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Perspective

Metal−Photoswitch Friendship: From Photochromic Complexes to Functional Materials

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ABSTRACT: Cooperative metal−photoswitch interfaces comprise an application-driven field which is based on strategic coupling of metal cations and organic photochromic molecules to advance the behavior of both components, resulting in dynamic molecular and material properties controlled through external stimuli. In this Perspective, we highlight the ways in which metal−photoswitch interplay can be utilized as a tool to modulate a system's physicochemical properties and performance in a variety of structural motifs, including discrete molecular complexes or cages, as well as periodic structures such as metal−organic frameworks. This Perspective starts with photochromic molecular complexes as the smallest subunit in which metal−photoswitch interactions can occur, and progresses toward functional materials. In particular, we explore the role of the metal−photoswitch relationship for gaining fundamental knowledge of switchable electronic and magnetic properties, as well as in the design of stimuli-responsive sensors, optically gated memory devices, catalysts, and photodynamic therapeutic agents. The abundance of stimuli-responsive systems in the natural world only foreshadows the creative directions that will uncover the full potential of metal−photoswitch interactions in the coming years.

■ INTRODUCTION

Cooperative metal−photoswitch (M−Φ) "friendship" is an application-driven concept that bridges cutting-edge research from the materials science and physical, inorganic, and organic chemistry communities.[1−27] Like good friends, metals (M) and stimuli-responsive organic molecules (e.g., photoswitches, Φ) possess individual strengths that can be synergistically combined to advance the behavior of both entities. For instance, M−Φ cooperation facilitates the development of stimuli-responsive homogeneous catalysts, while synergy of fast photoisomerization kinetics and M−Φ alignment in crystalline scaffolds is crucial to advance light harvesting.[28−31] These are only a few examples among a large span of applications ranging from optically gated memory devices and quantum-computing systems to photodynamic therapeutic agents.[29,32−35]

Commonly, M−Φ interplay is a cornerstone to not only harness and tailor metal−organic linker properties but also control the metal behavior through an organic counterpart. Incorporation of transition metals in such assemblies provides access to *d*-orbitals, resulting in a wider variety of geometries and electronic structures.[36] In particular, the presence of metal *d*-orbitals can alter the frontier molecular orbitals and corresponding electronic transitions associated with photoisomerization.[37] For instance, the absorbance bands for many organic photoswitches coordinated to metal cations are bathochromically shifted with respect to the uncoordinated ones.[37] Shifting absorbance into the visible region is particularly attractive for applications involving solar energy harvesting, for example.[38]

The enhancement of spin−orbit coupling caused by the presence of heavy atoms (i.e., transition metals or actinides) also plays an important role in M−Φ behavior. This enhanced coupling alters the photophysical behavior of the system by promoting spin-forbidden transitions, such as intersystem crossing.[39] As a result, M−Φ interactions are critical for the development of microscopy tags and active layers of bulk heterojunction solar cells, both of which often rely on long-lived triplet excited states.[40,41] In addition to the electronic transitions that occur during photoisomerization of organic molecules, ligand-to-metal and metal-to-ligand charge transfer (LMCT and MLCT, respectively) can change the magnetic properties of metal centers, promoting a pathway for switchable magnetism.[42] In the same realm, ligand photoisomerization can alter the ligand field strength around a metal center, resulting in switching between high- and low-spin states.[43]

Herein, we survey M−Φ interactions in a variety of structural motifs, starting from discrete structures such as molecular complexes and cages and expanding toward extended structures such as polymers and metal−organic frameworks (MOFs). Comprehensive reviews and books

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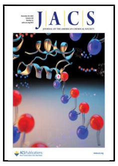

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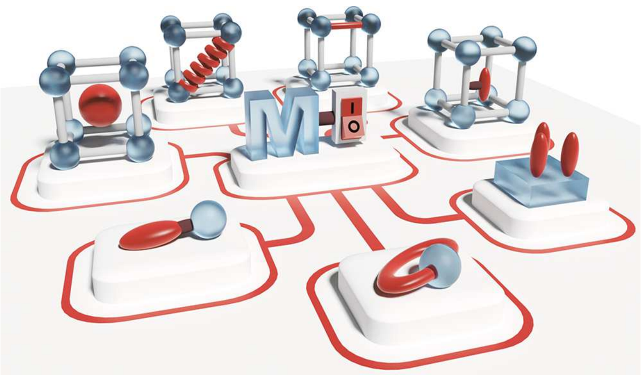
regarding photoswitches and photocatalysis can be found elsewhere.[29,30,44−50] Instead, in the current Perspective, we highlight the role of M−Φ interactions to control physicochemical properties and advance material development.[12,31,42,51−60] We look at five classes of stimuli-responsive molecules—spiropyran, spirooxazine, chromene, azobenzene, and diarylethene derivatives—in combination with a variety of transition metals. We shed light on the current state-of-the art in this area, highlighting the role of M−Φ interactions for tailoring specific material properties and corresponding applications. In addition, we outline the promising gaps, the fulfillment of which will result in the development of the next generation of stimuli-responsive devices.

■ MOLECULAR COMPLEXES

The smallest subunit in which M−Φ interactions could be realized is through direct bonding of M with a photochromic fragment, Φ, resulting in formation of M−Φ molecular complexes. The latter ones could be employed as efficient building blocks to engineer extended structures involving many instances of M−Φ cooperation and for fundamental understanding of their physicochemical properties.[49] Molecular complexes could also accommodate the structural dynamism of metal−ligand bonds associated with isomer switching, providing the flexibility necessary for efficient and reversible photoisomerization. In Scheme 1, several M−Φ binding motifs observed in molecular complexes that can cause significant perturbation of local geometries and electronic structures are shown.[49]

Scheme 1. Schematic Representation of the Discussed M−Φ Structural Motifs[a]



[a] Stimuli-responsive moieties are highlighted in red while the metal counterparts are emphasized in blue.

For instance, photoswitches functionalized with ligating groups could serve as monodentate ($M-\Phi_1$), polydentate ($M-\Phi_n$), or bridging ligands ($M-\Phi_\mu$, Figure 1). Thus, the overview of the M−Φ communications in this Perspective will begin with the exploration of the role of M−Φ interactions in discrete molecular complexes which have physicochemical properties that could be controlled as a function of external stimuli through Φ isomerization.

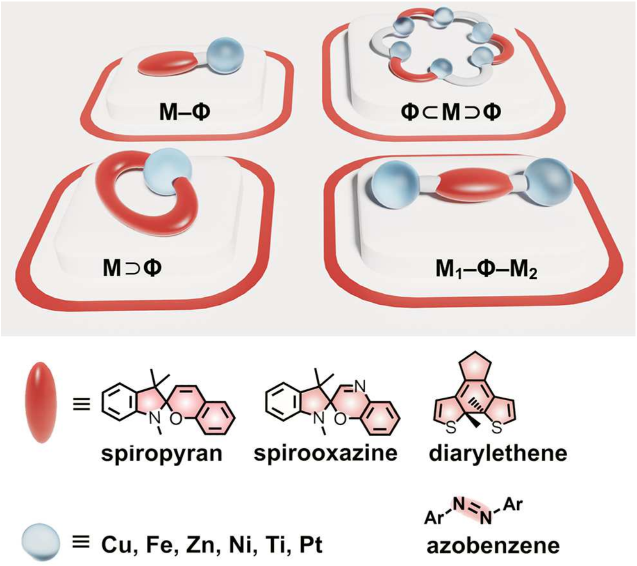


Figure 1. (*top*) Schematic representation of possible binding motifs in photochromic molecular complexes. (*bottom*) Classes of photoswitches and metals highlighted in the Molecular Complexes section.

The earliest studies of M−Φ interactions mainly relied on Φ isomerization accompanied by charge separation upon irradiation with a suitable excitation wavelength. The zwitterionic form can then bind metal cations in solution via electrostatic interactions.[47] For example, reports from as early as 1965 describe spiropyran derivatives (Figure 1) as light-responsive chelating agents for copper(II) and iron(II) cations.[61] Since then, numerous studies have shown reversible and selective metal ion binding by several classes of photochromic molecules, including spiropyran, spirooxazine, and chromene derivatives. While many of these fundamental studies were used to shed light on isomerization mechanisms, they also laid the groundwork for the field of highly sensitive and selective sensors for environmental toxins.[47] In fact, systematic modification of spiropyran- and chromene-based chelators with electron-donating groups has resulted in exceptionally high binding constants for toxic cations like copper(II), zinc(II), and nickel(II), while maintaining reversible binding behavior in solution. While selective binding of environmental contaminants has been a vital driving force in this field, challenges associated with Φ solubility and stability still require attention. In particular, rapid photodegradation caused by oxidation is known for some of the photoswitches employed in these studies.[47] Additionally, strategic coupling of visible-light-activated molecules with solubility in aqueous media is still a limiting factor in applying photochromic chelators for environmental sensing technologies.[50] Further studies regarding utilizing M−Φ interactions for ion and guest capture have been recently reviewed elsewhere.[62]

Tailoring of M−Φ interactions could be achieved through addition of other non-stimuli-responsive linkers, i.e., Φ implemented as one of multiple ligands in molecular complexes, resulting in a Φ−M−L structural motif (Figure 2).[42] Rational design of such Φ−M−L multi-component systems could result in cooperativity between the metal center and photochromic (Φ) as well as non-photochromic (L) ligands.[42] One of the examples demonstrating this concept is based on coupling of an optically bistable spirooxazine-based ligand with an electronically bistable cobalt-dioxalene complex shown in Figure 2.[42] Both photoisomers of the spirooxazine-based ligand were thermally stable, and, at the same time, the metal complex by itself could undergo spin state switching in response to other external stimuli (e.g., temperature or pressure). Therefore, slight changes in ligand field strength due to switching from the open or closed forms of the

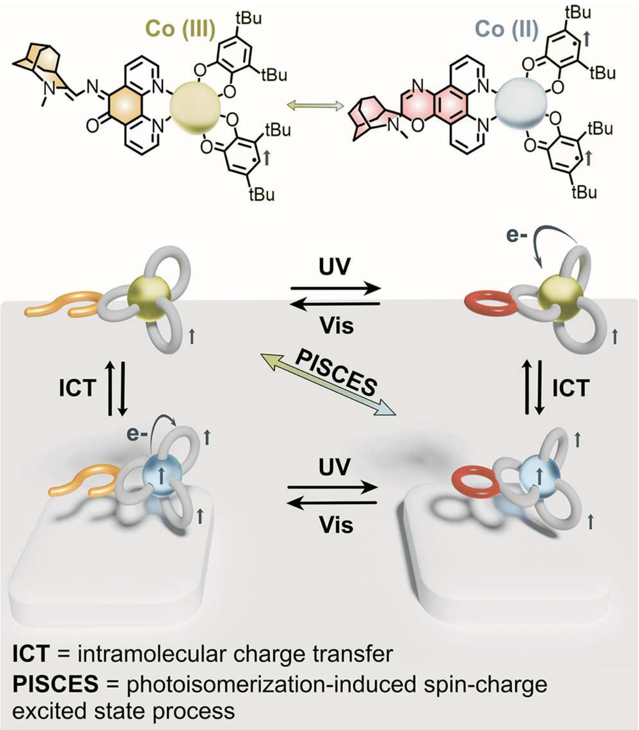


Figure 2. (*top*) A cobalt−dioxalene complex modified with a photochromic spirooxazine (Φ)-based ligand. (*bottom*) Schematic representation of a molecular complex undergoing a photoisomerization-induced spin-charge excited-state process caused by spirooxazine isomerization. Reproduced with permission from ref 42. Copyright 2018 American Chemical Society.

spirooxazine-based ligand resulted in reversible changes in the spin of the metal center. As such, M−Φ interactions provided access to control the electronic and magnetic properties of the system as a whole. Furthermore, efficient and reversible switching was detected not only in solution but also in a thin film, foreshadowing an avenue for the development of optically gated memory devices and quantum-computing systems.[34,35]

Photochromic bidentate ligands (e.g., functionalized azobenzene and diarylethene derivatives) can also serve to bridge two metal centers (M_1−Φ−M_2), allowing the spatial orientation of the metal cations to be modulated through irradiation (Figure 3).[51] Inspired by natural catalysis occurring through enzymes, which could involve cooperation between two metal centers, an azobenzene moiety has been used to control the spatial arrangement of two catalytically active sites.[63−65] As shown in Figure 3, the azobenzene-based ligand was used to bridge two chiral titanium(salen) complexes to catalyze asymmetric sulfoxidation reactions.[51] Specifically, irradiation with 365-nm wavelength resulted in formation of the *cis*-isomer, which brought the titanium centers in close proximity and catalyzed sulfoxidation reactions. At the same time, thermal relaxation in the dark promoted formation of the *trans*-isomer which separated the two titanium centers and inhibited catalysis. This interesting concept not only paves the way for light-controlled multi-metallic cooperative catalysis but also reveals how M−Φ interactions could translate an external stimulus (e.g., light or heat) into a chemical signal (i.e., product formation). These studies are the first steps toward synergetic utilization of stimuli-responsive selectivity and efficiency of biological enzymes through their coupling in synthetic M_1−Φ−M_2 systems.[51,66]

In addition to bridging two metal centers, ambidentate photochromic molecules can undergo self-assembly to form discrete metallacycles, Φ⊂M⊃Φ (Figure 4).[52] In the latter case, the photoswitch could not only modulate the spatial arrangement of metal centers as described above but also tune, for example, the aperture size and energy-transfer processes between organic-based donors and acceptors.[52] For example, combining a diarylethene-based photoswitch with a porphyrin-based photosensitizer in the presence of platinum(II) ions resulted in the formation of a "dual-stage" metallacycle capable of controlling singlet oxygen generation as shown in Figure 4.[52] In the open form, the diarylethene-based ligand (acceptor) does not possess a suitable excited state to promote energy transfer from the porphyrin-based photosensitizer, acting as a donor. In this case, the photosensitizer readily mediated the conversion of $^3O_2$ to $^1O_2$. In contrast, the closed form of the diarylethene acceptor promoted the energy-transfer process and severely suppressed the $^1O_2$ generation pathway. Remarkably, such behavior could be preserved even for metallacycles embedded in biologically compatible nanoparticles,[52] and controllable $^1O_2$ generation resulted in inhibition of tumor growth.[52] Based on demonstrated proof-of-concept related to medical treatment, it is feasible to anticipate that the future directions in this area will be associated with the development of similar systems working under excitation in the infrared region (instead of UV or visible), providing access to light-driven therapeutic agents.[52]

The foregoing results foreshadow a great potential toward different applications ranging from cation sensing to anticancer treatment using synergy of a metal (i.e., oxidation state, spin state, or coordination geometry) with the precise spatiotem-

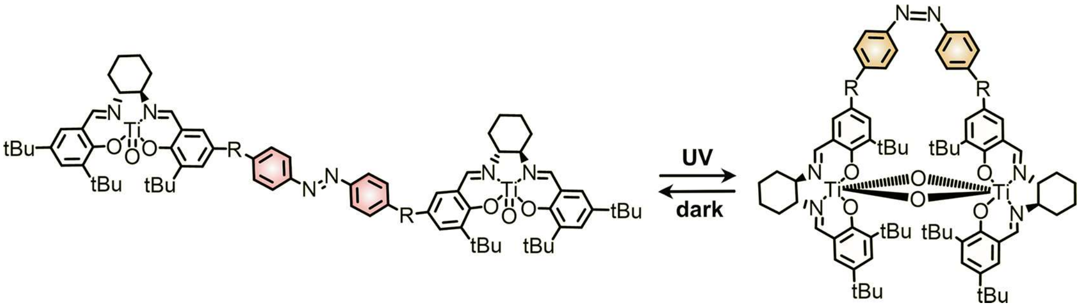


Figure 3. Azobenzene derivatives used as a bridging ligand between two metal complexes. UV irradiation results in the *cis*-isomer formation (highlighted in yellow), which leads to bringing the two metal complexes in close proximity and enables them to function as a cooperative catalyst in asymmetric sulfoxidation. Reproduced with permission from ref 51. Copyright 2020 Royal Society of Chemistry.

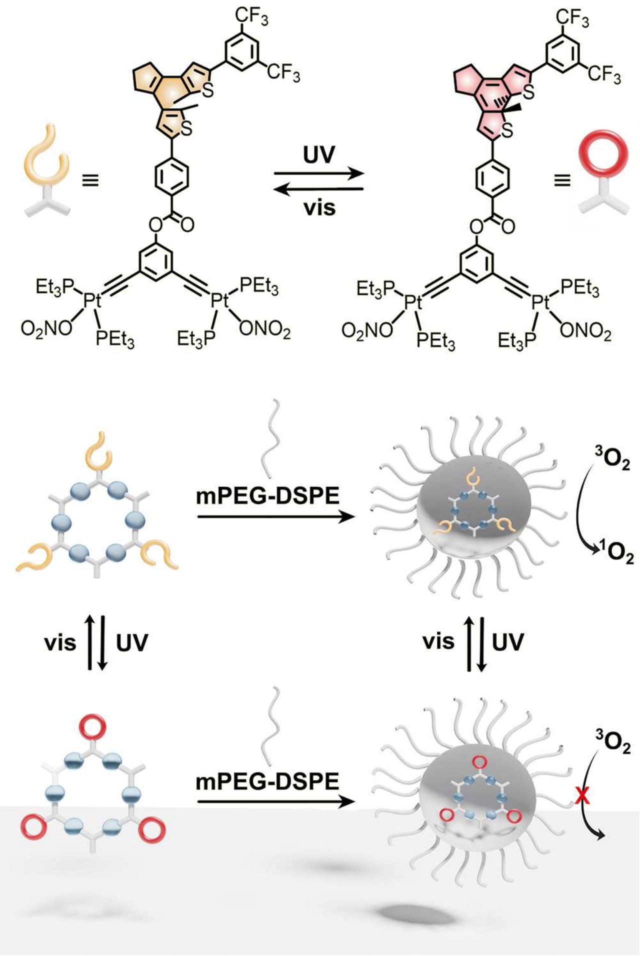


Figure 4. Schematic representation of diarylethene photoisomers (yellow and red) containing metallocene with Pt centers (blue spheres) encapsulated in a mPEG-DSPE self-assembling micelle for switchable $^3O_2$-to-$^1O_2$ conversion. The metal centers are shown in blue, the ligands and micelle are depicted by the gray color, and Φ is highlighted by yellow (open form) and red (closed form) colors. Reproduced with permission from ref 52. Copyright 2019 American Chemical Society.

poral control of organic stimuli-responsive molecules. However, in the reported studies, a majority of M−Φ interactions are limited to a few well-known classes of photochromic molecules, including spiropyran, spirooxazine, azobenzene, or diarylethene derivatives.[37,45,48,51,67−103] We envision that broadening the scope of stimuli-responsive molecules, their molecular geometries, and mechanisms of switching between one or multiple states would not only expand the scope of the M−Φ interaction portfolio but also reveal insights on the new forms of M−Φ "friendship" which could be translated into a novel twist of applications. Systematic studies of M−Φ systems, in which either M or Φ is used as a variable, are also crucial to reveal fundamental principles such as a possible effect of M or M−Φ interactions on isomerization kinetics of Φ. Another aspect which significantly limits recyclability of existing M−Φ-based systems in catalysis and sensing is Φ photobleaching. In addition, synthetic pathways for preparation of intriguing photochromic molecules on a large scale (beyond a few mg) are currently inaccessible. As a result, the mentioned challenges and perspective outlined a large scope of work necessary to realize the implementation of photochromic molecular complexes as long-term, efficient, and recyclable components of chemical industry.

■ METAL−ORGANIC CAGES AND POLYMERS

In this section, we will bridge the gap between discrete M−Φ units (e.g., molecular complexes) discussed in the section above and crystalline extended structures through surveying M−Φ interactions within metal−organic cages. While molecular cages are discrete structures for which conventional solution-state nuclear magnetic resonance (NMR) spectroscopic analysis could be applied, their size and cavities also make them the suitable candidates to model and probe different types of interactions (e.g., M−Φ) exhibited in extended periodic structures such as MOFs. In the latter ones, such studies are typically complicated by severe crystallographic disorder and the impossibility to employ solution NMR spectroscopy.[104] The aforementioned facts could explain a persistent interest in metal−organic cages and a plethora of reports in this area.[53,104−108] However, the number of studies with the main focus on photochromic molecules either as guests or as linkers intrinsic to the cage structure is significantly reduced, as shown by nearly 20,000 reports on molecular cages but only approximately 1% including photochromic moieties. There are several clear advantages of using photochromic cages as a platform for probing M−Φ interactions. First, it provides an opportunity to use single-crystal X-ray crystallography or NMR spectroscopic studies to shed light on not only the Φ structure but also its molecular conformation and orientation with respect to the tailorable cavity environment. Second, cages offer accessible voids to facilitate isomerization of the photochromic molecules under an external stimulus. Third, encapsulation of Φ in a cage could prevent aggregate formation and, therefore, promote photoisomerization. Despite these advantages, there are very few studies of photochromic metal−organic cages, especially in comparison with molecular complexes or extended structures such as MOFs. Ironically in many cases, cages are used as convenient models to probe molecular behavior in extended structures (e.g., MOFs), possessing similar pore geometries while remaining solution processable.

One of the approaches for utilizing M−Φ interactions in cages was realized by the Zhou group who developed an azobenzene-functionalized copper(II) cage exhibiting reversible capture and release of methylene blue as guest molecules (Figure 5).[53] In this study, a cuboctahedral cage constructed from 24 organic linkers was used to maximize Φ incorporation within each cage structure. The isomerization of azobenzene-based linkers occurred in the cage cavity since azobenzene moieties were attached as pendant groups (Figure 5). Notably, the pendant azobenzene functionalities interacted with neighboring cages via π−π stacking when in the *trans* state (highlighted in red in Figure 5), and as a result, the formed network was precipitated from polar solvents. Upon photoisomerization to *cis*-azobenzene (highlighted in yellow in Figure 5), the interactions between adjacent cages were weakened, resulting in dissolution. The observed reversible solubility was utilized to capture guest molecules within the cage network under visible light (i.e., *trans*-azobenzene) followed by release under UV light (i.e., *cis*-azobenzene).[53] Notably, arylazopyrazole-, diarylethene-, and diazocine-based photochromic cages have been also reported with similar guest capture and release capabilities.[104,109,110]

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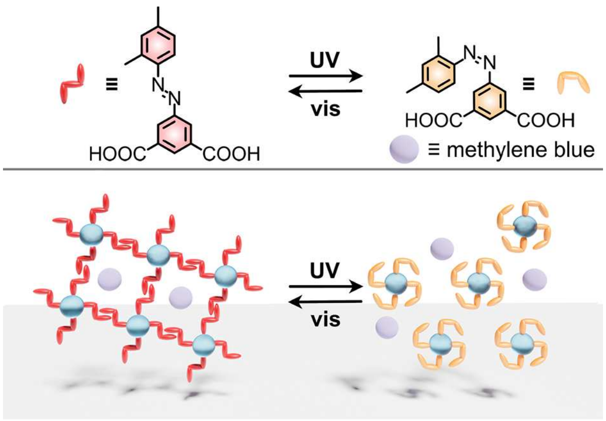

Figure 5. (*top*) Isomerization of azobenzene linkers used to construct a copper-based metal−organic cage. (*bottom*) Schematic representation of capture and release of guest molecules upon alternation with UV and visible light. The copper metal nodes are represented by blue spheres. Reproduced with permission from ref 53. Copyright 2014 John Wiley and Sons.

Such behavior highlights the potential for M−Φ interactions not only to influence confined 3D space but also to orchestrate the cooperative behavior of many discrete units or small assemblies.[53] Thus, these studies lay the foundation for remote manipulation of large numbers of highly complex entities. This approach also provokes an intriguing avenue for modulation of several properties at once (e.g., guest capture, optical behavior, or solubility) through integration of multiple stimuli-responsive units using an excitation wavelength as another variable. However, possible leaching of photochromic molecules is a remaining challenge. At the same time, embedding photochromic molecular complexes or cages within polymer matrices or grafting photochromic molecules to a polymer surface are possible solutions to prevent photochromic molecule leaching. Moreover, simultaneous control of multiple photochromic molecules could be addressed by integration within a polymer matrix.[54,55] For instance, 2D polymer layers grafted with photoswitches have been employed for selective metal cation extraction (Figure 6).[54,111] One study demonstrated the ability of spiropyran-grafted poly(methyl methacrylate) (PMMA)-based polymers to bind and release copper(II) cations. Notably, this example showed complete ejection of the bound metal cations upon isomerization from the zwitterionic merocyanine form to the neutral spiropyran form (Figure 6).[54] Such levels of reversibility are critical for implementation of M−Φ polymers as reusable sensors, for example. Moreover, the polymer support could result in decreased photodegradation. As a result, the grafted spiropyran derivatives, for instance, were able to bind and release metal cations several times without detectable photodegradation. Along these lines, chelation of metal cations by photoswitches anchored to polymer layers could allow for modulation of ionic conductivity controlled through an external stimulus (Figure 7).[55] Solid-state polymer electrolytes with grafted spiropyran units have been shown to exhibit reversible ionic conductivity based on chelation of metal ions by merocyanine, as described previously and illustrated in Figure 7. For that, a poly(ethylene oxide)-based polymer electrolyte was functionalized with spiropyran groups and complexed with $ZnCl_2$ salt under UV light (i.e., complexation by merocyanine).[55] Under UV excitation, the composite material exhibited low ionic conductivity due to immobilization of cations by merocyanine. Ionic conductivity was enhanced by exposure to visible light, which promoted decomplexation of cations through isomerization to the neutral spiropyran form. These studies illustrate that binding of metal cations by photoswitches is not constrained to sensing and extraction technologies, but rather can play an active role in modulation of bulk material properties, such as ionic conductivity.

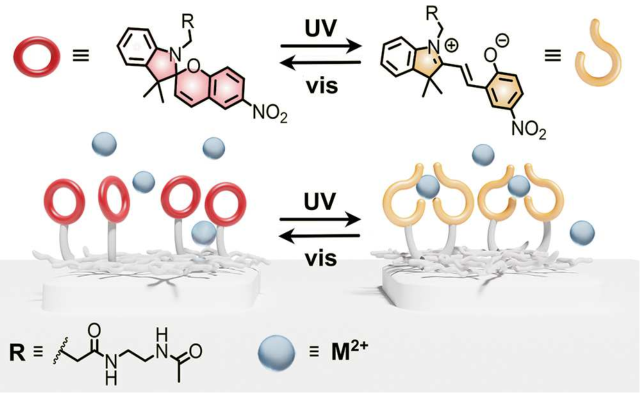

Figure 6. (*top*) Molecular structure of spiropyran derivative in the open (yellow) and closed (red) forms. (*bottom*) Schematic representation of the capture and release of metal cations by a spiropyran-grafted polymer upon alternation of UV and visible light. The blue spheres represent either Cu(II) or Co(II) cations. Reproduced with permission from ref 54. Copyright 2007 IOP Publishing, Ltd.

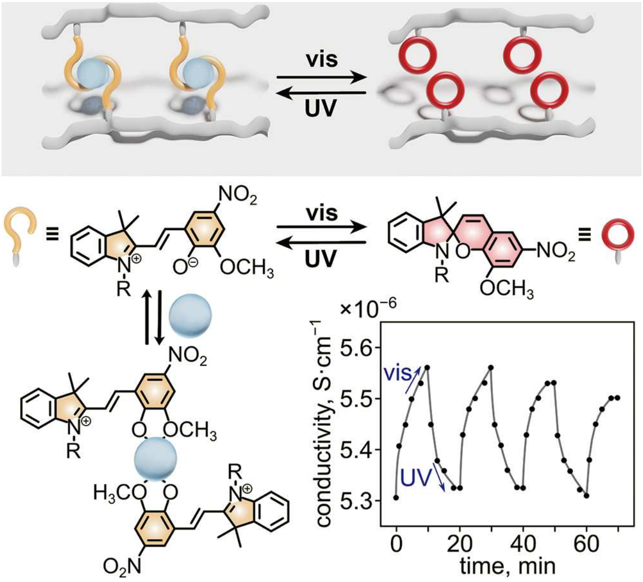

Figure 7. (*top*) Schematic representation of metal cation binding by spiropyran-grafted polymer layers. (*bottom*) Molecular structure of spiropyran derivatives upon photoisomerization and zinc(II) cation (blue spheres) binding. Switchable ionic conductivity was observed upon alternation with UV and visible light. Reproduced with permission from ref 55. Copyright 1995 Elsevier.

Rather than grafting photochromic units to polymer supports for metal cation chelation, a different approach is to embed larger entities such as photochromic molecular complexes (M−Φ) within a polymer matrix.[56] For instance, de Angelis and co-workers embedded platinum(II) complexes with a diarylethene-based ligand in a PMMA-based film to advance switchable non-linear optical (NLO) properties in the solid state (Figure 8).[56] In this study, switching from the open to closed form of the diarylethene derivative resulted in an extension of conjugation that altered the optical properties of the complex. Nanoorganization of the complexes within the polymer matrix amplified the effects of photoisomerization, resulting in a large NLO contrast.

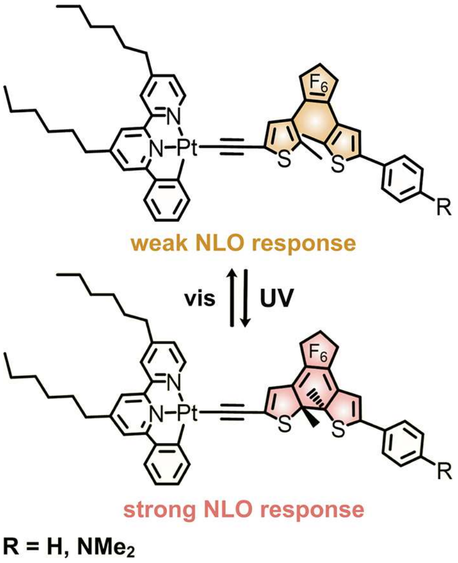

Figure 8. Molecular structure of a diarylethene moiety bound to a Pt-based molecular complex. Switching between the closed (red) and open (yellow) forms of diarylethene derivatives modulated the NLO response. Reproduced with permission from ref 56. Copyright 2014 American Chemical Society.

While grafting of photochromic molecules and embedding complexes in polymer matrices are effective approaches for preparation of functional materials, an alternative direction is a combination of photochromic cages and polymers within one material.[107] For instance, Johnson and co-workers functionalized a polymer backbone with diarylethene moieties. Exposing the polymer to palladium cations caused formation of photochromic cages at the junctions of the resulting polymer network.[107] In this case, photoisomerization of the diarylethene photoswitch from the open to closed forms drastically altered the cage structure from Pd_3L_6 to $Pd_{24}L_{48}$, where L represents the photochromic polymer ligands (poly(ethylene glycol) functionalized with diarylethene groups). Remarkably, the change in cage topology (i.e., changes in polymer cross-linking) affected the mechanical properties of the polymer. In particular, the $Pd_{24}L_{48}$ junctions resulted in a more mechanically robust material than the Pd_3L_6 junctions, and the Pd_3L_6 junctions produced a material with self-healing properties.[107] Thus, switching of the diarylethene moieties allowed for alternation between a mechanically strong state ($Pd_{24}L_{48}$) and a highly processable, self-healing state (Pd_3L_6). As such, these studies highlight not only the benefits of the M−Φ relationship but also the exciting opportunities to combine multiple structural motifs (e.g., photochromic cages and polymers) for tailoring material properties and overall material development.[107]

Overall, M−Φ interactions in cages and polymers exemplify two significant achievements: organization of photoswitches in a three-dimensional space and possibility of photoisomerization in a solid-state material. While photochromic cages allow for organization of several M−Φ interactions, polymer matrices are an industrially accessible platform for photoswitch integration required for product commercialization. Despite these advantages, alignment of chromophores in complex assemblies is made more challenging by the amorphous nature of most polymers. For example, it is nearly impossible to orchestrate the precise alignment and orientation of multiple M−Φ species, which are critical for many energy-transfer and catalytic processes, without the support of a crystalline scaffold where angles and distances between M and Φ or multiple M−Φ are defined. Additionally, the absence of organized voids to promote photoisomerization in polymers could limit advancements in this direction, especially for classes of photochromic molecules for which isomerization between different states is accompanied by large structural rearrangements (e.g., spirooxazine).

■ METAL−ORGANIC FRAMEWORKS

Integration of photoswitches in porous matrices is one avenue to address limited photoisomerization in the solid state. Moreover, the limitations observed in some polymers related to precise M−Φ alignment, distance/angle determination, and control of the molecular conformation could be resolved in well-defined crystalline porous matrices. Thus, MOFs are modular and suitable platforms to study and advance novel pathways for M−Φ interactions in the solid state through coordination of photochromic molecules of interest to metal nodes (Scheme 1). This approach is also an opportunity to probe topologically different voids or interframework space to promote fast photoisomerization for classes of stimuli-responsive molecules for which isomerization is sterically restricted in the solid state because of large structural rearrangements (e.g., spiropyran or hydrazone).[112] Moreover, MOFs allow for tailoring a framework environment through skeleton modification or wall grafting (Scheme 1).[12,28−30,43,46,58−60,90,112−171] Furthermore, photoswitch behavior can be tuned by incorporation of different guest molecules within framework cavities, including the presence or absence of solvent molecules of different polarity.[57,145,172−189] Thus, in this section, we discuss the advantages of coordination of photoresponsive molecules to metals in well-defined crystalline scaffolds and the corresponding effects on physicochemical properties of the material, as well as outline the potential scientific gaps in this area.

One of the simplest pathways for photoswitch immobilization in MOFs is incorporation of photochromic molecules within the pores (i.e., as a guest).[57] The realization of concepts like "breathing" MOF behavior associated with dynamism of some MOF structures could be utilized for control of gas sorption processes, for example. The combination of these two concepts was successfully implemented by Kitagawa and co-workers. For instance, they showed that *trans*-to-*cis* isomerization of azobenzene guests altered the structure of the composite host−guest material, resulting in capture and release of N_2 gas (Figure 9a).[57]

For that, azobenzene was encapsulated in the channels of a flexible zinc-based MOF, $[Zn_2(\text{terephthalate})_2(\text{triethylenediamine})]_n$. The *trans*-to-*cis* isomerization was induced by excitation with UV light and resulted in conversion from an orthorhombic to an expanded tetragonal lattice system. Subsequent gas sorption studies

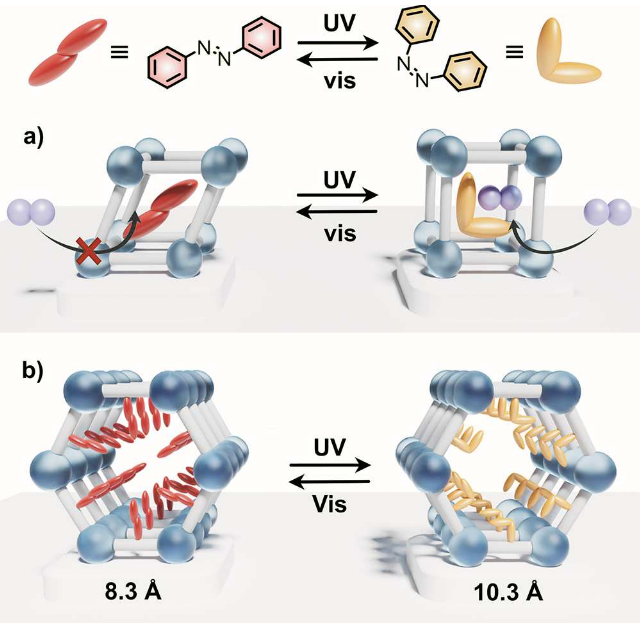

Figure 9. (*top*) Schematic representation of azobenzene molecules immobilized in a MOF pore. *Trans*-to-*cis* isomerization results in increased gas sorption abilities. The blue spheres represent zinc metal nodes, and the purple spheres represent N_2 gas. Reproduced with permission from ref 57. Copyright 2012 American Chemical Society. (*bottom*) Schematic representation of azobenzene groups grafted to a MOF backbone, allowing for control of pore size upon alternation with UV and visible light. The blue spheres represent magnesium metal nodes. Reproduced with permission from ref 58. Copyright 2013 Royal Society of Chemistry.

revealed that the MOF containing *trans*-azobenzene exhibited negligible N_2 gas adsorption, which the authors attribute to the blocking of pores by close contact between the MOF and azobenzene guest molecules. In contrast, treatment with UV-light promoted formation of *cis*-azobenzene and the corresponding tetragonal lattice system, which exhibited an 8.3-fold increase in N_2 adsorption when compared to *trans*-azobenzene. Incorporation of photochromic guest molecules is surely a powerful method for tuning gas sorption properties of MOFs since it could be applied to a variety of flexible MOFs without the need to synthesize new linkers, but the question of how to balance the degree of guest loading with ample void space for gas sorption is not fully addressed in this direction.

A conceptually different approach to dynamic control of pore size is by grafting of azobenzene groups to the MOF backbone, as shown by the Yaghi group (Figure 9b).[58] In this case, azobenzene was incorporated into a MOF-74-based structure, which forms one-dimensional channels. Isomerization of the grafted azobenzene groups resulted in direct control of the MOF pore size. In this system, grafting of azobenzene to the backbone allowed for even spacing of the photochromic units between metal nodes, which enhanced switching ability. Moreover, the *trans*-to-*cis* conversion caused widening of the pore aperture from 8.3 to 10.3 Å. As a next step, the described system was evaluated for the ability to trap and release cargo molecules on demand. For this, a luminescent dye was chosen such that the dimensions of the dye allowed for facile loading into the MOF pores under UV excitation (i.e., *cis*-azobenzene, 10.3 Å pore diameter) accompanied by restricted diffusion out of the pores upon exposure to visible light (i.e., *trans*-azobenzene, 8.3 Å pore diameter). Thus, loading and release of the dye could be promoted by UV irradiation to form the *cis*-isomer, whereas leaching of the dye did not occur in the case of the *trans*-isomer. Finally, irradiation at the isosbestic point of the azobenzene-grafted ligand resulted in simultaneous *cis*-to-*trans* and *trans*-to-*cis* "wagging", which increased dye molecule mobility and effectively expelled the dye from the pores on demand. The presented study goes beyond capture and release of guest molecules by diffusion-controlled processes to include light-induced molecular motion as a method to expel guests from the pores.[58]

Combining the concepts of light-induced structural deformation in flexible MOFs with precise arrangement of photoresponsive units through their coordinative immobilization leads to a recent study by Kaskel and Feringa, in which azobenzene groups were embedded in the backbone of a flexible MOF (Scheme 1, Figure 10).[12] Taking advantage of the mentioned *cis*-to-*trans* isomerization of the azobenzene functionality, these studies showed that light-induced "buckling" of the DUT-163-based MOF backbone resulted in "breathing" behavior. That is, irradiation with appropriate excitation wavelengths caused sequential pore expansion, contraction, and negative gas adsorption, mimicking the respiration process of living beings. Notably, this "breathing" behavior was made possible by the presence of dynamic M−Φ coordination bonds. In addition, theoretical modeling shed light on the mechanistic details of azobenzene photoisomerization in the presented system. In fact, coordination of the azobenzene-based linker between metal nodes provided access to a conformation (e.g., "buckling") that has not been

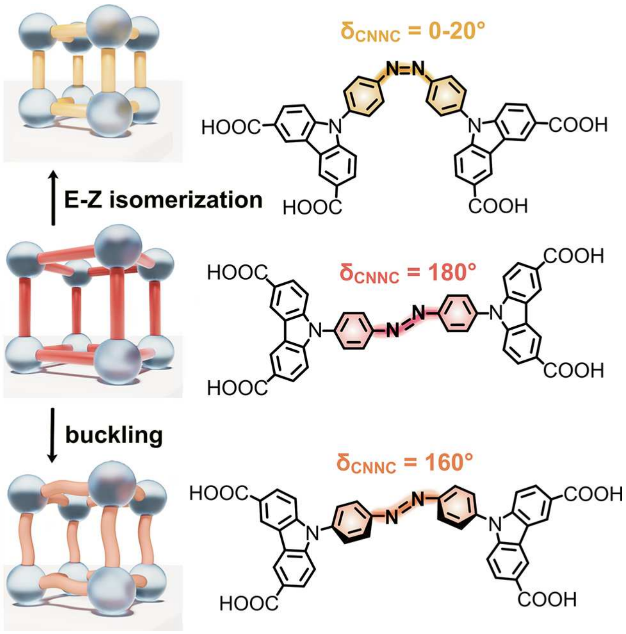

Figure 10. (*left*) Schematic representation of MOFs constructed from copper metal nodes (blue spheres) and azobenzene-based linkers (yellow, orange, and red rods). *E*/*Z* isomerization followed by "buckling" of the *E*-isomer changes the MOF pore size and causes "breathing" gas sorption behavior. (*right*) Molecular structures of the azobenzene linker with corresponding dihedral angles (δ). Adapted with permission under a Creative Commons Attribution 4.0 International (CC-BY 4.0) License from ref 12. Copyright 2022 Springer Nature.

detected in solution. The presented studies focusing on stimuli-responsive gas adsorption illustrate that traditional applications in the MOF field have room for further creative exploration, including the development of on-demand cargo release and biomimetic "breathing" MOFs. In addition to the examples highlighted above, many groups are taking this opportunity to expand the realm of functional materials for gas sorption processes to include light-responsive MOFs for directed gas transport[49] and emission-responsive MOFs for environmental monitoring.[190]

Especially in recent years, applications of M−Φ interactions in MOFs have been expanded beyond gas sorption.[117] For instance, direct cooperation between metal nodes and photoswitches has been shown to alter the electronic structure of the bulk material.[59] In particular, recent work[59] revealed that photoisomerization of spiropyran- and diarylethene-based linkers caused metal node reduction from copper(II) to copper(I), as shown in Figure 11.[59] Thorough analysis supported the hypothesis that photoinduced electron transfer from a photoresponsive linker to a corresponding metal node resulted in reduction of the metal nodes.[59] Remarkably, the detected change in metal oxidation states was completely reversible, showcasing the power of M−Φ interactions for dynamic control of material properties. Likewise, grafting of spiropyran-based Φ to a MOF backbone could also be used to modulate proton conductivity as a function of excitation wavelength (Figure 12).[60] Taking advantage of the large change in dipole moment upon formation of the merocyanine isomer, the proton conductivity of a MOF thin film could be precisely tuned in both alcoholic and aqueous media. For instance, irradiation with 365-nm wavelength promoted the formation of merocyanine and decreased proton conductivity, whereas thermal relaxation to spiropyran resulted in an 82-fold increase in proton conductivity. These studies demonstrate stimuli-responsive ionic conductivity in the presence of water, which is a critical component for the next steps in development of efficient proton exchange membrane fuel cells, for example. Photoresponsive linkers provide a pathway for remote control of not only metal node oxidation state and conductivity but also spin-state and the corresponding magnetic properties.[43] For instance, one of those studies leveraged redox-activity of the tetrathiafulvalene linker in the backbone of an iron(II)-based MOF to convert between low- and high-spin states of the metal nodes.[43] The controllable switching between redox properties of MOF metal nodes illustrates an opportunity to utilize stimuli-responsive MOFs in photoswitchable catalysis and conductivity, or for on-demand drug delivery.[31]

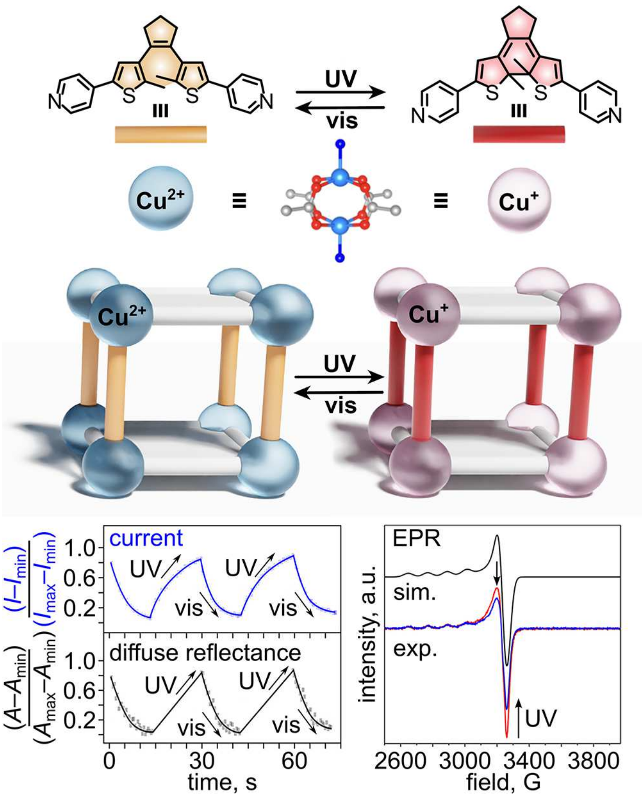

Figure 11. (*top*) Schematic representation of a MOF containing a diarylethene-based linker. Isomerization from the open (yellow) to closed (red) isomers results in reduction of Cu^{2+} (blue spheres) to Cu^{+} (pink spheres). (*bottom left*) Current and diffuse reflectance spectra over time and two switching cycles as well as (*bottom right*) the electron paramagnetic resonance spectra upon UV irradiation. Reproduced with permission from ref 59. Copyright 2022 American Chemical Society.

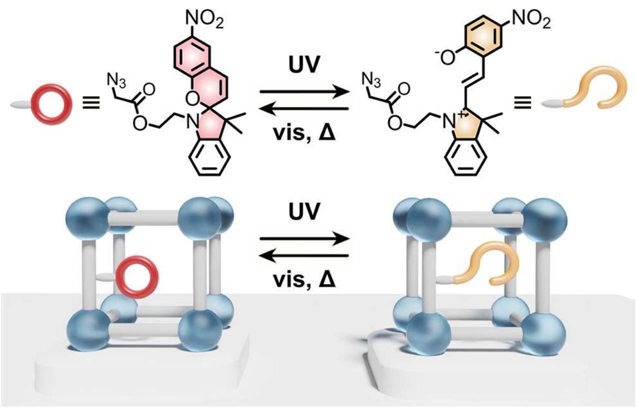

Figure 12. (*top*) Molecular structures of the isomers of a spiropyran-based Φ to be grafted to a MOF backbone. (*bottom*) Schematic representation of spiropyran isomerization within the void space of MOF pores upon alternation with UV and visible light. The blue spheres represent copper metal nodes. Reproduced with permission from ref 60. Copyright 2020 Royal Society of Chemistry.

Building on dynamic control of spin-states, Zhou and coworkers[31] employed both diarylethene- and porphyrin-based linkers to prepare a MOF for controllable singlet oxygen generation (Figure 13). In the described system, the porphyrin linker, tetrakis(4-carboxyphenyl)-porphyrin (TCPP), acts as a photosensitizer, which converts $^3O_2$ to $^1O_2$ when in the triplet excited state. At the same time, the diarylethene-based linker, 1,2-bis(2-methyl-5-(pyridine-4-yl)thiophen-3-yl)cyclopent-1-ene, (BPDTE) possesses different energy levels for the open and closed isomers. For instance, the excited state of the open form of BPDTE is higher in energy than the triplet excited state of TCPP, preventing energy transfer from TCPP to BPDTE in the open form and promoting singlet oxygen generation. In the closed form, the excited state of BPDTE is lower in energy, providing an alternative pathway for TCPP relaxation and quenching $^1O_2$ generation. That is, relaxation of excited TCPP linkers can be directed toward either energy transfer or $^1O_2$ generation based on excitation wavelength. In addition, the same MOF was implemented for dynamic control of the photooxidation of 1,5-dihydroxynaphthalene (DHN) by

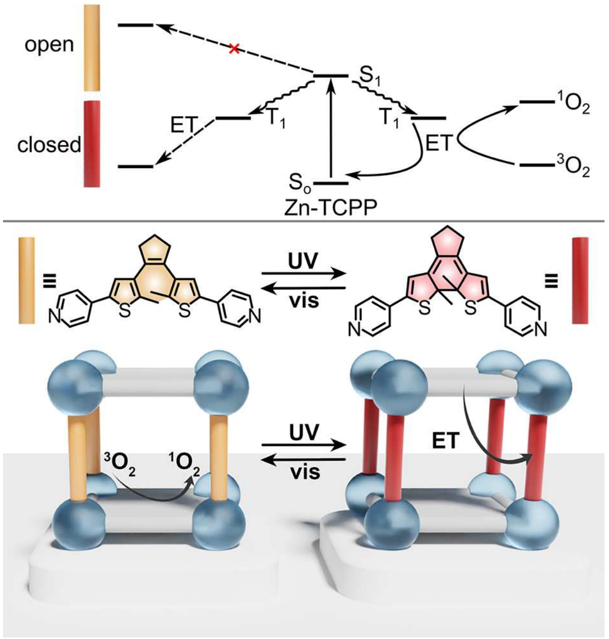

Figure 13. (*bottom*) Schematic representation of a MOF constructed from zinc metal nodes (blue spheres), diarylethene-based pillars (yellow and red rods), and porphyrin-based layers (gray). The open form diarylethene (yellow) promotes $^1O_2$ generation, while isomerization to the closed form promotes energy transfer and suppresses the $^1O_2$ generation pathway. (*top*) Energy level diagram emphasizing the proposed energy-transfer and $^1O_2$ generation processes. Reproduced with permission from ref 31. Copyright 2014 John Wiley and Sons.

the same mechanism as described above. Generation of $^1O_2$, as promoted by the open form of BPDTE, resulted in photooxidation of DHN, illustrating the power of photochromic MOFs for heterogeneous catalysis in multi-faceted systems.

As detailed above, MOFs offer a variety of methodologies to pre-organize metal−photoswitch interactions to form dynamic, functional materials.[30,46] Although we have described only a few exceptional studies, significant effort from numerous groups has proven that fundamental studies of photochromic MOFs could be a pathway toward on-demand drug delivery systems, spatially and temporally resolved sensors, optoelectronic devices, and heterogeneous catalysis, among many other applications.[30,46,190] In addition, these works show that synergy of M−Φ interactions within an extended structure goes beyond the properties of the individual molecular building blocks. Thus, continued work in this field will uncover unexpected photophysical behavior and unique material design principles. Some challenges remain, however, which must be addressed in the coming years to realize the mentioned applications. For example, development of suitable methods for determining photoisomerization quantum yield of bulk materials, which is a key parameter used in solution-based studies, is a critical step in fully characterizing dynamic materials.[29] Furthermore, the interplay between two unique photoswitches coordinated to metals within the same extended structure has been largely unexplored, indicating that a wealth of fundamental knowledge of these systems is left to uncover in the coming years.

■ CONCLUSIONS AND OUTLOOK

Strategic coupling of metals and photochromic molecules provides access to control properties as a function of an external stimulus in a variety of structural motifs, including molecular complexes, cages, polymers, and crystalline extended structures. Taking as examples five classes of photochromic molecules in combination with a variety of transition metals, we outline the potential for M−Φ interactions to impact areas like stimuli-responsive sensing, homogeneous and heterogeneous catalysis, switchable gas sorption and magnetism, tunable conductivity, and photodynamic therapies. Each of these directions takes advantage of light as a non-invasive stimulus with high spatiotemporal resolution to precisely alternate between discrete states. Current studies are the first steps toward manipulation of material properties with an external stimulus; however, strategic design in combination with synthetic and theoretical approaches could advance this area toward switching between "on" and "off" states, for instance, between conductors and insulators or a gradual transition from insulating−semiconducting−conducting material behavior. It is plausible to suggest that these avenues require more than one type of M−Φ interactions (i.e., more than one type of photoswitch) or novel structural motifs to advance the existing M−Φ "friendship"; however, all of them require a deeper fundamental understanding of Φ photoisomerization kinetics and thermodynamics, and advancement of synthetic strategies for preparation of novel Φ on a scale suitable for the development of new materials. Furthermore, a majority of the discussed M−Φ interactions are controlled through alternation of an excitation wavelength, which is a significant gap in terms of applications of other stimuli such as temperature, pH, magnetic and electric fields, etc., especially since light-driven systems impose inherent challenges. For example, the efficacy of the described light-responsive functional materials depends on penetration depth, and therefore, the thickness of the irradiated area for device development and fabrication should be taken into account. In particular, penetration depth depends on the excitation wavelength of the material and, therefore, the chosen chromophore.[191] Other variables like chromophore distribution should also be considered. In addition, scattering of light by particles of varying sizes in bulk powders should be taken into consideration when performing photophysical analyses.[190] One of the solutions to this challenge is the growth of high-quality thin films, but the methodology for their preparation using photochromic molecular complexes, cages, or stimuli-responsive frameworks should be not only developed but also optimized for many classes of photoresponsive materials. For instance, one of the emphases should be shifted toward preservation of fast photoisomerization kinetics in molecular complexes integrated into thin films. The use of multiple stimuli offers another direction to control material properties in a more uniform fashion compared to the use of light exclusively.

In addition to expanding the choice of stimuli, broadening the scope of metals involved in M−Φ interactions is an exciting and fruitful direction. For instance, the studies highlighted in this Perspective utilize transition metals, which have dominated the field thus far; however, incorporation of actinides or lanthanides will undoubtedly uncover fundamentally interesting and challenging phenomena.[128] Therefore, systematic studies and exploration of lanthanide integration in each of the structural motifs described herein could reveal novel M−Φ "friendship", allowing for tailoring of structure−property correlations. For instance, studies involving photochromic actinide-based MOFs illustrate the potential for actinide−Φ interplay to impact their optoelectronic behavior.[128] Moreover, the growing interest toward lanthanides and actinides, including transuranic elements, illustrates the unrevealed potential for M−Φ interplay.[128]

Thus, this Perspective only outlines the exciting and intriguing directions that were mainly inspired by dynamic adaptation of nature as a function of a variety of external stimuli: color of a chameleon toward its surrounding environment, orientation of plants as a reaction to sunlight, or reversible camouflage of marine creatures. Due to the complexity of stimuli-responsive materials, the M−Φ interface will require a multi-disciplinary approach and, therefore, will be based on successes occurring at the intersections of the materials science and physical, inorganic, and organic chemistry communities. The combined effort of these communities has already resulted in significant achievements in leveraging M−Φ "friendship" as a tool to uncover valuable fundamental knowledge for design of multi-functional materials. Although the full potential of M−Φ interfaces remains largely unknown, the natural world contains an abundance of inspiring stimuli-responsive materials, which only foreshadows the fundamental knowledge and creative directions to be uncovered in the coming years.

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Notes

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ABBREVIATIONS

LMCT, ligand-to-metal charge transfer; MLCT, metal-to-ligand charge transfer; MOF, metal−organic framework; NMR, nuclear magnetic resonance; PMMA, poly(methyl methacrylate); NLO, non-linear optics; TCPP, tetrakis(4-carboxyphenyl)porphyrin; BPDTE, 1,2-bis((2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene; DHN, 1,5-dihydroxynaphthalene

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