COMMUNICATION
Sourav Saha et al.
Modulating the electrical conductivity of metal–organic framework films with intercalated guest \( \pi \)-systems
Modulating the electrical conductivity of metal–organic framework films with intercalated guest \(\pi\)-systems†

Zhiyong Guo,‡§ K. Panda,‡§ Krishnendu Maity,‡ David Lindsey,‡ T. Gannon Parker, a Thomas E. Albrecht-Schmitt, a Jorge L. Barreda-Esparza, b Peng Xiong, b Wei Zhou c and Sourav Saha*a

The access to electroactive metal–organic frameworks (MOFs) and the ability to manipulate their electrical properties with external stimuli are vital for the realization of MOF-based electronic and photonic devices. To this end, we have constructed a new blue colored pillared-paddlewheel (PPW) MOF, namely BMOF composed of redox-active \(N,N'\)-bis(4-pyridyl)-2,6-dipyrrolidyl naphthalenediimide (BPDPNDI) struts and \(1,2,4,5\)-tetrakis-(4-carboxyphenyl)benzene (TCPB) struts, and grown stable, uniform BMOF films on ZnO substrates via a bottom-up method for device integration and testing. The electrical conductivity (\(\sigma\)) of BMOF films is \(6 \times 10^{-5} \text{ S m}^{-1}\) (25 °C), which surges up to \(2.3 \times 10^{-3} \text{ S m}^{-1}\) upon infiltration of \(\pi\)-acidic methyl viologen (MV\(^{2+}\)) guests, but remains unaffected by large \(C_{60}\) molecules that are size excluded. These results demonstrate for the first time that the conductivity of MOFs can be fine-tuned by complementary guest \(\pi\)-systems that can promote long-range electron delocalization by forming extended \(\pi\)-stacks with the redox-active ligands.

Introduction

Owing to their innate ability to capture and concentrate guests selectively via size-exclusion, porous metal–organic frameworks\(^1\) have emerged as nanoscale containers that show great promise in a wide gamut of separation, storage, and delivery applications.\(^2\)\(^-\)\(^4\) The evolution of MOFs as electronic, photonic, and magnetic materials, however, has been sluggish, largely because of the dearth of sophisticated molecular recognition and signal transduction capabilities.\(^5\) Furnishing these hybrid materials with redox- and photoactive building blocks should not only enrich them with intrinsic electronic and optical properties, but also enable them to communicate with and respond to various stimuli, such as guest entities, applied electric and magnetic fields, and light. Signals stemming from these interactions could then propagate through the extended networks, emanating new properties and functions that are non-native to the molecular building blocks or the parent materials. Much of these possibilities, however, remain to be cultivated, but once realized, MOFs would turn into powerful sensors,\(^5\)\(^6\) semiconductors,\(^8\)\(^-\)\(^11\) and photonic materials\(^12\) that could be deployed in batteries, transistors, solar cells, and myriads of other molecular electronics devices.

Electrical conductivity has become one of the most sought after amenities in functional materials because of an increasing demand for energy efficient electronic devices. Although the ordered structures of MOFs bode well for long-range charge transport and electrical conductivity, suggesting that they could eventually rival conducting polymers that suffer from structural defects and disorder, in reality, electrically conducting MOFs\(^9\)\(^-\)\(^11\) are few and far between, since engineering and manipulating conductivity in porous MOFs remain a difficult task to pull off.

Chief among the reasons behind these limitations is the scarcity of redox-active ligands that deprive MOFs of effective

---

\(\sigma\) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA, E-mail: saha@chem.fsu.edu

‡ Department of Physics, Florida State University, Tallahassee, FL 32306, USA

§ NIST Center for Neutron Scattering, National Institute of Standard and Technology, Gaithersburg, MD 20899, USA

† Electronic supplementary information [ESI] available: Experimental details, characterization, crystallographic data. CCDC 1413970. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5tc02232k

‡ Z.G. and D.K.P. contributed equally.
charge carriers and the signal transduction capability. Furthermore, the large spatial distance between the MOF-bound ligands prevents through-space charge transport, while the adjoining metal clusters restrict resonance delocalization, conspiring together to suppress the conductivity in most porous MOFs. One way to overcome these challenges is to construct certain planar and columnar MOFs, in which the redox-active building blocks can support long-range charge delocalization either via resonance or through the π-stacked ligands. Another way to enhance the charge mobility in MOFs is to introduce appropriate guests that can either oxidize the built-in redox centers or crosslink the nodes. The success of both strategies notwithstanding, the former requires certain planar and columnar architectures that only a handful of ligands and metal clusters can afford, whereas the node crosslinking strategy requires coordinatively unsaturated nodes, otherwise poses the risk of disrupting their structures and compositions altogether due to guest-induced ligand displacement. Therefore, there exists a need for new strategies that would not only afford intrinsically (semi)conducting MOFs but also allow us to manipulate their conductivity with certain stimuli without disrupting their structures. The π-donor/acceptor interactions between the redox-active ligands and complementary guests leading to the formation of extended π-stacks offer such opportunity, but they have yet to be exploited to boost the conductivity of MOFs.

Furthermore, successful integration and operation of MOFs in devices require stable, uniform, and electrically controllable films. Most existing film growth protocols, however, are MOF specific, and do not necessarily afford suitable films for electrical measurements. For instance, the MOF films grown on self-assembled monolayers (SAMs) are hardly responsive to electrical fields, as the insulating SAMs impair electrical contact between MOFs and the underlying electrodes. Elegant electrochemical and photochemical deposition methods are emerging, but the question remains whether the redox- and photoactive ligands can withstand such invasive preparative conditions.

**Results and discussion**

Addressing each of these grand challenges, in this all-encompassing work, we have (i) synthesized a new electroactive PPW-MOF, namely BMOF, using TCPB struts and electron rich BPDPNDI pillars (Fig. 1a), (ii) grown stable BMOF films on ZnO-coated substrates in a bottom-up fashion under solvothermal conditions (Fig. 1b), and (iii) demonstrated for the first time that the electrical conductivity of BMOF films can be fine-tuned by introducing different π-acidic guests, such as MV, dinitrotoluene (DNT), and 1,5-difluoro-2,4-dinitrobenzene (DFDNB) that can intercalate between the BPDPNDI pillars and thereby promote electron delocalization through the resulting π-stacks (Fig. 1c).

Unlike unsubstituted NDIs, which are electron deficient colorless compounds, the core-substituted NDIs (cNDIs) possess tunable electronic, optical, and guest recognition properties that make them attractive building blocks of various functional materials. Although the unsubstituted NDI-based MOFs are not so uncomman anymore, the cNDI ligands have been rarely used in MOFs, and their guest-induced optical and electrical properties have yet to be explored systematically. Furthermore, bulky ligands are known to prevent catenation in PPW-MOFs. Taking these factors into account, we envisioned that the bulky BPDPNDI ligand adorned with two electron donating pyrrolidine pendants should not only endow BMOF with the desired optoelectronic properties, but also yield a noncatenated architecture that can accommodate fairly large electroactive guests inside its cavities. With this goal in mind, we synthesized the BPDPNDI ligand (Scheme S1, ESI†) by installing two pyrrolidine rings on the naphthalene core via an SNAr reaction, followed by introducing the pyridyl groups on the imide-N atoms via a Cu(n)-mediated coupling reaction.

The navy-blue colored BMOF [Zn2(TCPB)(BPDPNDI)] crystals were obtained from a reaction between Zn(NO3)2·6H2O (0.2 mmol), TCPB (0.1 mmol), and BPDPNDI (0.1 mmol) in DMF (10 mL) at 80 °C for 24 h (Fig. 2a). The structure of BMOF was first solved partially from single-crystal X-ray (XRD) data, and then optimized by density functional theory calculations to assign the atomic coordinates of the disordered pyrrolidine rings of BPDPNDI pillars. Overall, the noncatenated cubic architecture of BMOF (Fig. 2a) is composed of TCPB-linked Zn2 paddlewheel nodes located in the crystallographic ab-plane and bridged by the BPDPNDI pillars aligned along the c-axis, making it isostructural to a known PPW-MOF, [Zn2(DBTCPB)(DPNDI)] (DBTCPB = dibromo-TCPB). The distances between the Zn2-nodes—16, 11, and 19 Å along the a-, b-, and c-axes, respectively—are consistent with the lengths of the respective ligands. The powder diffraction pattern of bulk BMOF crystals conforms to its simulated PXRD profile (Fig. 2b).

The PXRD studies further reveal that (Fig. S1, ESI†) while the as-synthesized BMOF is highly crystalline, its crystallinity suffers upon solvent evacuation but returns to full glory upon reintroduction of DMF. Such reversibility indicates that despite the loss of crystallinity upon solvent loss, the structure and connectivity of the evacuated BMOF remain intact under ambient conditions.

The thermogravimetric analyses (Fig. S2, ESI†) show that BMOF loses 70% of its initial weight at 120 °C due to DMF loss before decomposing at a much higher temperature (375 °C).
The permanent porosity of BMOF is evident from its CO$_2$ adsorption capacity—65 cm$^3$ g$^{-1}$ at 273 K, 1 bar (Fig. S3, ESI†)—which is comparable to that of isostructural [Zn$_2$(DBTCPB)-(DPNDI)]. The porous structure of BMOF bodes well for guest encapsulation and the subsequent guest-induced conductivity changes (vide infra).

Having constructed electroactive BMOF, we turned our attention to prepare its films for device integration and testing. Unable to grow BMOF films on glass, FTO, and ITO surfaces, we introduced annealed ZnO-coated substrates envisioning that the covalent attachment of the tetracarboxylate struts onto the oxide surface should subsequently promote the formation of BMOF films. The ZnO films were prepared by spin-coating FTO and glass slides with a ZnO/EtOH suspension, followed by sintering them at 350 °C for 0.5 h (Fig. 3a). To construct four-probe electrical devices, four Au electrodes (~100 nm thick) were vapor-deposited 1 mm apart on the ZnO-coated glass slides using patterned masks (Fig. 3b). After initiating the nucleation of BMOF by heating DMF solutions of its precursors placed in screw-capped vials at 80 °C for 2 h, the ZnO-coated slides were immersed at upright positions and the entire setups were kept in a 80 °C oven for different durations. Within 1 h, only the ZnO coated areas became selectively covered with uniform BMOF films (Fig. 3b), which grew thicker with longer immersion time, while the rest of the slides including the Au-electrodes deposited on the ZnO layer remained completely BMOF-free. The BMOF films are stable in DMF, MeNO$_2$, MeCN, and toluene, as well as under ambient conditions. The PXRD profiles of the resulting blue films match nicely with that of the bulk BMOF powder (Fig. 2b), confirming that they are indeed composed of the surface-bound BMOF microcrystals.

The scanning electron microscopy (SEM) images show a uniform coverage of amorphous ZnO nanoparticles in bare ZnO films (Fig. 3c) and densely packed BMOF crystals covering the ZnO layer in BMOF/ZnO films (Fig. 3d). The cross-sectional (CS) SEM images (Fig. 3e) show that the annealed ZnO films are ca. 3 µm thick and the BMOF films grown on the ZnO films for 1 h are ca. 20 µm thick. These BMOF films are mechanically stable, and retain their crystalline morphology even after becoming dry and being doped with different guests (Fig. 3 and Fig. S4, ESI†).

The BMOF films display (Fig. S5, ESI†) strong visible absorption ($\lambda_{\text{max}} = 615$ nm) and redox properties ($E_{\text{ox}} = +920$ mV, $E_{\text{red}} = -850$ mV vs. Ag/AgCl) that resemble those of the BDNDI ligand ($\lambda_{\text{max}} = 610$ nm; $E_{\text{ox}} = +880$ mV, $E_{\text{red}} = -850$ mV vs. Ag/AgCl). The electrochemical studies of BMOF films grown on the ZnO-coated FTO electrodes suggest that, unlike insulating SAMs, the ZnO layer provides sufficient electrical contact between the BMOF film and the underlying FTO electrode.

Finally, the electrical conductivity of BMOF films before and after infiltration of different guest π-systems were determined from the current–voltage (I–V) profiles (Fig. 4a and Fig. S6, ESI†) of the corresponding BMOF/ZnO devices measured via four-probe method. Although single crystal electrical measurement was not possible on tiny BMOF crystals, the stable BMOF films grown on the ZnO-coated glass slides equipped with four Au-electrodes allowed us to determine how their conductivity changes upon infiltration of different guests. The four-probe measurements on BMOF films not only eliminated the contact resistance associated with the two-probe measurement but also circumvented the technical problems associated with using pellets in this comparative study. Since the BMOF (undoped and doped) and ZnO layers in BMOF/ZnO devices constitute two parallel connections between the Au electrodes, and the charges can flow proportionately through both layers depending on their respective conductivities, the actual resistance of the BMOF films ($R_{\text{component}}$) was first extracted from the net resistances of the devices ($R_{\text{Device}}$) by excluding the resistance of the bare ZnO films ($R_{\text{ZnO}}$) using eqn (1): $R_{\text{component}} = R_{\text{Device}}R_{\text{ZnO}}/(R_{\text{ZnO}} - R_{\text{Device}})$. Then, from the resistance of each component, and taking probe-spacing ($d$), film thickness ($t$), and the lengths of Au electrodes ($l$) into account, the electrical conductivity of the corresponding materials was calculated using eqn (2): $\sigma_{\text{component}} = d/l\cdot R_{\text{component}}$ (Tables S1 and S2, ESI†). The net resistances of the ZnO and BMOF/ZnO devices are thickness-dependent, indicating that the charges actually move through the entire BMOF and ZnO films, not just their surfaces. Therefore, to ensure that the resistances of the entire devices and each layer are consistent and reproducible, i.e., they do not vary drastically from sample to sample (Tables S1 and S2, ESI†), the thickness of the ZnO films was maintained at 3 µm, and that of the BMOF films at 20 µm during their preparation.

The electrical conductivity of undoped BMOF films is ca. 6 × 10$^{-5}$ S m$^{-1}$ (25 °C), which is an order of magnitude greater than that of HKUST-1 that lacks redox-active ligands, but lower than that of intrinsically conducting planar and columnar networks. The poor intrinsic conductivity of the undoped BMOF films can be attributed to the lack of charge delocalization through the BDNDI pillars, as they are located too far apart from each other (ca. 16 and 11 Å along the crystallographic $a$- and $b$-axes, respectively).
Crystal grain boundaries also diminish the conductivity of MOFs. Overcoming this limitation, herein, we demonstrate that the conductivity of BMOF films can be improved and fine-tuned by infiltrating them with guest π-systems that have appropriate sizes and electronic properties required for the formation of extended π-donor/acceptor stacks.

Envisioning that intercalation of π-acidic guests between the electron rich BPDPNDI pillars could activate long-range electron delocalization through the resulting π-stacks, we immersed the BMOF devices into MV²⁺, DFDNB, DNT, and C₆₀ solutions and re-measured their I–V profiles under the same conditions (Table S1, ESI†). The conductivity of the BMOF films soaked in a MV²⁺ solution (30 mM/MeNO₂) increased gradually with the immersion time before reaching the maximum at 2.3 × 10⁻³ S m⁻¹ after 70 h of soaking (Fig. 4a), displaying an impressive 35-fold improvement from that of the undoped BMOF films. In comparison, the conductivity of the BMOF films soaked in less π-acidic guests (MV²⁺, DFDNB, and DNT) were not able to enhance the BMOF’s conductivity as effectively as the stronger π-donor/acceptor stacks. The latter shows new CT bands in the NIR region indicating π-donor/acceptor CT interactions between BPDPNDI ligands and MV²⁺ guests.

Conclusions

In summary, we have (i) constructed a new electroactive BMOF by introducing a new electron rich cNDI ligand, (ii) developed stable BMOF films on ZnO-coated substrates via a new protocol that could be adopted to grow other MOF films, and (iii) devised a new strategy to fine-tune the electrical conductivity of BMOF films by doping them with different π-acidic guests. The new bottom-up film growth method should simplify device integration and testing of MOFs, while the ability to control the conductivity of MOFs with intercalated guests should expand their utility as sensors, semiconductors, and magnetic materials. Since electron transfer through the π-donor/acceptor stacks can be triggered by light, light-harvesting and photoconducting MOFs could also be realized. Ongoing studies in our laboratory and elsewhere probing how different guests influence the optical and electronic properties of electroactive MOFs should bring the MOF-based electronic and photonic devices closer to reality.

Acknowledgements

SS acknowledges the donors of the American Chemical Society Petroleum Research Fund for proving financial support for a major part of this work (grant # 51734-DNI4).
Notes and references


26 The BMOF pellets disintegrate easily when soaked in guest solutions. The packing densities of the undoped and different doped BMOF in pellets are different. The contact resistances between the electrodes and undoped and doped BMOF pellets may not be the same either, but they can be neither quantified nor nullified by the two-probe method. These factors render two-probe pellet measurements more error-prone and less suitable especially for the comparison of the conductivity of the undoped and doped BMOF. Four-probe measurements on BMOF films on the other hand circumvent or eliminate these issues, enabling a fair comparison.

27 The electron rich tetrathiafulvalene and N-methyl-phenothiazine compounds failed to enhance the conductivity of BMOF films, plausibly because of their repulsive interaction with the electron rich BPDPNDI pillars that hindered the formation of extended π-stacks needed for long-range charge delocalization. These control studies emphasized the importance of the redox complementarity between the electroactive ligands and guests in promoting the conductivity of MOFs.

ELECTRONIC SUPPLEMENTARY INFORMATION

Modulating electrical conductivity of metal–organic framework films with intercalated guest π-systems


Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA
Department of Physics, Florida State University, Tallahassee, FL 32306, USA
NIST Center for Neutron Research, National Institute of Standards & Technology, Gaithersburg, MD 20899, USA

†Equal Contribution Authors
Corresponding Author Email: saha@chem.fsu.edu

I. Materials

Starting materials, such as Zn(NO₃)₂·6H₂O, 1,2,4,5-tetrakis-(4-carboxyphenyl)benzene (TCPB) struts, precursors of N,N'-bis(4-pyridyl)-2,6-dipyrrolidinynaphthalenediimide (BPDPNDI) pillar, ZnO/EtOH suspension (40 wt%), solvents and electrolytes were purchased from Sigma-Aldrich, Acros Organic, EMD Chemicals, and Cambridge Isotope Laboratory, and used as obtained. FTO-glass slides were purchased from Hartford Glass Co. The electrodes (Ag/AgCl, Pt-mesh, Pt-disk, and glassy-carbon disc) and electrochemical cells were procured from BASi.

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

II. Synthesis of and Characterization of BPDPNDI Pillar

BPDPNDI was synthesized from 1,4,5,8-tetracarboxylic dianhydride (NDA) in four-steps via modified literature protocols (Scheme S1). The ¹H and ¹³C NMR spectra were recorded at 298 K in appropriate deuterated solvents using Bruker Avance 400 MHz and 700 MHz spectrometers. MALDI-TOF data were recorded on a Bruker Autoflex-II instrument. FT-IR spectra were collected on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Elemental analysis was conducted on a PerkinElmer 240 CHN analyzer.

2,6-Dibromo-NDA (DBrNDA). NDA was first converted to DBrNDA via controlled bromination following a literature protocol. Briefly, to a solution of NDA (2.68 g, 10 mmol) in concentrated H₂SO₄ (10 mL), a solution of dibromoisocyanuric acid (11.48 g, 20 mmol) in concentrated H₂SO₄ (10 mL) was added slowly and the resulting mixture was stirred at 100 °C for 15 h. After cooling the reaction mixture to room temperature, it was poured on ice and the resulting yellow precipitate was filtered and washed thoroughly with H₂O and hot MeOH to obtain DBrNDA as the major product (4.0 g, yield ≈ 95%). MS (MALDI, –ve mode), m/z: observed: 423.20 [M⁺], calculated: 423.82 [M⁺]. This sparingly soluble intermediate was used in the next step without further purification.

2,6-Dibromo-NDI (DBrNDI). DBrNDA diimide was converted to corresponding diimide DBrNDI following a literature protocol. A suspension of DBrNDA (4.0 g, 9.4 mmol) and NH₄OAc (15.5 g, 188 mmol) in AcOH (40 mL) was stirred under reflux for 3 h. After cooling the reaction mixture to room
temperature, the resulting yellow precipitate was filtered and washed thoroughly with AcOH (80 mL) and then diethyl ether (120 mL) to obtain DBrNDI (3.2 g, yield ≈ 80 \%) as a yellow powder. MS (MALDI, –ve mode) \( m/z \): observed: 421.24 [M]\(^+\), calculated: 421.85 [M]\(^+\). This sparingly soluble intermediate was carried over to the next step without further purification.

2,6-Di-pyrrolo-NDI. A \( \text{S}_{\text{N}}\text{Ar} \) reaction of DBrNDI with pyrrolidine following a literature protocol\(^1\) afforded 2,6-bispyrrolo-NDI. Upon addition of pyrrolidine (20 mL) to yellow DBrNDI (2.0 g, 4.7 mmol) it immediately turned dark red and then purple. The mixture was then stirred under reflux for 16 h to drive the reaction to completion. After evaporating excess pyrrolidine with a rotary evaporator, the resulting purple solid was washed successively with copious amounts of hexanes and MeOH to remove the red impurity and obtain a reasonably pure, albeit sparingly soluble 2,6-di-pyrrolo-NDI as a navy blue solid (1.5 g, yield ≈ 73 \%). MS (MALDI, +ve) \( m/z \): observed: 404.48 [M]\(^+\), calculated: 404.15 [M]\(^+\). This sparingly soluble intermediate was carried over to the next step without further purification.

**BPDPNDI Ligand.** The BPDPNDI pillar ligand was prepared by a slightly modified Cu(II)-mediated coupling reaction\(^1\) between 2,6-di-pyrrolo-NDI and 4-pyridineboronic acid, which installed the pyridine groups on imide rings. To a suspension of 2,6-di-pyrrolo-NDI (1.3 g, 3.2 mmol), 4-pyridineboronic acid (3.96 g, 32.3 mmol), Cu(OAc)$_2$ (5.83 g, 32.3 mmol), and molecular sieves (4 Å) in anhydrous DMF (100 mL) purged with O$_2$ for 30 min, Et$_3$N (4.5 mL, 32.3 mmol) was added, and the resulting reaction mixture was stirred at 55 °C under an O$_2$ environment for 2 d. Additional amounts of 4-pyridineboronic acid (1.98 g, 16.2 mmol), Cu(OAc)$_2$ (2.92 g, 16.2 mmol), and Et$_3$N (2.3 mL, 16.2 mmol) in DMF (25 mL) were then added to the reaction mixture, which was stirred at 55 °C under O$_2$ environment for another 3 d. After 5 d, the reaction mixture was cooled to room temperature, filtered, and washed with DMF (100 mL) to obtain a blue solid residue, in which the desired product was trapped. This residue was boiled in CHCl$_3$ (250 mL × 3) and filtered hot to extract the crude product in the filtrate. After concentrating the crude product from the combined blue filtrates, it was purified by SiO$_2$ column chromatography (CHCl$_3$/MeOH 100:1 to CHCl$_3$/MeOH 100:1.5) to obtain pure BPDPNDI (0.72 g, yield ≈ 40 \%) as a vibrant navy blue-colored solid. \(^{1}\)H NMR (400 MHz, CD$_2$Cl, 25 °C): \( \delta = 8.84 \) (dd, 4H$_{\text{pyridine}}$), \( \delta = 8.42 \) (s, 2H$_{\text{NDI-core}}$), \( \delta = 7.33–7.29 \) (m, 4H$_{\text{pyridine}}$), \( \delta = 3.49 \) (dd, 8H$_{\text{pyridine}}$), \( \delta = 2.06 \) (m, 8H$_{\text{pyridine}}$) ppm. \(^{13}\)C NMR (175 MHz, DMSO-\( d_6 \), 25 °C): \( \delta = 162.81, 161.81, 160.90, 152.45, 151.02, 144.78, 125.17, 121.74, 114.64, 40.51, 31.05 \) ppm. MS (MALDI-TOF, +ve) \( m/z \): Observed 558.95 [M]\(^+\), [M]\(^+\) _{\text{calc}d} = 558.60. Elemental analysis: Calculated for (C$_{28}$H$_{28}$N$_{12}$O$_{4}$)(CH$_3$OH)$_{0.75}$(H$_2$O)$_{0.5}$: C 66.47, H 5.11, N 24.70; Found: C 66.90, H 4.98, N 14.14. IR (cm$^{-1}$): 2921 (m), 2863 (m), 2835 (m), 1692 (m), 1653 (s), 1564 (s), 1448 (s), 1415 (m), 1329 (m), 1283 (m), 1208 (s), 1137 (m), 909 (m), 776 (s).

### III. Solvothermal Synthesis and Characterization of BMOF [Zn$_2$(TCPB)(BPDPNDI)]

**BMOF Synthesis.** A DMF (10 mL) solution of Zn(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol), TCPB strut (56 mg, 0.1 mmol), and BPDPNDI pillar (56 mg, 0.1 mmol) placed in a 20 mL screw-capped vial was kept inside an 80 °C oven for 24 h.\(^4\) After cooling down the reaction mixture to room temperature slowly over 6 h, rod-shaped, navy blue colored crystals suitable for SXRD analysis were obtained (60 mg, yield ≈ 35 \%). On the basis of the crystal data and CHN elemental analysis (calculated for C$_{164}$H$_{105}$O$_{78}$N$_{32}$Zn$_{2}$: C: 45.67, H: 7.95, N: 11.95; observed: C: 45.71, H: 7.92, N: 11.90) the molecular formula of BMOF was calculated to be [Zn$_2$(TCPB)(BPDPNDI)]·(DMF)$_{27}$(H$_2$O)$_{36}$. IR (cm$^{-1}$): 2929 (m), 2863 (m), 1654 (s), 1384 (s), 1253 (m), 1092 (s), 862 (m), 783 (s).

**Crystal Structure Analysis of BMOF.** Single-crystal X-ray diffraction (SXRD) data of rod-shaped BMOF crystals were collected on a Bruker D8 Quest X-ray diffractometer (MoK\( \alpha \), \( \lambda = 0.71073 \) Å). Indexing was performed using APEX2 (Difference Vectors method). Data integration and reduction were conducted with SaintPlus 6.01. Absorption correction was done by multiscan method implemented in SADABS. The structure was solved using SHELXL-2013 (direct methods) and refined using SHELXL-2013 (full-matrix least-squares on F$^2$) contained packages. The powder X-ray diffraction (PXRD) data
were recorded on a Panalytical X'Pert Pro diffractometer with CuKα radiation (\(\lambda = 1.5418 \, \text{Å}\)) operated at 45 kV and 40 mA with a scan rate of 1 °/min at room temperature.

To optimize BMOF structure, density functional theory (DFT) calculation was performed with a Quantum-Espresso package using Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof (PBE) exchange correlation.\(^5\) A cutoff energy of 544 eV and a 2×2×2 k-point mesh (generated by Monkhusrt-Pack scheme) were enough for the total energy to converge within 0.01 meV/atom.

The structure of BMOF was first solved partially based on the SXRD data, which revealed a noncatenated pillared paddlewheel (PPW) architecture consisting of layers of TCPB-linked Zn\(_2\) paddlewheel nodes (in crystallographic ab-planes), coordinated axially by the pyridyl rings of linear BPDPNDI pillars along the c-axis. However, the atomic coordinates of fluxional pyrrolidine rings and naphthalenediimide core of BPDPNDI were not fully resolved from the experimental SXRD data largely due the presence of disordered solvent molecules in as-synthesized crystals. Nevertheless, the distances between the Zn-nodes in BMOF (16, 11, and 19 Å along the a-, b-, and c-axes, respectively) are fully consistent with the lengths and geometry of TCPB and BPDPNDI ligands, and its overall network connectivity and dimensions are identical to that of a known isostructural noncatenated PPW-MOF composed of dibromo-TCPB (DBTCPB) struts and DPNDI pillars that have the same lengths and geometry as the TCPB and BPDPNDI ligands present in BMOF. On the basis of this insight, we optimized the atomic positions of pyrrolidine rings and naphthalenediimide core of BPDPNDI ligand in BMOF, using first-principle DFT calculations\(^5\) to depict a complete picture of the noncatenated BMOF structure. The simulated PXRD pattern of this optimized BMOF crystal structure compares well with the experimental PXRD pattern of as-synthesized bulk material, validating the structural model. Cambridge Crystallographic Data Centre (CCDC) contains the supplementary crystallographic data of BMOF presented in this paper, which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

The PXRD profile of BMOF shows [001] reflection at 2\(\theta \approx 4°\), which corresponds to the distance between the layers of the TCPB-linked Zn\(_2\) paddlewheel nodes and is correlated to the lengths of the axially coordinated pillar ligands that connect these layers. This signal matches perfectly with that of a known isostructural noncatenated [Zn\(_2\)(DBTCPB)(DPNDI)] MOF\(^4\) that has the same dimensions as BMOF, but a doubly interpenetrated [Zn\(_2\)(TCPB)(DPNDI)] MOF does not display this signal.\(^4\) Like other bulky pillars,\(^6\) bulky BPDPNDI was able to prevent catenation in a BMOF when used in conjunction with TCPB strut. The PXRD analyses further showed that while as-synthesized and MeNO\(_2\)-exchanged BMOFs are highly crystalline materials, they lose crystallinity upon evacuation of solvents, but regains this feature after being re-soaked in DMF, indicating that structural integrity of BMOF remains intact under ambient conditions and upon solvent loss (Fig. S1). The PXRD profile of BMOF microcrystals soaked in a methyl viologen solution (MV\(^2+\)-2PF\(_6\), 30 mM/MeNO\(_2\)) for several days remained practically unchanged (Fig. S1), indicating that the structure of BMOF remained intact after MV\(^2+\) doping.

**Thermogravimetric analysis (TGA).** The TGA profile of BMOF was recorded under a N\(_2\) atmosphere with a heating rate of 5 °C/min using a TA Instrument Q50 thermogravimetric analyzer.

**Gas Adsorption Analysis.** A Micromeritics ASAP 2020 surface area analyzer was used to measure CO\(_2\) (Airgas, ultra-high purity grade) adsorption isotherms of BMOF. As-synthesized BMOF crystals were first washed with fresh DMF six times over 3 days. To replace DMF, BMOF crystals were then soaked in more volatile THF and the solvent was refreshed several times over 3 days. The THF-soaked BMOF powder was activated under high vacuum at room temperature for 24 h until the outgas rate was <5 \(\mu\)mHg/min prior to measurements. The activated BMOF sample was used for the CO\(_2\) sorption measurement. The sorption measurement was conducted at constant 273 K maintained with an ice-water bath. The CO\(_2\) uptake capacity of BMOF is 65 cm\(^3\)/g at 273 K, 1 bar (Fig. S3), which is comparable to that of isostructural [Zn\(_2\)(DBTCPB)(DPNDI)],\(^4\) indicating its permanent porosity.
IV. Preparation and Characterization of BMOF Films and Devices

Preparation of ZnO Films. Annealed ZnO-coated conducting (FTO) or nonconducting glass slides were used to grow uniform BMOF films. The FTO-coated and nonconducting glass slides (ca. 6 cm × 4 cm) were first covered along the two opposite lengths with four layers of scotch tapes creating a 1 cm wide margin on each side and an exposed rectangular area (ca. 6 cm × 2 cm) in the middle. A ZnO/EtOH suspension (40 wt%, ZnO particle size ~130 nm, Sigma Aldrich) was then spin-coated (1000 rpm, 50 s) on the exposed midsections of these slides using a Laurell Technologies spin-coater, the scotch tape-covered margins remained ZnO-free. After removing the tapes, the ZnO-coated slides were annealed at 350 °C for 30 min in a Vulcan 3-550 PD programmable oven and then cooled slowly to room temperature to obtain smooth, transparent, and uniform ZnO films covering the rectangular midsections (6 cm × 2 cm). These slides were then cut into smaller pieces (the final dimension of slides: ca. 4 cm × 1.1 cm; the ZnO-coated area: 2 cm × 1.1 cm in the middle) that were used for growing BMOF films or for depositing Au electrodes before growing BMOF films on the exposed ZnO-covered areas.

Depositing Au Electrodes on ZnO-Glass Films. In order to incorporate BMOF films into electrical devices and to measure their electrical conductivity by four-probe method, four Au electrodes (~100 nm thick Au pads on top of ~10 nm thick Ti pads) were deposited 1 mm apart through thermal evaporation technique (Edward Auto 306 Vacuum Coater) on ZnO-coated nonconducting glass slides covered with patterned stainless steel shadow masks (1 cm × 1 cm). After depositing the Au-electrodes on annealed ZnO films, the exposed ZnO-covered areas were available for growing BMOF films.

Preparation of BMOF Films and Devices. In order to grow BMOF films, DMF (10 ml) solutions of Zn(NO$_3$)$_2$.6H$_2$O (15 mg, 0.5 mmol), TCPB (14 mg, 0.25 mmol), and BPDPNDI (14 mg, 0.25 mmol) taken in 20 mL screw-capped vials were placed in an oven preset at 80 °C for 2 h to initiate the formation of BMOF. Once the BMOF microcrystals started to form in the precursor solutions, the ZnO films were immersed into them at upright position or in a slightly slanted fashion with the ZnO-coated side facing down to prevent precipitation of BMOF crystals on the active side. The entire setups were then kept in an 80 °C oven for different durations. The ZnO-coated areas became selectively covered with uniform BMOF films within 0.5–1 h of growth period and the thickness of BMOF films increased gradually with longer immersion time. The rest of the areas that did not have an exposed ZnO layer, i.e., the bare FTO and glass areas as well as the Au-electrodes deposited on the ZnO layer remained completely BMOF-free. The initial formation of BMOF in solution ensured a rapid growth of its films on ZnO surfaces. Typically, the slides were withdrawn from the reaction medium after allowing film growth for ca. 1 h to obtain uniform blue films of BMOF on the ZnO-coated areas. These BMOF films and devices were then soaked in fresh DMF to remove any unreacted precursors that may have been trapped, and then immersed in MeNO$_2$ to remove DMF before drying and/or immersing into guest solutions. The BMOF/ZnO films stored in DMF or MeNO$_2$ at room temperature remain intact for months. The PXRD profile of blue films grown on ZnO-coated slides matched with that of as-synthesized bulk BMOF microcrystals deposited in vials, confirming that the blue films are indeed made of the same material.

Doping BMOF Films with Guest π-Systems. The BMOF/ZnO films were immersed into MV$^{2+}$, 1,5-difluoro-2,4-dinitrobenzene (DFDNB), dinitrotoluene (DNT) (30 mM / MeNO$_2$), and C$_{60}$ (saturated in toluene) solutions to allow the appropriate guest molecules to enter into BMOF. While MV$^{2+}$, DFDNB, and DNT were able to penetrate into BMOF, as reflected from the enhanced conductivity of BMOF films doped with these guests, large C$_{60}$ was size-excluded and did not influence the BMOF’s conductivity.

Field-Emission Scanning Electron Microscopy (FE-SEM). Morphologies and the thickness of ZnO, BMOF, and doped BMOF films were analyzed by JEOL SM 7401F high resolution FE-SEM. For cross-sectional SEM analysis, BMOF films were sputtered with a conducting Pt layer (~3 nm). SEM images (Fig. S4) also show that the crystalline morphology of BMOF films remained intact after being doped with guest π-systems.
V. Electrical and Optical Measurements of BMOF Films Before and After Doping with Guests

**UV/Vis Spectroscopy.** The UV/Vis spectra of BPDNDI, BMOF films (undoped and doped) were recorded on a PerkinElmer Lambda-25 UV/Vis spectrophotometer. While the absorption spectra of BMOF/ZnO films are essentially identical to that of the BPDNDI ligand, the MV²⁺-doped BMOF films show prominent, albeit broad and weak as expected, charge-transfer (CT) bands in the NIR region, indicating CT interaction between electron rich BPDNDI pillars and electron deficient MV²⁺ guests.

**Electrochemical analysis.** Cyclic voltammograms (CV) of BPDNDI, MV²⁺, DFDNB, and DNT (1 mM solutions in 0.1 M Bu₄NPF₆ / MeCN) were recorded (Fig. S5) at room temperature on a Princeton Applied Research VersaStat-3-200 potentiostat/galvanostat instrument using a standard electrochemical cell, consisting of a glassy carbon as working electrode, Pt-wire counter electrode, and Ag/AgCl reference electrode. CV of BMOF was recorded using a BMOF/ZnO-FTO film as working electrode, Pt-mesh as counter electrode, Ag/AgCl as reference electrode, and a 0.1 M Bu₄NPF₆ solution as a supporting electrolyte. The redox potentials of BMOF match closely with that of redox-active BPDNDI ligand.

**Conductivity Measurement.** To determine electrical conductivity (σ) of BMOF films (before and after exposure to different guest π-systems) the current-voltage (I-V) relationships of ZnO-glass and BMOF/ZnO-glass devices equipped with four Au electrodes were measured at room temperature and under ambient conditions (Table S1) through standard four-probe technique using Keithley 2400 source meter and LabView program. Before measuring the I-V relationship of the devices, the Au-plated areas outside the active device areas (ZnO and BMOF/ZnO) were scraped off to eliminate the possibility of any current leakage. The total electrical resistance (R = V/I) of at least three devices of each type—(i) bare ZnO film, (ii) undoped BMOF/ZnO film, and BMOF/ZnO films soaked separately in (iii) MV²⁺, (iv) DFDNB, (v) DNT, and (vi) C₆H₆ solutions—were measured from the output voltage (V) between two inner probes in response to current applied (I) at the two outer electrodes under the same conditions. Since the BMOF and ZnO layers in BMOF/ZnO devices constitute two parallel connections between the Au-electrodes and charges can move between the electrodes through both of these layers, the contribution of the ZnO layer (R_{ZnO}) measured from a bare ZnO device was mathematically eliminated from the total resistance of the BMOF-containing devices (R_{Device}) to extract the actual resistance of the BMOF films (before and after soaking in guest solutions), namely R_{component}, using equation 1: R_{component} = R_{device}·R_{ZnO} / (R_{ZnO} – R_{device}). This treatment follows a standard protocol for determining an unknown resistance (R₁) in an electrical circuit consisting of two parallel resistances R₁ and R₂, when the net resistance (R) and R₂ are known [R = R₁R₂ / (R₁ + R₂)].

All devices of any given type displayed consistent values of resistance, and the average resistance of each component (R_{component}) derived from equation 1 was used to calculate its electrical conductivity (σ_{component}) using equation 2: σ_{component} = d / R_{component}·t_{film}·l, where d = probe-spacing, t_{film} = film thickness measured by CS-SEM, and l = the effective length of Au electrodes (Table S1). The conductivity of each undoped and doped BMOF films was also calculated from the resistance of individual devices after eliminating the contribution of the underlying ZnO layer. The conductivity values of any given component obtained from three identical devices (Table S2) are in excellent agreement with each other and with the average value calculated from the average resistance of the corresponding material (Table S1).

The electrical conductivity of the undoped BMOF films is 5.8 × 10⁻⁵ S/m. Upon soaking in MV²⁺ solutions (30 mM/MeNO₂) the conductivity of the MV²⁺-doped BMOF films increased gradually with longer immersion time, displaying 17-fold (0.98 × 10⁻³ S/m) and 34-fold (1.95 × 10⁻³ S/m) improvements after 24 and 48 h, respectively, before reaching the saturation point at 2.3 × 10⁻³ S/m after 70 h soaking, which accounted for an impressive ~35-fold upsurge from undoped BMOF films (6.8 × 10⁻⁵ S/m). Similarly, the conductivity of BMOF films soaked in DFDNB and DNT solutions (30 mM/MeNO₂ for 24 h) reached 3.5 × 10⁻⁴ S/m (a 6-fold improvement from the undoped BMOF films) and 1.5 × 10⁻⁴ S/m (a
2.6-fold upsurge), respectively, and remained practically unchanged after a longer exposure to these dopants. These results suggested that the smaller guest molecules percolated into BMOF faster than larger MV$^{2+}$, as the conductivity of DFDNB and DNT-doped BMOF films reached the saturation point after a shorter immersion time than the MV$^{2+}$-doped BMOF films. In contrast, the conductivity of BMOF films soaked in a saturated C$_{60}$/toluene solution remained practically unchanged (4 × 10$^{-5}$ S/m) even after a prolonged soaking (7 d), suggesting that the large C$_{60}$ molecules were size-excluded by BMOF.

The conductivity of the MV$^{2+}$-, DFDNB-, and DNT-doped BMOF films after quick washing (by dipping the doped BMOF films into fresh solvents and withdrawing them immediately) remained practically unchanged from that of the corresponding unwashed films, suggesting that the intercalated guests molecules adhered to the BPDPNDI pillars did not leak out readily. However, after soaking the doped BMOF devices in fresh solvents for a prolonged time (72 h), their conductivity values dropped significantly, i.e., close to that of the undoped BMOF films, indicating a gradual loss of the guest molecules from its pores. For example, after soaking the MV$^{2+}$- and DNT-doped BMOF films in fresh solvents for several days, their conductivity went down to ca. 3.75 × 10$^{-5}$ S/m, a value that is closer to that of undoped BMOF films than the fully doped ones. Upon soaking blank devices, i.e., those devoid of BMOF/ZnO films in these dopant solutions, their I-V relationships did not display any measurable changes, as they fell beyond the detection limit of the Keithley source meter. These results suggest that MV$^{2+}$, DFDNB, and DNT themselves have extremely low conductivity values that are practically impossible to measure, which is fully consistent with the highly insulting nature of the redox-active small organic molecules. These experiments served as nice controls showing that these guests were able to enhance the conductivity of the BMOF films only after being intercalated between the preorganized BPDPBDI pillars, which improved electron delocalization through the resulting π-stacks.

**Energy Dispersive X-ray Spectroscopy (EDS).** To verify the influx of MV$^{2+}$·2PF$_6^-$ into BMOF, EDS data (Fig. S7) were collected using a JEOL 5900 SEM instrument coupled with a PGT Prism SiLi EDS detector calibrated with AlKα and CuKα. The EDS spectrum of BMOF revealed all of its elements (Zn, C, O, and N), whereas the same doped with MV$^{2+}$·2PF$_6^-$ (after a quick wash with a fresh solvent to remove the extraneous guests) displayed additional diagnostic P and F signals confirming the presence of the dopant. It is worth noting that EDS is a semiquantitative method for heavy elements and does not reflect the actual amount of the lighter ones, but just their presence.

**References:**


Scheme S1. Synthesis of BPDPNDI ligand: (a) dibromoisocyanuric acid, conc. H₂SO₄, 110 °C, 15 h (~95 %); (b) NH₄OAc, AcOH, reflux, 3 h (~80 %); (c) pyrrolidine, reflux, 16 h (~73 %); (d) 4-pyridinylboronic acid, Cu(OAc)₂, Et₃N, molecular sieves (4 Å), DMAc, 55 °C, 5 d. (40%).

Fig. S1. PXRD profiles of (a) BMOF, simulated from SXRD data, (b) bulk as-synthesized BMOF powder (experimental), (c) known noncatenated isostructural [Zn₂(DBTCPB)(DPNDI)] PPW-MOF powder for a comparison, (d) fully evacuated BMOF, (e) BMOF powder exchanged with MeNO₂, (f) MV²⁺-doped BMOF powder, (g) after re-soaking the evacuated BMOF powder in DMF.
**Fig. S2.** The TGA profiles of BMOF (black: as synthesized, red: evacuated) show ~70% weight loss at 135 °C due to DMF loss.

**Fig. S3.** The CO$_2$ adsorption capacity of BMOF at 273 K shows its permanent porosity.

**Fig. S4.** SEM images of doped BMOF films show that their crystalline layered structures remain intact after being exposed to ambient conditions.
Fig. S5. Cyclic voltammograms (vs. Ag/AgCl) of (a) BPDPNDI ligand (1 mM in 0.1 M Bu$_4$NPF$_6$/MeCN): left: reduction, right: oxidation, (b) BMOF/ZnO-FTO film: left: reduction, right: oxidation, (c) MV$^{2+}$·2PF$_6^-$ (0.5 mM in 0.1 M Bu$_4$NPF$_6$/MeCN), (d) DFDNB (1 mM in 0.1 M Bu$_4$NPF$_6$/MeCN), and (e) DNT (1 mM in 0.1 M Bu$_4$NPF$_6$/MeCN).
**Fig. S6.** Current-Voltage (I-V) relationship of BMOF-ZnO films: blue: undoped and green: doped with (a) DFDNB and (b) DNT guests.

**Fig. S7.** The EDS spectra of BMOF (a) before and (b) after being doped with (MV$_{2}^{+}$·2PF$_{6}^{-}$).
Table S1. Electrical measurements of ZnO and BMOF/ZnO devices before and after soaked in different guest solutions. The net electrical resistance ($R_{\text{Total}} = V/I$) of ZnO-glass and BMOF/ZnO-glass devices (before and after soaking in different guest solutions) were measured under ambient conditions (25 °C) through four-probe method: i.e., from output voltage (V) between two inner probes in response to applied current (I) between two outer electrodes. Since the BMOF and ZnO films in BMOF/ZnO devices constitute two parallel connections between the Au-electrodes, the contribution of BMOF films before and after soaking in guest solutions—i.e., $R_{\text{Component}}$—was determined using the equation: $R_{\text{Component}} = R_{\text{Total}} \cdot \frac{R_{\text{ZnO}}}{(R_{\text{ZnO}} - R_{\text{Total}})}$. Based on the resistance of individual components ($R_{\text{Component}}$), and taking the thickness ($t_{\text{film}}$) of ZnO (~3 µm) and BMOF films (~20 µm), probe-spacing ($d$: 1.6 mm (center-to-center) for bare ZnO films, 1 mm (edge-to-edge) for BMOF films grown on ZnO films pre-patterned with Au electrodes), and the effective length of Au electrodes ($l = 4$ mm) into account, electrical conductivity ($\sigma_{\text{Component}}$) of each component was derived from the equation: $\sigma_{\text{Component}} = \frac{d}{R_{\text{Component}} \cdot t_{\text{film}} \cdot l}$.

<table>
<thead>
<tr>
<th>Four-Terminal Electrical Devices</th>
<th>$R_{\text{Device}}$ (MΩ)</th>
<th>Device Components</th>
<th>$R_{\text{Component}}$ (MΩ)</th>
<th>$\sigma_{\text{Component}}$ ($10^{-4}$ S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-glass</td>
<td>220 ± 9.6</td>
<td>ZnO</td>
<td>220</td>
<td>6.3</td>
</tr>
<tr>
<td>BMOF/ZnO-glass (Before soaking in any guests)</td>
<td>109 ± 1</td>
<td>BMOF Film (Undoped)</td>
<td>216</td>
<td>0.6</td>
</tr>
<tr>
<td>BMOF/ZnO-glass soaked in MV$^{2+}$ (30 mM / MeNO$_2$) for 70 h</td>
<td>5.3 ± 0.8</td>
<td>MV$^{2+}$-Doped BMOF Film</td>
<td>5.4</td>
<td>23</td>
</tr>
<tr>
<td>BMOF/ZnO-glass soaked in DFDNB (30 mM / MeNO$_2$) for 44 h</td>
<td>31 ± 4.3</td>
<td>DFDNB-Doped BMOF Film</td>
<td>36</td>
<td>3.5</td>
</tr>
<tr>
<td>BMOF/ZnO-glass soaked in DNT (30 mM / MeNO$_2$) for 48 h</td>
<td>60 ± 6.5</td>
<td>DNT-Doped BMOF Film</td>
<td>83</td>
<td>1.5</td>
</tr>
<tr>
<td>BMOF/ZnO-glass soaked in C$_{60}$ (saturated/PhMe) for 7 d</td>
<td>132 ± 10.9</td>
<td>C$_{60}$-soaked BMOF Film</td>
<td>325</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table S2. Electrical conductivity ($\sigma$) of undoped and doped BMOF films from individual devices:

<table>
<thead>
<tr>
<th>Films</th>
<th>Sample 1 $\sigma$ (S/m)</th>
<th>Sample 2 $\sigma$ (S/m)</th>
<th>Sample 3 $\sigma$ (S/m)</th>
<th>Average $\sigma$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$6.59 \times 10^{-4}$</td>
<td>$6.07 \times 10^{-4}$</td>
<td>$6.15 \times 10^{-4}$</td>
<td>$(6.3 \pm 0.3) \times 10^{-4}$</td>
</tr>
<tr>
<td>BMOF (Undoped)</td>
<td>$5.60 \times 10^{-5}$</td>
<td>$5.86 \times 10^{-5}$</td>
<td>$5.89 \times 10^{-5}$</td>
<td>$(5.8 \pm 0.2) \times 10^{-5}$</td>
</tr>
<tr>
<td>MV$^{2+}$-Doped BMOF</td>
<td>$1.96 \times 10^{-3}$</td>
<td>$2.34 \times 10^{-3}$</td>
<td>$2.65 \times 10^{-3}$</td>
<td>$(2.3 \pm 0.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>DFDNB-Doped BMOF</td>
<td>$4.21 \times 10^{-4}$</td>
<td>$3.22 \times 10^{-4}$</td>
<td>$3.12 \times 10^{-4}$</td>
<td>$(3.5 \pm 0.6) \times 10^{-4}$</td>
</tr>
<tr>
<td>DNT-Doped BMOF</td>
<td>$1.33 \times 10^{-4}$</td>
<td>$1.53 \times 10^{-4}$</td>
<td>$1.71 \times 10^{-4}$</td>
<td>$(1.5 \pm 0.2) \times 10^{-4}$</td>
</tr>
<tr>
<td>C$_{60}$-soaked BMOF</td>
<td>$4.80 \times 10^{-5}$</td>
<td>$4.81 \times 10^{-5}$</td>
<td>$3.48 \times 10^{-5}$</td>
<td>$(4.4 \pm 0.7) \times 10^{-5}$</td>
</tr>
</tbody>
</table>