CHEMICAL REVIEWS

Review

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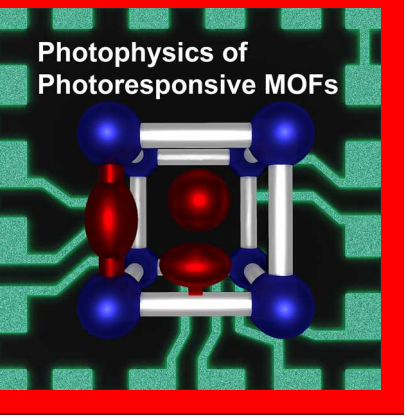
Photophysics Modulation in Photoswitchable Metal−Organic Frameworks

Allison M. Rice, Corey R. Martin, Vladimir A. Galitskiy, Anna A. Berseneva, Gabrielle A. Leith, and Natalia B. Shustova*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

In this Review, we showcase the upsurge in the development and fundamental photophysical studies of more than 100 metal−organic frameworks (MOFs) as versatile stimuli-responsive platforms. The goal is to provide a comprehensive analysis of the field of photoresponsive MOFs while delving into the underlying photophysical properties of various classes of photochromic molecules including diarylethene, azobenzene, and spiropyran as well as naphthalenediimide and viologen derivatives integrated inside a MOF matrix as part of a framework backbone, as a ligand side group, or as a guest. In particular, the geometrical constraints, photoisomerization rates, and electronic structures of photochromic molecules integrated inside a rigid MOF scaffold are discussed. Thus, this Review reflects on the challenges and opportunities of using photoswitchable MOFs in next-generation multifunctional stimuli-responsive materials while highlighting their use in optoelectronics, erasable inks, or as the next generation of sensing devices.



CONTENTS

1. INTRODUCTION

The development of stimuli-responsive materials that undergo changes in their physical−chemical properties upon exposure to external stimuli (e.g., light, pressure, or pH) encompasses next-generation advancements in the technological sector. A particular interest can be found in photochromic compounds, which have the ability to switch between two discrete states upon irradiation,[1−5] portending the ability for the photophysical properties of materials to be tuned as a function of an excitation wavelength. In other words, photochromic molecules can enhance the photophysical, mechanistic, electronic, or thermal properties of materials upon photoisomerization. Photoswitch utilization can facilitate the development of photoresponsive drug carriers, bioadhesive mediators, polymer−enzyme switches, electronic devices, and molecular machines.[6−13]

The importance of photoswitch technology development is emphasized by its recent role in visual restoration as a result of degenerative retinal diseases, microscale medicine, as well as molecular machines, progress in which was denoted by the 2016 Nobel Prize.[14−17]

Photochromic molecule incorporation has been probed for zeolites, polymers, hydrogels, covalent−organic frameworks (COFs), supramolecular host−guest systems, and metal−organic frameworks (MOFs). The description of these systems can be found elsewhere.[12,13,18−24]

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The focus of this Review is specifically on photoswitchable frameworks because MOFs:

(i) allow for large geometrical rearrangements of photoswitches (e.g., spiropyran-based derivatives) to occur inside their pores;[25−27]

(ii) possess a unique structural modularity promoting the capability of photoresponsive molecules to be incorporated as a part of a framework backbone, as a linker side group, and as a guest molecule and the study of the differences in their behavior;[26,28]

(iii) provide an opportunity to study geometrical transformation upon photoisomerization by single-crystal X-ray crystallography and therefore open a pathway for more accurate theoretical modeling;[26]

(iv) possess exceptional structural tunability allowing for tailoring of photoswitchable properties and systematic studies of photoswitch dynamics through isoreticular MOF topologies.[29−31]

Figure 1 demonstrates a multifaceted MOF platform[4,32−41] allowing for different pathways for the integration of photoresponsive moieties such as a side group of the organic linker, guest molecules inside the pores, or a part of the linker skeleton. Overall, the well-defined spatial arrangement of MOF linkers promotes metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), or ligand-to-ligand charge transfer (LLCT),[42,43] while the integration of photochromic molecules inside the scaffold can provide an intriguing twist. For instance, solid-state photoswitching, made possible in MOFs, is highly appealing for the design of smart windows, sensors, erasable inks, and data storage;[44−48] therefore, it is anticipated that the combination of photochromic properties with the inherent properties of MOFs can foreshadow engineering principles for next-generation multifunctional materials.

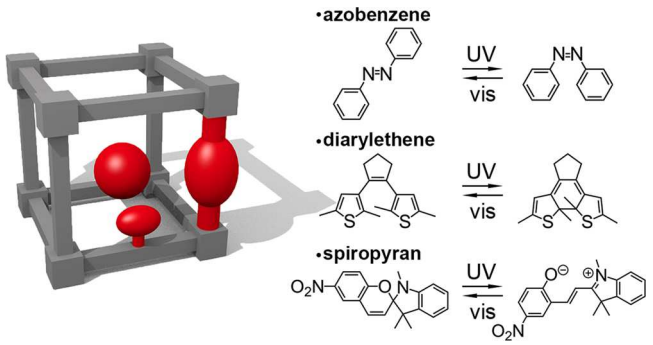

Figure 1. (left) Schematic representation of integrated photochromic moieties as a framework backbone, side group, and guest molecule. (right) Three classes of photoresponsive molecules that undergo structural changes as a function of the excitation wavelength.

Even though there is great interest in stimuli-responsive MOFs as well as photophysical studies in general,[25,49] this is the first Review, to the best of our knowledge, specifically focusing on the photophysics of photochromic MOFs. There are other reviews including some photoswitchable frameworks in general,[2,3,49−53] but the purpose of this Review is to highlight the synergistic effects and the corresponding impact of photochromic molecules on MOF photophysics. There are five classes of photochromic molecules covered in this Review containing diarylethene-, spiropyran-, azobenzene-, naphthalenediimide-, and viologen-based groups. The chosen classes of photochromic compounds are known for different mechanisms for photoisomerization upon light irradiation. For example, spiropyran undergoes a 6π-electron electrocyclic rearrangement accompanied by a large structural change, whereas a radical formation was observed in the case of viologen-based derivatives.

This Review is divided into three main sections covering the three integration methods for photochromic compounds and each section is divided into subsections containing the different classes of photoswitchable molecules. Furthermore, the differences in the photophysical response for each type of MOF are highlighted in the context of this Review. Because the main focus of this Review is centered on photophysical studies of photoresponsive MOFs, they are summarized in the comprehensive Table 1,[25−31,54−92] whereas other photoswitchable frameworks for gas sorption as the main application are summarized in Table 2,[46,93−112] thus providing a glimpse into all photoswitchable MOFs known to date.

2. PHOTORESPONSIVE MOIETIES AS A FRAMEWORK BACKBONE

One of the challenges for the incorporation of photoswitchable linkers as a MOF backbone is the preservation of framework integrity during possible structural transformations of the photoswitch. Not all MOF motifs can accommodate geometrical transformations of photoactive linkers while preserving framework crystallinity.

In this section, we discuss linkers with photoactive moieties incorporated within a framework backbone (e.g., diarylethene derivatives, Figure 1) leading to significant structural changes of a ligand upon irradiation as well as molecules in which the photoresponsive behavior is a result of electron transfer (e.g., chromophores with naphthalenediimide and viologen cores; Figure 2 and Table 1). Thus, there are three distinct classes of photochromic molecules that are highlighted in this section: diarylethene, naphthalenediimide, and viologen derivatives (Figure 2).

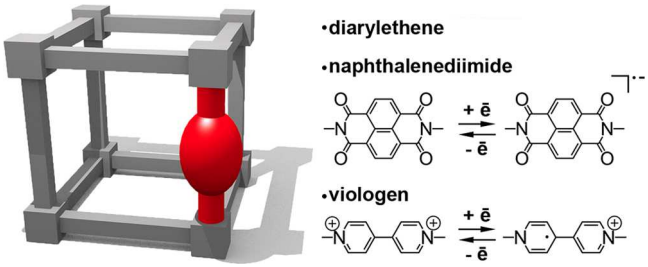

Figure 2. Photoactive moieties incorporated as a framework backbone.

Although azobenzene has been incorporated into a MOF backbone, oftentimes photoinduced switching is hindered because of the geometrical constraints imposed for trans−cis isomerization[60] (Figure 3), resulting in numerous examples with the azobenzene moiety as a side group attached to a linker (discussed later). The examples involving azobenzene as a framework backbone that are focused on gas sorption will be only briefly mentioned and are shown in Table 2.[93,99,104,106,107]

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Table 1. Photochromic Building Blocks and Corresponding Frameworks Discussed in the Review

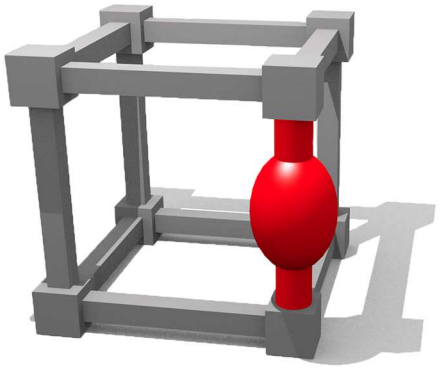
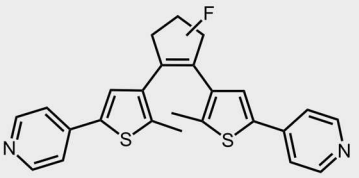
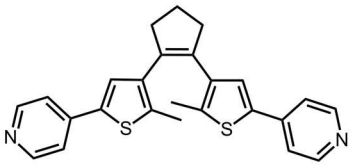
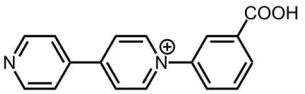
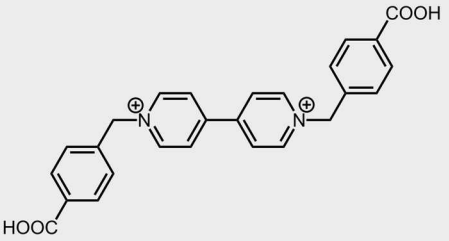
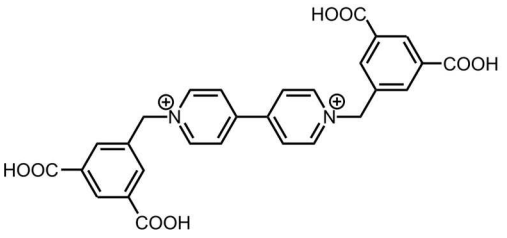
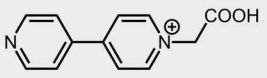
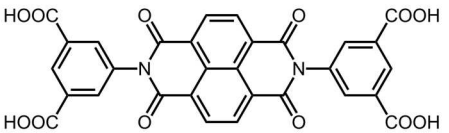
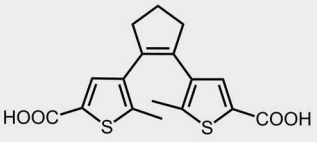
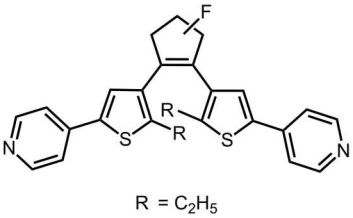
	photochromic unit and MOF	ref.		photochromic unit and MOF	ref.
	framework backbone				
			10.	 $[Zn_2(BPMTFC)(OBA)_2]\cdot 3DMF$ (DMOF2)	81
1.	 $[Zn_2(ZnTCPP)(BPMTC)_{0.85}(DEF)_{1.15}]\cdot 5.15DEF\cdot 7.25H_2O$	74	11.	 $[Zn_3(CPBPY)_2(BDC)_{2.5}(OH)]\cdot 5H_2O$	90
2.	$Zn_2(DBTD)(BPMTC)$	25	12.	 $[Eu(BA)(BPYBC)_{1.5}(H_2O)](NO_3)_2\cdot 5H_2O$	91
3.	$Zn_2(BPDC)_2(BPMTC)$	25, 26	13.	 $[Eu_2(OH)_2(H_2O)_2(BPYBDC)]Cl_2\cdot 8H_2O$ (LVMOF-1)	92
4.	$Zn_2(DBTD)(BPMTC)$ (PC-PCN)	88	14.	 $[Zn_3(CEBPY)_2(HBTC^a)(H_2BTC^a)_2(OH)_2]\cdot 4H_2O$	86
5.	$Zn_2(ZnTCPP)(BPMTC)$ (SO-PCN)	88	15.	$[Zn_4(CEBPY)_2(IPA)_3(OH)_2]\cdot 2H_2O$	86
6.	$Zn_2(SDC)_2(BPMTC)$	26	16.	 $Mg_4(BIPA\text{-}TC)_2(OH)(DMF)_3$ (Mg-NDI)	55, 56
7.	 $Zr_6(Me_2BPDC)_4(BCMTC)_{0.5}$	25, 26			
8.	 $R = C_2H_5$ $[Zn_2(BPETFC)(BPDC)]\cdot 2DMF$ (DMOF1)	81			
9.	$[Zn_2(BPETFC)(OBA)_2]\cdot 4DMF$ (DMOF3)	81			

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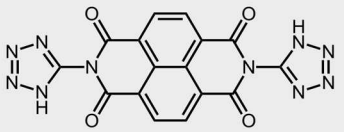
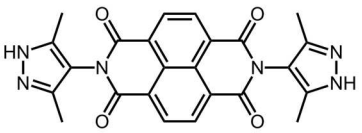
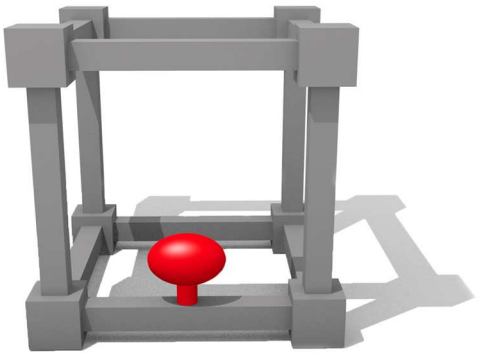
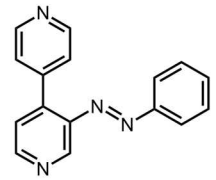
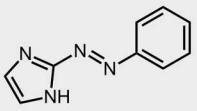
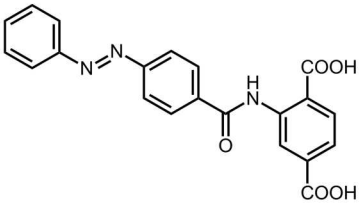
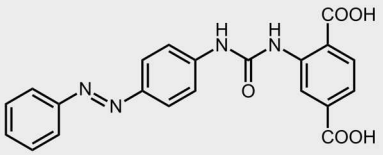
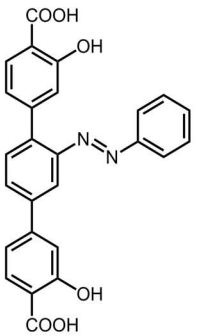
Table 1. continued

	photochromic unit and MOF	ref.
17.	$[Sr_2(BIPA\text{-}TC)(DMF)_x]\cdot yH_2O$ (Sr-NDI)	56
18.	$[Ca_2(BIPA\text{-}TC)(DMF)_4]\cdot 2DMF$ (Ca-NDI)	56, 58
		
19.	$Zn(NDI\text{-}ATZ)(DMF)_2$ (NBU-3)	57

	photochromic unit and MOF	ref.
		
20.	$Cd(BDC)(H_2NDI)$ (FJU-67)	59
21.	$Cd(NH_2\text{-}BDC)(H_2NDI)$ (FJU-68)	59
22.	$Cd(NDC)(H_2NDI)\cdot 2H_2O$ (FJU-69)	59

side group

		
		
23.	$Zn_2(NDC)_2(AzBIPY)$ (CAU-5)	60
24.	$Co_2(NDC)_2(AzBIPY)$	62
25.	$Cu_2(NDC)_2(AzBIPY)$	62, 66
26.	$Zn_2(BPDC)_2(AzBIPY)$	62
27.	$Zn_2(CCA)_2(AzBIPY)$	62
		
28.	Zn(IM)(AIM)	61

		
29.	$[Cr_3O(OH)(H_2O)_2(AzABDC)_3]\cdot xH_2O$ (Cr-MIL-101-amide)	63
		
30.	$[Cr_3O(OH)(H_2O)_2(AzUBDC)_3]\cdot xH_2O$ (Cr-MIL-101-urea)	63
		
31.	$Mg_2(DHAzTPDC)$ (Azo-IRMOF-74-III)	64

DOI: 10.1021/acs.chemrev.9b00350
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Table 1. continued

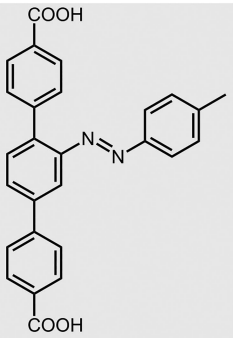
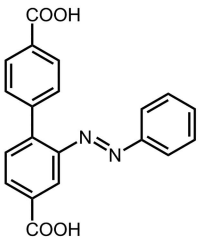
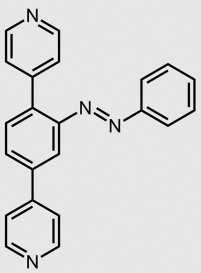
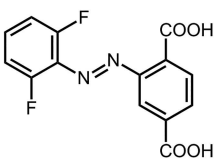
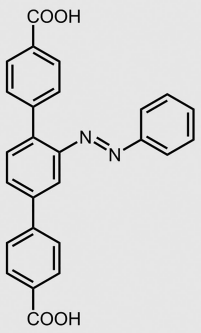
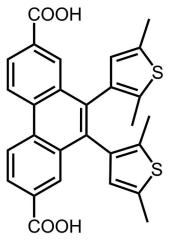
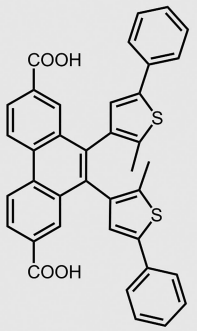
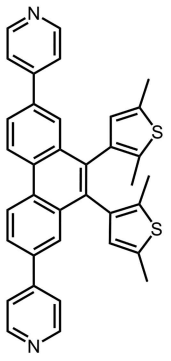
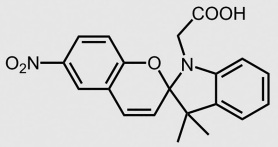
	photochromic unit and MOF	ref.
32.	 $[Zr_6O_4(OH)_4(TAzTPDC)_6$ (UiO-68-azo)	65
33.	 $Cu_2(AzBPDC)_2(BPY)$	66
34.	 $Cu_2(BDC)_2(AzBIPYB)$	67
35.	$Cu_2(Me_2TPDC)_2(AzBIPYB)$	67
36.	 $Cu_2(F_2AzBDC)_2(DABCO)$	68
37.	 $DySc_2N@C_{80}@Zr_6O_4(OH)_4(AzTPDC)_6$	69
38.	$Sc_3C_2@C_{80}@Zr_6O_4(OH)_4(AzTPDC)_6$	69
39.	 $Zn_4O(TPDC)_3$ (UBMOF-1)	70
40.	 $Zn_4O(PhTPDC)_3$ (UBMOF-2)	71
41.	 $Zn_3(BDC)_3(TPDPY)(DMF)_{1.5}$ (UBMOF-3)	72
42.	 $Zr_6O_4(OH)_4(BTC^a)_2(HCOO)_{5.95}(P)_{0.03}(SP)_{0.02}$ (MOF-808-SP)	27

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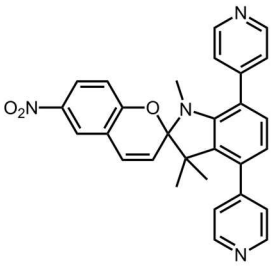
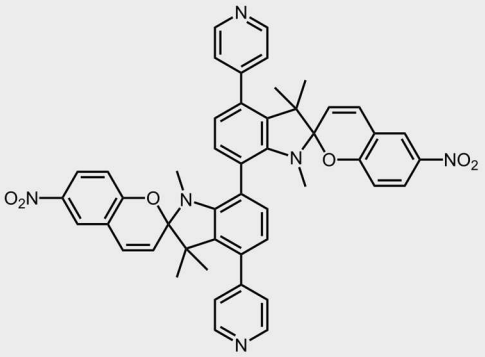
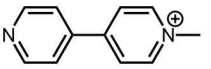
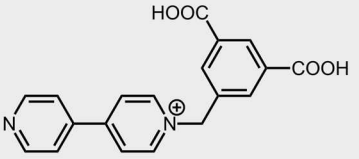
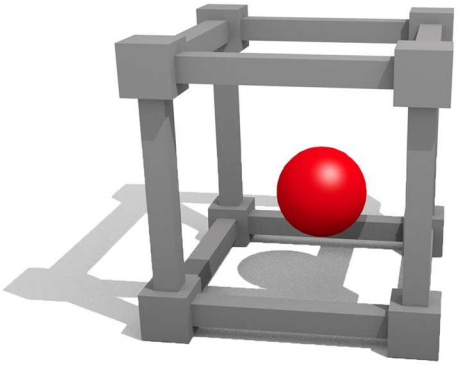
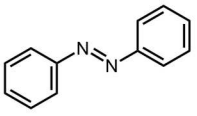
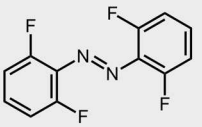
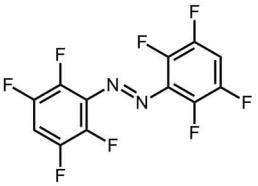
Table 1. continued

	photochromic unit and MOF	ref.
43.	 Zn_2(DBTD)(TNDS)	25, 26
44.	 Zn_2(DBTD)(HDDB)	25
45.	 [Zn(MeBPY)(HBTC[a])Cl]·$2H_2O$	86
46.	 [Eu(OH)(DCBBP)(H_2O)]NO_3·H_2O (Eu-MOF)	73
47.	$[Tb_4(OH)_4(DCBBP)_3(H_2O)_7]Cl_{0.63}(NO_3)_{4.37}\cdot 3H_2O$	54

	guest	ref.
48.	  AzB@$Zn_4O(BDC)_3$ (MOF-5)	29
49.	AzB@Al(OH)(BDC) (MIL-53-(Al))	29
50.	AzB@[Ga(OH)(BDC)]·0.9DMF·xH_2O (MIL-68-(Ga))	29
51.	AzB@[In(OH)(BDC)]·DMF·xH_2O (MIL-68-(In))	29
52.	AzB@$Cu_3(BTC^a)_2$ (HKUST-1)	75
53.	 *tF*-AzB@$Zn_4O(BDC)_3$ (MOF-5)	30
54.	*tF*-AzB@Al(OH)(BDC) (MIL-53-(Al))	30
55.	*tF*-AzB@Ga(OH)(BDC) (MIL-53-(Ga))	30
56.	*tF*-AzB@[Ga(OH)(BDC)]·0.9DMF·xH_2O (MIL-68-(Ga))	30
57.	*tF*-AzB@[In(OH)(BDC)]·DMF·xH_2O (MIL-68-(In))	30
58.	 *oF*-AzB@$Zn_4O(BDC)_3$ (MOF-5)	30
59.	*oF*-AzB@Al(OH)(BDC) (MIL-53-(Al))	30

DOI: 10.1021/acs.chemrev.9b00350
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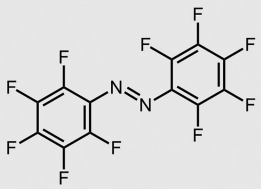
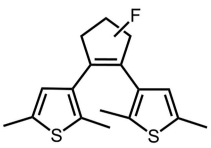
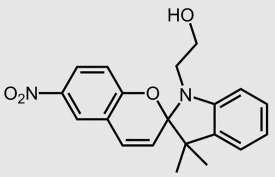
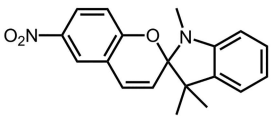
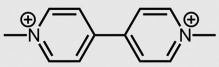
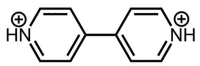
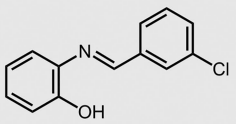
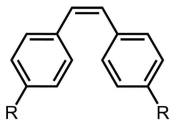
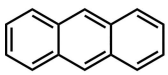
Table 1. continued

	photochromic unit and MOF	ref.
60.	*oF*-AzB@Ga(OH)(BDC) (MIL-53-(Ga))	30
61.	*oF*-AzB@[Ga(OH)(BDC)]·0.9DMF·xH_2O (MIL-68-(Ga))	30
62.	*oF*-AzB@[In(OH)(BDC)]·DMF·xH_2O (MIL-68-(In))	30
63.	 *pF*-AzB@$Zn_4O(BDC)_3$ (MOF-5)	30
64.	*pF*-AzB@Al(OH)(BDC) (MIL-53-(Al))	30
65.	*pF*-AzB@Ga(OH)(BDC) (MIL-53-(Ga))	30
66.	*pF*-AzB@[Ga(OH)(BDC)]·0.9DMF·xH_2O (MIL-68-(Ga))	30
67.	*pF*-AzB@[In(OH)(BDC)]·DMF·xH_2O (MIL-68-(In))	30
68.	 DTE@$Zn_2(BDC)_2(DABCO)$	76
69.	 BSP@$[In_3O(OH)(BTC^a)_2]\cdot H_2O$ (JUC-120)	77
70.	 SP-1@$Zn_4O(BDC)_3$ (MOF-5)	31
71.	SP-1@[Ga(OH)(BDC)]·0.9DMF·xH_2O (MIL-68-(Ga))	31
72.	SP-1@[In(OH)(BDC)]·DMF·xH_2O (MIL-68-(In))	31
73.	SP-1@Al(OH)(BDC) (MIL-53-(Al))	31
74.	SP-1@$Zr_6O_4(OH)_4(BDC)_6$ (UiO-67)	28
75.	 MV@$Zn_3(BDC)_4$	78
76.	MV@$[Zn_3(BTC^b)_2(H_2O)_2]\cdot H_2O$	79
77.	 H_2BPY@$[Cd_3(BTC^b)_2]\cdot 2H_2O$	80
78.	 CBIAP·*t*BuOH@$(ZnI_2)_3(TPT)_2$	83
79.	 R = H, CH_3, Br STa(b,c)@$(ZnI_2)_3(TPT)_2$	87
80.	$(CH_3)_2NH_2^+$ $((CH_3)_2NH_2)_2$@$[Zn_3(BTC^b)_2]$	84
81.	 ANT@$Zn(MeIM)_2$ (ZIF-8)	85

Another class of photochromic molecules, spiropyran derivatives, is completely unexplored as a component of a framework skeleton, probably due to large structural transformations associated with its photoisomerization requiring spiropyran rearrangement from orthogonal to planar geometry.[113,114] However, it does not impede the incorporation of spiropyran fragments as photoactive components of a linker side group or as a guest in a MOF. (Both aspects will be discussed later in this Review.)

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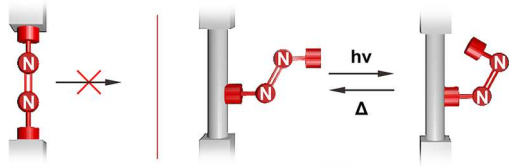

Figure 3. (left) Azobenzene moiety as a part of a framework backbone with hindered photoswitching. (right) Azobenzene moiety as a side group facilitating photoisomerization. Reproduced with permission from ref 60. Copyright 2011 Royal Society of Chemistry.

2.1. Diarylethene Derivatives as a Framework Backbone

Photochromic linkers with a diarylethene (DAE) core are attractive candidates for the development of photoactive materials because of their fatigue-resistant photochromic performance, thermal stability, and rapid response in the solid state.[45,115−117] This class of photoswitches has two isomeric forms: colorless ("open") and colored ("closed", Figure 1), where the "open" form of DAE can be irradiated with UV light, causing bond formation between two heterocyclic thiophenes, which results in the formation of the "closed" form.[45] To coordinatively immobilize DAE as a framework backbone into a framework, the DAE core is modified with anchors such as pyridyl groups or carboxylic acid arms to enable coordination to a metal center. The photoisomerization process can occur without the loss of framework integrity when DAE derivatives are integrated within a rigid scaffold because photoisomerization occurs within the plane of the molecule. Because this Review is focused on the changes in the photophysics of MOFs, the examples of DAE-based ligands as a framework backbone focused on gas sorption modulation will only be highlighted in Table 2.[108,109]

In 2014, we studied energy transfer (ET) in a MOF, which was constructed from a DAE-based derivative with two terminal pyridyl groups as pillars installed between light-harvesting layers (Figure 4 and Table 1: no. 1).[74] In this case, DAE-based ligands acted as the acceptor (A) coordinatively immobilized between porphyrin-based donor (D) layers. When DAE linkers are in the open form, the framework fluoresces, whereas when the "closed" form is produced upon UV irradiation, it opens a pathway for ET, and as a result, emission was quenched. Thus, the photophysical properties of the DAE-containing framework were controlled as a function of the excitation wavelength. Time-resolved photoluminescence (PL) spectroscopy along with spectral overlap function calculations were used to probe the possibility of Förster resonance energy transfer (FRET) in the prepared scaffold. The measurements showed a decrease in the average porphyrin emission lifetime upon the integration of the photoswitch (from 1.46 to 1.24 ns), which is consistent with a resonance ET mechanism. As a result, the ET efficiency and rate constant were found to be 13% and 1.21 × 10^8 s^{-1}, respectively. This concept demonstrated the possibility to control the photophysical response of porphyrin-containing light-harvesting assemblies through photoactive moieties as a function of external stimuli.

As a next step, we quantified the observed photoswitching behavior by the estimation of photoisomerization rates (Table 1: no. 2, 3, and 7).[25] We probed the photoisomerization kinetics in MOFs containing DAE-based linkers and compared their behavior with the photophysics observed for the same derivatives in solution and in the solid state.[25] It was found that the photoisomerization rate of DAE derivatives incorporated in a framework is slower in contrast with that in the solid state. For instance, the closed-to-open form transformation was ∼70 times slower than that of the same DAE derivatives in the solid state. This fact could be explained due to the linker being tethered inside a framework, which could impede the structural transformations associated with the photoisomerization process. We applied the gained fundamental knowledge about photoisomerization kinetics to study changes in material properties, in particular, for monitoring material aging or structural deterioration.[25]

Barbour and coworkers developed a series of DAE-based frameworks using either the common biphenyl-4,4′-dicarboxylic acid (H_2BPDC) or the more adjustable 4,4′-oxidibenzoic acid (H_2OBA) to study whether the flexibility of the second nonphotochromic ligand ($BPDC^{2-}$ or OBA^{2-}) could aid in the modulation of the photoisomerization rate (Table 1: no. 8−10).[81] They showed that the use of the more flexible OBA^{2-} linker resulted in the formation of a 3D, two-fold interpenetrated MOF, which corresponded to lower steric hindrance for photoswitching and therefore resulted in an enhanced photoisomerization rate. This concept opens a pathway for tuning the photoisomerization rate as a function of framework topology.

Zhou and coworkers shifted the above findings toward the application of a DAE-based MOF for the control of singlet oxygen generation and the development of a controllable photocatalyst (Figure 4 and Table 1: no. 4 and 5).[88] Two photochromic frameworks, PC-PCN (photochromic porous coordination network) and SO-PCN (singlet oxygen-generating porous coordination network) containing DAE-based linkers were developed.[88] Once photochromic behavior was probed in PC-PCN, SO-PCN consisting of both a photochromic switch and a photosensitizer was prepared, where $^1O_2$ generation was a result of the ET process activation (Figure 4). For instance, one of the pathways for the ET proposed for the generation of $^1O_2$ is based on the ET process occurring from the excited state of ^{3}[Zn-TCPP]* (H_4TCPP = tetrakis(4-carboxyphenyl)-porphyrin) in the open form of SO-PCN to $^3O_2$. It was also found that SO-PCN possessed catalytic activity toward the photooxidation of 1,5-dihydroxynaphthalene.

Further investigations of DAE-based MOFs were performed by our group in 2019, which demonstrated the possibility of preparing stimuli-responsive materials with dynamically controlled electronic behavior (Figure 5 and Table 1: no. 3, 6, and 7).[26] The electronic properties were studied as a function of photoisomerization in two structurally similar DAE MOFs where the DAE core was used as a pillar, (Zn_2(BPMTC)($BPDC)_2$ and Zn_2(BPMTC)-($SDC)_2$; BPMTC = bis(5-pyridyl-2-methyl-3-thienyl)-cyclopentane and H_2SDC = stilbene-4,4′-dicarboxylic acid; Table 1: no. 3 and 6).[26] The correlation between the photophysical properties and the electronic structure was established by the utilization of a combination of conductivity measurements, diffuse reflectance (DR) spectroscopy, and theoretical calculations. For instance, upon 365 nm irradiation, the shift of the optical band gap from 1.72 to 1.65 eV was detected, which was further supported by theoretical calculations. Conductivity measurements of photoresponsive MOFs were performed in the dark and after 365

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Table 2. Photochromic Moieties and Photoresponsive MOFs Discussed Elsewhere

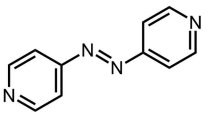
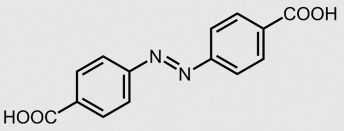
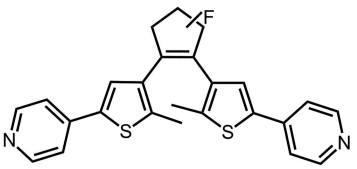
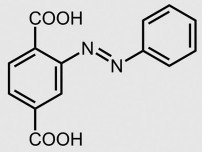
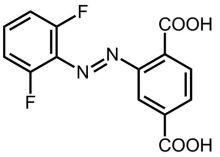
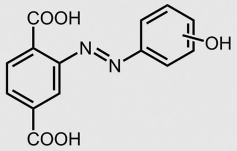
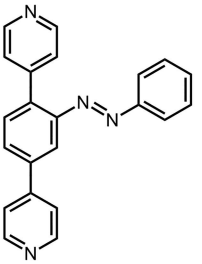
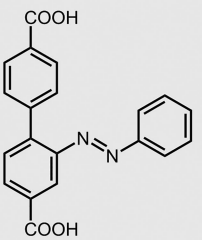
	photochromic unit and MOF	ref.
	framework backbone	
		
1.	[Cd(AzBPY)(MeSUC)]·2.5H_2O	*99*
2.	[Cd(AzBPY)(MeGLU)]·5H_2O	*99*
3.	[$Cd_{1.5}$(AzBPY)$_2$(GLU)]NO_3·MeOH	*99*
4.	[Cd(AzBPY)(SUC)]·2H_2O	*99*
		
5.	[In(AzDC)$_2$]·[$(CH_3)_2NH_2$] (ECUT-50)	*103*
6.	Zn(AzDC)$(BPE)_{0.5}$	*93*
7.	$Zr_6O_4(OH)_4$(AzDC)$_6$	*106*
8.	[Co_3(DPIPA)$_2$(AzDC)$_3$]·2DMF·4H_2O (ECUT-15)	*107*
9.	[Zn(AzDC)$(BPMTFC)_{0.5}$]·1.5DMF (ECUT-30)	*104*
		
9'.	[Zn(AzDC)$(BPMTFC)_{0.5}$]·1.5DMF (ECUT-30)	*104*
10.	[Zn(BPMTFC)(BPDC)]·2DMF·H_2O	*109*
11.	[Zn_4(BDC)$_4$(BPMTFC)$_2$]·4DMF·H_2O	*108*
	side group	
		
12.	Zn_4O(AzBDC)$_3$ (PCN-123)	*110, 97*
13.	$Zr_6O_4(OH)_4$(AzBDC)$_6$ (Azo-UiO-66)	*111*
		
14.	Cu_2(F_2AzBDC)$_2$(DABCO)	*98*
		
15.	[$Cr_3O(OH)$(HAzBDC)$_3$(H_2O)$_2$]·xH_2O (MIL-101(Cr)-azo)	*95*
		
16.	Cu_2(BDC)$_2$(AzBIPYB)	*46, 112*
17.	Cu_2(Me_2TPDC)$_2$(AzBIPYB)	*112*
18.	Cu_2(AzBPDC)$_2$(AzBIPYB)	*112, 96*
		
18'.	Cu_2(AzBPDC)$_2$(AzBIPYB)	*112, 96*
19.	Cu_2(AzBPDC)$_2$(DABCO)	*112*
20.	Cu_2(AzBPDC)$_2$(BP)	*94*
21.	Zn_4O(AzBPDC)$_3$ (IRMOF-10)	*97*

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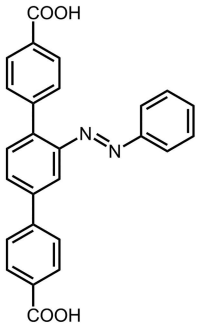
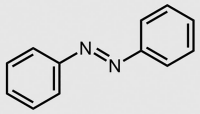
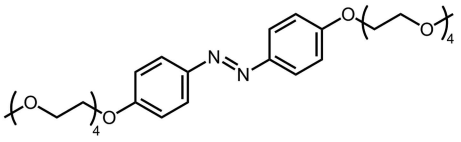
Table 2. continued

	photochromic unit and MOF	ref.
22.	 $Cu_2(AzTPDC)_2(DABCO)$	112

guest

23.	 $AzB@Zn_2(BDC)_2(DABCO)$	100
24.	$AzB@Cu_3(BTC^a)_2$ (HKUST-1)	101
25.	$AzB@Zr_6O_4(OH)_4(BPDC)_6$ (UiO-67)	102
26.	 $PEG\text{-}AB@Zn_2(BDC)_2(DABCO)$	105

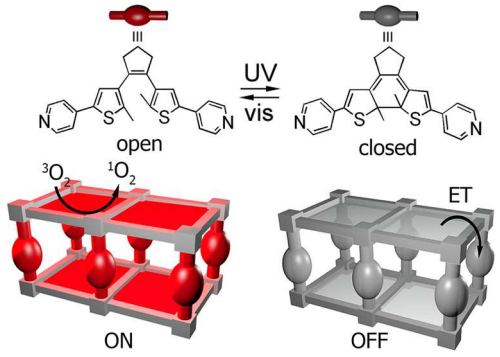


Figure 4. (top) BPMTC molecule in the "open" and "closed" forms as a function of an excitation wavelength. (bottom) MOF in the ON and OFF states depending on the wavelength of the incident light (Table 1: no. 1). This MOF was also used for the reversible control of $^1O_2$ generation. Reproduced with permission from refs 74 and 88. Copyright 2014 American Chemical Society and 2015 Wiley-VCH.

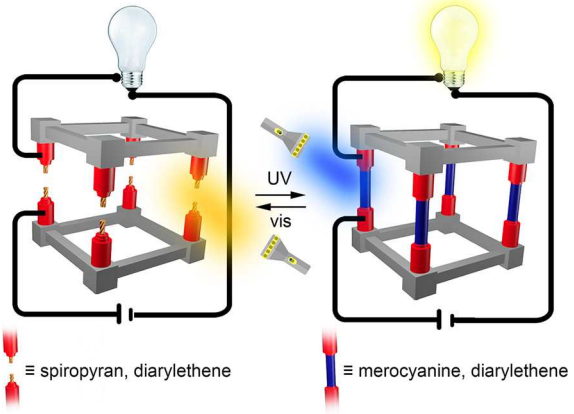


Figure 5. "Wiring" stimuli-responsive linkers as a function of excitation wavelength, resulting in framework electronic structure modulation (Table 1: no. 3, 6, 7, and 43). Reproduced with permission from ref 26. Copyright 2019 American Chemical Society.

nm irradiation. It was shown that the conductivity was enhanced from 6.4 (±0.87) × 10^{-7} to 1.7 (±0.34) × 10^{-6} S·cm^{-1} in the case of $Zn_2(BPMTC)(BPDC)_2$ and from 9.5 (±2.1) × 10^{-7} to 2.9 (±0.67) × 10^{-6} S·cm^{-1} in the case of $Zn_2(BPMTC)(SDC)_2$. The proposed strategy can be utilized for tuning the electronic properties of hybrid materials as a function of external stimuli.

An intriguing concept for the utilization of a DAE-based polymer metal−organic cage (polyMOC, not MOF) as a route to topology switching materials was introduced by Johnson and coworkers (Figure 6).[89] They showed that in the presence of Pd^{2+}, the reversible photoswitching of the MOCs from small Pd_3L_6 rings to $Pd_{24}L_{48}$ rhombicuboctahedra was possible upon irradiation with UV light, resulting in an alteration of the network topology. Moreover, it was possible to reverse the MOC structure to the small Pd_3L_6 rings with the application of green light (λ_{ex} = 490 nm), thus regenerating the original network topology. The material maintained the switching behavior for up to seven cycles, which can open avenues for its application in soft robotics.

2.2. Viologen Derivatives as a Framework Backbone

Unlike DAE-based compounds, whose photochromic behavior is associated with a structural transformation, viologen compounds undergo photoinduced electron transfer to the viologen dication from a counteranion upon irradiation.[118] Previous studies indicate that photochromism in viologen-

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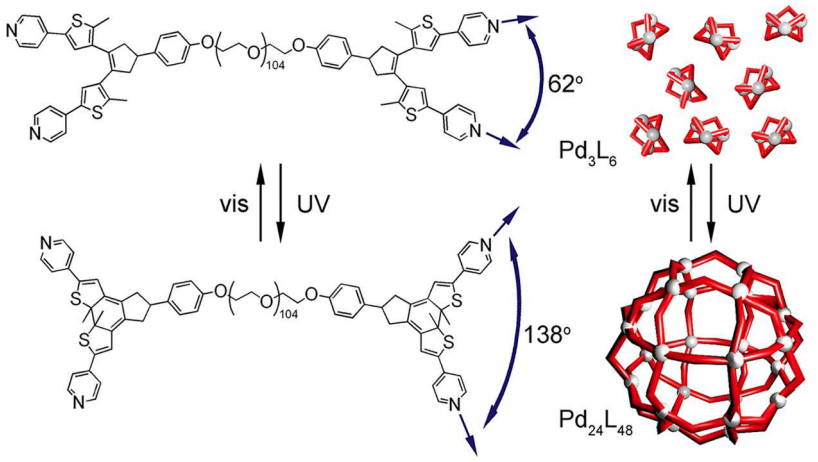

Figure 6. (left) Long photoresponsive linkers. (right) Schematic representation of polyMOC interconversion. Reproduced with permission from ref 89. Copyright 2018 Nature Publishing Group.

based compounds is mainly dictated by three factors: (1) short distances between the pyridinium nitrogen atom and the donor atom, (2) the presence of certain bonds (e.g., O−H···N, C−H···O, or C−H···X (X = Cl, Br) hydrogen bonds) between the pyridinium ring and the donor, and (3) the presence of $\pi-\pi$ or C−H$-\pi$ interactions between the pyridinium ring and the adjacent aromatic ring.[90,119−121] In addition, viologen-based compounds have the potential to undergo facile photochemical reactions in the solid state,[118] which opens a pathway for studies in a MOF matrix.

In an early report, Fu and coworkers studied photochromism in a 3D viologen-based Zn-MOF (Table 1: no. 11).[90] This Zn-MOF was prepared from viologen and dicarboxylic acid linkers, serving as an electron acceptor and an electron donor, respectively. The distances between the ligands were determined to be in the range of intermolecular charge transfer (CT),[122] thus displaying that it is possible to tune the photophysical properties through tailoring the ligand alignment. Moreover, the stabilization of viologen radicals generated upon irradiation within the MOF matrix provides a pathway for electronic structure modulation.

The other application of viologen-based MOFs for a nondestructive readout was demonstrated by Zhang and coworkers on the example of europium-containing MOF (Eu-MOF, Figure 7 and Table 1: no. 12).[91] The MOF acted as a switch due to ET from the excited state of Eu^{3+} to the colored state of the viologen-based ligand. The initial PL response was restored through the exposure of the MOF to atmospheric oxygen. The switching behavior of the Eu-MOF was maintained for at least seven cycles without a noticeable loss of luminescence intensity (Figure 7).

Those studies provided the Gao research team with a necessary platform to reveal the versatile responsive properties of an ionic viologen-based Eu-MOF (LVMOF-1), including the photochromic, piezochromic, and hydrochromic behavior (Table 1: no. 13).[92] The origin of such properties was attributed to CT or ET. The observed behavior involved viologen as an electron acceptor, a guest anion as an electron donor, luminescing Eu^{3+} as a donor in ET process(es), and the anion−viologen CT complex or ET-generated radical as an acceptor in ET process(es) (luminescence quencher). Such multifaceted responsive properties could be utilized for

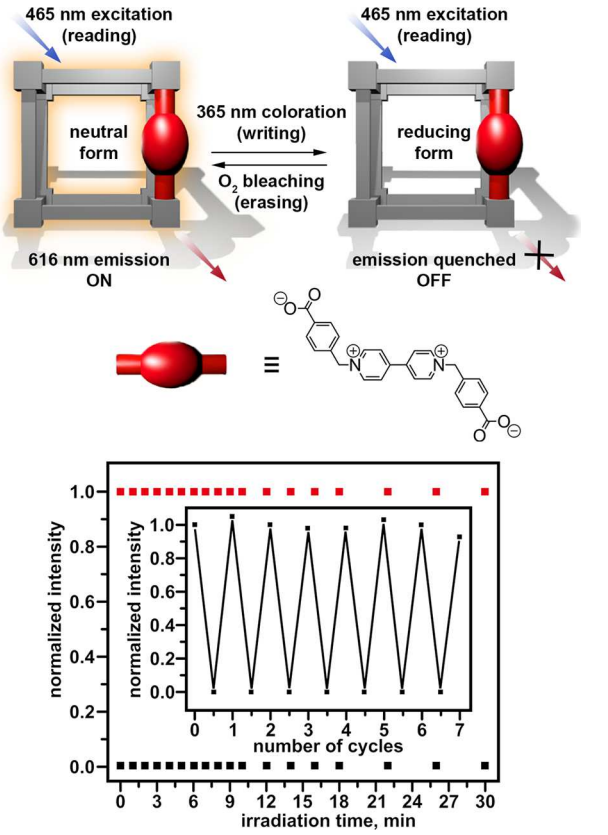

Figure 7. (top) Photoswitching of a viologen-based ligand incorporated inside the Eu-MOF (Table 1: no. 12). (bottom) Nondestructive readout capability of the MOF in the initial state (red dot) and colored state (black dot), λ_{ex} = 465 nm. The modulation of fluorescence intensity is shown at 616 nm based on alternating UV irradiation and O_2 exposure. Reproduced with permission from ref 91. Copyright 2011 Royal Society of Chemistry.

the development of multimode switches, pressure sensors, or chemical logic gates.

Very recently, Sun and Zheng reported the possible utilization of viologen-containing frameworks as inkless and erasable printing media. They prepared three viologen-based MOFs with different dimensionalities (1D−3D) exhibiting reversible photochromism through the mechanism of photo-

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generated radicals caused by photoinduced electron transfer (Table 1: no. 14, 15, and 45).[86] The photochromic moieties were integrated as a part of a ligand backbone (Table 1: no. 14 and 15)[86] and as a side group of linkers (Table 1: no. 45).[86]

2.3. Naphthalenediimide Derivatives as a Framework Backbone

It has been found that redox-active naphthalenediimide (NDI) exhibits reversible photochromism through a photoinduced electron transfer and is subsequently converted into the radical species (NDI*), which can be generated by electrochemical and photochemical methods.[123,124] Radical formation upon irradiation is associated with a drastic color change and the corresponding appearance of new absorption bands found in irradiated NDI-based MOFs.[59] These NDI compounds are useful candidates for the construction of photochromic MOFs due to the ability to derivatize the organic core for subsequent metal coordination as well as reversible electron transfer.[125]

In 2015, Banerjee and coworkers developed a porous photochromic Mg-MOF using an NDI linker that exhibited not only reversible photochromism through radical formation but also reversible solvatochromic behavior in solvents with differing polarities (Table 1: no. 16).[55] The reported MOF was used for effective amine detection because a drastic color change and PL quenching were accompanied by this process, which was attributed to donor−acceptor electron transfer between the amines and the NDI-based MOF. As a continuation of this work, the Banerjee group reported three MOFs (Mg-NDI, Ca-NDI, and Sr-NDI) with ligands containing a 1,4,5,8-NDI core to be used for inkless and erasable printing (Figure 8 and Table 1: no. 16−18).[56]

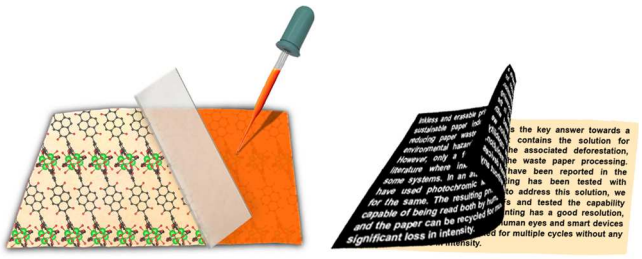

Figure 8. (left) Schematic representation of NDI-based MOF coated paper. (right) Representation of printing on the coated paper with a stencil through controlling the incidence of sunlight on the MOF coated paper (Table 1: no. 16−18). Reproduced with permission from ref 56. Copyright 2016 Royal Society of Chemistry.

Because NDI-containing chromophores typically display fast discoloration, inclusion inside of the extended MOF structure could resolve this issue.[39] Electron paramagnetic resonance (EPR) analysis revealed that the as-synthesized framework does not contain radicals, but with application of sunlight, a sharp resonance appears, verifying the formation of NDI* upon irradiation.

Due to the stability of the photogenerated NDI* within the MOF backbone, MOF-coated paper was prepared for inkless and erasable printing, disappearing after 24 h and rendering the blank paper reusable for printing. Furthermore, the color of the irradiated MOF crystals can be modulated as a function of structure according to spectroscopic studies, demonstrating the feasibility to tune ink color. At the same time, Han and coworkers explored a multifunctional MOF with a tetrazole-based NDI backbone (NBU-3) exhibiting, for the first time in an extended matrix, both reversible photochromic and electrochromic properties for the development of materials for electro-optical switches and memory devices (Table 1: no. 19).[57] The PL measurements revealed a blue shift of the MOF emission in comparison with that of the free ligand, which could be attributed to LLCT from the $\pi-\pi$ stacking in the MOF or LMCT.

A Ca-MOF with an NDI-based polycarboxylate ligand was developed by Zou and coworkers, which underwent a reversible photochromic transition from yellow to dark green upon irradiation (Table 1: no. 18).[58] This MOF has a doubly interpenetrated 3D porous network, leading to strong intermolecular $\pi-\pi$ stacking between π-deficient NDI rings, which reinforced the stability of the structure. The photophysical studies revealed a broad absorption band that could originate from photoinduced electron transfer. In addition, the photochromic capability of this MOF may result from the photoinduced radical generation from the NDI ligand, as confirmed by EPR spectroscopy. As a further development, a series of Cd-MOFs with NDI-based linkers were studied by Zhang, Xiang, and coworkers to feature the role of how interpenetrating packing could affect photoinduced electron transfer (Table 1: no. 20−22).[59] The molecular conformation of the secondary linker (in addition to NDI) was used as a tool to tune the degree of interpenetration. In addition to a detectable color change occurring upon irradiation, the absorbance spectrum revealed the appearance of a shoulder at ∼534 nm that could be a result of intermolecular electron transfer such as an MLCT.[126] Notably, there is no color change in the H_2NDI linker (H_2NDI = 2,7-bis(3,5-dimethyl) dipyrazol-1,4,5,8-naphthalene tetracarboxydiimide) itself upon irradiation, giving credence to the necessity of the framework for the promotion of photoswitching. The kinetics of the photochemical reactions for two of the MOFs were compared, which indicated that the photoresponsive rate was higher for the interpenetrated framework because the $\pi-\pi$ stacking from the adjacent NDI moieties was more beneficial for the transfer of electrons and the formation of free radicals.

3. PHOTORESPONSIVE MOIETY AS A LIGAND SIDE GROUP

The isomerization of photoswitchable linkers integrated as a framework backbone could result in framework degradation due to possible structural changes associated with ligand transformation upon irradiation. Moreover, few to no studies on azobenzene or spiropyran derivatives with this integration method exist. The challenge of preserving the MOF integrity can be remedied through the addition of a photoresponsive side group to the linker backbone in the MOF; therefore, linker photoisomerization can occur within the framework pores or on the MOF surface. Due to this fact, there are more examples of photochromic moieties integrated into a MOF as side groups (Figure 9), in contrast with the cases discussed in the section above.

3.1. Azobenzene Moiety as a Linker Side Group

Azobenzene and its derivatives undergo a trans−cis isomerization when irradiated with UV−visible light[127] associated with significant structural reorganization, as discussed before (Figure 3). Therefore, it is beneficial to anchor azobenzene

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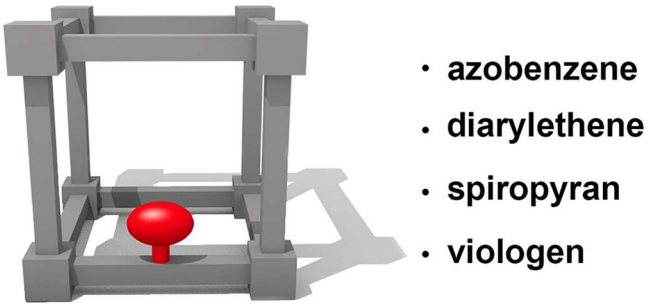

Figure 9. Photoactive moieties attached to the MOF linker as a side group.

species from only one side, leaving the other side as dynamic to maintain the structural integrity of the MOF. Stock and coworkers investigated how variations in metal and size or shape of the linkers influence the switching properties of MOFs containing an azobenzene unit as a linker side group.[62] As noted in a previous work by this research team, the switching effect was improved through avoiding the interpenetration of the network. This improvement could be attributed to the switching effect and the available pore size. Furthermore, these studies led to the preparation of four new MOFs that were made using the same synthetic procedure as CAU-5 while varying only the metal ion or organic linker (Table 1: no. 24−27).[62] Because interpenetration can potentially be suppressed through the usage of functionalized linkers, the azobenzene-based linker was paired with varying linkers to tune the overall structure. It was shown that the variation of metal ions had no significant effect on the switching behavior of the MOF.

The same group explored the possibility of introducing an azobenzene moiety inside of a framework postsynthetically (Table 1: no. 29 and 30).[63] As a starting point, the MOF, Cr-MIL-101-NH_2, was chosen due to the presence of a reactive amino group as well as it being a framework with high chemical stability and with large, accessible pores. The postsynthetic modification (PSM) of Cr-MIL-101-NH_2 was pursued with 4-phenylazobenzoyl chloride and 4-(phenylazo)-phenylisocyanate in a microwave oven to introduce an amide-based azobenzene derivative and a urea-based azobenzene derivative to form Cr-MIL-101_amide and Cr-MIL-101_urea, respectively. As evident through absorption measurements, the degree of functionalization played a role in the cis−trans isomerization, as more distinct changes in the spectra were observed in the case of the amide compared with urea. Interestingly, in the two explored MOFs (Cr-MIL-101_amide and Cr-MIL-101_urea), only partial reversibility of the photoswitching process was detected, which was attributed to a photobleaching or a steric hindrance effect. In addition, the influence of the host was confirmed by observation that the cis−trans isomerization of the extracted PSM reaction products in solution was fully reversible. This study can be beneficial for photoswitchable MOF engineering as the effect of linker functionalization was examined.

To overcome potential steric restrictions for azobenzene photoisomerization, Yaghi, Brown, and coworkers chose a MOF (IR-MOF-74-III) with large, noninterpenetrated 1D hexagonal pores (Table 1: no. 31).[64] The main goal of this study was to probe the ability of the MOF to store and release cargo, in which a luminescent dye (e.g., propidium iodide) was loaded into the channels of the MOF so that its release upon photoisomerization could be monitored spectroscopically. As expected, no release of the luminescent dye was found without irradiation, whereas the isomerization of the azobenzene side group triggered dye release under MOF irradiation. In general, this concept could be applied to the development of the MOF-based "smart vessels" in which "opening or closing" is triggered by an external stimulus. A similar type of "on-demand" cargo release was studied by Meng and Gui (Table 1: no. 32)[65] on the example of a Zr-MOF containing an azobenzene moiety as a linker side group, rhodamine B as a guest molecule, and β-cyclodextrin as a capping moiety. The controllable cargo release was achieved by modulating the binding of β-cyclodextrin to the protruding azobenzene linker. Upon irradiation, the dissociation of β-cyclodextrin was observed due to a drastically reduced binding affinity of β-cyclodextrin for *cis*-azobenzene compared with *trans*-azobenzene.[128] In other words, photoisomerization from trans to cis can drive β-cyclodextrin away from the azobenzene linkers, prompting the release of the cargo, rhodamine B guest molecules.

Heinke and coworkers studied how linker variation affects photophysics through the construction of two different azobenzene-containing pillared MOFs in which photoisomerization takes place inside the pores (Table 1: no. 25 and 33).[66] In the two different MOFs, photoswitching was enabled in only one scaffold because in the other case, steric hindrance did not allow for the trajectory of photoisomerization. As a follow-up study, the same group studied the activation barrier for cis−trans isomerization because it is a fundamental parameter dictating the properties of photoswitchable linkers (Table 1: no. 34 and 35).[67] Recent studies from the same group showed that remote control over the proton conduction of guest molecules (1,4-butanediol and 1,2,3-triazole) in a Cu-based surface-mounted MOF (SURMOF) was enabled by the photoisomerization of the azobenzene side groups of the MOF linker (Table 1: no. 36).[68] Switching between a relatively high-proton-conductivity (trans) and a low-conductivity (cis) state was demonstrated. The conductivity of the 1,2,3-triazole guest in the SURMOF switched between 1.2×10^{-4} S/m (trans) and 7.9×10^{-5} S/m (cis), resulting in a 1.5 times conductivity enhancement.[68] Because switching of proton conductivity was relatively fast in these thin films, this work can foreshadow new directions for using MOFs as an active material in field-effect transistors.

In recent studies performed by Wang, magnetic endohedral metallofullerenes were incorporated inside a photoresponsive MOF with linkers containing azobenzene as a side group to optically control the MOF magnetic properties (Figure 10 and Table 1: no. 37 and 38).[69] Metallofullerenes were chosen for the incorporation into MOF due to the ability to tune their magnetic properties based on their responsive electron spin character, thus rendering them as ideal candidates for the response to external stimuli.[129−132] Upon irradiation with UV light, the isomerization of the azobenzene groups in the pores of the MOF was able to modulate the spin relaxation of the endohedral metallofullerene, $Sc_3C_2@C_{80}$, while improving the single-molecule magnetic behavior, $DySc_2N@C_{80}$. Ultimately, these studies can foretell the development of "smart" molecular magnetic materials based on the response to external stimuli, which could benefit applications from information processing to its storage. In addition to the examples discussed in this Review, there are many examples

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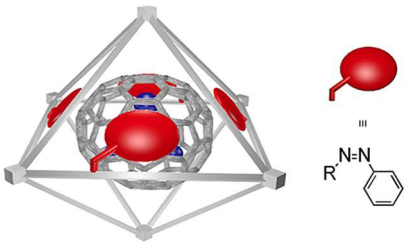

Figure 10. Schematic representation of metallofullerene@^{Azo}MOF with azobenzene moieties protruding into the pores (Table 1: no. 37 and 38). Reproduced with permission from ref 69. Copyright 2018 American Chemical Society.

employing azobenzene as a side group in a MOF linker for gas sorption studies that can be found elsewhere (Table 2: no. 12−22).[46,94−99,110−112]

3.2. Diarylethene Moiety as a Linker Side Group

Benedict and coworkers have spearheaded the inclusion of DAE as a side group in a MOF through the construction of a series of DAE-based frameworks (Table 1: no. 39).[70] It was found that whereas the photochromism of the ligand in solution was fully reversible, the cycloreversion reaction was suppressed upon incorporation of the linker into the MOF. These changes in photochromic properties could be a result of changes in the linker environment and the stabilization of the colored form of the photoswitch by the MOF. Whereas this study reinforced the potential to add photoswitching functionality through ligand design without changing the topology of the MOF, the suppression of the photochromic behavior in the MOF emphasizes challenges that need to be overcome in this sector to achieve maximum material performance. The same group further studied the effect of the MOF on the photoswitching ability of DAE-based derivatives after their integration as a side group through the functionalization of the DAE core with bulkier phenyl groups instead of methyl groups (Table 1: no. 40).[71]

Again, the linker itself exhibited photoswitching in solution, but the repeated cycling of the MOF resulted in loss of photoresponsivity. In a more recent report, Benedict and coworkers synthesized a pyridyl-based DAE derivative to utilize as pillars in a 2D layered MOF (Table 1: no. 41).[72] On the basis of this different approach from previous examples, the increased spacing between the photoswitching moieties could have potentially led to linker photoisomerization inside the pores, but a nonreversible behavior was still detected.

3.3. Spiropyran Moiety as a Linker Side Group

The photoisomerization of spiropyran-based derivatives within a framework, even with the immobilization of the photoswitch as a side group, is still challenging because of the large structural changes associated with this transformation. The allure of studying spiropyran-based photoswitches is centered on the fact that their isomeric forms (i.e., the closed-ring isomer is spiropyran and the open-ring isomer is merocyanine) have vastly different physicochemical properties.[114] Spiropyran is hydrophobic and uncharged, whereas merocyanine is a hydrophilic zwitterion, which gives rise to a large electric dipole moment in comparison with the former. In addition, the spiropyran isomer is optically transparent in the visible region, whereas merocyanine appears deep blue with an absorption maximum at λ = 550−600 nm. To date, there have been very few investigations of spiropyran-based compounds incorporated in MOFs through either integration as a side group or as a guest in the pores, rendering this subsection of photoswitching MOFs both an open and intriguing research area. D'Alessandro and coworkers tackled this challenge through the development of a spiropyran-incorporated MOF synthesized through metal-node PSM in MOF-808, as shown in Figure 11 (Table 1: no. 42).[27] This

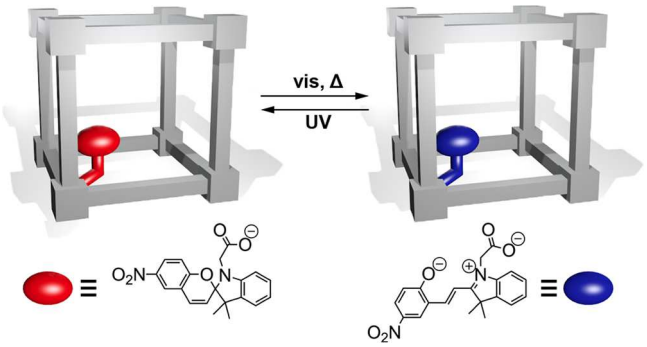

Figure 11. Schematic representation of a spiropyran-containing MOF prepared via a two-step modification of the metal nodes in MOF-808 (Table 1: no. 42). Reproduced with permission from ref 27. Copyright 2016 Royal Society of Chemistry.

powerful approach is "complementary" to the integration of photoresponsive moieties as linker side groups; however, a small degree of PSM on the level of several percent is still a noteworthy challenge.

In a recent study, we reported two novel photochromic linkers with spiropyran groups attached to a ligand backbone (Table 1: no. 43 and 44).[25] Through this approach, the solid-state photoisomerization of spiropyran moieties was achieved despite large structural rearrangements associated with this transformation. However, the photoisomerization of the linker with two spiropyran moieties still remains a challenge because the sterically hindered photoisomerization requires a much larger MOF aperture (Table 1: no. 44). In addition, the effect of a rigid scaffold on photoisomerization kinetics was also probed. The studies revealed that the coordinatively immobilized spiropyran derivative could mimic solution-like photophysical behavior. These findings were translated toward mapping changes in material properties. As shown in Figure 12, upon treatment with acid, the degradation of the framework resulted in linker release and therefore limited the photoisomerization typically observed in the solid state. The loss of isomerization reversibility resulted in a permanent mark on the surface of the material, thus serving as an indicator for necessary material replacement or repair.

In attempts to develop stimuli-responsive materials with dynamically controlled electronic behavior, a MOF with a spiropyran side group was also investigated by us (Table 1: no. 43).[26] In both single-crystal and bulk measurements, the MOF conductivity was found to increase upon irradiation, which could be due to the formation of the charge-separated merocyanine form under UV irradiation.[28] To visualize the MOF electronic structure modulation, an electric circuit with the spiropyran-integrated MOF was constructed, resulting in LED switching as a function of incident light (Figure 5). This work can lead to new avenues for the development of stimuli-responsive materials with controllable electronic properties.

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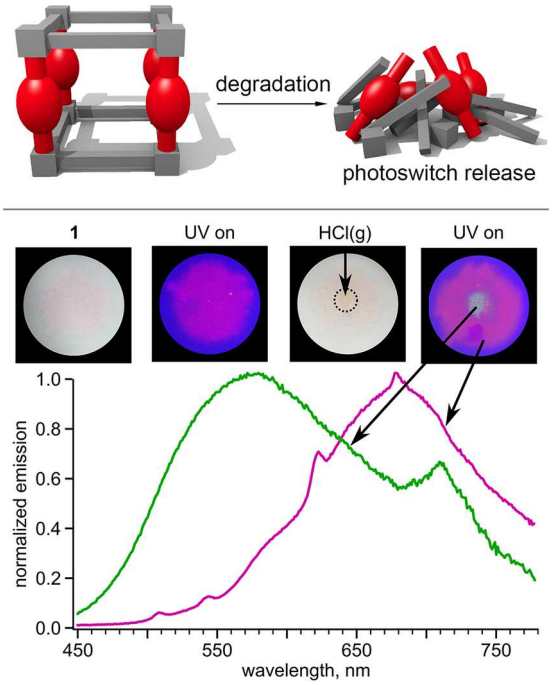

Figure 12. (top) Schematic representation of photochromic linker release due to framework degradation upon acid treatment. (bottom) Visible evidence of MOF degradation at the point of acid contact as well as the PL spectra of Zn_2(TNDS)(HDDB) before (purple) and after (green) exposure to HCl vapors. Reproduced with permission from ref 25. Copyright 2018 American Chemical Society.

3.4. Viologen Moiety as a Linker Side Group

Although viologen-based materials do not undergo a structural photoisomerization, alleviating a steric hindrance issue, there have still been few examples of a MOF with a linker containing a viologen moiety as a side group. In contrast with a previous Eu-MOF with viologen-based framework linkers,[91] Zang and coworkers investigated a viologen-functionalized chiral Eu-MOF that exhibited multifaceted properties, from photochromism and photomodulated luminescence to photoswitchable nonlinear optics (NLO) and piezoelectric properties (Table 1: no. 46).[73] The MOF displayed a reversible color change from light yellow to pale blue in which the framework emission was controlled, leading to photoinduced luminescence switching. The photoregulated piezoelectric switching was found to accompany the reversible photochromic process, as the MOF piezoelectric reversibility was maintained after six cycles. Furthermore, reversible photoswitching behavior that lasted for up to eight cycles was reported for the Tb-MOF-containing photoresponsive viologen moieties (Table 1: no. 47).[54]

4. PHOTOCHROMIC COMPOUND AS A GUEST

Spatial restrictions observed for photoinduced isomerization in the solid state could potentially be resolved through the inclusion of photochromic compounds in the porous scaffold of a MOF (Figure 13).

The organization of guests in the uniform pores of MOFs can enable the control of photophysical properties of the guests themselves or the host−guest interactions, which can be translated to photoswitch integration, as highlighted in this section. In addition, the exploration of photoswitch@MOF

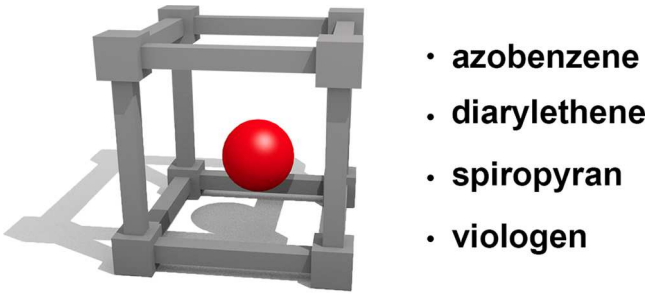

Figure 13. Photoactive moieties incorporated as a guest molecule inside MOFs.

could help to overcome synthetic challenges because the derivatization of a photochromic core could be complex, expensive, and labor-demanding as opposed to the guest-based alternative. Several photoswitches are commercially available, and thus guest inclusion can occur without the aforementioned synthetic limitations.

4.1. Azobenzene as a Guest

Although the majority of azobenzene@MOFs are focused on gas sorption studies, as highlighted elsewhere (Table 2: no. 23−26),[100−102,105] there are few examples involving the modulation of the photophysical properties of MOFs. For instance, Ruschewitz and coworkers reported the successful trans−cis isomerization of azobenzene integrated in MOF-5.[133] An expansion of that work followed to study the influence of host materials on the switching potential of azobenzene guests, in which Ruschewitz and coworkers examined a range of MOFs (MOF-5, MIL-68(Ga), MIL-68(In), and MIL-53(Al)) loaded with azobenzene (Table 1: no. 48−51)[29] to study the possible dependence of the photoisomerization rate on the MOF pore aperture and/or choice of the photochromic linker. The photoisomerization process of embedded azobenzene was investigated through monitoring the appearance of resonances associated with trans-to-cis conversion after irradiation by infrared spectroscopy. The trans-to-cis conversion occurring within the confined pores of the MOF was improved compared with that of azobenzene in the solid state, highlighting one of the main advantages of MOFs, their intrinsic porosity. This work also demonstrated the guiding principles for future photoswitch@MOF engineering, highlighting frameworks (e.g., MIL-53(Al)) that are not suitable for photoswitch isomerization due to the specific aperture of their channels. The Ruschewitz team demonstrated the power of the aforementioned approach on the examples of 15 photochromic MOFs through the loading of various fluorinated azobenzenes inside frameworks (e.g., MOF-5, MIL-53(Al), MIL-53(Ga), MIL-68(Ga), and MIL-68(In)) to prepare *F*-AZB@MOFs (Table 1: no. 53−67).[30] All of the F-AZB@MOFs are photoresponsive to visible light, whereas in some of them, 95% photoisomerization between the *E* and *Z* forms with no degradation after several cycles was detected.

In 2016, Gu, Chen, and coworkers explored a new photoswitch guest integration concept through a liquid-phase epitaxial method to prepare thin films of HKUST-1 with azobenzene included as a guest (Table 1: no. 52).[75] Similar to the bulk phase, azobenzene-containing guest molecules encapsulated into the film were able to isomerize between the trans and cis forms upon irradiation with either UV or visible light. Furthermore, the prepared photoswitch@

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MOF materials possess temperature-dependent photoluminescence properties, providing a platform for the development of multifunctional noninvasive thermometers.

4.2. Diarylethene as a Guest

In 2013, Benedict and coworkers reported one of the first examples of a MOF with a DAE-based derivative included as a guest (Table 1: no. 68).[76] The inclusion of the DAE-based guest was confirmed not only through a change in the absorption profile upon irradiation but also through the linear dichroism present in the irradiated crystals, which showed the preferential alignment of the guests within the host pores. In contrast with solution-based studies, their approach was based on the incorporation of molten diarylethene guests into evacuated MOFs, affecting the guest alignment. This strategy is beneficial for engineering optoelectronic devices in which precise guest alignment is a key factor for performance enhancement.

4.3. Spiropyran as a Guest

Because of the large structural changes occurring during spiropyran photoisomerization, studies of its integration as a linker backbone are nonexistent, whereas its appearance as a side group has only recently become feasible.[25−27,77] The inclusion of spiropyran as a guest could accommodate the structural changes necessary for photoswitch photoisomerization.

In an early example, Zhu and coworkers investigated In-MOF (JUC-120) films with the inclusion of spiropyran derivatives through microwave-assisted crystallization (Table 1: no. 69).[77] The film was found to have high photochromic reversibility, as no significant loss in the intensity or degradation was evident after 10 cycles. Interestingly, the metastable open merocyanine form was found to be stabilized in the pores, promoted by the specific MOF−guest interactions. The Ruschewitz group continued their investigations on how a host (MOF) can affect the optical properties of a spiropyran-based guest (Figure 14 and Table 1: no. 70−73).[31] They loaded the spiropyran-based molecule into various MOFs, MOF-5, MIL-53(Al), MIL-68(In), and MIL-68(Ga), selected based on the pore aperture; that is, not only should the spiropyran-based guest fit in the pores, but also the structural transformation of the guest associated with its photoisomerization should occur. Moreover, the MOF photophysical profile should not interfere with the absorption properties of the photoresponsive guest. As a result, the observed photoswitching behavior of integrated spiropyran guests was in line with their behavior in solution rather than in the solid, rendering MOFs as "solid solvents".

The preceding studies of spiropyran@MOFs provide sufficient background for the modulation of electronic profiles of such materials through guest photoisomerization (Figure 15 and Table 1: no. 74).[28] Similar to the aforementioned MOF in which a spiropyran moiety was integrated as part of a linker side group, conductivity enhancement by one order of magnitude was also detected in the spiropyran@UiO-67 film. The electronic properties of such a film could potentially be tailored through the optimization of the distance and the orientation of the spiropyran derivatives inside the MOF matrix.

4.4. Viologen as a Guest

In addition to viologen-based compounds being studied as a framework backbone or as a side group in a MOF, there are also studies of its inclusion as a guest and its ability to modulate the corresponding MOF photophysical properties.

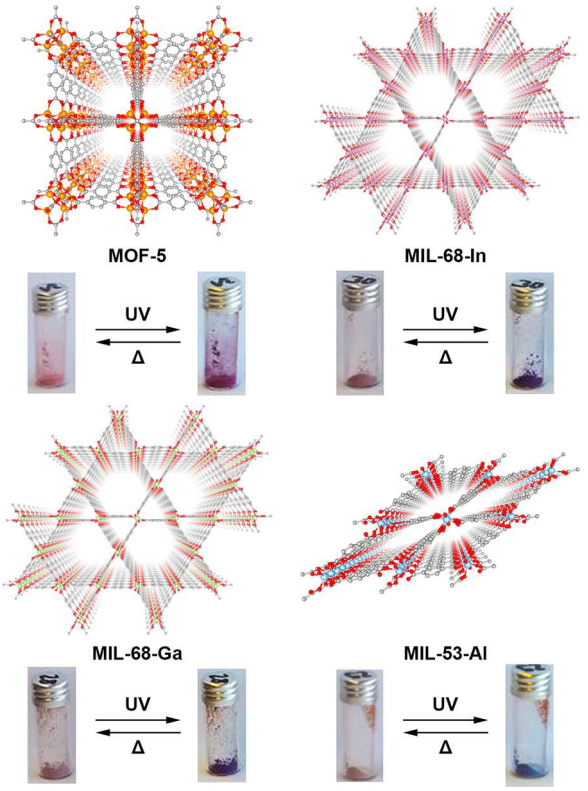

Figure 14. MOF hosts, MOF-5, MIL-68-In, MIL-68-Ga, and MIL-53-Al, affect the optical properties of spiropyran-based guests (Table 1: no. 70−73). The material color change is shown upon material irradiation. Reproduced with permission from ref 31. Copyright 2017 American Chemical Society.

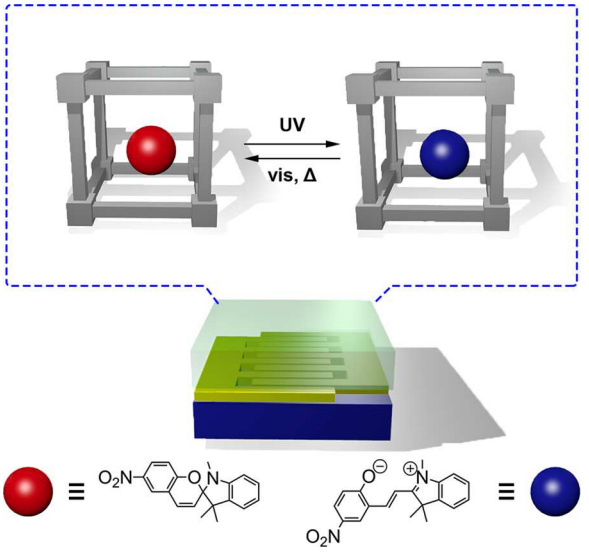

Figure 15. (top) Photoswitchable UiO-67 film with embedded spiropyran as a guest, highlighting the isomerization between spiropyran (red) and merocyanine (blue) forms (Table 1: no. 74). (bottom) Schematic representation of the MOF film deposited on an interdigitated gold electrode (yellow) and quartz (blue). Reproduced with permission from ref 28. Copyright 2019 Wiley-VCH.

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Studies by Fu and coworkers focused on the modulation of emission color of MOFs through photochromic viologen CT complexes (Table 1: no. 75).[78] A Zn-MOF with incorporated methyl viologen was constructed for the alignment of electron-donating and electron-accepting counterparts, resulting in photoinduced and thermally induced electron transfer.[78] The π-stacking arrangements in the MOF allowed for the precise donor−acceptor alignment that resulted in the formation of long-lived charge-separated states. In a more recent study by the same group, an anionic Zn-MOF (host) was used to include methyl viologen dications (guest, Figure 16 and Table 1: no. 76).[79] In this case, a donor−acceptor

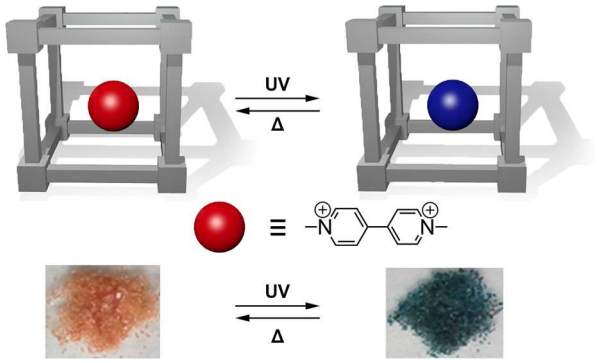

Figure 16. (top) MOF with viologen cations embedded in the channels. (bottom) Photographs of the sample before and after irradiation (Table 1: no. 76). Reproduced with permission from ref 79. Copyright 2016 American Chemical Society.

MOF was constructed; the carboxylate group of the linker acted as the donor, whereas the methyl viologen dication behaved as the acceptor, leading to the formation of a CT complex.

Remarkably, in the viologen@MOF developed by Wang, Guo, and coworkers (Table 1: no. 77),[80] the detected charge-separated state was stable in the dark for more than 2 months. On the basis of a number of compelling examples, viologen-based compounds could potentially open novel strategies for the development of MOF-based tools for bioimaging, for data storage, or as the next generation of "smart" barcodes.

4.5. Other Photochromic Molecules as a Guest

There are also some examples of guest@MOFs involving photoswitches that are not discussed in the preceding section. For example, a remarkable feature of anthracene lies in its ability to photodimerize under UV irradiation, leading to significant changes in photophysical properties.[134] Utilizing anthracene as a guest in zeolites and in MOFs/COFs has been realized,[135−137] but their photoswitching capacity is still in the rudimentary phases.

Another less studied class of photochromic molecule is stilbene, in which the Z to E isomerization has been investigated in MOFs. An example in this category are salicylideneanilines, which have been found to exhibit photochromism in both the solid state and solution based on the geometrical rearrangement of the molecule.[82] In 2007, Fujita and coworkers reported the ability to switch between the thermochromic and the photochromic behavior of salicylideneanilines due to their inclusion in a Zn-based porous framework constructed from tris(4-pyridyl)triazine ligands (Table 1: no. 78).[83] The inclusion inside a rigid matrix led to a significant twist of the dihedral angle in salicylideneaniline and therefore caused a shift in its photophysical profile. Fujita and coworkers also developed another example of a Zn-MOF with a tris(4-pyridyl)triazine ligand and a (*Z*)-stilbene guest (Table 1: no. 79).[87] In the latter example, it was shown that the electron-deficient pyridyl-based ligand can participate in the formation of host−guest CT complexes and promote photoinduced energy or electron transfer.[138] Interestingly, in the absence of the host, photoisomerization did not occur, and the individual components were not able to catalyze the conversion.

Zhang and coworkers developed a photochromic MOF exhibiting electron transfer due to host−guest interactions (Table 1: no. 80).[84] The photoresponsive system was constructed from a Zn-based anionic MOF (host) and $(CH_3)_2NH_2^+$ cations (guest) rather than "classical" photochromic molecules previously featured in this Review. This MOF underwent a rapid color change in response to irradiation, which is reversible, whereas the structural integrity was unchanged. The photochromic process is thought to be derived from a photoinduced electron transfer between the electron-rich anionic framework and the electron-deficient guest cations. The prepared MOF also exhibited photoregulated luminescence switching modulated by ultraviolet−visible light irradiation.

Very recently, Ameloot showed that the integration of anthracene in a MOF (ANT@ZIF-8) could lead to reversible yellow−purple emission photoswitching (Table 1: no. 81).[85] The photoresponsive host−guest system was proposed to be the result of anthracene photodimerization promoted by the pore aperture and flexibility of the host (ZIF-8). The solid-state photoswitching accessibility in ANT@ZIF-8 led to a proof-of-concept for the design of photopatternable, erasable, and rewritable paper. The patterns were found to be invisible under ambient light, whereas the patterns could be read under UV light, thus portending advancements in the realm of "hidden labels" with important information (e.g., serial numbers).

5. SUMMARY AND PERSPECTIVES

Through the combinatorial advantages of the intrinsic properties of photochromic molecules with the inherent properties of MOFs, such as their modularity, versatility, porosity, and structural tunability, the opportunity to devise novel classes of photoswitching MOFs has come to the forefront. To date, MOFs have been studied extensively for more "classic" applications involving gas storage and separations, but there has been a more recent "switch" toward their utilization for photocatalysis, optoelectronics, thermoelectrics, or battery development that could possibly be improved through the advent of photoresponsive MOFs. Although there has been premier interest in MOFs and photochromic molecules as well as their "marriage", this Review is the first account solely highlighting the underlying photophysical studies and their dependence on the type of MOF or photoactive moiety. This Review summarizes the first steps toward the control of optical, magnetic, electronic, or catalytic properties as a function of immobilized photoswitchable molecules. Although an impressive list of properties has proven to succumb to photoswitch modulation, there are typically only one or two reports on each subject. The translation of the observed findings to a plethora of systems must be realized to propel the development of

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photoresponsive MOF-based materials. The ability for MOFs to be a multifunctional platform, for instance, by merging photoresponsivity with redox activity or photocatalysis, could provide further development in this growing area. However, a number of synthetic challenges associated with the photochromic unit incorporation and limited by the framework rigidity should be addressed first. For instance, photochromic ligands integrated as a backbone typically possess a DAE, NDI, or viologen core, primarily due to the absence of drastic structural changes associated with the photoisomerization process. For this reason, spiropyran-based derivatives still remain unexplored as a ligand backbone. Similarly, hindered photoisomerization is typically observed for azobenzene derivatives upon their integration as a part of the MOF backbone.[93,99,103,104,106,107] One of the possible directions to address this challenge can rely on the preparation of multifunctional MOFs containing a second flexible linker complementary to a photoresponsive ligand; the former one will provide flexibility to a scaffold that is necessary for efficient photoisomerization to occur. For that reason (the absence of structural hindrance), MOFs with photochromic molecules integrated as a side group is the most comprehensively studied class. Moreover, the synthetic preparation of such ligands is usually relatively straightforward, in contrast with coordinatively immobilized photochromic linkers. In fact, the only photoswitch class not represented thus far in this area is NDI-based linkers.

Even though guest inclusion can occur without the need for multistep organic synthesis of a complex photoswitch, there are surprisingly fewer accounts in the guest category than expected. For this avenue, establishing the correlation between photoswitch molecular geometry and MOF topology is a key component for any photoresponsive MOF-based material development. Furthermore, a strategy including the variation of photoswitch structure or molecular geometry within the same MOF as opposed to the more common method of integrating the same photoswitch in different MOFs is an intriguing direction to pursue.

Another area of future interest to these systems relies on the development of multicomponent systems, that is, frameworks incorporating two or more photoresponsive molecules and possessing an orthogonal response from distinct photochromic units, allowing for simultaneous tuning of different properties of MOFs. This strategy can also be modified for the modulation of a MOF photophysical profile in different regions of the absorption spectrum because different photoresponsive molecules can isomerize upon irradiation with one or several excitation wavelengths. There is only one example of a similar system to date,[104] demonstrating the feasibility of this strategy and, at the same time, the great potential of the proposed concept.

The ability for the electronic structure modulation as a function of external stimuli has also recently started to gain more esteem. The advantages of optically controlled conductive materials have been partially highlighted in photoswitchable polymers.[139−141] This method could potentially provide the foundation for a revolutionary projection of MOF-based electronic devices that would benefit from the combination of modularity, porosity, and electrical conductivity. Further research in the area of photoresponsive frameworks could also result in a drastic conductivity enhancement, shifting MOFs away from being mainly porous insulating materials. For instance, photoswitch integration in porous frameworks with redox-active secondary linkers or heterometallic metal nodes could be a pathway for pursuing this avenue.

A noteworthy direction only briefly grazed that has a high potential for advanced device integration is photoswitchable magnetism in 3D MOFs. The modularity of MOFs provides a unique opportunity to use a combination of conjugated or radical-producing linkers and magnetic metal centers to tailor magnetic ordering from the short range (i.e., single-molecule or single-chain magnets) to the long range (ferromagnetic, ferrimagnetic, or antiferromagnetic phases). The addition of a photoswitchable linker in a MOF material promotes control between two magnetic states that opens an avenue for the future development of devices. Furthermore, porous photoswitching magnetic MOFs could behave as good molecular sensors to coordinate small molecules, especially paramagnetic ones (e.g., O_2 and NO). A combination of magnetic and photoswitching properties can lead to the concept of magnetochromism, which now is known only for some inorganic multiferroics and hybrid materials with molecular architectures.

Many factors dictating device compatibility are contingent on a fundamental knowledge of photoisomerization kinetics and the long-term stability of photoresponsive molecules; however, the photoisomerization rates (forward and reverse) are rarely reported. Furthermore, the long-term stability of photoswitches is sparsely studied as well. Fatigue products and photobleaching are mentioned in some reports but are often avoided, even though they are common and important issues for material development. Moreover, the chemical and thermal stabilities of photoresponsive linkers are often unaddressed altogether; however, these are important factors to consider for the development of devices and to enhance the overall performance.

In terms of processability, several key challenges still remain to be resolved for MOF development to increase the applicability of these materials. Because MOFs are typically grown as single crystals or polycrystalline powders, thin films of photoswitch-integrated MOFs should be prepared. Moreover, the ability to integrate a photoswitchable MOF into a device is a difficult feat alone, which leads to the necessity of a multidisciplinary approach toward materials development and device fabrication.

Lastly, there are a number of classes of photochromic molecules that have not yet been explored for immobilization inside a framework, including quinones, fulgides, hydrazone, and perimidinespirocyclohexadienone derivatives.[142,143] Broadening the family of photoswitchable MOFs could also provide untold opportunities for the improvement of MOF-based switching devices.

Ultimately, both the opportunities and the challenges of the surveyed MOFs are indicative of the increased interest in pushing the boundaries of fundamental understanding and experimental studies, which can play a role in "switching" the MOF application landscape.

AUTHOR INFORMATION

Corresponding Author

*E-mail: shustova@sc.edu.

ORCID

Natalia B. Shustova: 0000-0003-3952-1949

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Allison M. Rice received her B.S. degree in chemistry from Westminster College in 2014 and her Ph.D. degree in inorganic chemistry from the University of South Carolina (USC) in 2018. Her research at USC was focused on the exploration of novel fulleretic materials and their photophysical properties as well as stimuli-responsive materials.

Corey R. Martin received his B.A. degree in chemistry from Florida Gulf Coast University in 2017. He is currently pursuing his Ph.D. in inorganic chemistry at the University of South Carolina. He is investigating utilization of photochromic ligands to direct chromophore behavior in large light-harvesting ensembles.

Vladimir A. Galitskiy received his B.S. degree in materials science as well as his M.S. degree in applied mathematics and physics from Moscow State University in 2014 and 2018, respectively.

Anna A. Berseneva received her B.S. degree in materials science from Moscow State University in 2018. She is currently pursuing her Ph.D. degree in inorganic chemistry at the University of South Carolina (USC). Her research at USC is focused on the exploration of hybrid structures as a novel class of stimuli-responsive materials with dynamically controlled electronic behavior.

Gabrielle A. Leith received her B.A. degree in chemistry from Hanover College in 2017. She is currently pursuing her Ph.D. degree in organic chemistry at the University of South Carolina (USC). Her research at USC is focused on the development of graphitic hybrid materials.

Natalia B. Shustova is a Peter and Bonnie McCausland Associate Professor at the University of South Carolina. She received her M.S. degree in materials science from Moscow State University (MSU), Russia, a Ph.D. degree in physical chemistry from MSU, and a Ph.D. degree in inorganic chemistry from Colorado State University. Her postdoctoral research was conducted at the Massachusetts Institute of Technology. Her current research interests include graphitic hybrid materials for sustainable energy conversion, stimuli-responsive materials, sensors, and artificial biomimetic systems.

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ABBREVIATIONS

ANT	anthracene
AzB	1,2-diphenyldiazene
AzBIPY	3-azo-phenyl-4,4′-bipyridine
AzBPY	4,4′-azobispyridine
AzBIPYB	4,4′-(2-(phenyldiazenyl)-1,4-phenylene) dipyridine
BPE	1,2-bis(4-pyridyl)ethylene
BPETFC	1,2-bis(5-pyridyl-2-ethyl-3-thienyl)perfluoro cyclopentene
BPMTC	bis(5-pyridyl-2-methyl-3-thienyl) cyclopentene
BPMTFC	1,2-bis(5-pyridyl-2-methyl-3-thienyl) perfluorocyclopentene
BPY	4,4′-bipyridine
BSP	1-(2-hydroxyethyl)-3,3-dimethylindolino-6′-nitrobenzopyrylospiran
CBIAP	2-((3-chlorobenzylidene)amino)phenol
DABCO	1,4-diazabicyclo[2.2.2]octane
DEF	*N*,*N*-diethylformamide
DMF	*N*,*N*-dimethylformamide
DPIPA	N^1,N^3-di(pyridin-4-yl)isophthalamide
DTE	1,2-bis(2,5-dimethyl-thien-3-yl)-perfluoro cyclopentene
H_2AzABDC	2-(4-(phenyldiazenyl)benzamido) terephthalic acid
H_2AzBDC	2-(phenyldiazenyl)terephthalic acid
H_2AzBPDC	3-azobenzene-4,4′-biphenyldicarboxylic acid
H_2AzDC	4,4′-(diazene-1,2-diyl)dibenzoic acid
H_2AzTPDC	2′-(phenyldiazenyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid
H_2AzUBDC	2-(3-(4-(phenyldiazenyl)phenyl)ureido)-terephthalic acid
H_2BCMTC	4,4′-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carboxylic acid)
H_2BDC	1,4-benzenedicarboxylic acid
H_2BPDC	biphenyl-4,4′-dicarboxylic acid
H_2BPYBCCl$_2$	1,1′-bis(4-carboxybenzyl)-4,4′-bipyridinium-dichloride
H_2BPYBDCCl$_2$	1,1′-bis(3,5-dicarboxybenzyl)-4,4′-bipyridinium dichloride
H_2CCA	4-carboxycinnamic acid
H_2DCBBPCl	1-(3,5-dicarboxybenzyl)-4,4′-bipyridinium chloride
H_2DHAzTPDC	3,3′′-dihydroxy-2′-(phenyldiazenyl)-[1,1′:4′,1′′-terphenyl]-4,4′′-dicarboxylic acid
H_2F_2AzBDC	2-((2,6-difluorophenyl)diazenyl) terephthalic acid
H_2GLU	glutaric acid
H_2HAzBDC	2-(hydroxyphenyldiazenyl)terephthalic acid
H_2IPA	isophthalic acid
H_2MeSUC	2-methylsuccinic acid
H_2Me_2BPDC	2,2′-dimethylbiphenyl-4,4′-dicarboxylic acid
H_2Me_2TPDC	2,2″-dimethyl-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid
H_2MeGLU	2-methylglutaric acid
H_2NDC	2,6-naphthalenedicarboxylic acid
H_2NDI-ATZ	2,7-di(1*H*-tetrazol-5-yl)benzo[*lmn*][3,8]-phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone
H_2NDI	2,7-bis(3,5-dimethyl) dipyrazol-1,4,5,8-naphthalene tetracarboxydiimide
H_2NH_2-BDC	2-aminoterephthalic acid
H_2OBA	4,4′-oxybis(benzoic acid)
H_2PhTPDC	9,10-bis(2-methyl-3-phenylthiophen-3-yl)-phenanthrene-2,7-dicarboxylic acid
H_2SDC	stilbene-4,4′-dicarboxylic acid
H_2SUC	succinic acid
H_2TAzTPDC	2′-*p*-tolyldiazenyl-1,1′:4,4′-terphenyl-4,4″-dicarboxylic acid
H_2TPDC	9,10-bis(2,5-dimethylthiophen-3-yl) phenanthrene-2,7-dicarboxylic acid

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H_3BTC[a]	1,3,5-benzenetricarboxylic acid
	5,5′-(1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(1*H*,3*H*,6*H*,8*H*)-diyl)-diisophthalic acid
H_4BIPA-TC	
H_4BTC[b]	1,2,4,5-benzenetetracarboxylic acid
H_4DBTD	3′,6′-dibromo-4′,5′-bis(4-carboxyphenyl)-1-[1,1′:2′,1″-tetraphenyl]-4,4″-dicarboxylic acid
H_4TCPP	tetrakis(4-carboxyphenyl)porphyrin
HAIM	2-phenylazoimidazole
HBA	benzoic acid
HCEBPYCl	*N*-carboxyethyl-4,4′-bipyridinium chloride
HCPBPYCl	*N*-(3-carboxyphenyl)-4,4′-bipyridinium chloride
HDDB	1′,1‴,3′,3′,3‴,3‴-hexamethyl-6,6″-dinitro-4′,4‴-di(pyridin-4-yl)-7′,7‴-bispiro-[chromene-2,2′-indoline]
HIM	imidazole
HMeIM	2-methylimidazole
HSP	2-(3′,3′-dimethyl-6-nitrospiro-[chromene-2,2′-indolin]-1′yl) acetic acid
MeBPYCl	*N*-methyl-4,4′-bipyridinium chloride
o*F*-AzB	1,2-bis(2,3,5,6-tetrafluorophenyl)diazene
o*F*-AzB	1,2-bis(2,3,5,6-tetrafluorophenyl)diazene
PEG-AB	1,2-bis(4-((2,5,8,11-tetraoxatridecan-13-yl)-oxy)phenyl)diazene
PI	1-(carboxymethyl)-2,3,3-trimethyl-3*H*-indol-1-ium iodide
t*F*-AzB	1,2-bis(2,6-difluorophenyl)diazene
TNDS	1′,3′,3′-trimethyl-6-nitro-4′,7′-di(pyridin-4-yl)spiro-[chromene-2,2′-indoline]
TPDPY	4,4′-(9,10-bis(2,5-dimethylthiophen-3-yl) phenanthrene-2,7-diyl)dipyridine
TPT	2,4,6-tri-4-pyridyl-1,3,5-triazine
SP-1	1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran
STa	1,2-diphenylethene
STb	1,2-di-*p*-tolylethene
STc	1,2-bis(4-bromophenyl)ethene

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