Lowering Band Gap of an Electroactive Metal–Organic Framework via Complementary Guest Intercalation

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Supporting Information

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ABSTRACT: A new honeycomb-shaped electroactive metalorganic framework (MOF) has been constructed from an electron deficient naphthalenediimide (NDI) ligand equipped with two terminal salicylic acid groups. π -Intercalation of electron-rich planar tetrathiafulvalene (TTF) guests between the NDI ligands stacked along the walls lowers the electronic band gap of the material by ca. 1 eV. An improved electron delocalization through the guest-mediated π -donor/acceptor stacks is attributed to the diminished band gap of the doped material, which forecasts an improved electrical conductivity.



Letter

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KEYWORDS: metal-organic frameworks, naphthalene diimides, π -donor/acceptor interaction, band gap, conductivity

wing to their vital roles and widespread applications in advanced electronic devices, low-band-gap semiconductors having tunable electrical conductivity have become one of the most coveted materials. Although crystalline inorganic semiconductors and conjugated organic polymers dominate the landscapes of modern electronics industry, high production costs of the former and structural disorder and flexibility of the latter underscore the need of new high-performance materials that are easier to prepare and process. Self-assembled under solvothermal conditions from metal ions and organic ligands, metal-organic frameworks (MOFs)¹ possess highly ordered repetitive structures that could, in principle, support long-range charge movement if the required conditions were met. However, because of their poor charge carrier density and charge mobility, low-band-gap semiconducting MOFs are extremely rare.²⁻⁷ Although the mere presence of redox-active building blocks introduce charge carriers and endow MOFs with electrochromic, photochromic, light-harvesting, lightemitting, and other stimuli-responsive behaviors,⁸⁻¹³ the lack of resonance across metal cluster nodes and large spatial gaps between ligand π -systems continue to impede both throughbond and through-space charge transport pathways. Among various MOF architectures, planar graphitic frameworks composed of mixed-valence metal ions and ligands display the highest charge mobility and conductivity;^{5,14,15} however, there is a growing interest for transforming 3D porous MOFs into low band gap semiconductors. To this end, Allendorf et al.¹⁶ enhanced the conductivity of an insulating HKUST-1 framework by a million fold by cross-linking its unsaturated Cu₂ nodes with tetracyanoquinodimethane guests that activated

Cu–Cu electronic coupling, whereas Dincă¹⁷ and Wang¹⁸ constructed tetrathiafulvalene (TTF)-based columnar MOFs and an anthracene-based double-walled framework, respectively, which displayed respectable intrinsic conductivity owing to facile charge-delocalization through π -stacked ligands. It is worth noting that the node cross-linking strategy is safe to adopt only when the nodes are coordinatively unsaturated or else it poses a risk of guest-induced ligand displacement.¹⁹ On the other hand, adequate intrinsic conductivity of porous MOFs cannot be guaranteed in advance since a slightest (sub-Å) increase of interligand distance could plummet their conductivity by orders of magnitude.¹⁷

We recently conceived and demonstrated²⁰ that intercalation of complementary guest π -systems between electroactive ligands activate long-range charge delocalization through resulting π -stacks and thereby enhance the conductivity of doped material. We previously employed a pillared-paddlewheel MOF containing electron rich amine-tagged naphthalenediimide pillars to demonstrate this novel strategy, given that many MOF architectures are replete with parallel ligands and capable of forming guest-mediated π -stacks, we surmise that this strategy could be adopted broadly to transform them into low band gap semiconductors. Demonstrating the versatility of this strategy, herein, we report the construction of a new electroactive MOF-74 analog (Figure 1) based on an electron deficient NDI ligand and its band gap suppression via TTF

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Figure 1. Structure of a DSNDI-based MOF-74 architecture.

intercalation between the parallel NDI ligands stacked along the walls. Electron deficient NDI units are known to form π donor/acceptor charge transfer (CT) complexes with electron rich π -systems.^{21–24} CT complexes enjoy significantly lower energy gaps between frontier molecular orbitals than individual donors and acceptors due to facile electron delocalization. We exploited this phenomenon to lower the band gap of an electron deficient NDI-based MOF-74 architecture by infiltrating it with complementary TTF guests, which intercalated between the parallel NDI ligands forming extended π -donor/ acceptor stacks along the walls of hexagonal channels.

To construct an electroactive MOF-74 analog, we designed and synthesized a new NDI ligand equipped with two salicylic acid groups (DSNDI) by treating naphthalene dianhydride (NDA) with 4-aminosalicylic acid (Supporting Information).²⁵ The resulting DSNDI ligand is a regioisomer of a recently reported NDISA ligand derived from NDA and 5-aminosalicylic acid,⁸ in which the relative positions of -COOH and -OH groups are swapped. Although both ligands yielded MOF-74 architectures, unlike NDISA the topology of DSNDI ligand matches exactly with that of traditional MOF-74 ligands.²⁶ Solvothermal reaction of DSNDI and $Zn(NO_3)_2$. 6H₂O in a mixture of DMF, EtOH, and H₂O at 90 °C for 24 h yielded a yellow microcrystalline material (Figure 1). The activated material displayed powder X-ray diffraction (PXRD) pattern consistent with a MOF-74 topology having trigonal R3 space group. Le Bail structural refinement of PXRD data confirmed the phase purity of the material and revealed that its lattice parameters ($a = b \approx 53$ Å) were comparable to that of known MOF-74 analogs having similar dimensions.^{8,26} Due to the low intensities of high angle peaks in experimental PXRD data, the c-parameter (~6.7 Å) and precise atomic coordinates were determined from first-principles density functional theory (DFT) calculations (vide infra). The simulated diffraction pattern was in excellent agreement with the experimental data (Figure 2a), confirming a MOF-74 architecture. The framework contains large hexagonal channels with an average pore diameter of ~3.1 nm. The DSNDI ligands are stacked along the walls with interplanar distance of \sim 5 Å. The solid-state ¹³C NMR and FT-IR spectra (Figures S1 and S2) of the MOF are in excellent agreement with those of DSNDI ligand.

The N₂ sorption isotherms (77 K) of activated DSNDI-based MOF-74 show type IV sorption behavior (Figure S3), revealing a Brunauer–Emmett–Teller (BET) surface area of 2044 m^2/g and pore volume of 1.01 cm³/g. These values are comparable to other MOF-74 analogs having similar dimensions.^{8,26} The TTF-doped MOF-74 displayed a similar N₂ sorption profile (Figure S3), but diminished gas uptake, BET surface area (1698 m^2/g), and pore volume (0.85 cm³/g) due to the presence of TTF guests inside the MOF.



Figure 2. (a) PXRD profiles of activated DSNDI-based MOF-74: experimental (circles), Le Bail fitted (red line), and the difference between observed and simulated data (black line). The vertical bars indicate the calculated positions of Bragg peaks. Goodness of fit: $R_p = 0.0453$, $R_{wp} = 0.0595$. Inset: Comparison of experimental and simulated PXRD patterns of the activated MOF. (b) UV–vis–NIR spectra of DSNDI ligand (black), TTF guest (green), DSNDI-based MOF-74 (blue), and TTF-doped DSNDI-based MOF-74 (red).

Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) revealed that (Figure S4) both undoped and TTF-doped MOF-74 are thermally stable. According to DSC analysis, the former did not undergo any phase transition until 380 °C, while the latter remained unaffected until 420 °C, after which they underwent significant weight loss and phase changes.

Having confirmed the mesoporous structure of the DSNDIbased MOF-74, we turned our attention to determine its electronic property and how that is influenced by infiltration of electron rich TTF guests using UV–vis–NIR spectroscopy, electrochemical analysis, and computational studies. Although electrochromism of an NDISA-based MOF-74 has recently been reported,⁸ to our knowledge, these studies represent the first demonstration of band gap manipulation of a framework via complementary guest intercalation. The onset of the longest wavelength absorption peak of DSNDI ligand is at ~500 nm (Figure 2b), which corresponds to an optical band gap of ~2.5 eV. DSNDI undergoes a fully reversible electrochemical reduction at $E_{\text{Red}} = -450$ mV (vs Ag/AgCl, in 0.1 M Bu₄NPF₆/DMF, Figure S5), revealing its electron accepting nature. The LUMO of DSNDI (-3.9 eV) and the HOMO of TTF (-4.8 eV based on $E_{\rm Ox}$ = +460 mV vs Ag/AgCl, in 0.1 M Bu₄NPF₆/DMF) are such that they can engage in π -donor/ acceptor charge transfer interaction.

The UV-vis-NIR absorption characteristic and optical band gap of yellow DSNDI-based MOF-74 were determined from diffuse reflectance spectra.^{27,28} The UV-vis absorption of MOF-74 ($\lambda_{max} = 410$ nm) stems from DSNDI ligands. From the onset of this signal at 600 nm, the optical band gap of the MOF-74 was calculated to be 2.1 eV, which is slightly lower than that of free DSNDI ligand. After being soaked in a TTF solution for 2 days, the MOF-74 turned brownish and its UVvis-NIR spectrum (Figure 2b) revealed a new CT band centered at 900 nm. From the onset point of the new CT band (1250 nm), the optical band gap of TTF-doped MOF-74 was estimated to be \sim 1 eV, which was 1.1 eV lower than that of the parent material. Such a dramatic drop in optical band gap was attributed to intercalation of electron rich TTF guests between electron deficient DSNDI ligands leading to the formation of π donor/acceptor stacks.

Further evidence of electronic communication between TTF guests and DSNDI ligands in MOF-74 came from electron paramagnetic resonance (EPR) spectroscopy. While the pristine MOF-74 was EPR silent, the TTF-doped MOF-74 became EPR active indicating partial charge-transfer from TTF to DSNDI (Figure S6). The splitting pattern of EPR spectrum indicated coexistence of both TTF radical cations and DSNDI radical anions.²⁹ Such electronic interaction requires close proximity and adequate orbital overlap of donor and acceptor units, which was enabled by the intercalation of TTF guests between the DSNDI ligands leading to formation of π -donor/acceptor stacks. The TTF molecules located in the channels but not intercalated are unlikely to engage in CT interaction due to lack of orbital overlap with DSNDI ligands.

In addition to compelling spectroscopic evidence showing CT interactions between TTF guests and DSNDI ligands, energy-dispersive X-ray spectroscopy (Figure S7) and elemental analysis (Table S1) also confirmed the presence of TTF in the doped MOF-74, as sulfur was found in the doped material but not in the pristine MOF.

To gain further insights into (i) where the TTF guests are located within the MOF, (ii) how they interact with DSNDI ligands, and (iii) how these interactions influence the electronic band structure, especially the valence and conduction bands of the material, we turned to computational studies.³⁰⁻³³ DFT calculations were performed on primitive cells of MOF crystals with periodic boundary conditions, using Quantum Espresso package to ensure that the results correspond to 3D crystal structures, not just isolated unit cells. We applied normconserving pseudopotentials with Perdew-Burke-Ernzerhof (PBE) exchange correlation.³⁴ A cutoff energy of 544 eV and kpoint grid of $4 \times 4 \times 4$ generated by Monkhosrt-Pack scheme were found to be enough for the total energy to converge within 0.01 meV/atom. We started from MOF geometry relaxations. Once the MOF structure was fully optimized with respect to atomic coordinates and lattice parameters, its electronic band structures were determined from single-point calculations. Since DFT/PBE calculations typically underestimate fundamental band gaps of MOFs, we further performed single-point calculations on DFT/PBE-optimized structures using hybrid HSE06 functionals,³⁵ which are known to predict band gaps more accurately.³² To identify the benefits of having electron deficient DSNDI ligands in a MOF-74

architecture, we compared its estimated electronic band gap with that of an IRMOF-74-IV analog²⁶ composed of a tetraphenyl ligand having two terminal salicylate groups, which matches in length with DSNDI but is not electroactive.

The fundamental band gaps of our DSNDI-based MOF-74 and IRMOF-74-IV²⁶ estimated by HSE06 (PBE) calculations are 2.5 (1.6) and 3.7 (2.9) eV, respectively, indicating that the presence of DSNDI ligands stacked along the walls indeed led to much lower band gap (\sim 1.2 eV). As expected, the PBEpredicated band gaps were consistently smaller than those predicted by HSE06 method. But more importantly, the trend was the same according to both methods, i.e., the framework made of electroactive DSNDI ligand always displayed lower band gap. A similar trend was observed previously for an in silico generated MOF-74 architecture containing electron-rich thiophene ligands.³² The density of states diagram of DSNDIbased MOF-74 (Figure 3a) reveals that its total valence and



Figure 3. Simulated structures (left) and the corresponding band structures (right) of DSNDI-based MOF-74 (a) in the absence and (b) in the presence of guest TTF molecules intercalated between DSNDI cores. Upon TTF intercalation the band gap of the MOF drops from 2.5 to 1.5 eV. The total and partial density of states (DoS) with relative contributions from different atoms are color-coded and listed in insets.

conduction band wave functions are composed of C, O, and N p-orbitals of DSNDI ligand and have no contribution from Zn(II), indicating that there is no metal–ligand electronic coupling with the d^{10} Zn(II) ions. The conduction band of DSNDI-based MOF is located near the Fermi level, revealing its n-type semiconductor nature caused by electron deficient DSNDI ligands. This behavior is opposite to an electron rich thiophene-based MOF-74, which was predicted to behave like a p-type semiconductor.³²

The DFT calculations also provided critical insights into favored locations of TTF guests inside the DSNDI-based MOF-74. Although the estimated interplanar distance between the neighboring NDI planes in activated MOF-74 is \sim 5 Å, the dihedral angles between central NDI plane and terminal salicylate groups are flexible enough to allow the gaps to widen further to accommodate planar TTF guests between DSNDI ligands. At the outset of structure optimization of TTF-doped MOF-74, the TTF molecules were placed in a way that only

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half of each molecule was inserted between two successive DSNDI ligands. During the optimization process the MOF structure relaxed slightly, twisting the DSNDI ligands such that the core NDI planes became more parallel to crystallographic a-b plane. As a result, the interplanar distance between the ligands expanded to ~6.4 Å, allowing TTF molecules to become fully inserted between DSNDI ligands and form TTF/ NDI stacks along the walls. In the fully optimized structure, the TTF center of mass is located very close to the central axis of NDI stacks, an arrangement that provides maximum orbital overlap and π -donor/acceptor electronic (CT) interactions. The PXRD profile of the TTF-doped MOF-74 matched well with that of the undoped MOF (Figure S8), revealing that the structure of the material remained intact after TTF infiltration. However, the diffraction patterns were dominated by large lattice parameter *a*, and the lack of strong peaks at large angles corresponding to *c* parameter made it difficult to experimentally demonstrate lattice expansion along the c-axis upon TTF intercalation.

The HSE06 (PBE) estimated band gap of the optimized TTF-doped MOF-74 structure is 1.5 (0.9) eV, almost 1 eV lower than that of undoped material estimated by respective methods. The density of states diagram shows (Figure 3b) that the valence and conduction bands of TTF-doped MOF-74 are composed of *p*-orbitals of DSNDI ligands (C and O) as well as of TTF guests (C and S), indicating a significant orbital overlap between them. While the conduction band of TTF-doped MOF remained near the Fermi level, its valence band energy rose significantly, shrinking the band gap and suggesting that the electrons injected by TTF guests and facile charge delocalization through donor/acceptor stacks contributed to this desired phenomenon. While we recognize that DFT calculations usually underestimate fundamental band gaps, gratifyingly, the calculated electronic band gap values for our undoped and TTF-doped materials showed good agreement with the respective optical band gaps and followed the same trend.

It is worth noting that previously an in silico generated MOF-74 analog containing electron-rich thiophene ligands was predicted to host spherical fullerene guests inside the hexagonal channels and undergo ligand-to-guest photoinduced electron transfer,³² whereas our DSNDI-based MOF-74 preferentially accommodates electron-rich planar TTF molecules between the π -acidic NDI planes forming TTF/NDI stacks along the walls. The latter fosters efficient orbital overlap and long-range charge dispersion leading to significant band gap reduction. Furthermore, although electrochromic behavior of another NDI-based MOF-74 has been reported recently,⁸ the foregoing experimental and computational results revealed for the first time how the intercalation of complementary guest π -systems affected the band gaps of the material. Not only do these MOFs differ in terms of their composition, electronic properties, guest recognition, and stimuli-responsive behaviors, but also exhibit diverse functions and applications that could catapult them as cornerstones of future electronic and photonic devices.

In summary, we constructed a new MOF-74 architecture using an electron-deficient DSNDI ligand, and demonstrated through experimental and computational studies that intercalation of electron rich TTF guests between the NDI ligands dramatically suppressed its electronic band gap, making it a far better n-type semiconductor than the parent material. In principle, this concept can be extended to virtually any MOF architectures that furnish parallel electroactive ligands at regular intervals and are capable of forming guest-mediated π -donor/ acceptor stacks. Studies are underway in our laboratory to build upon this concept and develop new light-harvesting, photo-conducting, and semiconducting MOFs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07292.

Experimental details, synthesis of ligand and MOF, crystallographic data (PXRD and CIFs), ss-NMR, FT-IR, BET, EPR, TGA, DSC, EDX, CV data (PDF) Crystallographic information file for NDI MOF-74 (CIF) Crystallographic information file for TTF-doped NDI MOF-74 (CIF) Crystallographic information file for activated NDI MOF-74 (CIF)

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

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Experimental Procedures

General Materials and Methods

All chemicals, including $Zn(NO_3)_2.6H_2O$, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), 4aminosalicylic acid, solvents (DMF, EtOH, MeOH, DMSO- d_6), and electrolytes (Bu₄NPF₆) were purchased from Sigma-Aldrich, Acros Organic, TCI America, EMD Chemicals, and Cambridge Isotope Laboratory, and used as obtained.

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. The solidstate NMR of the MOF was recorded on a Bruker AVIII HD NMR spectrometer operating at a magnetic field strength of 11.74 T, equipped with a 4 mm Bruker Magic Angle Spinning probe.

The mass spectra (MS) were recorded with a Bruker Autoflex-II MALDI-TOF instrument.

Elemental analysis was conducted on a PerkinElmer 240 CHN analyzer.

Powder X-ray diffraction (PXRD) analysis was conducted on MOF samples placed in glass capillaries using a Rigaku X-ray diffractometer with Cu K α source.

The UV/Vis/NIR spectra of the ligand, MOF, and guests and were recorded with a Perkin Elmer Lambda-900 and a Shimadzu UV-2600 spectrophotometers equipped with integrated spheres for diffuse reflectance measurements (200–1400 nm range). The UV-Vis-NIR spectra of MOF-74 in the absence and presence of TTF guests were obtained from diffuse reflectance spectrum. The optical band gaps of the materials were determined from the onset of their longest wavelength absorption bands using following equation: $E_g = 1240 / \lambda eV$.^{S1,S2}

The FT-IR spectra were collected on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

The electrochemical measurements were conducted on a Princeton Applied Research Versa-Stat 3-450 instrument using Ag/AgCl reference electrode, Pt counter electrode, and Pt or glassy-carbon disc working electrode in electrochemical cells procured from BASi.

The gas adsorption isotherms and surface area of the MOF were measured with a Micromeritics ASAP 2020 surface area analyzer using N₂ and CO₂ gases (Airgas, ultra-high purity grade). A MeOH-exchanged MOF powder was activated under high vacuum initially at room temperature and then by heating at 100 °C for 24 h until the outgas rate was <5 μ mHg/min prior to measurements. An activated MOF sample (40 mg) was used for N₂ sorption measurement, and was maintained at 77 K with liquid N₂.

Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were conducted under a N₂ atmosphere using a TA Instrument SDT Q600 instrument.

Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) and elemental (CHNS) analysis used to determine the chemical compositions of DSNDI-based NDI-74 before and after doping with TTF. The EDX spectra of materials were recorded on a Hitachi Variable Pressure SEM S3400 instrument and elemental analysis was conducted by Atlantic Microlab Inc.

[Disclaimer: Certain commercial equipment, instruments, techniques, and materials identified in this paper are to foster understanding. Such identifications do not imply recommendation or endorsement by the National Institute of Standards and Technology, nor that they are the best available for the purpose.]

Preparation of DSNI ligand, the corresponding MOF-74, and TTF-doped MOF-74

DSNDI Ligand. Following a literature protocol,^{S3} a mixture of NDA (2.68 g, 10 mmol), 4-aminosalicylic acid (4.6 g, 30 mmol), and Me₃SiCl (6.4 mL, 50 mmol) in DMF (12 mL) was heated under reflux (150 °C) for 14 h. After allowing the mixture to cool to room temperature, the solid precipitate was filtered and washed first with EtOAc, then with an aqueous NaOH solution (1 M), and finally with H₂O and MeOH to obtain a yellow solid (0.27 g, yield = 5 %). ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C): δ = 8.72 (s, 4H), δ = 7.88–7.86 (d, 2H), δ = 6.94 (s, 2H), δ = 6.85–6.83.06 (m, 2H) ppm. ¹³C NMR (175 MHz, DMSO-*d*₆, 25 °C): δ = 174.97, 172.46, 164.32, 161.86, 141.02, 130.54, 126.65, 125.12, 122.20, 118.30, 113.02 ppm. IR (cm⁻¹): 3547 (m), 3479 (m), 3078 (m), 1712 (s), 1667 (s), 1445 (m), 1348 (m), 1244 (s), 1200 (s), 979 (m), 776 (s). MALDI-TOF-MS: *m/z*: [M]⁻_{observed} = 537.59, [M]⁻_{calcd} = 538.42.

DSNDI-based MOF-74. A 20 mL sealed scintillation vial containing $Zn(NO_3)_2 \cdot 6H_2O$ (21 mg, 0.07 mmol) and DSNDI ligand (17 mg, 0.03 mmol) in a DMF/EtOH/H₂O (3 : 0.5 : 0.5 mL) solvent mixture was sonicated for 5 min. The reaction mixture was then heated at constant 90 °C for 24 h. Within an hour, the reaction mixture became transparent as all the precursors dissolved completely, and after overnight heating bright yellow colored microcrystalline powder deposited on the vial floor. After allowing the reaction mixture to cool down gradually to room temperature, the solvent was decanted and the yellow solid was soaked in fresh DMF (10 mL) for 5 h. The solvent was then decanted and the process was repeated three times a day for 3 days. This same washing protocol was repeated with MeOH to obtain a yellow microcrystalline solid with a washed interior. The solvent molecules trapped within the MOF were removed under dynamic vacuum initially at room temperature and then by heating at 80 °C for 24 h to obtain a yellowish orange powder (yield = 76 % based on DSNDI ligand). The guest free sample was analyzed by PXRD, FT-IR, and solid-state ¹³C NMR spectroscopies, and its surface area was determined by N₂ sorption experiments.

TTF-doped MOF-74. To infiltrate DSNDI-based MOF-74 with TTF, 15 mg of activated sample was immersed in a TTF / MeOH solution (20 mM, 3 mL) and kept in the dark for 2 days. After decanting the solvent, the solid was washed with MeOH to remove excess TTF molecules that were not entrapped inside the MOF and dried under vacuum for 16 h.

Density Functional Theory Calculations for Structure Simulation and Band Gap Estimation.

To simulate the structure of DSNDI-based MOF-74 analog, a known IRMOF-74-IV^{S4} was used as starting point and the ligand was replaced with DSNDI while preserving the space group symmetry. Solvent molecules were excluded for structure simulation. The simulated data are consistent with typical R3 crystal symmetry of MOF-74 architectures. A Le Bail structural refinement was performed to confirm the phase purity and to derive lattice parameters. The refined lattice constants of our material are in good agreement with that of IRMOF-74-IV. Due to the large dimension of DSNDI-based MOF-74 unit cell, the precise atomic positions were calculated from first-principles DFT calculations. The final structural model and corresponding simulated diffraction pattern matches quite nicely with experimental PXRD pattern, attesting the accuracy of simulated structure.

In order to decipher how the electronic band structure of our MOF analog was dictated by the redoxactive DSNDI ligand and affected by TTF guests, we performed DFT calculations using the Quantum-Espresso package.^{S5} We used norm-conserving pseudopotential with Perdew-Burke-Ernzerhof (PBE) exchange correlation. A cutoff energy of 544 eV and a $4 \times 4 \times 4$ k-point mesh (generated by using the Monkhosrt-Pack scheme) were found to be enough for total energy to converge within 0.01 meV/atom. All calculations were done on the primitive cells of the MOF crystals with periodic boundary conditions. Therefore, the results correspond to 3D crystal structures, not just an isolated unit cell. The structures were first fully optimized with respect to atomic coordinates and lattice parameters. Then, electronic band structure analysis was carried out. Since DFT/PBE calculations are known to typically underestimate the band gaps, we further performed single-point calculations on the DFT/PBE-optimized structures using higher-level hybrid HSE06 functionals,^{S6} which are known to predict band gaps more accurately.^{S7} Due to the significant computational cost associated with the hybrid functionals, no further structural optimizations were performed on the MOF structures, and band gaps were directly obtained from the single-point calculations.

The crystal unit cell of our DSNDI-based MOF-74 is very large (a = b = 53 Å, c = 6.7 Å). Therefore, the electronic bands in both valence and conduction bands are quite flat with very small dispersion, which is common for porous materials. In such cases, the DOS plot provides an accurate estimate of the band gap, as shown in Figure 3. Upon TTF intercalation, the lattice parameter c is expected to increase. However, in the experimental PXRD diffraction patterns, all strong diffraction peaks at low angle ($2\theta < 13$ deg) are solely related to lattice parameter a. At high angle, the diffraction peaks are rather broad with quite small intensities. Therefore, lattice expansion along the c axis upon TTF intercalation could not be confirmed from experimental PXRD patterns, but it was found in the computational model. Furthermore, the CT band in UV-Vis-NIR spectrum strongly supports the intercalation of electron rich TTF guests between electron deficient DSNDI ligands of MOF-74.

Elements	Pristine Zn-NDI-74 Zn ₂ (C ₂₈ H ₁₀ N ₂ O ₁₀)(H ₂ O) ₅ (C ₃ H ₇ NO) _{1.5}		Pristine Zn-NDI-74TTF-doped Zn-NDI-74 $(C_{28}H_{10}N_2O_{10})(H_2O)_5(C_3H_7NO)_{1.5}$ $Zn_2(C_{28}H_{10}N_2O_{10})(H_2O)_5 \cdot (C_6H_4S_4)_{0.2}$	
	Calculated	Found	Calculated	Found
Zn	45.13	44.72	44.06	43.29
Н	3.55	3.40	2.63	2.82
Ν	5.67	6.00	3.52	3.69
S			3.22	3.40

Table S1. The elemental analysis data of DSNDI-based NDI-74 before and after TTF doping.



Figure S1. The solid-state ¹³C NMR spectra of DSNDI ligand (bottom) and DSNDIbased MOF-74 (top).



Figure S2. The FT-IR spectra of DSNDI ligand (black) and DSNDI-based MOF-74 (red).



Figure S3. The N_2 sorption isotherms of DSNDI-based MOF-74 before (black) and after (red) TTF infiltration.



Figure S4. The TGA (solid lines) and DSC (dotted lines) profiles of DSNDI-based MOF-74 before (black) and after (red) TTF infiltration.



Figure S5. The CV profiles of (A) DSNDI ligand's first reduction and (B) TTF guest's first oxidation processes (vs. Ag/AgCl, 1 mM in 0.1 M Bu_4NPF_6 / DMF).



Figure S6. Solid state EPR spectra of undoped (black) and TTF-doped MOF-74 (red). The latter shows the coexistence of TTF radical cations and DSNDI radical anions generated by partial charge transfer.



Figure S7. SEM-EDX data of undoped (top) and TTF-doped MOF-74 (bottom). The latter shows the presence of S of TTF.



Figure S8. The PXRD profiles of undoped (black) and TTF-doped MOF-74 (red).

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