

EXCITATION BAND DEPENDENCE OF FLUORESCENCE FOR SOME CHLORO-AZOMONOETHERS

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The fluorescence behavior of a series of chloro-azomonoethers was studied under four distinct UV excitation bands: 275 nm, 365 nm, 385 nm, and 400 nm. These excitation wavelengths were selected to explore their varying capabilities to induce/not induce isomerization in azocompounds. Notably, excitation at 275 nm produced fluorescence through a distinct mechanism, although the specific chromophore could not be identified. A correlation between the presence of chlorine atoms and the emergence of bimodal fluorescence behavior was observed. In addition, spectral red-shifting indicated the presence of J-type (head-to-head) molecular aggregation.

Keywords: fluorescence, azo dye.

1. Introduction

Azobenzene and its derivatives are widely studied due to their light-induced reversible isomerization, which alters molecular geometry. Ultraviolet light initiates a transition from the thermodynamically stable *trans* form to the less stable *cis* form, a process reversible by visible light or thermal relaxation [1–3]. This photoisomerization affects numerous physical properties, including aggregation behavior, which differs between the two isomeric states due to structural changes. Typically, azobenzene derivatives exhibit low fluorescence quantum yields [4,5], as non-radiative *trans*–*cis* interconversion pathways dominate. However, when isomerization is suppressed—such as in rigidified or metal-coordinated systems [6]—fluorescence intensity may increase. Studies have shown that fluorescence can also arise in azobenzene-based systems where chromophores adopt ordered arrangements, such as head-to-tail packing within self-assembled bilayers [7]. Moreover, long-term UV exposure has been associated with enhanced fluorescence in azobenzene compounds that form stable aggregates [8,9].

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In this context, fluorescence efficiency and its stability become critical parameters for evaluating organic chromophores, especially since aggregation often leads to quenching. This study investigates how fluorescence intensity and behavior depend on the excitation band in chloro-azomonoether derivatives, particularly in relation to *trans*–*cis* isomerization and molecular aggregation phenomena.

2. Experimental sections

Materials and their structural formulas

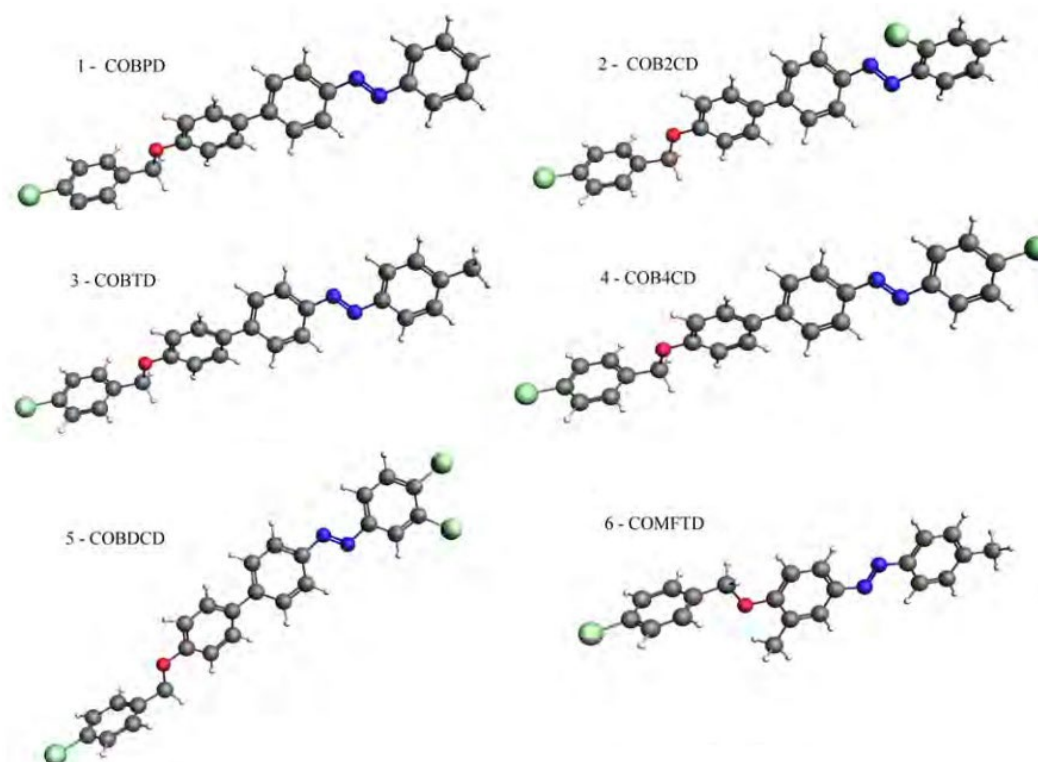


Fig. 1. Optimized structures of compounds 1-6 in *trans* form calculated by sTDDFT/B3LYP/TZP (Amsterdam DFT - Amsterdam Modeling Suite 2023.1)

The study focused on six chloro-azomonoether derivatives (Figure 1), each incorporating structural variations in the diazene substituents: 1-COBPD: 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-phenyldiazenes; 2-COB2CD: 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(2-chlorophenyl)diazenes; 3-COBTd: 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(p-tolyl)diazenes; 4-COB4CD: 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(4-chlorophenyl)diazenes; 5-

COBDCD: 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(3,4-dichlorophenyl) diazene; 6-COMFTD: 4-(4-chlorobenzyloxy)-3-methylphenyldiazene.

These compounds were synthesized to probe the influence of halogen substitution and steric configuration on their optical properties, particularly under UV excitation.

UV-Vis absorption spectra of studied substances

The electronic absorption spectra were recorded using an Ocean Optics HR4000 spectrometer (Figure 2). Measurements were conducted in acetone solution at concentrations between 10^{-6} and 10^{-5} M. The spectra revealed three primary absorption bands consistent with azo chromophores [3]: B-band ($\pi \rightarrow \pi^*$): Observed at wavelengths between ~ 320 – 343 nm, associated with aromatic ring transitions; second band $\pi \rightarrow \pi^*$ transition: Detected in the ~ 360 – 392 nm range; $n \rightarrow \pi^*$ transition: a partially forbidden transition attributed to the azo group, appearing in the visible range (~ 420 – 468 nm).

An additional high-energy UV sub-band (~ 260 nm) was suppressed due to acetone's strong absorbance in this region. Nonetheless, during fluorescence experiments, this level can still be populated via high-intensity UV excitation. In alternative solvents like dioxane, this deep-UV band becomes more accessible [3].

Experimental set-up

Fluorescence measurements were performed using a custom-designed experimental setup, incorporating both traditional and colinear optical configurations. The core assembly consisted of a plastic composite sample holder integrating:

- a fiber optic coupler with a converging lens,
- a quartz cuvette containing the sample,
- and a UV LED mounted on a thermally regulated platform.

In the standard geometry, excitation light was delivered perpendicularly to the fluorescence collection axis, with detection performed via an optical fiber (Thorlabs, Newton, NJ) placed close to the cuvette surface and connected to the HR4000 spectrometer.

However, due to limitations such as weak fluorescence signal intensity and attenuation within the medium, especially under 270 nm excitation, this perpendicular method proved suboptimal. The low optical power of the LED and acetone's UV absorption further reduced signal clarity.

Consequently, we employed a 180-degree head-on configuration, where excitation and emission paths are aligned oppositely. This geometry enhanced signal collection efficiency but introduced the risk of excitation light contaminating the emission spectrum. To mitigate this, the sample concentration was carefully adjusted to ensure complete absorption of excitation light within the cuvette, thus minimizing direct transmission artifacts.

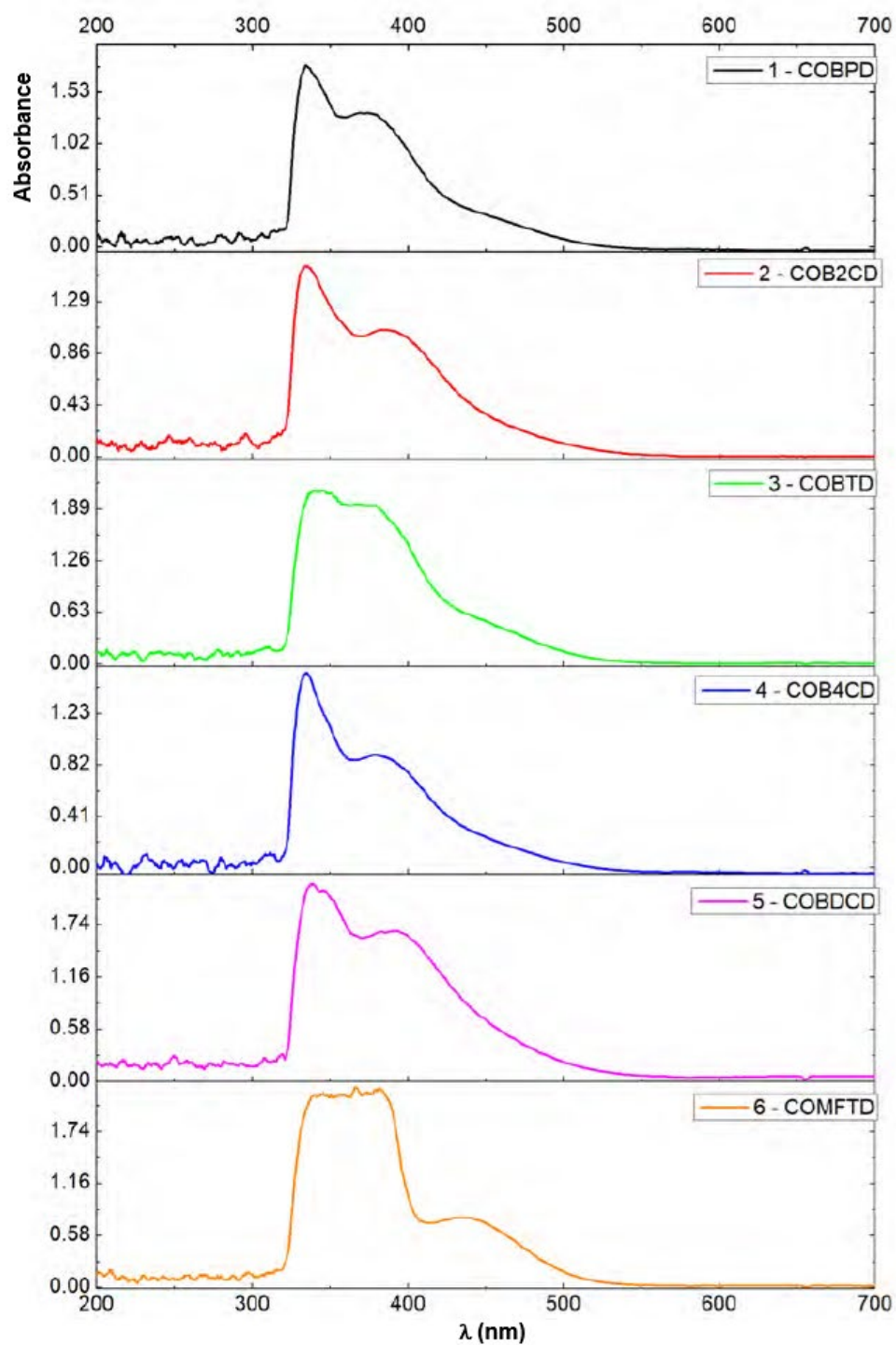


Fig. 2. UV-Vis spectra for studied azocompounds in pure acetone.

Fluorescence Response of Chloro-Azomonoethers Under Variable UV Excitation

We successfully obtained a well-defined fluorescence response for five of the six studied compounds. Compound 6 (COMFTD) displayed perturbations under three of the four excitation wavelengths, likely due to structural differences affecting its chromophore environment.

To ensure data consistency, fluorescence spectra were normalized with respect to: a) the integration time of fluorescence acquisition (reference: 1000 ms), b) the luminous flux of the UV-LED sources (reference: 1000 mW), and c) the emission angle of the LEDs (reference: 120°).

The UV LEDs used were as follows [10]:

1. REFOND RF-C37P0-URH-AR (UV-C 270–280 nm; 15 mW),
2. LITEON LTPL-0034UVH365 (UV-A 365 nm; 665 mW),
3. HONGLI ZHIHUI HL-C3535-F8-385 (UV-A 380–390 nm; 700 mW),
4. ProLight Opto PK2B-3JLE-NV (UV-A 390–410 nm; 1310 mW).

Spectral distributions of the LEDs (not shown) confirmed consistency with manufacturer data.

Influence of excitation band on the fluorescence spectrum

Solutions of the chloro-azomonoethers were prepared in high-purity acetone at concentrations of 10^{-6} – 10^{-5} M. Fluorescence spectra were recorded after short exposure times (~1 second) by using varying UV excitations. The principal characteristics of the fluorescence spectra are shown in Table 1 and Figures 3 and 4, where notable shifts in emission spectra as a function of excitation wavelength are observed.

Table 1

Fluorescence characteristics: maximum emission (nm)/ amplitude/ spectral shape changes

Compounds	Excitations			
	270 nm	365 nm	380–390 nm	390–410 nm
1 COBPD	578.8/H/SC	579.04/VH/SSC	574.6/M/RSC	571.8/L/LSC
2 COB2CD	579.3/VH/SC	589.6/H/SSC	579/M/SSC	579L/LSC
3 COBTD	579.04/VH/SC	569.7/H/SC	566.6/H/SSC	562.2/L/LSC
4 COB4CD	579/M/SC	566.3/M/SSC	574.4/M/SSC	564.3/L/LSC
5 COBD CD	584.8/H/SC	579.0/VH/SSC	574.6/M/SSC	577.7L/LSC
6 COMFTD	564.6/VH/SC	553.4/M/SSC	538.9/M/RSC	524.4/L/LSC
Very high (VH) >50000 a.u., 20000<High (H)<50000 a.u., 2000<Moderate (M)<20000 a.u., Low (L)<2000 a.u., SSC- significant spectral shape changes, SC-spectral shape changes, RSC- reduced spectral shape changes, LSC- low spectral shape changes				

Observations:

- Azo compounds showed characteristic fluorescence behavior, in agreement with prior studies [11–13].

- Notably, excitation at 365 nm led to significant spectral shape changes across most samples; the 270 nm excitation had a subtler but similar impact.

- An unexplained fluorescence band, centered around 700 nm, emerged under some conditions and remains under investigation.

- The most pronounced shape change was observed for compounds 4 (COB4CD), 5 (COBD CD), and 2 (COB2CD), which contain more chlorine atoms symmetrically distributed across the molecular structure. Compounds 1, 3, and 6 showed reduced intensity.

The correlation between fluorescence intensity and chlorine content suggests that substitution patterns on the molecular backbone influence emission, possibly via changes in planarity and chromophore conjugation [14–20].

Excitation-Wavelength Dependence and Molecular Aggregation

A red shift in fluorescence emission maxima was observed with increasing excitation wavelength (Figures 3-4), likely resulting from J-type (head-to-head) aggregation due to intermolecular interactions [14]. According to aggregation-induced emission (AIE) theory, such rigid aggregation can suppress non-radiative decay and enhance fluorescence [21,22]. Observations:

- At 270 nm excitation, five compounds showed a common emission band at 579 nm, indicating a central chromophore origin.

- COMFTD (Compound 6) deviated, showing a blue-shifted band at 564 nm, consistent with its modified central core.

- At longer excitation wavelengths, red-shifted emissions increased progressively in the order: COMFTD < COBTD < COB4CD < COBPD < COBD CD < COB2CD, suggesting growing influence of side-chain structure on emission.

This trend supports the idea that different chromophoric environments, possibly altered by isomerization or aggregation, contribute variably to emission characteristics.

The fluorescence experiment involves a complex series of photophysical and photochemical processes. Some of these processes occur simultaneously, while others follow one another in a sequential manner. Initially, a UV-induced isomerization takes place, as previously described in the literature [3]. The same ultraviolet radiation also plays a crucial role in the fluorescence mechanism. These experimental conditions affect the conformational state and molecular arrangement of the isomers within the solution.

The *cis* isomer formed under UV exposure exhibits fluorescence immediately upon generation. Fluorescence emission is observed from both *cis* and *trans* isomeric forms.

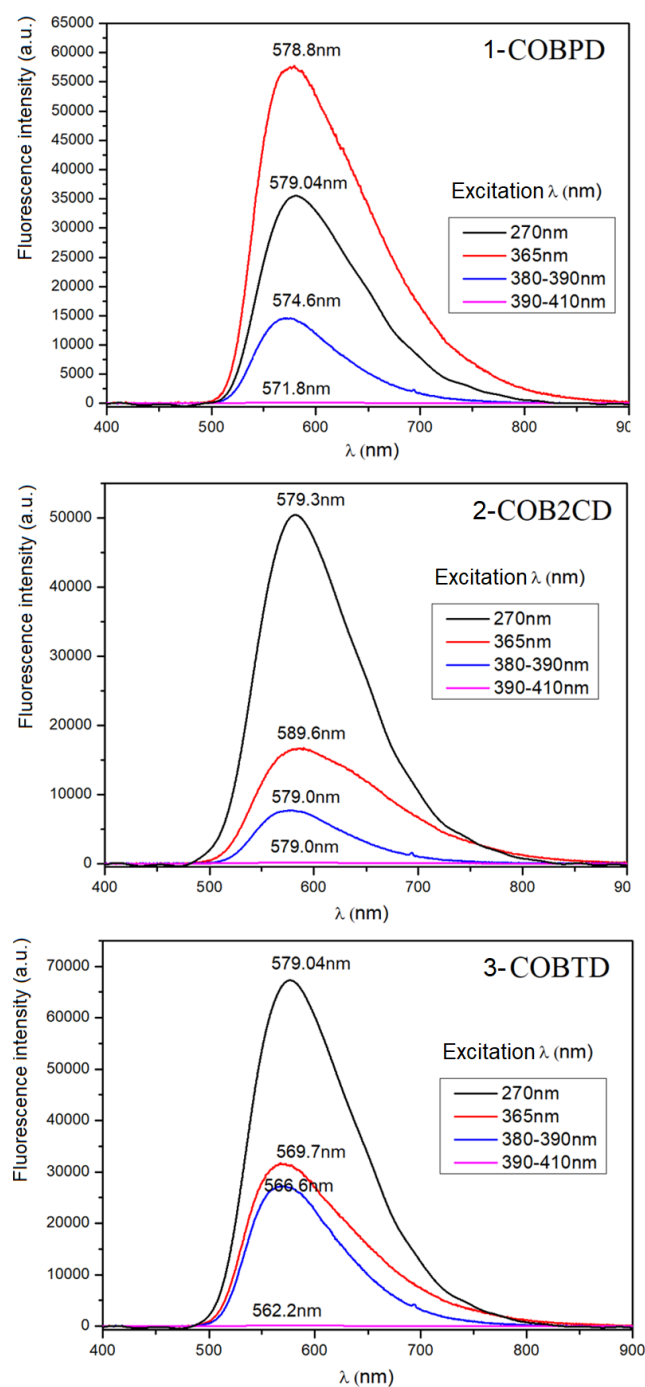


Fig. 3. Normalized emission spectra of fluorescence for azocompounds 1-3 in acetone for the four excitation radiations.

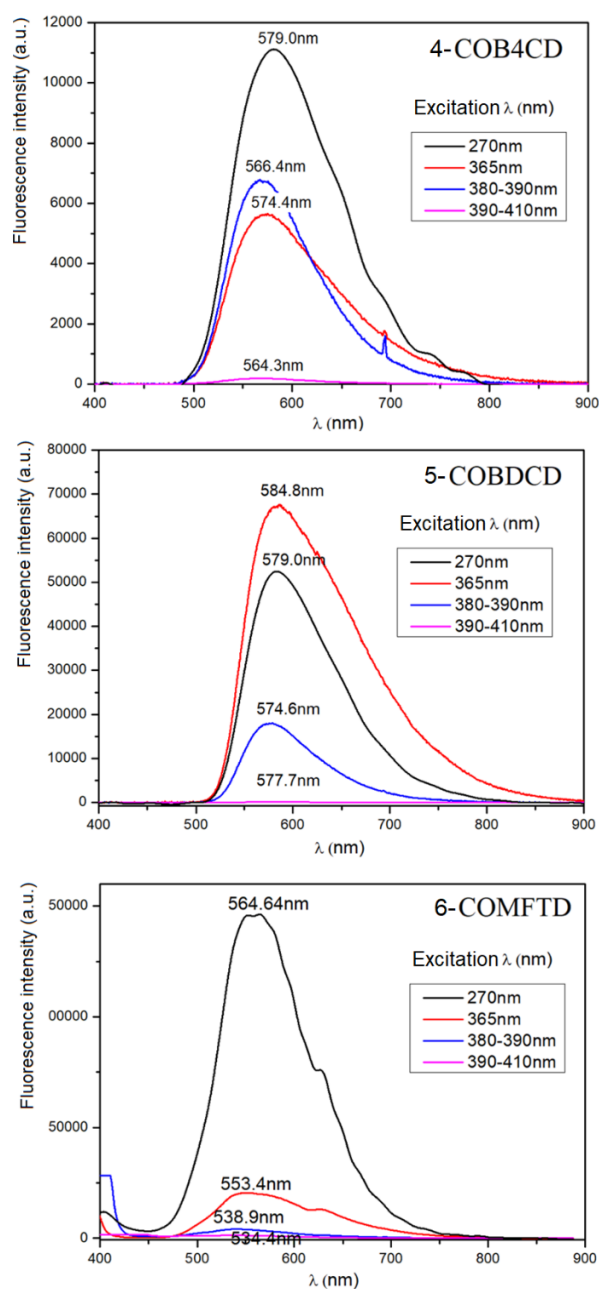


Fig. 4. Normalized emission spectra of fluorescence for azocompounds 4-6 in acetone for the four excitation radiations.

The isomeric species can organize into three distinct configurations: as isolated molecules (monomeric state), H-aggregates characterized by lateral alignment, and J-aggregates defined by a head-to-tail arrangement [23]. The distinct geometrical

conformations of the *cis* and *trans* isomers in solution can facilitate the formation of either H-type or J-type molecular aggregates, the latter representing a more loosely associated configuration. Given the substantial difference in dipole moments between the two isomeric forms, it is highly plausible that their modes of aggregation differ accordingly. Previous studies have demonstrated that the type of molecular assembly influences the absorption characteristics: H-aggregates typically induce a hypsochromic (blue) shift, while J-aggregates cause a bathochromic (red) shift in comparison to the absorption maximum of the monomeric state [23].

This observation likely accounts for the red shift noted in the experimental UV absorption spectra (Figure 2 from reference [3]), when compared to theoretical spectra generated using quantum chemical calculations based on sTDDFT/B3LYP/TZP functionals within the Amsterdam DFT framework (data not shown). These aggregation states also play a significant role in modulating both the kinetics of photoisomerization and the intensity of fluorescence, as discussed further below.

Highly compact H-type aggregates tend to exhibit slower photoisomerization dynamics due to the restrictive nature of their molecular packing. In contrast, isomers arranged in J-aggregates or present in monomeric form undergo much more rapid photoisomerization. As a result, during UV irradiation and fluorescence measurements, H-aggregates show delayed isomerization over extended timescales. Meanwhile, J-aggregates and monomeric species, which quickly convert to the *cis* configuration upon UV exposure, are more actively involved in fluorescence emission. Prior studies on block copolymers incorporating azobenzene moieties have also reported states characterized by both high photoisomerization efficiency and strong fluorescence emission [24–29].

The interplay between isomerization and fluorescence in azobenzene derivatives is well documented. These compounds generally exhibit low fluorescence efficiency due to rapid non-radiative deactivation of the excited state via isomerization. Notably, azobenzene does not conform to Kasha's rule, which posits that fluorescence arises predominantly from the lowest vibrational level of the first excited singlet state (S_1), and phosphorescence from the lowest vibrational level of the first triplet state (T_1). At room temperature, the fluorescence quantum yield for the $S_1 \rightarrow S_0$ transition in azobenzene is reported to be exceptionally low, approximately 2.53×10^{-5} [30]. Nevertheless, under specific conditions where steric constraints inhibit internal conversion from the S_2 ($\pi\text{--}\pi^*$) to the S_1 ($n\text{--}\pi^*$) state, emission from the S_2 state becomes more favorable, resulting in an observable increase in fluorescence intensity [31].

Azo compounds offer a compelling application in conformational locking through the formation of specific molecular interactions that restrict rotational freedom,

thereby enhancing fluorescence emission and enabling their use as molecular markers [32,33].

Dual or bimodal fluorescence is a rare and unconventional photophysical phenomenon exhibited by a limited number of chromophores. It involves the emission of photons from two distinct excited electronic states, typically resulting in two separate fluorescence bands [11–13, 34–36].

This behavior is generally attributed to either the formation of two distinct emissive conformers through excited-state electronic rearrangement or the generation of separate fluorescent species via photochemical transformation. Both mechanisms conform to Kasha's rule. In the current context, the observed bimodal fluorescence may arise from radiative transitions from both the S_1 and S_2 states, with emission from S_2 being significantly less probable. Experimental data confirm that excitation at higher-energy UV wavelengths (270 nm and 365 nm) is necessary to populate the S_2 (π – π^*) state. In contrast, lower-energy excitation near the UV-visible boundary (380–410 nm) yields a single, lower-intensity emission band, which decreases further as the excitation wavelength increases.

This dual-emission behavior holds potential for biosensing applications, as proposed in previous studies [36].

3. Conclusions

Fluorescence in azomonoether compounds is strongly influenced by both excitation wavelength and molecular structure.

Excitation at 270 nm initiates a distinct emission mechanism, possibly involving a yet-unidentified chromophore.

Chlorine substitution patterns contribute to bimodal emission, likely through their role in aggregation and chromophore stabilization.

The observed red shifts support J-type aggregation, which enhances fluorescence and modulates isomerization kinetics.

The coupled dynamics of isomerization and fluorescence in these systems open avenues for photochemical control and sensor applications.

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