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Thermally activated delayed fluorescence (TADF) compounds in energy transfer processes. A general alternative to metal-based complexes

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Recently, TADF (thermally activated delayed fluorescence) compounds have expanded their role beyond materials chemistry, enriching the field of photocatalysis and offering a cost-effective and environmentally friendly alternative to classical metal-based complexes. However, while their role in photoredox catalysis is well-established, research on their use in EnT reactions is sparse. In this tutorial review, we discuss and summarise the observed reactivity trends for some leading families of TADF compounds. Further, we examine their structure–property relationships and explore the development of synthetic methods for greener, more sustainable protocols in which TADF molecules serve as crucial catalytic systems.

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Green foundation

1. We discuss the use of organic molecules that present TADF as photosensitizers. The discussion is focused on the structure-properties relationship for the rational design, and also considering green parameters like the replacement of metal-based photosensitizers obtaining similar or highest yields, the use of safer solvents, and less energetic light sources.
2. The use of TADF compounds in photocatalysis has been studied more for the photoinduced electron transfer process than for the photoinduced energy transfer process. Therefore, it is essential to understand the potential of these molecules when analyzing overall trends in the design process. This knowledge will help synthesize new photosensitizers to modernize old methods more sustainably and to develop new ones aligned with green chemistry principles.
3. Despite the increasing application of TADF compounds in photocatalysis, their potential as photosensitizers continues to be a fascinating research area. This tutorial review aims to enhance understanding of how to rationally design new TADF-based photosensitizers that could replace metal-based alternatives, offering comparable or higher efficiency in a more environmentally friendly manner.

1. Introduction

In recent years, photocatalysis has emerged as a tool to perform innovative chemical transformations in a more sustainable manner.¹ However, when looking at light-driven energy-transfer (EnT) processes, many reactions are catalyzed by transition-metal based complexes. While these molecules are important for developing new transformations, they can often be replaced by metal-free alternatives, such as purely organic photosensitizers (PSs). In this context, some molecules that exhibit thermally activated delayed fluorescence (TADF) have emerged as promising candidates due to their ability to mimic metal-to-ligand charge transfer (MLCT) *via* a long-lived charge-transfer (CT) state (Fig. 1A and B). Generally, the photoexcitation of TADF compounds can lead to two distinct mechanisms: electron transfer (ET) or energy transfer (EnT), with the latter being much less used and less investigated.

TADF molecules are characterized by a small gap between S_1 and T_1 (commonly lower than 0.3 eV), which favors ISC (intersystem crossing) and RISC (reverse intersystem crossing) while suppressing internal conversion (Fig. 1E). In this regard, the synthesis and design of organic TADF compounds is based on donor and acceptor units (D–A, Fig. 1C) or molecules that incorporate heteroatoms with lone pair electrons (Fig. 1D).² Both strategies are related to Spin–Orbit Coupling (SOC) values, which depend on the nature of the excited states, orbital types, and the heavy-atom effect.³ Based on this, a common strategy for the design of D–A molecules is characterized by highly twisted structures (Fig. 1C) that promote a well-defined delocalization of the HOMO and LUMO orbitals, decreasing their overlap and the ΔE_{ST} . Additionally, substitutions in donor and acceptor structures tune the molecular energy levels, enabling a rational study of structure–property relationships. On the other hand, incorporating heavy atoms (Fig. 1D) can also induce SOC, facilitating the ISC (Fig. 1E).

However, the ΔE_{ST} character of TADF molecules is more peculiar than only considering the spatially separated HOMO–LUMO. In particular, has been studied that in carbazolycyano-

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benzene-based compounds, the energy of the S_1 state is reduced more significantly than T_1 state, while incorporating carbazole units. Moreover, the T_1 state has both contributions of the locally excitation (LE) and charge transfer (CT), the latter can be increased as the $\Delta E_{\text{HOMO-LUMO}}$ decreases.⁴ This duality CT/LE provides them with interesting properties for applications in materials chemistry and photocatalysis.

For example, TADF compounds can undergo energy transfer processes *via* the Förster resonance energy transfer (FRET) and Dexter energy transfer (DET) mechanisms. The first one is related to the dipole–dipole coupling mediated over long distances. While DET is based on simultaneous intermolecular electron exchange of the excited state of the photosensitizer (PS) and the ground state of the substrate.

In contrast, the heavy-metal-based complexes are more limited, typically achieving only DET, exemplifying the importance and versatility of organic TADF-PS for future applications. The FRET pathway mediated by TADF molecules and facilitated by a higher energy triplet has recently been explored in the development of hyperfluorescent OLEDs.⁵

In organic synthesis, the ability of TADF compounds to act as photosensitizers has been more extensively exploited *via* DET processes (*e.g.*, alkene photoisomerization). This reactivity can be attributed to their ISC quantum yields and long delayed-triplet lifetimes, making the Triplet–Triplet Energy Transfer (TT-EnT) thermodynamically feasible.

However, there are certain target properties of metal-based structures that the design of more effective TADF photosensitizers must aim to outperform:

- (1) An efficient SOC, facilitating an ultrafast ISC from $^1\text{MLCT}$ to $^3\text{MLCT}$.⁶
- (2) Structural rigidity through the incorporation of ligands, preventing the distortion, the chemical decomposition and increasing the excited states lifetime.⁷

(3) An extended wavelength window is achieved by modulating the electronic nature of the ligands, facilitating the use of less energetic light sources.⁷

In response to this, the synthetic community has been focused on the study and design of TADF compounds that can offer more sustainable methodologies, emulating or improving the photophysical and photochemical properties of metal-based compounds. These efforts are leading to new synthetic pathways in line with the need for greener chemistry.

1.1. About this tutorial review

While several review articles have discussed the theoretical aspects of TADF molecules and their synthetic importance based on photocatalysis,⁸ this tutorial review highlights the most common trend found in the structure–reactivity relationship on different families of TADF compounds that efficiently catalyze EnT manifold. We will present reports on the design of TADFs to achieve the desired triplet energy for EnT mechanisms, and we will compare the most recent methodologies that utilize TADFs with previous reports that used metal-based photosensitizers or harsh conditions. This review is organized with particular emphasis on the structure-properties relationships in TADF compounds that have been utilized in EnT processes. The work is divided into two main chapters: (i) TADF photosensitizers with donor–acceptor (D–A) structure and (ii) other types of TADF compounds.

TADF photosensitizers with donor–acceptor (D–A) structure. This D–A configuration has been widely used in materials chemistry to develop new organic emitters and luminescent materials. In particular, the family of carbazolocyanobenzene-based compounds has seen remarkable use in photocatalysis, mediating EnT processes (section 2.1). The ability to modify the number and positions of cyano and N-based groups has



Katy Medrano-Urbe

Katy Medrano-Urbe obtained her Master's and PhD degrees at the Universidad Nacional Autónoma de México (UNAM) under the mentorship of Prof. Luis Demetrio Miranda Gutiérrez. The main focus of her projects was the derivatization of multicomponent dehydroamino acids via polar and free-radical reactions. In 2022, she was awarded the MSCA Seal of Excellence and the Young Researchers-SoE (MUR-PNRR)

funding through the NextGenerationEU program. She joined the Dell'Amico group at the University of Padua as a junior assistant professor (RTDa). Her research interests involve studying and controlling the photophysical behavior of organic molecules to discover new photochemical reactivity.



Luca Dell'Amico

Luca Dell'Amico completed his PhD in 2014 at the University of Parma under the supervision of Prof. Franca Zanardi, including a spell with Prof. Karl Anker Jørgensen at Aarhus University. Then, he was a Marie-Curie COFUND fellow with Prof. Paolo Melchiorre at ICIQ. In 2017, he began his independent career as an assistant professor at the University of Padova. In 2019, he was awarded the Giacomo Ciamician Medal from the

Italian Chemical Society. In 2022, he received an ERC StG to investigate new pathways in organophotoredox catalysis. His research focuses on developing and elucidating the mechanisms of novel photochemical processes.



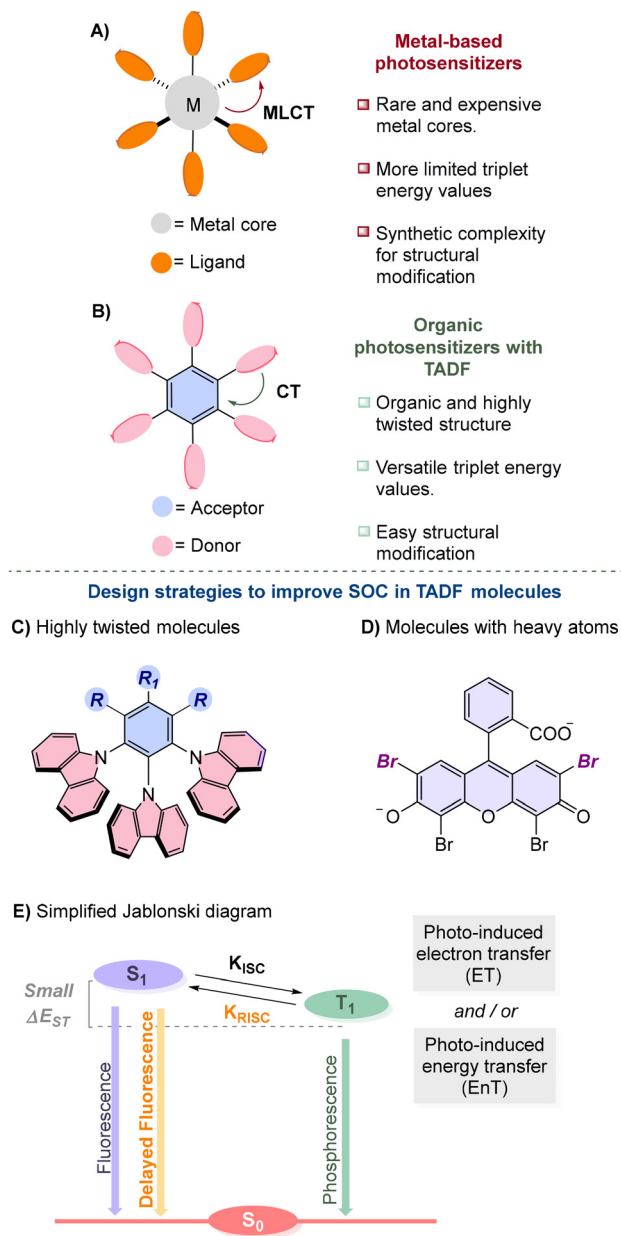


Fig. 1 Design strategies in TADF molecules used in photocatalysis.

enabled multiple combinations that can modulate the reactivity of the PS, facilitating the attainment of the target products.

Recently, the exploration of triplet energy in nitrogen-based cores has emerged as a novel alternative. In imidazoacridine- and imidazophenothiazine-based compounds (section 2.2), the dependence of ET values on structural modifications in the donor and acceptor moieties has been highlighted. Studies of these D–A compounds have examined the presence of various nitrogen-based heterocycles (modifying donor strength), and the influence of spin–orbit coupling SOC on PS reactivity. The triplet energy of more complex structures, such as diindoloquinoline-based compounds, has been studied (section 2.2). The structural diversification facilitates, for example, improvements in excited-state lifetimes. Also, an

excellent example of how the design of new photosensitizers can be addressed is presented in section 2.2, where the PS was specifically designed for the development of a new methodology, rather than its application in benchmark reactions.

While sulfur-based acceptors have been extensively reported in materials chemistry, only a few examples have been applied in photocatalysis. Interestingly, a dual role as a photocatalyst/ photosensitizer has also been explored (section 2.3), expanding the application field of this type of D–A compounds.

Other TADF compounds. TADF behavior is not limited to donor–acceptor compounds. Other examples include molecules in which a small energy gap between the singlet and triplet states arises from factors such as heavy atoms in the structure. For instance, thioxanthone (section 3.1), a core used in optoelectronic materials exhibiting TADF, has been studied for asymmetric induction. Additionally, xanthene-based compounds (section 3.2), and multiresonant structures (section 3.3) used in oxidation and isomerization processes are included.

2. TADF photosensitizers with D–A structure used in EnT processes

2.1. Carbazolycyanobenzene-based compounds

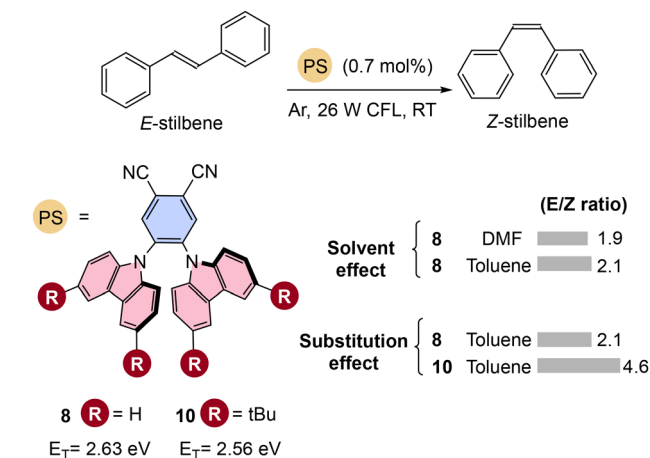
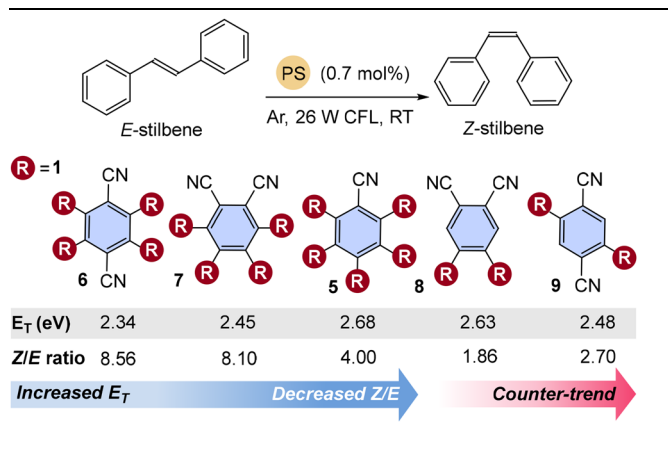
The rational design of efficient PSs is challenging. The difficulties mainly stem from the fact that several characteristics can influence the required physicochemical properties, such as the T_1 lifetime or the ISC quantum yield. However, Zhang and co-workers reported in 2018 an excellent example of how the modulation of the triplet excited states can be achieved.⁹ The authors synthesized carbazole-cyanobenzene fluorophores (D–A type), varying the number and position of cyano and carbazole groups. A clear tendency can be discerned by analyzing compounds within the same family. For example, the introduction of more electron-donating groups (EDGs) decreases the E_T from 3.03 eV to 2.68 eV (Table 1).

The E_T and λ values served as initial criteria for selecting the fluorophores involved in the isomerization of *E*-stilbene ($E_T = 2.2$ eV) to *Z*-stilbene ($E_T = 2.5$ eV). D–A compounds with a high E_T showed a lower isomerization rate, possibly due to the simultaneous activation of the *Z*-isomer (see the tendency in 6, 7, and 5 in Table 2). Interestingly, compound 8 and its 1,4-dicyanobenzene regioisomer, 2CzTPN (9),

Table 1 Impact of increasing the number of EDGs in carbazolyl-cyanobenzene-based compounds

E_T (eV)	3.03	2.77	2.70	2.68



Table 2 Trend and counter-trend found in the study of carbazoly-cyanobenzene-based compounds**Fig. 2** Solvent and substitution effect in molecules **8** and **10**.

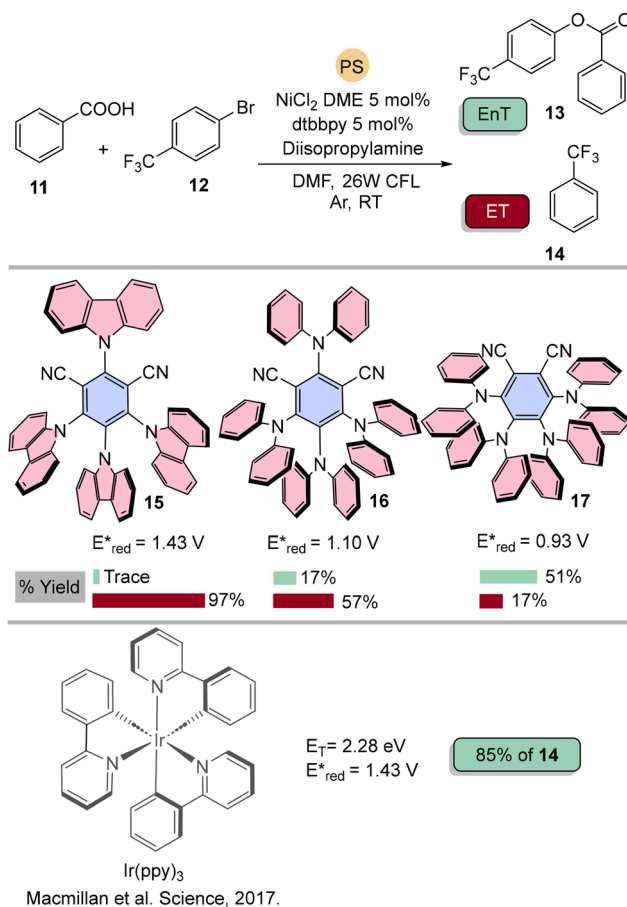
do not follow this trend, showing a Z/E ratio similar to that of compounds with higher E_T values (Table 1, for molecule **2**, Z/E ratio = 1.86). The authors identified strong 3LE (locally excited triplet state) character in compounds **8** and **9** based on theoretical calculations. This characteristic aligns with various reports describing that this type of TADF emitter with a D-A structure generally exhibits mixed local excitation (LE) and intramolecular charge transfer (CT) character.¹⁰

Spectroscopic analysis using femtosecond and nanosecond transient absorption spectroscopy confirmed the existence of two triplet states (3LE and 3CT). The 3LE state was more significant in those PSs with an unexpectedly low Z/E ratio. With this key information, the authors proposed two different strategies to modulate the 3LE / 3CT population by tuning the energy of 1CT : (i) change the solvent polarity and analyze the effect on the 3LE depopulation. (ii) Increase the electron-donating strength in the D-A structure, improving the charge transfer process. For molecule **8**, the Z/E ratio obtained in different solvents varied slightly due to a consistently lower-energy absorption band ($^1CT_{abs}$) with higher energy than 3LE . The addition of the *tert*-butyl group in **10**, which makes the carbazole core more electron-rich, shifted the $^1CT_{abs}$ below 3LE , increasing the Z/E ratio from 2.1 to 4.6. Ultimately, both strategies demonstrated that the 3CT population can influence the efficiency of TADF fluorophores in stilbene isomerization (Fig. 2).

It is worth mentioning that this transformation was originally carried out using higher temperatures or under UV light irradiation.¹¹ In this methodology, the authors showed that an organic PS and a CFL lamp can be efficiently used at ambient temperature.

The understanding of the origin of the triplet excited state and how to control the 3LE / 3CT population allows the use of D-A fluorophores in the cross-coupling reaction of carboxylic acids and aryl halides. The synthetic strategy involves modifying the redox potential by replacing the carbazole groups with better donor units, such as diphenylamines (see molecules **16** and **17**). This structural modification makes the PS less reactive toward dehalogenation of **12** ($E_{red} = -1.58$ V vs. SCE) via a

singlet-electron transfer (SET) process, while enhancing the EnT manifold that leads to product **13**. PS **17** represents a suitable alternative to Ir(ppy)₃ that was used in the seminal publication by Macmillan and co-workers,¹² in which the same compound **13** was obtained in 85% yield (Fig. 3).

**Fig. 3** Chemoselectivity in the synthesis of **13** and **14** and results obtained with Ir(ppy)₃.

In 2020, Miyake and colleagues employed Cinnamyl bromide as a bromine radical precursor to initiate a cascade *via* the EnT mechanism. This process involves the β -fragmentation of **20**, which produces a bromine radical that adds to vinyl or ethynylcyclopropane **18**, leading to ring opening with the subsequent addition to olefin **19** to produce the key intermediate (see Fig. 4).¹³ The involvement of an EnT mechanism is supported by the limited ability of the PS to promote a SET process, considering cinnamyl bromide's redox potential ($E_{\text{ox}} = +2.01$ V) and 4CzIPN (**15**) ($E_{\text{red}}^* = +1.37$ V). During the development of this methodology, three Iridium-based photosensitizers were tested. Notably, only Ir(dF-CF₃ppy)₂(dtbbpy)PF₆ exhibited results comparable to **15**, with yields of 95% and 93%, respectively. The authors then continued to optimize the reaction conditions using the latter to establish a metal-free approach.

The carbazolyl cyanobenzene compound **15** has been used for the [2 + 2] photodimerization of chalcone **22**, which has an E_{T} of 2.13 eV. Remarkably, the authors found that the *t*Bu-4CzIPN photosensitizer **25** showed the highest conversion among the IPN derivatives. They also emphasized that 4CzIPN (**15**) outperformed Ir(ppy)₃ upon irradiation at 425 or 455 nm. The reaction's success depends on the PS E_{T} value: the TADF photosensitizer **26** with the lowest E_{T} (2.27 eV), shows the lowest activity (see Fig. 5).¹⁴

All [4 + 2] cycloaddition reactions have been successfully photocatalyzed using 4CzIPN (**15**) with 2,3-dibromonaphthoquinone (**27**) and phenylbenzofurans (**28**).¹⁵ One of this methodology's most significant challenges was promoting the DA (Diels-Alder) reaction instead of the competitive [2 + 2] cycloaddition. Importantly, the authors found that adding a Lewis acid (SnCl₄) helps to diminish the competition between the two cycloadditions. Also, extending the aromatic system can help stabilize the 1,6-diradical intermediate **30**.

Although a clear trend in the triplet energy of the PS cannot be identified, the influence of solvent polarity is clear. The less polar solvent (benzene) provides the highest yield, whereas the more polar solvent (acetonitrile, MeCN) shows a decrease in yield (Fig. 6), probably due to a better stabilization of the excited state species.

The same D-A fluorophore (4CzIPN, **15**) has been used in the 6 π -photocyclization/defluorination process of *N*-aryl enam-

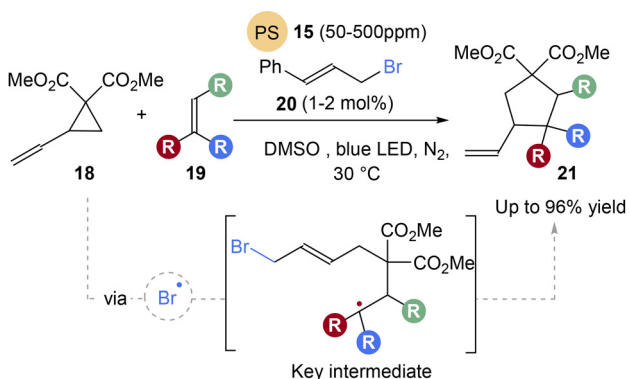
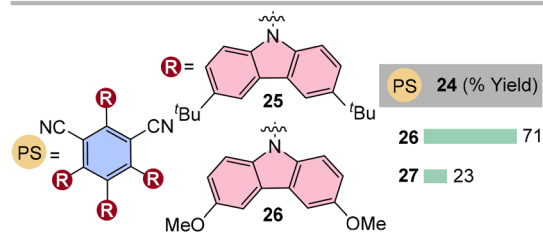
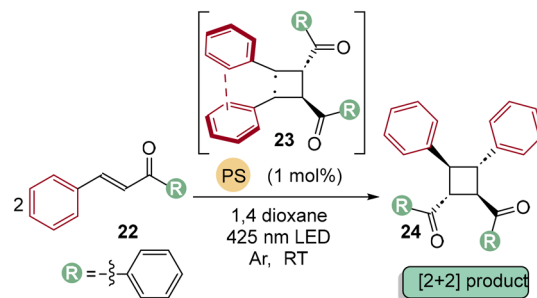


Fig. 4 Synthesis of **21** through bromine radical catalysis.



*For other chalcone derivatives studied in this methodology, the products (**24**) were obtained up to 83% yield.

Fig. 5 Comparison of the activity of the photosensitizers **25** and **26** for the synthesis of compound **24**.

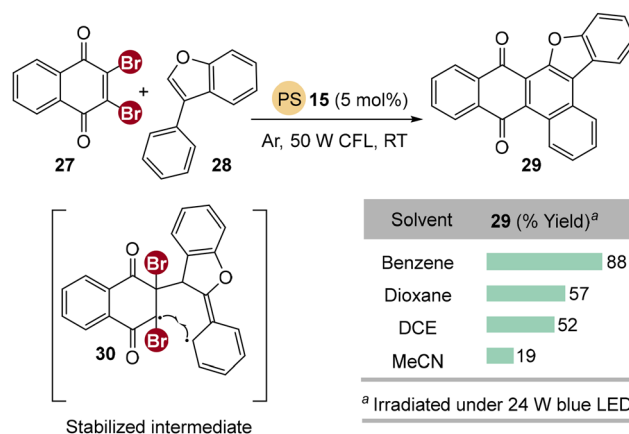


Fig. 6 Effect of the solvent in the [4 + 2] cycloaddition of **27** and **28**.

ines **31** ($E_{\text{T}} = 2.6$ eV) in the synthesis of indoles **32** (Fig. 7).¹⁶ Due to their similar triplet energies, the TADF compound demonstrated an equivalent performance in this reaction com-

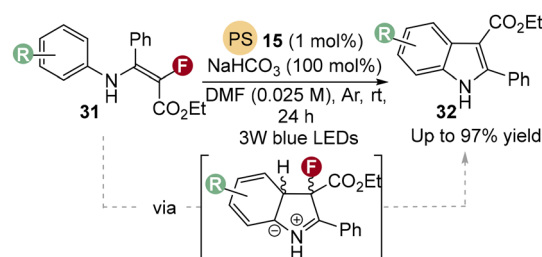


Fig. 7 Synthesis of indoles **32** through a 6 π -photocyclization/defluorination protocol.



pared with some metal-based triplet sensitizers, making this protocol a greener option.

Different photosensitizers with varying triplet energies were used to standardize the reaction conditions. In general, the photosensitizers with a small E_T value showed a lower yield or no reaction progress (Table 3).

The study of the EnT mechanism for the obtention of **32** was based on comparing the mismatched redox potentials of the substrate (**31**) and the photosensitizer during luminescence-quenching experiments. The latter showed that the *N*-aryl enamine **31** could quench the excited 4CzIPN. Also, using a triplet quencher like 2,5-dimethyl-hexa-2,4-diene inhibited the reaction progress.

In 2022, Kano and co-workers reported that the triplet energy of 4[Cz(CF₃)₂]IPN (**37**) is very similar to that of Ir-F (**35**) (a highly oxidizing and expensive photosensitizer, $E_{red}^* = +1.21$ V and priced at 152€ per 100 mg, Table 3). The purely organic photosensitizer performed well in the photocycloaddition of quinolinium triflate derivatives (**33**) with alkenes (**34**) (Fig. 8).¹⁷ The authors reported the triplet energy for **37** as 2.81 eV (64.8 kcal mol⁻¹), capable of sensitizing molecule **33** ($E_T = 2.44$ eV) to produce **35** with a 92% yield, slightly less than the 98% yield obtained using Ir-F (**36**).

The PS **8**, with a lower E_T value, performed poorly in achieving the transformation (Table 4).

In the same context, the use of **36** in the dearomative photocyclization can be replaced with the carbazolycyanobenzene compound **8**. Adachi reported an E_T of 2.63 eV for this molecule, a value similar to the 2.68 eV assigned to Ir-F (**36**). This similarity inspired Koenig and co-workers to explore the use of the organic TADF molecule **8** in previously reported dearomatization protocols for naphthol (**38**, $E_T \sim 2.59$ eV) and indole

Table 4 Dependency of product yield in the synthesis of **35**

E_T (eV)	2.63	2.68	2.81
% Yield (35)	55	98	92

derivatives (**40**).¹⁸ Additionally, compound **8** shows better solubility in the most commonly used solvents and can be recycled more efficiently than the Iridium complex (Fig. 9).

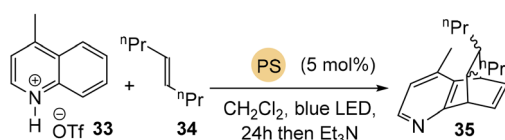
Interestingly, replacing 1,4-dioxane with chloroform led to the selective formation of molecule **39**, with the ratio increasing from 1.2 : 1 to 16 : 1. The involvement of the EnT process in this reaction can be attributed to the redox potential mismatch between the selected photosensitizer and the aromatic substrates, thereby ruling out an operative SET pathway.

2.2. N-heterocycles-based compounds

Hudson reported the synthesis of a new type of TADF emitter in 2020 based on an imidazole/acridine chromophore **42**.¹⁹ This report established that using *N*-phenylbenzimidazole constrained in a coplanar fashion is an efficient acceptor to allow a well-localized LUMO that, combined with a heterocyclic donor, can enhance a small ΔE_{ST} .

Table 3 Dependence of the molecule's yield **32** on the E_T value

E_T (eV)	1.88	1.92	2.01	2.5	2.6	2.61
% Yield (32)	0	0	0	31	70	75
Increased E_T			Higher yield			



*For other quinolinium triflate derivatives studied in this methodology, the products type **35** were obtained up to 97% yield using PS **37**.

Fig. 8 Intermolecular dearomative [4 + 2] cycloaddition for the obtention of **35**.

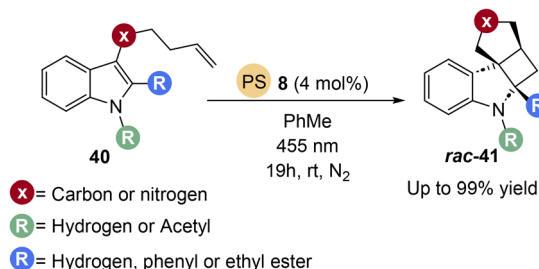
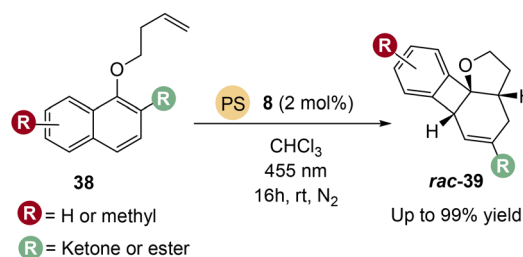


Fig. 9 Dearomative cycloaddition photocatalyzed by **8**.



In 2022, the author also reported using these D–A compounds in the [2 + 2] cycloaddition *via* an EnT process as a more sustainable alternative to Ir-based photosensitizers.²⁰ In this family of TADF compounds, the relationship between the strength of EDG and the E_T values remains unclear (Table 5); the worst EDG (**c**) is not the one with the highest E_T value.

The PS **42c** was shown to be highly efficient at activating compound **43** ($E_T = 2.54$ eV), thereby facilitating an intramolecular [2 + 2] cycloaddition to construct the tetracyclic **44** (Fig. 10). The D–A compound **42c** showed similar yields compared with the metal-based PS [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆, which is also one of the most expensive commercially available Ir-based photosensitizers (300€ per 100 mg). The authors proposed that the higher performance of compound **42c** is related to a more efficient ISC process.

In 2023, an extensive study was published to expose the impact of the SOC phenomenon in a family of new donor–acceptor molecules. The investigation included the study of three different sulfur-based acceptors (sulfide, sulfoxide, and sulfone) and diverse donors.²¹

In the acceptor unit, the presence of the sulfur atom in the imidazophenothiazine core increases the conjugation, allowing a red-shifted absorption compared to the imidazoacridine

Table 5 Impact of the EDGs on the E_T values of imidazoacridine-based photosensitizer

Structure	E_T (eV)
42	2.55
a	2.65
b	2.76
c	2.77
d	2.77

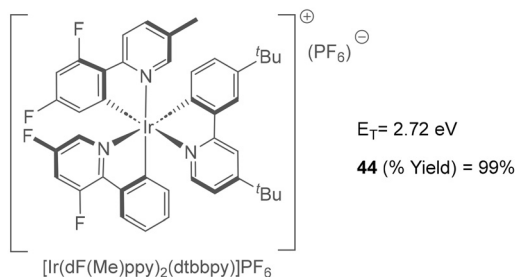
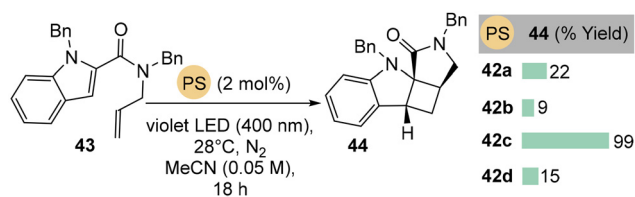


Fig. 10 Intramolecular [2 + 2] cycloaddition using **42** derivatives.

family before commented. In general, sulfur oxidation resulted in lower E_T parameter and SOC character values. Notably, this trend continued in the proportion of ³LE in the T₁ (Table 6).

This value was essential for effective performance as a photosensitizer across nearly all tested reactions, including thiolation of alkenes (Fig. 11a) and Ni-catalyzed esterification (Fig. 11b), in which molecule **46a** (higher E_T and SOC) delivered higher yields. In general, these new photosensitizers outperformed the reported **43** derivatives in all reactions studied, achieving better efficiency in each transformation.

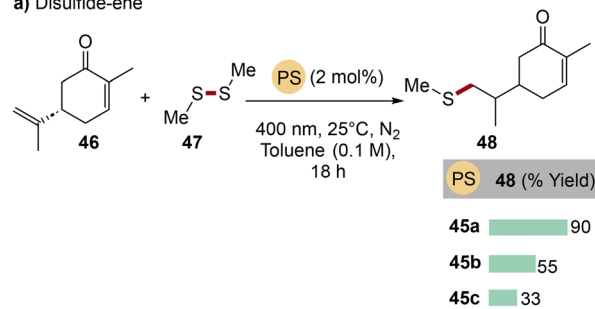
In 2023, Sengupta and collaborators synthesized four indoloquinoline-based TADF compounds, including phenyl carbazole **53** and diindolocarbazole (DiICz) **54**, as donors.²² The complete characterization was performed to explore their various properties. Specifically, the D–A compounds reported in this study exhibited similar E_T values. However, when the

Table 6 Effect of sulfur oxidation on the imidazophenothiazine family

Structure	E_T (eV)	SOC (cm ⁻¹)	T ₁ (³ LE% ³ CT%)
45	2.76	2.33	75.5/24.5
45a	2.71	1.00	7.2/92.8
45c	2.64	0.03	6.4/93.6

Decreased SOC → Decreased reactivity

a) Disulfide-ene



b) Esterification

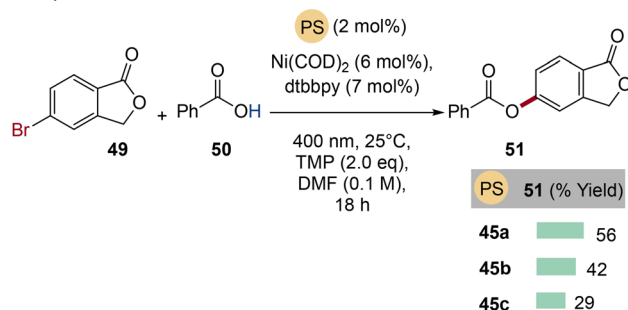


Fig. 11 Reactivity of **45** derivatives in representative examples.



photosensitization protocol for the isomerization of *E*-stilbene is used, a better performance was generally observed when the reaction time was extended to 30 hours. Interestingly, although compounds **53a** and **53b** have the same E_T value, their conversion (%) differed significantly (69% and 90%, respectively) (Fig. 12). The authors did not investigate the reason for this difference. Nonetheless, this exemplifies that the E_T parameter alone does not fully explain EnT efficiency.

The same group reported two more DiICz-based molecules with a donor-acceptor-donor structure using dibenzo[*a,c*]phenazine (**56a**) and phenanthrol[9,10-*d*]imidazole (**56b**) as donors (Fig. 13). In general, these molecules exhibited long excited-state lifetimes compared to **52** and **53**.²³ These compounds were tested in the photoisomerization of molecule **55a**, where **56b** presented the lowest yield, due to its capacity to activate the *cis*-isomer.

An interesting example of the synthesis and design of photosensitizers aimed at achieving challenging reactivity was reported by Dell'Amico and colleagues.²⁴ The goal of this synthesis was to produce azetidines **60** from azabicyclo[1.1.0]butanes **58**. During the reaction with compound **59**, the authors observed the formation of an imine dimer caused by the higher concentration of the iminyl radical in the reaction mixture. Controlling its formation was key to increasing the yield of the target product **60**. This was achieved by promoting RISC in molecule **57** by lowering the ΔE_{ST} to 0.05 eV, which was done by adding a *tert*-butyl group (compound **57b**) to increase steric hindrance (Fig. 14). In this particular case, it can be counterintuitive for the reader to see the benefit of RISC improvement when it decreases energy transfer efficiency. However, the reader must visualize that, for the pur-

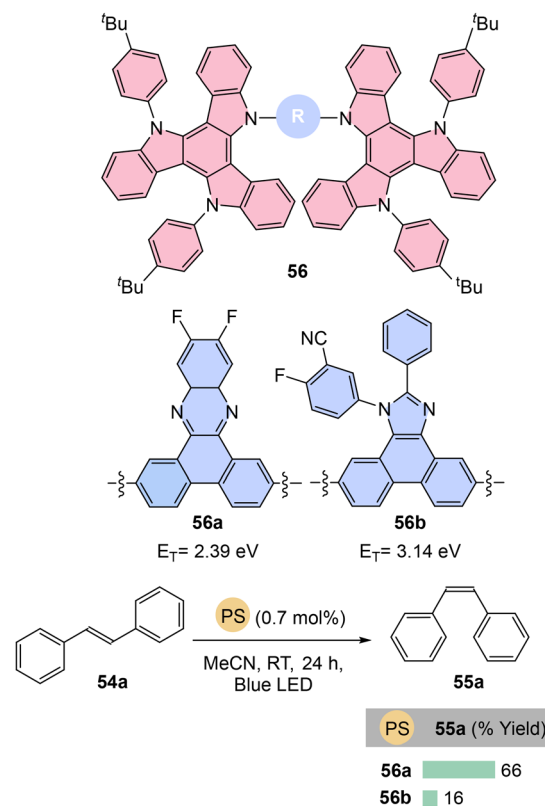


Fig. 13 Other TADF photosensitizers reported by Sengupta and colleagues.

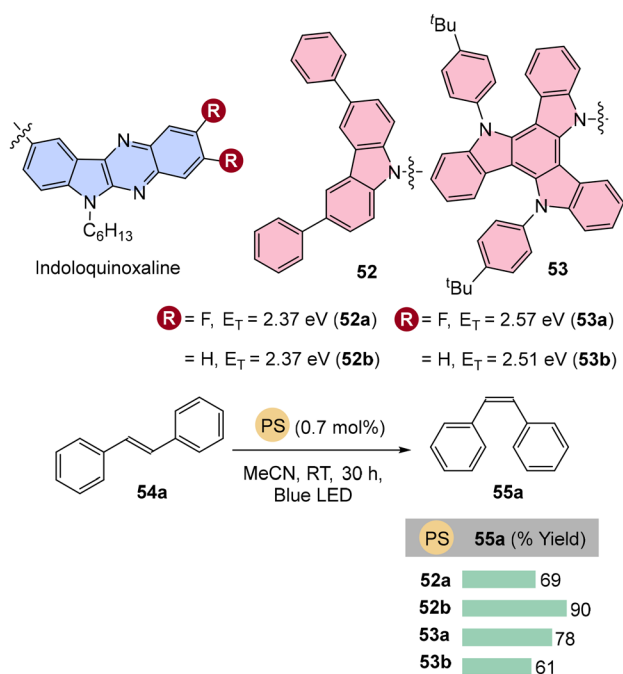


Fig. 12 *E/Z* isomerization using indoloquinoxalines-based compounds.

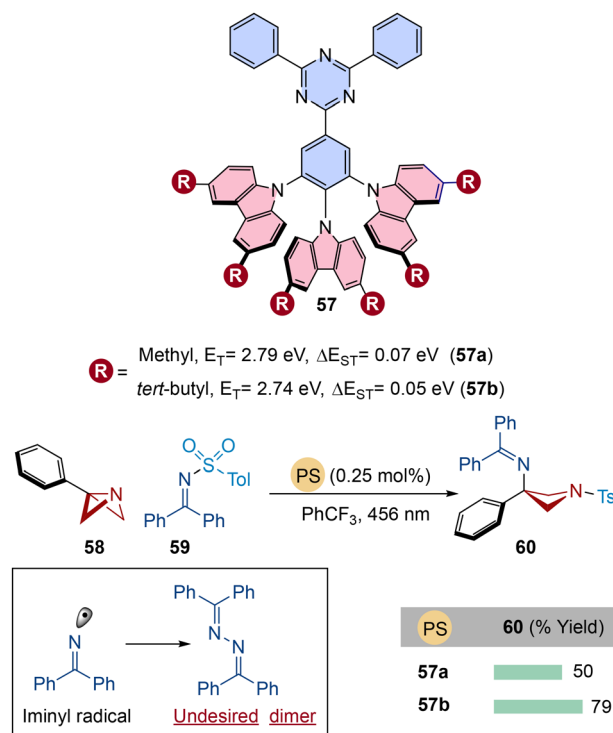


Fig. 14 Design of PS **57** for the synthesis of **60**.



poses of this synthetic methodology, it was a strategic way to access product **60** efficiently while avoiding dimerization.

This methodology offers an alternative approach for designing new photosensitizers based on the reactivity requirements needed for challenging chemical transformations. Unlike the traditional method of studying the reactivity of new photosensitizers in benchmark reactions such as cycloadditions and isomerizations, this approach emphasizes specific reactivity needs.

2.3. Sulfone-based compounds

In 2023, Zysman-Colman and colleagues reported sulfur-based molecule **61**, which can participate in ET and EnT processes.²⁵ The manuscript specifically compares the properties and photocatalytic reactivity of molecule **61** with the well-known 4CzIPN (**15**). Molecule **61** has a higher triplet energy ($E_T = 2.97$ eV) than 4CzIPN ($E_T = 2.59$ eV). The authors did not discuss the reason for this difference, such as whether a possible variance in the spin-orbit coupling nature in the two species might affect the E_T value. The benchmark reaction used to study EnT behavior was the isomerization of *E*-stilbene (**54a**). When using compound **61**, the *Z*-isomer (**55a**) was obtained in 63% yield, whereas 4CzIPN yielded 87%. The authors claimed that the lower performance is related to the higher E_T value, which can activate *Z*-stilbene ($E_T = 2.5$ eV), thus facilitating the reverse process. This selectivity issue is avoided when using an alkene with higher E_T values, such as diisopropyl fumarate **54b** (2.7 eV and 3.1 eV for the *E* and *Z*-isomers, respectively) (Fig. 15). Notably, the yield with **61** (81%) is the highest among those using 4CzIPN and $[\text{Ir}(\text{dFCF}_3)_2\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (6% and 58%, respectively).

3. Other TADF photosensitizers used in EnT processes

3.1. Thioxanthone-based compounds

The thioxanthone core has been used as an acceptor moiety in the construction of OLED devices. These TADF compounds are

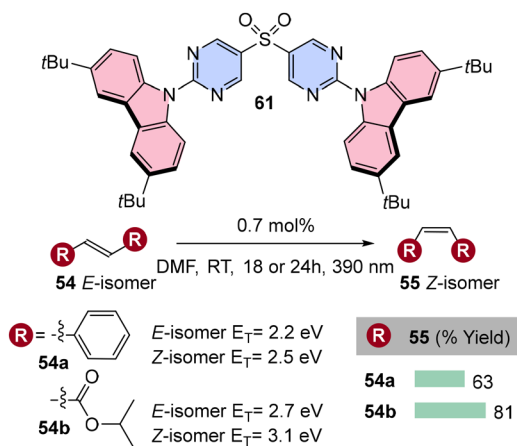


Fig. 15 Selectivity obtained for the *E/Z* isomerization using molecule **61**.

characterized by having high triplet energy and long triplet lifetimes.²⁶ These characteristics have opened the possibility of using them as organic photocatalysts in hydrogen atom transfer (HAT), single electron transfer (SET), and different EnT protocols. Furthermore, the literature includes examples illustrating the importance and versatility of the thioxanthone core, achieving different processes, even without any structural modification.²⁷

In general, modifying the thioxanthone core has focused more on enabling asymmetric reactions. The importance of adding a chiral auxiliary has allowed these thioxanthone-based derivatives to be used in different transformations with good yields and enantioselectivity. For the purposes of this tutorial review, we will highlight the most representative examples of this structural modification.

Inspired by their pioneering work on the cycloaddition [2 + 2] assisted by a chiral photosensitizer based on xanthone,²⁸ Bach and colleagues investigated the use of chiral thioxanthone **63**, which includes a 1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-2-one skeleton to promote hydrogen bonding interactions. Replacing xanthone with thioxanthone allows the use of the latter as a photosensitizer in the visible region, reducing the energy needed for substrate sensitization. The enantioselective reaction was mainly focused on modifying 2 (*1H*)-Quinolones **62**, which served as model substrates for various transformations (Fig. 16).

The first report involves synthesizing tetracyclic product **65** through an intramolecular reaction with extraordinary regio- and enantioselectivity. This work established, for the first time, the hydrogen-bonding interaction between molecules **62** and **63** in complex **64**, where the thioxanthone serves as an antenna that can donate energy to the absorbed photon (Fig. 16a).²⁹

The intermolecular reaction was reported using a variety of electron-deficient alkenes **66**. The successful conversion of the starting materials to product **67** was attributed to the hydrogen-bonding interaction in complex **64**, whose dissociation is responsible for the loss of enantioselectivity (Fig. 16b). Importantly, from a green perspective, the authors carried out this transformation using solar irradiation without compromising the ee.³⁰

Another tetracyclic **68** variant was obtained from 3-alkylquinolinones substituted with 4-*O*-tethered alkenes and allenes. Notably, the quinolinones α -substituted at the carbonyl showed a decrease in the E_T value, allowing the use of photosensitizer **63** and the reaction to proceed (Fig. 16c).³¹

The same group explored the possibility of using compound **62** not only in cycloaddition reactions. In 2019, they reported the synthesis of cyclopropanes **69** using allyl quinolone. Also, the authors demonstrated the capacity of thioxanthone **63** to racemize cyclopropanes enantiomerically pure (Fig. 16d).³² Even when this type of cycloaddition can be achieved by direct excitation of the substrates, the use of **63** facilitates the visible light irradiation (420 nm) and stereocontrol. Some years later, the EnT mechanism was corroborated using DFT calculations. It was also possible to establish that the first C–C bond for-



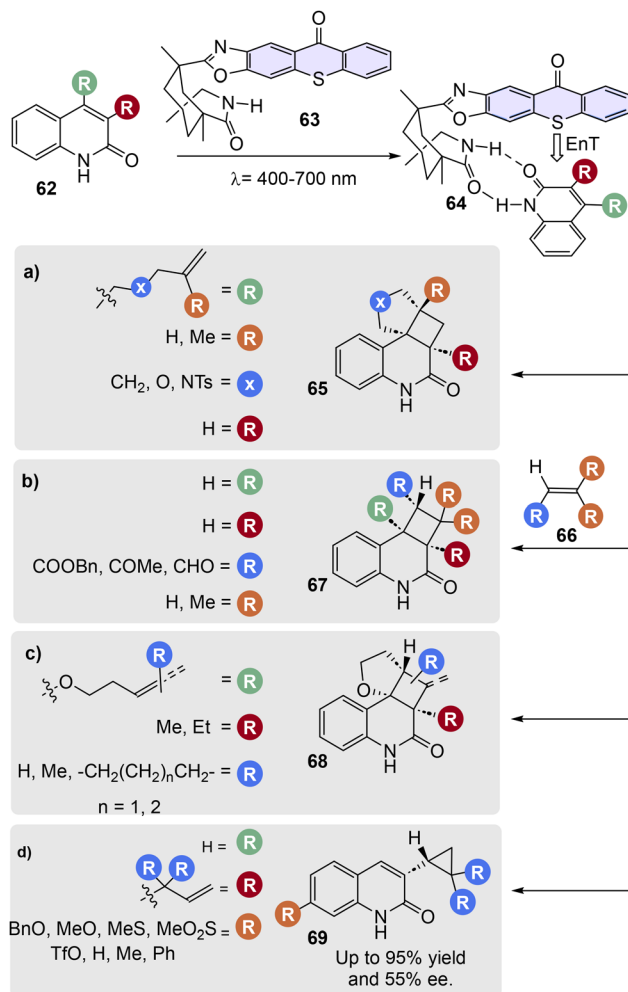


Fig. 16 Derivatization of compound **62** through [2 + 2] cycloaddition using alkenes (a and b), allenenes (c) and allyl quinolone (d).

mation is the critical step in the rate and selectivity performance.³³

To the best of our knowledge, there is only one report on the effect of structural changes on the capacity of thioxanthone to act as a photosensitizer. The work presented by Booker-Milburn and collaborators examines the structure–property relationships modifying the substitution patterns of the aforementioned core.³⁴ The UV-Vis absorption values of the synthesized molecules ranged between 300 and 450 nm, enabling their activation with various energy sources like UV and visible light. Additionally, the UV-Vis absorption and E_T values are inversely proportional, as shown in Table 7.

The study of the potential of these molecules as triplet energy photosensitizers involves intra- and intermolecular [2 + 2] cycloadditions. A general trend in reactivity is observed when a 125 Hg lamp is used as the light source; the molecule with the highest E_T value (**70**) performs better than molecule **74** (lowest E_T). However, molecule **74** could still be used in a visible light protocol to achieve the [2 + 2] cycloaddition with different substrates.

Table 7 Relationship between the absorption and E_T in thioxanthenes

λ_{abs} (nm)	354	367	385	399	405
E_T (eV)	3.08	2.93	2.72	2.50	2.39

Increasing λ_{abs} → Decreased E_T

3.2. Xanthene-based compounds

The family of xanthene has not been used as donor–acceptor compounds with TADF or in material chemistry, unlike other families previously studied. Nevertheless, this type of compound was initially explored in the study of this photoluminescence phenomenon. In this case, SOC, which is necessary for efficient ISC, is facilitated by the heavy-atom effect present in the structure. The most common approach to induce this effect is modifying the chromophore structure by adding metals (such as Ru, Ir, Pt) or halogens (such as Br, I). These elements are often located at the core of these traditional chromophores.

The synthetic application of this type of compound has been less explored using the EnT mechanism. Although Eosin Y was the first compound reported to exhibit TADF,³⁵ its synthetic applications following an EnT mechanism mainly involve generating singlet oxygen to mediate various oxidation reactions.

In this context, Ando and colleagues described the aerobic photooxidation of bulky tellurides to telluroxide using Eosin Y **75** and Rose Bengal **76**, replacing traditional methods such as 3-chloroperbenzoic acid (mCPBA). The weaker Te–O bond in mCPBA can transfer to various organic substrates, facilitating the oxidation of alcohols³⁶ and phosphite esters,³⁷ as shown in Fig. 17. This approach is notable for its environmental friendliness, as it uses ethanol—a safer solvent—compared to the solvents previously discussed. Additionally, it enables the *in situ* generation of toxic telluroxides.

Similarly, compound **75** has been used to synthesize phosphine oxide **78**, a versatile motif in organic, medicinal, and supramolecular chemistry. The reaction involves generating arylphosphadioxane **77**, which can produce the target compound **78** in the presence of a second molecule of the triarylphosphine (Fig. 18).³⁸

Another interesting reaction using Eosin Y (**75**) as a photosensitizer is the synthesis of Michael acceptors from the oxidation of the corresponding silyl enol ethers **79**. The TADF molecule facilitates the generation of O_2 , which undergoes an *ene* reaction with compound **79** to produce the cyclic intermediate **80**. The sub-



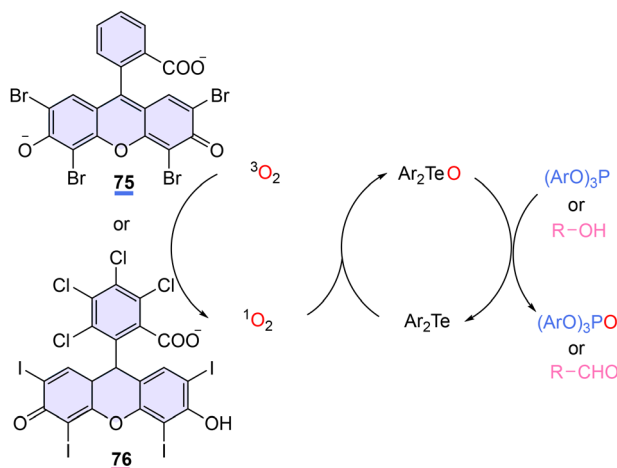


Fig. 17 Use of photosensitizers **75** and **76** in oxidation reactions mediated by telluroxides.



Fig. 18 Synthesis of phosphine oxide through aerobic oxidation.

sequent ring opening yields the hydroperoxy silyl hemiacetal **81**, followed by an intramolecular silyl transfer to form the α,β -unsaturated final product **82** (Fig. 19).³⁹

Furthermore, the photosensitizers **75** and **76** are widely used in the photooxidation reaction of furan **83**. Typically, this process involves a [4 + 2] cycloaddition to form the key intermediate **84**. This bicyclic compound (**84**) can react in two main ways: with a nucleophile, producing the molecule **85**, or with a base, forming the furanone core **86**. These two products can then be used in further transformations, increasing structural complexity and diversity (Fig. 20).⁴⁰ Notably, some of these transformations are performed using safer, less hazardous solvents such as water or ethanol.

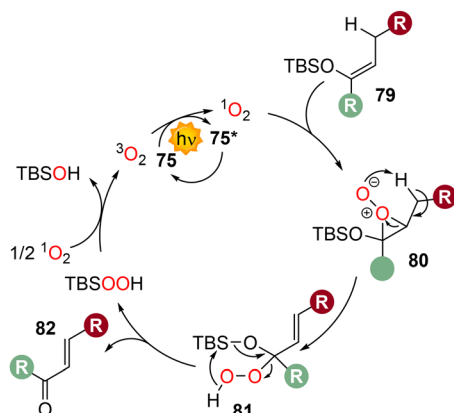


Fig. 19 Use of photosensitizer **75** in the synthesis of Michael acceptors.

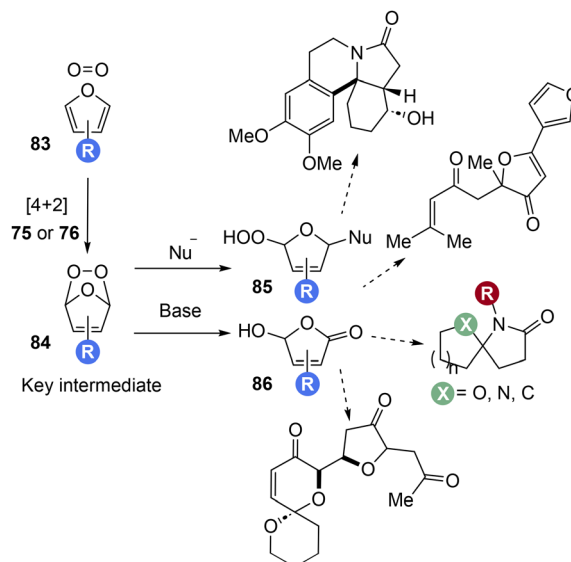


Fig. 20 Representative reactivity of furans in the presence of oxygen and xanthen-based photosensitizers.

3.3. MR-TADF compounds

The Zysman-Colman research group reported using the multi-resonant TADF compounds **87** and **88**, which yielded good results for ET and EnT. These molecules were studied as photosensitizers for the isomerization of the previously mentioned substrates (**54**), now using visible light, and decreasing the reaction time.⁴¹ In particular, these compounds have a small positive solvatochromism and higher absorptivity. Both characteristics were expected to enhance photocatalytic activity. In fact, due to their higher absorptivity, these molecules can be used at a low concentration (0.7 mol%) for alkene isomerization, improving process efficiency and catalytic performance. Like formerly reported Donor–Acceptor PS **61** (see section 2.3), better performance was achieved when using diisopropyl fumarate **54b** (90% yield) (Fig. 21).

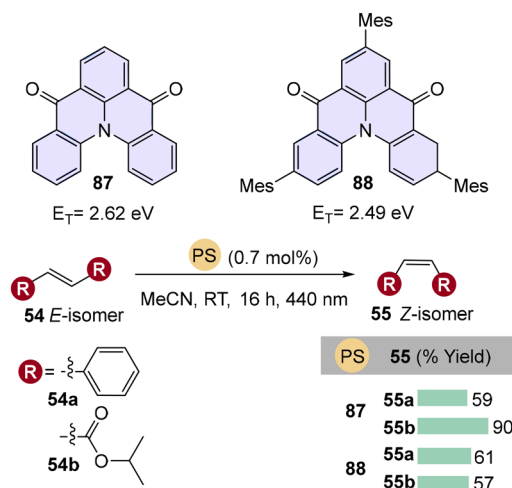


Fig. 21 *E/Z* isomerization in the presence of MR-TADF compounds **87** and **88**.



4. Conclusions and future perspectives

In this tutorial review, we have discussed the primary reactions mediated by energy transfer (EnT) processes in the presence of thermally activated delayed fluorescence (TADF) compounds, emphasizing their emerging role as efficient and sustainable photosensitizers in modern synthetic chemistry. These systems have demonstrated the capacity to promote a broad range of photochemical transformations under mild conditions, often relying on visible light irradiation and avoiding the need for precious metal complexes. A valuable feature of some of these molecules is their ability to also participate in electron transfer (ET) processes, which provides them with exceptional versatility for use in modern and sustainable synthetic protocols. This dual reactivity profile, in which a single photosensitizer can engage in either EnT or ET pathways depending on reaction conditions and substrate properties, represents a powerful conceptual and practical advance in photocatalyst design. Therefore, designing new molecules with this type of reactivity is a crucial focus in advancing photochemistry.

The coexistence of EnT and ET manifolds in TADF compounds originates from their distinctive electronic structure, typically based on donor–acceptor architectures that promote small singlet–triplet energy gaps (ΔE_{ST}). This feature enables efficient reverse intersystem crossing (RISC) and long-lived excited states, which are key parameters for productive bimolecular interactions, dictating exciton dynamics and providing long lifetimes that facilitate PS–substrate interactions (crucial for the DET mechanism), but not so long as to cause non-productive quenching. It is essential to study in depth the structure–property relationships influencing the fine-tuning of electronic and photophysical parameters that facilitate this interesting duality, ET/EnT. Subtle structural modifications, such as varying donor strength, acceptor identity, torsional angles, or regioisomerism, can alter charge-transfer (CT) character, locally excited (LE) character, and triplet energies (E_T). The former parameter has been utilized to analyze, in a general and easy way, if the EnT process between a donor (excited PS) and an acceptor (substrate) is thermodynamically feasible. Anyway, it is clear that the E_T value is not able to explain some inconsistencies in the reactivity (see discussion in section 2.1, Table 2), therefore, a deeper understanding and discussion of the physical properties of the reported TADF PS must be included in future publications. In other words, a systematic understanding of how these parameters correlate with reactivity will allow chemists to rationally design next-generation photosensitizers with predictable and programmable behavior.

Furthermore, by utilizing the structural derivatization of TADF PS, these molecules can both facilitate photoreactivity and incorporate chiral auxiliaries, leading to successful outcomes in certain asymmetric transformations. The modular nature of donor–acceptor scaffolds offers a unique opportunity to introduce stereochemical elements without compromising photophysical performance. However, only one family has been modified for these applications, leaving the potential to extend this reactivity to other TADF molecules. Expanding

asymmetric variants to structurally diverse TADF platforms could unlock new catalytic modes, particularly in enantioselective energy transfer catalysis, where precise control over substrate orientation and excited-state interactions is required.

The field is still in its early stages of development. Despite the rapid progress achieved in recent years, many mechanistic aspects remain insufficiently explored, particularly regarding the quantitative prediction of energy transfer efficiencies. It is vital to understand how we can connect the photochemical properties of these structures to the existing literature on TADF molecules in material chemistry to unlock new reactivity in EnT protocols. The extensive knowledge accumulated in the context of organic light-emitting diodes (OLEDs) and optoelectronic materials provides a valuable foundation for translating photophysical principles into synthetic applications.

In the coming years, we expect TADF compounds to become increasingly prominent, replacing traditional, costly metal-based PS and enhancing the performance of organic-based alternatives. Their tunability, structural diversity, and compatibility with visible light irradiation position them as highly attractive candidates for sustainable catalysis. Continued interdisciplinary collaboration between synthetic chemists, photophysicists, and materials scientists will be essential to fully exploit the potential of TADF-based photosensitizers and to establish them as central tools in energy transfer-driven synthetic methodologies.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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