

## Review

# Fluorescent Azobenzene-Containing Compounds: From Structure to Mechanism

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**Abstract:** The reversible photoisomerization of azobenzenes has been extensively studied to construct systems with optical responsiveness; however, this process limits the luminescence of these compounds. Recently, there have been many efforts to design and synthesize fluorescent azobenzene compounds, such as inhibition of electron transfer, inducing aggregation, and metal-enhancement, which make the materials ideal for application in fluorescence probes, light-emitting devices, molecular detection, etc. Herein, we review the recently reported progress in the development of various fluorescent azobenzenes and summarize the possible mechanism of their fluorescence emission. The potential applications of these materials are also discussed. Finally, in order to guide research in this field, the existing problems and future development prospects are discussed.

**Keywords:** azobenzene derivatives; fluorescence; photoisomerization



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## 1. Introduction

Since the discovery of azobenzene's isomerization in 1937 [1], it has shown great potential for use in liquid crystals [2–8], sensors [9–13], molecular photoswitches [8,14–18], information storage [19–21], etc. due to its unique and remarkable properties, including the ability to undergo reversible *cis*–*trans* isomerization upon photo-irradiation at specific wavelengths. In fact, when the molecule is excited from its ground state to an unstable excited state by irradiation, it releases energy to return to the ground state by various means, such as exciplex formation, intramolecular rotation of single bonds, internal transformation, intramolecular charge transfer (ICT), photoinduced electron transfer (PET), and photoinduced proton transfer and the other non-radiative transitions or emitting fluorescence/phosphorescence.

The photoisomerization of azobenzene molecules in the excited state is almost instantaneous, but its radiation deactivation is slow [22], which hinders the fluorescence of azobenzene derivatives [23], thus limiting further applications in multifunctional fluorescent probes, chemical sensors, and light-emitting devices. However, the rate of *cis*–*trans* isomerization depends on the chemical architecture of the system. Therefore, suppressing the photoisomerization or reducing the efficiency of other non-radiative transitions could enhance the fluorescence of these compounds.

Kunitake and Simomure reported the first fluorescent azobenzene-containing amphiphiles with aqueous-bilayer aggregates in 1987 [24]. Although many azobenzene-based chromophores that exhibit luminescence have been developed through exquisite molecular design, finding new luminous azoderivatives is still challenging. Thus, this field has at-

tracted considerable research attention over the past few years. To overcome this challenge, the following mechanisms have been attempted and classified.

1. Substituent effect;
2. Inhibition of the electron transfer;
3. Induced aggregation;
4. Other mechanism.

In this review, we discuss the different mechanisms for producing fluorescent azobenzene derivatives with respect to molecular design. We discuss the range of azobenzene molecules linked with electron acceptors that feature a “push-pull” structure as well as non-planar structures with improved rigidity that suppress PET, ICT, and intramolecular motion. Moreover, some azobenzene aggregates exhibit unique optical properties induced by photoexcitation or selective solvents. In particular, when metal nanoparticles are combined with azo derivatives, enhanced fluorescence can be achieved. The azobenzene compounds exhibiting the strongest fluorescence utilize B–N coordination. In addition, the design of fluorescent azobenzene provides a new insight in the design of smart fluorescence switches, fluorescent materials, and novel fluorescent probes. Here, we discuss their structures, characteristics, and the possible mechanisms involved.

## 2. Effect of Substituents on Azobenzene Isomerization

The reversible *cis*–*trans* transformation of azobenzenes is a remarkable photochemical phenomenon, which has been utilized for making smart switches [8,14–18,25–28], self-assembly materials [29–33], light-responsive liquid crystals [3,8,33–35], gels [4,36–39] etc. Upon exposure to UV light, *trans*-azobenzene transforms into its *cis*-isomer. In turn, *cis*-azobenzene can revert to its *trans* form upon irradiation by visible light or heat (Figure 1), with high efficiency.

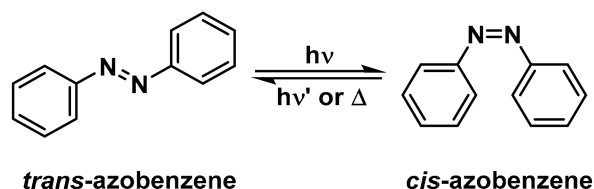
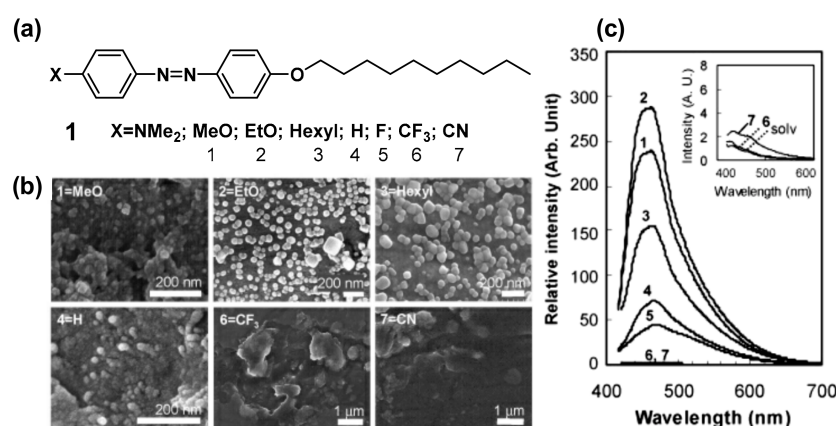


Figure 1. Reversible photoisomerization of azobenzene in two states.

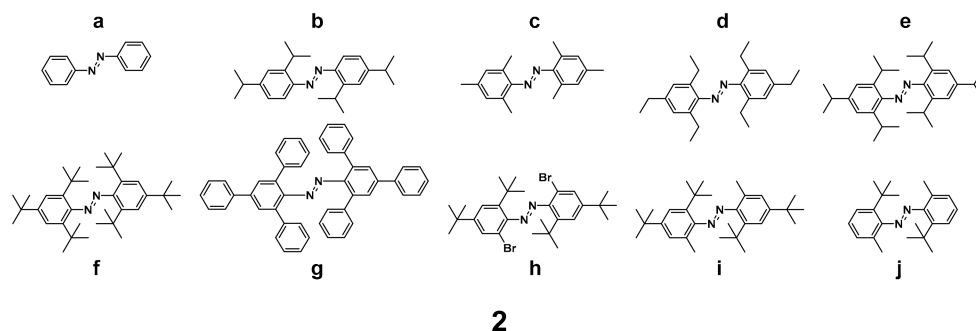
Two possible mechanisms have been proposed for the isomerization of azobenzene: inversion [40] and rotation [41]. In addition, azobenzene isomerization may be affected by various factors, such as the mode of excitation [42,43], radiation wavelength [44], solvent properties [45–48], substituents on the benzene ring [49–55], temperature [48], etc.

In particular, the sufficient lifetime of *cis*-azobenzenes, varying with different substituents at the *ortho* or *para* position, has been found to be one of the crucial factors favoring fluorescence enhancement (Figure 2c). Han et al. designed and synthesized a series of simple azobenzene derivatives **1** featuring substituents with various electronic properties to study the effects of substituents on the isomerization of azobenzene [50], as shown in Figure 2a. The substitution of electron-withdrawing groups on azobenzenes **1** indeed slowed the isomerization rate but obstructed the azobenzenes from aggregating (Figure 2b). On the other hand, azobenzenes **1** with more electron-donating substituents seemed to form aggregates more easily (Figure 2b), resulting in higher fluorescence quantum yield and obvious red shift of the  $\pi$ – $\pi^*$  transition [56,57]. Although the existence of strong electron-donating substituents leads to a significant increase in the photoisomerization rate, it tips the balance toward fluorescence quenching. If the azobenzene molecules are substituted by electron-donating and electron-withdrawing groups (e.g.,  $-\text{NH}_2$  and  $-\text{NO}_2$ ), respectively, the asymmetric “push-pull” electronic structure will favor higher isomerization rate and shorter lifetime of the *cis*-isomer [58], which greatly thwarts the fluorescence.



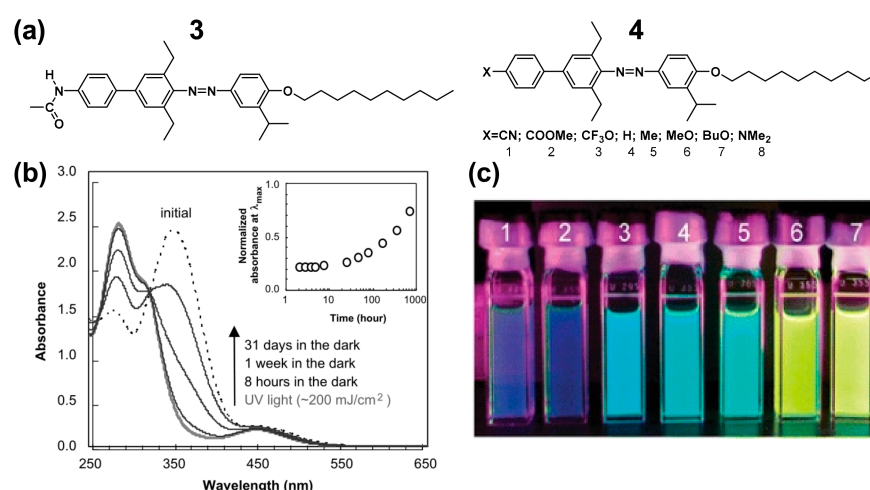
**Figure 2.** (a) The molecule structures of azobenzene derivatives **1** with different donor and acceptor substituents. (b) SEM images of **1** after UV irradiation for 300 min. (c) The fluorescence spectra of **1**. (b,c) were reproduced with permission from [50]. Copyright 2006 American Chemical Society.

Rau and Shen designed a series of azobenzene derivatives **2a–2j** containing steric hindrance [53], and found that the azobenzene derivatives **2f–2g** (Figure 3), bearing substituents with larger steric hindrance at *ortho* and *para* positions, had the lowest E→Z efficiency and showed almost no isomerization transition. The bulky *ortho*-substituents, such as isopropyl [51], *t*-isopropyl [52] and decyloxy [54] groups, often sterically restrict the molecular movement required for isomerization, and hence fluorescence emission occurs.



**Figure 3.** The molecule structures of a series of steric hindrance azobenzene derivatives **2a–2j**.

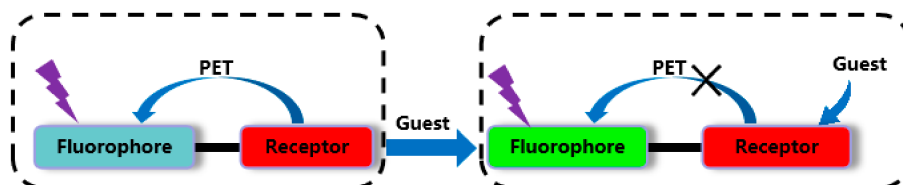
Slow thermal back isomerization and green fluorescence have been observed from one steric azobenzene derivative (**3**) featuring decyloxy groups due to the large *ortho* substituents [54] (Figure 4a,b). Thereafter, utilizing a series of derivatives of azobenzenes (**4**) substituted with electron-donating or electron-accepting groups resulted in appreciable change in fluorescence color from blue to yellow (see Figure 4c) [55]. The blue shift of its emission wavelength occurs with the electron-withdrawing ability of the substituent group becoming stronger. The emission wavelength of **4** was regulated by the electronic properties of the substituents, but its emission may be ascribed to the substituents with steric hindrance at the *ortho* and *para*-positions of the azobenzene molecules [55].



**Figure 4.** (a) The molecule structures of a series of steric hindrance azobenzene derivatives **3**, **4**. (b) Changes in UV-vis absorption spectral changes of azobenzene (**3**) solution ( $8 \times 10^{-5}$  M). After UV irradiation to reach a *cis*-rich photostationary state, the solution was stored in the dark at 20 °C for thermal *cis*-to-*trans* isomerization. Inset: changes in normalized absorbances at  $\lambda_{\max}$  as a function of time for thermal *cis*-to-*trans* isomerization. (c) Fluorescence of UV-exposed **4** solutions upon excitation at 365 nm. (b) was reproduced with permission from [54]. Copyright 2009, Elsevier. (c) Reproduced with permission from [55]. Copyright 2010 The Royal Society of Chemistry.

### 3. Inhibition the PET and ICT

Photoinduced electron transfer (PET) occurs between the electron acceptor (which behaves as a fluorophore) and the electron donor (which acts as the receptor unit) in the photoexcited state, which quenches the fluorescence. In a PET fluorescent molecular probe (Figure 5), once the receptor unit binds to the guest, the PET is inhibited or even completely blocked, and the fluorophore emits fluorescence.

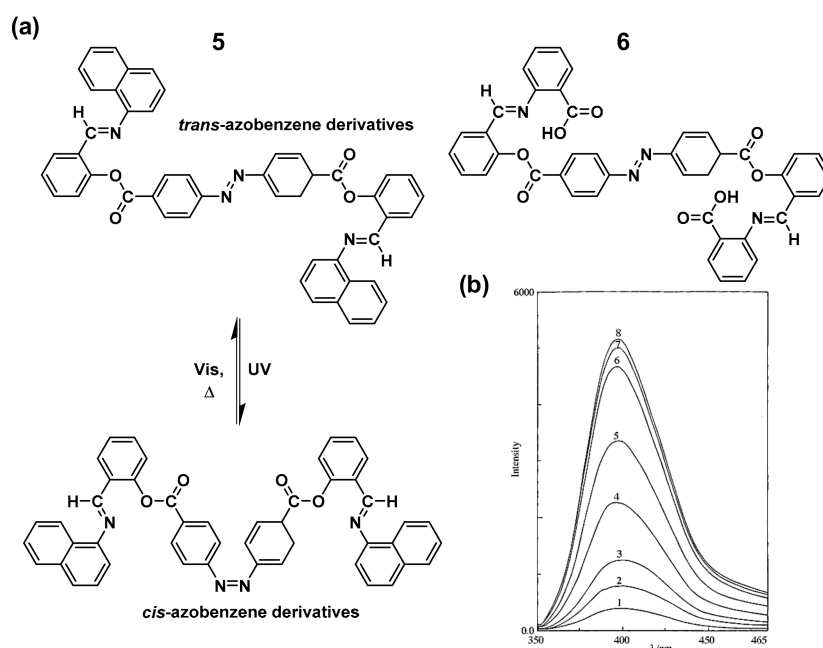


**Figure 5.** Working mechanism of the PET fluorescent molecular probe.

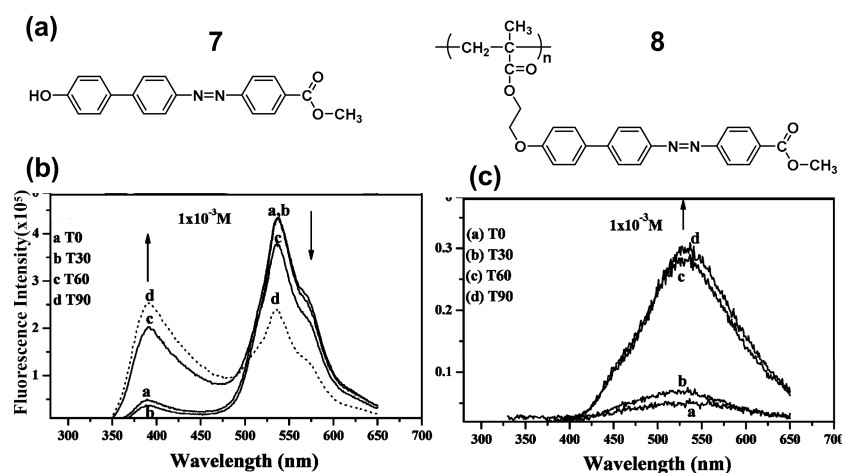
In compounds **5** and **6** (Figure 6a), PET occurs from the lone pair of electrons of the nitrogen atom in  $\text{N}=\text{N}$  to fluorophore 1-naphthyl and 2-carboxyphenyl moieties. The *cis*-isomers of **5** and **6** have a non-planar structure in the excited state, which limits the effective conjugation between  $\text{N}=\text{N}$  and the  $\pi$  electrons of the fluorophore, thus inhibiting electron transfer, albeit without binding to the guest. As shown in Figure 6b, the fluorescence of **5** increases significantly under UV irradiation [59].

Smitha and Asha synthesized a phenylphenol-bearing azobenzene **7** and its corresponding side-chain polymer **8** (Figure 7a) which exhibits the electron transfer from the  $\text{N}=\text{N}$  to the group of fluorophore, to a certain extent [60]. The unusually intense fluorescence spectra of the small molecule **7** showed that the aggregation peak at 535 nm decreased with continuous UV irradiation, while the emission intensity of the molecularly dissolved species at 390 nm increased, as shown in Figure 7b. Interestingly, the dilute solution of **8** also exhibited enhanced fluorescence under irradiation (Figure 7c), which can be attributed to the inhibition of PET from the *cis*-isomer with non-planar geometry.





**Figure 6.** (a) The molecular structure of **5** and **6**. (b) The corrected emission spectra of **5** as a function of irradiation time for forward E→Z process: (1) before irradiation; (2) irradiation for 5 min; (3) 15 min; (4) 30 min; (5) 45 min; (6) 60 min; (7) 75 min; (8) 115 min. (b) was reproduced with permission from [59]. Copyright 1998 The Royal Society of Chemistry.



**Figure 7.** (a) The molecular structure of phenylphenol azobenzene and its polymers (b) and (c) The fluorescence spectra of **7** and **8** upon UV irradiation after various time intervals (0 min, 30 min, 60 min, 90 min). (b,c) were reproduced with permission from [60]. Copyright 2007 American Chemical Society.

Furthermore, conjugated fluorophores having a strong “push-pull” electron effect mode providing a channel for electron transfer from the electron donor to the electron acceptor upon photoexcitation, which is known as intramolecular charge transfer (ICT), in a manner similar to PET. Mariyappan et al. designed and synthesized **9** and **10** (Figure 8), which when appended with  $Zn^{2+}$ , could be used in fluorescent chemosensors [61]. A significant increase in fluorescence intensity was observed, due to the synergy effects of chelation-enhanced fluorescence (CHEF) and ICT. After adding  $Zn^{2+}$ , the molecular structure of **9** and **10** becomes more planar and rigid, as well as inhibiting the intramolecular charge transfer from azo to hydroxyl groups.

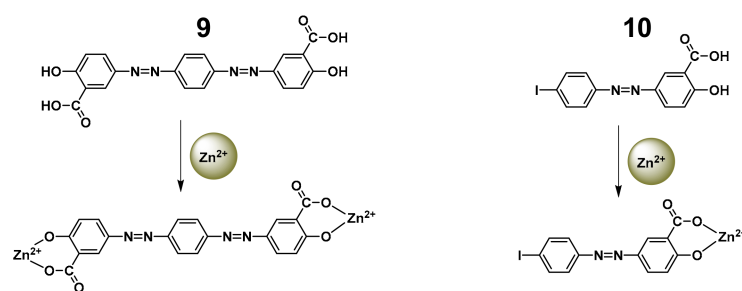


Figure 8. The molecular structure of azobenzene derivatives 9 and 10 which chelated with  $Zn^{2+}$ .

#### 4. Fluorescence from Aggregation

Extensive studies have revealed that reasonable fluorescence can be found in aggregates, such as micelles [62–70], vesicles [71–73], etc., of azobenzene derivatives in a manner similar to aggregation-induced emission (AIE), proposed by Tang et al. [74]. Herein, we compared the fluorescence of the AIE phenomenon to that of the aggregates of azobenzene compounds in detail, so as to understand the unusual fluorescence behavior of azobenzene derivatives with different methods of isomerization inhibition.

##### 4.1. Fluorescence from Aggregated Azobenzenes without Photo Irradiation

Theoretically, molecules with planar configuration are able to improve the luminous efficiency of molecular fluorescence to a certain extent; however, these molecules are prone to aggregate in face–face stacking, resulting in exciplex formation, which further leads to fluorescence quenching. However, the molecular structures with appropriate steric hindrance and available rotating or vibratory units, such as 1-methyl-1,2,3,4,5-pentaphenylsilole (Figure 9) [74], are the salient characteristics of AIEgens. Another factor reinforcing the AIE phenomenon is the restriction of intramolecular motion (including intramolecular rotation and intramolecular vibration) in the aggregates. In solution, non-radiative transition is the dominant deactivation process due to the rotational and vibrational motions in the unique AIE molecules, as shown in Figure 9. Upon addition of poor solvents, the solubility decreases, and aggregates start to appear, restricting intramolecular motions. At this point, radiative transition, the luminescence process, becomes the main mode of energy release from the excited state [75].

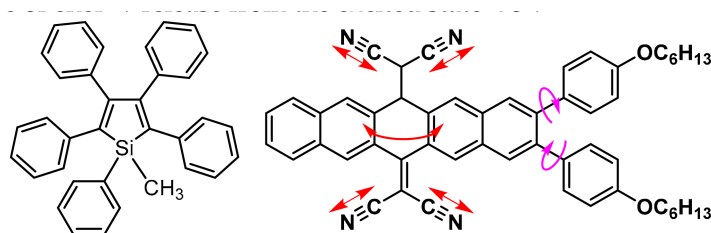
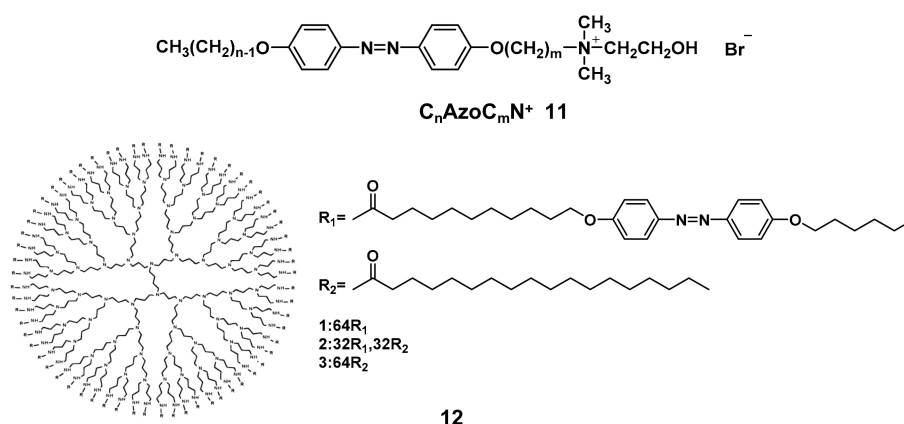


Figure 9. The molecular structure of 1-methyl-1,2,3,4,5-pentaphenylsilole and pentacenequinone derivatives.

Following the AIE mechanism, the aggregates of luminous azobenzenes achieved typically rigid molecular structures, and radiative decay was activated because of the restriction of intramolecular motion [76]. Increased fluorescence was achieved with azo compound 11 (Figure 10), the earliest luminescent azobenzene reported, via bilayer aggregates with a head-to-tail orientation [24]. However, fluorescence was significantly lower when the bilayer structure was replaced by a parallel arrangement in  $C_8AzoC_{10}N^+$ . In AIEgens, the intramolecular motion of dilute solutions and the steric hindrance or non-planar structures of the aggregated state generally prevent intermolecular  $\pi$ – $\pi$  stacking. In sharp contrast, fluorescence from azobenzene aggregates is more complicated, and  $\pi$ – $\pi$  stacking could exist in the aggregates [32,71]. Tsuda et al. demonstrated that dendrimer azobenzene 12 can self-assemble to form a large bilayer of vesicles stabilized by the  $\pi$ – $\pi$  stacking of

azobenzene moieties, leading to fluorescence, which was not observed in the previously reported AIEgens [71] (Figure 10).

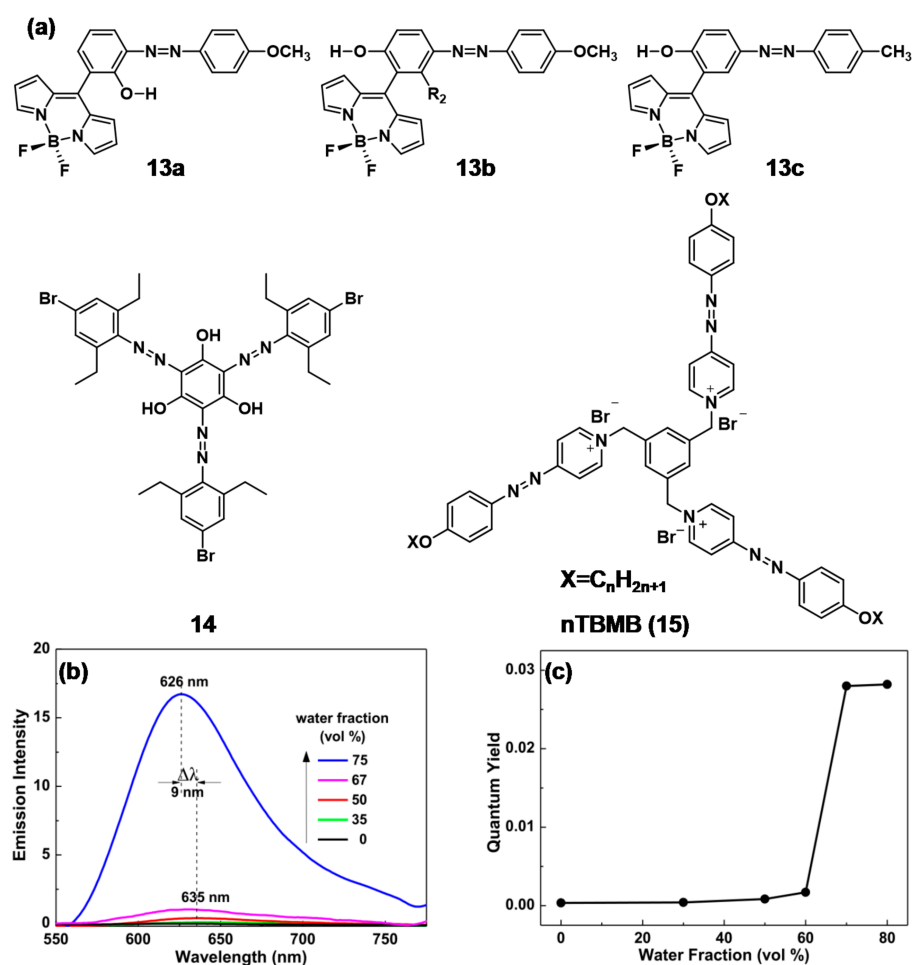


**Figure 10.** Molecular structure of azobenzene derivatives **11** and dendrimer azobenzene **12**.

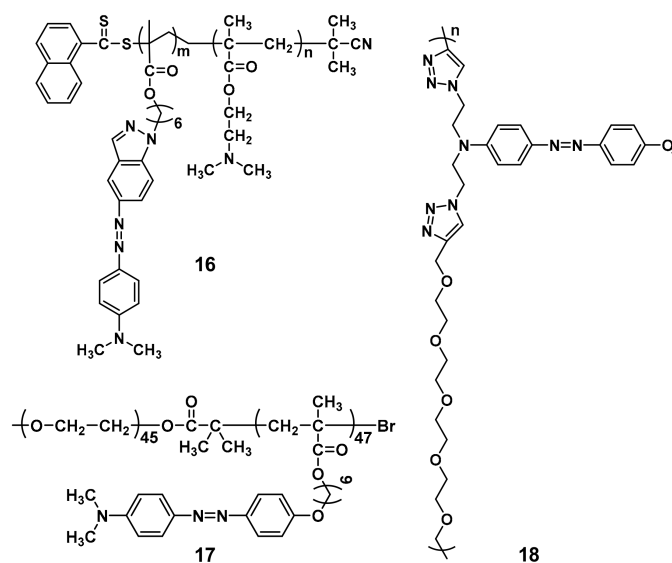
Motivated by the AIE phenomenon, the aggregation luminescence of azobenzenes has been extensively investigated [77–80]. Three fluorescent azo-phenol boron dipyrromethenes (BODIPYs), which have excellent fluorescent properties and are very amenable to modification [80–83], exhibited time-dependent AIE enhancement [77]. Nanoaggregates of **13b** and **13c** (Figure 11) initially demonstrated weak fluorescence after the addition of water, while favorable time-dependent fluorescence results were achieved. However, increasing the water content to >70% almost resulted in the elimination of the luminescence of **13a** in a manner similar to aggregation-caused quenching. Han et al. discovered the luminescent structure of azo nanofiber **14** (Figure 11) with multiple responses [78,79], and demonstrated AIE enhancement in polymer matrices (poly(methyl methacrylate) and poly(4-chlorostyrene)). These two examples demonstrate that the presence of *ortho* and *para* phenol groups may lead to the existence of an emissive tautomeric hydrazone form that restricts *cis-trans* isomerization [23,60,84].

As we have shown in our previous publications, a series of azopyridine-containing three-arm star salts nTBMB (**15**) [85] that exhibit a typical AIE effect upon addition of a poor solvent (Figure 11b,c), such as  $H_2O$ , were developed. The photoisomerization of **15** was completely blocked because of the formation of aggregates due to the high polarity of the water molecules and H bonding between  $H_2O$  and cationic azopyridinium moieties.

In addition to multiazobenzene-containing compounds, several other azobenzene-containing polymers that exhibit AIE fluorescence (Figure 12) have been reported. Zhu et al. fabricated the side-chain azoindole polymer (**16**), which exhibited strong fluorescence emission in a mixture of  $H_2O$  and THF and when irradiated with UV in  $CH_2Cl_2$  [86]. Fluorescence upon water addition was attributed to AIE, while the emission induced by UV may be caused by the inhibition of the PET of *cis*-**16**. The block copolymer (**17**), which belongs to the AIE system, easily self-assembles into luminescent vesicles in water because of its amphiphilic properties, which limit intramolecular motion owing to the tight stacking of the azo groups in the vesicles [72,73]. Azobenzene-containing side-chain alternating amphiphilic copolymer **18** features acidity-enhanced AIE in micelles because of the special alternating amphiphilic topology [87].

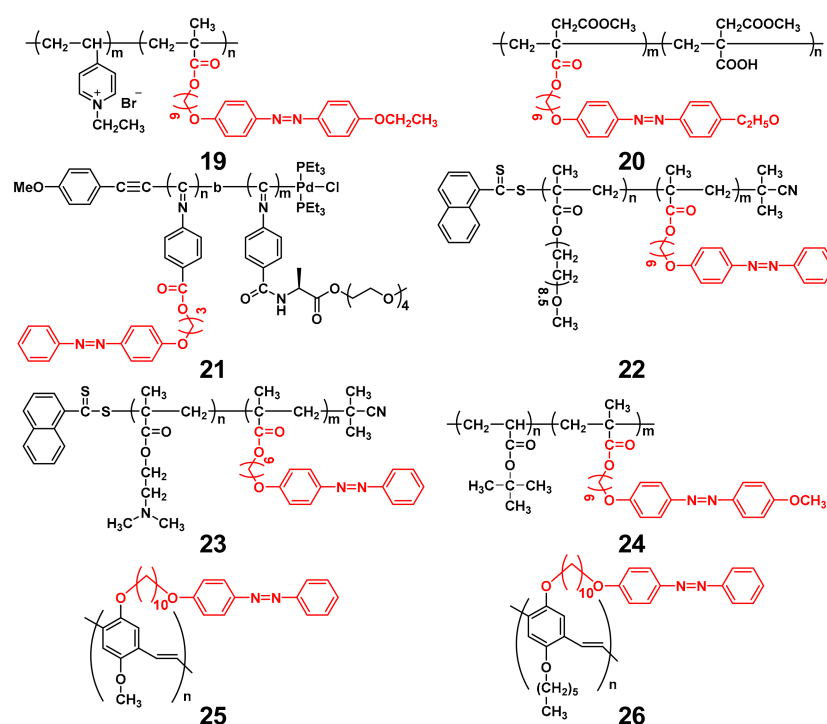


**Figure 11.** (a) The molecular structure of AIE azobenzene molecules **13**, **14**, **15**. (b) Emission spectra of the 10TBMB (**15**) in  $H_2O/THF$  mixtures with different water volume fractions ( $f_w$ , vol% volume fraction). (c) Changes in the fluorescence quantum yield ( $\Phi_F$ ) of 10TBMB (**15**) in  $H_2O/THF$  mixtures with  $f_w$ . (b,c) were reproduced with permission from [85]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 12.** The molecular structure of azobenzene-containing polymers **16**, **17** and **18** with AIE properties.

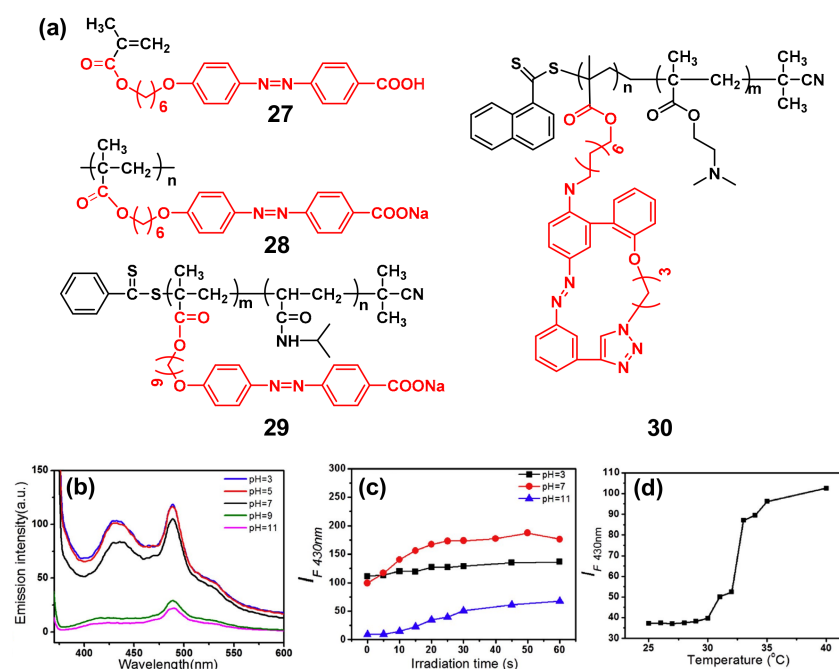
Fluorescence of azobenzene polymers has attracted considerable research attention because such polymers are applied as potential drug delivery carriers and fluorescent probes for living systems and possess smart multiple-response mechanisms that allow them to out-perform macromolecules. The azobenzene-containing amphiphilic polymers **19–30** (Figures 13 and 14), bearing long-chain ester groups between the polymer main chain and the azobenzene part, formed micelles in the presence of selective solvents [62–70,88]. Such polymers exhibit luminescence possibly because the azobenzene groups are confined to the core region of the micelles. In contrast, **25** and **26** may produce fluorescence because of the presence of the poly(p-phenylenevinylene) main chain in the place of the azobenzene moiety [88].



**Figure 13.** The molecular structure of azobenzene-containing polymers **19–26**.

Owing to the diverse plasticity of polymers, several multi-response fluorescent azobenzene polymers have been designed [69,70,72,73,89] (Figure 14). Azobenzene-containing monomer **27** and its homopolymer **28** exhibited fluorescence in response to UV radiation and pH changes in the mixtures of H<sub>2</sub>O and DMF [69,70]. In addition, multi-response fluorescence (due to pH and UV radiation changes) has also been reported in sphere micelles from another cyclic azobenzene-containing amphiphilic diblock copolymer **30** [89]. Fluorescence enhancement from micelle-like structure of block copolymer **29** has been observed. This was believed to be due to H bonding with azo carboxylic acid in response to changes in pH, UV radiation, and temperature [70]. The strong H bonding resulted in the formation of a tight micellar structure and considerable fluorescence under acidic conditions, while the response was adverse under basic conditions (Figure 14b). However, upon UV irradiation, the tighter stacking of the *cis*-isomer led to an increase in fluorescence under neutral and basic conditions (Figure 14c). Moreover, as the temperature rose above lower critical solution temperature, **29** underwent a thermal-induced transition from coil to sphere, which limited the rotation of the carboxyl azobenzenes and, thus, enhanced the fluorescence emission intensity (Figure 14d).

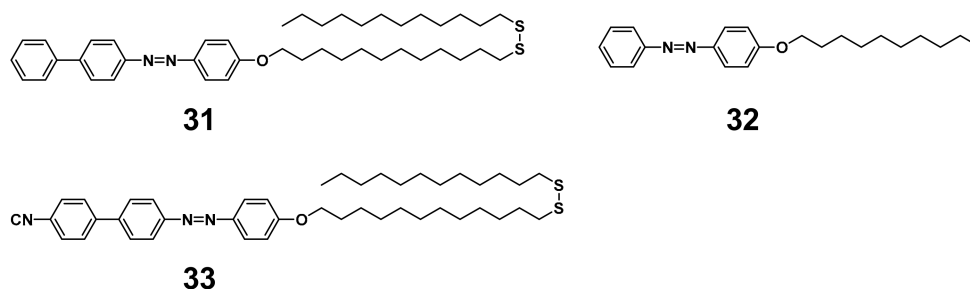




**Figure 14.** (a) The molecular structure of azobenzene-containing polymers **27–30**. (b) The change in fluorescence at 430 nm upon UV irradiation (365 nm, 70 mW/cm<sup>2</sup>). (c) The fluorescence emission spectra of **29** (5 mg/mL,  $\lambda_{\text{ex}}$ =360 nm, slit:10 nm) at different pH values. (d) The change in fluorescence of **29** at different temperatures ( $\lambda_{\text{ex}}$ =360 nm, slit 10 nm). (b–d) were reproduced with permission from [70]. Copyright 2016 Elsevier.

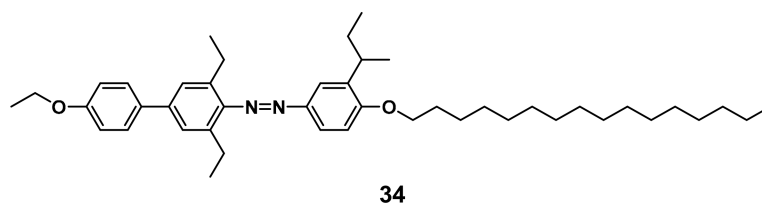
#### 4.2. Light-Driven Self-Assembly and Fluorescence Enhancement

Not only can aggregation occur spontaneously, but some nonfluorescent azobenzene derivatives **1**, **3**, **4**, **31–33** can self-assemble under photoirradiation into luminous spherical aggregates in their *cis* state (Figure 2, Figure 4, and Figure 15) [50,54,55,90,91]. The curved *cis*-isomer has higher polarity and hydrophilicity than the rod-shaped *trans*-isomer; in contrast, the long alkyl chains at *para* position of the azobenzene impart inherent hydrophobicity, resulting in the strong fluorescence due to spontaneous formation of spherical organic aggregates.



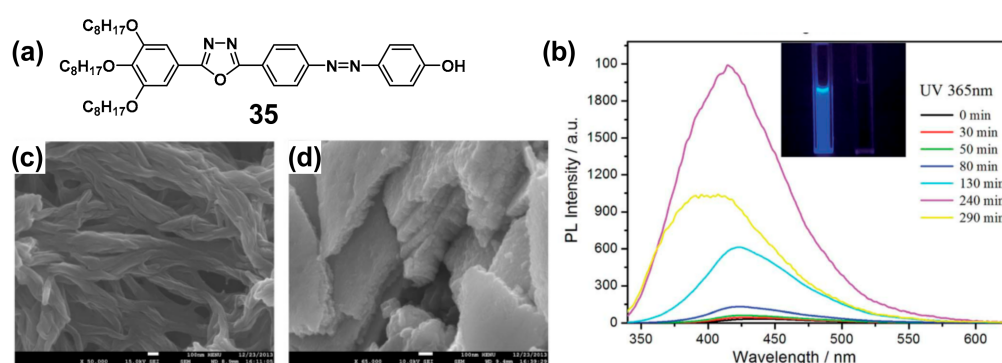
**Figure 15.** The molecular structure of azobenzene derivatives **30–33**.

A long-lived crystalline aggregate of striking fluorescent azobenzene derivative **34** was fabricated by Han et al. [32]. Unlike the luminescence of the previously mentioned AIEgens, the aggregates lying in their strong  $\pi$ – $\pi$  stacking between aromatic rings (Figure 16), as well as the van der Waals interaction between the long alkyl chains, significantly promoted the stacking of *cis*-**34**.



**Figure 16.** The molecular structure of **34**.

Guo et al. observed similar light-driven fluorescence enhancement in **35**, which is named AOB-t8 (Figure 17a) [92]. The *cis*-AOB-t8 solution exhibited 306-times higher fluorescence intensity than the *trans*-AOB-t8 solution (Figure 17b), because of the significant structural mutation from fiber-like *H*-aggregation in *trans*-AOB-t8 to layered *J*-aggregation in *cis*-AOB-t8 (Figure 17c,d).



**Figure 17.** (a) The molecular structure of azobenzene derivatives **35**. (b) Fluorescence spectra of **35** in ethonal ( $1 \times 10^{-3}$  M) under 365 nm irradiation for different times at room temperature. Inset: the image of **35** after (left) and before (right) UV irradiation. (c,d) SEM images of **35** in ethonal ( $1 \times 10^{-3}$  M) before exposure to UV light and under irradiation at 365 nm for 290 min, respectively. (b–d) were reproduced with permission from [92]. Copyright 2014 The Royal Society of Chemistry.

From small molecules to polymers, azobenzene-containing compounds can exhibit notable fluorescence behaviors either in a selective solvent or upon light irradiation.

## 5. Enhanced Fluorescence in Special Cases

Metal-enhanced fluorescence (MEF) refers to fluorescence enhancement of dyes in the vicinity of free or immobilized metal particles [93]. Our previous work observed that the fluorescence of azopyridine **36** (AzoPy) was enhanced upon addition of silver nanoparticles (Figure 18) [94]. Furthermore, when Br<sub>2</sub> was inserted into the AzoPy molecule and Ag NPs, the MEF effect became more intense. Compared with Ag⋯AzoPy, Ag⋯Br-Br⋯AzoPy showed three-times greater fluorescence emission enhancement owing to the extended distance between the azopyridine molecule and the Ag NP surface due to the added Br<sub>2</sub>.

Several azobenzene derivatives (**37–43**) with H-bonding or cyclic structure can also emit fluorescence via isomer locking (Figure 19). The existence of intra- and intermolecular H-bonding [95,96] and ring-constrained structure [97–101] in azobenzene compounds locked the molecule tightly, which increases the planarity and rigidity of the molecule, thus inhibiting the *cis*–*trans* isomerization rate.

Studies have demonstrated that azobenzene-containing heteroatomic coordination has a similar locking effect. In a series of organometallic azobenzene Pd(II) complexes **44** (Figure 20) [102–105], cyclopalladation increases the rigidity of the azo bonds, thus reducing the efficiency of photoisomerization and leading to fluorescence.

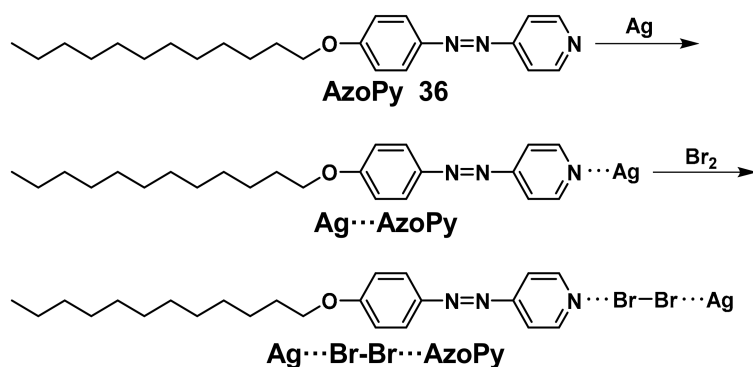


Figure 18. The molecular structure of azopyridine complex 36.

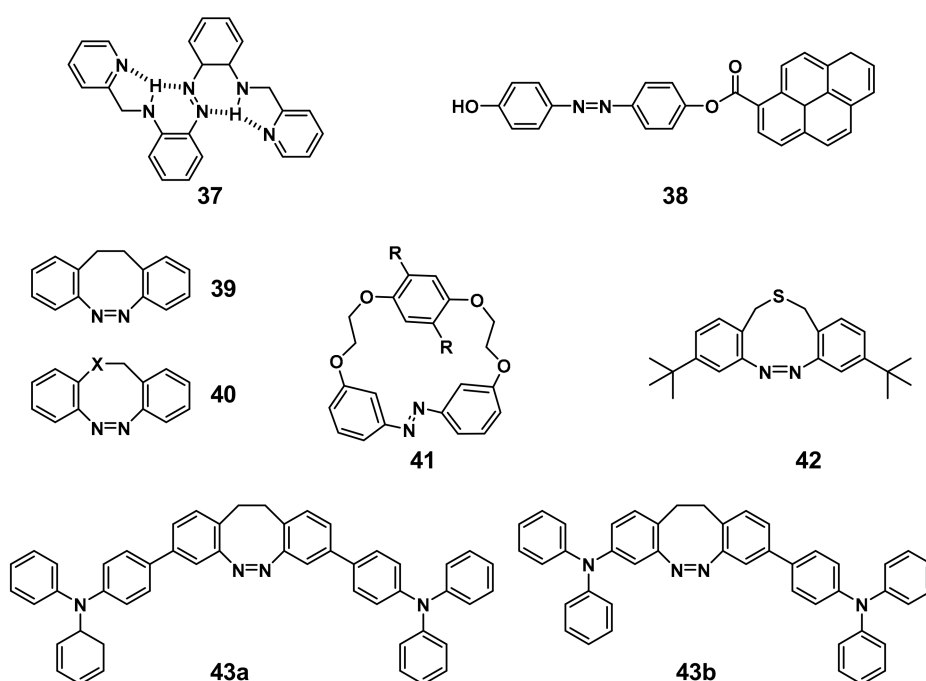


Figure 19. The molecular structure of azobenzene compounds 37–43.

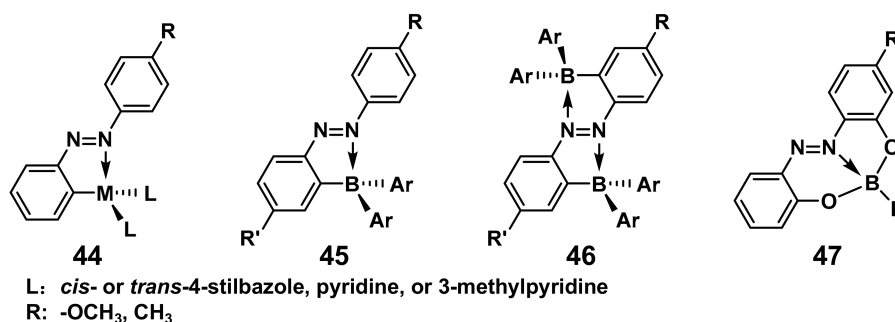


Figure 20. The molecular structure of a series heteroatomic coordination azobenzene complex 44–47.

The lone pair electrons of the N atom in boron-substituted azobenzenes 45–47 can be used to form an N–B coordination bond, and the N–B action restricts the rotation of the N–C bond, thus inhibiting photoisomerization. In addition, the N–B interaction perturbs the orbital energy levels, leading to significant fluorescence during the relaxation process of  $S_1$ – $S_0$  [106–110]. Kawashima et al. reported the most intensely flu-

orescent boron-substituted azobenzene (**45**), taking advantage of the B–N interaction (Figure 20) [57,106–109]. The B–N-coordinated structure is extremely compact, imparting extraordinary rigidity to the molecule, which considerably inhibits any conformational change of the azobenzene that might prevent the photoisomerization process. Hence, **45** exhibits intense green fluorescence with significantly high quantum yield.

## 6. Conclusions and Outlook

This paper reviewed methods that achieve luminescence in azobenzene, including those involving *ortho*- or *para*-substitution to equalize the rate of photoisomerization, inhibiting various possible non-radiative transitions (such as PET and ICT) and aggregation. It is possible to design a PET-type azobenzene molecule and then inhibit the PET moiety by inducing *cis*-isomerization through UV irradiation; the azobenzene molecules with a push-pull electronic structure are designed to match the metal ions that inhibit the ICT of azo molecules. These two mechanisms enable switchable fluorescence in azobenzene compounds. Studies have demonstrated that azobenzene exhibits AIE due to optical drive or in the presence of selective solvents. In particular, the azo molecules compounded with metal nanoparticles also exhibit enhanced fluorescence because of the MEF effect. Strong intermolecular forces such as those induced by H bonding, cyclic structures, metal coordination, and B atom coordination can be utilized to lock the azobenzene molecular structure, thus inhibiting its isomerization and causing fluorescence. Luminescence in azobenzene is not always caused by a single factor; it is often the result of multiple mechanisms. Although several cases of luminescence in azobenzene have been described herein, the luminescence efficiency in most of these examples is more limited compared to that of other existing organic fluorescent materials; consequently, improving the luminescence efficiency of azobenzene compounds is one of the main research goals of researchers in this field at present. This review highlights the close relationship between the molecular structures of azobenzenes and their fluorescence mechanisms to inspire research of fluorescent azobenzenes and to provide a detailed understanding of their remarkable luminescence capabilities.

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