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Temperature-Dependent Emission and Turn-Off Fluorescence Sensing of Hazardous "Quat" Herbicides in Water by a Zn-MOF Based on a Semi-Rigid Dibenzochrysene Tetraacetic Acid Linker

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ABSTRACT: A zinc metal-organic framework, i.e., Zn-MOF (Zn-DBC), with ca. 27% solvent-accessible void volume was synthesized from a rationally designed tetraacid based on sterically insulated dibenzo[g,p] chrysene core; the latter inherently features concave shapes. Due to rigidification of the fluorophore in the MOF, Zn-DBC exhibits a respectable fluorescence quantum yield of ca. 30% in the solid state. The fluorescent and water-stable Zn-DBC MOF was found to display intriguing temperature-dependent emission behavior with an activation barrier of 1.06 kcal/mol for radiationless deactivation from the singlet-excited state. It is shown that the Zn-MOF can be employed as an efficient sensory material for detection of hazardous "quat" dicationic herbicides in water by diffusion-limited "turn-off" fluorescence. Due to confinement of the cationic guest analytes within the pores of the MOF, the fluorescence quenching via excited-state charge transfer mechanism is shown to depend on the molecular size of the analyte in addition to the redox potentials. Remarkably, Zn-DBC permits sensing of DQ_i a well-known toxic "quat" herbicide, with a detection limit as low as 2.8 ppm in water. The unique structural attributes of the Zn-MOF for highly efficient fluorescence sensing of toxic herbicides in water are thus exemplified for the first time.

■ INTRODUCTION

One of the serious problems plaguing humankind today is the ever-increasing pollution of our ecosystem.¹ The toxic chemicals emanating from industrial processes, traffic emission, plant/animal protection, chemotherapy, etc. range from radioactive wastes to hazardous gases, chemical side products, herbicides, pesticides, drugs, etc.¹ There is thus a dire need to develop (i) sensitive analytical methods to monitor a large variety of chemicals that are detrimental to the ecosystem and (ii) efficient technologies to get rid of hazardous chemicals distributed in high dilution from the environment. In particular, there has been a relentless quest to develop methods to monitor concentrations of herbicides in the environment; herbicides, also termed weed killers, are widely used in agriculture and horticulture.²⁻⁶ Among the most commonly used herbicides, "quat" herbicides containing a diquaternary bipyridyl motif, e.g., paraquat (PQ, 1,1'-dimethyl-4,4'-bipyridinium) dichloride and diquat (DQ, 6,7dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium) dibromide (cf. Chart 1), have gained tremendous attention as nonselective and contact as well as quick-acting weed killers.^{6,7} The mechanism of their action has been established. Accordingly, the bipyridinium motifs of the dicationic species can accept electrons available from the plant photosynthetic system I (PSI), leading to generation of radicals, which in turn react with molecular oxygen.⁷ Although they are employed as aquatic or nonaquatic weed killers, the "quat" herbicides are regarded as water pollutants. In fact, the lethal dose (LD50) of PQ is reported to be ca. 20–40 mg/kg of body weight in

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Chart 1. Molecular Structures of Bipyridinium Dicationic $Quats^a$



humans.⁶ Further, it is known that direct contact and exposure to PQ via inhalation, ingestion, ocular, skin routes, etc. results in dangerous health consequences, which may include pulmonary fibrosis, pulmonary edema, erythema, dermatitis, mouth ulceration, brain damage, etc.⁶ Although the toxicity of DQ is relatively lower than that of PQ (the oral values of DQ and PQ in rats are 231 and 150 mg/kg, respectively⁶), the former is known to (i) instigate corrosion of tissues of skin and gastrointestinal tract upon exposure and (ii) cause kidney failure and central nervous system toxicity upon ingestion.⁶ Thus, efficient methods that detect toxic "quat" herbicides are of immediate relevance.

Molecular recognition of "quat" type dicationic systems by crown ethers involving supramolecular host-guest chemistry has long been known.⁸⁻¹⁵ The standard and traditional method for their detection, however, is spectrophotometry of their radical cations. This method necessitates meticulous experimental execution due to rapid oxidation of the latter by the dissolved molecular oxygen.⁷ Therefore, a number of laborious and time-consuming analytical methods, e.g., chromatography, capillary electrophoresis, immunoassay, etc., have been developed.⁷ However, the requirement of extremely sophisticated and expensive instruments in these techniques limits their practical applications. In this context, fluorescencebased sensing should provide the best possible analytical method in terms of sensitivity, speed, and portability. Only a few fluorescent chemosensors have been reported for detection of PQ and DQ^{7,16–19} some of them, for instance, are porphyrin-based receptors,^{16,17} coumarin-450-functionalized metallodendrimers,¹⁸ pyrene-appended bis(*m*-phenylene)-32crown-10 host,¹⁹ pyrene derivatives,⁷ etc. Two important drawbacks with these systems include (i) fluorescence sensing in organic solvents rather than in an aqueous medium, which completely precludes practical on-field detection of herbicides, and (ii) the inability of most of systems to distinguish between PO and DO.

Stimuli-responsive luminescent materials have gained enormous attention due to their emerging security applications, e.g., sensing, information storage, encryption, anticounterfeiting, etc.^{20–23} Although a variety of smart luminescent materials have been reported so far,^{21–23} there has been a surge of interest over the past decade to explore functional applications of luminescent metal–organic frameworks, termed popularly as LMOFs.^{24–27} The latter have been widely exploited for chemosensing applications due to several advantages such as tunabibility of structures based on ligand variations, framework stability, permanent porosity, high surface area, high thermal and chemical stability, functionality, etc.^{28–40} The photoluminescence in LMOFs is known to result from one or more of the following: organic linkers, metal ions (e.g., lanthanide ions), both organic linkers and metal ions at the same time, guest species bound in the porous MOFs, and scintillations.²⁴ Regardless of the origin of luminescence, LMOFs have been shown to be highly efficient fluorescence sensors for detection of small molecules, volatile organic compounds, explosive nitroaromatics, odorants, transition metal ions, temperature, pH, bioactive molecules, etc.^{24–40}

In continuation of our endeavors to develop functional MOFs in a "bottom-up" approach involving de novo design of organic fluorescent systems such as pyrene, bianthryl, triptycene, etc.,⁴¹⁻⁵¹ we designed a tetracarboxylic acid linker based on a twisted dibenzo[g,p]chrysene core, namely, 2,7,10,15-tetrakis[2,6-dimethyl-4-(α -carboxy)methoxyphenyl]-dibenzo[g,p]chrysene (H₄DBC), Figure 1. Our rationale for



Figure 1. Structure of the semirigid tetracarboxylic acid linker H_4DBC . Note that the dibenzo[g,p]chrysene (DBC) core is shown in blue.

the design of this linker was based on the following considerations. First, the linker H₄DBC is characterized by a rigid dibenzo [g,p] chrysene core and orthogonally oriented flat aromatic rings; the methyl groups installed strategically ensure inflexibility of the system. Such a structure features concave shapes, which have been demonstrated to facilitate guest inclusion in the solid state to permit access to multicomponent crystals.⁵²⁻⁵⁴ Second, the 4-connecting linker also features carboxymethyl groups at the periphery of the four orthogonal aromatic rings. The peripheral flexibility in the otherwise rigid linker may permit metal-assisted self-assembly successfully to afford MOFs without any structurally imposed constraints. Third, given the well-known excited-state properties of dibenzo[g,p]chrysene systems and their extensive applications in the development of luminescent materials,^{55–57} the LMOFs with d¹⁰ metal ions should be compelling materials for fluorescence sensing applications. Herein, we report that the self-assembly of H_4DBC in the presence of Zn^{2+} leads to a porous, water-stable, and fluorescent Zn-MOF, namely, Zn-DBC. The latter is shown to exhibit intriguing temperaturedependent emission behavior. The respectable fluorescence emission of Zn-DBC has been exploited for sensing of the dicationic "quat" herbicides. It is shown that the Zn-MOF is selective in that a distinction can be made between dicationic bipyridinium salts, solely based on size and redox properties of the analytes.

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Scheme 1. Synthesis of H₄DBC^a



^{*a*}Note that the dibenzo[g,p]chrysene (DBC) core is shown in blue.



Figure 2. (a) The coordination modes of the carboxylate groups of DBC and (b) the tetrahedral coordination environment of Zn^{2+} in Zn-DBC. Notice the twisted structure of the dibenzo[*g,p*]chrysene core in (a). (c) Crystal packing diagram of Zn-DBC down the *c* axis; notice that Zn, O, and N atoms are represented in cyan, red, and blue, respectively. The hydrogen atoms in (a–c) and the solvent molecules (water and DMF) in (c) have been omitted for clarity. (d) Simplified topology of the 3-nodal net of Zn-DBC represented down 001 direction.

RESULTS AND DISCUSSION

Synthesis of H₄DBC. The target linker H_4DBC was synthesized according to the route shown in Scheme 1. To begin with, 1,1,2,2-tetraphenylethene was brominated with neat Br_2 to access 1,1,2,2-tetrakis(4-bromophenyl)ethene

(1).⁵⁸ The latter was converted to 2,7,10,15tetrabromodibenzo[g,p]chrysene (2) by treatment with FeCl₃. Suzuki coupling reaction of 2 with 2,6-dimethyl-4methoxyphenylboronic acid under Pd(0)-catalyzed conditions furnished 2,7,10,15-tetrakis(2,6-dimethyl-4-methoxyphenyl)-

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Figure 3. Location of the DMA cations (represented as blue spheres) in the voids of Zn-DBC. Notice the strong N–H···O hydrogen bonding $(d_{N\cdots O} = 2.76 \text{ Å})$ of the DMA cation with the oxygen atom of one of the carboxylate groups of DBC.



Figure 4. (a) Steady-state fluorescence spectra ($\lambda_{ex} = 350 \text{ nm}$) of Zn-DBC and H₄DBC in the solid state at rt. Notice that the emission spectra ($\lambda_{em} = 420 \text{ nm}$) are identical for both cases. The insets show the photographs of the bulk crystals of pristine Zn-DBC under regular light (top) and blue fluorescence of the latter when exposed to 350 nm UV light (bottom). (b) Time-resolved fluorescence decay trace ($\lambda_{ex} = 308 \text{ nm}$) of Zn-DBC (dispersed in water) and H₄DBC (0.5 μ M in DMSO) at rt, cf. SI.

dibenzo[g,p]chrysene (3) in 82% yield. The resultant tetraanisyl derivative 3 was demethylated with BBr₃ to afford 2,7,10,15-tetrakis(2,6-dimethyl-4-hydroxyphenyl)dibenzo[g,p]chrysene (4) in almost quantitative yield. The tetraphenol 4 was subsequently subjected to alkylation with ethyl bromoacetate under basic conditions to get hold of 2,7,10,15tetrakis[2,6-dimethyl-4-(α -carboethoxy)methoxyphenyl]dibenzo[g,p]chrysene (5) in 74% yield. Base hydrolysis of the tetraester 5 led to the target tetraacetic acid H₄DBC in a nearquantitative yield.

Synthesis and X-ray Single Crystal Structure Analysis of Zn-DBC. Treatment of the solution of H₄DBC with $Zn(NO_3)_2$ ·6H₂O in DMF–DMSO–H₂O (3:1:1, ν/ν) solvent mixture at 90 °C in a tightly capped glass vial under autogenous solvothermal conditions led to flaky crystals of Zn-DBC after 2 days, cf. SI. Single crystal X-ray diffraction data collection and subsequent structure determination revealed that the crystals belong to the orthorhombic system with the *Pbcn* space group, cf. Table S1 in the SI. The asymmetric unit was found to contain 1.5 Zn²⁺ metal ions, one molecule of DBC linker, and three guests, namely, one uncoordinated water molecule, one uncoordinated DMF molecule, and one dimethylammonium (DMA) cation, cf. Figure S1. Thus, the chemical formula of the asymmetric repeating unit in Zn-DBC is $[Zn_{1.5}(DBC)\cdot(H_2O)\cdot(Me_2NCHO)\cdot Me_2NH_2]$. The crystal structure (cf. Figure 2) analysis shows that one molecule of DBC linker accounts for four units of negative charge, which is compensated by 1.5 units of Zn²⁺ ions and one DMA cation, such that the overall charge neutrality is maintained. Indeed, the DMA cation is found to be stabilized inside the voids of the MOF via strong N–H···O hydrogen bonding ($d_{N...O} = 2.76$ Å) with the oxygen atom of one of the carboxylate groups of DBC, cf. Figure 3. The structural analysis also shows that the Zn²⁺ metal ions in the framework exist in a tetrahedral geometry, whereby they are coordinated to four oxygen atoms of four carboxylate groups of DBC, cf. Figure 2. Thus, each Zn²⁺ metal ion behaves as a 4-connecting node. Figure 2 also shows the coordination motif of the tetracarboxylate DBC, which behaves as a 4-connecting linker. Thus, the assembly of Zn²⁺ ions and DBC leads a 3D porous anionic framework structure with the channels propagating down the c axis, Figure 2. Insofar as the central chrysene core is concerned, it is found to be significantly twisted.

The crystal lattice of Zn-DBC is found to be significantly porous with the dimensions of the pores ranging from ca. 8.4 to 17.9 Å, cf. Figure S3. PLATON⁵⁹ analysis shows that the



Figure 5. (a) Temperature-dependent fluorescence spectra of Zn-BDC in water. (b) Contour plot of the fluorescence intensity (I_{rel}) at 420 nm as a function of temperature. (c) Monoexponential diminution of quantum yields of fluorescence with increasing temperature. (d) Arrhenius-type plot for determination of activation energy for the activation-controlled nonradiative pathway.

solvent-accessible volume in the crystal lattice after removal of the two guest solvent molecules, i.e., water and DMF, is ca. 27%. The void volumes in the crystal lattice are generated in close proximity of the dibenzo[$g_{,P}$]chrysene core between the concave shapes, cf. Figure S4. Topological analysis using the TOPOS⁶⁰ program reveals that the 3D framework of Zn-DBC corresponds to a new topology with a point symbol of $\{6^2.8^4\}\{6^2.8\}2\{6^3.8^7\}2$. The framework corresponds to a three-centered nodal net, such that the stoichiometry is (3-c)2(4-c)(5-c)2. Figure 2 shows a simplified topological network of the three-centered nodal net of Zn-DBC down the 001 direction in a standard representation.

The synthesis of Zn-DBC could be scaled up quite readily. The material synthesized on a bulk scale was established to be identical to that of the X-ray determined single crystal by comparison of its PXRD profile of the pristine Zn-DBC with that simulated for the structure obtained by single crystal X-ray analysis, vide infra. The thermal stability of the MOF was established from TGA, which reveals solvent loss up to 350 °C corresponding to ca. 30% followed by decomposition, cf. Figure S7. Notably, the crystals of Zn-DBC were found to be remarkably stable both when immersed in water for 2 days at room temperature (rt) and when heated at 85 °C in water for 1 day, as revealed by PXRD analysis, vide infra. The stability of the MOF was further corroborated by a leaching experiment,

which reveals that the linker does not leach out from the MOF upon immersion of the crystals in water for 2 days at rt, cf. SI.

Temperature-Dependent Fluorescence Properties of Zn-DBC. The crystals of Zn-DBC were found to display brilliant blue emission upon exposure to UV light in the solid state. In Figure 4 is shown the solid-state fluorescence spectrum of Zn-DBC with an emission maximum at 420 nm $(\lambda_{\text{exc}} \text{ at } 350 \text{ nm})$; the full width at half-maximum (fwhm) of the emission was found to be 46 nm. The solid-state fluorescence emission spectrum of the precursor organic linker H₄DBC was found to be identical to that of Zn-DBC, cf. Figure 4. This is not surprising given that the orthogonally oriented aryl rings at the four corners of the dibenzo [g,p] chrysene moiety sterically insulate the fluorescent dibenzo[*g*,*p*]chrysene core, as has been found for an analogous system based on tetraarylpyrene;⁴⁵ fluorescence quantum yields for Zn-DBC and H₄DBC were determined in the solid state by an integrating sphere setup at 298 K to be ca. 30% and 16%, respectively. Significant enhancement of the fluorescence quantum yield of Zn-DBC when compared to that of the precursor linker H₄DBC should be reconciled from differences in their conformational rigidities and highly ordered structure of the dibenzo [g,p] chrysene fluorophore within the framework; structural rigidity is wellknown to attenuate nonradiative pathways that depopulate the singlet-excited state.45,61 This was further corroborated by time-resolved fluorescence studies using time-correlated single



Figure 6. (a) Changes in the UV–vis absorption spectra of the supernatant solution of MB in DMF with time in the presence of added crystals of Zn-DBC. Insets show the color of the supernatant solution of MB before and after 24 h of dye adsorption. (b) A plot showing the gradual decrease in absorbance at 664 nm of the MB solution with time. Notice the blue coloration of MOF crystals after 24 h of MB absorption in the inset; the photograph of the blue crystals was taken after thoroughly washing the crystals with DMF to remove any dye adhering to the surface.

photon counting (TCSPC), which reveal that the singlet lifetime of Zn-DBC (${}^{1}\tau = 7.8 \text{ ns}$) is comparatively longer than that observed in the case of H₄DBC (${}^{1}\tau = 5.0 \text{ ns}$), cf. Figure 4 and SI. This is a characteristic feature of LMOFs in which the fluorophoric linkers lose some degree of torsional freedom.^{45,61}

To further probe the nonradiative pathways that depopulate the singlet-excited state of Zn-DBC, the influence of temperature on the steady-state fluorescence properties was investigated for the crystals of Zn-DBC suspended as a dispersion in water, cf. Table S3. Interestingly, the fluorescence intensity of Zn-DBC was found to depend remarkably on temperature; of course, the emission maximum (420 nm) was found to remain affected with temperature. As shown in Figure 5, one observes a drastic decrease in the fluorescence intensity $(\lambda_{\text{max}} = 420 \text{ nm})$ with increasing temperature. Buoyed by this interesting observation, quantum yields of fluorescence (Φ_f) were determined for the aqueous suspension of the MOF at different temperatures in the range of 278-358 K; the stability of the MOF crystals in water at room temperature as well as at elevated temperatures was ensured to be unaffected by PXRD analysis, vide infra. The quantum yield was found to decrease rapidly from 35.5% at 278 K to 30% at 298 K and 25.4% at 358 K, cf. Table S3. The diminution in the quantum yield of fluorescence with absolute temperature (T in K) of the medium could be easily fitted to a monoexponential function with an excellent goodness-of-fit ($R^2 = 0.99$), cf. Figure 5.

On the basis of the definition of $\Phi_{\rm f}$ and the general assumption that the radiative decay constant $(k_{\rm r})$ is independent of temperature, $^{62-64}$ it could be reasoned that the influence of temperature on $\Phi_{\rm f}$ values must arise from some competitive activation-controlled nonradiative pathways $(k_{\rm nr})$. In fact, the mechanistic insights of the temperature dependence of $\Phi_{\rm f}$ due to operation of such activation-controlled radiationless processes have been comprehensively established by several groups.^{63,64} It is needless to mention that the relation of $\Phi_{\rm f}$ and T (K) can be expressed in the form of an Arrhenius-type equation (eq 1 and eq 2) as shown below:

$$\frac{1}{\Phi_{\rm f}} = \left(1 + \frac{k_{\rm nr}}{k_{\rm r}}\right) = 1 + \left(\frac{1}{k_{\rm r}}\right) k_{\rm nr}^{\rm o} \exp\left(\frac{-\Delta E}{RT}\right) \tag{1}$$

$$\ln\left\{\left(\frac{1}{\Phi_{\rm f}}\right) - 1\right\} = \ln\left(\frac{k_{\rm nr}^{\rm o}}{k_{\rm r}}\right) - \frac{\Delta E}{RT}$$
⁽²⁾

where $k_{\rm nr}^{0}$ is the pre-exponential factor and ΔE is the activation energy.

Following eq 2, the plot of $\ln\{(1/\Phi_f) - 1\}$ versus 1/T is indeed found to be linear with a respectable correlation of R^2 = 0.97, cf. Figure 5. Accordingly, the activation energy (ΔE) calculated from the slope of this linear fit turned out to be 1.06 kcal/mol for the radiationless deactivation of the singletexcited state of Zn-DBC. This clearly suggests that some activation-controlled radiationless relaxation mechanism is operative in the singlet-excited state of the latter. In this regard, the fact that the diminution in fluorescence intensity is not a consequence of the loss of crystallinity of the material was unambiguously established based on (i) similarity of the PXRD profiles of the material after heating/cooling cycles, vide supra, and (ii) the observation that the emission spectrum of the MOF suspension at 298 K is similar to the one recorded for the suspension heated at 358 K and cooled to 298 K, cf. Figure S8.

The observed temperature-dependent process should be reconciled from the structural features of Zn-DBC. As mentioned earlier, the carboxymethyl groups at the periphery of the four orthogonal aromatic rings offer structural flexibility to the DBC linker such that the latter behaves as a semirigid linker. Thus, one of the probable reasons behind the activation-controlled radiationless process could be torsional rotations of the conformationally flexible ether moieties (-O- CH_2 -), which are substituted at the *para* positions of the four orthogonally oriented aromatic rings in DBC linker. A similar instance of temperature-dependent torsional rotation and hence an activation-controlled fluorescence property has been reported for coumarin-151 dye; for the latter, the flipflop motion of the 7-amino group has been reported to serve as a nonradiative deactivation channel for the singlet-excited state in a nonpolar solvent.⁶³ Although the excited-state properties of LMOFs have been a subject of extensive investiga-tion, $^{24-40,43,45-47,50}$ the temperature-dependent fluorescence emission of LMOF due to an activation-controlled radiationless process is hitherto unknown.

"Turn-Off" Fluorescence Sensing of "Quat" Herbicides by Zn-DBC in Water. We were encouraged by respectable fluorescence quantum yield, appreciable void volume of ca. 27% in the crystals, and remarkable water stability of Zn-DBC to explore guest binding by fluorescence signaling. It was surmised that the electron-rich aromatic dibenzo[g,p]chrysene fluorophore that is part of Zn-DBC should relay information about its interaction with any electron-deficient (and π -acceptor) aromatic guest species through changes in fluorescence. However, the fluorescence of Zn-DBC was found to be unaffected whatsoever in the presence of various nitroaromatic compounds, e.g., nitrobenzene, 1,3-dinitrobenzene, 2,4,6-trinitrotoluene, etc.; the latter are well-known strong π -acceptor analytes, which have been employed routinely for "turn-off" fluorescence quenching of LMOFs.^{26,27,43} We reasoned that the lack of fluorescence quenching is presumably due to the anionic nature of the Zn-DBC framework, which warrants that the counter cations be located in the lattice for overall charge neutrality. Indeed, the DMA counter cations, as mentioned earlier, are found to be stabilized within the voids. The counter cations in the crystals of Zn-DBC may in principle permit transport of guests that are cationic in nature and capable of replacing the DMA cations in the voids. In other words, we surmised that the exchange of neutral and anionic guests in the anionic framework of Zn-DBC should be precluded.

To unambiguously establish the ability of the Zn-DBC crystals to undergo postsynthetic exchange (PSE)^{44,45} of the DMA cations, the MOF crystals were dispersed in the solution of a cationic dye, namely, methylene blue (MB). Indeed, the blue color of MB was found to fade with time in the presence of the MOF, cf. Figure 6. The gradual dye absorption process was also monitored by recording UV-vis absorption spectra of the supernatant solution of MB; as shown in Figure 6, the absorbance at the λ_{max} of MB (i.e., 664 nm) was found to undergo regular diminution over a period of 24 h. The dye exchange process was also corroborated by blue coloration of the colorless MOF crystals, which could be readily made out by the naked eye, cf. Figure 6. However, such a coloration was not observed whatsoever, when the MOF crystals were dispersed in the solutions of an anionic dye, namely, bromophenol blue (BB), and a neutral dye, namely, nile red (NR), even after 4 days, cf. Figure S15. It thus emerges that the anionic framework of Zn-DBC permits selective transportation of the cationic guests by exchanging DMA counter cations while precluding anionic and neutral guests. Additionally, the adsorption of cationic dye, e.g., MB, could be deadsorbed in a reversible manner by immersing the colored MOF crsytals in DMF containing ammonium chloride; the colorless MOF crystals reappeared slowly with the DMF turning intensely colored.

With the postsynthetic cation exchange in Zn-DBC established, we immediately sought to investigate the sensing of bipyridinium dicationic species and, hence, the "quat" herbicides. Thus, we comprehensively examined the binding/ sensing of four bipyridinium dicationic species as shown in Chart 1, namely, 1,1'-dimethyl-4,4'-bipyridinium (PQ), 6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium (DQ), 1,1'-dimethyl-2,2'-bipyridinium (OQ), and 1,1'-bis(3,5-di-tert-butyl-benzyl)-4,4'-bipyridinium (TBPQ); the analytes were used in the form of their hexafluorophosphate salts (cf. SI) with the advantage that the PF₆⁻ counteranion is non-coordinating in nature to interfere with the studies carried out.^{7,16-19} To begin

with, the fluorescence of the crystals of Zn-DBC suspended as a dispersion in water was examined in the presence of each of these analytes; of course, the structural integrity of the Zn-DBC crystals upon dispersion in water with and without the dicationic analytes was established to be intact by PXRD analysis, cf. Figure 7.



Figure 7. PXRD profiles: (a) simulated for the X-ray determined single crystal structure, (b) pristine MOF crystals synthesized in bulk, (c) crystals immersed in distilled water for 2 days, which were subsequently dried, (d) crystals immersed in distilled water and heated at 85 °C in water for 1 day, which were subsequently cooled to rt and dried, and (e) crystals immersed in a 5 mM aqueous solution of $DQ(PF_6)_2$, which were subsequently washed with water and dried.

With the addition of an increasing concentration of each of the dications, a gradual decrease in the fluorescence intensity of the aqueous suspension of Zn-DBC was observed, cf. Figure S9. A representative plot of fluorescence quenching titration of Zn-DBC with $DQ(PF_6)_2$ at rt is shown in Figure 8. Remarkably, the sensing of the dicationic analytes by the aqueous suspension of the MOF by fluorescence quenching can be readily made out with the naked eye, cf. Figure 8. The steady-state fluorescence quenching data for all four analytes could be readily subjected to a linear regression analysis following the Stern-Volmer plot. As established from timeresolved fluorescence titration experiments, the nature of quenching of fluorescence of Zn-DBC by the cationic analytes turns out to be dynamic, cf. Figure S10. Given that the dicationic analytes themselves do not absorb at the $\lambda_{ex} = 350$ nm, the observed fluorescence quenching of MOF with dicationic analytes is not contributed by competing light absorption due to the latter, cf. SI.

The Stern–Volmer quenching constants (K_{SV}) thus derived for all the analytes follow the order DQ (500 M⁻¹) > PQ (110 M⁻¹) > OQ (36 M⁻¹) > TBPQ (4 M⁻¹), cf. Table 1. The singlet lifetime of Zn-DBC in water (${}^{1}\tau = 7.8$ ns) determined from TCSPC (vide supra) was employed to evaluate absolute bimolecular quenching rate constants ($k_q = K_{SV}/{}^{1}\tau$) for each of the analytes, cf. Table 1. Thus, the order of quenching rate constants (k_q 's, × 10¹⁰ M⁻¹ s⁻¹) turns out to be DQ (6.41) > PQ (1.41) > OQ (0.46) > TBPQ (0.051). How can this observed order of fluorescence quenching data for the cationic quenchers be rationalized?

The fact that aromatic cations (acceptor) quench the fluorescence of e-rich fluorophores (donors) via excited-state charge transfer process by diffusion limited rates is well



Figure 8. (a) Quenching of the fluorescence intensity of Zn-DBC with increasing concentration of $DQ(PF_6)_2$ in water ($\lambda_{ex} = 350$ nm) at rt. Notice the changes in the fluorescence images (insets) of the aqueous dispersion of the MOF before and after quenching titration. (b) Corresponding Stern–Volmer quenching plot with increasing concentration of DQ.

Table 1. Fluorescence Quenching Data of Zn-DBC for Various Dicationic Analytes at rt

quencher ^a	$E_{\rm red}^{\circ} (V_{\rm V} vs_{\rm SCE})^{b}$	${K_{\rm SV} \choose {\rm M}^{-1}}$	$k_{q} (10^{10} M^{-1} s^{-1})$	η (%) at 12 mM conc. of quencher
DQ	-0.35	500	6.41	95.2
PQ	-0.45	110	1.41	55.2
OQ	-0.60	36	0.46	40.6
TBPQ	-0.37	4	0.051	1.7

^{*a*}The analytes were used in the form of their hexafluorophosphate salts. ^{*b*}The reduction potential in each case is reported for the first one-electron reduction (e.g., $E_{DQ^{2+}/DQ^{*+}}$) in deaerated acetonitrile using 0.1 M n-Bu₄NPF₆ as the supporting electrolyte. The first one-electron reduction potentials determined from differential pulse voltammetry (DPV) using Ag/AgCl as the reference electrode and platinum as the working electrode (scan rate = 20 mVs⁻¹) are eventually referenced to SCE by subtracting 45 mV from the values obtained versus the Ag/AgCl electrode, cf. Figure S16 and Table S5.

established.⁶⁵ In general, the quenching of fluorescence becomes progressively facile for more and more electrondeficient analytes for which the lowest-unoccupied molecular orbitals (LUMOs) are located between the valence band (VB) and conduction band (CB) of electron-rich MOFs.^{43,66–68} Photoexcitation leads to electron transfer from CB of the donor to the LUMO of the e-deficient analyte, leading to gradual diminution of fluorescence intensity due to increasing nonradiative decay rate.43,66-68 We have demonstrated this in our recent studies on LMOFs based on pyrene-tetracarboxylic acids.^{43,45} The observed order of k_{q} for fluorescence quenching of Zn-DBC by the bipyridinium dications in Chart 1 should, in principle, be traced to a bimolecular quenching process occurring as a consequence of charge transfer from the excited state of DBC fluorophore (donor) to the bipyridinium dications (acceptor); the latter becomes thermodynamically more favorable with increasing π -acceptor nature, and hence electron-deficiency of the analytes. Notably, the first oneelectron reduction potentials (E_{red}° vs SCE) of the bipyridinium salts measured from differential pulse voltammetry (DPV) analysis are found to follow the trend OQ (-0.60V) < PQ (-0.45 V) < TBPQ (-0.37 V) < DQ (-0.35 V), cf. Table 1, Figure S16 and Table S5. Interestingly, the LUMO energies of these dicationic salts, determined from their onset potentials of reduction, follow the trend OQ (-3.935 eV) >PQ(-4.085 eV) > TBPQ(-4.175 eV) > DQ(-4.205 eV), cf.Table S6. This trend suggests that in this series, OQ has the lowest reduction potential and hence highest LUMO energy such that this dication is the most difficult species to undergo one-electron reduction to the corresponding radical cation.



Figure 9. (a) A plot of quenching efficiency (η %) versus concentration of each of the dicationic quenchers. (b) A plot showing a similar trend in k_q and η % (at 12 mM concentration) for the dicationic quenchers; the reduction potentials versus SCE are also shown in green for the analytes.

Similarly, DQ with the highest reduction potential and hence lowest LUMO energy should be the easiest to reduce to the corresponding radical cation. The observed trend in the k_{q} $(10^{10} \text{ M}^{-1} \text{ s}^{-1})$ values, as mentioned before, is DQ (6.41) > PO (1.41) > OO (0.46) > TBPO (0.051). Thus, a ready correlation is observed for k_q with reduction potentials of the dications with the exception of TBPQ. In other words, for the three dications DQ, PQ, and OQ, the fluorescence quenching rates are diffusion limited and are guided by their reduction potentials, i.e., the higher the electron deficiency of the analyte, the greater is the value of k_{q} , cf. Figure 9. For example, the highest fluorescence quenching rate $(6.41 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ is observed for DQ, which has the highest E_{red}° (vs SCE) of -0.35 V, while the quenching rates are comparatively lower for PQ $(1.41 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ and OQ $(0.46 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ with $E_{\rm red}^{\circ}$ values of -0.45 V and -0.60 V, respectively. In stark contrast, one observes that TBPQ with almost a similar reduction potential (-0.37 V) as that of DQ shows the lowest fluorescence quenching rate of 5.1×10^8 M⁻¹ s⁻¹. The reason as to why TBPQ with a respectably high reduction potential exhibits such an unusually low fluorescence quenching rate should be reconciled from structural attributes. This is evidently due to the fact that TBPQ with two 3,5-di-tertbutylbenzyl groups is enormously large structurally such that it is not suitable to transport into the relatively smaller voids of the MOF to exchange the DMA cations. This clearly points to the fact that the fluorescent Zn-DBC MOF is size-selective in terms of cationic guest exchange.

To further corroborate the relative abilities of the dications to quench the fluorescence of Zn-DBC, change in the fluorescence quenching efficiency (η %) at rt was monitored with increasing concentration of each of the dications, cf. SI. As shown in Figure 9, η increases progressively with increasing concentrations of the quenchers in that the highest η value is observed for DQ. For instance, at a concentration of ca. 12 mM, one observes a quenching efficiency of ca. 95.2% for DQ, while the same turns out being ca. 55.2% for PQ, 40.6% for OQ, and only 1.7% for TBPQ, cf. Table 1. Thus, the trend of η values is the same as that observed for k_{α} , cf. Figure 9. In other words, for dications of almost similar size, i.e., DQ, PQ, and OQ, the fluorescence quenching rate/efficiency is dictated by the electron deficiency, i.e., reduction potential of the analyte. However, for TBPQ, a quencher with almost similar reduction potential as that of DQ but bulky in size, the lowest fluorescence quenching rate/efficiency is observed, understandably due to difficulty in its transportation to the fluorophoric dibenzochrysene sites in the crystals due to relatively smaller voids.

It is noteworthy that the Zn-DBC MOF offers a unique advantage over the precursor organic linker H₄DBC in terms of fluorescence sensing of the bipyridinium dications. For instance, the latter could be sensed by the MOF suspension in water without employing any organic solvent, whereas the same was not possible in the case of the organic linker due to its complete insolubility and obvious aggregation in aqueous media. For further comparison of the advantageous attributes of the MOF versus organic system, fluorescence quenching experiments were carried out with a model system, namely, tetramethoxy ether of dibenzo[g,p]chrysene, i.e., 3 in Scheme 1, which is devoid of carboxylic acid functionalities at the periphery. Notably, the reason for employing the tetraether 3 instead of the tetra-acid H₄DBC itself for quenching studies is that the latter was found to undergo aggregation even at a

concentration as low as 1 μ M in DMSO, due possibly to hydrogen-bonding interactions involving the carboxylic acid functionalities in the presence of water; complicated/abrupt fluorescence intensity changes were observed while carrying out the fluorescence titrations with aqueous solutions of the dications. Steady-state fluorescence quenching experiments were thus carried out with the solution $(1 \mu M)$ of 3 in DMSO $(\lambda_{ex} = 350 \text{ nm}; \lambda_{em} = 420 \text{ nm})$ and aqueous solutions of the dicationic analytes, cf. Figures S12 and S13 and Table S4. On the basis of the Stern-Volmer quenching constants thus derived and the singlet lifetime of 3 ($^{1}\tau$ = 7.0 ns) determined from a time-resolved study (Figure S11), bimolecular quenching rate constants (k_q) were calculated for the dications. The trend of k_q (10⁹ M⁻¹ s⁻¹) for fluorescence quenching of 3 thus turned out to be DQ (10.6) > TBPQ (8.0) > PQ (5.4) > OQ(3.9), which is in accordance with their redox potentials. This suggests that for the model system, the fluorescence quenching is dictated solely by the e-deficiency of the dicationic analytes and that the model system can not distinguish the latter by their size; in other words, a sterically bulky analyte (TBPQ) is sensed with a much faster rate than analytes of smaller size (PQ and OQ).

Overall, Zn-DBC MOF offers the following advantages over the pure organic system 3 in terms of fluorescence sensing of dicationic analytes: (i) The unique stability of the MOF in water permits sensing of the analytes in aqueous medium without the need of an organic solvent. (ii) Bimolecular quenching rates are much faster in case of the MOF (ca. 10¹⁰ M^{-1} s⁻¹) as compared to the model system (k_q on the order of 10^9 M⁻¹ s⁻¹), which points to better sensitivity of detection. (iii) Fluorescence sensing of the analytes with the MOF is controlled by both size and reduction potential, while for the model system, the same is dictated only by the reduction potential, and (iv) the MOF can distinguish between the two herbicides DQ and PQ better than the model system in terms of the ratio of fluorescence quenching rate constants, i.e., $k_{a}(DQ)/k_{a}(PQ)$; the latter are ca. 4.5 and 2.0 for the MOF and model system, respectively. Two plausible reasons²⁴⁻²⁷ for the observed contrasting differences between MOF and the organic model system are (i) rigidification of the fluorophore when present as part of the MOF and (ii) confinement of the cationic guests within the pores of certain size/shape.

To assess the sensitivity limits of Zn-DBC for detection of the dicationic herbicides, fluorescence quenching experiments were carried out at very low concentrations of DQ, a representative case, in water, cf. Figure S14. Accordingly, a plot of quenching efficiency $(\eta\%)$ versus the quencher concentration reveals that the minimum concentration for detection of DQ is ca. 15 μ M, cf. Figure S14. In other words, the Zn-DBC MOF permits fluorescence sensing of DQ with a detection limit of ca. 2.8 ppm. As mentioned at the outset, although LMOFs with tunable luminescence properties have been employed for diverse sensing applications, they have heretofore been not explored quite inexplicably for fluorescence detection of toxic herbicides. The results unveiled herein offer intriguing mechanistic insights of temperature-dependent emission behavior of an LMOF based on the dibenzo $[g_p]$ chrysene fluorophore and application of the latter for "turn-off" fluorescence sensing of toxic herbicides in water with a detection limit of ca. 2.8 ppm. The results thus constitute an invaluable addition to the gamut of ever-increasing applications being uncovered for MOFs in general.

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CONCLUSIONS

A fluorescent dibenzo [g,p] chrysene-based organic tetracarboxylic acid linker H₄DBC with inherent concave features was rationally designed and synthesized to access porous LMOFs via metal-assisted self-assembly. Treatment of H₄DBC with Zn(NO₃)₂ yielded a water-stable Zn-MOF, namely, Zn-DBC, with a solvent-accessible void volume of ca. 27% in the crystal lattice. The crystals of Zn-DBC exhibit fluorescence emission with a quantum yield of 30% and were found to exhibit intriguing temperature-dependent emission behavior with an activation barrier of 1.06 kcal/mol for radiationless deactivation of the singlet-excited state; the temperature-dependent deactivation should be reconciled from torsional rotations of the conformationally flexible ether moieties of DBC. It is shown that the fluorescent Zn-DBC MOF can be applied for "turn-off" sensing of toxic dicationic "quat" herbicides in water with diffusion-controlled rates. The quenching of fluorescence of the Zn-MOF has been rationalized based on exchange of the cationic DMA guests in the voids of the MOF crystals by the "quat" dicationic species. The latter, being extremely electronpoor aromatic systems, are proposed to be involved in chargetransfer interactions with the protected and e-rich singletexcited state of dibenzo [g,p] chrysene fluorophore of DBC to account for the observed quenching. It is further shown that the "turn-off" fluorescence quenching of Zn-DBC is dictated both by size and redox potential of the cationic guests. Indeed, Zn-DBC MOF is shown to efficiently distinguish between two common herbicides, DQ and PQ. The limit for sensing of DQ by Zn-DBC is remarkably low (2.8 ppm). The latter has been attributed to rigidification of the fluorophore in the MOF and confinement of the cationic analytes within the pores. Although LMOFs have been immensely explored for diverse sensing applications, the presently uncovered results constitute a first-ever demonstration of LMOF for "turn-off" sensing of toxic "quat" herbicides in water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00307.

Synthetic procedures for linker and MOF, details of Xray crystallography, table of crystal data and refinement, packing diagrams, PLATON analysis, topology, IR spectra, TGA profile, details of steady-state and timeresolved fluorescence spectroscopy, temperature-dependent fluorescence data, synthesis of hexafluorophosphate salts of bipyridinium dications, fluorescence quenching titration experiments with MOF and tetramethoxy ether model, determination of sensitivity limit, postsynthetic dye exchange studies, reduction potentials of bipyridinium salts, CheckCIF report, and NMR and ESI mass spectral reproductions (PDF)

Accession Codes

CCDC 1815196 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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