Chasing the rainbow: Exploiting photosensitizers to drive photoisomerization reactions

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REVIEW ARTICLE

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Chasing the rainbow: Exploiting photosensitizers to drive photoisomerization reactions

Zhihang Wang[1] | Lorette Fernandez[2] | Adil S. Aslam[3] | Monika Shamsabadi[3] |
Lidiya M. Muhammad[3] | Kasper Moth-Poulsen[2,3,4,5]

[1]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK

[2]The Institute of Materials Science of Barcelona, ICMAB-CSIC, Barcelona, Spain

[3]Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden

[4]Catalan Institution for Research & Advanced Studies, ICREA, Pg. Lluìs Companys 23, Barcelona, Spain

[5]Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE, Barcelona, Spain

Correspondence
Kasper Moth-Poulsen.
Email: kasper.moth-poulsen@upc.edu

Abstract

Photoswitchable molecules have garnered considerable attention for their versatility and diverse applications, spanning from solar energy harvesting and storage to drug delivery and molecular motors. The chemical conversions that make photoswitches a desirable system are driven by specific wavelengths of light, which often demand intricate molecular modifications. An alternative approach to achieve the photoisomerization reaction is through energy transfer with photosensitizers. Photosensitizers play a pivotal role in various light-induced processes and have demonstrated successful applications in photodynamic therapy, dye-sensitized solar cells, and activating photochemical reactions. Therefore, combining photoswitching systems with sensitizers presents an attractive alternative for advancing light-responsive material design and enabling innovative light-controlled technologies. This review summarizes the energy transfer mechanisms and strategies involved in sensitized molecular photoswitchable systems, emphasizing the performance of various combined systems, and potential applications. Furthermore, recent advances and emerging trends in this field are also discussed, offering insights into prospective future directions for the development of light-responsive materials.

Keywords
energy transfer, photosensitizers, photoswitchable molecules

1 | INTRODUCTION

An organic chromophore is a light-absorbing compound that undergoes a transition from its ground state to an excited state under irradiation. As a special type of chromophore, light-responsive materials are substances that can undergo specific structural changes or exhibit unique properties in response to light stimuli.[1] These materials can be designed to have reversible or irreversible light-induced responses, allowing for applications in various fields such as photonics,[2,3] optoelectronics,[4] sensing,[5] and actuation.[6] A typical example of these materials is photoswitchable

compounds, defined as a chemical entity, which can be converted into a photoisomer under light irradiation.[7] When the molecule is in its ground state, it can absorb light energy and transition to a higher energy state, resulting in an excited state. This excitation can then trigger a photoisomerization reaction, causing the parent molecule to transform into its high energy metastable photoisomer. The back-conversion of this photoisomer can also be induced by an appropriate trigger agent (light,[8] heat,[9] pH,[10] or catalyst[11]) allowing for recyclability of the system.[12–14] Therefore, light energy can be used to drive the activity of functional photoswitches for various purposes, such as solar energy storage,[12,15] pH

indicator,[16] and molecular motors.[17,18] In Figure 1, we highlight selected photoswitchable molecule structures in which photosensitizers have been used to drive the reaction. For instance, the [2 + 2] cycloaddition reaction of norbornadiene (NBD),[11,19,20] the dimerization of anthracenes,[21] the ring-closing reaction of diarylethene (DAE),[22] and the *E-to-Z* azobenzene (AZO) isomerization.[8,13]

Unfortunately, the activity or implementation of photosensitive molecules can sometimes be strictly limited by the need of specific wavelengths.[23] An interesting way to undergo a controllable photoconversion while expanding the properties of photoswitchable compounds, at the same time, retaining their intrinsic properties is the use of photosensitizers. Photosensitizers have been extensively studied in various applications, such as photodynamic therapy,[24] dye-sensitized solar cells,[25–29] and photocatalysis reactions.[30] By absorbing light and an energy transfer process, such excited chromophores can promote further reactions for different applications. This is achieved by transferring the energy to neighboring molecules with similar energy levels before returning to its ground state.[31] In general, photosensitizing reactions can be categorized into two main categories.[32] For the first category of reaction, the sensitizers transfer energy to molecular oxygen, which subsequently transfer its energy to surrounding molecules. This occurs as molecular oxygen naturally exists in a triplet state. Such energy transfer process facilitates successive reactions and effectively completes the sensitizing process.[33] For instance, in the advanced photo dynamic therapy, the sensitizing of oxygen has been used for cancerous cells and bacteria elimination.[34–36] The second category of photosensitizing reaction, which is also the focus on this review, involves a sensitizer and a target molecule, where the sensitizer's energy is directly transferred to the target molecules (for instance, a triplet-triplet energy transfer, TET),[37–39] thereby triggering subsequent reactions (Figure 2). In the context of organic materials, photosensitizers are primarily used to extend the

absorption of compounds to longer wavelengths. This is particularly important as soft material devices based on organic molecules can be susceptible to damage or limitations when exposed to ultraviolet (UV) light irradiation, especially in the field of photobiology.[36]

The combination of photoswitchable molecules and photosensitizers presents a compelling approach to tackle the challenge of enabling photoswitching using longer wavelength light. This approach offers the potential to facilitate chemical reactions without necessitating modifications to the molecular structure of the photoswitch molecule. In the following sections, a comprehensive review of various typical switchable compounds in the presence of photosensitizers is presented, showcasing their potential and discussing their photochemical behavior. Herein, Table 1 sums up the photoswitchables and the photosensitizing processes explored in this review. To be mentioned, we will mainly focus on the photosensitizing mechanism instead of detailing all photochemical parameters, such as the photoisomerization quantum yield, as well as triplet energy lifetime etc.
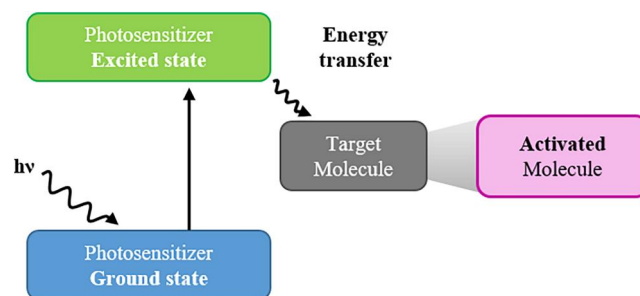

FIGURE 2 Photosensitizing reaction mechanism discussed in this review. The photosensitizer is initially excited from the ground state to the excited state upon absorption of incoming photons. Subsequently, the excited photosensitizer efficiently transfers energy to a substrate (photoswitchable molecule), triggering the activation of the photoisomerization reaction.
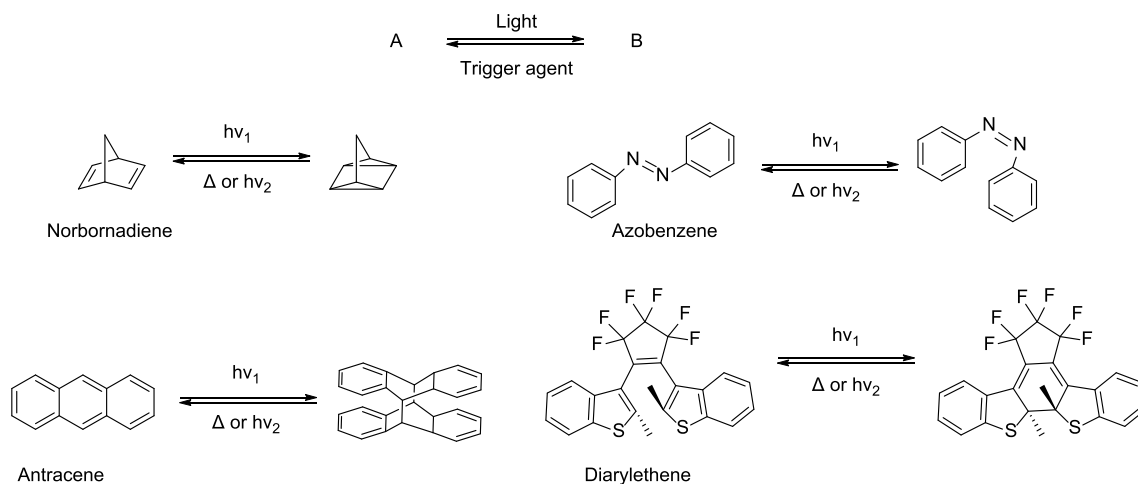

FIGURE 1 Examples of the most common types of molecular photoswitches where sensitizers have been used to drive photochemical conversion (norbornadiene, azobenzene, anthracene, and diarylethene).

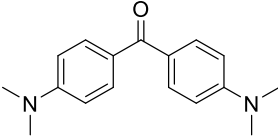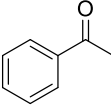**TABLE 1** Summary of the photoswichable molecules and the photosensitizer's combinations herein reviewed.
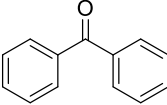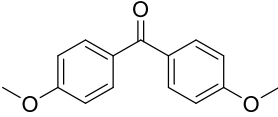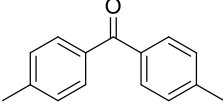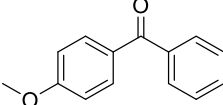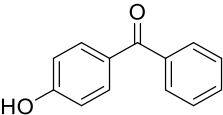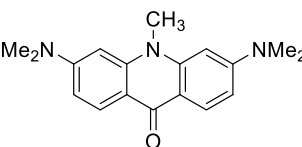
Photoswitchable molecules	Photosensitizing route	Photosensitizer unit	Initial Energy level (eV)	Solvent conditions
$E_T = 3.04$ eV	Triplet energy transfer (TET)		2.69	Solvent free[9] Acetonitrile[40, 41]
			3.19	Solvent free[9] Acetonitrile[40-43] Isopentane[43]
			3.00	Solvent free[9] Acetonitrile[40] Isopentane[43]
			3.05	Acetonitrile[40]
			3.01	Acetonitrile[40]
			3.00	Acetonitrile[40]
			2.99	Acetonitrile[40]
			2.96	Acetonitrile[40]
	Via exciplet		from 1.83 eV to 2.76 eV	Various[44]

And others.

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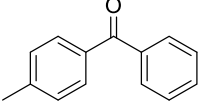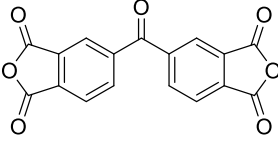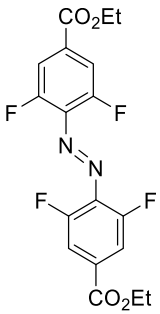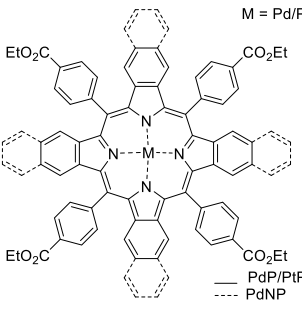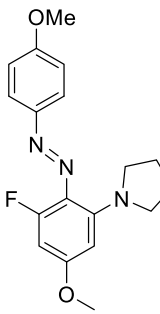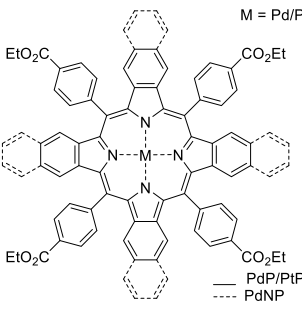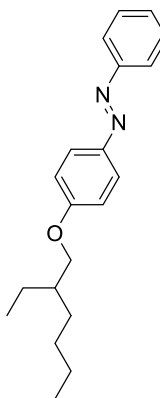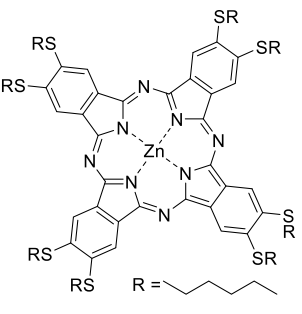
Photoswitchable molecules	Photosensitizing route	Photosensitizer unit	Initial Energy level (eV)	Solvent conditions
	Via metal-to-ligand charge-transfer (MLCT)	Cu	-	-[45]
	Via heavy atom exchanged zeolites	Zeolite	-	-[46]
	Via bond coupled electron transfer (BCET)		2.86 eV	-[47]
trans-Azobenzene derivatives $E_T = 1.49–1.52$ eV	Triplet energy transfer (TET)		$\Delta E_T = -1.3$ (PdP)/ -4.7 (PtP)	Dimethyl sulfoxide[48]
 $E_T = 1.58–1.63$ eV	Triplet energy transfer (TET)		$\Delta E_T = 1.1$ (PdP)/ 0.7 (PtP)	Dimethyl sulfoxide[48]
 $E_T = 1.26$ eV	Triplet energy transfer (TET)		1.12 eV	Bioplastic Film[49]

T A B L E 1 (Continued)

Photoswitchable molecules	Photosensitizing route	Photosensitizer unit	Initial Energy level (eV)	Solvent conditions
	Resonance energy transfer (RET)	Sensitizer is on the molecule – It is the pyrene part	-	Dimethyl sulfoxide[50]
	Photoinduced electron transfer (PET)	Sensitizer is on the molecule – It is the iridium complex	-	Acetonitrile[51]

Diarylethene derivatives

	Triplet energy transfer (TET)		2.63 eV	Toluene[22]
$E_T = 2.49$ eV				
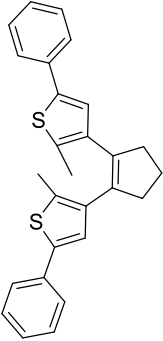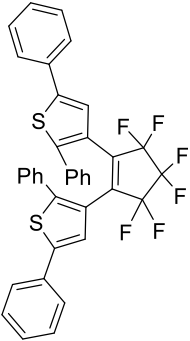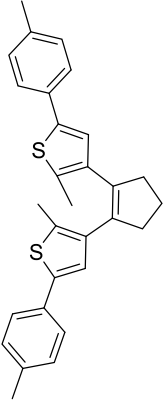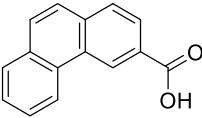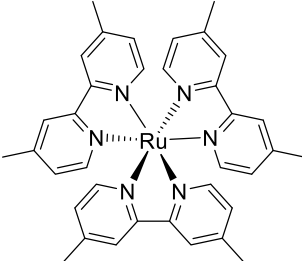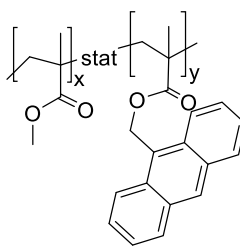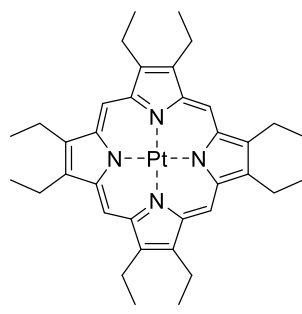
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T A B L E 1 (Continued)

Photoswitchable molecules	Photosensitizing route	Photosensitizer unit	Initial Energy level (eV)	Solvent conditions
	(non)trivial energy transfer	NaYF$_4$: TmYb and NaYF$_4$: ErYb	-	Acetonitrile[52]
	(non)trivial energy transfer	-	-	Tetrahydrofuran[53]
$E_T = 2.5$ eV	Triplet energy transfer (TET)	CdS NCs &	3.0 & 2.6 eV	Toluene[54]
Anthracene derivatives	Triplet energy transfer (TET)		-	Acetonitrile[55]

T A B L E 1   (Continued)

Photoswitchable molecules	Photosensitizing route	Photosensitizer unit	Initial Energy level (eV)	Solvent conditions
	Triplet energy transfer (TET)		-	Acetonitrile[56]

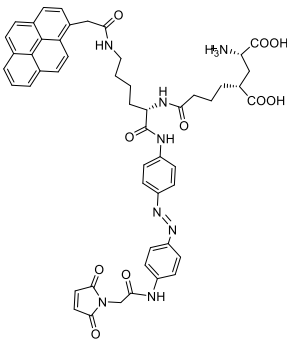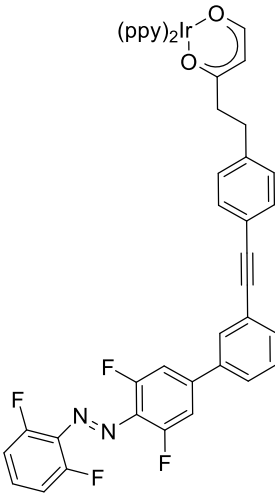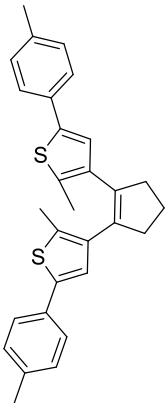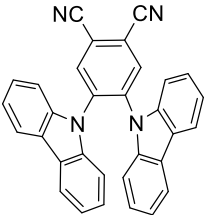Abbreviations: BCET, bond coupled electron transfer; MLCT, metal-to-ligand charge transfer; PET, photoinduced electron transfer; RET, resonance energy transfer; TET, triplet energy transfer.

2 | NORBORNADIENES AND SENSITIZERS

The conversion from NBD to quadricyclane (QC) has been extensively studied since the second half of the 20th century, particularly for applications in solar thermal energy storage. This system is highly sought after due to its remarkable energy storage density (up to 1 MJ kg^{-1}) and the ability to release heat on-demand.[19] A detailed analysis of needed molecular characteristics for energy applications has been reviewed previously.[12] It was found that the main limitation of this system is the absorptivity of the parent unsubstituted NBD, which is below 267 nm (>4.64 eV).[19,20] Additionally, the conversion of NBD to QC is impaired by a low quantum yield of conversion (<5%), meaning that direct conversion is difficult. Hence, considerable efforts have been dedicated to optimizing the system through a molecular design to red-shift the light absorption range and achieve a higher quantum yield. Unfortunately, the optimization process may also have an adverse effect on the energy storage density. For instance, incorporating heavy donor-acceptor chromophore units or linking a photosensitizer to red-shift the absorption profile, as demonstrated in the molecular composites reported by Meng et al., composed of a thermally activated delayed fluorescence core phenoxazine-triphenyltriazine (PXZ-TRZ) anchored with NBD, can negatively impact the energy storage density.[57] Consequently, an ideal NBD/QC couple for energy storage purpose is still under development.

To preserve the highest energy density of unsubstituted NBD and enable the photoisomerization reaction under sunlight, various photosensitizers have been reported. The most common type of organic sensitizers involves TET, a mechanism where the energy from an excited molecule in its triplet state is transferred to another molecule. This results in the promotion of the recipient molecule to an excited triplet state and facilitating subsequent photochemical processes. Considering the direct irradiation conversion from NBD to

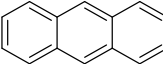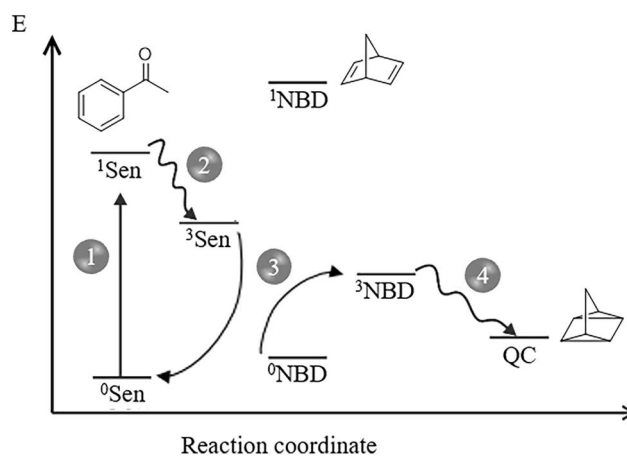**F I G U R E 3**   Jablonski diagram illustrating the whole process (1 = photon absorption leading to an excitation of the photosensitizer [Sen] to its singlet state, 2 = ISC to its triplet state, 3 = TET to the NBD triplet state, 4 = conversion into QC).[9] ISC, intersystem crossing; NBD, norbornadiene; QC, quadricyclane; TET, triplet energy transfer.

QC, it is important to highlight that this process hinges on the population of the high-energy singlet state of NBD. In this context, it is worth noting that the energy of the triplet-state NBD (^{3}NBD) is relatively low, measuring at only 3.04 eV.[40,58] This inherent characteristic of the triplet state NBD proves advantageous in facilitating the conversion process. In such case, a photosensitizer with a similar triplet energy to the switchable compound is required to assist the photoisomerization reaction via an energy transfer process (exothermic when ^{3}Sen > ^{3}NBD, and endothermic when ^{3}Sen < ^{3}NBD). As one example, acetophenone has a triplet state energy of 3.19 eV,[59] higher than that of ^{3}NBD.[9] The sensitization mechanism starts with the photoexcitation of the sensitizer to a vibrational level of the excited singlet state. Then, a non-radiative intersystem crossing (ISC) from the singlet to the triplet state occurs. An energy transfer then populates the triplet state of the NBD and converts it into the QC form (Equation 1, Figure 3).

$$h\nu$$
$$^0Sen \rightsquigarrow {}^1Sen$$
$$^1Sen \rightarrow {}^3Sen$$
$$^3Sen + {}^0NBD \rightarrow {}^0Sen + {}^3NBD \qquad (1)$$
$$^3NBD \rightarrow QC$$
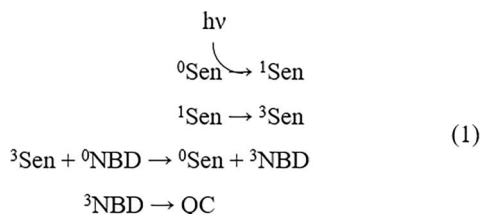
Thus far, several triplet energy photosensitizers have been studied. Among them, 4,4′-bis(*N*,*N*′-dimethylamino) benzophenone (Michler's ketone), acetophenone, and benzophenone were found to be efficient.[9,59] Table 1 includes a non-exhaustive list of benzophenone derivatives-based photosensitizers that have been used for NBD conversion. It was observed that both acetophenone and benzophenone exhibit a first-order reaction in the NBD conversion, where the reaction rate is controlled by the rate of energy transfer from the sensitizer to the NBD.[9] Acetophenone was used to demonstrate a remarkable capability to achieve 100% conversion of NBD into QC, primarily attributed to the narrow energy gap between its lowest excited singlet and triplet states.[9,60] This favorable energy alignment allows for efficient energy transfer and facilitates the conversion process. On the other hand, benzophenone, although comparable, can only achieve a conversion rate of 85%. The slight difference in conversion efficiency can be attributed to differences in the electronic properties and energy levels of benzophenone, affecting the energy transfer dynamics and overall photochemical behavior. This is likely due to the lower energy level of the latter's triplets, which results in an energy transfer via complex formation of the benzophenone and QC, thus inducing NBD regeneration.[60] Using Michler's ketone sensitizer, the rate of conversion is mainly controlled by the ISC to the triplet state-activated intermediate. Although its activity depends on the solvent polarity, by increasing the temperature, Michlers's ketone leads to a higher NBD/QC conversion rate.[9] However, it is important to note that the NBD/QC-photosensitizer system is primarily tailored for solar thermal energy storage applications. Unfortunately, many of these high triplet-state photosensitizers do not possess absorption capabilities at the most prevalent solar irradiation wavelengths. For instance, Michler's ketone absorbs light below 400 nm. This mismatch in absorption spectra ultimately results in low potential solar energy conversion efficiencies.[9,44] Another general aspect that reduces the conversion rate is the sensitivity of the used sensitizer to oxygen, which can lead to the formation of by-products. To overcome side reactions, Taoda et al. reported, for instance, the use of phenolic substances (as radical scavengers) while employing acetophenone. With such method, after irradiation, no polymer by-product was found.[60]

Instead of using a single TET sensitizer, Philippopoulos et al. investigated a mixture of three of these photosensitizers, aiming to achieve better performances than each one of them individually. However, its effectiveness was reduced possibly due to inter-sensitizer energy transfers.[9] As a step forward, using benzophenone in bichromophoric compounds has also been reported.[61] A bridge made of a crown ether, complexing a sodium ion, connects the sensitizer (donor) and the NBD (acceptor). Intramolecular TET occurs via a "through-space" mechanism and leads to the conversion of NBD into QC. More recently, Han et al. reported a similar remote TET process.[62] Nevertheless, the study involves a photosensitization via non-covalent bonds. The transfer is mediated by an amidinium-carboxylate salt bridge between benzophenone and NBD where a "through-bond" electron-exchange mechanism is assumed (Figure 4).

Another type of sensitizers that has been explored involves organic photosensitizers likely forming an exciplex.[44] An exciplex is an intermediate resulting from the electron donor–acceptor complexation of the excited sensitizer with the NBD, where the excitation energy is localized on the NBD molecule. For instance, Tinnemans et al. have reported a series of various acridinones presenting triplet-state energies from 1.83 to 2.76 eV (over an absorption range from 365 to 525 nm) attributed to the formation of exciplexes. Regarding the energy storage aspect, these acridinone-type sensitizers are more efficient due to their sensitivity to the visible region of the solar spectrum. However, the exciplex formation is solvent-dependent and may be limited to the conversion of the NBD into QC (Figure 5).

Transition metals capable of absorbing in the UV-Vis range were previously found to be very efficient for the back conversion of QC derivatives.[11] However, it can also be used as photosensitizers for NBD conversion. In such case, ligands around the metal core can coordinate with NBD, thus facilitating the conversion process. Kutal et al.[58] extensively investigated a series of complexes centered with ruthenium, iridium, or rhodium. Unfortunately, these complexes demonstrated low conversion efficiencies, likely can be attributed to the high triplet state energy of NBD. This observation emphasizes the necessity for tailored design of transition metal sensitizers to effectively catalyze the conversion reaction. Furthermore, the role of ligands is integral in shaping the outcome of the conversion. Notably, transition metals displaying two or more ligands can facilitate the coordination of multiple NBD molecules, culminating in the formation of dimers. These dimers effectively hinder the conversion process to QC. Additionally, the study revealed that certain metal sensitizers can engage in oxidative reactions in the presence of QC, instigating its back-conversion to NBD. Previously, it has been concluded that an optimal candidate for facilitating the NBD/QC conversion should ideally be a transition metal with oxidation states not exceeding +2. This metal should also exhibit a limited number of bonding sites, preferably less than two, with its d electrons actively engaging in π-back-bonding with NBD.[58] Later, it was found that copper (I) can meet the above-mentioned requirements, either
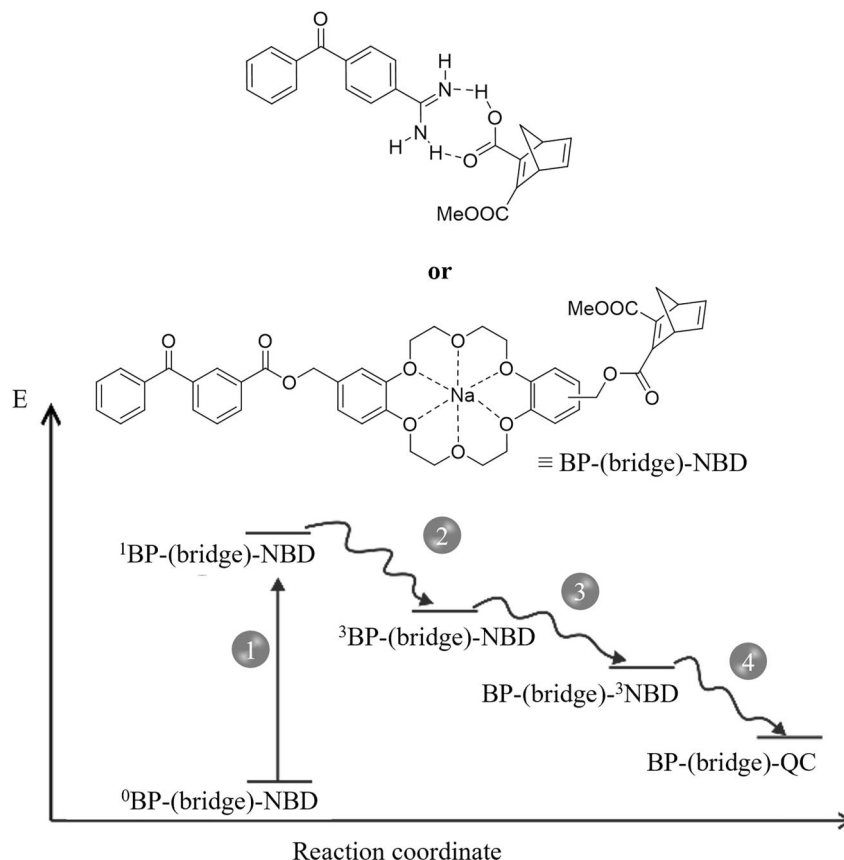
FIGURE 4 Jablonski diagram illustrating the whole process of the NBD-to-QC conversion's photosensitization via intramolecular triplet energy "through-space" transfers (1 = photon absorption leading to an excitation of the complex to its singlet state, 2 = ISC to its triplet state, 3 = intramolecular triplet energy "through-space" transfers, 4 = conversion to QC).[61,62] ISC, intersystem crossing; NBD, norbornadiene; QC, quadricyclane.
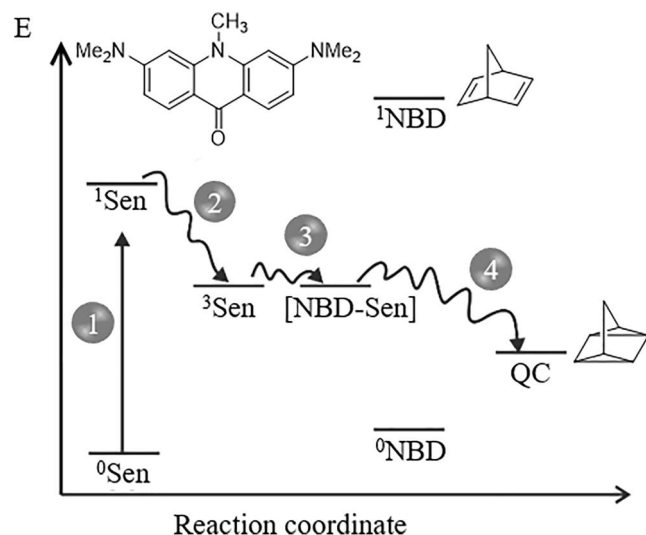
FIGURE 5 Jablonski diagram illustrating the whole process of the NBD-to-QC conversion's photosensitization via exciplet intermediate (1 = photon absorption leading to an excitation of the photosensitizer [Sen] to its singlet state, 2 = energy transfer to the exciplet, 3 = localization of the energy on the NBD moiety, 4 = conversion to QC).[44] NBD, norbornadiene; QC, quadricyclane.

a copper (I)-NBD complex is formed at the ground state, where the QC is generated and the sensitizer released upon the photon absorption (Equation 2), or the metal is first photo-excited and then interacts with the ground-stated NBD (Equation 3).[45] The preferred mechanism depends on the structural and electronic features of the complex. Additionally, the incorporation of π-delocalized ligands facilitates the creation of metal-to-ligand charge-transfer (MLCT) bands, enabling the utilization of visible light within the solar spectrum for NBD conversion. These MLCT bands are particularly pronounced in weakly polar solvents, and an elevation in temperature can also contribute to higher photoisomerization quantum yields in these systems.

$$CuL + {}^3NBD \rightleftarrows CuL\text{-}NBD \xrightarrow{h\nu} CuL + QC \qquad (2)$$

$$CuL \xrightarrow{h\nu} CuL^* \xrightarrow{NBD} [CuL^*,NBD] \rightarrow CuL + QC \qquad (3)$$
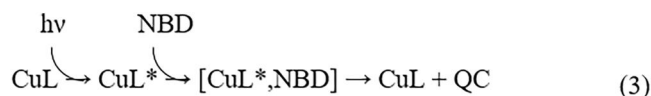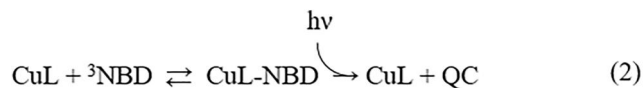
In addition to the above-mentioned common sensitizing methods, an unusual triplet photosensitization based on

heavy atom exchanged zeolites (Y) has been studied by Ghandi et al. It was observed that a conversion of up to 90% can be determined in the presence of thallium zeolite.[46] Cuppoletti et al. also reported another pathway involving an efficient bond coupled electron transfer to ^3QC, which then relaxes to QC via ISC, without an intermediate generation of ^3NBD.[47] The 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) is used as a photosensitizer to complete this conversion. A triplet $BTDA^{-\bullet}/NBD^{+\bullet}$ ion pair is formed by an electron transfer (Equation 4).

$$^3(BTDA^{-\bullet}/NBD^{+\bullet}) \xrightarrow{BCET} BTDA + {}^3QC \rightarrow BTDA + QC \qquad (4)$$
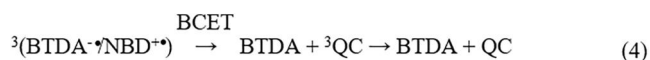
Furthermore, it is important to note that the presence of a photosensitizer does not affect the thermal or catalytic back-conversion process. For instance, Luchs et al. demonstrated a highly efficient one-pot system using acetophenone as a photosensitizer for the conversion from NBD to QC and $[Fe_3O_4-CoSalphen]$ as a catalyst in the back-conversion.[63] Similarly, Philippopoulos reported back-conversion rate constants at 180°C using Michler's ketone in the medium.[9] This eliminates the need for additional purification steps after the photoisomerization, and at the same time, provides a more suitable NBD/QC-interconversion system under specific wavelengths.

3 | AZOBENZENE AND SENSITIZERS

Azobenzene (AZO) derivatives are versatile systems that have seen lots of success within the expanding field of photoswitchable molecules. Discovered in the m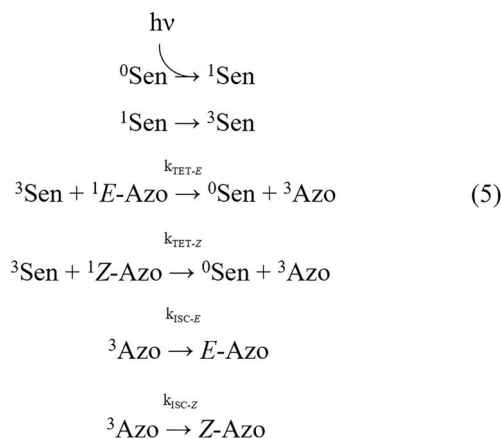id-1800s, E-AZOs have been prepared from many different methods throughout the years with the first report of E-to-Z photoisomerization in 1937 by Hartley.[64] The E isomer of AZOs is more stable than the Z isomer; however, it was reported that when exposed to UV light, AZO undergoes a E-to-Z photoisomerization through AZO π-π* excitation. Proceeding this discovery, extensive research has been carried out exploring AZOs as photoswitches, making them one of the most reported classes of photoswitches in literature.[8,64] Current research focuses on improving the photochemical properties for applications in the medical and the energy storage fields. Herein, the focus is on how sensitizers can be utilized to enhance the photoswitching properties of AZOs, whether they are incorporated through molecular modification or via solution mixture.

In 2021, Isokuortti et al. reported rapid Z-to-E photoisomerization of AZOs through the introduction of porphyrin photosensitizers.[48] The improved photoconversion efficiency was a result of TET similar to the cases of NBD, allowing for excitation up to 770 nm. Isokuortti et al. describe the mechanism of triplet-sensitized isomerization using the following Equation (5):

$$
\begin{aligned}
^0Sen &\xrightarrow{h\nu} {}^1Sen \\
^1Sen &\rightarrow {}^3Sen \\
^3Sen + {}^1E\text{-}Azo &\xrightarrow{k_{TET\text{-}E}} {}^0Sen + {}^3Azo \\
^3Sen + {}^1Z\text{-}Azo &\xrightarrow{k_{TET\text{-}Z}} {}^0Sen + {}^3Azo \\
^3Azo &\xrightarrow{k_{ISC\text{-}E}} E\text{-}Azo \\
^3Azo &\xrightarrow{k_{ISC\text{-}Z}} Z\text{-}Azo
\end{aligned}
\qquad (5)
$$

The mechanism involving TET from the photosensitizer is believed to be the primary pathway for most photosensitizers (Table 1). In this process, TET leads to the formation of a mixture of excited triplet states for both isomers in azobenzenes. Subsequently, an ultrafast ISC occurs between the triplet state and the ground state of the AZOs, resulting in the predominance of the Z-isomer.

From an energetic point of view, TET from the sensitizer to the target molecule is normally exothermic as seen in most of the cases in NBD-related conversion. However, such process can also be endothermic. In 2022, Moth-Poulsen and co-workers reported a method of low-energy excitation-based photoswitching process by developing a liquid-polymer composite bioplastic film with far-red/red sensitized AZO.[49] This was achieved via two strategies: (1) dispersing the liquid azobenzene inside a bioplastic matrix framework that enables structural flexibility and (2) the addition of a triplet sensitizer that increases the optical action spectrum of the photoswitch. This is possible as the dopants used, zinc phthalocyanine (ZnPc) and Pd(II) meso-tetraphenyl tetrabenzoporphine, allowed for the direct triplet sensitizing process via an endothermic TET between the sensitizer and the AZO, respectively (Figure 6, Table 1).

In AZO-based systems, photoswitching typically occurs through a one-photon excitation at shorter wavelengths, which can limit their practical applications. However, the excitation occurs via resonance energy transfer (RET) instead of a TET mechanism. RET occurs when the energy from an excited donor molecule is transferred to an acceptor molecule without the emission of light due to their electronic energy levels being in resonance or overlap. By leveraging this effect, the switching performance of AZOs can be finely controlled and optimized. For example, in the photo-pharmaclogical field, absorption at long wavelength light is preferable to increase penetration into living tissue. To tackle this challenge, Marta Gascon-Moya et al. reported an efficient transfer of electronic excitation via a two-photon absorption under NIR irradiation to the AZO chromophore by the introduction of a pyrene sensitizing unit (Figure 7).[50]
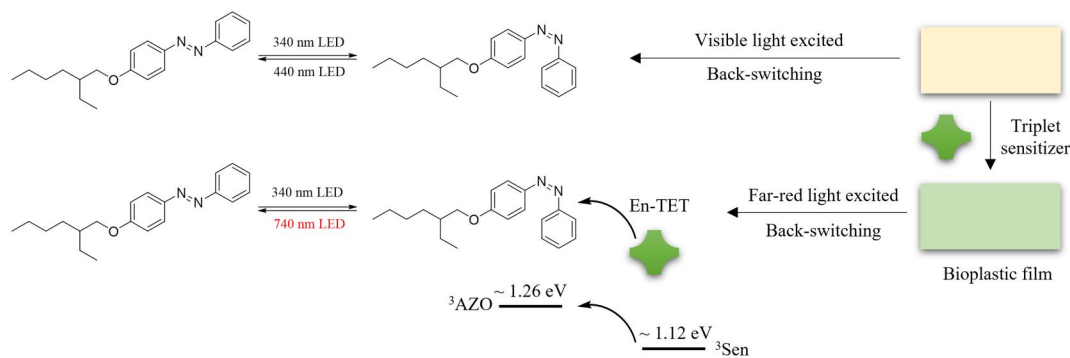
FIGURE 6 Illustration of the *Z-to-E* photoswitching of the AZO in the absence and presence of a far-red sensitizer in the liquid-polymer composite bioplastic film. En-TET is referred as endothermic TET. Reproduced from Ref. [49] with permission from the Royal Society of Chemistry. TET, triplet energy transfer.
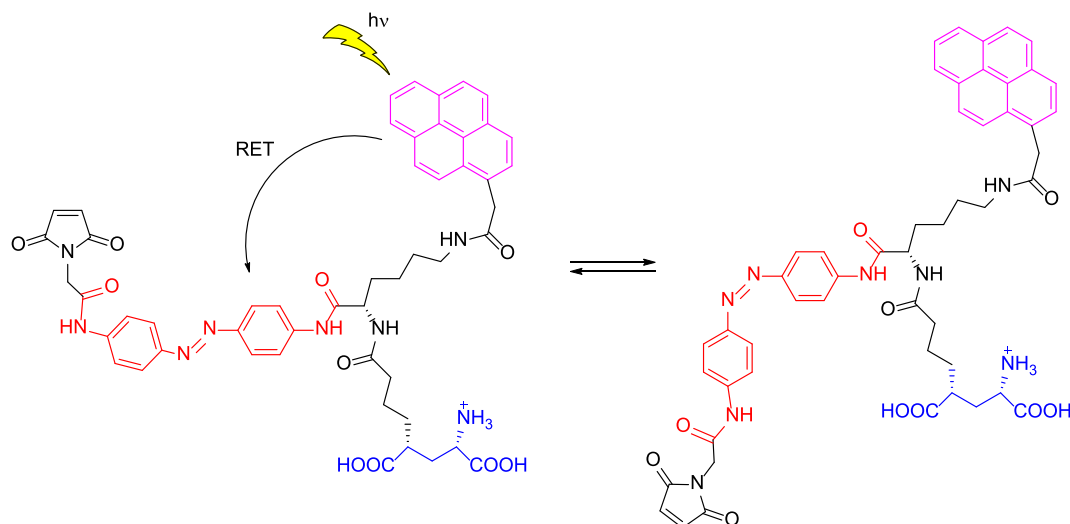

FIGURE 7 Illustration of the *E-to-Z* photoswitching of the AZO including the pyrene photosensitizer moiety. Reproduced from Ref. [50], Copyright © 2015, American Chemical Society.

They reported that by using this pyrene antenna, they could improve the photoconversion efficiency of their chosen AZO up to 60% while also improving the thermal stability of the *Z* isomer.

Photoinduced electron transfer (PET) is another process in which the absorption of light by a donor molecule (electron donor) leads to the transfer of an electron to an acceptor molecule (electron acceptor). This electron transfer is initiated by photon absorption and results in the formation of charged species, such as radical cations and radical anions. As a result, using metal-based complexes as photosensitizers to aid the PET process can be utilized as another effective strategy to achieve rapid *E-to-Z* isomerization in photoswitchable molecules. An example of this approach was demonstrated by Moreno et al., who synthesized an AZO compound coupled with an iridium-based complex. This system exhibited efficient photoswitching through selective irradiation of the MLCT band within the sensitizers (Figure 8).[51] However, the covalently linked sensitizing Ir(III) complex could only promote the initial intramolecular photoenergy transfer step.

4 | DIARYLETHENES AND SENSITIZERS

Diarylethenes (DAEs)[65] have found applications in various multiresponsive switchable devices,[66] bioimaging,[67] and photodynamic therapy.[68] Typically, UV light is used for the photocyclization (ring-closure) of DAEs. However, this approach has its drawbacks, including photo-oxidation and photodegradation. Moreover, the red-shifted absorption of DAEs leads to limited tissue depth penetration, which hinders their true potential in photopharmacology.[68]

To address these challenges, researchers have adopted two strategies. The first approach involves direct excitation by incorporating extended π-conjugation into the molecular structure.[69] The second approach employs sensitizers for indirect excitation. In this review, our primary focus will be on the latter strategy. Consequently, there is a considerable demand for molecular photoswitches that can be activated by visible light. For the indirect excitation, the sensitizer is responsible for energy transfer to the switch. The energy transfer pathway can occur via non-radiative Förster-type
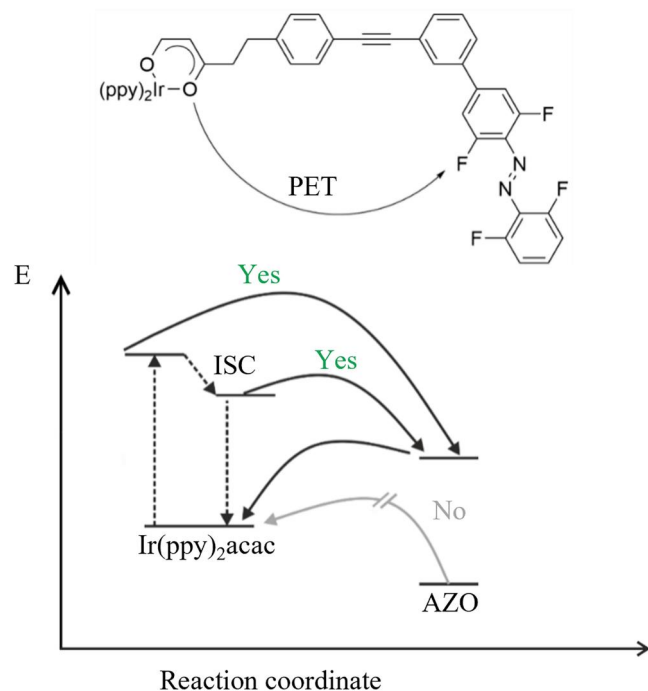
FIGURE 8 Energy levels of the dyad components in MeCN and the electron transfer steps.[51] Figure reproduced, © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

resonance energy transfer (FRET), in which the excited donor molecule transfers its energy to an acceptor molecule through dipole–dipole interactions at a molecular distance of approximately 10 nm, or through Dexter-type energy transfer, where molecules in direct contact (molecular distance <15 Å) enable electron exchange between their respective energy levels.[7] As one example, Zhang et al. used a narrow singlet–triplet energy gap sensitizer to demonstrate visible light photochromism in DAE.[22] A versatile approach to achieve triplet-sensitized/visible light photochromism using three narrow ΔE_{ST} molecules, namely 2CzPN, 4CzIPN, and PXZ-TRZ, as triplet sensitizers was demonstrated in Figure 9a. DAE 1o/2CzPN blend was irradiated with 405 nm light; around 530 nm, a rising absorption band was observed. Complete cycloreversion was observed as irradiated with visible light (550 nm, 3 min) displaying excellent photochromic performance as shown in Figure 9b.

Instead of using organic molecules, nanoparticles can also act as sensitizers. In 2009, it was demonstrated by the Branda group that NIR light from the upconverting nanoparticles (UCNPs) can be used to photoisomerize DAE.[52] The study elucidates the methodology of "remote ring opening and closure control" through the utilization of upconverting doped nanocrystals (NCs). The ring closure was induced by $NaYF_4$:TmYb (emitting UV light) photons, whereas cycloreversion was achieved by $NaYF_4$:ErYb (emitting green light, Figure 9c).

Later in 2010,[53] the same group demonstrated that by using low power intensity, one type of NIR light, and lanthanide-doped UCNPs, two-way switching of the photo switch

can be observed. The lanthanides Er^{3+} and Tm^{3+} were doped into separate layers of UCNPs, producing methodical upconversion processes and resulting in the back reaction (Figure 10a). A bidirectional photoswitching process was achieved using a single 980 nm excitation beam. A colorless solution can undergo a reversible transformation to a blue solution and vice versa when irradiated with 980 nm light at different power settings. When exposed to high power, the ring closure process generates blue and UV light, leading to the formation of the blue solution. On the other hand, low power irradiation produces green light, causing ring opening and restoring the original color, as depicted in Figure 10b.

Additionally, Hou et al. have reported the utilization of a hybrid photosensitizer made up of semiconducting NCs and a mediator.[54] A remarkable achievement was demonstrated with the reversible all-visible light photoisomerization of DAE derivatives both in the liquid and solid states. In this work, a cocktail strategy was adopted, where DAE was photoisomerized using the visible light irradiation populating excited state of CdS nanocrystals transferring the excitation energy to phenanthrene-3-carboxylic acid (3-PCA). This is referred to as triplet energy transfer (TET_1), followed by the second TET_2 from 3-PCA to open-DAE; thus, the photocyclization reaction was sensitized all through a triplet-state pathway. Remarkably, the presence of oxygen did not interfere with the photoisomerization process, making it a highly promising and versatile technique for various applications (Figure 11, Table 1).

It is noteworthy to mention that in addition to the first type of photosensitization involving energy transfer between a sensitizer and a triplet-state oxygen molecule, the combination of photosensitizers and photoswitches holds significance in photodynamic therapy for regulating the generation of singlet oxygen ($^1O_2$).[68] Typically, an energy transfer under irradiation occurs from the photosensitizer to triplet oxygen ($^3O_2$) can induce $^1O_2$ generation. As described above, photoswitchable compounds as DAE can exist either as a parent or as an isomer. By taking advantage of the competition between the triplet energy states of the oxygen and one of the switching forms, during the energy transfer from the photosensitizer, $^1O_2$ generation can be shut down. In this way, adjusting the DAE switches with light enables the regulation of $^1O_2$ generation.

5 | ANTHRACENE AND SENSITIZERS

First reported in 1909, anthracene photodimerization is one of the oldest known photochemical reactions.[70] When exposed to UV light, it undergoes [4 + 4] cycloaddition dimerization and this reaction is reversible via photolysis at lower wavelength, thermolysis, or a catalyst.[71] Although both anthracene and anthracene derivatives absorb in the UV region, photodimerization can also be achieved using low-energy photons by utilizing different kinds of photosensitizers like MLCT sensitizer ($[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine)),[55,72] platinum(II) octaethylporphyrin (PtOEP),[56]
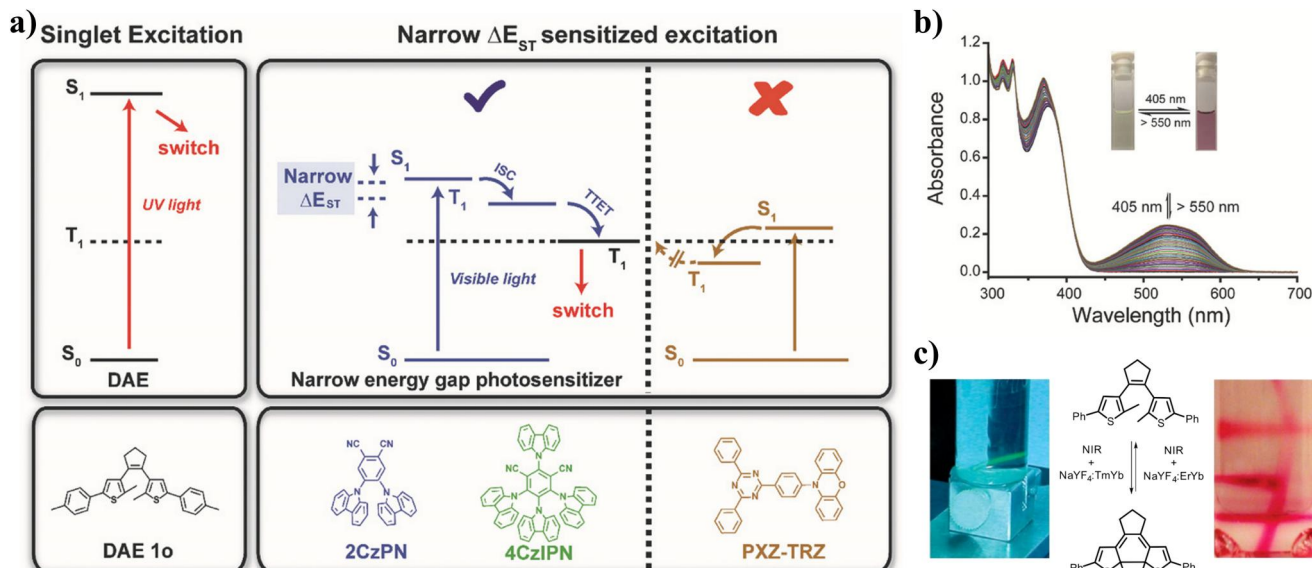
FIGURE 9 (a) Singlet excited photochromism (left top); the visible light photochromism mechanism with the sensitization of narrow ΔE_{ST} molecules 2CzPN and 4CzIPN (right top). Structure of the DAE 1o (left bottom) investigated narrow ΔE_{ST} molecules (right bottom). (b) Photochromic performance of DAE 1o/2CzPN couple. Insets: photographs of DAE 1o/2CzPN in deaerated toluene before and after irradiation. Reproduced from Ref. [22] with permission from John Wiley and Sons. (c) The ring closure (left picture) of DAE was induced by NaYF4:TmYb, whereas cycloreversion (right picture) was achieved by NaYF4:ErYb. Reprinted with permission from Ref [52]. © 2009 American Chemical Society. DAE, diarylethene.
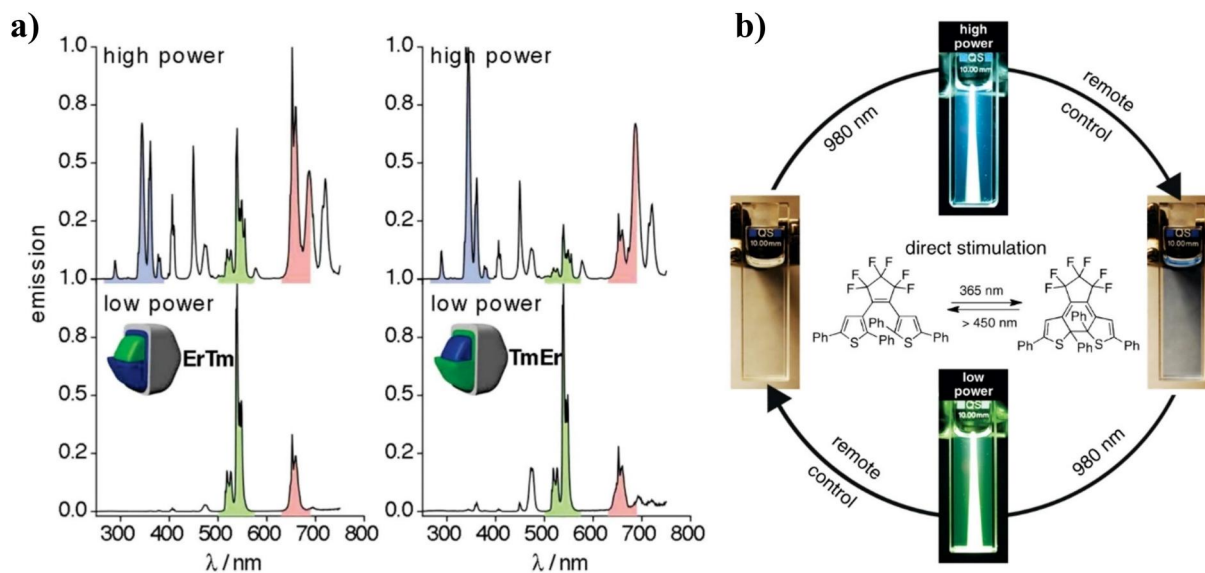

FIGURE 10 (a) ErTm and TmEr UCNPs at high and low power; (b) Bidirectional photoswitching of DAE in a THF solution dispersed with TmEr core-shell-shell NPs by manipulating the power intensity of NIR light. Reprinted with permission from Ref [53]. © 2010 American Chemical Society. DAE, diarylethene. THF, tetrahydrofuran; UCNPs, upconverting nanoparticles.

platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP),[73] and palladium (II) octaethylporphyrin (PdOEP).[74]

Similar to other TET sensitizer-assisted photoswitching reactions, the [4 + 4] cycloaddition of the two anthracene molecules can take place in three main steps. This was initially demonstrated by Islangulov et al., showing the Ru (bpy)₃-sensitized dimerization of anthracene and the advantageous utilization of diphenylanthracene as emitters of triplet-triplet annihilation upconversion process (TTA-UC).[55,72] The first step is selective excitation of the sensitizer using light at visible wavelength followed by a non-irradiative ISC. Then, this energy will be transferred to the anthracene molecule via TET forming excited triplet anthracenes (Equation 6).

$$^0Sen \xrightarrow{h\nu} {}^1Sen$$
$$^1Sen \rightarrow {}^3Sen$$
$$^3Sen + {}^0An \rightarrow {}^0Sen + {}^3An$$

$$(6)$$
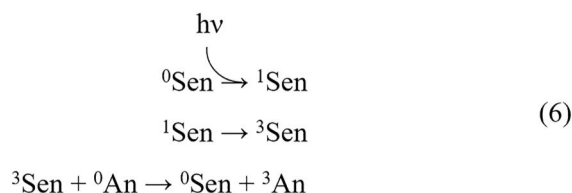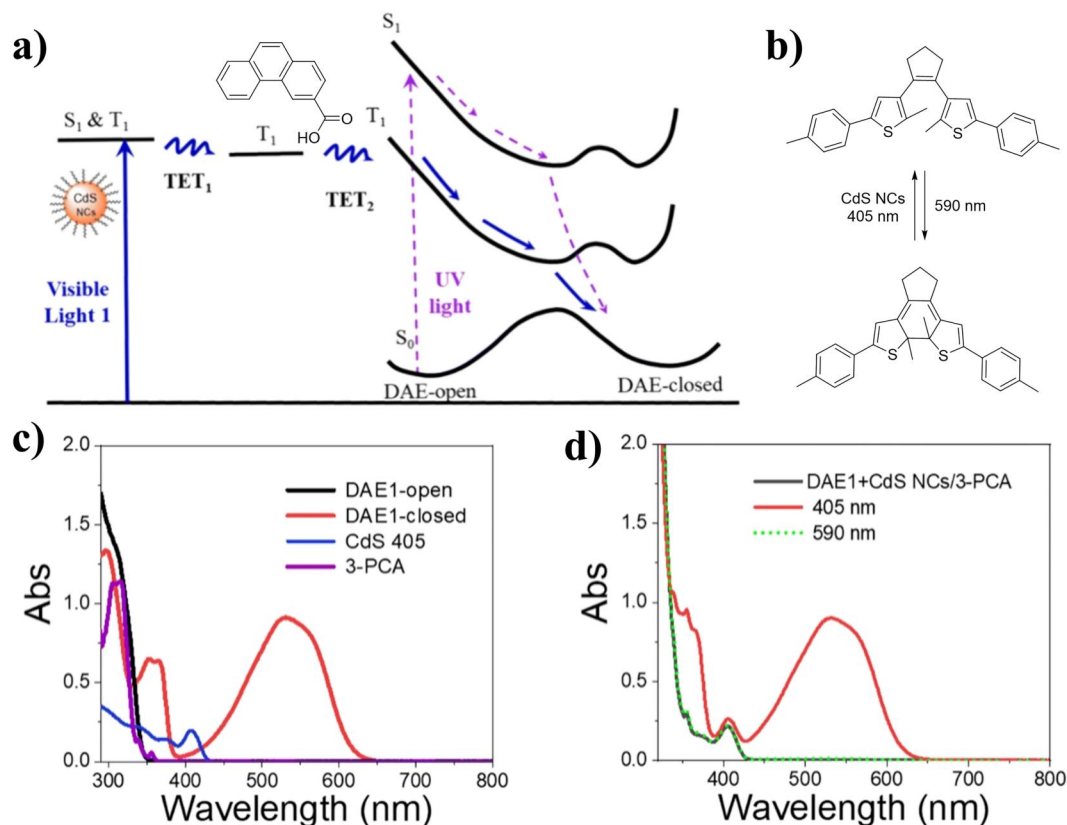
FIGURE 11 (a) DAE-open to DAE-closed photoisomerization mechanism under visible light irradiation via two triplet energy transfer steps [TET$_1$ and TET$_2$] indicated in blue lines. (b) Different absorption of CdS NCs, DAEs with varied absorption bands are used to achieve irradiation at specific wavelengths. (c) UV-Vis absorption profile: DAE1-open (50 μM, black), DAE1-closed (50 μM, red) irradiated using 302 nm UV light, CdS 405 (0.5 μM, blue) and 3-PCA (100 μM, purple) in toluene. (d) UV-Vis absorption spectra of a mixed solution of DAE1-open (50 μM), CdS 405 (0.5 μM), and 3-PCA (100 μM) in deaerated toluene, before (black) and after (120 s, red) light irradiated at 405 nm, followed by 590 nm light irradiation (90 s, green dot). Reproduced from Ref. [54] with permission from the Royal Society of Chemistry. 3-PCA, phenanthrene-3-carboxylic acid; Cds NCs, CdS nanocrystals; DAE, diarylethene; UV, ultraviolet.

FIGURE 12 Demonstration of the photodimerization of pendant anthracene group on a methacrylic polymer.

FIGURE 13 Jablonski diagram illustrating sensitized TTA-based upconversion occurring between PdOEP and anthracene. A, acceptor (anthracene); GS, ground state; PdOEP, palladium (II) octaethylporphyrin; S, sensitizer (PdOEP); TTA, triplet-triplet annihilation. Reproduced from Ref. [74].
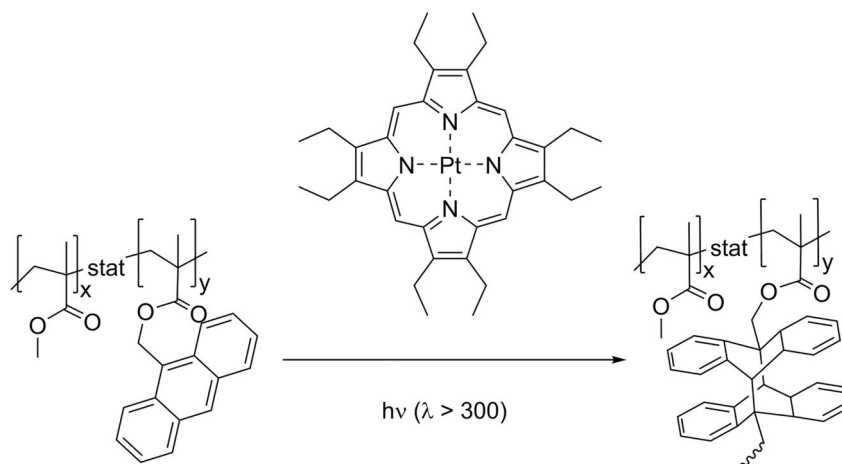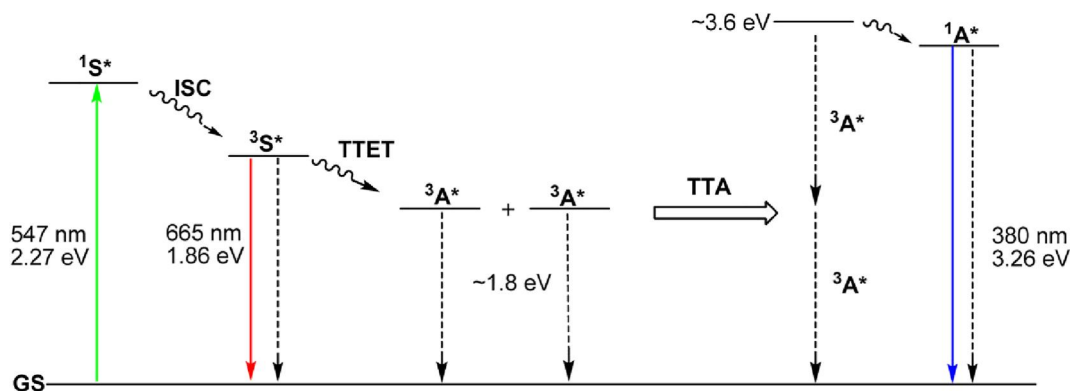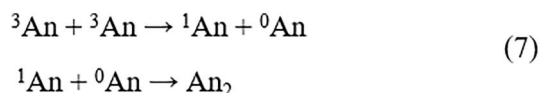
The photodimerization of anthracene occurs when an excited singlet anthracene interacts with an anthracene in the ground state (Equation 7).

$$^3An + {}^3An \rightarrow {}^1An + {}^0An$$
$$^1An + {}^0An \rightarrow An_2$$

$$(7)$$

In 2018, Chidanguro et al.[56] have reported the use of photosensitized dimerization of pendant anthracene chains for the formation of single-chain nanoparticles (Figure 12). Using a PtOEP sensitizer not only made it possible to synthesize nanoparticles without the need to use UV light, which is useful in situations where UV light is undesirable (e.g., photodynamic therapy), but also increased the rate of dimerization in the polymer solution.

Interestingly, two excited triplet anthracenes can then combine to give an excited singlet anthracene resulting in the TTA-UC. Such energy transfer process is also shown in the energy diagram below for the case of PdOEP sensitizer and anthracene (Figure 13).[74]

6 | CONCLUSION

The investigation and comprehension of sensitizers and their interactions with photoswitchable molecules offer exciting prospects for the advancement of innovative technologies and materials. The unique ability of sensitizers to absorb light energy and efficiently transfer it to neighboring molecules holds great promise for a wide range of applications in the field of photoswitching. These applications span diverse fields, including photodynamic therapy, molecular devices, and emerging areas like energy storage. Ongoing research in this domain will contribute to the discovery of novel sensitizers, advanced photoswitches, and integrated systems, resulting in improved performance and expanded applications across various disciplines. Moreover, the integration of

sensitizers with photoswitchable materials presents a remarkable opportunity to develop molecular-scale devices with unprecedented functionalities and responsiveness. The future holds immense potential for the utilization of sensitizers in the design of next-generation light-responsive materials and technologies.

AUTHOR CONTRIBUTIONS
Zhihang Wang: Writing – original draft (lead); writing – review and editing (lead). **Lorette Fernandez**: Writing – original draft (supporting); writing – review and editing (supporting). **Adil S. Aslam**: Writing – original draft (supporting); writing – review and editing (supporting). **Monika Shamsabadi**: Writing – original draft (supporting); writing – review and editing (supporting). **Lidiya M. Muhammad**: Writing – original draft (supporting); writing – review and editing (supporting). **Kasper Moth-Poulsen**: Writing – original draft (lead); writing – review and editing (supporting).

CONFLICT OF INTEREST STATEMENT
The authors declare no conflicts of interest.

ORCID
Zhihang Wang https://orcid.org/0000-0002-9961-3346
Lorette Fernandez https://orcid.org/0000-0002-6776-7359
Adil S. Aslam https://orcid.org/0000-0003-2498-3526
Monika Shamsabadi https://orcid.org/0009-0005-5530-6263
Lidiya M. Muhammad https://orcid.org/0000-0002-4706-3354
*Kasper Moth-Poulsen* https://orcid.org/0000-0003-4018-4927

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AUTHOR BIOGRAPHIES
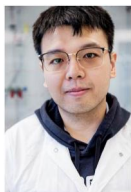
Zhihang Wang obtained his BSc (Physics) from Claude Bernard University Lyon 1, MSc (Optical Science) from the University of Paris-Saclay in France, and PhD (Materials Science) from Chalmers University of Technology in Sweden under the supervision of Prof. Kasper Moth-Poulsen. At present, he is working as a postdoctoral research associate at the University of Cambridge in the UK under the guidance of Prof. Rachel C. Evans. His ongoing research revolves around the development of spectral converters for solar energy harvesting applications.

Lorette Fernandez is working as a PhD student in Kasper Moth-Poulsen's group at the Institute of Materials Science of Barcelona (ICMAB-CSIC). She completed French training as a chemical technician at the University Institute of Technology of Montpellier-Sète (2017). She was then trained as a chemical engineer in France for 3 years at the National Superior Chemistry School of Mulhouse (ENSCMu) with an exchange at Sigma Clermont and she received her Master's Degree at the University of Clermont Auvergne at the same time (2020). Her current project focuses on the characterization of molecular solar thermal energy storage systems and their integration into devices.

Adil S. Aslam is a postdoctoral researcher working under the guidance of Kasper Moth-Poulsen at Chalmers University (Sweden). His research focuses on designing synthetic methodology (norbornadiene systems) for application in MOST. He obtained his BS from Forman Christian College (Lahore, 2009) and MS from COMSATS University (Abbottabad, 2011). In 2013, he received a Korean Government Scholarship award to undertake his PhD under the supervision of Prof. Dong Gyu-Cho at Inha University (South Korea). He obtained his PhD (2019) in Organic Chemistry.

Monika Shamsabadi was born in London, UK. She received her undergraduate education at University College London (UCL) in 2020 and was a Dean's List commendee. She worked within the research group of Professor Vijay Chudasama to develop a novel cysteine protecting group for her Master's Thesis. In 2021, Monika started her PhD studies in Kasper Moth-Poulsen's group at Chalmers University of Technology where her research interest is based on synthesis and characterization of organic compounds for molecular solar thermal energy storage.
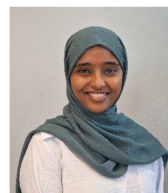
Lidiya M. Muhammad obtained both her BSc in applied chemistry (2018) and MSc in organic chemistry (2020) from Addis Ababa University (Ethiopia). During her master's degree program, she worked under the supervision of Professor Wendimagegn Mammo in the synesthetic organic chemistry laboratory where she focused on the synthesis of conjugated polymers for photovoltaic applications. She is currently doing her PhD in Kasper Moth-Poulsen's group at Chalmers University of Technology (Gothenburg, Sweden). Her research project is centered on the design, synthesis, and characterization of organic compounds for solar thermal energy storage materials.

Kasper Moth-Poulsen is an ICREA research professor at the Polytechnic University of Catalunya (UPC) and at the Institute of Materials Science of Barcelona, Spain (ICMAB-CSIC). He is also affiliated with Chalmers University of Technology in Gothenburg, Sweden. His research interest focuses on molecule synthesis, energy storage, photon up-conversion, and molecular materials. He received his MSc (2003) and PhD (2007) degrees in chemistry from the University of Copenhagen, Denmark. In 2009, he joined U.C. Berkeley as a Post-Doc. In 2011, he moved to Gothenburg, Sweden, to lead his research group at Chalmers. In 2021, he joined ICMAB-CSIC in Barcelona, Spain, as an ICREA professor, and from 2023, he joined the UPC.