

What Leads to Aggregation-Induced Emission?

Jianxin Guan, Chengzhen Shen, Jie Peng, and Junrong Zheng*

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 4218–4226

Read Online

ACCESS |

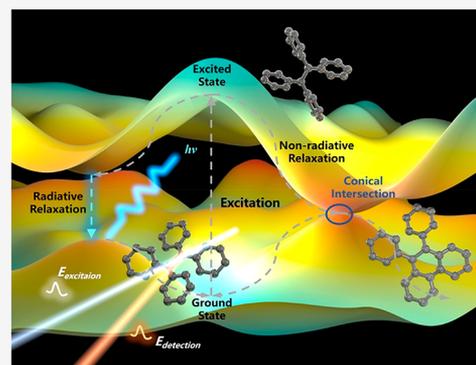


Metrics & More



Article Recommendations

ABSTRACT: Aggregation-induced emission (AIE), usually referring to the phenomenon in which molecules emit more strongly in the aggregate state than in the solution state, is intriguing and promising in various optoelectronic and biosensing applications. In this Perspective, the basic principles that can lead to AIE and experimental evidence to reveal the AIE mechanism of tetraphenyl ethylene (TPE)-type molecules are discussed. AIE is the consequence of two factors: (1) the fast energy dissipation by crossing a conical intersection (CI) in solutions but not in solids results in low luminescence efficiencies in the solutions, and (2) the weak intermolecular coupling and thus slow intermolecular energy/charge transfers in the AIE solids effectively prevent quenching and result in relatively high luminescence efficiencies. The key to AIE is that the luminescence efficiency is tuned by controlling molecules to cross or not to cross a CI by changing the phase of molecules. How fast a molecule can cross a CI is dependent on the energy barrier of isomerization, which can be tuned in many ways, including mechanical or electrical stimuli, in addition to changing phases. Barrier-dependent crossing CI also results in a very important consequence: excitation-wavelength-dependent fluorescence yield within one electronic excited state, an anti-Vavilov's rule phenomenon. In principle, there can be an alternative way to tune luminescence efficiency by manipulating the formation of CIs instead of crossing or not crossing them. This approach relies on the fact that the electronic ground state and the excited state have many different properties, e.g., dipole moment. By tuning the environment, e.g., dielectric constant, to favor or disfavor one state, one may be able to lift or lower the potential surface of one state so that the potential surfaces of two states can vary between intersected and not contacted.



The processes of molecules absorbing photons and releasing photons and heat have been considered not only as an important energy source for sustaining life but also as the basis of photoelectronic devices. Under different conditions or in different molecular systems, the photo-, electro-, and thermal conversion efficiencies in these processes can be highly different. For example, in most cases, luminescent molecules emit brightly in dilute solutions but dim with the increase of concentration or in solids, namely, aggregation-caused quenching (ACQ).^{1–3} In many practical applications, e.g., organic or polymer light-emitting diodes, ACQ is an undesirable factor.^{4–6} In sharp contrast, a group of molecules behave completely oppositely. The more they aggregate or solidify, the stronger their luminescence,^{7–12} which is the so-called aggregation-induced emission (AIE).^{1–3} AIE molecules have many desirable properties, such as good solubility and processability and high emission efficiency, attracting tremendous interest from fields like organic photoelectronics and bioimaging.^{13–19}

AIE has a fairly long history. It was already mentioned in an 1896 paper.^{10–12,20} In the following 100 years, it was discussed and studied mostly by photophysicists.^{9,10,12,20–22} In the early 2000s, accompanying the booming applications of organic electronics, material scientists and organic chemists began to be aware of this anti-intuitive phenomenon.^{23–25} Using their

unmatched capability of molecular design and imagination, they have promoted this once relatively unknown physical chemistry observation into a famous and fascinating topic.

In contrast, the mechanistic studies of AIE are not as advanced. Long before the AIE concept was well-received, the nonradiative decay of tetraphenylethylene (TPE), which is known as a prototypical AIE compound, and its derivatives in solution was portrayed in terms of E-Z photoisomerization,^{26–29} borrowing concepts from the well-studied ethylene and stilbene molecules. Systematic studies of tethered TPEs also suggested that the phenyl ring torsions probably play a major role in deactivation of the excited singlet state, as opposed to the traditionally assumed “olefinic twist” around the central double bond.^{30,31} Nevertheless, the argument that “In the excited state, the central olefinic double bond can be opened, generating two diphenylmethylene (DPM) units. The friction caused by their rotational or twisting motions against each

Received: December 31, 2020

Accepted: April 21, 2021

Published: April 26, 2021



other with the solvent media transforms the photonic energy to thermal energy, leading to radiationless relaxation of the excitons.” is still popular,¹ partially because molecules with high luminous efficiency have relatively rigid structures, e.g. perylene and 8-hydroxyquinoline, whereas molecules with flexible structures and rotatable groups seem to be weak in luminescence in liquids, like tetraphenyl ethylene (TPE) and vitamin A. Because of such a difference, it is natural and intuitive to assume that molecular motions associated with the flexible structures are the major energy acceptors of electronic excitation.

Previous studies have suggested that aggregation or solidification can significantly change the electronic transition dipole moments and selection rules, and the electronic structures of molecules, because of the orbital overlaps and the constraints of molecular symmetry that are imposed by the closely packed and aligned molecules in solids.^{32–34} The altered basic molecular properties, which may overwhelm the quenching effect of aggregation, can lead to enhanced luminescence in solids or aggregates, such as sugar molecules.^{8,35,36} This type of AIE with a well-defined mechanism is not within the scope of this Perspective. Herein, we focus only on AIE molecules that have no dramatic changes in these molecular parameters, e.g., TPE and its derivatives.

The competition between radiative and nonradiative decay pathways of electronic excitation plays a crucial role in the AIE phenomenon of these molecules, and therefore, this perspective starts from these fundamentals.

The competition between radiative and nonradiative decay pathways of electronic excitation plays a crucial role in the AIE phenomenon of these molecules, and therefore, this perspective starts from these fundamentals.

When a molecule absorbs a photon and is excited to an electronic excited state, its electronic energy can relax through electron transfer, radiative (fluorescence or phosphorescence), and/or nonradiative (energy conversions to heat including vibrations, rotations, and translations) pathways. Assuming no electron transfers which eventually also convert electronic energy into photons or heat, if the radiative decay rate constant (k_r) is larger than that of nonradiative decay rate constant (k_{nr}), the electronic energy mainly relaxes via emitting photons, and vice versa. k_r can be estimated by the spontaneous emission equation:^{37,38}

$$k_r = \frac{32\pi^3 \nu_{mn}^3}{3c^3 \hbar \epsilon} |\mu_{mn}|^2 \quad (1)$$

where c is the velocity of light, ν_{mn} the photonic frequency, μ_{mn} the transition dipole moment between electronic states m and n , and ϵ the dielectric constant. Using $\nu_{mn} = 6 \times 10^{14}$ Hz ($\lambda = 500$ nm for UV–vis) and $\mu_{mn} = 1$ D (typical parameters for organic molecules), eq 1 gives the time constant of radiative decay $\tau_r = 1/k_r$ to be about tens of nanoseconds (~ 47 ns).

The estimation of nonradiative decay rate is less straightforward. Under the Born–Oppenheimer approximation (BOA), electronic motions and nuclear motions are separable

and weakly coupled. If the coupling is assumed to be purely electronic, the conversion rate of electronic energy into molecular thermal motions (vibrations, rotations, and translations) can then be estimated with energy transfer and dipole–dipole coupling theories.^{39–42} A polyatomic molecule has $3n$ (n , number of atoms) nuclear motions, and these $3n$ motions can be the acceptors of the electronic energy. The gap between the fundamental transition energy of these acceptors and that of the donor is huge. For example, the gap between a donor of a 500 nm electronic absorption and a CH stretch (3000 cm^{-1}) acceptor is 17000 cm^{-1} , significantly larger than the thermal energy of ~ 200 cm^{-1} at room temperature, and is also too large to be efficiently compensated by phonons. Under such a condition, the energy transfer from the electronic energy donor to a vibrational acceptor in a condensed phase can be estimated with the theory of a dephasing mechanism.^{42–44} Under the weak coupling limit which requires the donor–acceptor coupling strength V to be much smaller than the homogeneous dephasing line width τ^{-1} , the energy-transfer rate constant is^{42–44}

$$k_{DA} = \frac{2}{1 + e^{-100hcN\Delta E/RT}} V^2 \frac{\tau^{-1}}{(\Delta E)^2 + 4V^2 + \tau^{-2}} \quad (2)$$

where ΔE (cm^{-1}) is the absolute value of energy difference between donor and acceptor, h Planck’s constant, c the speed of light in vacuum, N Avogadro’s constant, τ (fs) the dephasing time, V (cm^{-1}) the coupling strength, T (K) temperature, and R ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) the gas constant. At room temperature, the nonradiative decay time constant $\tau_{nr} = 1/k_{DA}$ is at the time scale of a few nanoseconds (~ 4.6 ns), using 17000 cm^{-1} as the energy difference between donor and acceptor, 20 fs as the dephasing time (15 nm ~ 583 cm^{-1} as the bandwidth of the donor, which is assumed to give a 20 fs dephasing time for the transfer process), and 25 cm^{-1} as the coupling strength (calculated based on the dipole–dipole interaction,^{42–45} using $1D$ for donor and $0.3D$ for acceptor, 2.4 Å as DA distance, and 0.5 for orientation factor). It is noted that the estimation here is only approximate, as the number, transition dipole moments, and orientations of the acceptors may change and lead to different coupling strengths. Nonresonant energy transfers can also occur via the phonon compensation mechanism,^{46,47} but the huge energy gap requires a very high-order compensation with, e.g., 100 phonons of 170 cm^{-1} , of which the efficiency is probably too low to be of any significance.⁴⁴

The above estimations give similar radiative and nonradiative decay rates, with the latter being slightly faster, which is consistent with the fact that the luminescence efficiencies of many molecules are at the order of tens of percent.^{48,49}

In dilute solutions of AIE molecules, their luminescence efficiencies can be very low, e.g., 0.1% , meaning that the nonradiative decay is at the time scale of picoseconds (ps) to tens of picoseconds, about 100 – 1000 times faster than the radiative decay. According to eq 2, there are two possibilities to increase k_{DA} : reducing the energy gap or increasing the coupling strength. If the energy gap decreases to zero, the coupling strength should be larger than 6 cm^{-1} in order for $1/k_{DA}$ to be about 5 ps. A very high-order vibrational combination band or overtone can have energy equal to that of the energy donor and eliminate the energy gap. However, because of its high order, this combination band or overtone has a very small transition dipole moment, which leads to a negligible donor–acceptor coupling strength.

Without changing the gap, if the coupling strength increases to 790 cm^{-1} , the nonradiative rate can be increased 1000-fold. However, under such a condition, the coupling strength surpasses the dephasing line width.⁴² The weak coupling limit is violated, and eq 2 does not apply any more.

The above analyses suggest that for the nonradiative decay to be at the time scale of picoseconds or faster, the electron–vibration coupling is so strong that the electronic and nuclear motions are inseparable and the BOA does not apply any more. This scenario was addressed as early as 1937 by Teller.⁵⁰

The breakdown of the BOA typically occurs when two electronic states are resonant (of the same energy), which can be illustrated by the following equation:⁵¹

$$\vec{F}_{ji} = \langle j(\vec{R}) | \nabla_{\vec{R}} i(\vec{R}) \rangle = \frac{\langle j(\vec{R}) | \nabla_{\vec{R}} \hat{H}_e | i(\vec{R}) \rangle}{E_i(\vec{R}) - E_j(\vec{R})} \quad (3)$$

which is derived from

$$\begin{aligned} \nabla_{\vec{R}} \langle j(\vec{R}) | \hat{H}_e | i(\vec{R}) \rangle &= E_i(\vec{R}) \vec{F}_{ji}^*(\vec{R}) + E_j(\vec{R}) \vec{F}_{ji}(\vec{R}) \\ &+ \langle j(\vec{R}) | \nabla_{\vec{R}} \hat{H}_e | i(\vec{R}) \rangle = 0 \end{aligned} \quad (4)$$

where $j(\vec{R})$ and $i(\vec{R})$ are two different electronic states in nuclear coordinate \vec{R} ; \hat{H}_e is the Hamiltonian of electronic states; $\nabla_{\vec{R}}$ is the first derivative operator over the nuclear coordinate; $E_i(\vec{R})$ and $E_j(\vec{R})$ are the energy eigenvalues of $i(\vec{R})$ and $j(\vec{R})$, respectively.

From eq 3, we can see that under normal conditions, the energy gap of two electronic states is large, and \vec{F}_{ji} is small. However, if the energy values of two states are the same, \vec{F}_{ji} can be very large, which means that any linear combination of the electronic wave functions is the solution of the Schrödinger equation. In other words, under such a resonant condition, the molecule has two indistinguishable identities: electronic states $j(\vec{R})$ and $i(\vec{R})$.

The above physical picture can be qualitatively understood in the following way using the electronic ground state and one electronic excited state as examples. Under normal conditions, the structure of the electronic ground state of a polyatomic molecule is distinctly different from that of its electronic excited states. However, when a molecule at its electronic ground state is highly vibrationally excited and its nuclear distances become larger, one of its conformations can be identical to some at its electronic excited state. In other words, at this particular conformation, the molecule has two indistinguishable identities: electronic ground state and excited state. The state duality of this conformation is because it can come from the rearrangements of nuclei, triggered, e.g., by vibrational excitations, followed by electronic motions, or from the rearrangement of electrons, triggered, e.g., by light, followed by nuclear motions. The conformation is the conical intersection (CI) at the potential surface. A CI will not exist in diatomic molecules because the existence of a CI requires at least two degrees of freedom and diatomic molecules have only one (nuclear distance).⁵² In general, the conformation (CI, the green or purple spot in Figure 1) has energy lower than the vertically excited one (the red spot in Figure 1).

After a molecule is vertically excited, as required by the Frank–Cotton principle, its conformation begins to evolve. If the energy barrier is low enough, it can isomerize into the structures of CIs before any substantial decay of electronic

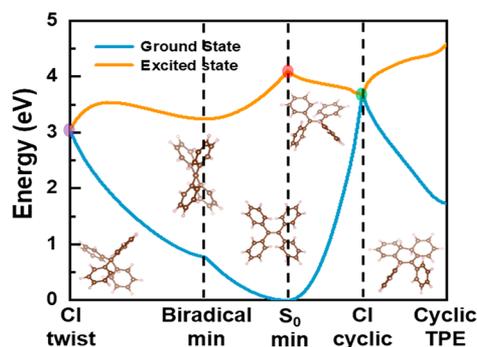


Figure 1. Potential surfaces of TPE excited state and ground state. The molecule absorbs a photon and is vertically excited to the red spot. The excited molecule can evolve to reach the green or purple spot (CI), where the electronic ground and excited states are degenerate. Reprinted with permission from ref 69. Copyright 2020, Wiley-VCH.

excitation. Once it reaches any CI, 50% of its identity is the electronic ground state, and the energy of this portion must relax in the form of nuclear motions; no UV–vis photon emission is involved because electrons cannot jump to a lower level from the ground state. It is well-known that the high-order molecular vibrations typically relax at the time scale of hundreds of femtoseconds to picoseconds in a condensed phase,^{53–57} which is much faster than fluorescence. Therefore, at a CI, most of the electronic energy must relax into vibrational energy within picoseconds. Certainly, the structural evolutions of the electronic excited state to reach CIs require conformational changes, which takes time and are dependent on molecular environments. They can be much slower than the energy conversion process at CIs, becoming the bottleneck determining the radiative/nonradiative decay ratio.

Crossing the CI, or the nonadiabatic coupling of vibrational and electronic degrees of freedom, is not a rare phenomenon. In fact, it is frequently involved in the excited-state dynamics of polyatomic molecular systems,⁵² and the energy associated with electronic excitations converted to vibrational energy within ultrafast time scales (femtoseconds to picoseconds) is often considered as the driving force for photochemical processes.⁵⁸ That conical intersections mediate nonradiative internal conversion processes has become a standard mechanism to justify their ultrafast time scales,⁵⁹ e.g., in chemical reactions and nonadiabatic luminescence processes,^{60–63} fluorescence quenching of organic molecules,^{64–66} and DNA bases.^{67,68} CIs also play key roles in AIE.

As discussed above, the luminescence efficiency of AIE molecules in solutions can be very low, e.g., <0.1%, which can be caused only by crossing CI. This mechanism was experimentally supported recently by monitoring the structural evolutions of TPE and its derivatives crossing CIs.⁶⁹ Upon UV photoexcitation, TPE in a dilute tetrahydrofuran solution shows an infrared response (Figure 2d) totally different from that of its solid (Figure 2c), though their infrared absorption spectra are very similar (Figure 2b). In the solid, two absorption peaks at 1486 and 1437 cm^{-1} appear after excitation (Figure 2c). The peaks reach maxima within 100 fs, the temporal resolution of the experiments, and diminish quickly. After 10 ps, their intensities have dropped significantly. These two peaks have frequencies that are slightly smaller than their respective peaks at 1489 and 1442 cm^{-1} in the FTIR spectrum, resulting from the excited-state absorptions of the

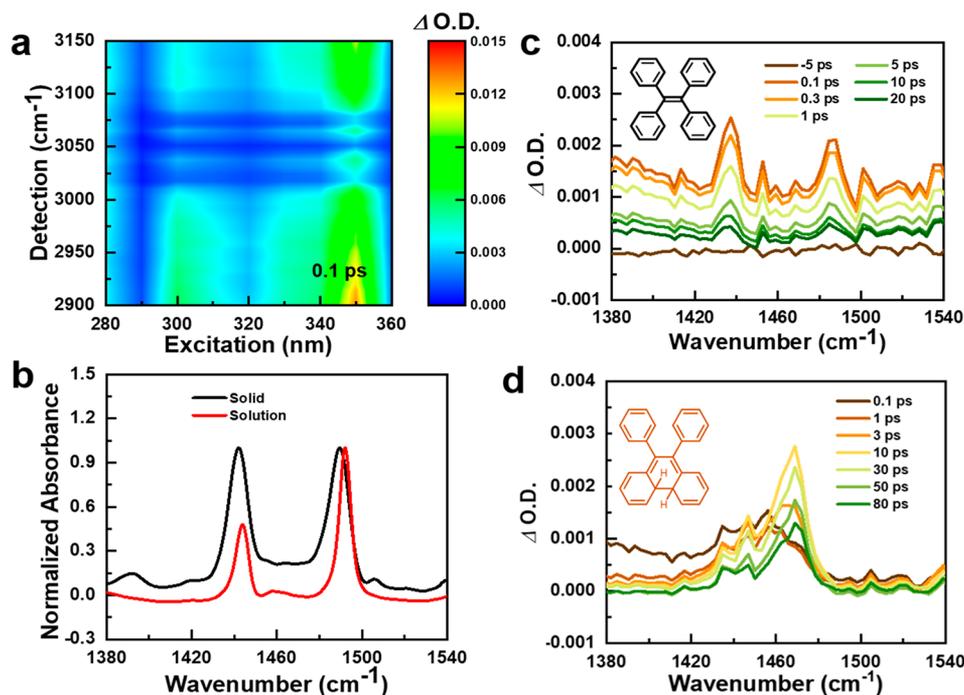


Figure 2. (a) UV/IR 2D plot of TPE at a waiting time of 0.1 ps. (b) FTIR spectra of TPE in the solid state (black) and a THF solution (red). The frequencies of the two major peaks are very similar, in contrast to the huge difference observed in the transient spectra in panels c and d. (c) Evolution of vibrational spectra of TPE in the solid state after excitation with photons at 290 nm and the molecular structure of TPE. (d) Evolution of vibrational spectra of TPE in a dilute THF solution after excitation with photons at 290 nm, and the structure is TPE cyclic intermediate. Reprinted with permission from ref 69. Copyright 2020, Wiley-VCH.

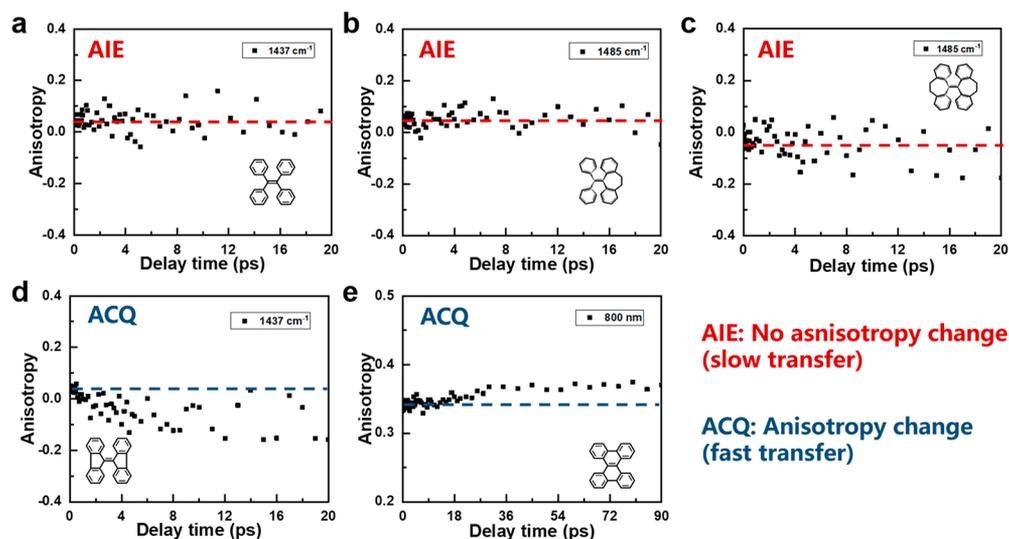


Figure 3. Time dependence of photoexcitation signal anisotropy of AIE and ACQ solids. Because molecular orientations in the solids are not identical for each molecule, intermolecular energy or charge transfers inevitably result in anisotropy change. No anisotropy change has occurred within 20 ps in AIE solids, whereas in ACQ solids, anisotropy change is clearly visible within 10 ps. Dots are data. Straight dashed lines are added for a better comparison effect. Reprinted with permission from ref 69. Copyright 2020, Wiley-VCH.

benzene skeleton vibrations and frequency shifts caused by the electronic excitation. Two corresponding small bleaching peaks grow in, appearing at slightly blue-shifted 1497 and 1447 cm^{-1} positions. In the dilute solution, its ultrafast spectral evolution is distinctively different. Upon electronic excitation, a new absorption peak at 1469 cm^{-1} (Figure 2d) grows in. It reaches a maximum at ~ 10 ps. This new peak is not caused by the photoexcitation-induced instantaneous frequency shift like those in the solid or energy transfer that requires the peaks

to be at the same frequencies as observed in FTIR.^{42–44} It is caused by the formation of a new molecular structure in the solution.⁶⁹ Systematic investigations, including multiple frequency mapping, comparison between theoretical and experimental vibrational frequencies, analyses of molecular masses of oxidized intermediates, and control samples, conclude that the new molecular structure is the unstable TPE Woodward–Hoffmann cyclic intermediate, diphenyl dihydrophenanthrene (DPDHP),⁶⁹ and over 70% of the

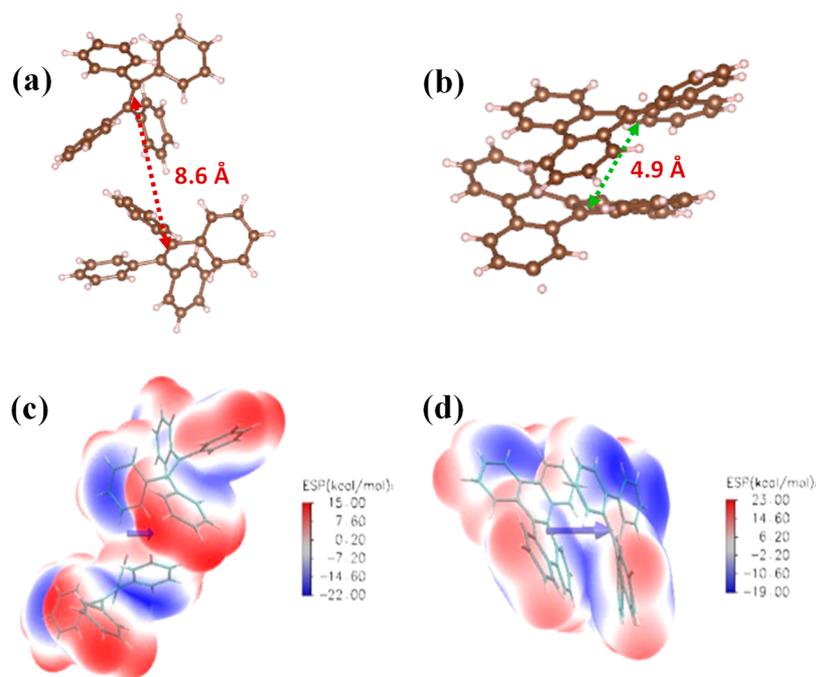


Figure 4. Center distance between two closest molecules in (a) TPE and (b) dibenzo[g,p]chrysene crystals; and surface electrostatic potential of two nearest molecules in TPE (c) and dibenzo[g,p]chrysene (d) crystals. Electrostatic potential is lower when the area is bluer. The blue arrow indicates the direction of the dipole moment. Panels c and d were calculated with Multiwfn and Gaussian09^{92–94} and drawn with VMD.^{88,89} The dimers are at their respective first singlet excited state where one molecule is at electronic ground state and the other is at the first excited state.

photoexcited molecules have been converted into the cyclic intermediate within 10 ps. Such a fast process can be possible only by passing through a CI, which has been predicted by theory.^{70–80}

In contrast, in the TPE solid, photoexcitation does not lead to the formation of new structures. This is because it is too costly in energy for benzene rings of TPE to rotate around in order to form the cyclic intermediate. Such a process requires the breakdown of the crystalline structure of the solid. Therefore, the fast dissipation pathway through a CI disappears in the TPE solid, and the electronic energy gained from photoexcitation is preserved.

Fast energy dissipation by crossing a CI well explains the low luminescence efficiencies of AIE solutions. The inability of reaching a CI in AIE solids allows electronic excitation to stay longer, but it does not preclude aggregation-induced quenching of luminescence caused by intermolecular coupling and charge/energy transfers. There has to be another factor leading to the luminescence efficiency of an AIE solid being higher than that of not only its solution but also many other organic solids.^{81,82} It is very likely that their bulky nonplanar side groups prevent the chromophore centers of two adjacent molecules from staying close or aligning well to each other, effectively weakening intermolecular coupling and thus slowing down intermolecular electron or energy transfers, both of which are major factors for luminescence quenching in solids. This structural effect is illustrated by the comparison of anisotropy measurements of AIE and ACQ molecular solids displayed in Figure 3. The orientations of molecules in solids are different from one to another. Energy or charge transfers inevitably cause the signal anisotropy of photoexcitation to change with time.⁸³ A slower anisotropy change indicates a slower energy/charge transfer. As displayed in Figure 3, no anisotropy change is observed in AIE solids within 20 ps,

whereas evolutions of anisotropy in ACQ molecules are clearly visible within 10 ps. Note that any initial anisotropy value in Figure 3 is determined by the relative orientation between the excited and the detected transition dipole moments, which varies dependent on what optical transitions are chosen in experiments. In Figure 3d, the anisotropy value changes from the initial ~ 0.05 to the final ~ -0.075 , indicating that the cross angle between the excitation and detection transition dipole moments changes from $\sim 49.8^\circ$ to $\sim 62.8^\circ$. The result implies that, on average, the donor molecule has a relative orientation $\sim 13^\circ$ different from that of the final acceptor molecules. Similarly, the result in Figure 3e indicates that the donor molecule has a relative orientation $\sim 6^\circ$ different from the final acceptor molecules. Detailed quantitative analyses to correlate the anisotropy changes with the crystalline structures and energy-transfer kinetics are subject to future studies.

Calculations based on molecular crystalline structures provide interesting insights for the different dynamics of AIE and ACQ solids observed in Figure 3. As displayed in Figure 4a,b, in the AIE solid of TPE, the center distance between two closest molecules is 8.6 Å, whereas in the ACQ solid of dibenzo[g,p]chrysene, the distance, 4.9 Å, is almost 50% shorter. Without considering other factors, the longer distance would cause the energy transfer in the AIE solid to be about 28 times slower than in the ACQ solid, assuming that the energy-transfer rate is inversely proportional to the sixth power of distance.^{42–45} Somewhat unexpectedly, the charge distribution between an excited molecule and its nearest ground-state neighbor also favors faster charge-transfer dynamics in the ACQ solid. As displayed in Figure 4c,d, not only is the dipole moment of the excited TPE dimer smaller than that of the dibenzo[g,p]chrysene solid (0.2431 D vs 0.5652 D), but also its direction is less desirable for charge transfer. In TPE, the direction is almost perpendicular to the connection line of the

two molecules, whereas in dibenzo[g,p]chrysene it is pointing from one molecule to the other.

According to the exciton model,⁸⁴ in organic solids or concentrated solutions, one major fluorescence quenching factor is the formation of aggregate (e.g., H-aggregate) exciton energy levels of which the separation between the bright and dark levels is typically within hundreds to a couple thousand cm^{-1} . Such a small gap allows a substantial portion of electronic excitation at the bright level to quickly relax to the dark level within a few picoseconds to hundreds of picoseconds, effectively quenching fluorescence. The fast bright-to-dark relaxation dynamics were recently experimentally illustrated.^{85,86} Such a quenching effect is closely correlated to the transition dipole/dipole coupling between adjacent molecules.⁸⁴ A larger coupling results in a larger bright/dark gap (typically smaller than a few thousand cm^{-1} , and an intra- or intermolecular vibrational normal mode is available as a resonant or quasi-resonant energy acceptor) and a larger portion of excitation at the dark level under equilibrium and thus a larger quenching effect. Certainly a larger coupling also indicates a fast energy or charge transfer, or vice versa. The dynamic processes of energy/charge transfers themselves can also quench fluorescence by various possibilities, e.g., transferred to and trapped at defects or hot spots, momenta altered during transfer, and it takes time for intermolecular charges to recombine on the same molecule. The anisotropy measurements discussed above not only imply a very slow energy/charge transfer but also a weak intermolecular coupling and a small exciton-quenching effect in the TPE solid. Although similar to the case of strong coupling where a fluorescence or absorption peak in the solid or a concentrated solution appears at a higher frequency than in a dilute solution,^{85,87,88} the fluorescence spectra of TPE are much more complicated because they are highly dependent on the temperature and solvent structures which may lead to different molecular conformations with different emissions.^{89–91}

Associated with this AIE mechanism, there is a natural photo physical consequence: the fluorescence quantum yields of the AIE molecules in liquid dilute solutions are dependent on excitation wavelengths, an anti-Vavilov's rule phenomenon.⁹⁵ Although it is known that anti-Vavilov's rule phenomena exist for molecules with multiple electronic excited states, e.g., S_1 and S_2 , the mechanism here is different. In the AIE molecules, different excitation wavelengths lead to different vibrational excited states at the first electronic excited state, which allows the electronic excited state to cross different barriers to reach the CI so that the nonradiative decay rates are different. A shorter excitation wavelength allows the molecule to be excited to a higher vibrational excited state, so the barrier to reach the CI is smaller and the nonradiative decay is faster; therefore, it results in a lower fluorescence quantum yield. Taking *trans*-stilbene which is also an AIE molecule as an example, its fluorescence quantum yields in a 5×10^{-5} mol/L hexane solution are 1.0% (260 nm excitation), 1.8% (280 nm excitation), 2.4% (300 nm excitation), and 4.5% (320 nm excitation). It is noted that such a phenomenon in which the fluorescence quantum yield is dependent on the excitation wavelength is not limited to AIE. Only if the electronic excited state has to cross a barrier that is close to the vibrational transition frequencies, e.g., a few kilocalories per mole, to reach a CI, a salient excitation wavelength-dependent fluorescence quantum yield is expected. Comprehensive studies on this topic are subject to future investigations.

In this Perspective, the theoretical principles and experimental evidence of the AIE mechanism of TPE and its derivatives are discussed. AIE results from two factors: (1) the fast energy dissipation by crossing a CI in solutions but not in solids results in low luminescence efficiencies in the solutions; and (2) the weak intermolecular coupling and thus slow intermolecular energy/charge transfers in the AIE solids effectively prevent quenching and result in relatively high efficiencies of luminescence. Crossing conical intersections is common and plays vital roles for nonradiative energy dissipation in molecules, not limited to AIE. The key to AIE

The key to AIE is that the luminescence efficiency is tuned by controlling molecules to cross or not cross a CI by changing the state of the molecule from dilute solution to aggregate.

is that the luminescence efficiency is tuned by controlling molecules to cross or not cross a CI by changing the state of the molecule from dilute solution to aggregate. How fast a molecule can cross a CI is dependent on the energy barrier of isomerization, which can be tuned in many ways, including mechanical or electronic stimuli. Although the conclusions are mostly from the work on TPE and a few of its derivatives, they are expected to be general for a much wider range of AIE molecules that have been applied in various applications^{13–19} where the luminescence efficiencies are highly different in the aggregate and liquid states.

The structural evolution of the electronic excited state occurs on the time scale of femtoseconds to picoseconds and can last for a very long time, and crossing a CI is typically within tens of picoseconds, both of which are well within the capability of ultrafast laser spectroscopy. However, CIs are not global or local energy minima in potential surfaces, and they are not reaction intermediates, which means that their relative concentrations are too low to be experimentally observed. Typical experimental observables are reaction intermediates after crossing a CI, like the cyclic intermediate of the TPE solution. Therefore, the combination of theoretical calculations and ultrafast experiments is necessary for determining CI structures. The evolution of vibrational frequencies and vibrational transition dipole directions obtained by polarization-selective ultrafast UV–vis/IR mixed frequency spectroscopy can provide rich structural and dynamic information about the process of crossing a CI.

Finally, in principle, there can be an alternative way to tune luminescence efficiency by manipulating the formation of CIs instead of crossing or not crossing them in AIE. This approach relies on the fact that the electronic ground state and the excited state have many different properties, e.g., dipole moment. By tuning the environment, e.g., dielectric constant, to favor or disfavor one state, one may be able to lift or lower the potential surface of one state so that the potential surfaces of two states can vary between intersected and not contacted.

■ AUTHOR INFORMATION

Corresponding Author

Junrong Zheng – College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular

Sciences, Peking University, Beijing 100871, China;
✉ orcid.org/0000-0002-4472-8576; Email: junrong@pku.edu.cn

Authors

Jianxin Guan – College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, Beijing 100871, China

Chengzhen Shen – College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, Beijing 100871, China

Jie Peng – College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, Beijing 100871, China

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jpcllett.0c03861>

Notes

The authors declare no competing financial interest.

Biographies

Jianxin Guan is a chemistry Ph.D. candidate at Peking University. He received his B.S. from Wuhan University. His research focuses on the ultrafast dynamics of electrons and excited molecules.

Chengzhen Shen is a chemistry Ph.D. candidate at Peking University. He received his B.S. from Nanjing University. His research focuses on electronic structure theory.

Jie Peng is a chemistry Ph.D. candidate at Peking University. She received her B.S. from Suda University. Her research focuses on the ultrafast dynamics of electrons and excited molecules.

Junrong Zheng is a professor of chemistry at Peking University. He received his B.S. and M.S. from Peking University and RPI and Ph.D. from Stanford. He was a faculty member at Rice University before joining Peking University. His research focuses on molecular dynamics and energy.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation of China (NSFC-21627805, 21673004, and 21821004) and MOST (2017YFA0204702) of China.

REFERENCES

- (1) Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- (2) Yuan, W. Z.; Lu, P.; Chen, S.; Lam, J. W. Y.; Wang, Z.; Liu, Y.; Kwok, H. S.; Ma, Y.; Tang, B. Z. Changing the Behavior of Chromophores from Aggregation-Caused Quenching to Aggregation-Induced Emission: Development of Highly Efficient Light Emitters in the Solid State. *Adv. Mater.* **2010**, *22*, 2159–2163.
- (3) Jenekhe, S. A.; Osaheni, J. A. Excimers and Exciplexes of Conjugated Polymers. *Science* **1994**, *265*, 765–768.
- (4) Hong, Y.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission: Phenomenon, Mechanism and Applications. *Chem. Commun. (Cambridge, U. K.)* **2009**, 4332–4353.
- (5) Voll, C.-C. A.; Engelhart, J. U.; Einzinger, M.; Baldo, M. A.; Swager, T. M. Donor-Acceptor Iptycenes with Thermally Activated Delayed Fluorescence. *Eur. J. Org. Chem.* **2017**, *2017*, 4846–4851.
- (6) Kawasumi, K.; Wu, T.; Zhu, T.; Chae, H. S.; Van Voorhis, T.; Baldo, M. A.; Swager, T. M. Thermally Activated Delayed Fluorescence Materials Based on Homoconjugation Effect of Donor-Acceptor Triptycenes. *J. Am. Chem. Soc.* **2015**, *137*, 11908–11911.

(7) Jelley, E. E. Spectral Absorption and Fluorescence of Dyes in the Molecular State. *Nature* **1936**, *138*, 1009–1010.

(8) Zink, J. I.; Hardy, G. E.; Sutton, J. E. Triboluminescence of Sugars. *J. Phys. Chem.* **1976**, *80*, 248–249.

(9) Fischer, G.; Fischer, E.; Stegemeyer, H. Fluorescence and Absorption Spectra of Sterically Hindered Arylethylenes in the Neat Glassy State. *Berichte der Bunsengesellschaft für physikalische Chemie* **1973**, *77*, 685–687.

(10) Stark, J.; Lipp, P. The Effect of Inner Molecular Relative Movement on the Intensity of Absorption of Fluorescent by Valence Electrons. *Z. Phys. Chem.* **1913**, *86*, 36–41.

(11) Schmidt, G. C. Beiträge Zur Kenntniss Der Fluoreszenz. *Ann. Phys.* **1896**, *294*, 103–130.

(12) Schmidt, G. C. Über Lumineszenz Von Festen Lösungen. *Ann. Phys.* **1921**, *370*, 247–256.

(13) Hong, Y.; et al. Fluorescent Bioprobes: Structural Matching in the Docking Processes of Aggregation-Induced Emission Fluorogens on DNA Surfaces. *Chem. - Eur. J.* **2010**, *16*, 1232–1245.

(14) Hu, F.; Xu, S.; Liu, B. Photosensitizers with Aggregation-Induced Emission: Materials and Biomedical Applications. *Adv. Mater.* **2018**, *30*, 1801350.

(15) Ding, D.; et al. Ultrabright Organic Dots with Aggregation-Induced Emission Characteristics for Real-Time Two-Photon Intravital Vasculature Imaging. *Adv. Mater.* **2013**, *25*, 6083–6088.

(16) Li, Y.; Xu, L.; Su, B. Aggregation Induced Emission for the Recognition of Latent Fingerprints. *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 4109–4111.

(17) Wang, D.; Su, H.; Kwok, R. T. K.; Hu, X.; Zou, H.; Luo, Q.; Lee, M. M. S.; Xu, W.; Lam, J. W. Y.; Tang, B. Z. Rational Design of a Water-Soluble Nir Aiegen, and Its Application in Ultrafast Wash-Free Cellular Imaging and Photodynamic Cancer Cell Ablation. *Chem. Sci.* **2018**, *9*, 3685–3693.

(18) Hu, R.; Leung, N. L. C.; Tang, B. Z. Aie Macromolecules: Syntheses, Structures and Functionalities. *Chem. Soc. Rev.* **2014**, *43*, 4494–4562.

(19) Luo, X.; Li, J.; Li, C.; Heng, L.; Dong, Y. Q.; Liu, Z.; Bo, Z.; Tang, B. Z. Reversible Switching of the Emission of Diphenyldibenzofulvenes by Thermal and Mechanical Stimuli. *Adv. Mater.* **2011**, *23*, 3261–3265.

(20) Würthner, F. Aggregation-Induced Emission (Aie): A Historical Perspective. *Angew. Chem., Int. Ed.* **2020**, *59*, 14192–14196.

(21) Oster, G.; Nishijima, Y. Fluorescence and Internal Rotation: Their Dependence on Viscosity of the Medium. *J. Am. Chem. Soc.* **1956**, *78*, 1581–1584.

(22) Sharafy, S.; Muszkat, K. A. Viscosity Dependence of Fluorescence Quantum Yields. *J. Am. Chem. Soc.* **1971**, *93*, 4119–4125.

(23) Luo, J.; et al. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole. *Chem. Commun.* **2001**, 1740–1741.

(24) Chen, J.; Xu, B.; Ouyang, X.; Tang, B. Z.; Cao, Y. Aggregation-Induced Emission Of cis, Cis-1,2,3,4-Tetraphenylbutadiene from Restricted Intramolecular Rotation. *J. Phys. Chem. A* **2004**, *108*, 7522–7526.

(25) Tong, H.; Dong, Y.; Häußler, M.; Hong, Y.; Lam, J. W. Y.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Tang, B. Z. Molecular Packing and Aggregation-Induced Emission of 4-Dicyanomethylene-2,6-Distyryl-4h-Pyran Derivatives. *Chem. Phys. Lett.* **2006**, *428*, 326–330.

(26) Ma, J.; Dutt, G. B.; Waldeck, D. H.; Zimmt, M. B. The Excited State Potential Energy Surface for the Photoisomerization of Tetraphenylethylene: A Fluorescence and Picosecond Optical Calorimetry Investigation. *J. Am. Chem. Soc.* **1994**, *116*, 10619–10629.

(27) Greene, B. I. Observation of a Long-Lived Twisted Intermediate Following Picosecond Uv Excitation of Tetraphenylethylene. *Chem. Phys. Lett.* **1981**, *79*, 51–53.

(28) Lenderink, E.; Duppen, K.; Wiersma, D. A. Femtosecond Twisting and Coherent Vibrational Motion in the Excited State of Tetraphenylethylene. *J. Phys. Chem.* **1995**, *99*, 8972–8977.

- (29) Zijlstra, R. W. J.; van Duijnen, P. T.; Feringa, B. L.; Steffen, T.; Duppen, K.; Wiersma, D. A. Excited-State Dynamics of Tetraphenylethylene: Ultrafast Stokes Shift, Isomerization, and Charge Separation. *J. Phys. Chem. A* **1997**, *101*, 9828–9836.
- (30) Shultz, D. A.; Fox, M. A. Spectroscopic Properties of [N.1]-Metacyclophanenylidenes. *Tetrahedron Lett.* **1988**, *29*, 4377–4380.
- (31) Shultz, D. A.; Fox, M. A. Effect of Phenyl Ring Torsional Rigidity on the Photophysical Behavior of Tetraphenylethylenes. *J. Am. Chem. Soc.* **1989**, *111*, 6311–6320.
- (32) Kang, H.; et al. Ultralarge Hyperpolarizability Twisted Pi-Electron System Electro-Optic Chromophores: Synthesis, Solid-State and Solution-Phase Structural Characteristics, Electronic Structures, Linear and Nonlinear Optical Properties, and Computational Studies. *J. Am. Chem. Soc.* **2007**, *129*, 3267–3286.
- (33) Misawa, K.; Minoshima, K.; Ono, H.; Kobayashi, T. Giant Static Dipole Moment Change on Electronic Excitation in Highly Oriented J-Aggregates. *Chem. Phys. Lett.* **1994**, *220*, 251–256.
- (34) Kano, H.; Saito, T.; Kobayashi, T. Dynamic Intensity Borrowing in Porphyrin J-Aggregates Revealed by Sub-5-Fs Spectroscopy. *J. Phys. Chem. B* **2001**, *105*, 413–419.
- (35) Wang, Y.; Nie, J.; Fang, W.; Yang, L.; Hu, Q.; Wang, Z.; Sun, J. Z.; Tang, B. Z. Sugar-Based Aggregation-Induced Emission Luminogens: Design, Structures, and Applications. *Chem. Rev.* **2020**, *120*, 4534–4577.
- (36) Shah, N. K.; Ludescher, R. D. Phosphorescence Probes of the Glassy State in Amorphous Sucrose. *Biotechnol. Prog.* **1995**, *11*, 540–544.
- (37) Strickler, S. J.; Berg, R. A. Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules. *J. Chem. Phys.* **1962**, *37*, 814–822.
- (38) Henderson, B.; Imbusch, G.F. In *Optical Spectroscopy of Inorganic Solids*; Oxford University Press.
- (39) Kobayashi, M.; Sakashita, M. Morphology Dependent Anomalous Frequency Shifts of Infrared Absorption Bands of Polymer Crystals: Interpretation in Terms of Transition Dipole–Dipole Coupling Theory. *J. Chem. Phys.* **1992**, *96*, 748–760.
- (40) Chen, H.; Wen, X.; Li, J.; Zheng, J. Molecular Distances Determined with Resonant Vibrational Energy Transfers. *J. Phys. Chem. A* **2014**, *118*, 2463–2469.
- (41) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Springer Science & Business Media, 2013.
- (42) Chen, H.; Wen, X.; Guo, X.; Zheng, J. Intermolecular Vibrational Energy Transfers in Liquids and Solids. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13995–4014.
- (43) Chen, H.; Bian, H.; Li, J.; Wen, X.; Zhang, Q.; Zhuang, W.; Zheng, J. Vibrational Energy Transfer: An Angstrom Molecular Ruler in Studies of Ion Pairing and Clustering in Aqueous Solutions. *J. Phys. Chem. B* **2015**, *119*, 4333–4349.
- (44) Chen, H.; Zhang, Q.; Guo, X.; Wen, X.; Li, J.; Zhuang, W.; Zheng, J. Nonresonant Energy Transfers Independent on the Phonon Densities in Polyatomic Liquids. *J. Phys. Chem. A* **2015**, *119*, 669–680.
- (45) Scholes, G. D. Long-Range Resonance Energy Transfer in Molecular Systems. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57–87.
- (46) Egorov, S. A.; Berne, B. J. Vibrational Energy Relaxation in the Condensed Phases: Quantum Vs Classical Bath for Multiphonon Processes. *J. Chem. Phys.* **1997**, *107*, 6050–6061.
- (47) Kenkre, V. M.; Tokmakoff, A.; Fayer, M. D. Theory of Vibrational Relaxation of Polyatomic Molecules in Liquids. *J. Chem. Phys.* **1994**, *101*, 10618–10629.
- (48) Gilmore, E. H.; Gibson, G. E.; McClure, D. S. Absolute Quantum Efficiencies of Luminescence of Organic Molecules in Solid Solution. *J. Chem. Phys.* **1952**, *20*, 829–836.
- (49) Melhuish, W. H. Quantum Efficiencies of Fluorescence of Organic Substances: Effect of Solvent and Concentration of the Fluorescent Solute. *J. Phys. Chem.* **1961**, *65*, 229–235.
- (50) Teller, E. The Crossing of Potential Surfaces. *J. Phys. Chem.* **1937**, *41*, 109–116.
- (51) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; Clarendon Press, 1988.
- (52) Yarkony, D. R. Diabolical Conical Intersections. *Rev. Mod. Phys.* **1996**, *68*, 985–1013.
- (53) Chen, H.; Bian, H.; Li, J.; Wen, X.; Zheng, J. Ultrafast Multiple-Mode Multiple-Dimensional Vibrational Spectroscopy. *Int. Rev. Phys. Chem.* **2012**, *31*, 469–565.
- (54) Burin, A. L.; Tesar, S. L.; Kasyanenko, V. M.; Rubtsov, I. V.; Rubtsov, G. I. Semiclassical Model for Vibrational Dynamics in Polyatomic Molecules: Investigation of Internal Vibrational Relaxation. *J. Phys. Chem. C* **2010**, *114*, 20510–20517.
- (55) Rubtsov, I. V.; Wang, J.; Hochstrasser, R. M. Vibrational Coupling between Amide-I and Amide-a Modes Revealed by Femtosecond Two Color Infrared Spectroscopy. *J. Phys. Chem. A* **2003**, *107*, 3384–3396.
- (56) Kurochkin, D. V.; Naraharisetty, S. R. G.; Rubtsov, I. V. A Relaxation-Assisted 2d Ir Spectroscopy Method. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 14209–14214.
- (57) Rosenfeld, D. E.; Gengeliczki, Z.; Smith, B. J.; Stack, T. D. P.; Fayer, M. D. Structural Dynamics of a Catalytic Monolayer Probed by Ultrafast 2d Ir Vibrational Echoes. *Science* **2011**, *334*, 634–639.
- (58) Michl, J.; Bonačić-Koutecký, V. *Electronic Aspects of Organic Photochemistry*; Wiley, 1990.
- (59) Yarkony, D. R. Conical Intersections: Their Description and Consequences. In *Conical Intersections*; **2004**, *15*, 41–127.
- (60) Gindensperger, E.; Bâldea, I.; Franz, J.; Köppel, H. Multi-State Vibronic Interactions in the Fluorobenzene Radical Cation: The Importance of Quadratic Coupling Terms. *Chem. Phys.* **2007**, *338*, 207–219.
- (61) van der Horst, M. A.; Hellingwerf, K. J. Photoreceptor Proteins, “Star Actors of Modern Times”: A Review of the Functional Dynamics in the Structure of Representative Members of Six Different Photoreceptor Families. *Acc. Chem. Res.* **2004**, *37*, 13–20.
- (62) Dugave, C.; Demange, L. Cis–Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* **2003**, *103*, 2475–2532.
- (63) Liang, J.; Nguyen, Q. L.; Matsika, S. Exciplexes and Conical Intersections Lead to Fluorescence Quenching in π -Stacked Dimers of 2-Aminopurine with Natural Purine Nucleobases. *Photochemical & Photobiological Sciences* **2013**, *12*, 1387–1400.
- (64) Sobolewski, A. L.; Domcke, W. Ab Initio Investigations on the Photophysics of Indole. *Chem. Phys. Lett.* **1999**, *315*, 293–298.
- (65) Sobolewski, A. L.; Domcke, W. Photoinduced Electron and Proton Transfer in Phenol and Its Clusters with Water and Ammonia. *J. Phys. Chem. A* **2001**, *105*, 9275–9283.
- (66) Sobolewski, A. L.; Domcke, W. Conical Intersections Induced by Repulsive $1\pi\sigma^*$ States in Planar Organic Molecules: Malonaldehyde, Pyrrole and Chlorobenzene as Photochemical Model Systems. *Chem. Phys.* **2000**, *259*, 181–191.
- (67) Nir, E.; Kleinermanns, K.; Grace, L.; de Vries, M. S. On the Photochemistry of Purine Nucleobases. *J. Phys. Chem. A* **2001**, *105*, 5106–5110.
- (68) Kim, N. J.; Jeong, G.; Kim, Y. S.; Sung, J.; Keun Kim, S.; Park, Y. D. Resonant Two-Photon Ionization and Laser Induced Fluorescence Spectroscopy of Jet-Cooled Adenine. *J. Chem. Phys.* **2000**, *113*, 10051–10055.
- (69) Guan, J.; et al. Direct Observation of Aggregation-Induced Emission Mechanism. *Angew. Chem., Int. Ed.* **2020**, *132*, 14903–14909.
- (70) Crespo-Otero, R.; Li, Q.; Blancafort, L. Exploring Potential Energy Surfaces for Aggregation-Induced Emission-from Solution to Crystal. *Chem. - Asian J.* **2019**, *14*, 700–714.
- (71) Prlj, A.; Doslic, N.; Corminboeuf, C. How Does Tetraphenylethylene Relax from Its Excited States? *Phys. Chem. Chem. Phys.* **2016**, *18*, 11606–11609.
- (72) Tran, T.; Prlj, A.; Lin, K. H.; Hollas, D.; Corminboeuf, C. Mechanisms of Fluorescence Quenching in Prototypical Aggregation-Induced Emission Systems: Excited State Dynamics with Td-Dftb. *Phys. Chem. Chem. Phys.* **2019**, *21*, 9026–9035.

- (73) Gao, Y.-J.; Chang, X.-P.; Liu, X.-Y.; Li, Q.-S.; Cui, G.; Thiel, W. Excited-State Decay Paths in Tetraphenylethene Derivatives. *J. Phys. Chem. A* **2017**, *121*, 2572–2579.
- (74) Tretiak, S.; Saxena, A.; Martin, R. L.; Bishop, A. R. Photoexcited Breathers in Conjugated Polyenes: An Excited-State Molecular Dynamics Study. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 2185–2190.
- (75) Maksimenka, R.; Dietzek, B.; Szeghalmi, A.; Siebert, T.; Kiefer, W.; Schmitt, M. Population Dynamics of Vibrational Modes in Stilbene-3 Upon Photoexcitation to the First Excited State. *Chem. Phys. Lett.* **2005**, *408*, 37–43.
- (76) Ortiz-Sánchez, J. M.; Gelabert, R.; Moreno, M.; Lluch, J. M. Electronic-Structure and Quantum Dynamical Study of the Photochromism of the Aromatic Schiff Base Salicylideneaniline. *J. Chem. Phys.* **2008**, *129*, 214308.
- (77) Hoffman, D. P.; Mathies, R. A. Photoexcited Structural Dynamics of an Azobenzene Analog 4-Nitro-4'-Dimethylamino-Azobenzene from Femtosecond Stimulated Raman. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6298–6306.
- (78) Li, Q.; Blancafort, L. A Conical Intersection Model to Explain Aggregation Induced Emission in Diphenyl Dibenzofulvene. *Chem. Commun. (Cambridge, U. K.)* **2013**, *49*, 5966–5968.
- (79) Zhou, P.; Li, P.; Zhao, Y.; Han, K. Restriction of Flip-Flop Motion as a Mechanism for Aggregation-Induced Emission. *J. Phys. Chem. Lett.* **2019**, *10*, 6929–6935.
- (80) Peng, X.-L.; Ruiz-Barragan, S.; Li, Z.-S.; Li, Q.-S.; Blancafort, L. Restricted Access to a Conical Intersection to Explain Aggregation Induced Emission in Dimethyl Tetraphenylsilole. *J. Mater. Chem. C* **2016**, *4*, 2802–2810.
- (81) Zhang, L.; Chen, Y.; Jiang, J. Solid State Fluorescent Functionalized-Triphenylamine Bodipy Detector for HCl Vapor with High Stability and Absolute Fluorescent Quantum Yield. *Dyes Pigm.* **2016**, *124*, 110–119.
- (82) Zhang, J. N.; Kang, H.; Li, N.; Zhou, S. M.; Sun, H. M.; Yin, S. W.; Zhao, N.; Tang, B. Z. Organic Solid Fluorophores Regulated by Subtle Structure Modification: Color-Tunable and Aggregation-Induced Emission. *Chem. Sci.* **2017**, *8*, 577–582.
- (83) Chen, H.; Zhang, Y.; Li, J.; Liu, H.; Jiang, D. E.; Zheng, J. Vibrational Cross-Angles in Condensed Molecules: A Structural Tool. *J. Phys. Chem. A* **2013**, *117*, 8407–8415.
- (84) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. The Exciton Model in Molecular Spectroscopy. *Pure Appl. Chem.* **1965**, *11*, 371–392.
- (85) Dean, J. C.; Oblinsky, D. G.; Rafiq, S.; Scholes, G. D. Methylene Blue Exciton States Steer Nonradiative Relaxation: Ultrafast Spectroscopy of Methylene Blue Dimer. *J. Phys. Chem. B* **2016**, *120*, 440–454.
- (86) Moretti, L.; Kudisch, B.; Terazono, Y.; Moore, A. L.; Moore, T. A.; Gust, D.; Cerullo, G.; Scholes, G. D.; Maiuri, M. Ultrafast Dynamics of Nonrigid Zinc-Porphyrin Arrays Mimicking the Photosynthetic "Special Pair". *J. Phys. Chem. Lett.* **2020**, *11*, 3443–3450.
- (87) Kordas, J.; El-Bayoumi, M. A. Excited State Intramolecular Torsional Relaxation. Viscosity, Temperature, and Medium Effects on the Fluorescence Characteristics of a Sterically Crowded Molecule. *J. Am. Chem. Soc.* **1974**, *96*, 3043–3048.
- (88) Zhao, Z.; et al. Steric Hindrance, Electronic Communication, and Energy Transfer in the Photo- and Electroluminescence Processes of Aggregation-Induced Emission Luminogens. *J. Phys. Chem. C* **2010**, *114*, 7963–7972.
- (89) Barbara, P. F.; Rand, S. D.; Rentzepis, P. M. Direct Measurements of Tetraphenylethylene Torsional Motion by Picosecond Spectroscopy. *J. Am. Chem. Soc.* **1981**, *103*, 2156–2162.
- (90) Ma, J. S.; Dutt, G. B.; Waldeck, D. H.; Zimmt, M. B. The Excited-State Potential-Energy Surface for the Photoisomerization of Tetraphenylethylene - a Fluorescence and Picosecond Optical Calorimetry Investigation. *J. Am. Chem. Soc.* **1994**, *116*, 10619–10629.
- (91) Shi, J.; Chang, N.; Li, C.; Mei, J.; Deng, C.; Luo, X.; Liu, Z.; Bo, Z.; Dong, Y. Q.; Tang, B. Z. Locking the Phenyl Rings of Tetraphenylethene Step by Step: Understanding the Mechanism of Aggregation-Induced Emission. *Chem. Commun. (Cambridge, U. K.)* **2012**, *48*, 10675–10677.
- (92) Li, D.; Hu, R.; Guo, D.; Zang, Q.; Li, J.; Wang, Y.; Zheng, Y.-S.; Tang, B. Z.; Zhang, H. Diagnostic Absolute Configuration Determination of Tetraphenylethene Core-Based Chiral Aggregation-Induced Emission Compounds: Particular Fingerprint Bands in Comprehensive Chiroptical Spectroscopy. *J. Phys. Chem. C* **2017**, *121*, 20947–20954.
- (93) Huang, D.-C.; Kuo, C.-H.; Ho, M.-T.; Lin, B.-C.; Peng, W.-T.; Chao, I.; Hsu, C.-P.; Tao, Y.-T. Contorted Tetrabenzoacenes of Varied Conjugation: Charge Transport Study with Single-Crystal Field-Effect Transistors. *J. Mater. Chem. C* **2017**, *5*, 7935–7943.
- (94) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
- (95) Klán, P.; Wirz, J. *Photochemistry of Organic Compounds: From Concepts to Practice*; Wiley-Blackwell, 2009.