Size-Dependent Properties of Solution-Processable Conductive MOF Nanocrystals

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Abstract. The diverse optical, magnetic, and electronic behaviors of most colloidal semiconductor nanocrystals emerge from materials with limited structural and elemental compositions. Conductive metal-organic frameworks (MOFs) possess rich compositions with complex architectures, but remain unexplored as nanocrystals, hindering their incorporation into scalable devices. Here, we report the controllable synthesis of conductive MOF nanoparticles based on $\text{Fe(1,2,3-trizolate)}_2$. Sizes can be tuned as small as 5.5 nm, ensuring indefinite colloidal stability. These solution-processable MOFs can be analyzed by solution-state spectroscopy and electrochemistry and cast into conductive thin films with excellent uniformity. This unprecedented analysis of MOF materials reveals a strong size-dependence in optical and electronic behavior sensitive to the intrinsic porosity and guest-host interactions of MOFs. These results provide a radical departure from typical MOF characterization, enabling insight into physical properties otherwise impossible with bulk analogs, while offering a roadmap for the future of MOF nanoparticle synthesis and device fabrication.

Introduction

The discovery of colloidal metal and semiconductor nanocrystals has led to a revolution in materials chemistry.¹ While the class of materials known as metal-organic frameworks (MOFs) attracts broad interest due to their high accessible surface areas and wide synthetic tunability, their preparation as stable, monodisperse nanoparticles remains an open frontier.² Nevertheless, recent research into the few examples of MOF nanoparticles has revealed enhanced properties compared to their bulk counterparts due to greater mass transport rates, higher ratios of exposed surface areas, and superior processability, leading to higher catalytic activities, improved gas permeability in separation membranes, more uniform integration into composite films, and utility as unique drug delivery agents.³⁻⁷ The controlled synthesis of MOF nanoparticles with precise sizes will therefore facilitate their application in myriad applications, while

enabling solution-state analysis to reveal size-dependent physical properties.⁸ Currently, the few MOFs that can be prepared as colloiddally stable nanoparticles with narrow size dispersities⁹ are electrical insulators, whereas conductive MOF nanoparticles will enable electronic technologies that benefit from the microporosity and high surface areas of MOFs and the processability and size-control of nanoparticles.¹⁰ Here, we address the long-standing challenge of making solution-processable conductive MOF nanoparticles (nanoMOFs) with controlled size and low polydispersity. Solution processability also enables solution-state spectroscopy for unprecedented analysis of electronic properties and thin film fabrication reveals unique insight into their redox chemistry and charge transport phenomena.

Results and Discussion

Size-tunable Synthesis of Iron Triazolate Nanoparticles

Figure 1: Overview of $\text{Fe(1,2,3-triazolate)}_2$ (Fe(TA)_2) nanocrystal synthesis. a) General synthetic route to Fe(TA)_2 nanoparticles using 1-methylimidazole (1-mIm) as a modulator. b) Equilibrium between metal ions (M), linkers (L), and modulators (Mod) that control MOF nanoparticle formation. c) PXRD patterns of the Fe(TA)_2 nanoparticles synthesized with varying amounts of 1-mIm. Grey lines indicate expected reflections. d) The SBU of Fe(TA)_2 . e) An idealized representation of a 5.5-nm Fe(TA)_2 particle based on the bulk crystalline structure

Nanoparticles of $\text{Fe}(\text{TA})_2$ were prepared with tunable sizes by modifying the standard bulk synthesis¹¹ through addition of 1-methylimidazole (1-mIm) as a “modulator” (Fig. 1). Although the use of “modulators,” usually monotopic analogs of the native MOF linkers,⁹ is common in MOF nanoparticle syntheses, their mechanistic role has been debated, especially because increasing modulator equivalents leads to smaller sizes in some systems, but larger sizes in others. Previous studies from our lab point to a “seesaw” model where modulators impact particle sizes by interfering with linker deprotonation (Figure 1, Eq. 1) and metal-linker complexation (Eq. 3). Based on a meta-data analysis of the literature⁹ this model contends that MOF particles result from kinetic trapping of metal ions by excess linker or modulator. Through deliberate control of the key parameters outlined by this model—proton activity, concentration, and ligand excess—excellent size reproducibility can be achieved for benchmark MOF materials.⁹ Using these insights, we can devise MOF syntheses previously inaccessible at the nanoscale. To access small and controllable particle sizes, we hypothesized that reversible bonds between Fe and 1-mIm (Eq. 4) would compete with the metal-linker complexation (Eq. 3) required to form the secondary building blocks (SBUs) of $\text{Fe}(\text{TA})_2$, shown in Figure 1c, thereby inhibiting MOF growth. Additionally, previous work with other MOF systems have shown promising nanosizing effects with the use of similar imidazole modulators.^{12,13}

In comparison to the bulk synthesis first reported by Yaghi *et al* in 2012,^{11,14,15} the synthesis of nanoparticles was conducted under dilute conditions, with stirring, and varying modulator equivalents. After heating the reaction mixture under air-free conditions in DMF at 120 °C, the reaction was terminated after 1.5 h by removing from heat and immediate centrifugation and washing. These reactions are low yielding (6 – 23%), which is further evidence of arrested growth of kinetically trapped particles, as has been observed in other nanoMOF systems (Fig. S4). Indeed, Figure 1d shows the expected PXRD pattern of $\text{Fe}(\text{TA})_2$ but with peaks that broaden with greater equivalents of modulator. Additionally, Figure 2 shows that particle sizes determined by Scherrer analysis of these data and by SEM imaging dramatically decrease with increasing equivalents of 1-mIm. At low equivalents of 1-mIm, the particle sizes decrease steeply: from 0.055 eq to 0.709 eq, the particle sizes reduce from 130 nm to 16 nm. Beyond 0.709 eq, the particle sizes level off abruptly, decreasing to 5.5 nm only with 10.9 equivalents of modulator (Fig. 2f, Fig. S5a).

Figure 2: Particle sizes of Fe(TA)₂ resulting from modulated syntheses. (a) – (e) SEM images of Fe(TA)₂ nanoparticles synthesized with 1-methylimidazole equivalents (with respect to Fe sites) ranging from 0.055 eq (a) to 10.9 eq (e). Images were set to greyscale using Adobe Illustrator. Insets: histograms of particle size distributions from >200 particles fitted to weighted gaussian distributions. f) Particle sizes using 1-mIm (red squares), 1-benzyl-2-methylimidazole (Benzyl, green triangle) 5-bromo-1-methylimidazole (Bromo, blue triangle), and *n*-butylamine (nBA, purple triangle). Filled data points were determined by SEM and open data points by Scherrer analysis.

To the best of our knowledge, the 5.5-nm particles represent some of the smallest reported MOF particle sizes synthesized by a facile one-pot modulator method, whereas the synthesis of nanoMOFs below 10 nm typically requires multiphase systems, dropwise additions, or multiple modulator ligands.^{16–18} Figure 1e depicts a simulated structure of 5.5-nm Fe(TA)₂, confirming that such a small size still includes many pores due to the unusually high density of this MOF. SEM analysis of the 16 and 25 nm particles reveals unimodal and symmetrical size distributions and essentially spherical morphologies (Fig 2). Microscopy of larger particles (0.055 eq 1-mIm, 130 nm), on the other hand, show octahedral faceting, akin to the bulk MOF product. Size distributions also skew towards larger sizes when the modulator equivalents are low, indicating that particles may grow by non-classical mechanisms such as digestive ripening or interparticle coalescence.¹⁹ The polydispersity index (PDI) from these histograms vary between 0.09 and 0.18, which are considerably lower than the typical PDI values of nanoMOFs, which are often as high as 0.6, and rival

the archetype of low-dispersity MOF particles, ZIF-8, which also exhibits values around 0.09.^{22–25} Whereas modulators may incorporate as internal defects or surface ligands in other MOF systems, ¹H acid digestion NMR indicates that 1-mIm does not incorporate in most cases (Fig S9). Remarkably, despite the lack of conventional capping ligands, particles of all sizes exhibit colloidal stability in DMF under anaerobic conditions for at least three months, even at relatively high concentrations of 10–20 mg/mL. Dynamic light scattering measurements of 25-nm particles stored for three months gave a solvated diameter of 60 ± 10 nm, a reasonable increase from the SEM images of dried particles that did not exhibit aggregation (Fig. S11). Therefore, these Fe(TA)₂ particles exhibit superior long-term stability compared to previously reported MOF systems, which, with the notable exception of ZIF-8 in methanol, must be coated with polymers or surfactants to achieve colloidal stability.^{26,27}

To explore the general application of this nanocrystal synthetic route, we investigated 5-bromo-1-methylimidazole, 1-benzyl-2-methylimidazole, and *n*-butylamine (nBA) as alternatives to 1-mIm. Due to their differences in Lewis and Brønsted-Lowry basicities, this series of modulators offers a platform for exploring the competing equilibria outlined in Figure 1b. Specifically, we expected that nBA, as the strongest ligand and proton acceptor, would yield the smallest sizes. Figure 2f plots the resulting particle sizes using 0.218 equivalents of each modulator, indicating that each of these alternative modulators produces nanoparticles, with nBA giving the smallest sizes and the bromo-substituted variant, i.e., the weakest ligand, producing the largest sizes. This trend correlates with the strength of the N-Fe bond, as the weakly electron-donating benzyl group allows the imidazole nitrogen to increase its sigma-donating ability, whereas the electronegative bromine moiety withdraws electron density from the N-Fe bond. This size trend therefore provides further evidence that modulators compete with the triazole MOF linkers. SEM images confirm that the resulting particles are also uniform (Fig. S3), but unlike particles synthesized with 1-mIm, their PXRD patterns indicate minor phase impurities (Fig S1) and accordingly 1-mIm was selected as the standard modulator for subsequent syntheses. Encouraged by the results with Fe(TA)₂, we explored the synthesis of Co(TA)₂ with the addition of 1-methylimidazole and observed a similar size trend by Scherrer analysis (Fig. S6). Although SEM images reveal that the morphology of these particles is not well-defined,

the addition of 1-mIm as a modulator may be a generally applicable method to synthesize nanoMOFs comprised of triazole linkers.

Size-Dependent Optical Properties of Colloidal Fe(TA)₂ Nanoparticles

The remarkable colloidal stability and small sizes of Fe(TA)₂ nanoparticles yielded suspensions with minimal light scattering, as seen in the inset photo of Fig. 3a. In fact, diluting colloidal suspensions of Fe(TA)₂ results in samples with sufficient transparency for solution-state UV-Vis absorption spectroscopy. In general, any spectroscopy of MOF materials involves analysis of solid-state samples, with UV-Vis analysis demanding diffuse reflectance methods. Figure 3a shows solution-state UV-Vis spectra for all Fe(TA)₂ particle sizes. These spectra comprise some of the only examples of solution-state spectroscopy of MOF materials, which include isolated reports of MOF-525, TMU-34, and Zn-MOF-74.^{28–30} To the best of our knowledge, this report is the first to quantify fundamental optical properties from the absorbance spectra of MOF particles in solution. The spectra exhibit the same two MLCT bands (ca. 27,000 cm⁻¹ and 34,000 cm⁻¹) as observed in the bulk material (Fig. 3a, shaded grey). Due to significant scattering that is observed in the spectra of larger particle sizes, the low-intensity d-d transition expected at 19,000 cm⁻¹ for the low-spin-state material from the bulk spectrum is obscured in all spectra. Notably, the spectra lack an inter-valence-charge-transfer (IVCT) band around 10,000 cm⁻¹ that arises from mixed Fe^{3+/2+} valency, suggesting the particles exist in a fully ferrous state.¹⁴

Close inspection of the solution-state spectra reveal that the peak maxima of the two charge transfer bands decrease in energy with increasing particle sizes, while a shoulder emerges at energies below the lower-energy band (Fig. 3). For the higher energy band (CT1), the maximum shifts a total of 1,750 cm⁻¹, while the lower band (CT2) maximum shifts 880 cm⁻¹. In the bulk material, the λ_{max} of CT1 appears at a lower energy of 32,182 cm⁻¹, and CT2 appears at 27,968 cm⁻¹, within range of the λ_{max} of the nanoparticles. Although the CT2 band is split in the bulk spectrum, the peak-to-peak separation appears more extreme in the nanoparticles, with the lower-energy shoulder appearing at much lower energies (Fig S15). *These data represent the first examples of size-dependent shifts to optical properties of MOF materials.* To determine whether the modulator plays a role in the size dependence, UV-Vis spectra were collected of particles

synthesized with *n*-butylamine and 1-benzyl-2-methylimidazole. Because modulated MOF syntheses often introduce defects, we anticipated the modulator identity to influence the extent of defect incorporation in Fe(TA)₂ nanoparticles.²⁹ Interestingly, the λ_{max} values for particles prepared with these alternative modulators are similar to Fe(TA)₂ particles prepared with 1-mIm. Therefore, the size-dependent optical behavior is unlikely due to modulator-induced defects and is reproducible (Fig 3d, 3g).

Figure 3: Solution-state UV-Vis absorption spectra of Fe(TA)₂ nanoparticles. a) Normalized spectra of colloidal Fe(TA)₂ nanoparticles of varying sizes suspended in DMF (colored traces) compared with the bulk MOF (filled grey area) as reported by diffuse reflectance.¹⁶ Smallest and largest particles traces are emphasized in bold. Inset contains a photo of the smallest and largest particles as solutions in cuvettes. b) CT1 (blue) and CT2 (black) peak maxima plotted as ϵ per particle versus particle diameter. Solid curves are fits of ϵ to cubic functions of diameter. Pre-factors for CT1 and CT2 fits are 18013 and 15081, respectively. c) Normalized CT2 band and d) Corresponding peak maxima versus particles sizes. e) UV-Vis traces for all particle sizes plotted as extinction coefficient ϵ per particle. f) Normalized CT1 band and g) corresponding peak maxima versus particles sizes. Peak maxima are reported for syntheses modulated by 1-mIm except for data labeled for *n*-butylamine (nBA) and 1-benzyl-2-methylimidazole (Benzyl). h) Oscillator strength determined per particle for the two charge transfer bands as well as the shoulder (sh) of CT2.

The shift in the peak maxima suggest that the electronic structure of FeTA₂ changes with particle size. Several physical scenarios might explain this observation. The first possibility is quantum confinement; particle sizes smaller than the excitonic Bohr radius of Fe(TA)₂ would exhibit blue-shifted absorption events. Previous electronic structure calculations of Fe(TA)₂, however, depict relatively shallow band curvatures and therefore low charge carrier mobilities, which would result in an insufficiently large excitonic radii for quantum confinement.³¹ Additionally, band-gap transitions of quantum-confined materials linearly increase with $1/r^2$, based on the effective mass approximation, or as $1/r$ due to Coulombic electron-hole interactions.³² However, a linear trend is not observed in this transition with respect to $1/r^2$ or $1/r$ (Fig. S15). A second explanation may be that the observed optical shifts arise from a size-dependent magnetic transition. Previous studies of bulk Fe(TA)₂ indicate that low-spin Fe²⁺ centers undergo spin-crossover transitions at 290 °C,¹⁵ but this transition temperature might occur at lower temperatures for smaller particles due to decreased cooperativity of smaller domain sizes. For example, the spin-crossover temperatures of related Fe-based 1-D coordination polymers decrease with decreasing particle sizes.³³ The distinct electronic configurations of high- and low-spin states would produce different sets of spectra, as is well-documented for spin-crossover materials.^{34,35} In other words, the size-dependent spectra of Fe(TA)₂ might arise from the particles existing in differing mixtures of low-spin and high-spin states, depending on the size-dependent transition temperatures. If the particles reside primarily in a high-spin state, this scenario would explain the absence of the expected d-d transition at 19,000 cm⁻¹ for a low-spin Fe(TA)₂. Preliminary PXRD analysis, however, suggests the nanoparticles exist in the denser low-spin crystallographic phase (Fig 1d).¹⁵ Partial oxidation of iron sites is another possibility, as a change in shape of the charge transfer bands has been reported for Fe(TA)₂ bulk powders after chemical oxidation.¹⁴ This scenario is unlikely, however, as the colloids are stored and measured air-free, and the spectra lack an intervalence charge-transfer band.¹⁴ Finally, structural distortions due to the high surface-to-volume ratios of small particles could be responsible for the size-dependent spectral shifts as optical shifts arising from surface restructuring has been reported in several metal-oxide nanoparticle systems.³⁵ Specifically, the localized orbitals of surface, sub-surface, and internal species in different geometries could contribute different absorption bands

to UV-vis profile, with surface species playing the greatest role in the smallest particles. Delocalized wavefunctions, on the other hand, might respond coherently to structural distortions, contorting the shapes of valence band and conduction band orbitals and shifting their relative energies. The presence of surface defects is supported by N₂ sorption experiments, which show that the 48-nm particles display a lower accessible surface area than the bulk material despite their higher surface area to volume ratio (Fig S8).

Conventional spectroscopy of MOFs lacks the ability to interpret absorption intensities, but solution state measurements allow for the determination of extinction coefficients (ϵ) for all Fe(TA)₂ particle sizes. Quantitative analysis of extinction coefficients has driven the quantum mechanical understanding of semiconductor nanocrystal optical phenomena by relating optical oscillator strengths (f) to physical excitation processes and by providing a practical estimation of particle concentrations from optical spectra.^{26,27} Such analysis is currently limited for MOF materials; to date only one report discusses the dependence of optical properties—in this case fluorescence—on particle size and defectiveness.²⁹ Figure 3b plots the extinction coefficients of peak maxima versus particle diameters, which increase by four orders of magnitude, from 10⁶ (cm⁻¹ M⁻¹) for 5.5 nm particles to 10¹⁰ (cm⁻¹ M⁻¹) for 130 nm particles (Fig S14). It is evident from the spectra alone that the extinction coefficients depend strongly on particle sizes, with larger sizes absorbing more intensely than smaller particles, as expected from the increased number of absorber units (Fig 3e). To explain this dramatic increase in absorber strength, the extinction coefficient data were fitted to cubic functions of particle diameters, as has been demonstrated for lead chalcogenide semiconductor nanocrystals based on the hypothesis that absorber strength per particle arises from increased particle volumes.³⁸ A cubic relationship produces an excellent fit except for larger sizes, in which the experimental data appears depressed in relation to the expected cubic trend, most likely due to light scattering (Fig. 3b). While greater extinction coefficients may be expected for larger particles, the absorption strength per Fe(TA)₂ formula unit depends on particle diameters as well, ranging from ~3000 – 7000 cm⁻¹ M⁻¹, which are typical values observed for molecular charge transfer bands (Fig. S13). For a deeper microscopic analysis of absorption intensities, oscillator strengths f can be determined for each of the absorption bands. When calculated per particle, f increases with particle sizes (Fig. 3e), as expected for

an increased number of absorbing units. Determined per formula unit, the oscillator strength changes minimally with particle sizes, with f values ranging from 0.05 to 0.27 (Fig. S16). In all cases, f per formula unit is on the order of 10^{-1} , as expected for a charge transfer that is both spin and parity allowed. Combined, these results show that colloidal stability enables powerful quantitative analysis of the optical properties of MOF nanocrystals. Although the analysis herein does not yet consider possible non-linear contributions of scattering to total extinction, this type of analysis represents a step forward for understanding the optical properties of MOF structures.^{39,40}

Size-Dependent Redox Chemistry and Charge Transport of Fe(TA)₂ Nanoparticles

Although solid-state techniques and additives such as polymer binders are required to study redox properties of bulk MOFs, the colloidal stability of Fe(TA)₂ nanoparticles enabled characterization by solution-state electrochemistry. Figure 4a shows cyclic voltammogram (CV) traces for several particle sizes using standard 3-electrode cell configurations. These four smallest-sized particles were stable in 0.1-M TBAPF₆ / DMF electrolyte mixtures under applied bias, while attempts to analyze 48-nm particles failed, likely due to aggregation, as the particles precipitated from the stored electrolyte solution over the course of a few days. Although we expected only a single redox event corresponding to Fe^{2+/3+} oxidation, all samples exhibited qualitatively similar traces with three quasi-reversible Faradic waves appearing at similar applied potentials. Cyclic voltammetry of the 1,2,3-triazole linker in 0.1-M TBAPF₆ / DMF reveals a chemically irreversible event at 0.31 V vs Fc^{0/+} (Fig. S18), supporting the assignment of the three redox waves to Fe^{2+/3+}. The 16-nm colloidal suspension was further investigated due to the well-defined features of its CV trace. As summarized in Figure 4d, variable scan rate measurements showed a strong dependence of the peak-to-peak separation ΔE for the lowest-potential redox event at around -0.61 V (blue closed triangles), ranging from 9.2 mV at 100 mV/s to 56 mV at 130 mV/s, while the second event, centered at -0.29 V (blue open circles), showed less reversibility, with ΔE of 126 mV at 100 mV/s to 144 mV at 130

mV/s (Fig. 4d), while ΔE for the highest-potential feature, centered around 0.13 V, could not be resolved. These data stand in stark contrast to two prior reports of bulk $\text{Fe}(\text{TA})_2$ cyclic voltammetry. In one study, scanning the material in an air-free environment in LiBF_4 / propylene carbonate showed a single redox feature at high potential, assigned to $\text{Fe}^{2+/3+}$.¹⁴ In the other report, the material was synthesized in aerobic

Figure 4: Cyclic voltammetry of $\text{Fe}(\text{TA})_2$ nanoparticles analyzed as colloids or thin films. Initial scan directions are indicated by arrows. a) CV traces collected at a 130 mV/s scan rate for four particle sizes prepared as colloids in 0.1-M TBAPF_6 / DMF; current density is normalized to the second faradaic event. Scan rate dependence of 16-nm particles drop-casted onto glassy carbon in 0.1-M TBAPF_6 / MeCN (b) and TBABF_4 / MeCN (c). Light to dark greyscale traces correspond to 10 mV/s – 500 mV/s. Relevant peaks are marked with filled triangles (first peak analyzed) or open circles (second peak analyzed) in all panels. d) Peak-to-peak separation with respect to scan rate. e) Peak current with respect to scan rate for two reduction peaks in each of the 16 nm particle CVs. Dashed lines correspond to linear fits. CV traces collected at 100 mV/s with a Pt QCM electrode for 16-nm particles in TBAPF_6 / MeCN (f) and TBABF_4 . (g) Colored open circles refer to the right axis, moles of anions with respect to moles FeTA_2 on the QCMs.

conditions and scanned in 0.1-M KOH, showing several redox events assigned to varying Fe surface species.⁴¹ Here, we assign all redox events to $\text{Fe}^{2+/3+}$ even though the redox couples span more than one volt. We envision several possible causes for such an unusual difference in the potentials. For example, similar behavior has been observed in redox-active iron clusters that display intramolecular electronic cooperativity such that redox chemistry of one site influences the subsequent redox potential of neighboring sites despite similar chemical environments.⁴² Another possible origin of the three redox events is that they correspond to Fe species at the surface, sub-surface, and interior, where deeper species require higher potentials due to their inaccessibility by charge-balancing counterions.

To investigate the origin of these redox events and to demonstrate that the solution processability of colloidal $\text{Fe}(\text{TA})_2$ nanoparticles will facilitate their use in MOF-based electrochemical devices, 16-nm $\text{Fe}(\text{TA})_2$ were drop-casted onto the surface of glassy carbon electrodes. Figure 4b shows the variable-scan rate CVs of the particle films in 0.1 M TBAPF_6 / MeCN. Despite the difference in solvent, which was chosen to discourage particle delamination, the CV traces resemble those of the free-standing colloids in Figure 4a. Due to the small pore size of $\text{Fe}(\text{TA})_2$, we hypothesized that the broad redox waves observed with TBAPF_6 reflect the hindered ability of the bulky PF_6^- anion to diffuse through the material. Therefore, these experiments were repeated on particle films using TBABF_4 , as shown in Figure 4c, producing markedly different traces. In contrast to voltammetry with TBAPF_6 , the use of TBABF_4 causes all peaks to sharpen and induces new redox events, most notably a sharp, reversible feature at 1.2 V (Fig. 4c). For direct quantitative comparison, we investigated two well-defined redox events from each set of electrolyte experiments, as indicated by open circles and shaded triangles throughout Fig 4. Figure 4d shows that in both electrolyte media, ΔE is always smaller for the lower-potential event, supporting the assignment of this peak to a surface species which benefits from both better ion-pairing and faster kinetics of ion diffusion. Additionally, the second event (green circles) for a film in TBAPF_6 shows the largest ΔE among all conditions, including the colloidal suspension in TBAPF_6 / DMF (blue circles). Interestingly, as shown in Figure 4e, the peak current for the events in all experiments exhibit a linear dependence with respect to scan

rate. Therefore, even if the particles are employed as colloids, the redox events are adsorption-controlled.⁴³ To precisely quantify the role of ions in the redox chemistry of Fe(TA)₂ particles, we employed quartz crystal microbalance (QCM) electrodes. Spin-coating 16-nm particles onto the QCMs yielded uniform multi-layer nanoparticle films (Fig. S22), which allowed us to measure their voltammetric responses and simultaneous mass changes in either TBAPF₆ or TBABF₄ environments. The frequency of the quartz crystal oscillation is sensitive to mass changes at the crystal surface, allowing monitoring of film loading and ion flux while the potential is scanned. Figures 4f and 4g show both the CV traces and the number of moles of anion adsorbed to the particles based on the mass change of the QCM electrode, using the Sauerbrey equation⁴³ and assuming that all mass change is due to unsolvated PF₆⁻ and BF₄⁻ anions. Once again, the redox waves of the sample analyzed with TBAPF₆ exhibits broad features in comparison to the same size nanoparticles in TBABF₄ (Fig 4, Fig S21). Additionally, substantially more current passes to the particles in the presence of TBABF₄. Charge integration shows nearly seven-fold enhancement, with stoichiometric oxidation of nearly all Fe sites, *i.e.*, $e^-:\text{Fe} = \sim 0.9$ when using TBABF₄, whereas TBAPF₆ yields only $e^-:\text{Fe} = \sim 0.3$. This comparison suggests that more Fe sites are electrochemically accessible in the TBABF₄ experiment, which we attribute mainly to the ability of the smaller anions to diffuse through the porous MOF particles. A further contribution may be differences in thin thickness and morphology, although films were homogenous for both cases (Fig S22, Table S6). The mass of the particle films increases in both experiments with oxidizing potentials, as expected for incorporation of charge-balancing anions, but far more anions incorporate when using the smaller BF₄⁻ ions. Approximately four times as many moles of BF₄⁻ adsorb compared to PF₆⁻, yielding PF₆:Fe = 0.1 and BF₄:Fe = 0.4 (Table S6). We expect that surface ions provide additional charge-balancing anions needed for stoichiometric oxidation of all Fe sites. Comparing mass changes to redox waves at a given potential provides deeper insight into the nature of the redox chemistry. Most notably, the coincidence of a sharp increase in mass and current at ~ 1.2 V strongly suggest this redox event corresponds to ion-coupled charge transport to interior Fe sites enabled by the smaller size of the BF₄⁻ anion in comparison to the gradual mass changes and broad redox waves of the TBAPF₆ experiments. Although ion intercalation and ion pairing are frequently invoked to understand MOF

redox chemistry, charge storage and sensing, these data represent some of the only direct measurements of ion intercalation processes by employing quartz crystal microbalance electrodes.^{45,46} They also show that nanosizing MOFs can improve the availability of redox-active sites, thus lowering redox potentials through improved ion pairing, a key insight into designing electronic MOF devices.

Figure 5: Charge transport measurements of $\text{Fe}(\text{TA})_2$ nanoparticle thin films. a) Photographs and optical microscope image of a thin film prepared by doctor-blading 84-nm nanoparticles. b) I-V curves and the corresponding four-contact DC conductivity values of four FeTA_2 thin films. d) FIB-SEM image of a cross-section of the 84 nm particle film.

Thin film fabrication and solid-state measurements are enabled by the long-term colloidal stability and solution-processability of $\text{Fe}(\text{TA})_2$ nanoparticles. Doctor blading high-concentration suspensions onto glass slides afforded uniform films with smooth surfaces, as shown in the optical microscope image of Figure 5a and the cross-sectional FIB-SEM image in Figure 5c. Additional SEM images and photos of particle films can be found in the SI (Fig. S23, S24). The dark brown color occurs due to oxidation of Fe^{2+}

in air, whereas the particle suspensions are tan (Fig. 5a, S23). Figure 5b shows I - V curves of thin films for the two largest particle sizes, 130 nm and 84 nm, giving DC conductivities of 48 $\mu\text{S}/\text{cm}$ and 150 $\mu\text{S}/\text{cm}$, respectively. For comparison, the conductivity of bulk $\text{Fe}(\text{TA})_2$ thin films were determined to be 11 $\mu\text{S}/\text{cm}$, in good agreement with the first reported value of 77 $\mu\text{S}/\text{cm}$, which was also handled in air.¹¹ Subsequent studies of bulk $\text{Fe}(\text{TA})_2$ reported values of 1×10^{-10} S/cm for a sample kept air-free, and therefore lacking $\text{Fe}^{2+/3+}$ mixed-valency, and 0.31 S/cm when the material was chemically oxidized to contain 33% Fe^{3+} . These measurements suggest a size-dependence in the charge transport behavior of $\text{Fe}(\text{TA})_2$, with the lowest conductivities observed in the bulk and the highest for the 84 nm particles. Although this effect is unexpected because smaller particles should introduce more grain boundaries and therefore electron scattering, cross-sectional SEM images of the films made from the bulk material display far more interparticle void space in comparison to the densely packed nanoparticle films (Fig. S24). Another possibility for the increase in conductivity is that the smaller particles contain more Fe^{3+} centers as a result of a higher surface-area to volume ratio, allowing for more iron centers to oxidize in air. A greater degree of mixed valency in the material would facilitate charge hopping and increase bulk conductivity, as has been previously reported for the chemical oxidation of the bulk MOF.¹⁴ Finally, as a proof-of-concept for future MOF-based electrochemical devices, composite films were easily prepared by adding 5% w/w of each carbon black and polyvinylidene fluoride (PVDF) as a binder, yielding smooth and homogenous materials (cross-sectional SEM images in Fig. S24) with improved conductivities of 630 $\mu\text{S}/\text{cm}$. Further investigations are ongoing into the charge transport mechanisms of $\text{Fe}(\text{TA})_2$ nanoparticles, including the dependence on size, redox-state, and guest-host interactions for technologies ranging from charge storage to electrochemical sensing and separation.

Conclusions

In summary, conductive $\text{Fe}(\text{TA})_2$ nanoparticles can be prepared reproducibly with excellent colloidal stability. The solution processability of this unprecedented class of semiconductor nanocrystals enables solution-state spectroscopy and electrochemistry, whereas MOF characterization typically requires

solid-state techniques. These measurements enable the first analysis of MOF extinction coefficients, which scale with particle size. Fe(TA)₂ particles can be probed by colloidal and thin-film voltammetry; results show redox chemistry sensitive to ion pairing and intercalation effects within the porous materials. Finally, we showed that the particles can be easily processed into thin films for charge transport measurements that reveal increased conductivity compared to the bulk material.

Experimental Methods

PXRD measurements and analysis. PXRD data was collected in air in the range 3.5 – 35° 2θ with a Bruker D2 Phaser. Patterns were matched to the low spin Fe(TA)₂ cif file.¹⁵ Gaussian fitting was performed using the Multipeak 2.0 package in Igor 6.3. Scherrer analysis was performed to determine crystallite size, with K = 1.

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

In the Scherrer equation above, τ is the crystallite size, K is the shape factor, λ is the source X-ray wavelength (Cu K α , 0.154 nm), β is the full width at half max in radians, and θ is the half of the peak position in radians. A shape factor (K) of 1 is used, as the particles change shape as size decreases, from octahedral to nearly spherical shapes.

Synthesis of Fe(TA)₂ nanoparticles. Controlling the size of iron triazolate nanoparticles was achieved by changing the amount of 1-methylimidazole added to the synthesis. In a N₂ glovebox, 1-methylimidazole was added to a solution of anhydrous iron (II) chloride in DMF (0.805 mmol, 0.0575 M, 14 mL). The amount of 1-methylimidazole varied from 3.5 μ L (0.044 mmol, 0.055 eq) to 700 μ L (8.78 mmol, 10.9 eq); all equivalents are with respect to iron (II) chloride. Syntheses performed with 5-bromo-1-methylimidazole and 1-benzyl-2-methylimidazole were also performed with these equivalents. Initial exploratory synthesis, conducted with 1-methylimidazole, n-butylamine, and sodium formate were performed with 1 equivalent (1.15 mmol). Under stirring, 1,2,3-triazole (2.42 mmol, 140 μ L, 3 eq) was added to the reaction solution. Vials were capped and sealed with electrical tape, then placed in an

aluminum block pre-heated to 120 °C. The solutions stirred for 1.5 hours, after which time they were immediately centrifuged and washed twice with DMF.

UV-Vis experiments and calculations. All UV-Vis data were collected using custom-made air-free quartz cuvettes with a pathlength of 1 cm. Long-range scans (1350 – 265 nm, 1.0 nm resolution) were used for gaussian fitting, performed with the Multipeak Fitting 2.0 package in Igor 6.3. For Beer's Law experiments, measurements were collected only from 900 – 265 nm with 0.5 nm resolution. The particles were diluted until the maximum absorbance was less than 1, then further diluted four times. A linear relationship between absorbance and concentration, determined either in formula unit molarity or particle molarity, gave the extinction coefficient. Peak maxima reported in the main text were the absolute maximum of the trace determined without a gaussian fit; gaussian fit data is available in Fig S15. The extinction coefficient per particle trend was fitted to a cubic equation in Igor 6.3. The last data point, at 130 nm, was excluded to maintain a good fit. The y intercept was set to zero. For CT1, the pre-factor is 23810 and for CT2, the pre-factor is 26160. To determine the oscillator strength, the gaussian fits for CT1, CT2, and the shoulder of CT2 were used. The following relation gives the oscillator strength as a unitless quantity, where $\epsilon_{\max}$ is the extinction at the peak of the band, and $\nu_{1/2}$ is the full-width-at-half-maximum of the peak.

$$f = 4.61 \times 10^{-9} \epsilon_{\max} \nu_{1/2}$$

Preparation of Fe(TA)₂ nanoparticle thin films. The preparation of thin films was performed in aerobic ambient conditions. Substrates, either glass or Si wafers, were rinsed copiously with isopropyl alcohol and dried with pressurized nitrogen. Substrates were taped to glass slides with electrical tape (U-Line Listed E50292 590J) such that the edges of the tape created a barrier on either side, with a total exposed area of 1 inch square. A 200 μ L aliquot of a dispersion of particles was added to one side of the blade, and a razor blade was used to slowly wipe the particles across the glass. To create the composite film, 5% w/w suspensions were created of carbon black and PVDF in DMF. The suspensions were then added to a concentrated 83.9 nm particle suspension and the total volume was diluted to create an overall concentration

of 20 mg/mL. The bulk sample film was created by dispersing the bulk powder in DMF at a concentration of 20 mg/mL and sonicating for 10 min; the film was created directly after the sonication step. Samples were allowed to dry in ambient conditions.

Cyclic voltammetry experiments. For solution state experiments, cyclic voltammetry was collected in DMF with 0.1 M TBAPF₆ or TBABF₄ as the supporting electrolyte in a standard three electrode cell with a glassy carbon working electrode, a silver wire pseudo-reference electrode, and a platinum wire counter electrode. Electrodes were polished immediately before use. The blank CV scans showed no faradaic events within the electrochemical window scanned. Particles were added in aliquots until sufficient peaks appeared at 70 mV/s. The total concentration of particles in these experiments is not known and is estimated to be between 0.01 and 0.05 mg/mL. Data was collected within window of a few hours, as particles suspended in 0.1 M TBAPF₆ for several days were observed to aggregate significantly. Data was collected from -0.325 V to 1.325 V against Ag/Ag⁺, then ferrocene was added to act as a reference. Scans were collected at rates of 10, 40, 70, 100, and 130 mV/s. For experiments with FeTA₂ on the working electrode, experiments were conducted in ACN with either TBAPF₆ or TBABF₄ as the electrolyte. A standard three electrode cell was used, with the particle-coated glassy carbon (GC) was the working electrode, silver wire as a pseudo-reference electrode, and carbon cloth as a counter electrode. To prepare the working electrode, particles (0.709 eq 1-methylimidazole, 16 nm) were suspended in DMF at a concentration 7.7 mg/mL, then drop-casted (7 μ L) onto the polished GC surface. For the bulk material, it was necessary to dilute the dispersion to a concentration of 0.6975 mg/mL. The dispersion was allowed to dry under ambient conditions for a few hours, then placed under vacuum to dry completely. Scans were collected at rates of 10, 100, 300, and 500 mV/s. The bare GC electrode was replaced in the cell and a blank scan was collected to show that no significant particle delamination occurred. Finally, ferrocene was added as a reference and a scan was collected using the particle-coated electrode. Current density data is normalized to the area of the bare GC working electrode, as the particle dispersion runs off the edges of the electrode and as such the exact amount of material on the electrode is less than the amount drop-casted. For QCM experiments, the PT/Ti-coated 5 MHz AT-cut quartz crystal microbalance (QCM) working electrodes were first soaked in acidic piranha

solution for ~5 minutes, then rinsed copiously with 18.2 MΩ nanopure water, followed by isopropyl alcohol, and lastly dried under N₂ pressure. Suspensions of 16-nm particles in DMF were spin-coated onto the QCM electrodes until a minimum of 4 μg was obtained on the surface. An electrochemical cell was set up with 0.1-M TBAPF₆ or TBABF₄ in MeCN (80 mL), the QCM as the working electrode, glassy carbon as the counter electrode, and a bare silver wire as a pseudo-reference electrode. Frequency data was collected simultaneously with CV scans using a SRS QCM200 apparatus. The frequency was converted to mass using the Sauerbrey equation below, in which Δf is the experimental change in frequency, C_f is the sensitivity factor (56.6 Hz cm² μg⁻¹ for 5 MHz AT-cut crystals), and Δm is the change in mass.

$$\Delta f = -C_f * \Delta m$$

Once the mass change is obtained, the value is converted to moles of anions (PF₆⁻ or BF₄⁻); potential solvation of the anions was not taken into account. These values are then compared to the total number of moles of FeTA₂ deposited onto the microbalance. Additional analysis is included in Table S6.

Conductivity measurements. The conductivity of the thin films was determined using a four-point probe method in aerobic ambient conditions. The four probes (distance = 1 mm) were placed on the film close to the center of the 1-inch square surface. Two separate resistivity measurements were collected, with either forward or reverse bias. Film thickness was measured using FIB-SEM within a few millimeters of where the probes were set for conductivity measurements. To calculate the resistivity of the films, the following relation was used.

$$\rho = \frac{\pi t}{\ln(2)} \left(\frac{V}{I} \right) = 4.532t \frac{V}{I}$$

In the expression, V/I is the slope of the IV curve and t is the film thickness. Thin films were of sufficient length and thin enough such that further geometric corrections were not needed.¹

Dynamic Light Scattering (DLS) experiments. DLS data was collected using a Wyatt Mobius instrument with a custom-made airfree quartz cuvette with a pathlength of 1 mm. Samples suspended in DMF were filtered through 0.45-μm PTFE filters, and the solvent itself was prepared by filtration through a 0.10-μm PTFE filter. A normal 50-mW laser mode was used, and the samples were diluted such that the

measured counts were between 1 and 8 million, and the correlation function was reproducible over the course of 6 measurements 1 minute apart.

N₂ sorption measurements. For gas sorption measurements, the samples were further washed with MeCN twice, and DCM five times. A typical washing process proceeded over the course of 1 week. Samples were dried under vacuum in tared ASAP tubes. Samples were degassed under high vacuum and 120 °C heat on an ASAP 2020 instrument; degassing was considered complete when the pressure in the closed manifold rose less than 2.5 μ torr/min. BET analysis was based on a linear fit in the BET plot to N₂ isotherm data at relative pressures between $10^{-5} - 10^{-1}$ P/P₀. Data for these experiments can be found in Figure S8.

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