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## Ultrafast nonradiative decay from higher-lying excited states in azulene-dimers

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The anti-Kasha fluorescence nature of azulene has been explained by the large energy gap between the second excited state and the lowest excited singlet state. While such property is expected to be perturbed in the presence of electronic interchromophore interactions without a change in the  $S_n$ – $S_1$  energy gap, the study of the excited-state dynamics of azulene assemblies or oligomers remains scarce. In this study, we designed dimers with diverse rigid bridge structures with controlled intermolecular interactions. Based on the ultrafast spectroscopy, we reveal that nonradiative deactivation from  $S_2$  states was markedly accelerated upon conjugation, indicating that anti-Kasha behavior is highly sensitive to interchromophoric coupling. The results strongly suggest that careful optimization of interchromophore interactions is crucial for utilizing anti-Kasha-type molecules for energy or charge transport.

### Introduction

Excited-state relaxation is a fundamental phenomenon upon molecular excitation. According to Kasha's rule, rapid internal conversion from a higher-lying excited state leads to emission from the lowest excited electronic state of a given multiplicity,<sup>1</sup> regardless of the excitation energy. However, some molecules with significant energy gaps between higher-lying singlet excited states ( $S_n$ ) and the lowest singlet excited state ( $S_1$ ) deviate from this rule and exhibit fluorescence from the  $S_n$  state, known as "anti-Kasha fluorescence". Anti-Kasha fluorescence has been widely reported since its discovery.<sup>2–6</sup> Beyond being a subject of scientific curiosity, efforts to control this phenomenon have opened new avenues for manipulating photophysical and photochemical processes,<sup>7</sup> including photochemical reaction<sup>3,8,9</sup> and singlet fission,<sup>10–12</sup> making the use of higher energy states increasingly essential.

Azulene, a structural isomer of naphthalene composed of fused five- and seven-membered rings, has long been recognized as a prototypical example of anti-Kasha fluorophores (Fig. 1a).<sup>13</sup> Since the first report of anomalous fluorescence characteristics,<sup>6</sup> extensive studies have focused on controlling azulene's  $S_2$  fluorescence by introducing heavy atoms,<sup>14–16</sup> breaking molecular symmetry,<sup>5,17</sup> and reducing the  $S_2$ – $S_1$

energy gap.<sup>3</sup> Recent advances in quantum chemical calculations, notably the work by Dunlop and colleagues, have highlighted the importance of ground and excited-state (anti-) aromaticity in determining the degree of geometric relaxation in the excited state.<sup>13</sup>

While the excited-state property of azulene is also affected by interchromophore interaction, there are few reports on azulene in aggregated or oligomeric systems. Stevens *et al.* reported the ultrafast (<ps) relaxation from the  $S_2$  state in calix[4]azulene, suggesting strong electronic interaction among azulene units.<sup>18</sup> Given the recent synthetic progress in azulene-fused molecular backbones<sup>19–30</sup> and the observation of  $S_n$  emission from some of them,<sup>31</sup> a systematic investigation of azulene multichromophoric systems with tunable electronic interactions would be a crucial milestone toward its potential applications in photonic and optoelectronic systems where azulene units often aggregate.

In this work, we synthesized a series of azulene dimers with various bridge structures and investigated their excited-state dynamics from the  $S_2$  state with ultrafast spectroscopy (Fig. 1b). Molecular conjugates with rigid bridge structures serve as ideal models for studying processes among chromophores, as the complex intermolecular processes can be suppressed in diluted conditions, and electronic interactions among chromophores can be finely controlled. We employed xanthene and phenylene linkers because of their synthetic feasibility. For the dimer with suppressed electronic interaction between azulene units, we used a durylene bridge, which is nearly orthogonal to the azulene plane at the potential minimum.<sup>32,33</sup> This systematic structural variation enables us to evaluate the effect of interchromophore interactions in the excited-state relaxation.

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Fig. 1 (a) Chemical structure of azulene and the schematic diagram of the anti-Kasha fluorescence. (b) Chemical structures of **A1**, **A2**, **A3**, **A4** and **A5**.

By comparing the  $S_2$ -state relaxation dynamics across these molecular architectures using ultrafast spectroscopy, we aim to elucidate the underlying principles that govern anti-Kasha behavior in azulene and its multichromophoric systems. We found that anti-Kasha emission in azulene is highly sensitive to interchromophore interactions and can be readily quenched even when the  $S_2$ - $S_1$  energy gap remains relatively large. Our ultrafast measurements revealed that the internal conversion from  $S_2$  to  $S_1$  accelerates to the picosecond timescale upon aggregation or through-bond coupling. These findings enhance our understanding of azulene photophysics and offer critical design guidelines for developing next-generation photoresponsive materials that exploit higher-lying excited states.

## Experimental section

### Compounds

Detailed synthesis procedure and characterizations of **A1**, **A2**, **A3**, **A4** and **A5** are available in SI.

### Instrumentation

$^1\text{H-NMR}$  (400 MHz) spectra were measured on a JEOL JNM-ECZ400S using TMS as the internal standard. Elemental analyses were conducted at the Elemental Analysis Center, Kyushu University. UV-Vis absorption spectra were recorded on a JASCO

V-670 spectrophotometer and a Horiba Fluoromax 4 fluorometer utilising a Xenon lamp. PL spectra were measured using a JASCO FP-8700 NIR spectrofluorometer.

## Results and discussion

### Steady-state spectra and fluorescence quantum yields

The absorption spectrum of the azulene monomer was consistent with previously reported data,<sup>34</sup> showing a weak and broad  $S_0 \rightarrow S_1$  transition (attributed to the HOMO-LUMO excitation) along the molecular  $y$ -axis over the range of approximately at 550–700 nm, and a more intense  $S_0 \rightarrow S_2$  band around at 340 nm, which includes transitions such as HOMO  $\rightarrow$  LUMO+1 and HOMO-1  $\rightarrow$  LUMO (Fig. 2a). The strongest absorption peak at around 275 nm corresponded to the  $S_0 \rightarrow S_5$  transition, also involving contributions from nearby transitions such as  $S_0 \rightarrow S_3$  and  $S_0 \rightarrow S_6$ . Fluorescence measurements confirmed  $S_2$  emission at around 375 nm (Fig. 2b), and the quantum yield was determined to be  $\Phi = 2.7\%$ , in agreement with literature values.<sup>18</sup>

To investigate the effect of substitution on optical properties, we synthesized the phenyl-substituted azulene (**A1**) as a reference. The absorption spectrum of **A1** exhibited a pronounced red shift compared to that of azulene, which is attributed to the extended  $\pi$ -conjugation introduced by the phenyl group (Fig. 2a). The photoluminescence quantum yield of **A1** was significantly reduced ( $\Phi_{\text{A1}} < 0.3\%$ ), which can be rationalized by the acceleration of internal conversion due to a reduced  $S_2$ - $S_1$  energy gap.

In the case of the dimers (**A2**–**A5**), nonradiative decay rates differ depending on the degree of electronic interaction among the chromophores. **A2**, where two azulene units are fixed in a face-to-face configuration, exhibited more red-shifted and broadened  $S_0 \rightarrow S_2$  absorption than **A1** possibly due to the exciton coupling among the azulene units and extended  $\pi$ -conjugation (Fig. 2a).<sup>35–37</sup> As evident from the fluorescence spectra, the emission intensity of **A2** was unexpectedly low (Fig. 2b). Despite a similar  $S_2$ - $S_1$  energy gap as **A1**, this pronounced quenching cannot be attributed solely to the substituent effect and indicates additional nonradiative decay pathways induced by dimerization. In **A3**, which features minimal steric hindrance with a phenylene bridge, a broad absorption around 380 nm due to the extended conjugation was observed (Fig. 2c). Consistent with the previous results, fluorescence was substantially quenched, reinforcing the conclusion that dimerization consistently leads to significant fluorescence suppression.

In contrast, the absorption spectra of **A4** and **A5** with the durylene bridge did not show much red-shift and broadening (Fig. 2c), implying suppressed electronic interactions between azulene units. This behavior was attributed to the twisted geometry between the azulene and durylene bridge, which disrupts conjugation with the azulene  $\pi$ -system. Consequently, it is anticipated that the interaction is less governed by “through-bond” interactions between the chromophores. We note the subtle spectral differences in the tail region of the  $S_0 \rightarrow S_2$  absorption (375–400 nm) should not be overlooked. Particularly in **A5**,



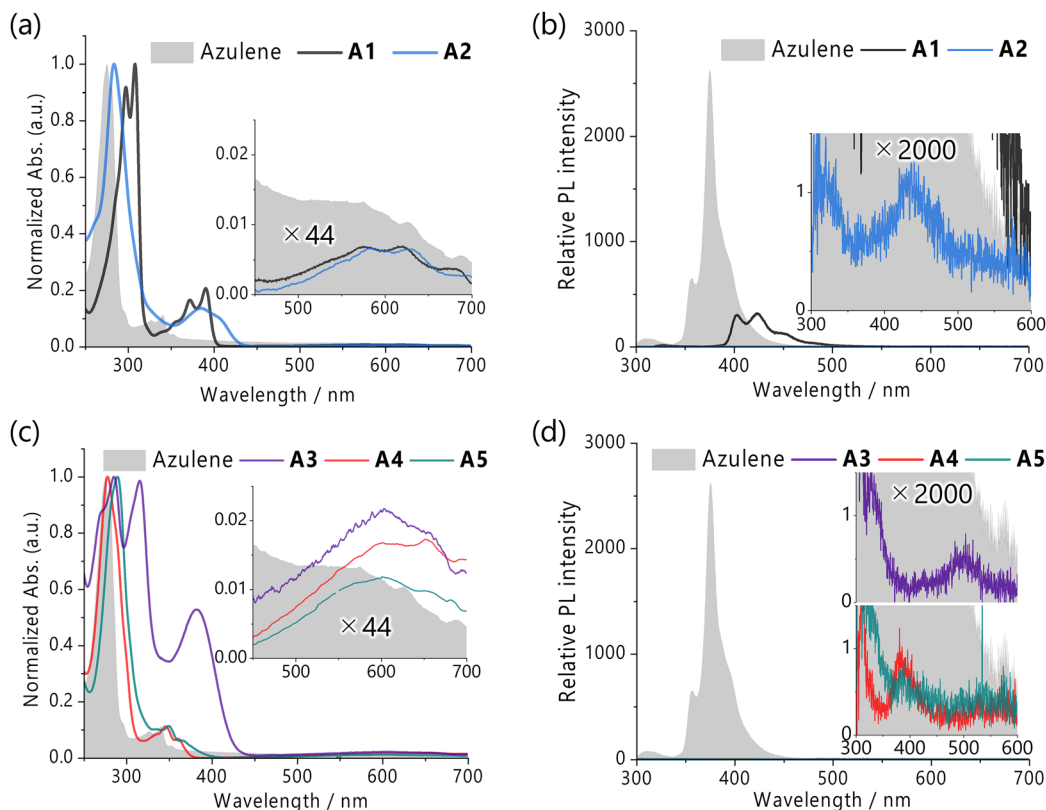


Fig. 2 (a) Absorption spectra and (b) fluorescence spectra of azulene, **A1** and **A2** in THF ([Azulene] = 100  $\mu$ M, [**A1**], [**A2**] = 50  $\mu$ M), (c) Absorption spectra and (d) fluorescence spectra of azulene, **A3**, **A4** and **A5** in THF ([Azulene] = 100  $\mu$ M, [**A3**], [**A4**], [**A5**] = 50  $\mu$ M).

the substituent introduced at the 2 position of azulene was presumed to lower the rotational barrier of the azulene, thereby affording greater structural flexibility. This increased freedom is likely responsible for the observed extended absorption edge in **A5** compared to **A4**, demonstrating that even slight modifications in molecular structure can have a significant impact on optical properties. We note that fluorescence from **A4** and **A5** was so weak and was nearly undetectable (Fig. 2d). Despite the introduction of steric hindrance aimed at increasing molecular rigidity and suppressing chromophore-linker motion, the fluorescence was markedly suppressed. These results strongly suggest that fluorescence quenching is fundamentally attributed not to increased structural flexibility, but rather to the dimerization itself. We also attempted to evaluate the fluorescence quantum yields. But reliable values could not be obtained with our instrumentation due to extremely low emission intensities ( $\Phi_{\text{A2-A5}} \ll 1\%$ ). Therefore, regardless of the bridge structure, fluorescence quenching was observed upon dimerization. This behavior contrasts sharply with the widely accepted view that unique  $S_2$  fluorescence in monomeric azulene is retained even in the presence of various substitutions.<sup>16,38</sup> Fluorescence quenching seems to be an intrinsic feature of dimeric systems of azulene chromophores.

### Ultrafast spectroscopy

To uncover the origin of this ultrafast excited-state dynamics and to understand what caused azulene to lose its unique

properties of the anti-Kasha emission, we conducted ps-TAS of the azulene and azulene derivatives in 2-methyltetrahydrofuran (2MeTHF, Fig. 3 and 4). All compounds exhibited transient absorption signals within the probe range of 480–980 nm. However, the most notable differences emerged in the excited-state lifetimes. While the monomeric azulene displayed relatively long-lived signals longer than 100 picoseconds, the other derivatives showed significantly faster decay—accelerated by more than an order of magnitude (Fig. 4). This trend highlights the drastic impact of dimerization and substitution on the photophysical properties of the  $S_2$  state.

In azulene monomer, only one transient was observed with a broad excited absorption band centered at 570 nm. The time constant of the decay of the TA signal was  $(7.3 \pm 0.2) \times 10^2$  ps, which correlates to the fluorescence lifetime of the  $S_2$  state in previous works ( $\sim 1$  ns).<sup>34,39</sup> Therefore, the TA signal was assigned as  $S_2 \rightarrow S_n$  transition. In contrast, the TA spectrum of **A1** was different from azulene monomer and showed quicker decay compared to azulene. Notably, other azulene derivatives (**A2–A5**) exhibited similar TAS but with even quicker decays than azulene and **A1**.

We estimated the time constants of the decays in azulene derivatives using global analysis assuming one component (Fig. S13, S14 and Table S1); the estimated time constants of the transition indicated as  $\tau_1$  in the global analysis were  $15.37 \pm 0.01$  ps,  $0.60 \pm 0.05$  ps,  $0.50 \pm 0.05$  ps,  $1.66 \pm 0.01$  ps, and,





Fig. 3 (a)–(f) ps-TAS of azulene in 5 mM and azulene derivatives in 2.5 mM 2MeTHF obtained after pulsed excitation at 350 nm (The range: 480–980 nm): (a) azulene, (b) **A1**, (c) **A2**, (d) **A3**, (e) **A4** and (f) **A5**.



Fig. 4 Temporal evolution of the transient absorption signals of azulene, **A1**, **A2**, **A3**, **A4**, and **A5**, presented as lin-log plots.

$0.81 \pm 0.01$  ps for **A1**, **A2**, **A3**, **A4** and **A5**, respectively. The trends can be summarized as follows: even with introducing a phenyl substituent, the lifetime was shortened to about 15 ps.<sup>40</sup> The shorter lifetime of **A1** compared to azulene was consistent with the increased nonradiative decay of **A1**. We also examined the possibility of contribution from the additional component on the TA signal, but the contribution from the second component was found to be negligible.

In all dimer cases, a single transient species with fast decay ( $< 10$  ps) was observed. As shown in Fig. 3, the time constants differed depending on the dimer chemical structures. The  $S_2$  lifetime estimated by fs-TAS exhibited a correlation with the degree of broadening and red-shift in absorption. Fig. 4 shows the relationship between the  $S_2$ – $S_1$  energy gap ( $\Delta E_{(S_2-S_1)}$ ) and the nonradiative decay rate constants ( $k_{nr}$ ) with reported closed-shell molecules.<sup>16,39,41</sup> For **A1**, the observed decay rate was

consistent with the estimated value from this linear relationship of the energy gap law. In contrast, the azulene dimer (**A2**–**A5**) exhibited significantly faster nonradiative decay constants than the energy gap law predicted. In comparison to other azulene dimers, **A4** exhibited slightly longer decays. The difference can be understood by the rigid duryl substituents and better symmetry of **A4**, which may contribute to the suppression of deactivation processes.

### Excited state dynamics

Based on the optical properties and the result of ultrafast spectroscopy, we discuss the fate of the  $S_2$  state in azulene dimers—an essential question for understanding the excited-state dynamics of higher-lying states in these systems. For the rational design of functional molecules that harness the  $S_2$  state of azulene, it is crucial not only to stabilize and utilize the  $S_2$  state, but also to elucidate the mechanisms underlying its anomalous acceleration of non-radiative decay and fluorescence quenching. The dynamics of the  $S_2$  states in these azulene dimers were not predicted from previous studies, and further work is needed to fully elucidate them.

In monomeric azulene derivatives, anomalous  $S_2$  fluorescence has demonstrated remarkable robustness even under structural perturbations such as substitution or symmetry breaking. As a result, suppressing this emission has remained a challenging task. Within this context, our observation that dimerization leads to a pronounced quenching of the  $S_2$  emission was unexpected and highly informative. This finding introduces a new paradigm for engineering azulene-based chromophores in photonic and electronic materials.



A primary hypothesis to consider is the acceleration of nonradiative  $S_2 \rightarrow S_1$  internal conversion, as exemplified by **A1**. This phenomenon may be attributed to the so-called “loose bolt effect”, wherein increased conformational flexibility of the chromophore facilitates nonradiative relaxation pathways. Indeed, as shown in Fig. 5, compounds such as **A1** and porphyrin derivatives that exhibit anti-Kasha emission tend to follow the energy gap law, with their decay rates correlating with the  $S_2-S_1$  energy gap. In contrast, the azulene dimers reported in this study exhibit  $S_2$ -state decay rates that significantly exceed this trend, suggesting that conformational flexibility alone cannot account for the observed dynamics. This deviation implies the emergence of alternative, previously unrecognized deactivation pathways specific to the dimer systems. Notably, this trend aligns with recent findings by Stevens *et al.* in azulene tetramers, where higher-order excitonic coupling was proposed to induce unexpected deactivation channels.<sup>18</sup> Such reports support that close spatial proximity between azulene units may trigger novel, collective decay mechanisms inaccessible in monomeric forms.

Another candidate mechanism involves triplet-mediated processes. These include intersystem crossing or even singlet fission, whereby a singlet excited state yields a pair of triplets.<sup>36</sup> Goener *et al.* reported that the  $T_1-T_n$  absorption of azulene occurs near 360 nm, a region outside the spectral window probed in our current setup.<sup>42</sup> Moreover, theoretical work suggests possible transitions between  $T_1$  and  $T_4$  around 550 nm, although these remain experimentally unverified.<sup>18</sup> As such, triplet-state contributions cannot be definitively ruled out or confirmed, highlighting the need for future studies.

Symmetry-breaking charge transfer between chromophores is yet another possibility.<sup>43–47</sup> If charge-separated states were involved, we would expect broad absorptions attributable to radical cations or anions in the long-wavelength region. Indeed, a broad transient absorption was observed beyond 650 nm in the dimers, but its time evolution matches that of the 550 nm feature, making it difficult to attribute this signal to distinct charge-separated species. Modulating redox potentials and precisely controlling interchromophoric distances and orientations may be key to realizing such states. At present, however,

the observed spectral behavior is more likely attributed to transitions between higher-lying singlet states originating from the  $S_2$  state.

Taken together, while several plausible decay mechanisms may account for the rapid loss of  $S_2$  emission upon dimerization, the available evidence remains insufficient to draw a definitive conclusion. Rather, a synergistic interplay of multiple deactivation pathways cannot be ruled out. In this sense, the present system provides fertile ground for uncovering new aspects of  $S_2$ -state photophysics and poses a challenge to current models, which have mainly been developed around isolated azulene chromophores. While many questions remain unresolved, the present work significantly highlights the vast and largely unexplored potential of anti-Kasha systems in molecular photophysics.

## Conclusions

In this work, we synthesized a series of four covalently conjugated, structurally defined azulene dimers, and their higher-lying excited-state dynamics were investigated by ultrafast spectroscopy. Regardless of the rigidity and relative intermolecular electronic interactions, dimerization leads to a pronounced suppression of  $S_2$  fluorescence and a predominance of nonradiative decay. A key conclusion is that the anti-Kasha behavior of azulene is remarkably sensitive to interchromophoric interactions. This introduces a critical constraint on the rational design of molecular architectures that aim to harness high-energy excited states. Any strategy that employs higher-lying excited states of chromophores in optoelectronic devices must carefully consider their mutual interactions, which are governed by the orientation and spatial arrangement of the chromophores.

## Author contributions

YS, KM, and NK designed the project. YS synthesized the compound. YS conducted steady-state experiments. AT and KM measured the transient absorption of the molecules. All authors wrote the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data underlying this study are available in the published article and its SI. Source data are provided with this manuscript. See DOI: <https://doi.org/10.1039/d5cp02571k>

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Fig. 5 The relationship between  $S_2-S_1$  energy gap and the nonradiative decay rate constant.



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