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Switching of Adsorption Properties in a Zwitterionic Metal-Organic Framework Triggered by Photogenerated Radical Triplets

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ABSTRACT: A new metal-organic framework (MOF) has been designed that features photo-reactive zwitterionic pyridinium-4-carboxylate units. Upon UV-light irradiation, these units form radical triplets enabled by intramolecular electron transfer between anionic carboxylate and cationic pyridinium groups. This reversible light-responsive behavior creates on/off switchable charge gradients localized at the MOF's major adsorption sites and thus, significant control of the gas sorption process. It is shown that this strategy offers new design routes to access stimuli-responsive materials.

■ INTRODUCTION

Stimuli-responsive properties are one of the most intriguing aspects of metal-organic frameworks (MOFs),¹ as the structure can undergo significant changes in response to physical or chemical stimuli such as temperature,^{2, 3} pressure,^{4, 5} light,^{6, 7} pH^{8, 9} or electricity.¹⁰⁻¹² Among these materials, optically responsive MOFs are receiving increasing attention due to the controllable release of gas molecules from their pores modulated by light irradiation.¹³⁻¹⁶ Herein, the vast majority of light-responsive MOFs^{17, 18} are azobenzene¹⁹⁻²⁴ or diarylethene^{25, 26} containing frameworks that exhibit drastic changes in their gas adsorption properties based on structural transformations through the reversible and light-driven cis/trans isomerization of azobenzene or ring opening/closing reactions of diarylethene units.

At the same time, the formation of radicals in MOFs have been studied extensively,²⁷ including N-substitutedpyridiniums and the better known N,N'-disubstituted-4,4'-bipyridiniums (viologens). While bipyridinium cations are not themselves radicals, they are often readily photo-reduced in a photochromic process to form deep blue colored radical species. Subsequent exposure to the atmosphere triggers a return to the diamagnetic state, a process that can also be accelerated thermally. Recently, it was demonstrated that such cations can be incorporated in cavities of anionic MOFs, leading to a new type of composite material which, upon UV irradiation, can maintain a radical character.²⁸⁻³⁰ In another approach, carboxylate-functionalized pyridinium cations are used as building-blocks in coordination polymers.³¹⁻³⁷ In both cases, the radical generation process was always described as a photo-induced intermolecular electron transfer from the donor carboxylate anion to the acceptor pyridinium

cation within seconds, exhibiting stability up to several months. None of

these materials are reported to be porous however.

In this vein, we recently reported a new design strategy to access zwitterionic (ZW) MOFs from anionic viologen derivatives.³⁸ We have shown that an electrostatic field gradient can be found on the zwitterionic molecular surface due to their well-separated intramolecular charges and therefore, their incorporation into MOFs can create charged organic surfaces (COSs) within the pore environment - a new means to polarize guest molecules.^{39, 40} This effect has the potential to increase host-guest interactions and, hence, to enhance adsorption enthalpies (Fig 1A). More importantly, the fact that pyridinium-based zwitterions can be reversibly photo-reduced to a radical species may lead to the elimination of any charge gradients, thus representing an unprecedented mechanism to design on/off switchable adsorption sites (Fig 1B). In the current study, we hypothesize that intriguing opportunities for tunable adsorption properties are possible if this behavior can be triggered in porous MOFs. In particular, it is expected that this process does not lead to any major structural changes, as only the electrostatic surface is modified as opposed to conformational changes in azobenzene-/diarylethene-based materials. In particular, this structurally inert behavior would be of interest for membrane and thin film applications. Therefore, our strategy is to introduce pyridinium moieties as light-switchable functionalities into a porous MOF. As a proof of concept, the effect of reversible radical formation of the ligand on the gas adsorption properties of the MOF was investigated by CO2 adsorption experiments since its adsorption in MOFs is typically significant at room temperature. This approach of implementing stimuli-responsive adsorption behavior based on the reversible photo-induced generation of radicals to produce a switchable electrostatic pore surface into a MOF is unprecedented, as none of the existing porous pyridinium-based ZW MOFs is reported to exhibit any light-



Figure 1. (A) Schematic representation of a ZW MOF pore showing well-separated charges on its surface. Their charge gradients yield into a well-aligned intramolecular electrostatic field which in turn leads to enhanced polarization effects on guest molecules and thus, strong host-guest inter-actions; (B) the ZW component can be reversibly transformed into a radical species upon exposure to external stimuli, switching off the COS and releasing adsorbed guest molecules; note: the intramolecular electron transfer process is indicated by the curved arrows in A; (C) structure of the tritopic ZW ligand.

responsive adsorption behavior.⁴¹⁻⁴⁷ Herein, we report the design of a unique tritopic pyridinium-based ZW ligand yielding a new ZW MOF, which exhibits an unprecedented light-responsive adsorption effect. We believe that our findings constitute a potential route towards the development of new CO₂ scrubber materials with an ultra-low energy requirement for their regeneration processes, as opposed to the state-of-the-art, energy intensive temperature- or pressure-swing routes.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were used as received without further purification. The zwitterionic ligand 1,1',1"-(benzene-1,3,5-triyl)tris(methylene)tris(4-carboxypyridinium) tribromide (H₃LBr₃) was synthesized as described below.

1. Synthesis of H₃LBr₃. Mesitylene (1.2 g, 10 mmol), *N*bromosuccinimide (4.43 g, 25 mmol) and benzoyl peroxide (0.06 g, 0.25 mmol) were dissolved in 20 mL benzene and refluxed at 95 °C for 12 h. The reaction mixture was filtered, and the filtrate was evaporated to yield a yellow oil. Crystals were formed after 3 days, collected by filtration, washed with an ethanol/hexane mixture, and dried under vacuum to give 1,3,5-tris(bromomethyl)benzene as a white powder (4.14 g, yield 57.1%). ¹H-NMR (400 MHz, CDCl₃): δ = 4.45 (*s*, 6H), 7.35 (*s*, 3H) (Figure S1).

A solution of 1,3,5-tris(bromomethyl)benzene (0.543g, 1.5 mmol) in DMF (1.5 mL) was treated dropwise with a

solution of isonicotinic acid (0.555 g, 4.5 mmol) in DMF (36 mL). After the mixture was stirred at 70 °C for 6 hours, the resulting precipitates were collected by filtration, washed with DMF and diethyl ether, and dried in vacuum to give H₃LBr₃ as a light yellow powder (0.411 g, yield 40.0%). Anal. Calcd for C₂₇H₂₄Br₃N₃O₆ (726.21): C 44.66%, H 3.33%, N 5.79%; found: C 44.05%, H 3.69%, N 5.38%. ¹H-NMR (400 MHz, D₂O): δ = 8.95 (*d*, 2H); 8.34 (*d*, 2H); 7.59 (*s*, 1H); 5.88 (*s*, 2H) (Figure S2).

2. Synthesis of $\{[CdBr(L)] \cdot (ClO_4) \cdot 2DMF\}_n$ (1). Bulk material was prepared by the following procedure: H₂LBr₃ (19.4 mg, 0.04 mmol) and Cd(ClO₄), 6H₂O (62.4 mg, 0.2 mmol) were dissolved in 2 mL of DMF and the pH value of the solution was adjusted to ~ 7 using 70 µL 1.0 mol L⁻¹ aqueous NaOH solution. Ivory colored polycrystalline precipitate was obtained after stirring the mixture in a closed glass vial on a heating plate at 80 °C for 3 days. The residue was removed by filtration, washed with water and diethyl ether, and air dried. The purity was confirmed by X-ray powder diffraction (Figure S₃). Yield based on the Calcd ligand: 14.5 mg (39.4%). Anal. for C₂₇H₂₅BrCdClN₃O₁₂ (811.267): C 39.97, H 3.11, N 5.18; found: C 39.29, H 3.23, N 5.32%. Note that this elemental composition is calculated based on a dihydrate, as opposed to the DMF solvate suggested by SC-XRD analysis. We assume that the prolonged handling time during elemental analysis promoted this solvent exchange. IR (KBr pellet, cm^{-1}): $\tilde{v} = 3121$ (w), 3057 (w), 1618 (s), 1563 (s), 1509 (w), 1455 (m), 1360 (s), 1255 (w), 1212 (w), 1181 (w), 1167(w), 1078 (s), 930 (w), 870 (m), 776 (s), 705 (m), 685 (m), 663 (w) (Figure S₄).

Single-crystals were prepared by the following procedure: H_3LBr_3 (9.7 mg, 0.02 mmol) and $Cd(ClO_4)_2$ · $6H_2O$ (31.2 mg, 0.1 mmol) were dissolved in a mixture of 0.5 mL water and 0.5 mL DMF. The pH was adjusted to 7 using 1.0 mol L⁻¹ aqueous NaOH solution. The reaction mixture was kept in a closed vial for three weeks at room temperature, forming colorless needle-shaped single crystals.

3. Powder X-Ray Diffraction. PXRD patterns were collected using a Bruker D2 Phaser diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å). Powder samples were dispersed on low-background discs for analyses. Simulations of the PXRD data were performed using single crystal data and the Powder Pattern module of the Mercury CSD software package.⁴⁸

4. Elemental analysis. Elemental analyses (C, H, and N) were completed by Atlantic Microlab, Inc.

5. Spectroscopy. FT-IR data were recorded on a Nicolet iSio from Thermo Scientific. 'H-NMR data were recorded on Avance DMX-400 from Bruker.

6. Magnetic Measurements. Magnetic characterization of the sample was carried out in a Quantum Design MPMS XL SQUID magnetometer under an applied magnetic field of 1000 Oe in the temperature range of 2-300 K. The activated sample was first measured in a sealed quartz tube. Then the same sealed sample was subjected to UV irradiation (365 nm, 100 W, lamp UVP B-100AP) for 48 h with frequent shaking.

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7. Single-Crystal Structure Analysis. Data collections were performed on single crystals coated with Paratone-N oil and mounted on Kapton loops. Single crystal X-ray data of all compounds were collected on a Bruker Kappa Apex II X-ray diffractometer outfitted with a Mo Xray source (sealed tube, $\lambda = 0.71073$ Å) and an APEX II CCD detector equipped with an Oxford Cryosystems Desktop Cooler low temperature device. The APEX-II software suite was used for data collection, cell refinement, and reduction.⁴⁹ Absorption corrections were applied using SADABS.⁵⁰ Space group assignments were determined by examination of systematic absences, Estatistics, and successive refinement of the structures. Structure solutions were performed using intrinsic phasing methods implemented with ShelXT,51 and structure refinements were performed by least-squares refinements against $|F|^2$ followed by difference Fourier synthesis using ShelXL;⁵² both pieces of software are part of the ShelX⁵³ program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $[U_{eq}(H) = -1.2 \cdot U_{eq}(C)]$ using a riding model with $d_{C-H} =$ 0.95 Å (aromatic) and 0.99 Å (methylene). It should be noted that one perchlorate and two DMF molecules could be found in the electron density maps. However, a reasonable structural model was only found for the perchlorate in 1. Thus, the data were corrected using the SQUEEZE option in PLATON.⁵⁴ SQUEEZE estimated a total count of 709.2 electrons per 1268.7 Å3 of solvent accessible volume, which is in good agreement with two DMF molecules (Z = 8; DMF = 40 e²; 709.2 e²/8 = 88.7 e² \approx 2 DMF molecules) per asymmetric unit of 1. Details of the structure determination are given in Table 1.

CCDC-1428227 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

8. Adsorption Analysis. Gas adsorption isotherms for pressures in the range 1.10^{-5} to 1.1 bar were measured by a volumetric method using a Micromeritics ASAP2020 surface area and pore analyzer. A pre-weighed analysis tube was charged with the sample, capped with a seal frit and evacuated by heating at 100 °C under dynamic vacuum for 12 h. Note that this activation process removes all guest molecules from the pores as evidenced by the TGA data (SI, Section S₅). The evacuated analysis tubes containing the activated samples were then carefully transferred to an electronic balance and weighed to determine the sample mass (121.0 mg). The tubes were then transferred to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). All gases used are UHP grade (99.999% purity). N2 and H2 isotherms at 77 K were measured in liquid nitrogen, isotherms at 273 K were measured using ice water and isotherms at 283 K and 295 K were measured using water baths. All temperatures and fill levels were monitored periodically throughout the measurement. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

The sequence of events for the characterization of the stimuli-responsive adsorption effect of 1 were performed using the same sample and are as follows: (1) the sample was activated; (2) a CO_2 isotherm was collected; (3) the sealed sample was irradiated by UV light (365 nm, 100 W, lamp UVP B-100AP) for 48 h with frequent shaking; (4) a CO_2 isotherm was collected; (5) the sample was exposed to ambient air for 12 h; (6) the sample was re-activated and (7) a final CO_2 isotherm was collected.

Table 1. Selected crystal data and details on the structure determinations from single crystal data for 1.

Formula	$\mathrm{C}_{33}\mathrm{H}_{35}\mathrm{BrCdClN}_{5}\mathrm{O}_{12}$
MW [g·mol ⁻¹]	921.42
Crystal system	Orthorhombic
Space group	Pbcn
a [Å]	28.9782(10)
<i>b</i> [Å]	17.9781(10)
c [Å]	12.4794(5)
α [deg]	90
β [deg]	90
γ[deg]	90
<i>V</i> [Å ³]	6501.4(5)
<i>T</i> [K]	170(2)
Ζ	8
$D_{\text{calc}} \left[\mathbf{g} \cdot \mathbf{cm}^{-3} \right]$	1.883
μ [mm ⁻¹]	2.061
Min/max transmission	0.657/0.746
θ_{\max} [deg]	25.027
Measured reflections	27896
Unique reflections	5749
Reflections $[F_o > 4\sigma(F_o)]$	1954
Parameter	388
R _{int}	0.1715
$R_{\rm i} \left[F_{\rm o} > 4 \sigma(F_{\rm o})\right]$	0.0686
wR ₂ [all data]	0.1892
GOF	0.804
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min} [{\rm e} \cdot {\rm \AA}^{-3}]$	1.916/-1.008

9. Thermogravimetric Analysis. TGA data were recorded using a TGA Q50 from TA Instruments. All measurements were performed using platinum crucibles in a dynamic nitrogen atmosphere (50 mL min⁻¹) and a heating rate of 3 °C min⁻¹. The instrument was corrected for buoyancy and current effects, and was calibrated using standard reference materials.

10. Differential Scanning Calorimetry. DSC data were recorded using a TGA Q20 from TA Instruments. All measurements were performed using T zero aluminum pans, a dynamic nitrogen atmosphere (50 mL min⁻¹) and a heating rate of 3 °C min⁻¹. The instrument was calibrated using standard reference materials.

11. Density Functional Theory Calculations. DFT calculations were performed using Gaussian o9 software⁵⁵, namely the B₃LYP exchange-correlation function⁵⁶ in combination with 6-31G* basis-set⁵⁷ to evaluate the distributions and energy levels of involved molecular orbitals. Spin densities were computed at the same level. The orbital and spin density maps were plotted by Multiwfn software version 3.3.8.⁵⁸

RESULTS AND DISCUSSION

1. Synthesis and Crystal Structure. The ZW ligand 1,1',1"-(benzene-1,3,5-triyl)tris(methylene) tris(4carboxypyridinium)tribromide (H₂LBr₂) was designed as an exemplary stimuli-responsive ligand, as its tritopic flexible nature is predicted to lead to interesting new MOF topologies with favorable intra/intermolecular carboxylate-O to pyridinium-N orientations enabling accessible electron transfer pathways for radical formation. Its reaction with $Cd(ClO_4)_2 \cdot 6H_2O$ in dimethylformamide at 80 °C leads to the formation of a new MOF material (SI, Section S1). Single crystal X-ray diffraction analysis reveals the composition $\{[CdBr(L)] \cdot (ClO_4) \cdot 2DMF\}_n$ (1). Powder Xray diffraction analysis confirmed phase-purity of the bulk material (SI, Fig. S₃). It crystallizes in the orthorhombic space group Pbcn, with the asymmetric unit consisting of one Cd(II) cation, one L ligand, one bromide and one perchlorate anion, and two non-coordinating DMF molecules (SI, Fig. S₅). All atoms are located on crystallographically independent general positions. In the crystal structure, each Cd(II) is hexa-coordinated with five carboxylate-O atoms of three symmetry-related bridging L ligands and one terminally bonded Br anion in a distorted trigonal prismatic geometry (Fig. 2A). Enabled by the three methylene groups of L, their pyridinium rings are significantly twisted from the central benzene moiety with dihedral angles of 77.3, 74.2 and 86.0° (angles listed in order ring-N11, -N21 and -N31). This arrangement facilitates the metal centers to be bridged by two bidentate and one monodentate carboxylate groups of L to form 2D layers (SI, Fig. S6), which are further linked by strong interlayer hydrogen bonding interactions (SI, Table S1) to form a 3D supramolecular framework with two pore types of similar diameter (~4 Å, Fig. 2B). The interlayer voids are partially occupied by the non-coordinating perchlorate anions, serving as interlayer hydrogen bonding acceptors outside the pores (SI, Fig. S₇).

2. Mechanism of Radical Formation. A crucial step towards the photo-induced radical formation in this MOF is the occurrence of suitable electron transfer reactions between the pyridinium acceptor units and organic electron donors. To determine the nature of such reactions,

we initially investigated potential intermolecular reaction pathways: In the present case, we identified the carboxylate groups and the bromide anions as potential electron donors. The perchlorate anions can be excluded as electron donor species due to their rather weak electrondonating ability. Favorable conditions for the electron transfer can be found if the electron donor is located perpendicularly and in close proximity to the pyridinium N atom. Note that inter-



Figure. 2 Crystal structure of **1** with view of the metal coordination environment (A) and 3D supramolecular coordination network showing two types of pores (B). Solvent accessible surfaces are shown in orange and hydrogen atoms are omitted for the sake of clarity. Color scheme: Cd, turquoise; Br, brown; Cl, green; C, grey; N, blue and O, red.

molecular geometries and distances between donor and acceptor units of 70-100° and 3.4-4.0 Å respectively are reported to be suitable for generation radicals.³¹⁻³⁷ A thorough structural analysis of 1 reveals that such orientations can be found for the carboxylate groups (SI, Table S2), whereas unfavorable distances of >4.5 Å are found for the bromide anion. However, it should be pointed out that the aforementioned favorable donor-acceptor orientations are solely reported for viologen derivates and that to the best of our knowledge an intermolecular electron transfer has never been reported for isonicotinate derivates. This is not surprising, as the direct linkage of the carboxylate group to the pyridinium unit results in an extended conjugation that delocalizes the carboxylate's negative charge over the pyridinium ring. Thus, this structural feature leads to the mitigation of both the electron-accepting ability of the pyridinium ring and the electron-donor ability of the carboxylate group,.33 Such structural attributes render the photoinduced electron transfer unfavorable and thus, an intermolecular electron transfer can be ruled out as a potential dominating radical forming mechanism.

Following this argument, density functional theory (DFT) calculations have been carried out to explore po-

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tential intramolecular charge transfer (CT) transitions in L. The ground state geometry was adapted from the X-ray data and further optimized (SI, Fig. S8). The computational calculations suggest that L exhibits a complete separation of the HOMOs and LUMOs. The majority of the electron distribution of the HOMOs was located on the carboxylate groups (Fig. 3A) and that of the LUMOs on the pyridinium units (Fig. 3B). The complete localization of HOMOs and LUMOs means the HOMO–LUMO transition becomes a typical photoinduced intramolecular CT



Figure. 3 Spatial representations of (A) the HOMOs, energy - 5.85 eV; and (B) the LUMOs, energy -3.25 eV in the ZW form of L. The orbital isosurfaces are given in isovalue of 0.03. Red and blue represent positive and negative orbital phases, respectively; (C) the spin density for the multiradical state of L, which is distributed on all three ligand branches evenly, with each branch having two unpaired electrons. For calculating spin density, the isovalue was set to 0.05.

transition.^{59, 60} Accordingly, upon excitation the HOMO donates one electron to the LUMO, resulting in the formation of one diradical per branch of L with each set of two unpaired electrons delocalized over the carboxylate group and pyridinium unit (Fig. 1B). Spin density calculations confirm the delocalization in all three branches (Fig. 3C). From their nature it can be assumed that a radical triplet is formed per branch with a total of six unpaired electrons evenly distributed over the three branches, also referred to as a radical septet. Interestingly, the formation of a second radical triplet would result in the pairing of radicals by Pauli Exclusion principles, thereby returning to the zwitterion ground state. In principle, the third excitation is observed, but is indistinguishable from the first, allowing us to conclude that even excitations are silent in this process with the observation of only the odd. Finally, although these conclusions are sound, it should be noted that the chemical environment of L in the framework of 1 may be a prerequisite for the quantum mechanical origin of these CT transitions, and, at the very least, it is impossible to decouple this effect. Nevertheless, even if one posits that the ligand-metal interactions could indeed perturb the linker's molecular orbitals, it is not expected to change their relative patterns. As a result, this type of ligand-only computation is sufficient in the current situation especially given the fact that the electronic excitation of interest is ligand-centered and not ligand-to-metal in nature.^{26, 61-63}

3. Photo-Induced Radical-Driven Adsorption Effect. The above findings provide the basis for the hypothesis that 1 should exhibit an optically induced radicaldriven adsorption effect. To test this hypothesis, the CO₂ adsorption properties were characterized before and after UV exposure. Note, that scattering from crystal defects and absorption from competing chromophores renders

photons unusually difficult to penetrate into the core of the crystals.⁶⁴ Thus, to enhance radical generation, the bulk crystals were irradiated with UV-light (365 nm) for an extended time of 48 h in air. In comparison to the pristine activated sample, a significant decrease of 43.2 % in CO₂ uptake at 273 K/1 bar was recorded for the UV irradiated sample (pristine: 18.3 cm³ g⁻¹, after UV irradiation: 10.4 cm³ g⁻¹). This change in uptake of 38.2% and 35.0% is slightly less pronounced at 283 K and 295 K, respectively (Figs. 4A and SI, Fig. S9). At the same time, it is worth mentioning



Figure. 4 CO₂ adsorption isotherms (A) and isosteric heats of adsorption (B) of 1 showing a reversible alteration of the adsorption behavior accompanied by a dramatic change in the heats of adsorption. Note that in (A) the data points are superimposed for the pristine (blue) and after UV/air exposure (red) sample.

that the isotherms of the pristine sample can be fitted using a dual-site Langmuir model, whereas the data after UV can be roughly fitted only using a single-site model (SI, Fig. S11, S12). This observation is in agreement with the relative adsorption behavior: two types of micro pores are present in 1, which are each strongly adsorbed by CO_2 in the pristine form, whereas after UV irradiation they become more or less equivalent to the CO_2 molecules as a result of their weak adsorption. In contrast, the adsorption amount of N₂ and H₂ is negligible at 77 K and 295 K (SI, Fig. S10, S14, S15). Although the pores are large enough to host these guest molecules, their weak polarizability may explain this unusual adsorption-exclusion.

To further quantify the observed stimuli-responsive adsorption effect, the heat of adsorption was calculated from CO_2 isotherms at three different temperatures (273, 283 and 295 K), exhibiting a significant decrease from 40.5 kJ mol⁻¹ at zero coverage before UV irradiation to 27.3 kJ mol⁻¹ afterwards (Fig. 4B). Note that these Qst values were derived from dual-site Langmuir fits and unfitted isotherms respectively (see SI, Fig. S13 for Qst data from single-site fit). Most importantly, as a result of this study, it is evident that the drastic change of the material's CO2 adsorption capacities is in accord with a drastic change in Qst data.

In addition, N2 isotherms of 1 collected at 77 K before and after UV irradiation (Fig. S14) do not indicate any change in the material's porosity. This observation strengthens the conclusion that the aforementioned stimuli-responsive adsorption effect is driven by changes of the linker's electrostatic charges rather than by any geometrical modifications of the material's pore space.

Subsequently, the reversibility of this stimuliresponsive phenomenon was investigated, as the oxidation of viologen radicals into their non-radical forms is known to be facilitated by air exposure via a process of oxidative quenching.^{28, 31-37} This experiment was initiated with the exposure of the UV irradiated sample to ambient air for 12 h followed by the characterization of CO2 adsorption. Although the measurements were performed sequentially using the same sample, the gas uptake at 295 K before UV irradiation and after returning from the radical back to the non-radical form were almost identical (Fig. 4A, compare blue and red squares), demonstrating the reversible alteration of CO₂ capture upon photochemical treatment. At the same time, this finding along with any significant changes of PXRD patterns before and after UV irradiation (SI, Fig. S16), exclude any significant structural collapse during and after UV irradiation.

Roughly similar performance values can be found for other light-responsive frameworks such as those reported by Zhou *et al.* with a 53.3% decrease in CO₂ uptake at 295 K upon UV irradiation of PCN-13 with pore walls lined by photosensitive azobenzene units.⁶⁴ An alternative approach was explored by Hill *et al.* by employing azobenzene units as building blocks into a MOF which resulted in a 64% dynamic change of CO₂ adsorption at 303 K.²² This approach was further adopted by Luo *et al.*²⁰ and later by Feng *et al.*¹⁹ to achieve a record decrease of 75% and 21.4% at 298 K in CO₂ capture/release under dynamic conditions in respective azobenzene-based MOFs. Guo *et al.* recorded a CO₂desorption capacity of 75% at 298 K by the design of a photochromic diarylethene MOF.²⁵ It is important to emphasize that these azobenzene- and diarylethene-based materials undergo major conformational changes upon photo-switching, whereas the current lightdriven reversible alteration of adsorption properties reported herein is driven solely by a switchable electrostatic pore surface – a new mechanistic approach that is unprecedented in literature for any sorbent.

We also investigated the potential of 1 as a sorbent for carbon capture. In general, for a sorbent competent in carbon capture, high selectivity of CO2 over N2 and energetically efficient sorbent regeneration are two prerequisites. The latter was extensively shown above, as light is abundant and a low-cost alternative towards temperature- or pressure-swing sorbent regeneration processes. The selectivity was investigated using IAST simulations of the mixed gas uptake (15% CO2, 85% N2), yielding remarkable selectivity values of 47.3 at 273 K and 26.1 at 295 K, respectively (SI, Fig. S17, S18, and Table S3, S4). These values fall in the mid-range of best performing MOFs,⁶⁵⁻⁶⁸ but significantly outperform well-known MOFs such as HKUST-1 (~12), ZIF-8 (~4), MOF-5 (~3) and PCN-11 (~21).⁶⁹ Another critical element in relation to the energy requirement is the activation of the sorbent. Whereas most promising MOF adsorbers require energy intense activation procedures such as solvent-exchange reactions,⁷⁰ the "as-synthesized" sample of 1 can be activated through a simple thermal activation process. Most importantly, the activated material can be kept in ambient laboratory air for several weeks without showing any signs of hydration, as indicated by TG experiments (SI, Fig. S20).

4. Magnetic Characterization. To provide incontrovertible evidence that this light-responsive adsorption effect is based on a radical generation mechanism with delocalized spins, variable temperature magnetic data were collected on 1 before and after 48 h of UV irradiation over the range 2-300 K at 0.1 T (Fig. 5).



Figure. 5 Temperature dependence of the magnetic susceptibility-temperature (χT) product of **1** (with sample holder) before (black squares) and after UV irradiation (blue squares). The difference is the contribution from the radicals of the sample only (red squares, the solid line represents the best fit to $\chi T = \chi_{TIP}T$).

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The sample before UV irradiation showed diamagnetic signals with negative χT values due to both the sample and sample holder. This is expected, as 1 is composed of diamagnetic Cd²⁺ cations (d¹⁰) and diamagnetic ligands. After UV irradiation, the sample exhibits paramagnetic signals, which is direct evidence of the presence of radicals. The difference in χT before and after UV irradiation allows for the subtraction of the diamagnetic contribution from the sample holder and diamagnetic atoms so one can evaluate the contribution from the radicals of the sample. It should be noted that the Curie Weiss Law is not obeyed below 300 K, neither can a dimer (Bleaney-Bowers) or alternating magnetic chain (Bonner-Fisher) model be fit to the data. Instead, the linear trend in the γT difference as the temperature changes can be described using the temperature-independent paramagnetism (TIP) term ($\chi T = \chi_{TIP}T$) with a χ_{TIP} of 8.7 × 10⁻³ emu mol⁻¹, which can be appropriately ascribed to delocalized radical spins. This magnetic behavior is typical for a Fermi gas-like state, also referred to as Pauli paramagnetism.⁷¹ Moreover, the absence of any exchange coupling between nearest neighbors is also consistent with the DFT calculations suggesting the even distribution of delocalized spins along all three isonicotinate branches of L.

However, it should be noted that the power and duration of UV irradiation as well as the nature of the sample in terms of crystallite size, may influence the magnetic properties of **1**. For example, preliminary studies indicate a decrease in the paramagnetic signal when the material was irradiated for only 12 h. This observation is not surprising, as scattering from crystal defects and absorption from competing chromophores renders photons unusually difficult to penetrate into the core of the crystals. Therefore, an extensive irradiation for 48 h could result in quantitative radical formation. Nevertheless, most importantly, this study reveals a drastic change of the relative magnetic behavior before and after UV irradiation, which is incontrovertible evidence of radical formation.

CONCLUSIONS

The reversible alteration of CO₂ capture upon light irradiation or oxidative quenching has been observed in a ZW MOF. The CO₂ adsorption capacity significantly decreases upon light irradiation as compared to the pristine material. This adsorption process can be reversibly triggered by ambient oxidative quenching as the sorbent returns to its pristine state. Thorough structural, computational and magnetic investigations have shown that the nature of this stimuli-responsive adsorption effect is based on the reversible generation of radicals. Interestingly, an intramolecular CT transition was found to be the dominating radical generation mechanism, resulting in a unique delocalized radical septet. Finally, we believe that this unprecedented stimuli-responsive adsorption effect is expected to have a major impact on the development of new design strategies for various gas capture and release processes based on low-cost alternatives as opposed to

current energy-intense state-of-the-art temperature- or pressure-swing sorbent regeneration processes.

ASSOCIATED CONTENT

Supporting Information

Experimental details, synthetic procedure, structural details, PXRD patterns, Langmuir fits, adsorption isotherms, TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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REFERENCES

1. Coudert, F.-X., Responsive Metal–Organic Frameworks and Framework Materials: Under Pressure, Taking the Heat, in the Spotlight, with Friends. *Chem. Mater.* **2015**, *27*, 1905-1916.

2. Ma, S.; Sun, D.; Yuan, D.; Wang, X.-S.; Zhou, H.-C., Preparation and Gas Adsorption Studies of Three Mesh-Adjustable Molecular Sieves with a Common Structure. *J. Am. Chem. Soc.* 2009, 131, 6445-6451.

3. Wriedt, M.; Yakovenko, A. A.; Halder, G. J.; Prosvirin, A. V.; Dunbar, K. R.; Zhou, H.-C., Reversible Switching from Antiferro- to Ferromagnetic Behavior by Solvent-Mediated, Thermally-Induced Phase Transitions in a Trimorphic MOF-Based Magnetic Sponge System. *J. Am. Chem. Soc.* **2013**, 135, 4040-4050.

4. McKellar, S. C.; Sotelo, J.; Greenaway, A.; Mowat, J. P. S.; Kvam, O.; Morrison, C. A.; Wright, P. A.; Moggach, S. A., Pore Shape Modification of a Microporous Metal–Organic Framework Using High Pressure: Accessing a New Phase with Oversized Guest Molecules. *Chem. Mater.* **2016**, *28*, 466-473.

5. Im, J.; Seoung, D.; Hwang, G. C.; Jun, J. W.; Jhung, S. H.; Kao, C.-C.; Vogt, T.; Lee, Y., Pressure-Dependent Structural and Chemical Changes in a Metal–Organic Framework with One-Dimensional Pore Structure. *Chem. Mater.* **2016**, DOI: 10.1021/acs.chemmater.6b01148.

6. Van Cleuvenbergen, S.; Stassen, I.; Gobechiya, E.; Zhang, Y.; Markey, K.; De Vos, D. E.; Kirschhock, C.; Champagne, B.; Verbiest, T.; van der Veen, M. A., ZIF-8 as Nonlinear Optical Material: Influence of Structure and Synthesis. *Chem. Mater.* **2016**, 28, 3203-3209.

7. Liu, M.; Quah, H. S.; Wen, S.; Yu, Z.; Vittal, J. J.; Ji, W., Efficient Third Harmonic Generation in a Metal–Organic Framework. *Chem. Mater.* **2016**, *2*8, 3385-3390.

8. Li, H.-Y.; Wei, Y.-L.; Dong, X.-Y.; Zang, S.-Q.; Mak, T. C. W., Novel Tb-MOF Embedded with Viologen Species for Multi-Photofunctionality: Photochromism, Photomodulated Fluorescence, and Luminescent pH Sensing. *Chem. Mater.* 2015, 27, 1327-1331.

9. Duan, L.-N.; Dang, Q.-Q.; Han, C.-Y.; Zhang, X.-M., An interpenetrated bioactive nonlinear optical MOF containing a coordinated quinolone-like drug and Zn(ii) for pH-responsive release. *Dalton Trans.* **2015**, **4**4, 1800-1804.

10. Zhang, Z.; Yoshikawa, H.; Awaga, K., Discovery of a "Bipolar Charging" Mechanism in the Solid-State Electrochemical Process of a Flexible Metal–Organic Framework. *Chem. Mater.* **2016**, 28, 1298-1303.

11. Fernandez, C. A.; Martin, P. C.; Schaef, T.; Bowden, M. E.; Thallapally, P. K.; Dang, L.; Xu, W.; Chen, X.; McGrail, B. P., An Electrically Switchable Metal-Organic Framework. *Sci. Rep.* **2014**, DOI: 10.1038/srep06114

12. Kung, C.-W.; Wang, T. C.; Mondloch, J. E.; Fairen-Jimenez, D.; Gardner, D. M.; Bury, W.; Klingsporn, J. M.; Barnes, J. C.; Van Duyne, R.; Stoddart, J. F.; Wasielewski, M. R.; Farha, O. K.; Hupp, J. T., Metal–Organic Framework Thin Films Composed of Free-Standing Acicular Nanorods Exhibiting Reversible Electrochromism. *Chem. Mater.* **2013**, 25, 5012-5017.

13. Sato, H.; Matsuda, R.; Sugimoto, K.; Takata, M.; Kitagawa, S., Photoactivation of a nanoporous crystal for ondemand guest trapping and conversion. *Nat. Mater.* **2010**, *9*, 661-666.

14. Yanai, N.; Uemura, T.; Inoue, M.; Matsuda, R.; Fukushima, T.; Tsujimoto, M.; Isoda, S.; Kitagawa, S., Guest-to-Host Transmission of Structural Changes for Stimuli-Responsive Adsorption Property. *J. Am. Chem. Soc.* **2012**, 134, 4501-4504.

15. Brown, J. W.; Henderson, B. L.; Kiesz, M. D.; Whalley, A. C.; Morris, W.; Grunder, S.; Deng, H.; Furukawa, H.; Zink, J. I.; Stoddart, J. F.; Yaghi, O. M., Photophysical pore control in an azobenzene-containing metal-organic framework. *Chem. Sci.* **2013**, **4**, 2858-2864.

16. Park, J.; Sun, L.-B.; Chen, Y.-P.; Perry, Z.; Zhou, H.-C., Azobenzene-Functionalized Metal–Organic Polyhedra for the Optically Responsive Capture and Release of Guest Molecules. *Angew. Chem., Int. Ed.* **2014**, **53**, 5842-5846.

17. Jones, C. L.; Tansell, A. J.; Easun, T. L., The lighter side of MOFs: structurally photoresponsive metal-organic frameworks. *J. Mater. Chem. A* **2016**, *4*, 6714-6723.

18. Mukhopadhyay, R. D.; Praveen, V. K.; Ajayaghosh, A., Photoresponsive metal-organic materials: exploiting the azobenzene switch. *Materials Horizons* **2014**, 1, 572-576.

19. Dang, L.-L.; Zhang, X.-J.; Zhang, L.; Li, J.-Q.; Luo, F.; Feng, X.-F., Photo-responsive azo MOF exhibiting high selectivity for CO2 and xylene isomers. *J. Coord. Chem.* **2016**, 69, 1179-1187.

20. Gong, L. L.; Feng, X. F.; Luo, F., Novel azo-Metal–Organic Framework Showing a 10-Connected bct Net, Breathing Behavior, and Unique Photoswitching Behavior toward CO₂. *Inorg. Chem.* **2015**, 54, 11587-11589.

21. Castellanos, S.; Goulet-Hanssens, A.; Zhao, F.; Dikhtiarenko, A.; Pustovarenko, A.; Hecht, S.; Gascon, J.; Kapteijn, F.; Bléger, D., Structural Effects in Visible-Light-Responsive Metal-Organic Frameworks Incorporating ortho-Fluoroazobenzenes. *Chem.- Eur. J.* **2016**, *22*, 746-752.

22. Lyndon, R.; Konstas, K.; Ladewig, B. P.; Southon, P. D.; Kepert, P. C. J.; Hill, M. R., Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release. *Angew. Chem., Int. Ed.* **2013**, 52, 3695-3698.

23. Park, J.; Yuan, D.; Pham, K. T.; Li, J.-R.; Yakovenko, A.; Zhou, H.-C., Reversible Alteration of CO₂ Adsorption upon Photochemical or Thermal Treatment in a Metal–Organic Framework. *J. Am. Chem. Soc.* **2012**, 134, 99-102.

24. Lyndon, R.; Konstas, K.; Thornton, A. W.; Seeber, A. J.; Ladewig, B. P.; Hill, M. R., Visible Light-Triggered Capture and Release of CO₂ from Stable Metal Organic Frameworks. *Chem. Mater.* 2015, 27, 7882-7888.

25. Luo, F.; Fan, C. B.; Luo, M. B.; Wu, X. L.; Zhu, Y.; Pu, S. Z.; Xu, W.-Y.; Guo, G.-C., Photoswitching CO₂ Capture and Release in a Photochromic Diarylethene Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2014**, 53, 9298-9301.

26. Patel, D. G.; Walton, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B., Photoresponsive porous materials: the design and synthesis of photochromic diarylethene-based linkers and a metal-organic framework. *Chem. Commun.* 2014, 50, 2653-2656.

27. Faust, T. B.; D'Alessandro, D. M., Radicals in metalorganic frameworks. *RSC Advances* **2014**, 4, (34), 17498-17512.

28. Zeng, Y.; Fu, Z.; Chen, H.; Liu, C.; Liao, S.; Dai, J., Photoand thermally induced coloration of a crystalline MOF accompanying electron transfer and long-lived charge separation in a stable host-guest system. *Chem. Commun.* **2012**, 48, 8114-8116.

29. Gong, Y.-N.; Lu, T.-B., Fast detection of oxygen by the naked eye using a stable metal-organic framework containing methyl viologen cations. *Chem. Commun.* **2013**, 49, 7711-7713.

30. Yu, J.; Cui, Y.; Xu, H.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G., Confinement of pyridinium hemicyanine dye within an anionic metal-organic framework for two-photon-pumped lasing. *Nature Commun.* **2013**, 4, 2719.

31. Yao, Q.-X.; Ju, Z.-F.; Jin, X.-H.; Zhang, J., Novel Polythreaded Coordination Polymer: from an Armed-Polyrotaxane Sheet to a 3D Polypseudorotaxane Array, Photoand Thermochromic Behaviors. *Inorg. Chem.* 2009, 48, 1266-1268.

32. Jin, X.-H.; Sun, J.-K.; Xu, X.-M.; Li, Z.-H.; Zhang, J., Conformational and photosensitive adjustment of the 4,4[prime or minute]-bipyridinium in Mn(ii) coordination complexes. *Chem. Commun.* **2010**, 46, 4695-4697.

33. Sun, J.-K.; Wang, P.; Chen, C.; Zhou, X.-J.; Wu, L.-M.; Zhang, Y.-F.; Zhang, J., Charge-distribution-related regioisomerism of photoresponsive metal-organic polymeric chains. *Dalton Trans.* **2012**, 41, 13441-13446.

34. Tan, Y.; Chen, H.; Zhang, J.; Liao, S.; Dai, J.; Fu, Z., Synthesis of a 3D photochromic coordination polymer with an interpenetrating arrangement: crystal engineering for electron transfer between donor and acceptor units. *CrystEngComm* **2012**, 14, 5137-5139.

35. Tan, Y.; Fu, Z.; Zeng, Y.; Chen, H.; Liao, S.; Zhang, J.; Dai, J., Highly stable photochromic crystalline material based on a close-packed layered metal-viologen coordination polymer. *J. Mater. Chem.* **2012**, 22, 17452-17455.

36. Zeng, Y.; Liao, S.; Dai, J.; Fu, Z., Fluorescent and photochromic bifunctional molecular switch based on a stable crystalline metal-viologen complex. *Chem. Commun.* **2012**, 48, 11641-11643.

37. Fu, K.; Ren, C.-X.; Chen, C.; Cai, L.-X.; Tan, B.; Zhang, J., Auxiliary ligand-controlled photochromism and decolourization of two bipyridinium-based metal-organic hybrid materials with various water clusters. *CrystEngComm* **2014**, 16, 5134-5141.

38. Aulakh, D.; Varghese, J. R.; Wriedt, M., A New Design Strategy to Access Zwitterionic Metal–Organic Frameworks from Anionic Viologen Derivates. *Inorg. Chem.* **2015**, 54, 1756-1764.

39. Higuchi, M.; Nakamura, K.; Horike, S.; Hijikata, Y.; Yanai, N.; Fukushima, T.; Kim, J.; Kato, K.; Takata, M.; Watanabe, D.; Oshima, S.; Kitagawa, S., Design of Flexible Lewis Acidic Sites in

Porous Coordination Polymers by using the Viologen Moiety. *Angew. Chem., Int. Ed.* **2012**, *51*, 8369-8372.

40. Aulakh, D.; Nicoletta, A. P.; Varghese, J. R.; Wriedt, M., The structural diversity and properties of nine new viologen based zwitterionic metal-organic frameworks. *CrystEngComm* **2016**, 18, 2189-2202.

41. Yao, Q.-X.; Pan, L.; Jin, X.-H.; Li, J.; Ju, Z.-F.; Zhang, J., Bipyridinium Array-Type Porous Polymer Displaying Hydrogen Storage, Charge-Transfer-Type Guest Inclusion, and Tunable Magnetic Properties. *Chem. -Eur. J.* **2009**, 15, 11890-11897.

42. Higuchi, M.; Tanaka, D.; Horike, S.; Sakamoto, H.; Nakamura, K.; Takashima, Y.; Hijikata, Y.; Yanai, N.; Kim, J.; Kato, K.; Kubota, Y.; Takata, M.; Kitagawa, S., Porous Coordination Polymer with Pyridinium Cationic Surface, [Zn2(tpa)2(cpb)]. J. Am. Chem. Soc. **2009**, 131, 10336-10337.

43. Sun, J.-K.; Yao, Q.-X.; Tian, Y.-Y.; Wu, L.; Zhu, G.-S.; Chen, R.-P.; Zhang, J., Borromean-Entanglement-Driven Assembly of Porous Molecular Architectures with Anion-Modified Pore Space. *Chem. -Eur. J.* **2012**, **18**, 1924-1931.

44. Sun, J.-K.; Ji, M.; Chen, C.; Wang, W.-G.; Wang, P.; Chen, R.-P.; Zhang, J., A charge-polarized porous metal-organic framework for gas chromatographic separation of alcohols from water. *Chem. Commun.* **2013**, 49, 1624-1626.

45. Kanoo, P.; Matsuda, R.; Sato, H.; Li, L.; Jeon, H. J.; Kitagawa, S., In Situ Generation of Functionality in a Reactive Haloalkane-Based Ligand for the Design of New Porous Coordination Polymers. *Inorg. Chem.* **2013**, 52, 10735-10737.

46. Lin, J.-B.; Shimizu, G. K. H., Pyridinium linkers and mixed anions in cationic metal-organic frameworks. *Inorg. Chem. Front.* 2014, 1, 302-305.

47. Toma, O.; Mercier, N.; Allain, M.; Kassiba, A. A.; Bellat, J.-P.; Weber, G.; Bezverkhyy, I., Photo- and Thermochromic and Adsorption Properties of Porous Coordination Polymers Based on Bipyridinium Carboxylate Ligands. *Inorg. Chem.* **2015**, 54, 8923-8930.

48. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A., Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* 2008, 41, 466-470.

49. SAINT and APEX 2 Software for CCD Diffractometers, Bruker AXS Inc., Madison, WI, USA: 2014.

50. Sheldrick, G. M., *SADABS, version 2014/4* **2014**, (Bruker AXC Inc., Madison, WI).

51. Sheldrick, G. M., SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Foundations and Advances* **2015**, 71, 3-8.

52. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect.C: Structural Chemistry* 2015, 71, 3-8.

53. Sheldrick, G. M., A short history of SHELX. Acta Crystallogr. Sect. A 2008, 64, 112-122.

54. Spek, A. L., Structure validation in chemical crystallography. *Acta Crystallogr. Sect. D* **2009**, 65, 148-155.

55. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.

W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.

56. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, 98, 11623-11627.

57. Hariharan, P. C.; Pople, J. A., The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **1973**, **28**, 213-222.

58. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, 33, 580-592.

59. Li, H.; Chi, Z.; Xu, B.; Zhang, X.; Yang, Z.; Li, X.; Liu, S.; Zhang, Y.; Xu, J., New aggregation-induced emission enhancement materials combined triarylamine and dicarbazolyl triphenylethylene moieties. *J. Mater. Chem.* **2010**, 20, 6103-6110.

60. Jin, X.-H.; Wang, J.; Sun, J.-K.; Zhang, H.-X.; Zhang, J., Protonation-Triggered Conversion between Single- and Triple-Stranded Helices with a Visible Fluorescence Change. *Angew. Chem., Int. Ed.* 2011, 50, 1149-1153.

61. Cox, J. M.; Walton, I. M.; Benedict, J. B., On the design of atropisomer-separable photochromic diarylethene-based metalorganic framework linkers. *J. Mater. Chem. C* **2016**, 4, 4028-4033.

62. Bichoutskaia, E.; Suyetin, M.; Bound, M.; Yan, Y.; Schröder, M., Methane Adsorption in Metal–Organic Frameworks Containing Nanographene Linkers: A Computational Study. *J. Phys. Chem. C* 2014, 118, 15573-15580.

63. Xu, G.; Guo, G.-C.; Wang, M.-S.; Zhang, Z.-J.; Chen, W.-T.; Huang, J.-S., Photochromism of a Methyl Viologen Bismuth(III) Chloride: Structural Variation Before and After UV Irradiation. *Angew. Chem., Int. Ed.* **2007**, 46, 3249-3251.

64. Park, J.; Yuan, D.; Pham, K. T.; Li, J.-R.; Yakovenko, A.; Zhou, H.-C., Reversible Alteration of CO₂ Adsorption upon Photochemical or Thermal Treatment in a Metal–Organic Framework *J. Am. Chem. Soc.* **2011**, 134, 99-102.

65. Schoedel, A.; Ji, Z.; Yaghi, O. M., The role of metalorganic frameworks in a carbon-neutral energy cycle. *Nature Energy* **2016**, 1, 16034-16046.

66. Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M., Low concentration CO₂ capture using physical adsorbents: Are metal–organic frameworks becoming the new benchmark materials? *Chem. Eng. J.* **2016**, 296, 386-397.

67. Wang, Q.; Bai, J.; Lu, Z.; Pan, Y.; You, X., Finely tuning MOFs towards high-performance post-combustion CO2 capture materials. *Chem. Commun.* **2016**, 52, 443-452.

68. Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B., Perspective of microporous metal-organic frameworks for CO₂ capture and separation. *Energy Environ. Sci.* **2014**, *7*, 2868-2899.

69. Simmons, J. M.; Wu, H.; Zhou, W.; Yildirim, T., Carbon capture in metal-organic frameworks-a comparative study. *Energy Environ. Sci.* 2011, 4, 2177-2185.

70. Liu, J.; Benin, A. I.; Furtado, A. M. B.; Jakubczak, P.; Willis, R. R.; LeVan, M. D., Stability Effects on CO₂ Adsorption for the DOBDC Series of Metal–Organic Frameworks. *Langmuir* **2011**, 27, 11451-11456.

71. Rizzuto, F. J.; Hua, C.; Chan, B.; Faust, T. B.; Rawal, A.; Leong, C. F.; Hook, J. M.; Kepert, C. J.; D'Alessandro, D. M., The electronic, optical and magnetic consequences of delocalization in multifunctional donor-acceptor organic polymers. *Phys. Chem. Chem. Phys.* **2015**, 17, 11252-11259. Table of Contents artwork

