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ARTICLE

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.

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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 multiplicity¹, 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". The anti-Kasha fluorescence has been widely reported since its discovery^{2–6}. Beyond being a subject of scientific curiosity, efforts to control this phenomenon have opened new avenues for manipulating photophysical and photochemical processes⁷, including photochemical reaction^{3,8,9} and singlet fission^{10–12}, 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 fluorophores¹³. Since the first report of anomalous fluorescence characteristics⁶, extensive studies have focused on controlling azulene's S_2 fluorescence by introducing heavy atoms^{14–16}, breaking molecular symmetry^{5,17}, and reducing the S_2 - S_1 energy gap³. 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 state¹³.

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 units¹⁸. Given the recent synthetic progress in azulene-fused molecular backbones^{19–30} and the observation of S_n emission from some of them³¹, 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. 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^{32,33}. This systematic structural variation enables us to evaluate the effect of interchromophore interactions in the excited-state relaxation. 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.

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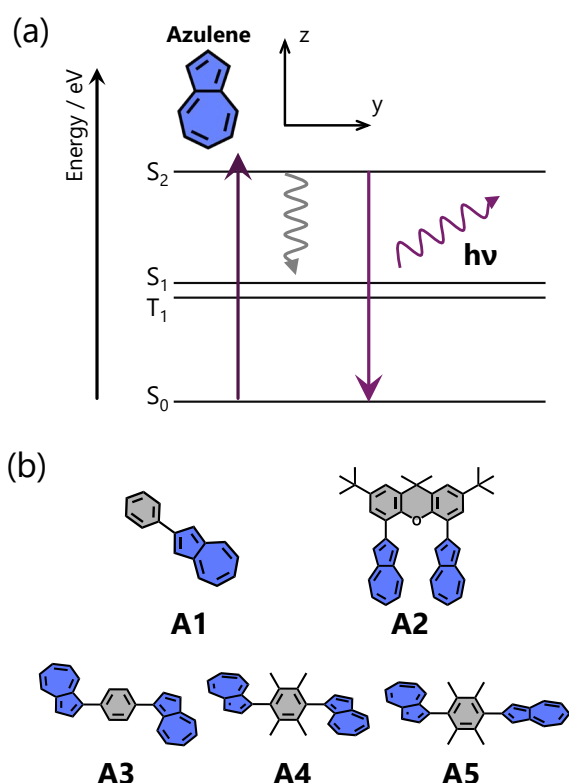
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Figure 1: (a) Chemical structure of azulene and the schematic diagram of the anti-Kasha fluorescence. (b) Chemical structures of **A1**, **A2**, **A3**, **A4** and **A5**.

Experimental Section

Compounds

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

Instrumentation

¹H-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 data³⁴, 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. 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, and the quantum yield was determined to be $\Phi = 2.7\%$, in agreement with literature values¹⁸.

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 π -conjugation introduced by the phenyl group. The photoluminescence quantum yield of **A1** was significantly reduced ($\Phi_{A1} < 0.3\%$), 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 π -conjugation.^{35–37} As evident from the fluorescence spectra, the emission intensity of **A2** was unexpectedly low. 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. 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, 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 π -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**, 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. 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

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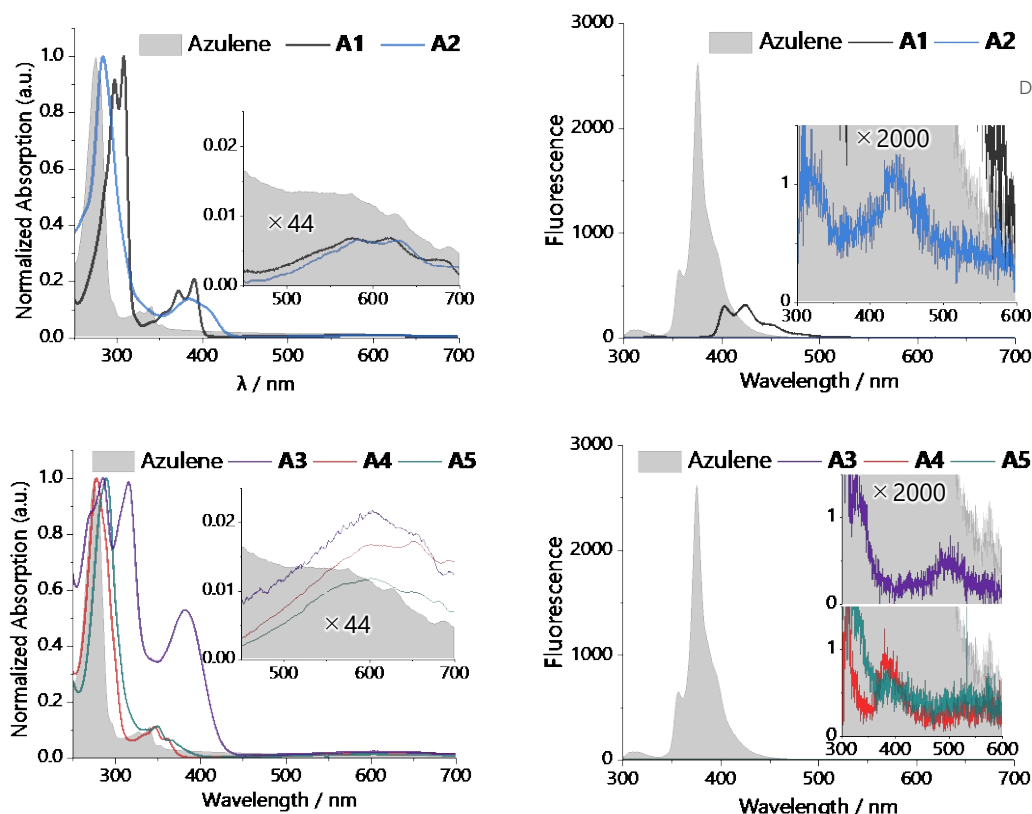


Figure 2. (a) Absorption spectra and (b) fluorescence spectra of azulene, **A1** and **A2** in THF ([Azulene]=100 μ M, [**A1**], [**A2**]=50 μ M), (c) Absorption spectra and (d) fluorescence spectra of azulene, **A3**, **A4** and **A5** in THF ([Azulene]=100 μ M, [**A3**], [**A4**], [**A5**]=50 μ M).

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^{16,38}. 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, Figure 3,4). 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 (Figure 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 (~ 1 ns)^{34,39}. 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 (Figure S13–S14, Table S1); the estimated time constants of the transition indicated as τ_1 in the global analysis were 15.37 ± 0.01 ps, 0.60 ± 0.05 ps, 0.50 ± 0.05 ps, 1.66 ± 0.01 ps, and 0.81 ± 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 ps⁴⁰. 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 Figure 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. Figure 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^{16,39,41}. 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.



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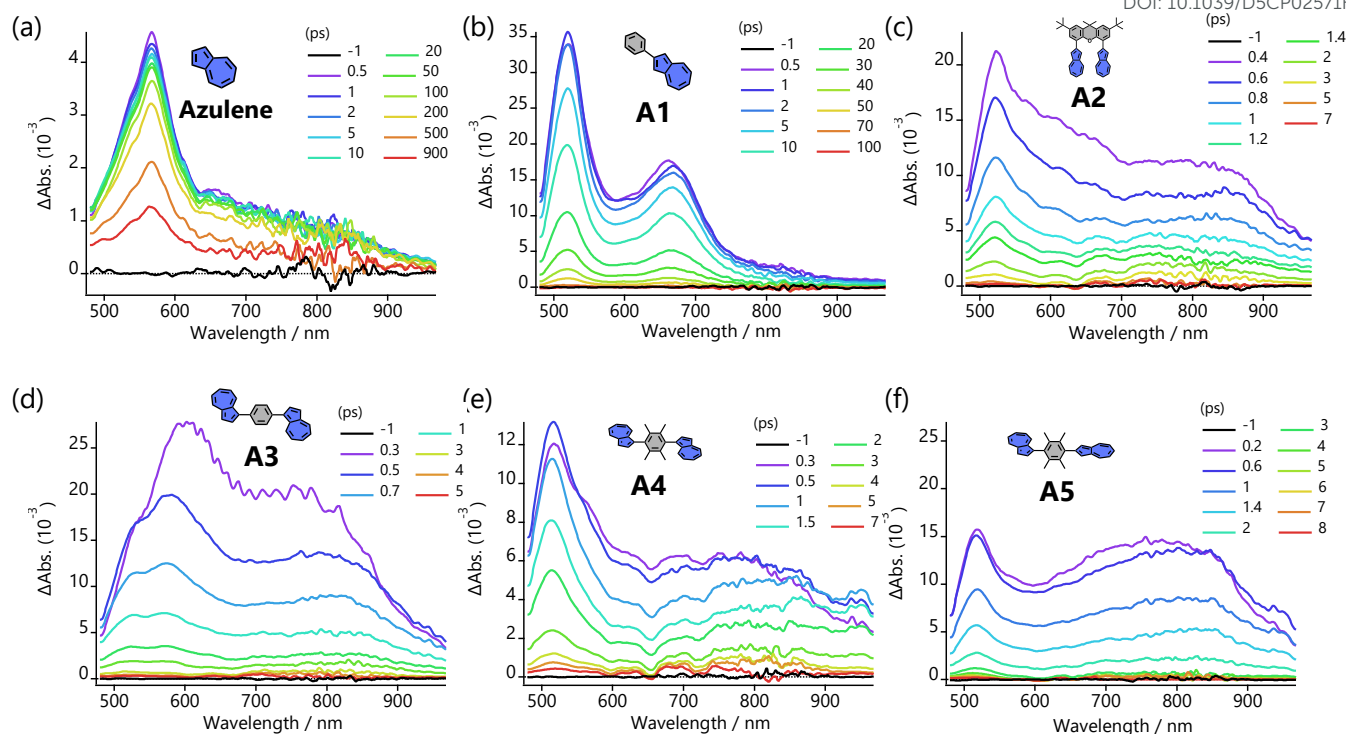
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Figure 3. (a–f) ps-TAS of azulene in 5 mM and azulene derivatives in 2.5 mM 2MeTHF obtained after pulsed excitation at 350 nm (The range: 480–980 nm): (a) azulene, (b) **A1**, (c) **A2**, (d) **A3**, (e) **A4** and (f) **A5**.

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,

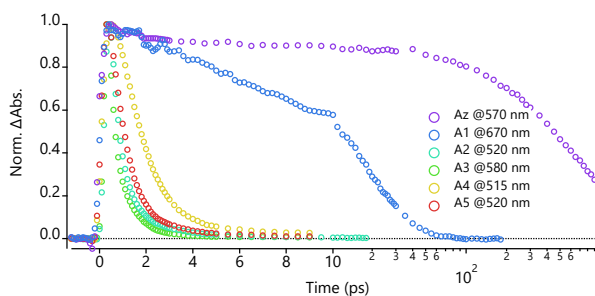


Figure 4. Temporal evolution of the transient absorption signals of azulene, **A1**, **A2**, **A3**, **A4**, and **A5**, presented as lin-log plots.

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 Figure 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 channels¹⁸. 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 triplets³⁶. 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 setup⁴². Moreover, theoretical work suggests possible transitions between T_1 and T_4

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around 550 nm, although these remain experimentally unverified¹⁸. 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.^{43–47} 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.

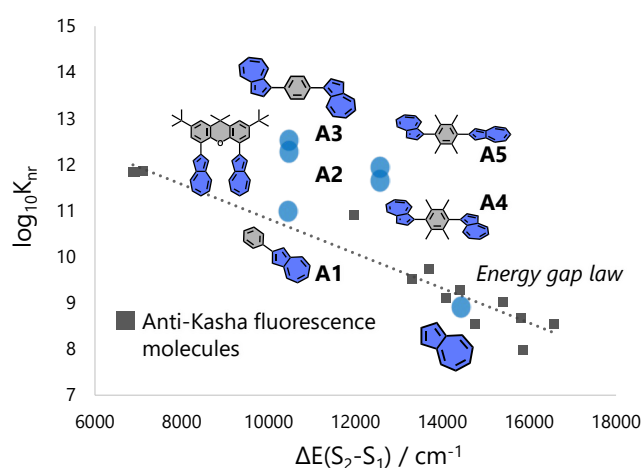


Figure 5. The relationship between S_2 - S_1 energy gap and the nonradiative decay rate constant.

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.

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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 Supporting Information. Source data are provided with this manuscript.

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Notes and references

- 1 M. Kasha, Characterization of electronic transitions in complex molecules, *Discuss. Faraday Soc.*, 1950, **9**, 14.
- 2 G. Viswanath and M. Kasha, Confirmation of the anomalous fluorescence of azulene, *J. Chem. Phys.*, 1956, **24**, 574–577.
- 3 N. J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, The effect of wavelength on organic photoreactions in solution. Reactions from upper excited states, *Chem. Rev.*, 1978, **78**, 125–145.
- 4 T. Itoh, Fluorescence and phosphorescence from higher excited states of organic molecules, *Chem. Rev.*, 2012, **112**, 4541–4568.
- 5 D. Malpicci, E. Lucenti, C. Giannini, A. Forni, C. Botta and E. Cariati, Prompt and long-lived anti-Kasha emission from organic dyes, *Molecules*, 2021, **26**, 6999.
- 6 M. Beer and H. C. Longuet-Higgins, Anomalous light emission of azulene, *J. Chem. Phys.*, 1955, **23**, 1390–1391.



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ARTICLE

- 7 H. Xin, B. Hou and X. Gao, Azulene-based π -functional materials: Design, synthesis, and applications, *Acc. Chem. Res.*, 2021, **54**, 1737–1753.
- 8 B. Pfund and O. S. Wenger, Excited organic radicals in photoredox catalysis, *JACS Au*, 2025, **5**, 426–447.
- 9 A. P. Demchenko, V. I. Tomin and P.-T. Chou, Breaking the Kasha rule for more efficient photochemistry, *Chem. Rev.*, 2017, **117**, 13353–13381.
- 10 K. Wang, X. You, X. Miao, Y. Yi, S. Peng, D. Wu, X. Chen, J. Xu, M. Y. Sfeir and J. Xia, Activated singlet fission dictated by anti-Kasha property in a rylene imide dye, *J. Am. Chem. Soc.*, 2024, **146**, 13326–13335.
- 11 M. B. Smith and J. Michl, Singlet fission, *Chem. Rev.*, 2010, **110**, 6891–6936.
- 12 K. Miyata, F. S. Conrad-Burton, F. L. Geyer and X.-Y. Zhu, Triplet pair states in singlet fission, *Chem. Rev.*, 2019, **119**, 4261–4292.
- 13 D. Dunlop, L. Ludvíková, A. Banerjee, H. Ottosson and T. Slanina, Excited-state (anti)aromaticity explains why azulene disobeys Kasha's rule, *J. Am. Chem. Soc.*, 2023, **145**, 21569–21575.
- 14 G. Eber, S. Schneider and F. Dörr, On the importance of intersystem crossing for the deactivation of the S2 state of halogeno derivatives of azulene, *Chem. Phys. Lett.*, 1977, **52**, 59–62.
- 15 O. K. Abou-Zied, D. R. M. Demmer, S. C. Wallace and R. P. Steer, Picosecond dynamics of the S2 excited state of azulene and its van der Waals complexes with Ar and Xe, *Chem. Phys. Lett.*, 1997, **266**, 75–85.
- 16 N. Tétreault, R. S. Muthyala, R. S. H. Liu and R. P. Steer, Control of the photophysical properties of polyatomic molecules by substitution and solvation: The second excited singlet state of azulene, *J. Phys. Chem. A*, 1999, **103**, 2524–2531.
- 17 P. M. Kozłowski, G. Rauhut and P. Pulay, Potential symmetry breaking, structure and definite vibrational assignment for azulene: Multiconfigurational and density functional results, *J. Chem. Phys.*, 1995, **103**, 5650–5661.
- 18 A. L. Stevens, C. Yeow, J. M. White, S. J. Bradley, K. P. Ghiggino and R. P. Steer, Electronic spectroscopy and photophysics of calix[4]azulene, *J. Photochem. Photobiol. A Chem.*, 2021, **405**, 112922.
- 19 A. Ong, T. Tao, Q. Jiang, Y. Han, Y. Ou, K.-W. Huang and C. Chi, Azulene-fused acenes, *Angew. Chem. Int. Ed Engl.*, 2022, **61**, e202209286.
- 20 M. Murai, S. Iba, H. Ota and K. Takai, Azulene-fused linear polycyclic aromatic hydrocarbons with small bandgap, high stability, and reversible stimuli responsiveness, *Org. Lett.*, 2017, **19**, 5585–5588.
- 21 T. Shoji, N. Sakata, R. Ishikawa, S. Mori, T. Okujima, R. Sekiguchi and S. Ito, AzUlene - fused polycyclic aromatic hydrocarbons: Synthesis, structural, optical, and electrochemical properties of azuleno[2,1 - a]phenalenes, *ChemistryEurope*, 2025, **3**, e202500039.
- 22 J. Guo, F. Du, B. Yu, P. Du, H. Li, J. Zhang and H. Xin, Heptacyclic aromatic hydrocarbon isomers with two azulene units fused, *Chem. Sci.*, 2024, **15**, 12589–12597.
- 23 H. Zhang and P. An, Azulene-fused seco-hexabenzocoronene-based nanographenes, *Org. Lett.*, 2025, **27**, 4411–4416.
- 24 M. Murai, S. Iba, S. Hamao, Y. Kubozono, H. Ota and K. Takai, Azulene-fused linearly π -extended polycyclic aromatic compounds: Synthesis, photophysical properties, and OFETs applications, *Bull. Chem. Soc. Jpn.*, 2023, **96**, 1077–1081.
- 25 M. Murai, M. Abe, S. Ogi and S. Yamaguchi, Diazulenylmethyl cations with a silicon bridge: A π -extended cationic motif to form J-aggregates with near-infrared absorption and emission, *J. Am. Chem. Soc.*, 2022, **144**, 20385–20393.
- 26 M. Murai, M. Ito, S. Takahashi and S. Yamaguchi, Germanium- and tin-bridged diazulenylmethyl cations: effects of group 14 elements on the structure and properties of π -extended cations, *Dalton Trans.*, 2023, **52**, 8631–8635.
- 27 B. Liu, M. Chen, X. Liu, R. Fu, Y. Zhao, Y. Duan and L. Zhang, Bespoke tailoring of graphenoid sheets: A rippled molecular carbon comprising cyclically fused nonbenzenoid rings, *J. Am. Chem. Soc.*, 2023, **145**, 28137–28145.
- 28 T. Tsuchiya, M. Higashibeppu and Y. Mazaki, Synthesis and properties of twisted and helical azulene oligomers and azulene-based polycyclic hydrocarbons, *ChemistryOpen*, 2023, **12**, e202100298.
- 29 J. Wang, F. G. Gámez, J. Marín-Beloqui, A. Diaz-Andres, X. Miao, D. Casanova, J. Casado and J. Liu, Synthesis of a dicyclohepta[a,g]heptalene-containing polycyclic conjugated hydrocarbon and the impact of non-alternant topologies, *Angew. Chem. Int. Ed Engl.*, 2023, **62**, e202217124.
- 30 S. Wang, M. Tang, L. Wu, L. Bian, L. Jiang, J. Liu, Z.-B. Tang, Y. Liang and Z. Liu, Linear nonalternant isomers of acenes fusing multiple azulene units, *Angew. Chem. Int. Ed Engl.*, 2022, **61**, e202205658.
- 31 G. Nöll, C. Lambert, M. Lynch, M. Porsch and J. Daub, Electronic structure and properties of poly- and oligoazulenes, *J. Phys. Chem. C Nanomater. Interfaces*, 2008, **112**, 2156–2164.
- 32 V. Kumar, S. Kushida, T. Inoue, K. Iwata, H. Yamagishi, H. Tsuji and Y. Yamamoto, Ultrafast energy transfer induced lasing from a coplanar donor - acceptor - donor molecule in a microspherical cavity, *Adv. Funct. Mater.*, 2025, 2502545.
- 33 S. Jhulki, S. Seth, A. Ghosh, T. J. Chow and J. N. Moorthy, Benzophenones as generic host materials for phosphorescent organic light-emitting diodes, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1527–1535.
- 34 P. Foggi, F. V. R. Neuwahl, L. Moroni and P. R. Salvi, $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ absorption of azulene: Femtosecond transient spectra and excited state calculations, *J. Phys. Chem. A*, 2003, **107**, 1689–1696.
- 35 R. E. Cook, B. T. Phelan, R. J. Kamire, M. B. Majewski, R. M. Young and M. R. Wasielewski, Excimer formation and symmetry-breaking charge transfer in cofacial perylene dimers, *J. Phys. Chem. A*, 2017, **121**, 1607–1615.
- 36 W. Ni, G. G. Gurzadyan, J. Zhao, Y. Che, X. Li and L. Sun, Singlet fission from upper excited electronic states of cofacial perylene dimer, *J. Phys. Chem. Lett.*, 2019, **10**, 2428–2433.
- 37 Y. J. Bae, D. Shimizu, J. D. Schultz, G. Kang, J. Zhou, G. C. Schatz, A. Osuka and M. R. Wasielewski, Balancing Charge Transfer and Frenkel Exciton Coupling Leads to Excimer Formation in Molecular Dimers: Implications for Singlet Fission, *J. Phys. Chem. A*, 2020, **124**, 8478–8487.
- 38 A. Olszowski, Pseudoazulenes: a new large group of compounds with anomalous fluorescence, *Chem. Phys. Lett.*, 1980, **73**, 256–262.
- 39 B. D. Wagner, D. Tittelbach-Helmrich and R. P. Steer, Radiationless decay of the S2 states of azulene and related compounds: solvent dependence and the energy gap law, *J. Phys. Chem.*, 1992, **96**, 7904–7908.

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- 40 G. Binsch, E. Heilbronner, R. Jankow and D. Schmidt, On the fluorescence anomaly of azulene, *Chem. Phys. Lett.*, 1967, **1**, 135–138.
- 41 U. Tripathy, D. Kowalska, X. Liu, S. Velate and R. P. Steer, Photophysics of Soret-excited tetrapyrroles in solution. I. Metalloporphyrins: MgTPP, ZnTPP, and CdTPP, *J. Phys. Chem. A*, 2008, **112**, 5824–5833.
- 42 H. Görner and D. Schulte-Frohlinde, Observation of a triplet state of azulene generated by energy transfer in solution, *J. Photochem.*, 1981, **16**, 169–177.
- 43 E. Vauthey, Photoinduced symmetry-breaking charge separation, *ChemPhysChem*, 2012, **13**, 2001–2011.
- 44 R. M. Young and M. R. Wasielewski, Mixed electronic states in molecular dimers: Connecting singlet fission, excimer formation, and symmetry-breaking charge transfer, *Acc. Chem. Res.*, 2020, **53**, 1957–1968.
- 45 I. Papadopoulos, M. J. Álvaro-Martins, D. Molina, P. M. McCosker, P. A. Keller, T. Clark, Á. Sastre-Santos and D. M. Guldi, Solvent - dependent singlet fission in diketopyrrolopyrrole dimers: A mediating charge transfer versus a trapping symmetry breaking charge separation, *Adv. Energy Mater.*, 2020, **10**, 2001496. DOI: 10.1039/D5CP02571K
- 46 E. Sebastian and M. Hariharan, Symmetry-breaking charge separation in molecular constructs for efficient light energy conversion, *ACS Energy Lett.*, 2022, **7**, 696–711.
- 47 A. Yahagh, R. R. Kaswan, S. Kazemi, P. A. Karr and F. D'Souza, Symmetry breaking charge transfer leading to charge separation in a far-red absorbing bisstyryl-BODIPY dimer, *Chem. Sci.*, 2024, **15**, 906–913.



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Fukuoka, July 4th, 2025

Dear Editor and Referees,

Attached herewith is the Data Availability Statement (DAS) of the following manuscript submitted to the journal Physical Chemistry Chemical Physics.

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

Authors: Y. Sawada, A. Takada, K. Onda, K. Miyata, Y. Sasaki, N. Kimizuka

The data of the following manuscript are available in the published article and its Supporting Information. The source data are provided as a separate "Source Data" with the manuscript.

Yours sincerely,

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