[Fe(CN)$_5$NO]$^{2-}$-Based MOIFs for Adsorption of Organic Pollutants and as a Self-Rotatory Motor

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ABSTRACT: Herein, we report metal–organic ionic frameworks (MOIFs; an ionic product of an anionic complex and an organic cationic head group) for the adsorption of toxic organic pollutants and as a self-rotatory motor. MOIFs were synthesized via the ion-exchange mechanism in water (without use of any toxic organic solvent) using Na$_3$[Fe(CN)$_5$NO] and [C$_n$H$_{2n+1}$N$^+$ (CH$_3$)$_3$]$^2$ and characterized through small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) techniques. Thermal gravimetric (TGA/DTA) and differential scanning calorimetric (DSC) studies of MOIFs have informed their activation energy, enthalpies of crystallization/melting, and specific heat capacity (SHC), which have also been correlated with their structural properties. MOIFs have shown the adsorption of toxic pollutants determined through the UV–visible method, two parameter isotherms, thermal kinetics, and activation parameters. The interaction between the adsorbate and adsorbent has been estimated with the equilibrium isotherm, which is characteristic of the adsorption system. Apart from this, we also found MOIF, especially dodecyltrimethyl ammonium cation + nitroprusside anion (Dt-NP), to be an autonomous motor, where it could develop a surface tension gradient at the water interface, and this gradient produced mechanical motion, as demonstrated with boat experiments.

1. INTRODUCTION

Recently, organic pollutants as industrial wastes, especially organic dye pollution, have become one of the most serious environmental issues because they are photochemically and chemically resistant. It not only harms the environment but also pollutes drinking water at the ground level and causes drinking water problem. Such dyes are not limited to use as coloring agents for textile, paper, pharmaceutical, food, leather, and cosmetic industries but also used as disinfectants in aquaculture as preservative for animals feed. Thus, the removal of organic dyes from wastewater prior to discharge is necessary for the protection of ecological environments and human health. In this context, many porous materials like metal–organic frameworks (MOFs) play an important role in the removal of pollutants via adsorption or degradation. However, there is still a great demand to develop new molecular frameworks for wastewater treatment due to their restriction with chemical and physical properties. Apart from this, MOFs are being projected for adsorption or degradation according to the Marangoni effect enabling them to be used as good adsorbents and also to create a good ST gradient at the water interface. The adsorption property of MOIFs is experimentally investigated with four dyes—methyl orange (MeO), methyl red (MeR), azo, and azo-hydroxy (azo-OH)—and analyzed with different isotherms. The direction mechanical motion of dodecyltrimethyl ammonium cation + nitroprusside anion (Dt-NP) MOIFs has been demonstrated with boat experiments and assessed by measuring the ST of water before and after rotations. Although the Marangoni effect is common, in this study, the Dt-NP MOIFs show this

Received: October 7, 2020
Accepted: December 8, 2020
Published: December 22, 2020

Published by American Chemical Society
2020
ACS Omega 2021, 6, 456–464
phenomenon directionally, which encouraged us to use it in the mentioned applications.

2. RESULTS AND DISCUSSION

2.1. Identification and Sustainability of Ionic Units in MOIFs. The ionic interactions of cationic quaternary ammonium and anionic [Fe(CN)₅NO]²⁻ moieties produced MOIFs such as Dt-NP, nitroprusside anion + tetradeclyltrimethyl ammonium cation (T-NP), and nitroprusside anion + hexadecyltrimethyl ammonium cation (H-NP). UV–vis spectroscopy was used to identify the sustainability of the anionic [Fe(CN)₅NO]²⁻ moiety into MOIFs where 270 nm (λ_{max} of [Fe(CN)₅NO]²⁻) was considered for comparative analysis (Figure 1A). The pure (absence of chosen quaternary cations, Figure S1B) [Fe(CN)₅NO]²⁻ showed maximum absorption (1.47) as compared to MOIFs ([Fe(CN)₅NO]²⁻ + quaternary cations, Figure 1A) due to a transition from 5T₂g to 5Eg having the maximum energy (Figure 1B). However, MOIFs showed lower absorption than earlier, shown in Figure 1B, due to the ionic interaction of [Fe(CN)₅NO]²⁻ and quaternary cations. The ionic association of quaternary nitrogen in MOIFs (Dt-NP, T-NP, and H-NP) with [Fe(CN)₅NO]²⁻ restricted the absorption of the [Fe(CN)₅NO]²⁻ ion as it was in the pure state. That is why a decrease in absorption was obtained, and this restriction was observed to be effective as H-NP < T-NP < Dt-NP, from which it can be inferred that the maximum restriction was caused by the 12 C alkyl chain. The crystal field splitting energy (CFSE) values for MOIFs were predicted on the basis of absorption where the δ low spin complex has a CFSE value of −2.4Δ_{dil}; thus, the result shows that MOIFs having a hexadecyltrimethyl ammonium ion are more stable than the others (Figure 1B). The characteristic vibration frequencies (CFSE) values for MOIFs were predicted on the basis of absorption where the δ low spin complex has a CFSE value of −2.4Δ_{dil}; thus, the result shows that MOIFs having a hexadecyltrimethyl ammonium ion are more stable than the others (Figure 1B).

2.2. Small-Angle X-ray Scattering (SAXS) and Powder X-ray Diffraction (PXRD). Small-angle X-ray scattering (SAXS) predicts the structural properties of MOIFs. Thus, on impinging the monochromatized X-rays on the sample, a sharp maximum in the scattered intensity is obtained, and the reciprocal lattice vectors are matched with the length of the scattering vector q. Thus, the periodicity of the structure is identified with the adequate numbers of peaks with relative positions at the q-axis, where the relative intensities of peaks reveal the actual arrangement of molecules within the unit cells. In SAXS, the lamellar phase is recognized by equidistant reflections occurring at qₙ = 2πn/L, where L is the lamellar period and n = 1, 2, 3, etc. in the two-dimensional (2-D)/three-dimensional (3-D) cases where the reflection peaks follow a (n) sequence. Generally, in the 2-D hexagonal case, the first values are n = 1, 3, 4, 7, 9, 12, 13, etc., while the cubic reflections lie in positions n = h² + k² + l², where h, k, and l are whole numbers. The SAXS curve (Figure S2) illustrates the intensity of SAXS from the MOIF, where the two reflections occurring at q = 2.2, 6.3 and 2.2, 4.2 nm⁻¹ for [C₁₂H₂₅N(CH₃)₃][Fe²⁺(CN)₅(NO)] suggest a lamellar structure. The electrostatic attraction between [Fe²⁺(CN)₅(NO)]²⁻ and cationic [(C₄H₂₉⁺₁)-N(CH₃)₃]⁺ caused the formation of MOIF. Here, the negative charge density (−2) on [Fe²⁺(CN)₅(NO)]²⁻ is satisfied by [C₄H₂₉⁺₁]⁺N(CH₃)₃ which resulted in highly ordered crystalline structures. The crystalline nature of MOIFs (Dt-NP) was also confirmed with powder XRD pattern, as illustrated in Figure S3, where many sharp peaks contributed to the crystalline nature. The lattice parameters are calculated using the below-mentioned equation and are tabulated in Table S1, supporting the crystalline nature of MOIFs. The powder XRD analysis was also compared to the crystallographic cards (references 01-0244 and 30-0483) and was found to be in accordance with the findings.
2.3. Thermal Analysis and Kinetics. The enthalpies of melting ($\Delta H_m$) and crystallization ($\Delta H_c$) were calculated by integrating the area under the curve, while the specific heat capacity (SHC) was calculated using the equation

$$\text{SHC} (C_p) = \frac{\text{(heat flow)} \times \text{(time)}}{\text{(weight)} \times \text{(temperature)} \text{ or } \text{(mW)} \times \text{(s)} \text{ or } \frac{\text{(J)}}{\text{(gC)}}}$$  

Figure 3 and Table S2 show the $\Delta H_m$ and $\Delta H_c$ as well as SHC in the order $\Delta H_m^{\text{SNP}} < \Delta H_m^{\text{Dt-NP}} < \Delta H_m^{\text{T-NP}} < \Delta H_m^{\text{H-NP}}$, $\Delta H_c^{\text{SNP}} > \Delta H_c^{\text{T-NP}} > \Delta H_c^{\text{H-NP}}$, and $C_p^{\text{SNP}} > C_p^{\text{T-NP}} > C_p^{\text{H-NP}} > C_p^{\text{SNP}}$. The melting enthalpy and SHC increased on increasing the carbon number of the alkyl chain. Thus, the ionic association increased the capability of MOIFs to hold the heat because the alkyl chain provides more space for the same. For instance, with $[\text{Fe}^{2+}(\text{CN})_5(\text{NO})]^2^-$, all ligands are bound to the Fe ion only, but with MOIFs, the same ligands are not only bound to the Fe ion but also surrounded by long alkyl chains. Thus, MOIFs are not free as $[\text{Fe}^{2+}(\text{CN})_5(\text{NO})]^2^-$ and have a high heat-holding capacity. In the DSC curve, the crystallization peak shows the crystalline nature of MOIFs, where the % crystallinity ($X_c$) values for Dt-NP, T-NP, and H-NP were calculated using the following equation and were found to be 7.85, 37.63, and 6.40%, respectively.

$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m(1 - x)} \times 100$$  

Figure 3. DSC analyses of (a) sodium nitroprusside (SNP), (b) Dt-NP, (c) T-NP, and (d) H-NP, where the enthalpy of melting, enthalpy of crystallization, and specific heat capacity were calculated through ORIGIN LAB software.

2.4. Dye Adsorption Thermodynamics. The % dye adsorption, as shown in Figure S5, was obtained using the following equation:

$$\% \text{adsorption} = \frac{C_i - C_a}{C_i} \times 100$$  

where $C_i$ is the initial concentration of dye and $C_a$ is the concentration of dye after adsorption.

The adsorption of chosen dyes was found for MOIFs such as SNP < Dt-NP < T-NP < H-NP, which informs that it is governed by hydrophilic and hydrophobic interactions. In the case of SNPs, only hydrophilic interaction was applicable because all hydrophilic ligands were attached to the Fe ion, so the adsorption was minimum, while in the case of MOIFs, both interactions were accountable so adsorption was greater than SNP. When comparing MOIFs with constant hydrophilicity, the hydrophobicity increased as Dt-NP < T-NP < H-NP due to an increase in the alkyl chain length in the same order. Due to this, the increased adsorption was found as a combined effect of hydrophilicity and hydrophobicity. The thermodynamics of dye adsorption informs about the effect of temperature on thermodynamic parameters such as Gibbs function change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$), and standard entropy.
\[ \Delta G^0 = -RT \ln K_D, \quad \text{where} \quad K_D = \frac{q_e}{C_e} \]  

(5)

\( K_D, q_e, \) and \( C_e \) are the thermodynamic equilibrium constant, equilibrium dye adsorption, and equilibrium dye concentration, respectively. The \( \Delta H^0 \) and \( \Delta S^0 \) were obtained from the slope and intercept of the linear plot of \( \ln K_D \) vs \( 1/T \). The effect of temperature on all thermodynamic parameters was evaluated at 303.15, 308.15, and 313.15 K, as shown in Figures 4 and 5. The \( \Delta G^0 \) was found to be SNP \( \Delta G_{Azo-OH}^0 > SNP \Delta G_{MeR}^0 > SNP \Delta G_{MeO}^0 > SNP \Delta G_{Azo}^0 \) at all chosen temperatures. It indicates the dependence of adsorption on the functional groups, interacting sites, and hydrophobic/hydrophilic domains of the chosen dyes. In the case of Azo-OH, the highly interactive group −OH with less hydrophobicity; for MeR, the highly interactive group −OH with high hydrophobicity; for MeO, the less interactive oxide group with high hydrophobicity; and for Azo hydrophobicity, lesser interactive groups affected their adsorption by MOIFs. On increasing the temperature, the \( \Delta G^0 \) increased in the order 313.15 \( \Delta G^0 > 308.15 \Delta G^0 > 303.15 \Delta G^0 \) because the increasing temperature restricted the interacting capability of dyes as well as MOIFs. The value of \( \Delta G^0 \) decreased with a decrease in temperature, indicating that dye removal was higher at low temperatures. The \( K_D \) values at different temperatures decreased, clearly showing that dye adsorption gradually decreased with the increase in temperature—an exothermic nature of dye adsorption. The positive values of \( \Delta G^0 \) at all of the temperatures indicated that the dye adsorption process was not spontaneous. Similarly, \( \Delta H^0 \) and \( \Delta S^0 \) were comparatively analyzed as shown in Figure 5, and it was found as MOIF \( \Delta H_{Azo-OH}^0 > MOIF \Delta H_{Azo}^0 > MOIF \Delta H_{MeR}^0 > MOIF \Delta H_{MeO}^0 \) and MOIF \( \Delta S_{Azo-OH}^0 > MOIF \Delta S_{Azo}^0 > MOIF \Delta S_{MeR}^0 > MOIF \Delta S_{MeO}^0 \). It indicated that interaction with Azo-OH produces the maximum internal energy as well as entropy compared to the others.

2.5. Adsorption Isotherm, Kinetics, and Activation Parameters. Adsorption isotherm models are important tools for describing the interaction between an adsorbate and adsorbent. With respect to this, the adsorption of chosen dyes on the surface of MOIFs was investigated through isothermal models. The Langmuir isotherm model is used to find out the monolayer adsorption, and adsorption only occurs at available sites. The equation of the Langmuir isotherm signifies homogenous adsorption where each molecule possesses a constant enthalpy and activation energy. The intercept and slope values of the linear plot of \( 1/Q_e \) and \( 1/C_e \) represent \( K_L \) and \( Q_{\text{max}} \), respectively, as shown in Table S4. The comparative analysis of the monolayer capacity of MOIFs is illustrated in Figure 6. It varies not only with MOIFs but also with dyes such as \( q_s = \Delta G_{Azo-OH} > q_s = \Delta G_{MeR} > q_s = \Delta G_{MeO} > q_s = \Delta G_{Azo} \).
temperature as 303.15 K.

The monolayer capacity of MOIFs increased on increasing the number of the dye and hydrophilic/phobic environments of MOIFs. The monolayer capacity of MOIFs is indicated that the dye has individual capacity to cover the surface of the individual MOIF and is influenced by the interacting sites of the dye and hydrophilic/phobic environments of MOIFs. The monolayer capacity of MOIFs increased on increasing the temperature as $Q_{\text{max}}^{\text{S15}} < Q_{\text{max}}^{308.15} < Q_{\text{max}}^{313.15}$. It may be because the increase in temperature expanded the surface area of MOIFs, where the dye has to be adsorbed. Similarly, the value of $R_1$ indicates the type of isotherm. If the value of $R_1 = 1$ is linear, $R_1 = 0$ corresponds to being irreversible, while $0 < R_1 < 1$ and $R_1 > 1$ indicate favorable and unfavorable isotherms, respectively.

Table S5 shows that the value of $R_1$ is $0 < R_1 < 1$ at all chosen temperatures, which indicates the favorability of the adsorption on the surface of MOIFs. The Freundlich isotherm defines the nonideal and reversible adsorption and is also applied to multilayer adsorption. The intercept $(K_F, \text{mg g}^{-1})$ and slope $(1/n)$ values of a linear plot of $q_e$ and $\log C_e$ are tabulated in Table S6. The trend of $K_F$ as H-NP/MR > T-NP/MO > DNP/Azo-OH > DNP/MA > T-NP/MA > H-NP/MA > T-NP/Azo-OH > H-NP/MO > DNP/MA > T-NP/Azo > SNP/Azo > SNP/MR > SNP/MO > SNP/Azo-OH shows that the adsorption capacity depends on interacting sites and alkyl chain length. The slope $(1/n)$ range $0–1$ is the measure of adsorption intensity or surface heterogeneity, where a value close to zero indicates the high heterogeneity of the surface. Figure 7 reveals the isotherm favorability on the basis of the $1/n$ value, where the value $0 < 1/n < 1$ confirms the favorability of the isotherm. Similarly, the Dubinin–Radushkevich (D–R) isotherm correlates the Gaussian energy distribution to the adsorption mechanism on a heterogeneous surface and is applicable to different concentration ranges. D–R is applied to differentiate the chemical and physical adsorption based on temperature. The D–R parameters’ intercept and slope, obtained by the linear plots of $\ln q_e$ vs $\varepsilon^2$, are listed in Table S7. In the case of MeR interaction with MOIFs, the mean free energy was found to be the maximum. A comparative analysis of $E$ was made, as illustrated in Figure 8, which indicates the effect of temperature on $E$, where on increasing the temperature, the $E$ also increased. Likewise, the Temkin isotherm takes into account the interaction between an adsorbate and adsorbent as well as the uniform distribution of binding energy. Therefore, Temkin constants were obtained by the linear plot of $\ln q_e$ vs $\ln C_e$ and are tabulated in Table S8. In the case of interaction between MOIFs and dyes, the higher values of $b$ and $k_f$ indicate the stronger interaction and binding between these two. Figure 9 reveals the binding constant at chosen temperatures, which is almost constant for all systems, indicating the validity of the experiment.

### 2.6. MOIF as a Self-Rotatory Motor.

Apart from the adsorption property, MOIF (Dt-NP) as an autonomous motor is shown in Figure 10a,b. For comparative rotations of neat MOIF, neat dodecyltrimethyl ammonium bromide (DTAB), and neat SNP, a small particle of each was dropped onto the surface of pure water. The neat SNP particle descended immediately to the bottom of the water with no translational or rotational motion. It slowly dissolved, characteristic of its rigidity of the selected constituents of MOIF is high enough to avoid motion. In fact, the neat DTAB also did not show motion (filled diamond blue color in Figure 10b). Such observations indicated that the rigidity of the selected constituents of MOIF is high enough to avoid motion. Figure 9 reveals the interaction between an adsorbate and adsorbent analyzed by the Temkin isotherm model.
MOIF particle is dropped onto water, it shows vigorous motion on the surface for more than $10^{-15}$ min (Figure 10b). This MOIF particle moved around on the surface at a maximum average speed of $38 \text{ mm s}^{-1}$ per volume ($1 \text{ mm}^3$) given the average diameter of the MOIF spherical particle being measured as $1 \text{ mm}$. The direction of motion is determined by the initial impulse of the MOIF, and at stabilization of the surface tension gradient, the MOIF particles quickly move along the direction of that gradient. For considering MOIF as a rotor in water, we performed boat experiments varying the mass of the MOIF to determine the mass effect on rotation of the MOIF at the water surface. On increasing the amount of MOIF, the rotation increased because of an increase in the mass and volume of the MOIF. Therefore, the MOIF system can be realized with a remarkably efficient fuel conversion as an autonomous motor.

Because the neat DTAB and SNP particles did not move at the water surface, the motion of the MOIF particle must be powered by some chemical changes that can be understood by a mechanism (Figure 11). The hydrophobic and hydrophilic domains of the MOIF misbalance themselves at the water surface, which develops an equilibrium gradient between hydrophobic and hydrophilic domains, causing the motion (Figure 11). During this process, maybe, the MOIF develops mechanical energy due to which some cationic molecules (maybe of excess) are dissociated and dissolve into water. This lowers the ST of water and creates an ST gradient, which reinforces the rotation of the MOIF as per the Marangoni effect, as shown in Figure 12.12

2.7. Investigation of the Marangoni Effect. The Marangoni effect was investigated by measuring the ST of water, before/after rotation, using the Survivimeter.50 The Survivimeter is a device using which physical properties such as surface tension and viscosity of a solution can be measured together without changing the solution once it is filled into the device. The rotation experiment was carried out in pure water and an aqueous DTAB solution with variable concentrations to see the effect on motion, confirming the Marangoni effect as illustrated in Figure 13. For instance, the ST of pure water was found to be $72.80 \text{ mN m}^{-1}$ before using it for rotation, while after rotation the ST values of the same water were found to be $69.23$ and $65.89 \text{ mN m}^{-1}$ with 2 and 5 mg weight of MOIF, respectively. Similarly, in aqueous DTAB (0.000125 M), the ST was $48.91 \text{ mN m}^{-1}$ before rotation and $45.04 \text{ mN m}^{-1}$ after rotation. After rotation, the ST of water or aqueous DTAB solution, in which rotation is performed, was found to be lower than before. It indicates that some surfactant molecules might have dissolved, which lowers the ST as explained in the above mechanism. In aqueous DTAB solutions, the rotation of the

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**Figure 10.** (a) Structure of the hybrid MOIF motor, a product of ionic combinations of dodecyltrimethyl ammonium and pentacyano nitrosyl ferrate (II) ions. (b) Illustration of rotation by the MOIF.

**Figure 11.** Illustration of motion produced due to an equilibrium gradient developed by hydrophobic and hydrophilic domains of the MOIF.

**Figure 12.** Illustration of development of surface tension gradient causing rotation.

**Figure 13.** Confirmation of the Marangoni effect, analyzed through surface tension measurements of mediums in which the rotation experiment was carried out.
MOIF became slow on increasing the concentration from 0.000125, 0.00025, 0.0005, and 0.001 M because the increase in concentration of the ST gradients developed by MOIF becomes weaker, as illustrated in Figure 14. The objective behind conducting this experiment is to be able to control the motion of the rotor as required, which can help us in artificial robotic systems. We also checked the UV−vis spectra of water and aqueous surfactant solutions before and after rotation to check whether or not the anionic part dissolves into the medium. This allowed us to avoid the unnecessary use of toxic and expensive organic solvents to prepare MOIFs like others.8 The MOIF is an advancement in autonomous rotor systems because it does not break down during rotation. Furthermore, it does not need any specific medium for developing ST gradients like others.8 This novel driving mechanism of MOIFs on a water surface includes the generation of an equilibrium gradient, contributing to the release of surfactant molecules that develops ST gradients, resulting in the swimming motion.

3. CONCLUSIONS

The present study reports the synthesis of multipurpose MOIFs in an aqueous medium and their application in dye adsorption. The adsorption was measured in terms of the Gibb's free energy, internal energy, and change in entropy and monolayer adsorption capacity. MOIFs were found to be good adsorbents with their remarkable adsorption of toxic organic pollutants up to 40%. The DSC and TGA analyses proved the thermal stability of MOIFs, where they also showed their crystallization nature. Apart from this, the Dt-NP has been found as an artificial self-rotatory motor in water, and this property can be utilized for electric energy production applying the concept of energy transformation from mechanical to electric. Both adsorption and motion studies open a new window for researchers of material science for developing multipurpose compounds.

4. EXPERIMENTAL SECTION

4.1. Materials and Measurements. Sodium nitroprusside (SNP), dodecyltrimethyl ammonium bromide (DTAB), tetradecyltrimethyl ammonium bromide (TTAB), hexadecyltrimethyl ammonium bromide (HTAB), and all dyes were procured from Sigma-Aldrich having more than 99% purity. All chemicals were used as received without any purification.

4.2. General Consideration for Preparation of MOIF. The mixtures of aqueous SNP and DTAB, SNP and TTAB, and SNP and HTAB in round-bottom flasks (1:2 molar ratio for each) were placed on a magnetic stirrer for 1 h at 700 rpm, separately. After complete precipitation, the compounds were found in glossy powdery forms and dried in a vacuum oven overnight. Three MOIFs were synthesized, named Dt-NP, T-NP, and H-NP, with the above-mentioned combinations separately, which were found to be soluble in methanol and ethanol.

4.3. Characterization. IR spectra were recorded on a Perkin Elmer spectrum two Fourier transform infrared spectrometer (FTIR). The powder XRD measurements were carried out using a Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube, and the wavelength of the X-ray was 0.154 nm (Cu Kα). The X-rays were detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector) where data were collected at 40 kV and 40 mA. Thermal analyses were measured on Perkin Elmer DSC and TGA instruments within the range of 30–350 °C and heating rate of 5 °C min⁻¹. 1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker machine (500 MHz). UV−vis spectra were recorded on a UV-1800 spectrophotometer (Shimadzu, Japan) equipped with a Lab sphere diffuse reflectance accessory.c

Dt-NP: elemental (calculated): C, 62.48; H, 10.19; N, 16.65; O, 2.38, (found) C, 62.08; H, 9.519; N, 15.87; O, 2.14. 1H NMR (MeOH): δ 3.233 (s, (CH₃)₂N⁺), 3.162 (t, 2H, −CH₂CH₃N⁺), 1.692 (m, 2H, −CH₂CH₂CH₂N⁺), 1.321–1.269 (remaining H of the alkyl chain), 1.112 (t, last 3H of the alkyl chain). T-NP:
elemental (calculated): C, 64.26; H, 10.51; N, 15.37; O, 2.19 (found) C, 63.26; H, 10.13; N, 15.07; O, 1.82. 1H NMR (MeOH): δ 3.198 (s, (CH2)3N+), 3.123 (t, 2H, −CH2CH2CH2N+), 1.589 (m, 2H, −CH2CH2CH2N+), 1.302–1.369 (remaining H of alkyl chain), 1.135 (t, last 3H of the alkyl chain). H-NP: elemental (calculated): C, 65.79; H, 10.79; N, 14.27; O, 2.04 (found) C, 65.21; H, 9.98; N, 13.25; O, 1.69. 1H NMR (MeOH): δ 2.969 (s, (CH2)3N+), 3.098 (t, 2H, −CH2CH2CH2N+), 1.458 (m, 2H, −CH2CH2CH2N+), 1.263–1.256 (remaining H of the alkyl chain), 1.102 (t, last 3H of the alkyl chain).

The adsorption experiments were performed on experiments were performed at 303.15, 308.15, and 313.15 K temperatures. The adsorption properties of each MOIF. The uptake kinetic

**4.4. Small-Angle Scattering.** SAXS is performed on the powder MOIF sample with the instrument Model SAXSspace (Anton Paar, GmbH, Austria). The Eiger R1 M Hybrid Photon counting detector having a line-collimation system using a Cu Kα source with a wavelength of 1.54 Å is used. Fujifilm (Greenwood, SC) image plates and a Perkin Elmer Cyclone (Covina, CA) image plate reader are used to acquire the data. GIFIT and DACON software are used to obtain the shape, Dmax, and electron density and to reduce the two-dimensional data to a one-dimensional, intensity (l) vs scattering vector (q) plot, respectively.

**4.4.1. Execution of SAXS Data.** SAXS analysis results in the scattering intensity (l(q)) as a function of the scattering vector q, which is defined as q = \( \frac{4\pi}{\lambda} \sin(\theta/2) \), where \( \lambda \) is the wavelength, \( \theta \) is the scattering angle, and the refractive index is \( n \approx 1 \) for X-ray scattering. The scattering intensity is related to the real space pair distance distribution function \( p(r) \) that gives information about the size, shape, and internal structure in real space.

\[
l(q) = 4\pi \int_0^{\infty} p(r) \frac{\sin qr}{qr} dr
\]

(6)

By the convolution square-root technique to deconvolute \( p(r) \) of the MOIF, the excess radial density profile, \( \Delta F(r) \), could be determined by assuming a spherical shape as follows, where \( \langle \rangle \) stands for the spherical average and \( ~2 \) is a symbol for the convolution square operation.

\[
p(r) = r^2 \langle \Delta \rho^2(r) \rangle = \left( \int p(r) \Delta \rho(r') \Delta \rho(r' - r) dr' \right)
\]

(7)

**4.5. Dye Adsorption and Isotherm Analysis.** MeO, MeR, Azo, and Azo-OH (Figure S1A) dyes were chosen to investigate the adsorption properties of each MOIF. The uptake kinetic experiments were performed at 303.15, 308.15, and 313.15 K temperatures. The adsorption experiments were performed on the basis of the decrease in the absorbance of dyes. The dye concentration was kept constant at 1 \times 10^{-3} M, while MOIFs were varied from 50 to 250 μM with an interval of 50 μM. For sample preparation, 2 mL of MOIF and 2 mL of dye solution were mixed separately and kept for half an hour before UV-visible measurements were performed. The UV–vis data were used in isothermal analysis. The Langmuir isotherm was used to find the monolayer adsorption at available sites\(^{20}\) as follows:

\[
Q_e = \frac{Q_{\text{max}}K_L}{1 + K_L C_e}
\]

(8)

\( C_e \), \( K_L \), and \( Q_{\text{max}} \) are dye concentrations at equilibrium. The shape of the Langmuir isotherm\(^{25,33}\) denoted by the dimensionless separation factor \( R_l \) was calculated by the following equation:

\[
R_l = \frac{1}{1 + K_L C_e}
\]

(9)

\( C_e \) and \( K_L \) are the initial dye concentration and the Langmuir constant, respectively. The Freundlich isotherm was obtained as

\[
Q_e = K_q C_e^{1/n}
\]

(10)

\( K_q \) (mg g\(^{-1}\)) is the adsorption capacity and \( n \) is the adsorption exponent. The Dubin-in–Radushkevich (D–R) isotherm was obtained using the equation as follows, where \( K_d \) and \( e \) are the D–R constant (mol\(^2\) kg\(^{-1}\)) and the D–R isotherm constant, respectively; \( R \) and \( T \) are the gas (8.314 × 10^{-3} kJ mol\(^{-1}\) K\(^{-1}\)) and temperature (K) constants, respectively; and \( q_m \) is the saturation capacity (mg g\(^{-1}\)).

\[
\ln q_e = \ln q_m - K_d e^2 \quad \text{and} \quad e = RT \ln \left[ 1 + \frac{1}{C_e} \right]
\]

(11)

The mean free energy, \( E \) (kJ mol\(^{-1}\)), is obtained from \( K_d \) and is expressed as

\[
E = \frac{1}{\sqrt{2K_d}}
\]

(12)

The Tempkin isotherm is obtained as

\[
q_e = \frac{RT}{b} \ln k_T C_e
\]

(13)

Here, \( b \) and \( k_T \) are the Tempkin isotherm constant (kJ mol\(^{-1}\)) and the equilibrium binding constant, respectively.

**4.6. MOIF as the Self-Rotatory Motor.** The boat experiments were performed to find the self-rotatory motion of Dt-NP, where 2 and 5 mg of Dt-NP were taken and trapped in a silt of paper boat; then, the boat was kept in a Petri dish with dimensions 1 cm height and 9 cm width. The rotation of MOIF was recorded by a high-resolution camera as a movie. The ST measurements before and after rotations were done using Survismeter.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04896.

Lattice parameters; DSC parameters; TGA thermal event data; Langmuir constant and separation factor at various temperatures; Freundlich isotherm constant at various temperatures; Dubinin–Radushkevich constant at various temperatures; Tempkin isotherm constant at various temperatures; structures of chosen dyes; SAXS pattern; powder XRD pattern; TGA/DTA curves; % dye adsorption; FTIR spectra; and XRD pattern (PDF)

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Notes
The author declares no competing financial interest.

**ACKNOWLEDGMENTS**

The author is grateful to the Kadi Sarva Vishwavidyalaya, Gandhinagar, and the Central University of Gujarat, India, for infrastructure support. The author is also thankful to K. M. Sachin, SCS, CUG, India, for conducting DSC and TGA experiments. The author is also thankful to SIAF, Chandigarh, Punjab University, India, for SAXS analysis and interpretation.

**REFERENCES**

(1) Okesola, B. O.; Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting self-assembled gels as smart materials for pollutant removal. *Chem. Soc. Rev.* 2016, 45, 4226–4251.

(2) Ameta, R. K.; Singh, M. Co(III) based surfactant complexes and their Dye, BSA and Free radical activities. *Heliyon* 2019, 5, No. e01568.

(3) Wang, C. C.; Li, J. R.; Lv, X. L.; Zhang, Y. Q.; Guo, G. S. Photocatalytic organic pollutants degradation in metal-organic frameworks. *Energy Environ. Sci.* 2014, 7, 2831–2867.

(4) Chen, C. C.; Ma, W. H.; Zhao, J. C. Semiconductor-mediated photodegradation of pollutants under visible-light irradiation. *Chem. Soc. Rev.* 2010, 39, 4206–4219.

(5) Khin, M. M.; Nair, A. S.; Babu, V. J.; Murugan, R.; Ramakrishna, S. A review on nanomaterials for environmental remediation. *Energy Environ. Sci.* 2012, 5, 8075–8109.

(6) Herney-Ramírez, J.; Vicente, M. A.; Madeira, L. M. Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Appl. Catal., B* 2010, 98, 10–26.

(7) Gonzalez-Olmos, R.; Holzer, F.; Kopinke, F. D.; Georgi, A. Indicators of the reactive species in a heterogeneous Fenton-like reaction using Fe-containing zeolites. *Appl. Catal., A* 2011, 398, 44–53.

(8) Ikezoe, Y.; Washino, G.; Uemura, T.; Kitagawa, S.; Matsu, H. Autonomous motors of metal–organic framework powered by reorganization of self-assembled peptides at interfaces. *Nat. Mater.* 2012, 11, 1081–1085.

(9) Marangoni, C. About the spread of drops of one liquid on the surface of another. *Ann. Phys. Chem.* 1871, 219, 337–354.

(10) Ikezoe, Y.; Fang, J.; Wasik, T. L.; Uemura, T.; Zheng, Y.; Kitagawa, S.; Matsu, H. Peptide Assembly-Driven Metal–Organic Framework (MOF) Motors for Micro Electric Generators. *Adv. Mater.* 2015, 27, 288–291.

(11) Hanczyc, M. M.; Toyota, T.; Ikegami, T.; Packard, N.; Sugawara, T. Fatty acid chemistry at the oil–water interface: Self-propelled oil droplets. *J. Am. Chem. Soc.* 2007, 129, 9386–9391.

(12) Sumino, Y.; Magome, N.; Hamada, T.; Yoshikawa, K. Self-running droplet: Emergence of regular motion from nonequilibrium noise. *Phys. Rev. Lett.* 2005, 94, No. 068301.

(13) Nakata, S.; Murakami, M. Self-motion of a camphor disk on an aqueous phase depending on the alkyl chain length of sulfate surfactants. *Langmuir* 2010, 26, 2414–2417.

(14) Bachand, G. D.; Hess, H.; Ratna, B.; Satir, P.; Vogel, V. Smart dust® biosensors powered by biomolecular motors. *Lab Chip* 2009, 9, 1661.

(15) Wang, W.; Duan, W.; Ahmed, S.; Mallouk, T. E.; Sen, A. Small power: Autonomous nano- and micromotors propelled by self-generated gradients. *Nano Today* 2013, 8, 531.

(16) Catchmark, J. M.; Subramanian, S.; Sen, A. Directed rotational motion of microscale objects using interfacial tension gradients continually generated via catalytic reactions. *Small* 2005, 1, 202.

(17) Sallapu, S. K.; Chattopadhyay, A. Induction of electromotive force by an autonomously moving magnetic boat. *Angew. Chem., Int. Ed.* 2014, 53, 1521.

(18) Mitsuuma, T.; Ikeda, K.; Gong, J. P.; Osada, Y. Controlled Motion of Solvent-Driven Gel Motor and Its Application as a Generator. *Langmuir* 2000, 16, 307.

(19) Ameta, R. K.; Rohit, R. K.; Akshay, V.; Chirag, R.; Nitin, K. S.; Man, S. [Fe(CN)₆]₃⁻/[Fe(CN)₆]⁴⁻ based Metal Organic Ionic Frameworks and impact of Fe²⁺/Fe³⁺ on Material-Medicinal-Properties. *J. Mol. Liq.* 2018, 268, 677–684.

(20) Duan, Y. T.; Sangani, C. B.; Ameta, R. K. Thermal, SEM, AFM, BET and biological analysis of newly synthesized Fe²⁺/Fe³⁺ based MOFs. *J. Mol. Liq.* 2019, 295, No. 111709.

(21) Saruchi, Kumar, V. Adsorption Kinetics and Isotherms for the Removal of Rhodamine B Dye and Pb²⁺ Ions from Aqueous Solutions by a Hybrid Ion-Exchanger. *Arab. J. Chem.* 2019, 12, 316–329.

(22) Ikikala, O.; Brinke, G. B. Hierarchical self-assembly in polymeric complexes: Towards fundamental materials. *Chem. Commun.* 2004, 19, 2131–2138.

(23) Hof, F.; Rebek, J., Jr. Molecules within molecules: Recognition through self-assembly. *Proc. Natl. Acad. Sci. U.S.A.* 2002, 99, 4775–4777.

(24) Gissot, A.; Campl, M.; Grinstaff, M. W.; Barthelemy, P. Nucleoside, nucleotide and oligonucleotide based amphiphiles: a successful marriage of nucleic acids with lipids. *Org. Biomol. Chem.* 2008, 6, 1324–1333.

(25) Brown, D. B. “Nitrogen- and oxygen-bonded nitrosyl Metal complexes of the nitroprusside ion. *Inorg. Chem.* 1975, 14, 2582–2584.

(26) Klang, P. H.; Alexander, E. L. X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed.; John Wiley & Sons: Hoboken, NJ, 1974.

(27) Mu, B.; Walton, K. S. Thermal Analysis and Heat Capacity Study of Metal Organic Frameworks. *J. Phys. Chem. C* 2011, 115, 22748–22755.

(28) Ameta, R. K.; Singh, M. NO and -CN directed Metal Organic Ionic Framework used for Concentration Responsive Adsorption of Organic Pollutant, Bovine Serum Albumin and 2,2-Diphenyl-1-Picrylhydrazyl. *ChemistrySelect* 2019, 4, 1922–1929.

(29) Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 1918, 40, 1361–1403.

(30) (a) Malik, P.; Ameta, R. K.; Singh, M. Preparation and characterization of bionanoemulsions for improving and modulating the antioxidant efficacy of natural phenolic antioxidant curcumin. *Chem.–Biol. Interact.* 2014, 222, 77–86. (b) Malik, P.; Ameta, R. K. A Green and Sustainable Tool for Physicochemical Analysis of Liquid Solutions: Survisimeter; CRC Press, 2019.

(31) Hooshary, H.; Sadeghi, R. Influence of Sodium Salts on the Micellization and Interfacial Behavior of Cationic Surfactant Dodecyltrimethylammonium Bromide in Aqueous Solution. *J. Chem. Eng. Data* 2015, 60, 983–992.

(32) Mittal, H.; Kumar, V.; Saruchi, Ray, S. S. Adsorption of methyl violet from aqueous solution using gumxanthan/Fe₂O₃-based nanocomposite hydrogel. *Int. J. Biol. Macromol.* 2016, 89, 1–11.

(33) Gupta, V. K.; Patania, D.; Agarwal, S.; Sharma, S. Removal of Cr(VI) onto Ficus carica biosorbent from water. *Environ. Sci. Pollut. Res.* 2013, 20, 2632–2644.