived from the single-crystal structure. (f) Optical micrographs of single crystals of AQM-H<sub>2</sub>L-Zn MOF.

Powder X-ray diffraction (PXRD) patterns of bulk samples matched simulated data, confirming phase purity (Figure 2e and Figure S12). N<sub>2</sub> sorption at 77 K yielded a BET surface area of 245 m<sup>2</sup> g<sup>-1</sup> with a dominant pore size of 1.76 nm (NLDFT) (Figure S13), providing ion-accessible channels compatible with confined electrolyte transport. The frameworks remain thermally stable up to ~260 °C (TGA, Figure S14) and display uniform prismatic morphologies under FE-SEM (Figure S15). Elemental mapping confirmed homogeneous distribution of C, N, O, S, and Cu, with measured Cu content (1.55 at%) in close agreement with theoretical values (1.78 at%), corroborating the proposed coordination model. For comparison, the pore structure and thermal stability of the isostructural AQM-H<sub>2</sub>L-Zn MOF were also characterized by BET and TGA (Figure S16). The AQM-H<sub>2</sub>L-Zn MOF exhibits a substantially lower specific surface area than the Cu analogue, indicating less accessible porosity within the framework. Thermogravimetric analysis shows that the AQM-H<sub>2</sub>L-Zn MOF begins to decompose at around 280 °C, displaying thermal stability comparable to that of the AQM-H<sub>2</sub>L-Cu MOF.

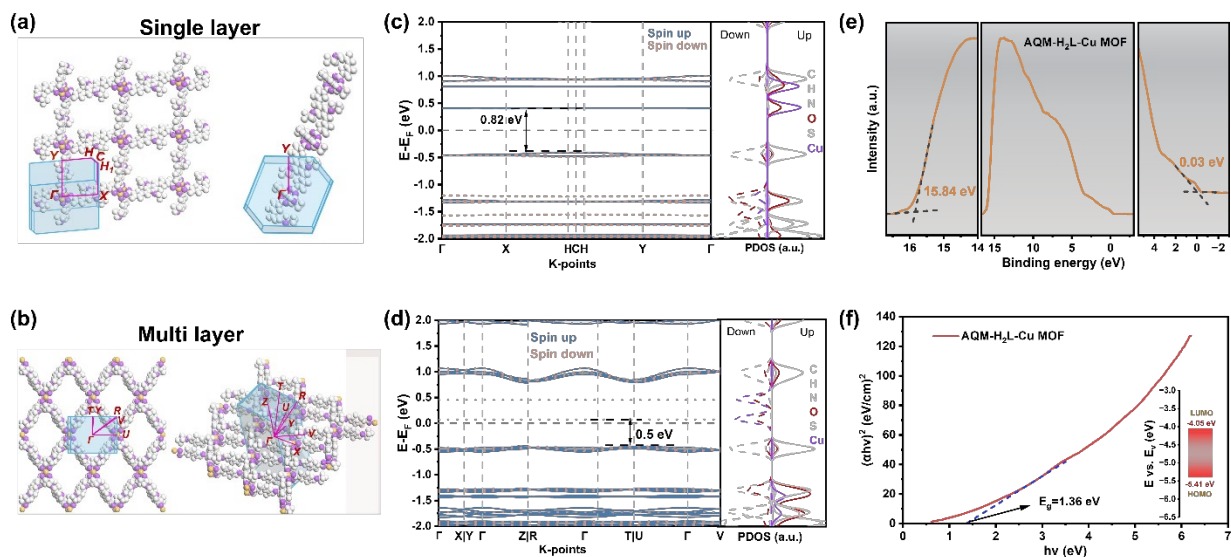
### Electronic structure and spectroscopic characterization

To rationalize the unusual combination of redox activity and crystallinity, we performed DFT calculations on monolayer and multilayer structural models derived from SCXRD coordinates (Figure 3a-d). The calculated monolayer band structure shows a relatively flat valence and conduction band with a direct bandgap of ≈0.82 eV, indicating localized frontier states primarily associated with the AQM ligand and Cu-O coordination environment. By contrast, a multilayer model displays pronounced band dispersion and a reduced bandgap

( $\approx 0.50$  eV), especially along directions that sample interlayer coupling (Figure 3c and 3d). Projected density of states (PDOS) analysis reveals significant contributions from Cu 3d and carboxylate O orbitals near the Fermi level, demonstrating metal-ligand hybridization in the stacked lattice. Spin-resolved calculations indicate weak spin polarization localized at Cu centers, consistent with ligand-to-metal and metal-to-ligand charge redistribution.

Ultraviolet photoelectron spectroscopy (UPS) locates the valence band maximum ( $E_{vb}$ ) at -5.41 eV for the bulk AQM-H<sub>2</sub>L-Cu framework (Figure 3e), consistent with the PDOS analysis that indicates deep-lying valence states stabilized by strong metal-ligand coordination. Solid-state UV-vis diffuse reflectance spectroscopy (UV-vis DRS) combined with Tauc-plot analysis yields an optical bandgap ( $E_g^{opt}$ ) of  $\approx 1.36$  eV (Figure 3f and Figure S17), from which the conduction band minimum ( $E_{cb}$ ) was estimated at -4.05 eV. These values confirm the semiconducting nature of the framework and its narrowed bandgap relative to most carboxylate-based MOFs, reflecting efficient  $\pi$ -d hybridization within the quinoidal coordination environment. Cyclic voltammetry (CV) in N<sub>2</sub>-saturated acetonitrile (Figure S18) provided an electrochemical bandgap ( $E_g^{elec}$ ) consistent with these spectroscopic estimates, further validating the electronic structure. The energetic alignment of  $E_{vb}$  (-4.75 eV) and  $E_{cb}$  (-3.9 eV) underscores the robustness of quinoidal linker-metal orbital hybridization, a key feature that facilitates rapid and reversible redox charge transfer. Notably, the observed proximity-dependent narrowing of the bandgap upon multilayer stacking provides a mechanistic basis for enhanced out-of-plane charge delocalization: interlayer orbital overlap mediated by the  $\pi$ -conjugated quinoidal backbone lowers charge-transfer barriers and enriches the density of states near the Fermi level, collectively underpinning the framework's high pseudocapacitive response.

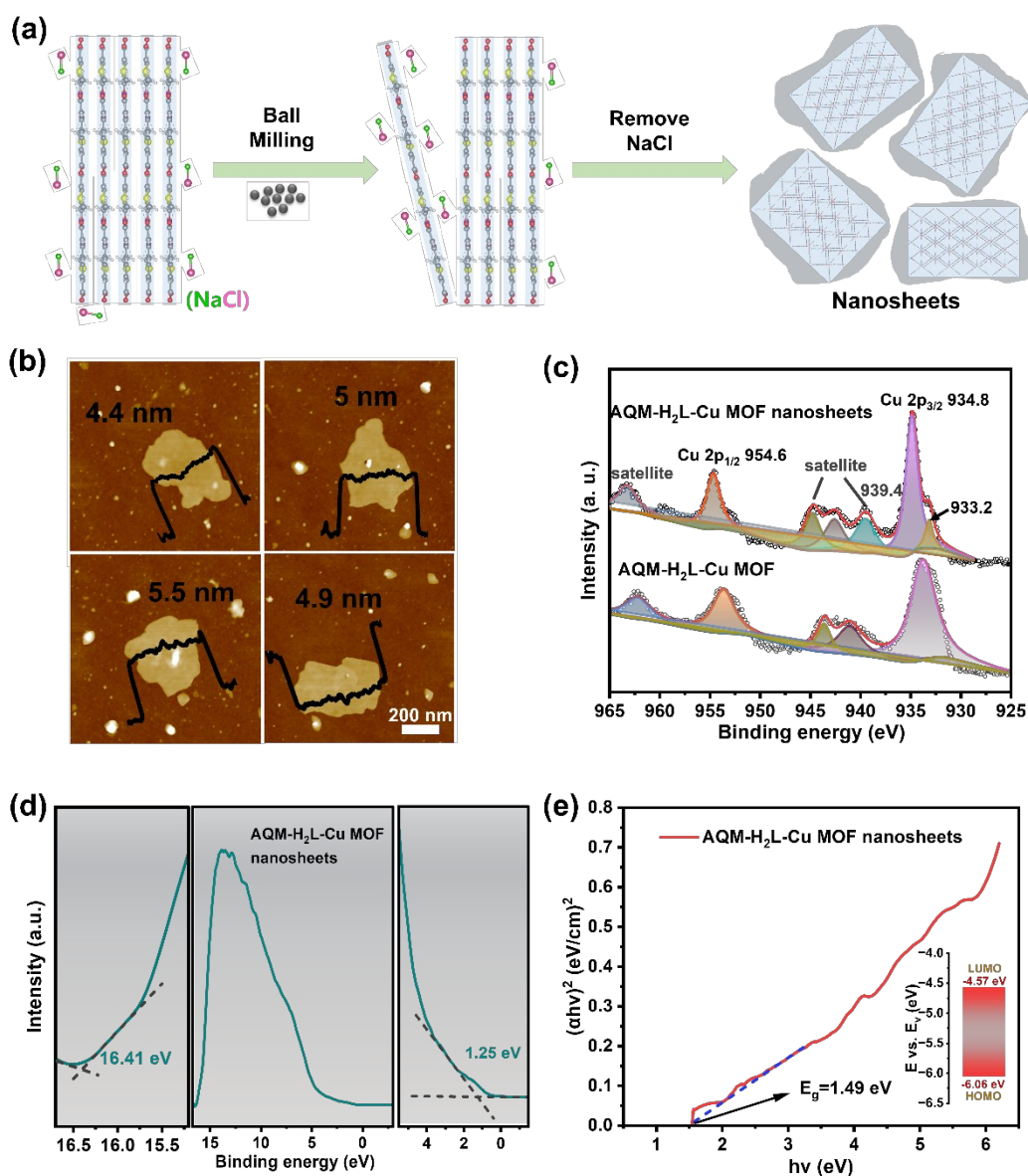
In comparison, the solid-state UV-vis diffuse reflectance spectrum of the isostructural AQM-H<sub>2</sub>L-Zn framework shows a wider optical bandgap of 2.19 eV (Figure S19), indicating a less delocalized electronic structure and reduced interlayer charge-transfer capability relative to the Cu analogue. This broader bandgap suggests weaker  $\pi$ -d orbital hybridization and lower electronic conductivity, which are unfavorable for fast redox-coupled charge storage. Consequently, the AQM-H<sub>2</sub>L-Cu MOF, with its narrower bandgap and enhanced charge-transport characteristics, was selected as the primary candidate for subsequent electrochemical device evaluation, including micro-supercapacitors and solid-state lithium batteries.



**Figure 3.** Electronic band structure and optical properties of AQM-H<sub>2</sub>L-Cu MOF. First Brillouin zone and high-symmetry K-points of monolayer (a) and multilayer (b) AQM-H<sub>2</sub>L-Cu MOF. Calculated electronic band structures and corresponding projected density of states (PDOS) for the monolayer (c) and multilayer (d). (e) Ultraviolet photoelectron spectroscopy (UPS) spectrum of AQM-H<sub>2</sub>L-Cu MOF. (f)  $T_{auc}$  plot derived from the absorption spectrum, used to estimate the optical bandgap. Inset: energy-level diagram with the extracted bandgap ( $E_g = 1.36$  eV) determined from the intersection of the baseline and tangent.

## Exfoliation and characterization of 2D AQM-H<sub>2</sub>L-Cu MOF nanosheets

To improve ion accessibility and enable solution processability, bulk crystals were exfoliated using a low-energy ball milling followed by ultrasonication in the presence of NaCl as a protective milling medium (Figure 4a). The process yields stable colloidal dispersions of nanosheets (100-300 nm lateral size, thickness  $\approx$  5 nm by AFM, Figure 4b) that exhibit the Tyndall effect (Figure S20). XPS shows Cu 2p<sub>3/2</sub> and 2p<sub>1/2</sub> features characteristic of Cu<sup>2+</sup> (Figure 4c and Figure S21). After exfoliation, an additional Cu 2p shoulder at  $\approx$ 933.2 eV appears, attributed to under-coordinated or surface-exposed Cu species, while satellite intensities shift subtly, commensurate with modified surface electronic structures.



**Figure 4.** Exfoliation of bulk AQM-H<sub>2</sub>L-Cu MOF into nanosheets. (a) Schematic illustration of the exfoliation process. (b) Atomic force microscopy (AFM) images of exfoliated nanosheets. (c) Cu 2p XPS core-level spectra of AQM-H<sub>2</sub>L-Cu MOF before and after exfoliation. (d) Ultraviolet photoelectron spectroscopy (UPS) spectrum of exfoliated nanosheets. (e)  $T_{auc}$  plot used to estimate the optical bandgap. Inset: energy-level diagram with extracted bandgap ( $E_g = 1.49$  eV), determined from the intersection of the baseline and tangent.

Exfoliation also produces a measurable change in electronic properties: UPS of nanosheets indicates a downward shift of the valence band maximum to 6.06 eV (Figure 4d), and UV-vis DRS indicates an increased optical gap ( $E_g \approx 1.49$ ) (Figure 4e and S22), consistent with quantum confinement and increased localization. In agreement with these optical observations, cyclic voltammetry further confirms the modification of the electronic structure upon exfoliation. The exfoliated AQM-H<sub>2</sub>L-Cu MOF nanosheets exhibit oxidation and reduction onset potentials of 0.95 V and -0.35 V versus Ag/AgCl, respectively (Figure S23), corresponding to an electrochemical

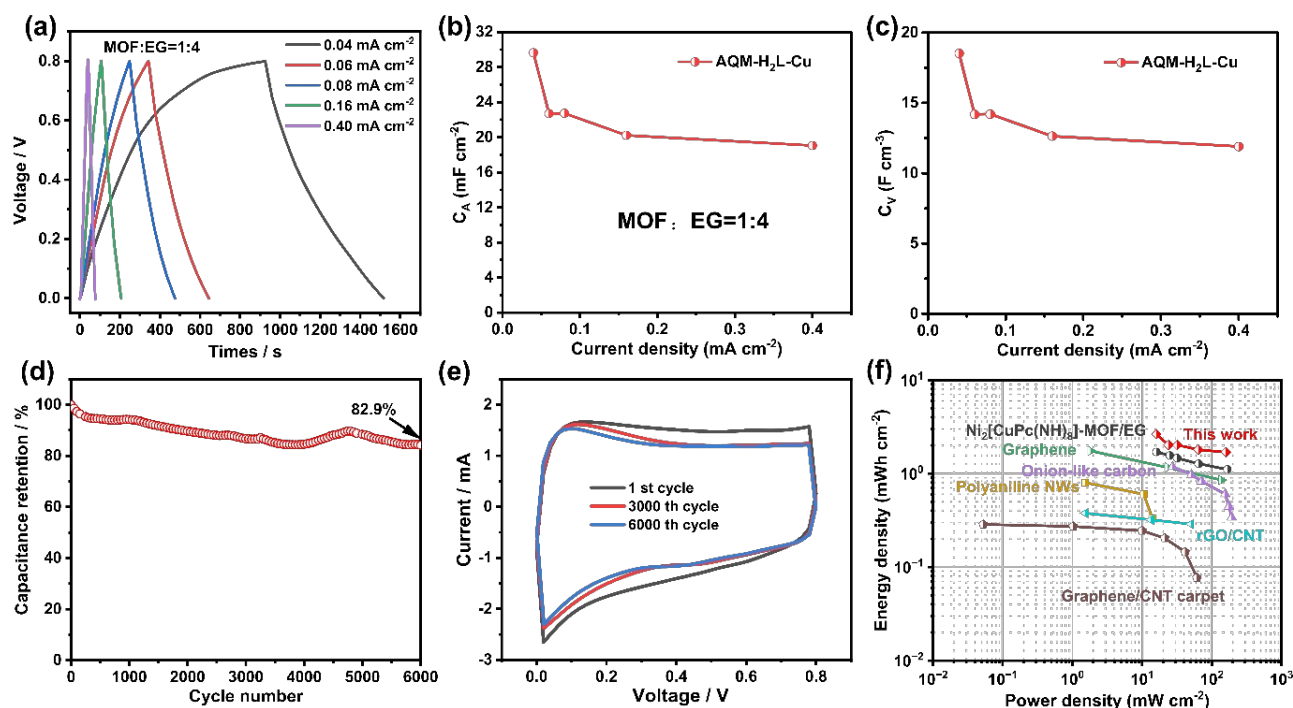
bandgap of approximately 1.30 eV. This value is slightly larger than that of the bulk MOF, which can be ascribed to reduced interlayer electronic coupling and weakened orbital overlap after exfoliation. The consistent trends observed for the optical and electrochemical bandgaps provide convergent evidence that exfoliation leads to a moderate bandgap widening while preserving favorable redox accessibility. From a mechanistic perspective, two opposing electronic effects emerge: multilayer stacking promotes band dispersion and out-of-plane transport, while nanoscale exfoliation increases site accessibility and introduces reactive surface Cu centers that can participate in fast faradaic processes. Device-level performance benefits from a balanced interplay between these effects: nanosheets provide ion accessibility and abundant active surface area while the residual multilayer regions and interparticle contacts maintain electronic pathways when blended with conductive graphene.

### Micro-supercapacitor (MSC) integration and device performance

Exfoliated AQM-H<sub>2</sub>L-Cu MOF nanosheets were integrated with electrochemically exfoliated graphene (EG) in a 1:4 mass ratio to form flexible hybrid films by vacuum filtration (film thickness ~16  $\mu\text{m}$ ) (Figures S24-S26). Interdigital Au contacts were thermally evaporated and laser-patterned to create MSCs, which were completed using a H<sub>2</sub>SO<sub>4</sub>-doped poly(vinyl alcohol) gel electrolyte. This hybrid design yields intimate electrical contact between the electronically active MOF and a high-conductivity graphene network while retaining porosity for ion ingress. To directly evaluate the acid stability of AQM-H<sub>2</sub>L-Cu MOF under realistic operating conditions, equal masses of the MOF were immersed in the same acidic electrolyte used for MSC fabrication. The concentration of leached Cu<sup>2+</sup> ions was quantitatively determined by ICP-MS as a function of immersion time (Table S5). Even after prolonged exposure for 72 h, the total amount of Cu released into the electrolyte was only 0.168  $\mu\text{g}$ , which is several orders of magnitude lower than the theoretical Cu content of the MOF sample ( $\approx 0.165$  mg), indicating negligible framework degradation and strong chemical robustness in acidic environments.

Galvanostatic charge-discharge (GCD) analysis gives an areal capacitance ( $C_A$ ) of 29.6  $\text{mF cm}^{-2}$  at 0.04  $\text{mA cm}^{-2}$ , corresponding to a volumetric capacitance ( $C_V$ ) of 18.1  $\text{F cm}^{-3}$ , surpassing most state-of-the-art MSCs based on conducting polymers and 2D frameworks (Figure 5b and 5c and Table S6).<sup>[4b, 9]</sup> CV curves retained quasi-rectangular shapes even at scan rates up to 50  $\text{mV s}^{-1}$  (Figure S27), indicating rapid ion transport through the nanosheet network. Capacitances of 18  $\text{mF cm}^{-2}$  ( $C_A$ ) and 11.8  $\text{F cm}^{-3}$  ( $C_V$ ) were obtained at 2  $\text{mV s}^{-1}$ . Long-term cycling tests (Figure 5d and 5e) confirmed decent durability, with 82.9% capacitance retention after 6000 cycles at 50  $\text{mV s}^{-1}$ . Ragone analysis (Figure 5f) showed ultrahigh areal power density (160  $\text{mW cm}^{-2}$ ) at an energy density of 2.6  $\text{mWh cm}^{-2}$ , surpassing most reported MSCs based on 2D MOFs, graphene, and carbons.<sup>[4b, 9]</sup> Trasatti analysis revealed nearly equal contributions from pseudocapacitance (49.2%) and double-layer capacitance (50.8%), underscoring the synergistic interplay between the quinoidal MOF and graphene (Figure S28).

Mechanistically, the pseudocapacitive behavior originates from the intrinsic quinoidal resonance of the AQM linker, which delocalizes charge across the  $\pi$ -conjugated lattice and couples synergistically with redox-active Cu centers in the dinuclear SBUs. The alignment of ligand redox potentials with the device operating window, together with Cu d-states near the Fermi level revealed by PDOS, confirms dual ligand-metal participation in charge storage. The high rate capability and low internal resistance stem from ultrashort ion-diffusion pathways within the nanosheet/graphene hybrid, an electronically continuous network, and a dense population of near-surface redox sites that minimize solid-state transport limitations.



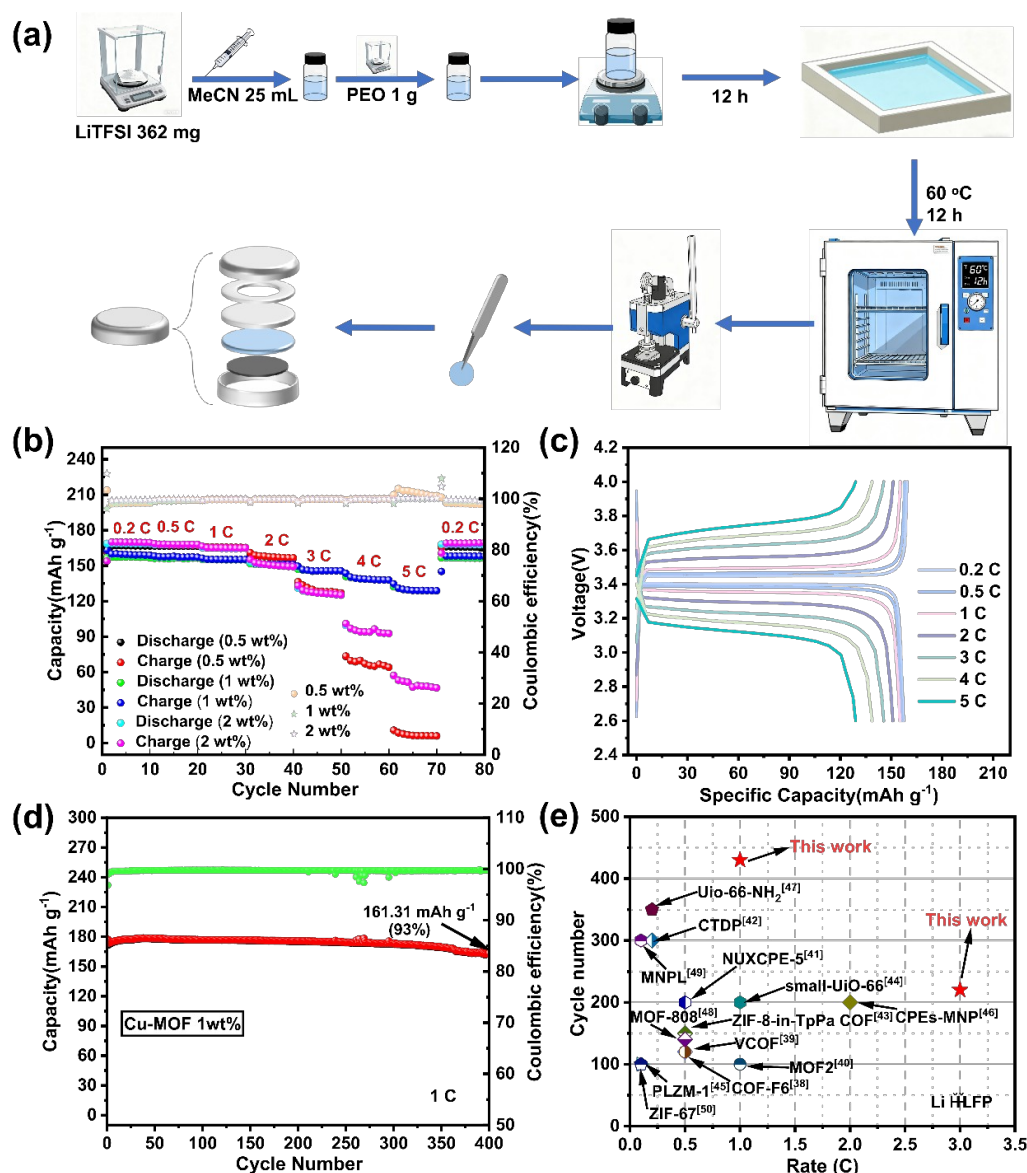
**Figure 5.** Electrochemical performance of AQM-H<sub>2</sub>L-Cu MOF-based micro-supercapacitors (MSCs). (a) Galvanostatic charge-discharge (GCD) curves at different current densities. Specific areal (b) and volumetric (c) capacitances as functions of current density, derived from GCD curves. (d) Cycling stability measured at 50 mV s<sup>-1</sup> within a voltage window of 0.8 V. (e) Cyclic voltammetry (CV) curves recorded at 1<sup>st</sup>, 3000<sup>th</sup>, and 6000<sup>th</sup> cycles. (f) Ragone plots comparing the energy and power densities of AQM-H<sub>2</sub>L-Cu MOF-based MSCs with those of previously reported 2D MOFs, carbon/graphene materials, and other framework-based electrodes.

## Solid polymer electrolytes and lithium battery performance

The multifunctionality of AQM-H<sub>2</sub>L-Cu nanosheets was further demonstrated by their use as ion-conductive fillers in PEO-based solid polymer electrolytes (Figure 6). Inclusion of 1 wt% nanosheets into PEO/LiTFSI matrices forms mechanically coherent SPEs that were assembled into Li/SPE/LiFePO<sub>4</sub> cells and tested at 60 °C. The 1 wt% loading was critical: at lower loadings percolation of ion-conductive pathways is incomplete, while higher loadings (>2 wt%) promote aggregation and pore blockage.<sup>[10]</sup>

Rate capability tests show capacities of 169.8 mAh g<sup>-1</sup> (0.2 C), 167.4 mAh g<sup>-1</sup> (0.5 C), 165.5 mAh g<sup>-1</sup> (1 C) and 127.9 mAh g<sup>-1</sup> (5 C), with the capacity largely recovered upon returning to 0.2 C. Long-term cycling yields 93% capacity retention after 400 cycles at 1 C and ≈150 mAh g<sup>-1</sup> over 200 cycles at 3 C (Figure 6d and S29). These performances exceed those of conventional PEO-based electrolytes and most reported MOF-based SPEs (Figure 6e and Table S7).<sup>[11]</sup> EIS shows reduced interfacial resistance relative to pristine PEO SPEs, and CV profiles show highly overlapping redox peaks (Figure S30), consistent with stable interfacial chemistry. The improved Li<sup>+</sup> transport and interfacial stability are primarily attributed to the following features: (i) heteroatom-rich pore walls (O, N, S) that provide solvating sites and transient coordination to Li<sup>+</sup>, lowering activation barriers for ion hopping; (ii) ordered nanochannels that enable continuous pathways across the electrolyte matrix; and (iii) suppression of large-domain polymer crystallinity in PEO near the MOF surfaces, which increases segmental mobility and Li<sup>+</sup> conductivity. The combined effect mimics aspects of ceramic fillers (structure and coordination) while preserving the processability and mechanical compliance of polymer electrolytes. In addition, post-cycling XPS analysis was performed to probe the chemical stability and redox behavior of the AQM-H<sub>2</sub>L-Cu MOF after prolonged lithium battery operation (Figure S31). The Cu 2p spectrum shows a pronounced attenuation of the Cu<sup>2+</sup> satellite features, while the Cu LMM Auger spectrum reveals the emergence of a Cu<sup>+</sup> signal at 569.0 eV, indicating partial and reversible Cu<sup>2+</sup>/Cu<sup>+</sup> redox conversion during repeated charge–discharge processes. This redox activity suggests that the metal nodes actively participate in electrochemical processes while maintaining the integrity of the coordination framework. Such a redox-tolerant metal–ligand environment, enabled by the quinoidal linker and robust coordination geometry, allows the MOF to accommodate charge compensation without irreversible degradation, thereby contributing to the sustained cycling stability and high-rate performance of the solid-state lithium battery.

The electrochemical performance of the bulk Cu-MOF was further evaluated in a solid-state lithium battery (Figure S32). Rate-capability tests show discharge capacities of 153.1, 148.5, 140.7, and 120.9 mAh g<sup>-1</sup> at 0.5, 1, 2, and 3 C, respectively, dropping sharply to 3.6 mAh g<sup>-1</sup> at 5 C, with partial recovery upon returning to 1 C. Long-term cycling at 3 C reveals gradual capacity decay, falling below 60% of the initial capacity by 80 cycles. This performance degradation is attributed to limited electronic connectivity, sluggish charge-transfer pathways, and structural stress accumulation coupled with interfacial degradation. In contrast, exfoliated nanosheets offer shortened charge-transport pathways, improved interfacial contact with graphene, and enhanced structural compliance, resulting in the markedly improved electrochemical performance observed in both MSCs and solid-state lithium batteries.



**Figure 6.** Electrochemical performance of AQM-H<sub>2</sub>L-Cu MOF-based lithium battery. (a) Schematic illustration of the assembly process of the Li/AQM-H<sub>2</sub>L-Cu MOF solid polymer electrolyte (SPE)/LiFePO<sub>4</sub> battery. (b) Rate capability and (c) charge-discharge profiles at various current rates (0.2-5 C) measured at 60 °C. (d) Long-term cycling stability at 1 C. (e) Ragone plot comparing the energy-power performance of the AQM-H<sub>2</sub>L-Cu MOF-based lithium battery with conventional PEO-based electrolytes and representative MOF-based SPEs. The plot illustrates the C-rate dependence of cycling performance (capacity retention as a function of charge-discharge rate).

## Conclusion

The results presented here reveal a direct molecular-to-device correlation in which the chemistry of quinoidal linkers governs the concurrent electronic and ionic functions of two-dimensional metal-organic frameworks. The AQM-H<sub>2</sub>L-Cu framework exemplifies how molecular design centered on  $\pi$ -conjugated quinoidal scaffolds can simultaneously enable redox delocalization, band structure tunability, and ion transport, properties that define multifunctional energy materials.

The aza-quinodimethane core introduces energetically aligned frontier orbitals that mediate reversible multi-electron processes within device-relevant potentials. In contrast to conventional MOFs, where redox activity is confined to metal centers, AQM-H<sub>2</sub>L-Cu exhibits a delocalized pseudocapacitive network arising from cooperative ligand and metal participation. Density-of-states calculations and XPS spectra reveal the coexistence of ligand-centered redox transitions and Cu<sup>2+</sup>/Cu<sup>+</sup> processes in close energetic proximity, allowing fast charge exchange between  $\pi$ -conjugated linkers and metal nodes. This distributed redox framework expands the density of electrochemically active sites and mitigates kinetic limitations typical of localized metal-centered charge storage. The quinoidal backbone therefore functions not only as a redox reservoir but also as an electronic bridge that couples molecular and extended conduction pathways.

Electronic coupling between adjacent layers further enhances charge transport. Density functional theory and spectroscopic analyses reveal that interlayer proximity narrows the bandgap and increases band dispersion, promoting out-of-plane delocalization crucial for fast electrode kinetics. Conversely, exfoliation into few-layer nanosheets increases site accessibility and introduces under-coordinated Cu sites that accelerate surface redox reactions. The experimentally optimized hybrid of AQM-H<sub>2</sub>L-Cu nanosheets and conductive graphene embodies a balance between these effects, ensuring nanoscale accessibility without sacrificing electronic continuity. This proximity-tunable electronic structure offers a powerful design principle: by modulating interlayer spacing, substituent sterics, or co-ligand incorporation, one can systematically tailor the interplay between electronic conductivity and ionic permeability in layered frameworks.

Ion transport within the framework follows an equally rational molecular basis. The large interlayer spacing and ordered nanochannels embedded with O, N, and S atoms establish stable ionic highways that facilitate Li<sup>+</sup> solvation and migration. These heteroatom-rich environments lower activation barriers and stabilize interfacial chemistries, while simultaneously suppressing polymer crystallization when embedded in PEO matrices. As a result, even minimal incorporation (1 wt%) of AQM-H<sub>2</sub>L-Cu nanosheets generates continuous Li<sup>+</sup> conduction networks, delivering high rate capability and exceptional cycling stability in LiFePO<sub>4</sub> full cells. Such ionic transport enhancement, achieved at an order of magnitude lower filler loading than in typical ceramic-based solid polymer electrolytes, highlights the efficiency of molecular-level ionic coordination within the framework.

These results establish a unified mechanistic picture in which ligand-centered redox activity, interlayer orbital coupling, and ordered heteroatom coordination act synergistically to merge electronic and ionic transport in a single crystalline lattice. The AQM motif thus functions as a molecular transducer, storing charge through  $\pi$ -conjugated redox states while simultaneously facilitating electron and ion movement across the material. This dual functionality directly translates to macroscopic device performance: micro-supercapacitors exhibit high areal and volumetric capacitance with robust cycling stability, while solid-state lithium batteries achieve enhanced rate capability and long-term retention. The concurrent optimization of these orthogonal functionalities within one reticular framework underscores the conceptual advance of this work, a molecularly integrated strategy that bridges the traditional divide between electrode and electrolyte materials.

Beyond performance metrics, the significance of this study lies in the generalizable design principle it introduces. The incorporation of redox-accessible quinoidal units into ordered coordination lattices provides a molecular blueprint for constructing frameworks with tunable band alignment, hybridized electronic states, and controlled ionic pathways. The quinoidal linker acts as a structurally encoded electronic relay, while the metal-ligand coordination defines directional ion channels and mechanical robustness. Notably, the ligand is derived from commercially available precursors, and the MOF is assembled from earth-abundant copper under mild conditions, suggesting compatibility with scalable synthesis and future optimization. These attributes highlight the potential of this molecularly integrated platform to bridge the traditional divide between electrodes and electrolytes, providing a pathway toward practical, high-performance energy materials.

## Acknowledgements

The authors gratefully acknowledge the financial supports from the National Key R & D Program of China (2024YFB4206300), the National Natural Science Foundation of China (U22A20426, 22122801, 22408017), and Beijing-Tianjin-Hebei Natural Science Foundation Cooperation Project (25JJJC0046). Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Y.L. and C.Y. acknowledge the support from the Laboratory Directed Research and Development (LDRD) Program.

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.<sup>[12]</sup>

**Keywords:** Quinoidal metal-organic frameworks • Redox-active ligands • Two-dimensional nanosheets • Microsupercapacitors • Solid-state lithium batteries

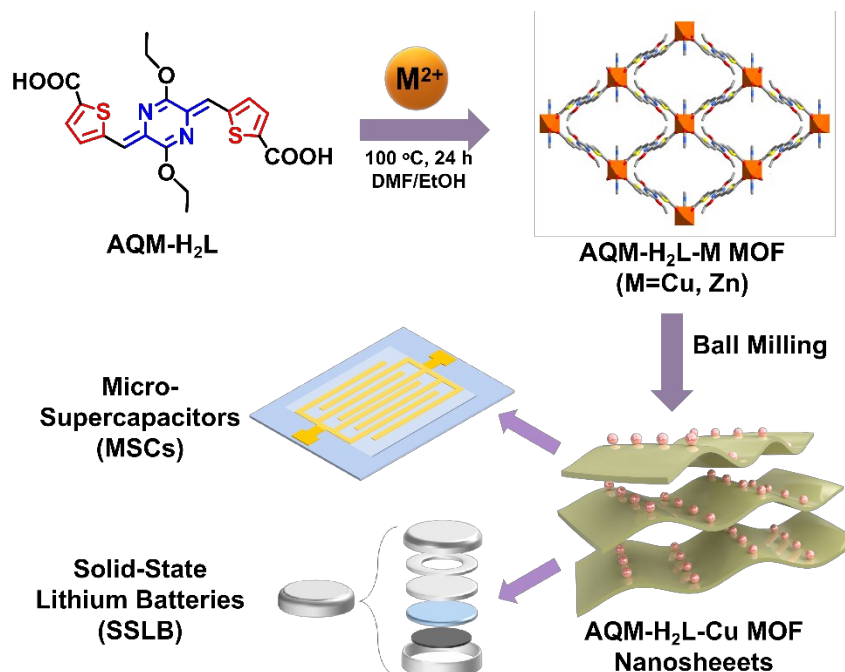
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[12] Deposition Number(s) (<https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/anie.2025XXXXX>) 2499051 (for AQM-H<sub>2</sub>L-Cu MOF), 2499057 (for AQM-H<sub>2</sub>L-Zn MOF) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service (<http://www.ccdc.cam.ac.uk/structures>).

## Entry for the Table of Contents



Quinoidal redox ligands enable the construction of layered Cu-based two-dimensional metal-organic frameworks with abundant redox sites and ordered ion channels. Exfoliated nanosheets exhibit outstanding capacitive and ionic transport properties, empowering high-performance microsupercapacitors and solid-state Li-ion batteries with exceptional energy density and long-term cycling stability.