REVIEW

Recent advances in dynamically photo-responsive metal complexes for optoelectronic applications

Yanyan Qin,[1,2,3] Pengfei She,[1,2,3] and Wai-Yeung Wong[1,2,*]

*Correspondence: wai-yeung.wong@polyu.edu.hk

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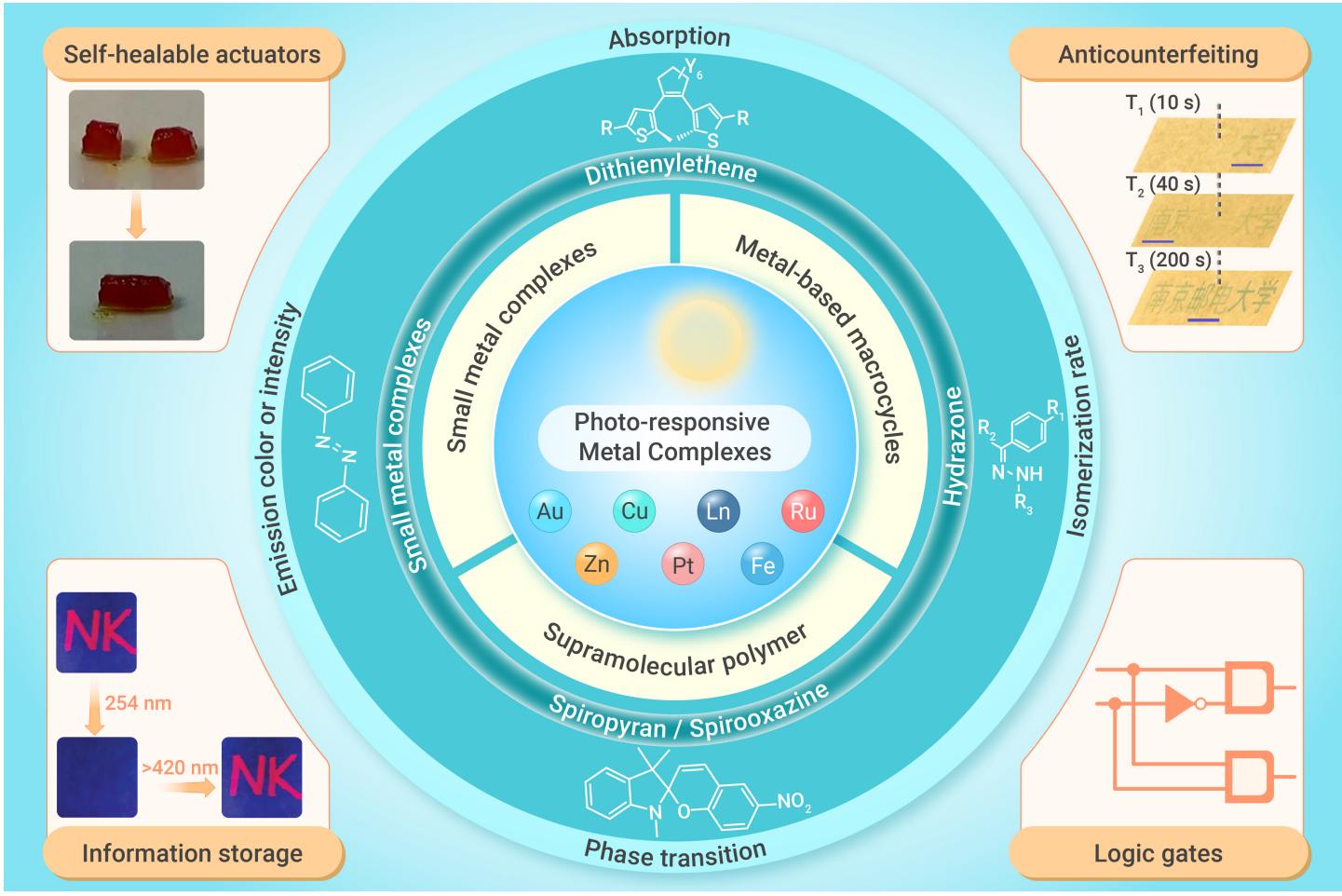
GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Material category, design strategies and responsive behaviors of photo-responsive metal complexes are summarized.
- Research progress of photo-responsive metal complexes in optoelectronic applications is discussed.
- Challenges and opportunities in photo-responsive metal complexes are presented.

REVIEW

Recent advances in dynamically photo-responsive metal complexes for optoelectronic applications

Yanyan Qin,[1,2,3] Pengfei She,[1,2,3] and Wai-Yeung Wong[1,2,*]

[1]Department of Applied Biology and Chemical Technology and Research Institute for Smart Energy. The Hong Kong Polytechnic University, Hong Kong SAR, China

[2]The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, China

[3]These authors contributed equally

*Correspondence: wai-yeung.wong@polyu.edu.hk

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Photo-responsive metal complexes, which connect certain photo-switches with the distinctive metal ions, have aroused extensive interest in the fields of optoelectronic functional applications. Upon photoisomerization, these metal complexes exhibit dynamically tunable photophysical properties in terms of their absorption ability and range, emission color and intensity, photoisomerization rate, mechanical property, and so on. This review will provide an overview of the recent advances in photo-responsive metal complexes, including small molecules, metal-based macrocycles and supramolecular polymers. Moreover, the responsive mechanisms and design strategies, along with the applications of these photo-responsive metal complexes in optoelectronic devices are also discussed. Finally, the challenges and perspectives on future synthesis and extensive applications of photo-responsive metal complexes are also presented. This review shall offer important guidelines for designing novel photo-responsive metal complexes with controllable responsive behaviors for advanced optoelectronic applications.

INTRODUCTION

Smart-responsive materials, which exhibit dynamic absorption, luminescence and electroconductivity under various external stimuli such as light, temperature, humidity and pressure, are widely utilized in various cutting-edge photonic applications.[1-11] Among all stimuli-responsive materials, photo-responsive materials have garnered significant attention due to the facile and expedient stimulus of light, which enables control over responsive behaviors in a high spatiotemporal precision and noninvasive manner and applies in different areas of switching, sensing, imaging, photodynamic therapy, catalysis, optoelectronics, etc.[12-18] Recently, photo-responsive metal complexes, including small molecules, metal-based macrocycles and supramolecular polymers, have been constructed by bridging molecular switches with diverse metals, i.e., Pt(II), Zn(II), Fe(II), Cu(II), Eu(III), Au(I), Ru(II), etc.[19-23] The construction process involves various bonding types, such as covalent bond, coordinate bond, and weak interactions, which are determined by the structures of the photo-switches (Figure 1A). Typically, covalent bonding, which primarily involves the bonding reactions (Pt-acetylide, Ru-acetylide, or Au-acetylide, etc.) between molecular switches and organometallic spacers, allows the formation of robust and stable metal complexes. The terpyridine, pyridine and pyrrole units in the photoswitchable monomers provide effective coordinate sites to bond with diverse metals. Additionally, the formation of metal-based macrocycles, cages, and supramolecular polymers are synergistically facilitated by host–guest interaction, electrostatic interaction, hydrogen bonding, π–π stacking together with the above covalent or coordinate bonds.

At present, the best-known organic photo-switches consist of spiropyran/spirooxazine, azobenzene/stilbene, hydrazone and diarylethene/dithienylethene.[24-29] Upon photoirradiation, these photoswitchable molecules can undergo the reversible isomerization process, including *trans–cis* conversion, cleavage of C-O bond, photocyclization, and photooxygenation (Figure 1B), accompanied with appreciable changes in morphology, color, conformation, and spectroscopic property. Furthermore, the connection of photoswitches with metal ions represents a highly effective strategy for the regulation and enhancement of photo-responsive performance, such as absorption ability and range, emission color and intensity, photoisomerization rate, mechanical property, and so on. Thus, compared with pure organic photoswitches, these photoswitch-based metal complexes could exhibit unique optoelectronic properties and advantages. For instance, photoswitch-based metal complexes always possess the enhanced light absorption ability and extended light absorption range induced by the metal-to-ligand charge transfer (MLCT) transition that enables photoswitches respond to visible light in the initial state, thereby achieving convenient remote control of isomerization due to the higher permeability of visible light than UV light.[30] Additionally, rapid energy transfer between metal center and photochromic units during the photoisomerization process would be favored, which allows the precise control of the photochromic responsive behaviors by energy manipulation. To date, great efforts have been dedicated to modulate the photochromic responsive behaviors of metal complexes, such as varying the position of coordination sites, tuning the substituent groups, altering the ancillary ligands, introducing redox-active metal and even lanthanide ions with long-lived emission, etc.[31-33]

Recent progress of photo-responsive metal complexes in the fields of chemical and biological sensing and imaging, as well as catalysis applications have been surveyed.[34-37] For example, the utilization of light can induce a change in the state of catalyst, providing a pathway for immediate control of reaction yield, possible modulation of reaction intermediates and mechanistic pathways, thereby enabling fine-tuning of the product selectivity. Previous reviews of photo-responsive metal complexes do not predominantly cover all the aspects of materials science and engineering. They have covered only one aspect of application either in the biological science or in the catalysis aspect or morphology aspect. Nevertheless, how the key features of photo-responsive molecular structures tune the photophysical performance (i.e. photoconversion yield, photoisomerization rate, photoluminescence efficiency, etc.) of metal complexes and their optoelectronic applications has not been reviewed yet. For this reason, we will begin our discussions with a focus on the material category of photo-responsive metal complexes, considering examples of metal-containing small molecules, metal-based macrocycles and supramolecular polymers, as well as the assembling photo-responsive composite systems in the last six years. Herein, we specifically focus on the typical design strategies, responsive properties and functionalities of various photo-responsive metal complexes, establishing the connections among material structural features, photophysical properties, and functionalities. Figures 2-3 summarize some representative molecular structures of photo-responsive metal complexes. In addition, we also address the potential applications of photo-responsive metal complexes in logic gates, anticounterfeiting, self-healable actuators, information storage, and so on. Finally, the challenges and prospects in this research area are also thoroughly discussed. We expect that this review shall provide valuable insights and serve as an indispensable guidebook for researchers in the field.

PHOTO-RESPONSIVE METAL COMPLEXES

Dithienylethene-based metal complexes

Dithienylethene (DTE), one of the most popular and blossoming photoswitches, has been extensively studied during the past few decades due to its high photoisomerization quantum yield, excellent fatigue resistance and high stability of both isomers.[38-42] Recently, the controllable responsive behaviors of photochromic metal complexes based on DTE, including absorption, luminescence and conversion rate through MLCT, intermolecular fluorescence resonance energy transfer (FRET) between metal center and ligand as well as

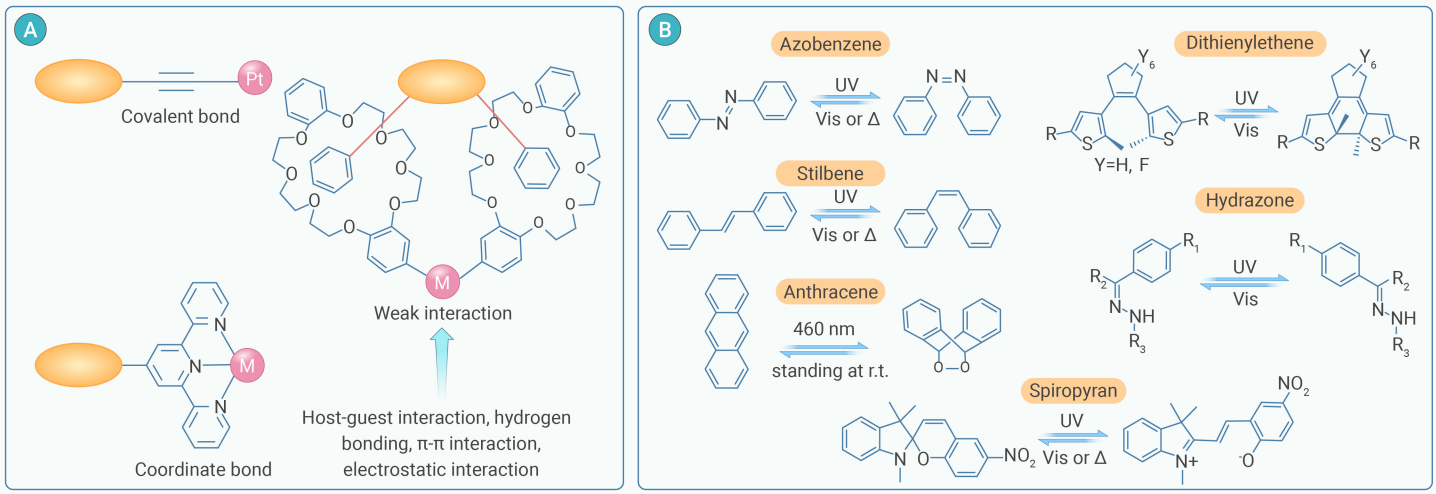

Figure 1. The molecular design of photo-responsive metal complexes (A) Illustration of the construction of photo-responsive metal complexes by covalent bond and coordinate bond as well as weak interaction. (B) Photo-responsive switches including azobenzene, stilbene, dithienylethene, spiropyran, hydrazone, and anthracene units.

switching on/off of DTE units, have been reported. These tunable properties have greatly facilitated the successful applications of DTE in optical switches, optoelectronics, smart surfaces, photoinduced shape-memory polymers, functional vesicles, bionanodevices, sensing, bioimaging and information storage.[43-47] In this section, we will summarize and discuss the photochromic behaviors of the representative DTE-based metal complexes, encompassing absorption, emission intensity, photoisomerization rate, as well as thermostability in relation to both the type of the metal and the electronic structure of the DTE molecule.

Recently, various DTE-based Pt(II) complexes have been developed and their photo-responsive behaviors have been discussed. For example, Boixel et al. designed and synthesized two Pt(II) complexes (**1** and **2**) with the same DTE core but different coordination sites.[30] Unlike the conventional design of **1**, complex **2** was synthesized through the integration of cyclometalated Pt(II) acetylide units into the reactive carbon atoms. Before UV light irradiation, **1** and **2** exhibited similar absorption spectra at 300-400 nm and 400-500 nm, which could be assigned to intraligand charge transfer (ILCT) and MLCT transitions, respectively. Upon irradiation at 350 or 450 nm, a new absorption band appeared at 640 nm due to the generation of a ring-closed form of **1**, while no photochromic behavior was observed in **2**. Density functional theory (DFT) calculations proved that ring-closed **2** displayed the lower thermostability than its ring-opened form. This result demonstrates that the regulation of the reactive carbon atom exerts an influence on both the thermostability and photochromic property of metal complex.

To explore the inductive effect of the substituent groups on photo-responsive behaviors, Chan et al. synthesized three Pt(II) complexes (**3**, **4** and **5**), which contained different electron-withdrawing or -donating units (F, H and ^{t}Bu) in the 5-position of tridentate 1,3-bis(N-alkylbenzimidazol-2'-yl)benzene (bzimb) ligand.[48] These Pt(II) complexes exhibited a similar green phosphorescence in degassed benzene solution, which can be attributed to the triplet intraligand (^{3}IL) excited state of bzimb. Compared to complexes **3** and **4**, complex **5** exhibited a slightly red-shifted phosphorescence because the negative inductive effect of fluorine group could stabilize the lowest unoccupied molecular orbital (LUMO) energy level of the complex. However, the attempt to fine-tune the absorption and luminescence intensity in their photoisomerization processes through inductive effect of the substituent groups proved unsuccessful. Instead of the robust connected mode, Zhao et al. employed a nonconjugated and flexible ethylene glycol bridge to construct a novel photochromic Pt(II) complex (**6**).[49] Similar to complex **7** with an insulator link, the weak emission of complex **6** could be attributed to the existence of an opened isomer, indicating that the flexible linker separating the DTE unit and the N^C^N ligand did not significantly affect the luminescence quenching. Nevertheless, temperature-dependent emission spectra exhibited distinct luminescence quenching temperature of 155 K for **7** and 250 K for **6**, respectively. Experimental and theoretical investigation demonstrated that efficient photoisomerization of **6** upon visible light excitation was rationalized by intramolecular energy transfer between the (N^C^N)PtCl and DTE parts. As a whole, inductive effect of the substituent groups or connected mode make a little effect on their photophysical properties in the above examples.

In order to evaluate the competitive photoisomerization of different photoswitches, Li et al. designed two *trans*/*cis* linked-hybrid photochromic Pt(II) complexes **8** and **9** containing two DTE and B(ppy)Mes$_2$ (ppy = 2-phenylpyridyl, Mes = mesityl) units.[50] When B(ppy)Mes$_2$ (Φ = 85%) was selected as the reference compound, **8** and **9** exhibited high photocyclization quantum efficiency (PCQY) of 41% and 55%, respectively. Compared with *cis*-linked **9**, the lower PCQY of *trans*-linked complex **8** could be attributed to the existence of low-lying emissive transitions caused by the extended π-conjugation backbone. Besides, the isomerized DTE unit could effectively absorb excitation energy, thereby inhibiting the photochemical reaction of the boryl units. Furthermore, theoretical calculations have indicated that efficient intramolecular energy transfer could enhance photochemical reaction through the triplet pathway, and the boryl unit acted as an antenna ligand to enhance the photoisomerization quantum efficiency of the DTE unit. Recently, Wang et al. synthesized a new Pt(II) dendrimer (**10**) containing up to twenty-one photochromic DTE units. Notably, complex **10** displayed both high photochromic efficiency and individual switching properties, thus providing a novel approach for the arrangement of multiple chromophores into a highly ordered system by the straightforward synthetic pathway.[51]

Furthermore, the incorporation of other metal ions into DTE may rationally tune the photo-responsive behaviors. For example, Wu et al. were the first to report a series of photochromic and mechanochromic benzo[b]phosphole alkynyl Au(I) complexes (**11**-**14**) through simultaneously incorporating a photo- and a mechano-responsive unit.[52] As shown in Figure 4A, upon UV light irradiation, complexes **11**, **12** and **14** exhibited significant color changes from colorless and yellow to pale red, deep blue and deep green, respectively. The ring-closed forms, along with their corresponding colors, could also recover to their open forms through the photoirradiation at around 500–600 nm. Besides, upon grinding, complexes **11**, **12** and **14** exhibited prominent color changes from pale yellow and orange to yellow and red, respectively (Figure 4B). Meanwhile, these varied colors could restore to their initial states in the presence of solvent vapors such as diethyl ether. Due to the absence of the short Au···Au distance, the mechanochromic behavior should be attributed to the planarization of the triphenylamine-containing alkynyl unit, which enhanced π-conjugation and increased planarity in the ground samples of Au(I) complex through reducing the interplanar angle between the triphenylamine moiety and the neighboring π systems. Moreover, the pristine and ground samples both exhibited reversible solid-state photochromism under UV or visible light irradiation. This work provides a new insight for developing mechanochromic and photochromic metal complexes.

Apart from modifying the DTE skeleton chemically, the photo-responsive behaviors can also be tailored by altering the ancillary ligands of metal complexes. In 2018, Xu et al. synthesized a series of Cu(I) complexes (**15**-**19**)

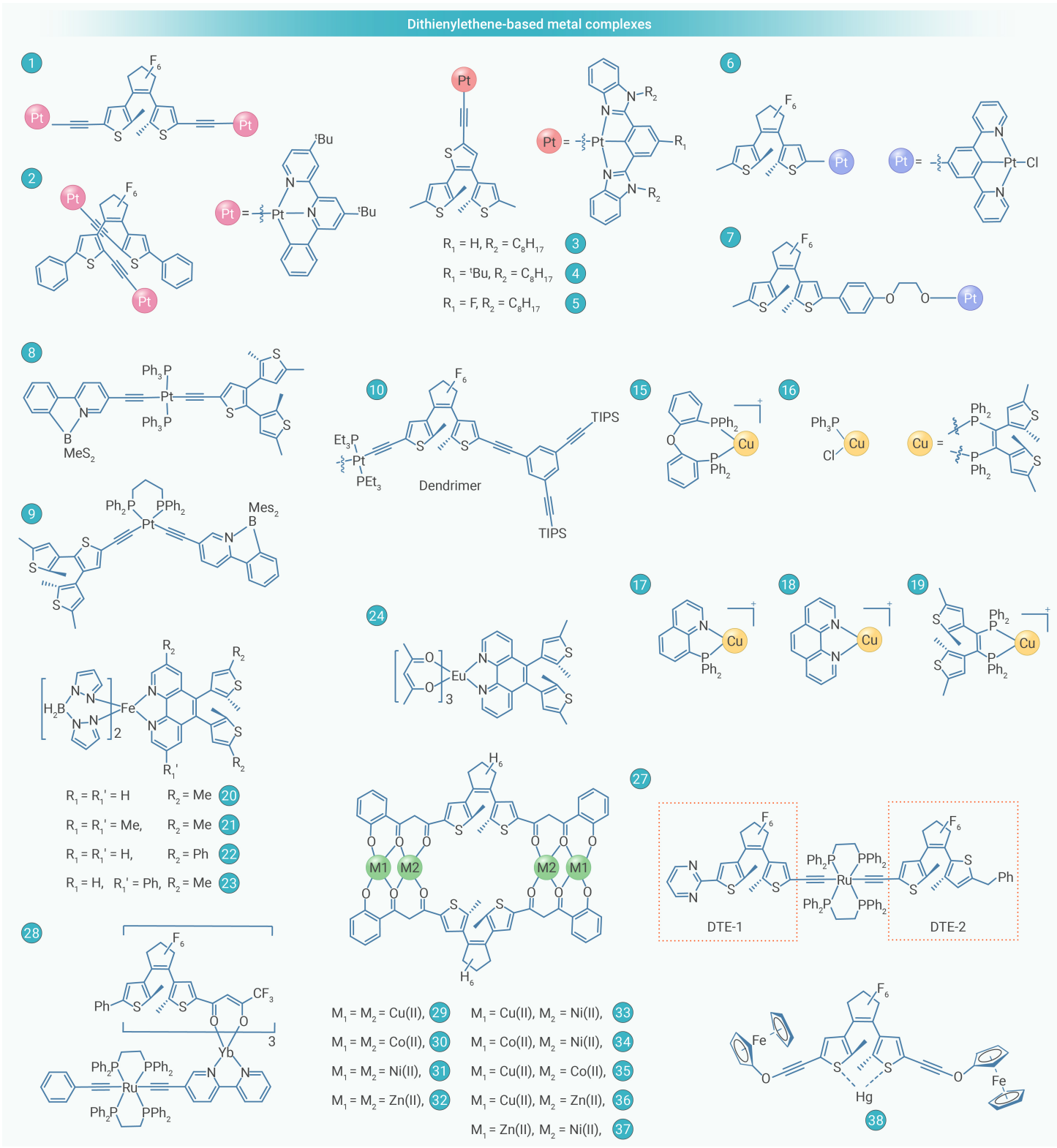

Figure 2. Partial molecular structures of dithienylethene-based metal complexes.

via the reaction of a DTE-based Cu(I) dimer with different ancillary ligands, displaying tunable photochromic properties.[53] For example, complex **15** showed a PCQY of 45%, while the PCQYs of **17** and **18** complexes were very low. DFT calculations demonstrated that the quantum yields of the photoreactions could be influenced by different MLCT transitions. Their highest occupied molecular orbitals (HOMOs) were primarily localized at the *d* orbitals of Cu and a π orbital of the DTE-based phosphine ligand, while the LUMOs of complexes **17** and **18** were distributed across the atomic orbitals of the quinoline and 1,10-phenanthroline ligands, respectively. This strong MLCT transition from Cu to the heterocycles imposed the limitation on the photoreactivity of **17** and prevented the cyclization of **18**.

Some DTE-based Fe(II) complexes have been developed to investigate their photocycloreversion reactions and thermodynamic stability. For example, by introducing methyl substituent into the phenanthroline backbone and phenyl group into the photoactive DTE unit, Mörtel et al. developed three Fe(II) spin-crossover molecular photoswitches (**20**, **21** and **22**) with different

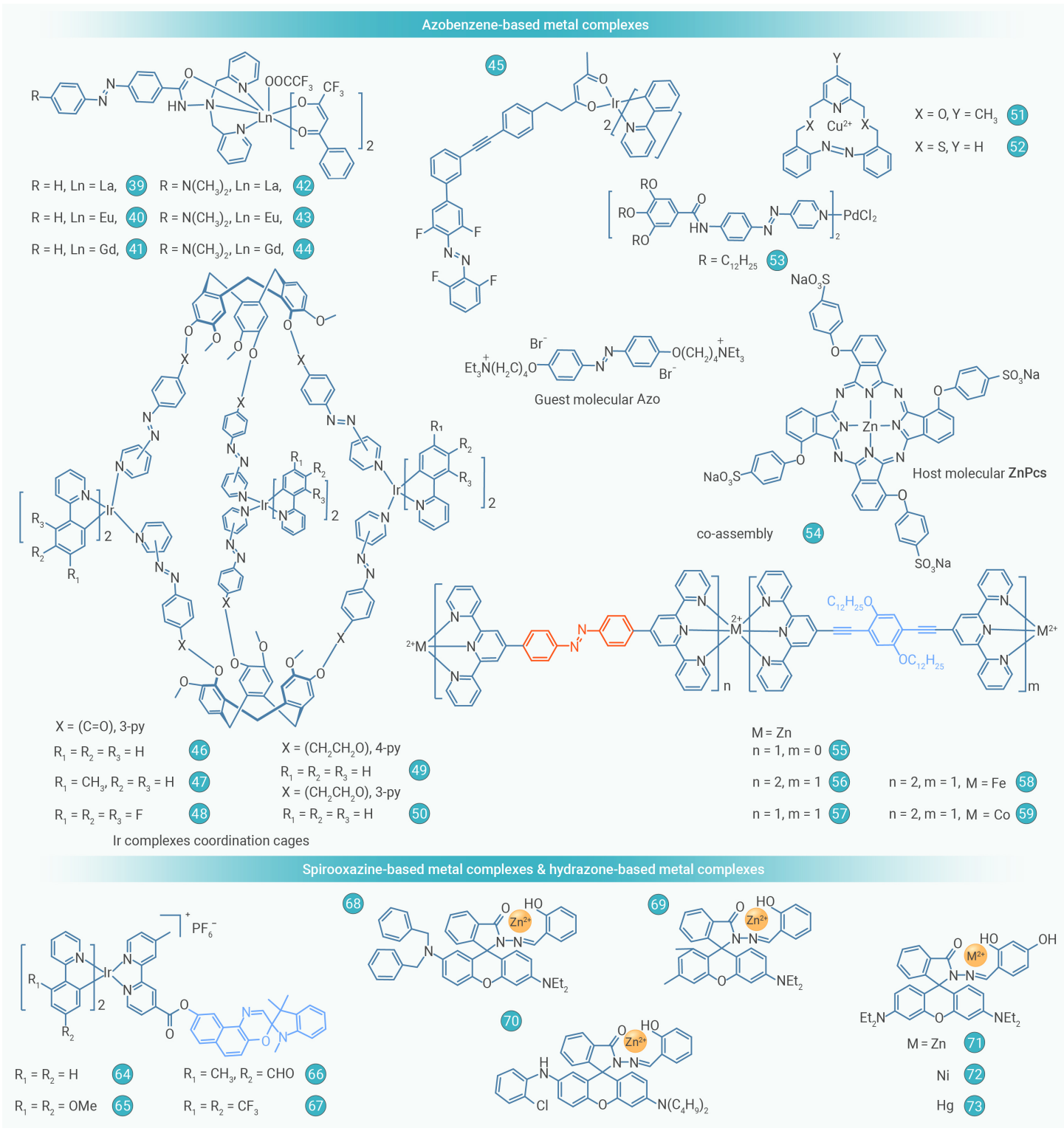

Figure 3. Partial molecular structures of other photo-responsive metal complexes.

photochromic behaviors.[54] Upon UV light irradiation at 282 nm, the absorption spectra of **22** presented the most red-shifted new band at 586 nm due to the formation of large conjugation system when compared with **20** and **21**. Upon irradiation with visible light (λ ≥ 400 nm), the cycloreversion reactions of **20** and **21** were not fully completed in the persistent absorption of the ring-opened forms within the visible range, while those of **22** could be fully completed within 135 s. Furthermore, the half-lives of the ring-closed **20**-c, **21**-c and **22**-c were 421 h, 199 h, and 3.3 min, respectively, demonstrating that modifications of the phenanthroline backbone could fine-tune the photocycloreversion reactions and thermodynamic stability. Subsequently, with the same photoswitchable backbone, Mörtel et al. synthesized an asymmetric photoswitchable phenanthroline DTE ligand and the corresponding Fe(II) complex **23** showing excellent photoswitchability at room temperature.[55] Particularly, the ring-closed **23** in solution exhibited a remarkably extended half-life of up to 533 hours (22 days).

The characteristic emission of lanthanide ion can be modulated by the photoswitching of the DTE units. For example, Mei et al. designed and synthesized a photo-responsive Eu(III) complex **24** with 5,6-dithienyl-1,10-phenanthroline ligand (L).[31] In the initial state, **24** exhibited characteristic emission peaks at 580, 594, 614, 654 and 704 nm in the ethanol solution,

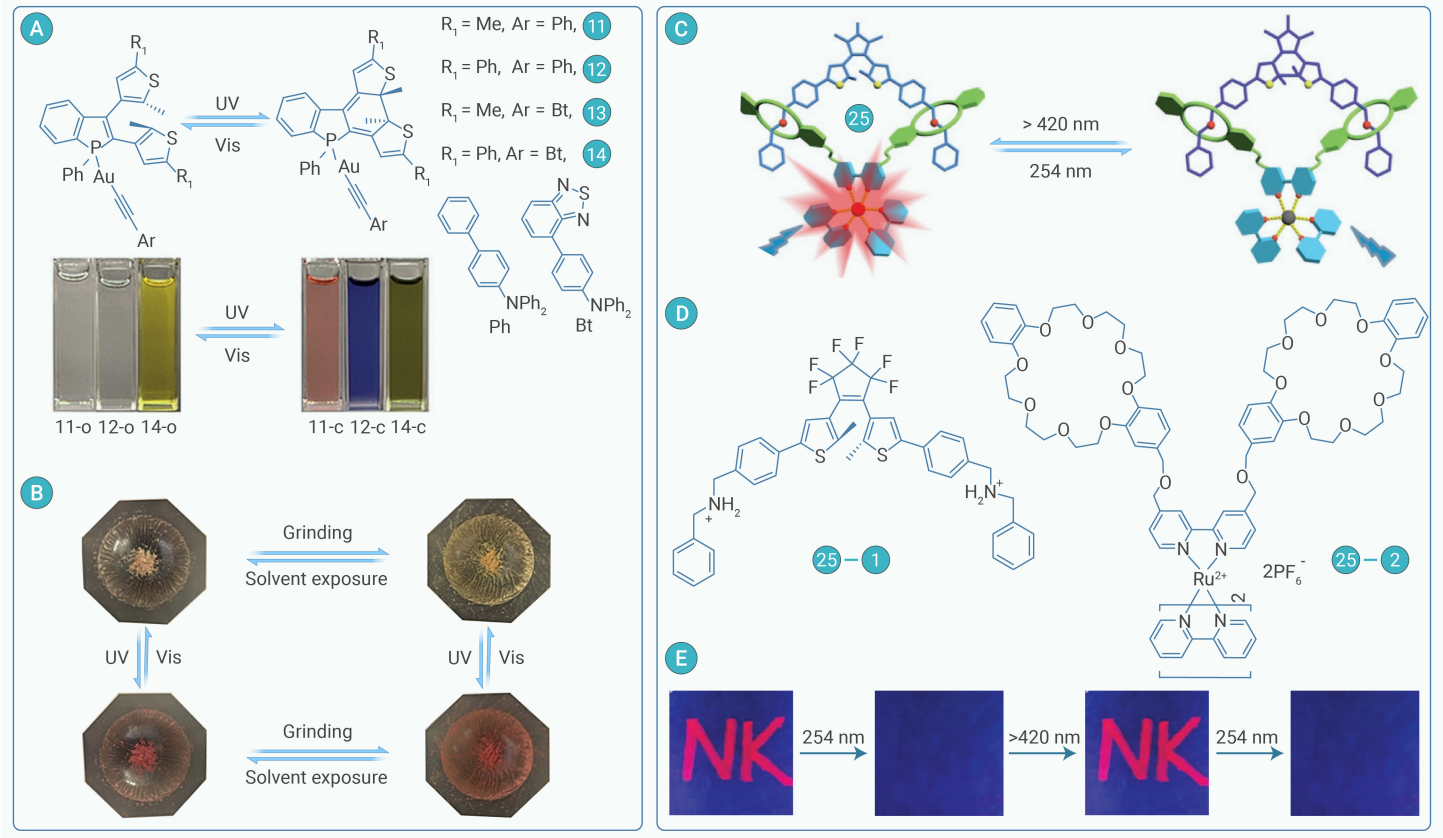

Figure 4. DTE-based Au(I) and Ru(II) complexes (A) Photochromic reactions with their color changes in degassed benzene solution upon UV excitation. (B) Solid-state mechanochromism and photochromism of **11** upon grinding and UV excitation, respectively. Reproduced with permission.[52] Copyright 2019, Wiley-VCH. (C and D) Schematic illustrations of the reversibly photoswitchable supramolecular assembly, and the chemical structures of corresponding components. (E) Fluorescence images of characters written by the assembly of **25** before and after irradiated with UV or visible light. Reproduced with permission.[56] Copyright 2017, Wiley-VCH.

which were originated from the $^5D_0$-^7F_j (j = 0-4) transitions of the Eu(III) ion. Upon UV light irradiation at 254 nm, the conversion of the ring-opened L to its closed form could result in a reduction of the lowest triplet state level, thereby disturbing the intermolecular energy transfer process between L and Eu(III) ion. Therefore, the luminescence intensity of **24** gradually decreased with increasing irradiation time. Meanwhile, the ligand L and complex **24** displayed similar absorption changes at 365 nm and 530 nm before and after photoirradiation, respectively. Based on this unique luminescence properties, the multi-level encryption application was prepared. The encrypted information could not be observed under visible light irradiation, but red-light structure image of ring-opened L appeared under UV light. Subsequently, red luminescence disappeared and the dynamic C–C bond appeared with increasing photoirradiation time, attributed to the formation of closed form. Finally, true encrypted information was read under natural light.

The luminescence intensity of DTE-based metal complexes can be finely modulated through intermolecular FRET process. For example, Wu et al. constructed a photo-responsive supramolecular assembly (**25**) by the noncovalent association of dialkylammonium in DTE units with dibenzo-24-crown-8 in $[Ru(bpy)_3]^{2+}$ moiety (Figures 4C-D).[56] Considering the significant spectral overlap of the absorption band of ring-closed **25-1** with the emission band of **25-2**, the FRET process between **25-1** and **25-2** could be realized by photoirradiation, leading to the dynamic control of luminescence of **25**. Upon UV light (254 nm) irradiation for 5.5 min, the fluorescence intensity of the resultant ring-opened **25** assembly was gradually quenched by 91%, indicating the efficient FRET process. Meanwhile, the fluorescence color of the solution could restore to red color after visible light irradiation (>420 nm). Importantly, the reversible switch on/off of luminescence of **25** could also be realized in polymethylmethacrylate (PMMA) film and solid state. Based on this reversible photoswitching intermolecular FRET behavior, information encryption application was developed by using **25** as ink (Figure 4E). The characters with red emission could only be observed under UV light at 365 nm, and it could be erased by UV light at 254 nm.

Based on a similar FRET strategy, Li et al. also developed a photo-responsive supramolecular coordination polyelectrolyte (**26**) as a smart anticounterfeiting ink.[57] In their design, the synthesis of **26** involved the electrostatic interactions between an anionic Eu(III) coordination polymer and a cationic DTE-containing photochrome (Figure 5A). The ring-closed DTE (CF-1) exhibited an absorption band that was perfectly aligned with the emission band of Eu(III), leading to luminescence quenching. As shown in Figure 5B, the as-prepared **26** presented the characteristic red emission of Eu(III). Upon UV light irradiation, the luminescence of Eu(III) gradually disappeared, indicating that the efficient FRET process between Eu(III) and CF-1 has taken place. After 20 consecutive cycles, no obvious decrease in luminescence intensity could be observed, indicating its outstanding reversibility. Furthermore, security printing was developed using **26** as ink. As depicted in Figure 5C, no discernible pattern was visible under daylight, while a bright red luminescent QR code could be observed upon 254 nm UV light. Then, the red luminescence could be effectively quenched by 300 nm UV light, rendering the QR code invisible under UV light or daylight, and the QR code could appear by visible light, demonstrating the promising potential of **26** in anticounterfeiting applications.

To achieve multi-responsive properties, such as interconvertible states and a wide range of colors, Chen et al. designed an asymmetric Ru(III) complex (**27**) with two distinct DTE units (DTE-1 and DTE-2), and the two units possessed the well-separated ring-closed absorption bands.[33] In the initial state, the doubly ring-opened form (**27**oo) of complex **27** in toluene presented the main absorption bands at about 290-370 nm. Upon exposure to UV light at 365 nm, new absorption bands at 426-850 nm appeared, which could be ascribed to the absorptions of the ring-closed forms of two DTE units (DTE-1c and DTE-2c), suggesting the presence of a mixture of singly ring-closed species (**27**co and **27**oc). Then, the colorless toluene solution gradually transformed into a blue-black hue with increasing irradiation time, attributed to the formation of a mixture of **27**co and the doubly ring-closed form **27**cc. Importantly, upon photoirradiation at 730 nm, complex **27**oc could be

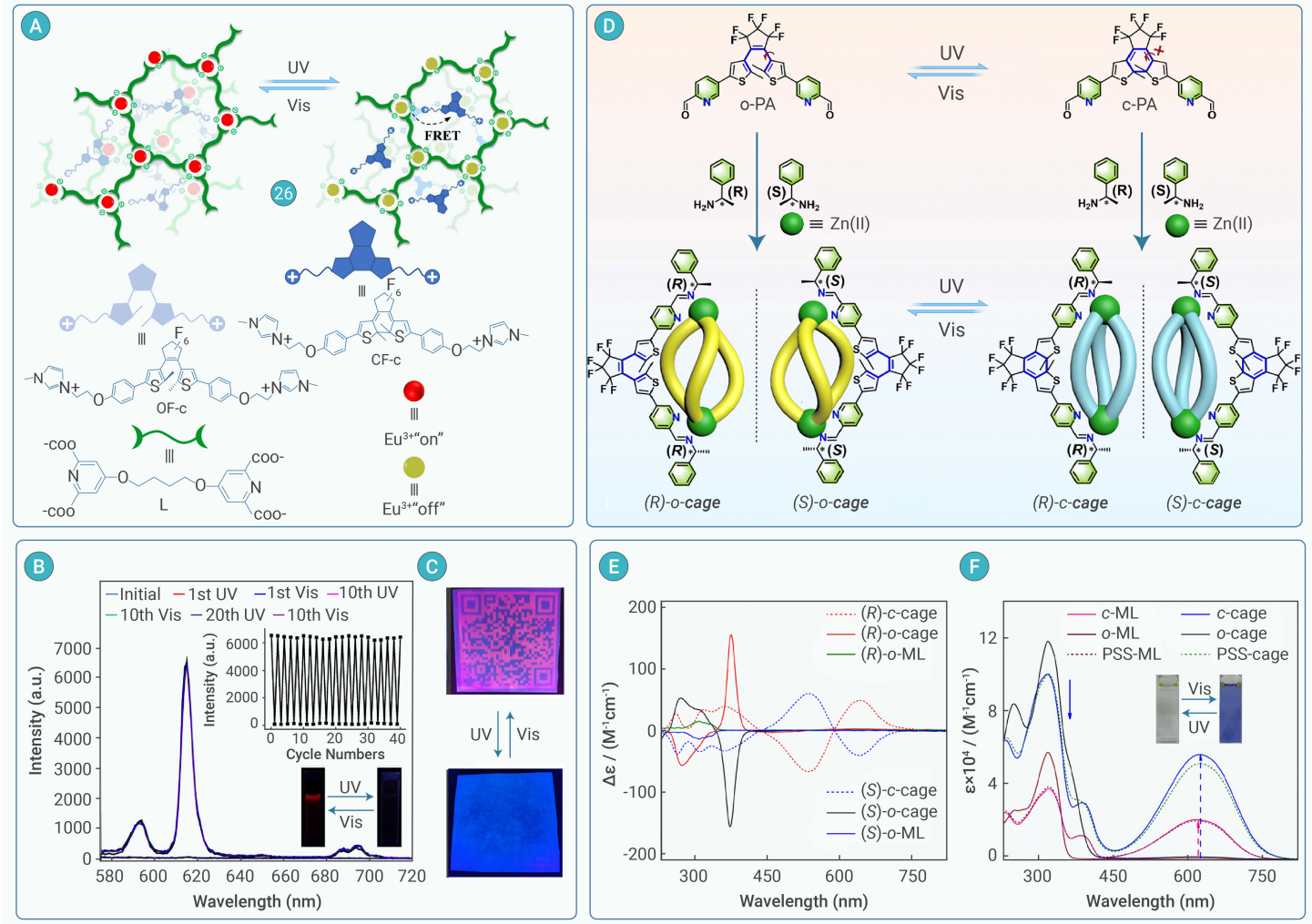

Figure 5. DTE-based Eu(III) and Zn(II) complexes (A) Schematic illustrations of the reversibly photochromic supramolecular coordination polyelectrolyte, and the chemical structures of corresponding components. (B) Luminescence emission changes of **26** upon exposure to UV and visible light. (C) Digital photos of **26**-based luminescent QR code on commercial blue PET film upon alternating UV and visible light. Reproduced with permission.[57] Copyright 2021, Springer Nature. (D) Self-assembly representation of DTE units, chiral amines, and zinc ions into chiral [3 + 2] metallacages and graphical representation of light-induced transformation between an (*R/S*)-o-cage and (*R/S*)-c-cage. (E) CD (top) and UV/Vis (bottom) spectra of the (*R/S*)-cage and (*R/S*)-model ligands in CH_3CN. (F) CD spectra of the (*R/S*)-cage (λ = 630 nm) in CH_3CN upon irradiation of UV light (λ = 313 ± 10 nm) and visible light (λ > 510 nm), respectively. Reproduced with permission.[61] Copyright 2023, Royal Society of Chemistry.

obtained through the cycloreversion of ring-closed DTE-1c to ring-opened DTE-1o, accompanied with the color change from blue-black to red. Similarly, **27**co could be achieved with the color changed from blue-black to blue upon photoirradiation at 530 nm. Furthermore, when irradiated at >460 nm, complex **27**cc in solution at the photostationary states (PSS) finally could convert into a colorless **27**oo. Furthermore, the photo-responsive behaviors of oxidized **27**oo$^+$ were also investigated through the oxidation of Ru(II) to Ru(III). Finally, eight interconvertible states were achieved through light and redox stimulation.

Besides single metal-based complexes, the incorporation of two or more metal ions was observed in DTE switches. Rigaut et al. realized efficient photocontrol of bright near-infrared (NIR) luminescence and multifunctionality of complex **28** by combining Yb(III) and Ru(II) ions.[58] Upon photoirradiation at 450 nm, **28** in CH_2Cl_2 exhibited a characteristic emission, originating from the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb(III), in the NIR spectral range at λ_{max} = 980 nm, suggesting an effective energy transfer from the Ru(III) moiety to the Yb(III) center. Meanwhile, this "pure" NIR emission could be reversibly turned on/off upon irradiation at 350 nm or 650 nm. Notably, excitation at 450 nm could offer a highly efficient and nondestructive means for reading the system state. Additionally, the initial cyclic voltammetry curves and spectroelectrochemistry measurements revealed that a single reversible wave corresponding to the one-electron oxidation of Ru acetylide subunit at 0.049 V (E_1^+), and the disappearance of the absorption band centered at 460 nm and the appearance of a new broad absorption band at 1060 nm were observed. Thus, the reversible transformation of the ring-opened **28**o into the oxidized **28**o$^+$ enabled precise control over the switching on/off of the bright NIR emission by effectively suppressing sensitization through an electron transfer mechanism or the new transition at ca. 1060 nm. Consequently, dual light and redox control of NIR luminescence was successfully achieved.

By exploiting the selective coordination of different metals at distinct binding sites within the ligand, Uber et al. successfully synthesized a series of heterometallic architectures (**29**-**37**).[59] These heterometallic complexes consisted of two separate dimers of closely spaced metal centers interconnected by laterally disposed L^{4-} ligands. Interestingly, the heterometallic [MM'···M'M] topology revealed a selective distribution of two types of metals. The central positions in the structure exhibited an octahedral coordination environment, while the external positions adopted a square-pyramidal geometry. However, the switching process of these heterometallic complexes was not fully reversible due to the structural rearrangements caused by the variations in coordination geometries and pyridine ligands. Therefore, stability and reversibility of photochromic heterometallic architectures needed to be enhanced.

Unlike the majority of reported DTE-based metal complex photoswitches, Hg(II) ion can directly coordinate with the S atoms of thiophene rings in the photochromic unit, and intervene directly the dynamics of the photoisomerization process.[60] After adding Hg(II) ion to 1 equiv of the ring-opened ligand and ring-closed ligand in CH_3CN solutions, respectively, distinct color changes from pale yellow and violet to blue and green were observed. The

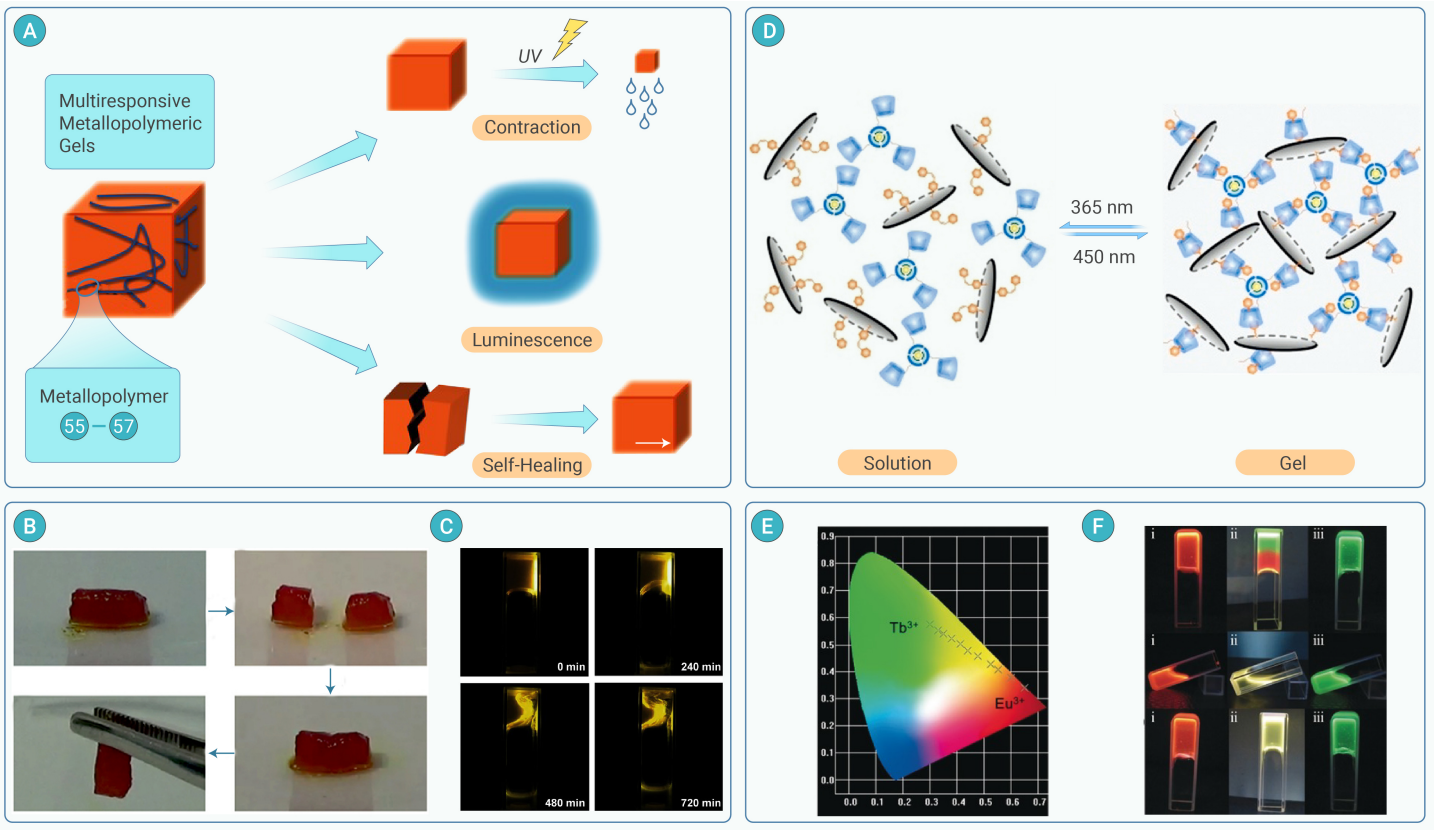

Figure 6. Light-powered soft actuators and phase transition (A) Schematic representation of the properties of the supramolecular coordination polymers. (B) Photograph of self-healing behaviors of supramolecular gel. (C) Contraction of the gel upon continuous UV photoirradiation showing the macroscopic photomechanical response. Reproduced with permission.[77] Copyright 2016, Wiley-VCH. (D) Proposed photoinduced sol-gel phase transition of photo-responsive hybrid hydrogels formed by the hierarchical self-assembly of host–guest. (E) CIE 1931 chromaticity diagram within the coordinates of the supramolecular hydrogels excited at various Tb^{3+}/Eu^{3+} molar ratios. (F) Photographs of luminescent supramolecular hydrogels upon UV light under 254 nm and after irradiation at 365 nm then 450 nm. Reproduced with permission.[32] Copyright 2018, Wiley-VCH.

binding constant values were calculated as 4.779×10^4 and 2.149×10^4 M^{-1} for **38**o and **38**c, respectively, suggesting that ring-opened ligand displayed the slightly stronger binding ability. Compared with free DTE ligand, **38**o exhibited slower ring-closed process, which was consistent with the regenerated irreversible wave of **38**o complex upon photoirradiation. Moreover, theoretical studies demonstrated that the complexation of **38**o showed a significantly higher exergonicity (−22.7 kJ/mol) compared to the formation of **38**c (−4.8 kJ/mol), thereby providing an explanation for the low conversion in **38**o.

Recently, through the coordination-driven self-assembly of DTE units with octahedral Zn ions, Guo's group developed a series of dynamic chiral photoswitches based on supramolecular metallacages (Figure 5D).[61] Inspiringly, these metallacages exhibited an ultrahigh photoconversion yield of 91.3%, which indicated that flexibility of coordination bonds contributed to the relative independence of inner responsive units. Importantly, a 10-fold enhancement of chirality and redshift of about 60 nm were achieved in (*R/S*)-o-cages in contrast to model ligands, suggesting that the point chirality of the phenylethylamine was successfully transferred to the helix chirality through the metal coordination (Figures 5E-F). Unlike (*R/S*)-o-cage, (*R/S*)-c-cage displayed two strong absorption peaks at 400–800 nm with characteristic Cotton effects. This dynamic chiral model, incorporating chirality transfer, significantly contributed to the understanding and simplification of the chirality effects at the supramolecular level.

In summary, the reported photo-responsive DTE-based metal complexes, including single-component metal complexes and multi-component composites, display switchable responsive behaviors. Incorporation of metal into DTE-based switches has been demonstrated as a successful strategy to immediate control of the optical signal and switching efficiency by delicate manipulation of their energy transfer pathways. Different types of metal ions endow the multifunctionality of metal complex (such as dual luminescence and redox properties), which is beneficial to construct photo-responsive multifunctional materials. Moreover, by virtue of the photoswitchable nature, DTE-based photochromic metal complexes offer numerous advantages, enabling them to provide additional information on optical anticounterfeiting applications.

Azobenzene-based metal complexes

Azobenzene (AB) is well known for its *trans(E)*-to-*cis(Z)* isomerization upon UV light irradiation, and the reverse isomerization can be induced by visible light or heating.[62-69] When AB was combined with a metal ion, the obtained metal complexes would exhibit distinct photochromic properties upon UV light or visible light. Particularly, *trans*-ABs have a planar structure with nearly zero dipole moment, while *cis*-isomers are less flat and have larger dipole moments. Therefore, the significant geometry variation of ABs, along with the associated host–guest interactions and synergistic metal-coordination, can effectively manipulate the assembly or disassembly behaviors of metal supramolecular polymers, such as phase transition, hierarchical organization and tunable luminescence.

To evaluate the effect of the electron-donating group on the AB-based metal complexes, Lin et al. constructed a series of AB-derived β-diketonates Ln(III) complexes (**39-44**), and explored their photo-responsive behaviors.[70] Upon photoirradiation, the absorption variations revealed that the Ln(III) complexes lacking electron-donating substituent exhibited higher isomerization quantum yields compared to the corresponding Ln(III) complexes with the electron-donating *para* substituent. Meanwhile, two Eu(III) complexes showed red luminescence at around 614 nm in both solution and solid state *via* the good antennae effect of the dionate ligand. Therefore, photo-responsive luminescence behavior could not be observed in this work. To improve the photoisomerization of AB, Moreno et al. designed and synthesized an Ir(III) complex (**45**) using a covalently tethered AB fragment.[71] Due to the absence of electronic communication between the metal center and the AB unit in the ground state, selective irradiation of the ^{1}MLCT band of the Ir(III) complex could induce an efficient $Z \rightarrow E$ photoisomerization over a wide concentration range and even at concentrations below 10^{-5} M.

For the first time, AB-based metal coordination cages were also

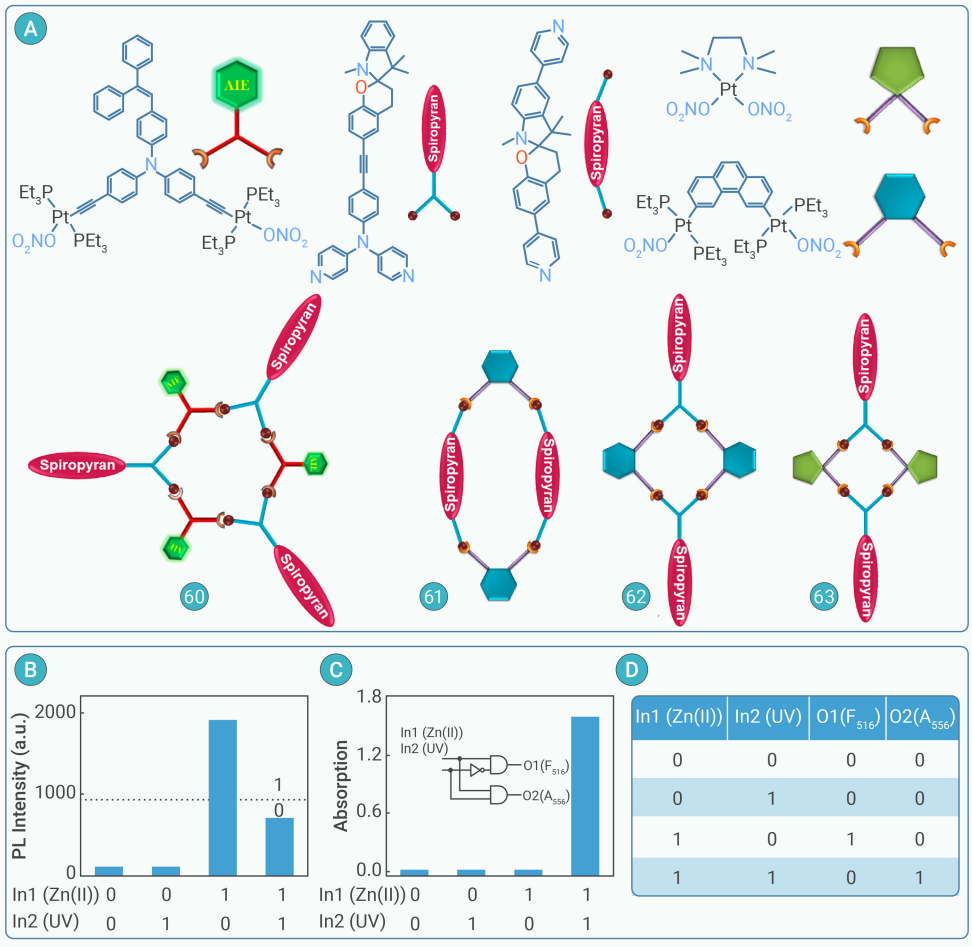

Figure 7. Photo-responsive macrocycles and logic gates application (A). Self-assembly of the macrocycles **60**–**63** from their corresponding building blocks. Reproduced with permission.[92] Copyright 2020, American Chemical Society. Bar diagrams of (B) fluorescence and (C) absorbance changes in response to Zn ions and UV light irradiation. Inset: Schematic diagrams of the logic gates with different inputs. (D) The corresponding truth tables of the logic gates based on the utilization of Zn ions and UV light irradiation. Reproduced with permission.[100] Copyright 2020, Elsevier.

developed.[72] For instance, Oldknow et al. synthesized a series of M_3L_2 Ir(III) coordination cages (**46**-**50**) featuring photo-isomerising azo-aromatic linkers, where M was a C^N type cyclometallating ligand and L was cyclotriguaiacylene (CTG) derived pyridyl-AB-phenyl group. Meanwhile, each M_3L_2 Ir(III) cage, equipped with six AB-type linkages, exhibited different photoisomerization property. Particularly, the $E \rightarrow Z$ photoisomerization of the pyridyl-AB-phenyl groups in cages could reach 40% under photoirradiation at 355 nm. Moreover, the cages showed reversible structure-switching while maintaining their compositional integrity owing to the presence of rotational flexibility, thereby resulting in the relatively low photoluminescence quantum yields of these blue emitting cages.

Unlike the classical photo-induced AB, the metal ion can also facilitate the $Z \rightarrow E$ isomerization of AB in the absence of light. In 2021, Hossain et al. designed a pair of novel macrocyclic AB-based photoswitches, namely, **51** (O-containing) and **52** (S-containing), which possessed three additional donor atoms around the -N=N- bond to facilitate coordination with the metal ion.[73] Initially, two Cu^{2+} complexes existed in *E*-isomers at 298 K. Subsequently, their *Z*-forms were attained under continuous irradiation with UV light and then immediately went back toward their initial states upon cessation of light. This phenomenon can be attributed to the favorable interaction distance between the -N=N- bond and the metal ion in the *Z*-form, which leads to a significant reduction of the N–N bond and subsequent isomerization towards the thermally stable *E*-form. It is anticipated that this instant metal ion-induced switching of these macrocycles will open up newer opportunities for fast photo-responsive materials.

In order to explore the impact of metal coordination on hierarchical supramolecular structures of light-responsive building blocks, Kartha et al. designed two novel light-responsive AB-containing pyridyl ligands, featuring an amide group for hydrogen bonding and a pyridyl ligand responsive to Pd(II) ion.[74] Before photoirradiation, the ligand self-assembled in an antiparallel manner into long twisted fibers driven by hydrogen bonding and π-stacking *via* the formation of dimer species. However, upon exposure to UV light, disassembly occurred, leading to the formation of shorter rigid rods with a new non-H-bonded packing mode. In contrast, when complexed with Pd(II) ion, the molecular rearrangement occurred, and the aggregation mode changed from antiparallel to slipped stacks driven by N–H/Cl interactions due to the enhanced cooperativity of the supramolecular growth, accompanied by the formation of long thin fibers. Upon light irradiation, these long thin fibers transformed into thinner, shorter rods *via* a reorganization into a different *trans* conformation of the Pd(II) complex (**53**). The findings have unraveled the influence of metal coordination and light irradiation on hierarchical self-assembly processes, paving the way towards the design of novel supramolecular photochromic systems combining the properties of metal ions and light.

By co-assembling phthalocyanine and AB amphiphiles, Cheng et al. developed new photoswitchable nanoparticles for controlled double-lock photodynamic therapy by precisely regulating the stoichiometric ratio of the components and light irradiation.[75] Upon addition of more than 2 equiv. of amphiphilic azobenzene (Azo 1) to zinc(II) phthalocyanines (ZnPcS), a significant decrease in the absorption intensity of ZnPcS, accompanied by enhanced fluorescence emission, was observed at around 600–800 nm, indicating robust interactions within the co-assembled host–guest nanosystem ZnPcS–Azo (**54**), which promoted complex formation. Meanwhile, the disassembly of **54** could be triggered by visible light stimulation. This novel co-assembled phthalocyanine-AB nano-photosensitizer could effectively promote the death of red light irradiated bacteria cells, which served as a smart photosensitizer for controlled photodynamic therapy.

The preparation of soft actuators with self-repair capability and directional motion is a challenging research goal.[76] In 2017, Borre et al. designed and prepared the light-powered soft actuators with Zn–based supramolecular polymers (**55**, **56** and **57**) bearing photoisomerizable di-AB units and solubilizing luminescent phenylene–ethynylene moieties (Figure 6A).[77] The mechanical and gelation properties of the material could be precisely controlled by simply varying the ratio of photoswitchable/solubilizing ligand. The low critical gelation concentration for **56**, which was as low as 0.12 wt% in a solvent mixture of DMF:EtOH (1:20 v/v), demonstrated the exceptional organogelating capability of the designed metal supramolecular polymers. Owing to the reversible and dynamic metal–ligand coordination bond, the photo-responsive organogels exhibited remarkable self-healing abilities. When exposed to UV light, the prepared supramolecular gels displayed luminescent properties and mechanical actuation (orientation-dependent volume reduction and syneresis) due to the presence of photo-responsive moieties within the metallopolymer backbone (Figures 6B-C). After photoirradiation, the reduced flatness of the *cis*-AB in the metallopolymer units decreased the π–π interchain interaction, inducing the production of macroscopic collapse of the organogel. However, after solvent removal and redissolution in DMF, the *trans* form of **56** could be regenerated through heat, enabling its reusability while retaining both its organogelation ability and photomechanical prop-

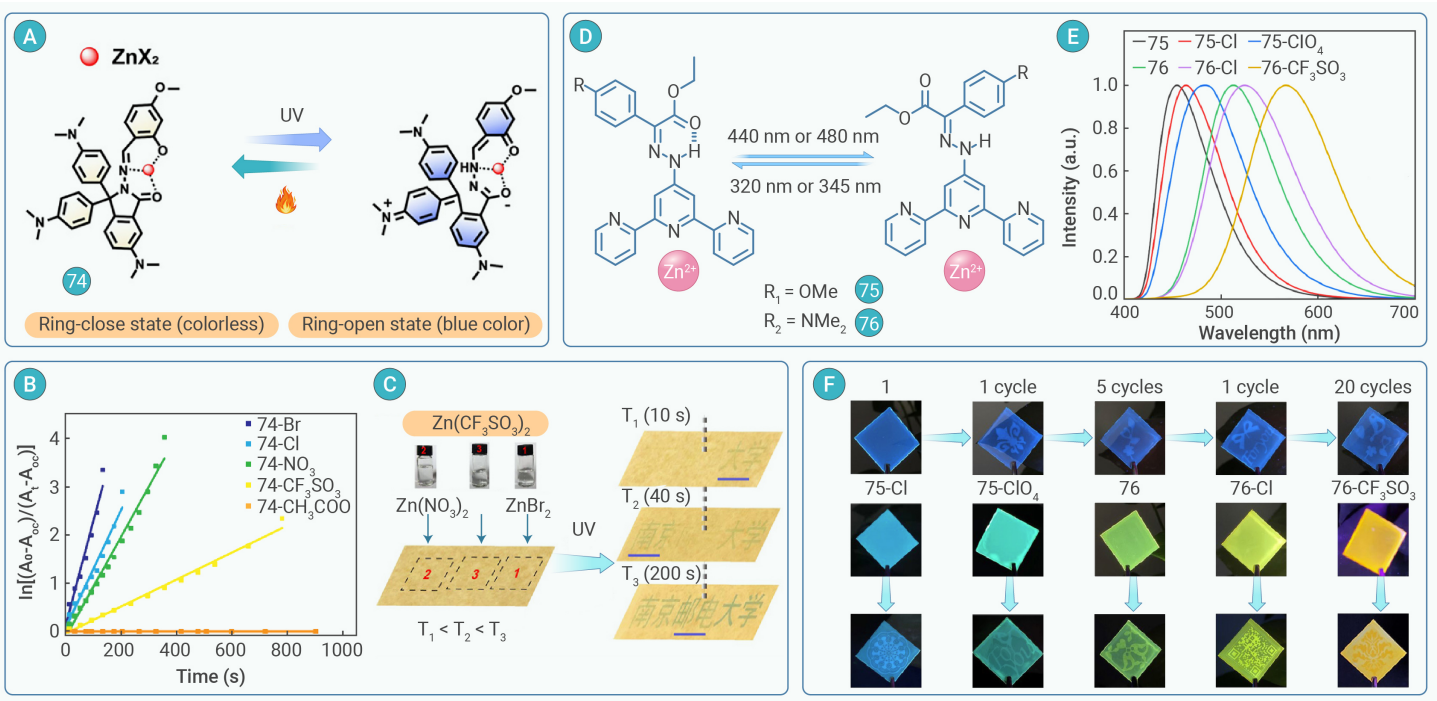

Figure 8. Hydrazone-based Zn(II) complexes for information storage and anticounterfeiting (A) Reversible photo-induced ring-opening and ring-closing reaction process for **74**-X. (B) Calculated coloration rate of **74**-X during the dynamic manipulation process. (C) Multilevel security information printing was realized by using various zinc salts as the inks. Reproduced with permission.[101] Copyright 2020, Amer Assoc Advancement Science. (D) Photo-induced *E*/*Z* isomerization of hydrazones **75** and **76**. (E) Normalized emission spectra (λ_{ex} = 365 nm) of drop-casted films of hydrazones **75**, **75**-Cl, **75**-ClO_4, **76**, **76**-Cl and **76**-CF_3SO_3. (F) Multicolor printing patterns on the various transparent films. Reproduced with permission.[104] Copyright 2022, Wiley-VCH.

erties for multiple cycles. Next year, with the same photoisomerizable AB unit and luminescent moiety, Borre et al. further synthesized two novel metal supramolecular polymers **Fe–P** (**58**) and **Co–P** (**59**).[78] However, the as-prepared **58** gel sample did not show photomechanical responses or phase transition under identical excitation conditions, which was ascribed to the ultrafast energy transfer from the excited donor AB to the acceptor MLCT band of the $[Fe(tpy)_2]^{2+}$ moiety.

Using the strikingly distinct binding abilities of *trans*- and *cis*-AB toward α-cyclodextrins (α-CDs), precise remote control over the reversible phase transition of α-CD-based supramolecular assemblies can be achieved. For example, Li et al. designed a robust luminescent hybrid hydrogel by rationally selecting Ln ions and AB units as emitting ions and photoswitches, respectively.[32] This design effectively resolved the excitation conflict between luminescent centers and photochromic units by allowing independent excitation, thus endowing hydrogels with luminescent and photo-responsive properties simultaneously (Figure 6D). Host–guest inclusion complexes consisting of α-CDs and AB as critical cross-linking bridges were employed for the formation of hydrogels. The emission colors of the resulting hydrogels could also be precisely tailored through altering the molar ratio of Tb^{3+} to Eu^{3+} ions (Figure 6E). As expected, the colorful supramolecular hydrogels presented a distinct reversible sol ↔ gel phase transition upon photoirradiation with UV and visible-light (λ = 450 nm). Notably, the luminescence at the interface of the supramolecular hydrogel, containing Eu^{3+} and Tb^{3+} ions at a 1:1 ratio, was no longer observed, and a compromised yellow emission appeared after UV irradiation, demonstrating the remote control over a reversible phase transition of tough luminescent hybrid hydrogels throughout the entire hydrogel monolith rather than just at the interface (Figure 6F).

In 2022, using the similar host–guest complexation approach, Yu et al. synthesized a new cross-linked supramolecular hydrogel *via* free-radical copolymerization in the presence of acrylamide-modified α-CD (AAm-α-CD) and 2,6-pyridinedicarboxylic acid-modified AB-based Eu(III) complex.[79] Upon excitation, the obtained hydrogel presented a bright red luminescence together with the quantum yield of 2.5% and lifetime of 155.6 μs, respectively. Similar to the solution phase, upon irradiation with UV light, the photoswitchable luminescence behavior of the hydrogel was observed with the luminescence quenching of 90%, and then recovered to the original state when exposed to visible light. This reversible luminescence change was attributed to the confinement effect, immobilizing the encapsulated *trans*-AB within the α-CD cavity and reviving the emissive pathway of Eu(III) complex, thus leading to a significant enhancement in the photoluminescence efficiency. The macrocycle-confined photoisomeric Ln complex is an appealing candidate for the creation of light-responsive intelligent materials.

Like the ABs, stilbenes exhibit similar *trans* to *cis* photoisomerization. Recently, several *fac*-Re complexes with stilbene units have been designed and synthesized.[80–84] Research has primarily focused on the photo-responsive behaviors in the *trans*-to-*cis* isomerization, including the modulation of isomerization quantum yield. However, reversible assembly materials incorporating stilbenes have not been adequately developed owing to the irreversible nature of *trans*/*cis* isomerization.

In short, a series of photoresponsive AB-based metal complexes, including small molecules, metal-macrocycles, metal-coordinated supramolecular polymers and host–guest inclusion complexes, have been realized by metal ligand coordination and host–guest interactions. It's found that the morphologies of supramolecular hydrogel based on photo-responsive AB-based metal complex could be dynamically tuned, where host–guest interactions capable of improving the ability of phase transition and photoswitchable luminescence upon alternating light irradiation. However, the supramolecular hydrogel should possess stretchable and flexible characteristics in order to fulfill the practical requirements. Therefore, developing photo-responsive supramolecular hydrogel with stretchable and flexible properties is highly desirable.

Spiropyran/spirooxazine-based metal complexes

Spiropyran (SP), a kind of typical photochromic molecules, exhibits reversible interconversion between colorless non-fluorescent SP and colored fluorescent merocyanine (MC). Upon UV irradiation, the ring-closed SP can convert into the ring-opened MC by heterolytic cleavage of the spiro C–O bond, which can be reversed by visible light or thermal energy.[85] Besides, protonated MC could release and subsequently re-capture H^+, thereby achieving acidochromic properties. Importantly, SP is commonly coordinated with diverse metal ions to form versatile metal-containing materials. Through structural modifications, use of functional building blocks, acid treatment, and

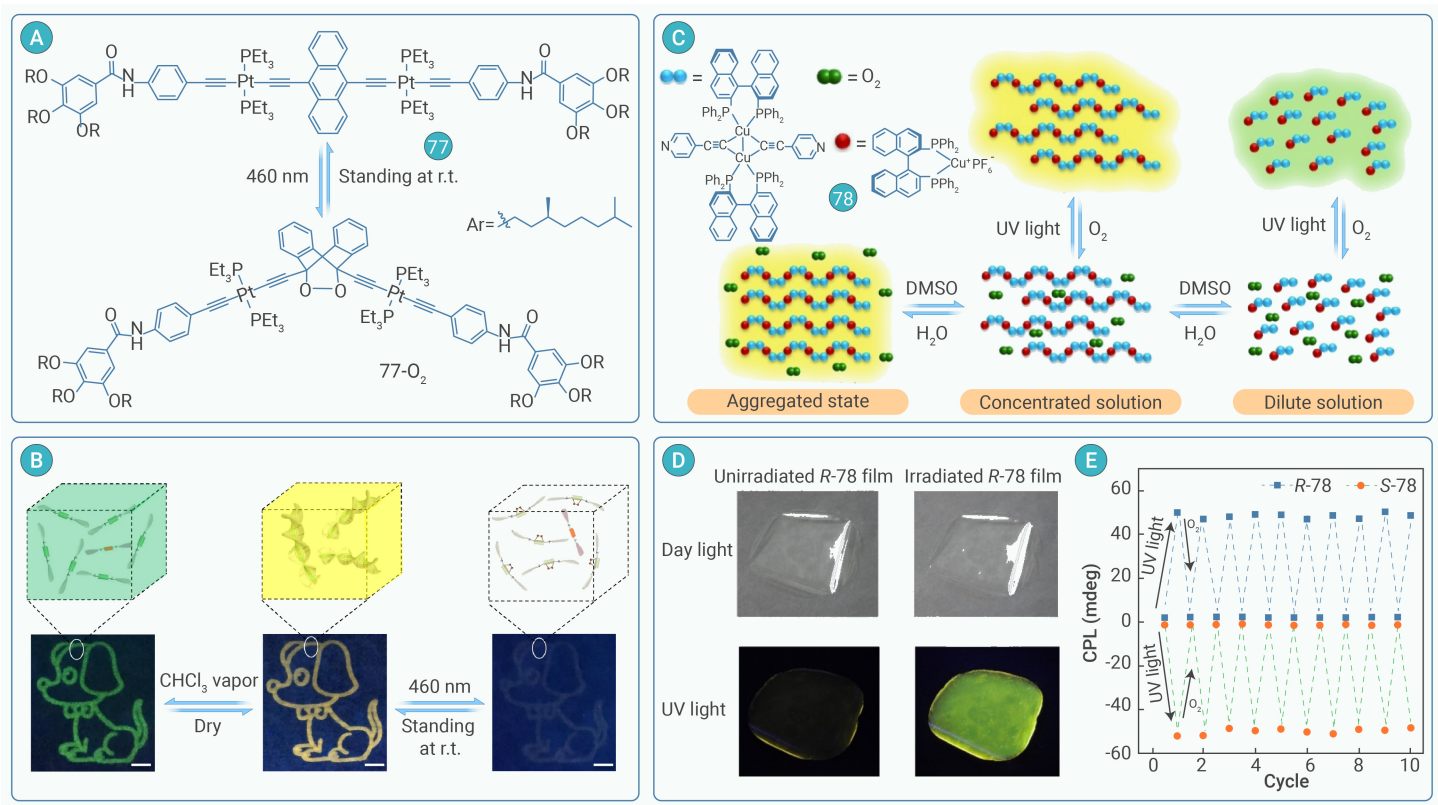

Figure 9. Other photo-responsive metal complexes (A) Schematic illustration of monomer **77** with anthracene–endoperoxide photoswitching. (B) Dual-stimuli responsive dog pattern. Reproduced with permission.[105] Copyright 2018, Springer Nature. (C) Proposed mechanism for AIE and concentration-dependent photo-response characteristics of *R/S*-**78**. (D) Photo of the R/S-**78** contained PMMA film before and after UV light irradiation. (E) Fatigue resistance of *R/S*-**78** contained PMMA film upon UV light irradiation and standing in air alternately. Reproduced with permission.[107] Copyright 2023, Wiley-VCH.

varying counterions, the photochromic properties of SP-based metal complexes could be tailored for versatile chemical and biological sensing applications.[86-89] Herein, we mainly focus on the discussion about the photo-responsive mechanisms of SP-based metal complexes. Discussions on the detection of metal ions of spiropyran-based sensors have been well reviewed in previous literature reports and thus will not be summarized in this part.[90]

To incorporate dual functions within a single coordination architecture, Mukherjee et al. devised a self-assembled Pt(II) macrocycle **60** with aggregation-induced emission (AIE)-active triphenyl group on the periphery, endowing this macrocycle with simultaneous AIE, photochromic, and acidochromic properties (Figure 7A).[91] Compared with **60** in 10% hexane in DCM, its emission intensity increased by 5-fold in 90% hexane in DCM because the steric congestion restricted the rotation of the aryl rings in the aggregate state. Meanwhile, N–Pt bond, which functioned as an electron-withdrawing group, enabled **60** to achieve stable and reversible photochromic behaviors. Besides, using the inherent protonation–deprotonation equilibrium of the SP units, the macrocycle **60** also showed reversible acidochromic behavior. By adding dilute nitric acid (2 M) into DMSO solution of **60**, no obvious changes could be observed. Upon UV light irradiation at 365 nm, the color of the solution changed from faint to intense yellow. After adding the dilute solution of triethylamine, an immediate color change from intense yellow to bluish-green was observed, indicating the deprotonation of the open form. Upon exposure to visible light, a color change from green to the original faint yellow was achieved, demonstrating the significant reversible acidochromic behavior of macrocycle **60**. Furthermore, Mukherjee et al. constructed three reversible SP-based-Pt(II) macrocycles (**61, 62** and **63**),[92] and exploited the influence of the position of the SP unit on the photostability of macrocycles (Figure 7A). By monitoring their photochromic behaviors, it was observed that **62** exhibited excellent photostability in 20 cycles, while **63** presented a good reversible photoswitch for up to 10 cycles. However, the degradation of **61** appeared after only 5 cycles. Therefore, it is concluded that the SP unit in the backbone of **61** could facilitate the macrocycle shrinking and swelling, disturbing the self-assembly of the closed and open forms of SP.

Like SP, spirooxazine also exhibits photoswitchable behaviors. In general, its open form is thermally unstable and rapidly undergoes bleaching reaction back to the closed form. However, the bleaching reaction rate of spirooxazine can be modulated through coordination with metal ion. For example, by combination of Ir(III) complexes with the photochromic spirooxazine ligand, a series of Ir(III) complexes (**64**, **65**, **66** and **67**) with tunable photochromic behaviors were designed and synthesized by Yam's group.[93] The bleaching reaction rates of these complexes presented a decreasing trend (**65** > **64** > **66** > **67**) with increasing the electron deficiency of the C^N ligands (−OMe < −H < −CHO < $-CF_3$). This was due to the electron-deficient nature of the C^N ligands, stabilizing the merocyanine form.

Apart from the SP-based sensing for metal ions, the SP- or spirooxazine-based metal complexes are rarely reported. Generally, the photo-responsive behaviors of SP- or spirooxazine-based metal complexes are currently dominated by photoswitchable unit. Their photostability and photoisomerization rates are modulated by reversible interconversion between open and closed form of SP or spirooxazine molecule. Through structural modifications (such as introducing electron-donating or electron-withdrawing group) and use of functional building blocks (such as AIE nature), it is feasible to construct versatile smart materials exhibiting switchable and desirable functionalities by employing appropriate molecular design strategy.

Hydrazone-based metal complexes

In comparison to the aforementioned molecular switches, hydrazone derivatives represent a relatively recent class of photochromic switches, which undergo *E*-to-*Z* isomerization around a central imine bond upon exposure to UV irradiation accompanied by significant structural changes.[94-98] Through rational molecular structure modulation, various hydrazone derivatives have been designed, including the violet lactone salicylaldehyde hydrazine, rhodamine B salicylaldehyde hydrazone, fluoran salicylaldehyde hydrazone, and so on. Additionally, employment of metal–ligand coordination proves to be an effective strategy in manipulating the responsive behaviors of hydrazone photoswitches. This section discusses the material categories, photostability, photochromic behavior, fatigue resistance, isomeriza-

tion lifetime and rate of photo-responsive hydrazone-based metal complexes.

In 2017, Li et al. designed and prepared a series of fluoran salicylaldehyde hydrazone Zn(II) complexes (**68**, **69** and **70**), which showed excellent reversible photochromism with remarkable fatigue resistance both in solution and solid matrix.[99] Upon UV light irradiation, the colors of these Zn complexes in DCM solution quickly changed from faint yellow or colorless to green (**68**), orange (**69**), and black (**70**), respectively. After removing the UV light, these solutions gradually returned to their initial states within 10 min. The distinct color changes arose from the tautomerism of different salicylaldehyde hydrazone moieties, transitioning from the enol form to the keto form. Meanwhile, distinct luminescence quenching was observed after photoirradiation. Besides, the photochromisms of these complexes were only observed in $CHCl_3$, DCM and DCE, while no color changes were detected in other solvents. Notably, the recovery rate constants transitioning from colored **69** to the leuco **69** were significantly higher than those of complexes **68** and **70** in all solvents, indicating the inherent instability of complex **69** as a result of the steric hindrance of the methyl group near the spirolactam ring. Thus, different patterns were successfully visualized by impregnating a thin layer of silica gel with these complexes, which demonstrated their potentials as promising candidates for photo-patterning. In the following year, Li et al. reported other three rhodamine B-based metal complexes (**71**(Zn), **72**(Ni) and **73**(Hg)) with photoswitchable behaviors, and evaluated the influence of different metal ions on the luminescence properties.[100] Upon UV light irradiation, these metal complexes presented similar absorption changes but distinct photo-induced luminescence behaviors. Before photoirradiation, **71** exhibited a strong green emission, and **73** showed weak orange emission, while **72** displayed almost negligible luminescence. After photoirradiation, the luminescence of **71** was quenched, while **73** presented enhanced luminescence. Again, there was still no emission observed for **72** due to the paramagnetic Ni(II) quenching effect. The luminescence quenching of **71** could be explained by the intense self-absorption of the conjugated rhodamine B moiety. Before photoirradiation, the weak fluorescence emission of **73** came from the spirolactam part of the rhodamine B part in the ring-opened form induced by the strong polarization of Hg(II), while the generation of more ring-opened form molecules resulted in an enhanced fluorescence emission after photoirradiation. Meanwhile, these complexes also showed the good fatigue resistance and excellent reversible photo-responsive properties. Thus, different logic gates were facilely designed by simply varying the inputs of metal ions (In1) and UV light (In2). The presence of inputs (In1 and In2) was defined as "1", while their absence was "0". The fluorescence intensity and absorbance acted as the output signals of O1 and O2, respectively. The constructed logic gates as well as the corresponding truth table were shown in Figures 7B-D. Taking **71** as an example, for the output of O1, fluorescence intensity at 516 nm was chosen as "1" before UV light, and the turn-off emission was defined as "0" after UV light (Figure 7B). For the output of O2, the absorbance at 556 nm was set as "1" after UV light while the absent absorbance was the "0" signal (Figure 7C). As shown in Figure 7C inset and Figure 7D, only the input with Zn(II) (In1 = 1, In2 = 0) can induce a fluorescence output signal (O1 = 1) while both the presence of Zn(II) and UV light (In1 = 1, In2 = 1) resulted in a colored state with an intense absorbance (O2 = 1). This work provides a new strategy for developing multifunctional photo-responsive materials, which is beneficial for constructing photo-controlled logic gates with tunable performance.

Apart from tuning different metal ions or structural modulation, varying counterions is a simple and convenient manner for modulating the photochromic behaviors of metal complexes. In 2020, based on crystal violet lactone salicylaldehyde hydrazine (CVLSH) ligand, Ma et al. reported a facile and effective strategy to engineer the photochromic properties of Zn complexes (**74**-X, X = CH_3COO^-, $CF_3SO_3^-$, NO_3^-, Cl^-, or Br^-) by varying the counterions (Figure 8A).[101] The coordination of Zn and CVLSH ligand could significantly mitigate the negative charge density on the nitrogen atom through inductive effects, thereby enhancing the stability of the ring-opened isomers. Considering the direct influence of counterions on the charge density of the metal center that resulted in different photochromic properties, Ma et al. investigated the influences of various counterions on the ring opening reaction rate of Zn complexes. As shown in Figure 8B, the calculated UV-induced ring opening reaction rate constants (k_{UV}) of these photochromic complexes followed the order of **74**-Br (0.01887 s^{-1}) > **74**-Cl (0.01093 s^{-1}) > **74**-NO_3 (0.00875 s^{-1}) > **74**-CF_3SO_3 (0.00208 s^{-1}) > **74**-CH_3COO (approximately 0), suggesting an increase in the energy would be required to stabilize the ring-opened form as the basicity of counterions increased. Therefore, the variations of the charge density around the spiro-C-N moiety caused by altering the counterions would have remarkable influences on their photochromic behaviors. Based on the remarkable tunability in photochromic rates of **74**-X complexes, multilevel information encryption was further developed. As shown in Figure 8C, $ZnBr_2$, $Zn(NO_3)_2$, and $Zn(CF_3SO_3)_2$ in aqueous solutions were used as inks for security information storage. Upon exposure to UV light for 10 s, the paper displayed the chinese characters of "Nanjing". After irradiation for more than 30 s, two other chinese characters of "University" appeared. Thus, "Nanjing University of Posts and Telecommunications" was revealed after UV irradiation for 200 s. These findings show that it is possible to develop smart materials with dynamically controllable responsive behavior in advanced optoelectronic applications.

For most of the luminescent photoswitches, the transition between on and off switching of emission intensity is often accompanied by a significant color change,[102,103] which is unsuitable for high-level information encryption. Additionally, the isomerization half-life of the majority of photochromic molecules is relatively short, thereby limiting their applications in real-world scenarios. Recently, Ma et al. designed and synthesized two novel hydrazone photoswitches **75** and **76** (Figure 8D), where anisole and N, N-dimethylaniline (electron donors) were used as the rotor, and the terpyridine group (electron acceptor) was used as the stator.[104] The "donor-acceptor" structure endowed hydrazone photoswitches with decent emission quantum yields, good reversible photoisomerization properties, and extremely long thermal half-lives. The coordination of Zn(II) salts and the terpyridine group of hydrazones **75** and **76** could vary the electron-withdrawing ability of the stator part and tune their luminescence properties. As displayed in Figure 8E, under UV light, obvious different luminescence colors (blue, cyan, green, yellow, and orange) were observed on **75**, **75**-Cl, **75**-ClO_4, **76**, **76**-Cl, and **76**-CF_3SO_3 doped PMMA films. Importantly, photo-induced luminescence quenching was also observed in the polymer matrices. Besides, these hydrazone-based metal complexes revealed their excellent isomer reversibility and remarkably long thermal half-lives (>5000 and 240 years). Moreover, the photo-controlled rewritable printing of invisible multicolor images with high resolution on transparent substrates was realized by using these photoswitches (Figure 8F). Importantly, the legibility of the printed patterns could last for more than 3 months without any detectable emission intensity loss under ambient conditions.

Based on above research, the approaches to achieve switchable photochromic behaviors of hydrazone-based metal complexes have been demonstrated by tuning different metal ions, structural modulation, or varying counterions. The reversible photo-responsive behaviors of hydrazone-based metal complexes offer an opportunity to be applied in advanced optoelectronic applications (such as logic gates and information encryption).

Other photo-responsive metal complexes

Compared with the above classical photoswitches, anthracene–endoperoxide interconversion becomes another promising photochromic switch for a variety of purposes. In 2018, Gao et al. designed and synthesized Pt(II)-based supramolecular polymer **77** with the attachment of $Pt(PEt_3)_2$ moiety on both ends of 9,10-diacetylide anthracene and investigated the double mode responsive behaviors for fluorescent anti-counterfeit applications (Figure 9A).[105] Upon irradiation with a 460 nm LED lamp, the absorption and emission band of **77** in $CHCl_3$ solution rapidly vanished within 20 s due to the occurrence of photo-oxygenation reaction (**77**-O_2). Different from the reported deep UV light (254 nm) or heating conditions, the reversible conversion from **77**-O_2 to **77** was spontaneous at room temperature, attributed to the presence of the larger hindrance imposed by two neighboring $Pt(PEt_3)_2$ units. Then, photoirradiation at 460 nm led to the complete collapse of supramolecular gels of **77** (10 mM in MCH) within 4 min, accompanied by a reduction of the green emission intensity. Upon standing at room temperature, highly emissive supramolecular gels reformed owing to the complete deoxygenation of **77**-O_2. Moreover, based on the two-component co-assem-

bly strategy, efficient FRET process was utilized to prepare the dual-mode anti-counterfeiting ink. As shown in Figure 9B, yellow emission signals of the dog pattern significantly decreased upon 460 nm light irradiation and could restore to the initial state within 3 min at 40°C through the synthetic effect of the interconversion between **77** and **77**-O_2, along with deactivated/reactivated the FRET effect. Additionally, $CHCl_3$ vapor could trigger the appearance of green emission of monomer anthracene, while yellow emission could be restored upon drying.

Different from the reversible color change between states of distinct isomers, some novel photochromic metal complexes have also been reported. For example, Jin et al. reported that photo-irradiation triggered the coordination transition between the carbonate groups and Mg(II) ion from bidentate to the more stable bridging mode, which varied the conformation of the remote diphenyldibenzofulvene, thereby modulating the emission colors from cyan to dark yellow.[106] Notably, the photo-activated powder exhibited bistable thermal and photochemical stability under continuous daylight exposure, high temperature or fuming with various vapors. However, this photo-responsive behavior was not reversible. Recently, Zang's group designed and synthesized a pair of chiral Cu(I) cluster-assembled materials (*R/S*-**78**), whose solution state and doped PMMA films both exhibited the unique photo-responsive luminescence characteristic (Figure 9C).[107] When *R/S*-**78** was irradiated in DMSO by UV light, an obvious "turn on" luminescence was observed. Considering that the phosphorescent metal cluster could be regarded as a photosensitizer capable of converting the triplet O_2 into singlet O_2, a singlet O_2 indicator of DCFH-DA was used to monitor the luminescent properties of the *R/S*-**78** in DMSO solution. The emission intensity of DCFH-DA with *R/S*-**78** in DMSO solution rapidly increased under continuous UV light exposure, demonstrating the efficient photosensitizing ability of *R/S*-**78** for singlet O_2 production. Furthermore, the *R/S*-**78** doped films also exhibited photo-responsive behaviors due to the photo-induced deoxygenation process (Figure 9D). Besides, the turning on/off process could be repeated for 10 times, indicating an excellent fatigue resistance (Figure 9E). This work provides a novel avenue for the future design of photo-responsive metal complexes without necessitating structural changes.

Above studies enrich the types of photo-responsive metal-based switches and offer new strategies for the construction of novel photo-responsive metal complexes for optoelectronic functional applications.

CONCLUSION AND OUTLOOK

In this review, we exhaustively summarize the recent advances made in photo-responsive metal complexes combining reversible molecular switches, including DTE, AB, stilbene, SP, spirooxazine and other photoswitches. The responsive behaviors and design strategies as well as their potential applications in various optoelectronic applications are presented. Two primary factors have to be addressed when modulating the photochromic properties of photo-responsive metal complexes: (i) Molecular switches provide the prerequisites for the defined stimulus; (ii) Metals that promote the ^{3}MLCT states or characteristic excited states resulting in distinct luminescence and photochromism. Although remarkable advances have been achieved in the fabrication and applications of various photo-responsive metal complexes in functional devices, some challenges still remain. For example, due to the intriguing photocolorimetric and photofluorometric behaviors, several DTE- and hydrazone-based metal complexes materials have been exploited in the development of anticounterfeiting labels. In contrast to their exceptional photoswitchable behaviors in dilute solution, the photoswitching properties of these metal complexes exhibit limited repetition in doped films or solid states due to the presence of the rigid environment that hinders the photoisomerization of switches. Therefore, it is vital to build a loose molecular environment in order to enhance the feasibility of photo-switchable metal complexes in doped film. Besides, short isomerization half-life and low reversibility of the major photo-responsive metal complexes weaken their responsive performances. Therefore, exploiting new photo-responsive metal complex with bistable properties and high cycle lifetimes as well as good performances in film state is necessary. Considering the continuous structure variation and possible degeneration of traditional molecular switches in response process, new photo-responsive mechanisms without structure changes are vital to produce smart photo-responsive metal complexes with long cycle lifetimes.

In addition, the majority of metal complexes with photo-responsive properties are unsuitable for biomedical applications due to the harmful effect of UV light stimulus on living cells. Moreover, reports on metal complexes that exhibit responses to multiple stimuli are still rare. Therefore, based on the above considerations, several strategies for the future design of such novel photo-responsive metal complexes could be adopted: (a) To introduce photo-induced stable radical cation in metal complexes, such as carbonyl derivatives,[108] triphenylphosphine derivatives,[109] and triarylamine derivatives,[110] which will not cause structure damage during the isomerization process; (b) To develop the photo-activated metal complexes through oxygen consumption enhancing phosphorescence; (c) To decorate the metal complexes with multifunctional units that can simultaneously respond to two or more external stimuli with different behaviors. For instance, the emission lifetime of organic phosphors, as the candidate, could be well controlled by temperature, oxygen content or water molecule; (d) To prepare the visible and NIR light-activated molecular switches in metal complexes to broaden the application scope, especially for biomedical applications. For instance, the absorption in the NIR region of molecular switches could be achieved by extending the π-conjugated molecular skeleton or compositing with upconversion nanoparticles (UCNPs), thereby the NIR light-activated molecular switches can be obtained. Under NIR irradiation, the UCNPs are capable of emitting visible light, thus inducing isomerization of the molecular switches and subsequently modulating the photophysical properties of the responsive system.

Modulating photophysical process is a fundamental way for tuning the performance of many optoelectronic devices. In addition to above optoelectronic functional areas, by virtue of the advances of "on/off" photoswitchable molecules that are capable of modulating excited states, absorption or mechanical properties based on geometric and electronic changes, the smart photo-thermoelectric devices or X-ray scintillators based on the photo-responsive metal complexes could also be explored in the near future.

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AUTHOR CONTRIBUTIONS

W.-Y. W. supervised and revised the manuscript. Y. Y. Q. and P. F. S. wrote and edited the manuscript. All authors contributed to the article and approved the submitted version.

DECLARATION OF INTERESTS

Wai-Yeung Wong is an Editorial Board member of The Innovation Materials and was blinded from reviewing or making final decisions on the manuscript. Peer review was handled independently of this member and their research group. The other authors declare no conflicts of interest.

DATA AND CODE AVAILABILITY

Not applicable.

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https://www.polyu.edu.hk/abct/people/academic-staff/prof-wong-wai-yeung-raymond/