Kinetic and thermodynamic control of tetraphenylethene aggregation-induced emission behaviors

Nanoscience: Special Issue Dedicated to Professor Paul S. Weiss

Xiancheng Nie | Wenhuan Huang | Dingcheng Zhou | Tao Wang | Xiao Wang | Biao Chen | Xuepeng Zhang | Guoqing Zhang

Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, China

Correspondence
Xuepeng Zhang and Guoqing Zhang, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 96 Jinzhai Rd., Hefei, 230026, China. Email: zhangxp@ustc.edu.cn; gzhang@ustc.edu.cn

Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 21975238, 22103077; University of Science and Technology of China, Grant/Award Number: KY234000139

Abstract
Many aggregation-induced emission (AIE) systems exhibit broad and structureless luminescence emission spectra resembling the Gaussian distribution, which is likely due to kinetically locked molecular conformers in the condensed phase. To verify the hypothesis, a series of tetraphenylethene (TPE) derivatives are synthesized and characterized as aqueous nanoparticle suspensions. It is found that the unsubstituted TPE exhibits reduced fluorescence intensity accompanied by a blueshift of the emission maximum, after the temperature of the aqueous suspension is elevated and cooled to room temperature again. For a naphthalimide-substituted TPE compound, thermal treatment of the AIE aqueous suspension results in complete, irreversible aggregation-caused quenching (ACQ) of fluorescence, which can be restored by a redissolving-precipitation process of thermally treated aggregates. The phenomenon is ascribed as a relative population shift of a kinetic AIE (k-AIE) state to a thermodynamic AIE (t-AIE) or ACQ state, evidenced by differential scanning calorimetry, dynamic light scattering, and scanning electron microscopy. The phenomenon may be universal for many other AIE systems and could be explored as stimuli-responsive materials.

KEYWORDS
aggregation-induced emission, kinetic, phase change, thermodynamic

1 | INTRODUCTION

The complexity of organic systems arises from a rich variety of dynamic, energy-dissipating pathways even for discrete molecules at a finite temperature.[1-7] The situation is aggravated when organic molecules aggregate in the condensed phase in which many new degrees of freedom are created with old ones being randomly inhibited conforming to the laws of statistics.[8-10] However, new fascinating phenomena are usually born into such high complexities, which in turn provide new means for tuning physical properties.[11-13] One example is aggregation-induced emission (AIE): it harnesses the dominant radiative electronic transitions only possible in the aggregate state, because major thermal or collisional quenching pathways that take advantage of large free volumes in the solution state are no longer accessible.[14-20] In addition, classical AIE molecules are typically non-planar and are weakly interacting excitonic systems, and should thus yield luminescence emissions characteristic of individual molecules locked into various structural conformations.[21-23] The hypothesis could be further backed by the fact that AIE spectra are usually Gaussian-like and lack distinct vibronic features, compared to those of emissive organic crystals.[24,25] We reason that if AIE indeed contains a contribution from various kinetic aggregates that are otherwise stable at room temperature, it is possible to expedite the equilibrium state with thermodynamic aggregates either by supplying energy to the kinetic aggregates at elevated temperatures, or by reducing the kinetic barrier such as in the presence of an organic solvent, that is, accelerate the relative intensity change of different emitting states after subjecting the AIE systems to environmental changes.

Herein, we employ a series of AIEgens, including tetraphenylethene (TPE) and its naphthalimide (TPENI) derivatives, to show that AIE generated from two of these derivatives consists of significant contribution from...
kinetically stable but thermodynamically unstable nanosized aggregates at room temperature. We picked N-substituted naphthalimide (NI) as the chemical conjugate to TPE because it has been previously shown that (1) N-substitution with strongly electron-donating species such as N,N-dimethylaminophenyl or trimethoxyphenyl[26–28] quenches fluorescence in solution due to a forbidden charge-transfer (CT) state from the phenyl to the nearly orthogonal NI ring as the lowest singlet excited state, (2) multiple polymorphs with temperature-dependent fluorescence[29] have been observed for the NI derivatives due to their nonplanarity and various types of weak nonbonding interactions, and (3) certain NI compounds exhibit distinct photoluminescence colors from different polymorphs at room temperature[30]. It is quite possible that the inclusion of the NI moiety into the TPE structure could lead to multiple polymorphs with varying free-energy states with different AIE characteristics. Furthermore, different substituents on the NI moiety should lead to different strength of CT states as well as different degrees of rotational freedom of resulting molecules that will tune the photoluminescence properties. We here show that, indeed, after thermal treatment of TPE and TPENI nanoaggregate aqueous suspension, the AIE can be color-switched, unaltered, abated, or even entirely converted into aggregation-caused quenching (ACQ), depending on the substituent groups; the process may be accelerated in the presence of increased organic solvent fraction. To understand the kinetic versus thermodynamic AIE processes, luminescence lifetimes, quantum yields, differential scanning calorimetry (DSC), dynamic light scattering (DLS), and scanning electron microscopy (SEM) are also used.

2 RESULTS AND DISCUSSION

The synthesis of TPE derivatives is straightforward via a one-step coupling reaction between NI derivatives and 4, 4, 5, 5-tetramethyl-2-(1, 2, 2-triphenylvinyl)-1, 3, 2-dioxaborolane (Supporting Information, Scheme S1–2, S1), with their chemical structures (Scheme 1) and purity verified by 1H-NMR spectroscopy, high-resolution mass spectrometry and high-performance liquid chromatography (HPLC). In the THF solution and under UV excitation, these TPE derivatives are either non-fluorescent or exhibit weak photoluminescence to the naked eye (Figure S1), presumably due to the rotational and vibrational dissipation of excited-state energy. When water was added as a co-solvent from zero to 0.9 (water/THF, v/v) at an increment of 0.1, TPE exhibited typical AIE[31] and the NI derivatives possessed AIEE behaviors, where the changes in fluorescence spectra, quantum yields, and lifetimes were monitored for 10 incremental ratio points (Figure 1; Figure S1), given the similarity in the AIEE spectroscopic feature for the three NI-substituted TPE molecules, only the results of the trimethoxyphenyl variant, TPENI-Ph(OMe), are provided in Figure 1. From the 3D-stick model of TPENI-Ph(OMe)3 (Figure 1A), a high degree of rotational freedom from both TPE and NI moieties may render the complex structure weakly fluorescent in THF (Figure 1B). With increased water content in the mixed solvent, the photoluminescence intensity first dimmed to a minimum at a water fraction of 0.6 and saw a sudden change beyond 0.7; concomitantly, the red emission turned to green at the point of abrupt change. The emission spectra of the AIE process were collected and are provided in Figure 1C, where the wavelength at the maximal intensity is first red-shifted from 532 to 630 nm, before commencing a jump to a hypsochromic shift back to 532 nm at a water volume fraction of 0.9. In Figure 1D, the fluorescence intensity and quantum yield changes are consistent with a visual inspection, where the minima occur at a water fraction of 0.6. However, the intensity and quantum yield maxima were observed at a water fraction of 0.8, instead of 0.9. To understand the complicated spectral and intensity change over water content of the mixed solvent, the intrinsic fluorescence lifetimes are calculated (Figure 1E; Figures S1–S4 and Table S1). In pure THF, an intrinsic lifetime of τ0 = 7.83 ns indicates a rather typical singlet π∗–π* transition state. A slight increase from 7.83 to 7.96 ns is noted when the water content is 10%, and the possibility of a specific solvent effect such as hydrogen bonding or excited-state reactions can be excluded. The intrinsic lifetime is drastically lengthened to 150 ns with 0.3 water, which could be due to a strong CT emission. The intrinsic lifetime is reduced to 100 ns at 70% water content, followed by a sharp drop to 10.42 ns with 80% water in the mixed solvent. To probe the presence of a strong CT state, the emission spectra of TPENI-Ph(OMe)3 in toluene, ethyl acetate, tetrahydrofuran, chloroform, and acetonitrile were recorded (Figure S5), where it was found that the emission maxima are red-shifted to 500, 550, 560, 570, and 635 nm, respectively, with a longest-lived intrinsic fluorescence lifetime up to 192.8 ns in acetonitrile (Figure S6; Table S2). The results clearly demonstrate that water first facilitates a strong CT fluorescence state as a polar co-solvent of individual TPENI-Ph(OMe)3 before causing AIE as a bad co-solvent. It must be noted that the AIE intensity is slightly reduced when the water content is further added to 0.9, which could suggest that a stronger fluorescence state is favored for “loose” aggregates in the presence of THF molecules versus “tight” aggregates in pure water, which is supported by the fact that the intrinsic lifetime slightly increases when water content increases from 0.8 to 0.9, presumably due to stronger intermolecular interactions.

To investigate whether these organic aggregates exhibit multiple energetic states, the aqueous suspension from four samples (TPE, TPENI-Ph, TPENI-PhOMe, and TPENI-Ph(OMe)3) were thermally treated by heating the liquids in glass vials with closed caps (in order to maintain the solvent
FIGURE 1  (A) Stick-model representation of TPENI-Ph(OMe)₃ showing multiple freedoms of rotation of aromatic rings; (B) images showing progressively red-shifted fluorescence emission color and enhanced intensity as the water ratio (v/v) increases in a mixture of water/THF solvent; (C) steady-state photoluminescence emission spectra of TPENI-Ph(OMe)₃ in mixed water/THF solvent, where the water fraction is indicated by a decimal number ($\lambda_{ex} = 385$ nm); (D) fluorescence intensity (left vertical axis) /quantum yield (right vertical axis) change as a function of water volume ratio in mixed water/THF solvent; (E) intrinsic fluorescence lifetime ($\tau_0 = \tau/\phi$, where $\tau$ is the measured apparent lifetime and $\phi$ is the measured absolute fluorescence quantum yield) change over water volume ratio.

FIGURE 2  (A–D) Evolution of steady-state emission spectra of TPE ($\lambda_{ex} = 320$ nm), TPENI-Ph(OMe)₃, TPENI-Ph ($\lambda_{ex} = 385$ nm), and TPENI-PhOMe ($\lambda_{ex} = 385$ nm) in water-THF mixed solvent (10⁻³ M, water volume fraction = 0.95) recorded at different times after heating at 100°C, where the change of wavelength and maximum intensity is shown in (E–H). (I–P): The experiment was repeated in a water-THF mixed solvent with a water volume fraction of 0.99 composition). We first studied the fluorescence response in a THF/H₂O mixed solvent with a water volume fraction of 0.95 (Figure 2A–H). The AIE suspensions were submerged in a heat bath of 100°C for 15 min and were let cool for another 15 min to room temperature, when photoluminescence measurements were carried out. The heating-and-measurement cycles were repeated six times (up to $t = +180$ min). For TPE without any substituent, repeated heating not only progressively abates the fluorescence intensity of the AIE suspension, it also blue-shifts the spectral maximum from 474 to
448 nm (Figure 2A,E). For TPENI-Ph(OMe)₃, however, a 15-min heating period is almost sufficient enough to quench the AIE by a factor of 91; repeating the thermal treatment procedures result in further intensity losses (Figure 2B,F). Nonetheless, the weakened fluorescence spectra after each heating cycle have largely maintained similar energy distribution compared to the generated AIE in situ at room temperature. To verify that the loss of intensity was not due to unwanted chemical damages (e.g., oxidation, hydrolyzation, and so forth) to the molecules, the non-fluorescent suspension was diluted with additional THF until a homogenous solution was yielded. When water was added to the THF solution, the AIE characteristic of TPENI-Ph(OMe)₃ could be observed again (Figure S7). The results suggest that TPENI-Ph(OMe)₃ aggregates exhibit an AIE-ACQ dichotomy, which is very likely due to the existence of at least two types of aggregation states with distinct optical properties. For the other two TPENI derivatives, TPENI-Ph and TPENI-PhOMe, however, the same physical manipulation induces very little change to their AIE spectra (Figure 2C,D,G,H). In fact, the initial heating cycle has increased the AIE intensity for both aggregates without changing the emission spectral profiles while the remaining heating cycles appear to only cause the AIE intensity to slightly fluctuate, which is well within the range of measurement errors. When the same experiment was repeated in a mixed solvent with a THF volume fraction of only 0.01, the trend in AIE change over heating time is slower, and the AIE fluorescence emissions for all three TPENI derivatives are consistently blue-shifted by 2 nm presumably due to more compact aggregates.

To provide a mechanistic understanding of heating-induced changes in TPE and TPENI-Ph(OMe)₃, we performed a series of additional characterizations shown in Figure 3. First, the purity of each TPE derivative was thoroughly verified with HPLC using eluents from various combinations of CH₃CN and water, where only one single component could be observed (Figure 3A–D; Figure S8), ensuring that no unsolicited impurity photoluminescence emission would interfere with the sample AIE. Then the average aggregates sizes were also compared before and after the thermal treatment (for 180 min at 100°C). All of these AIE aggregates generated in situ at room temperature by adding water to their THF solutions exhibit average diameters in between 100 and 200 nm from the result of DLS measurements (Figure 3E,F; Figure S9). However, post thermal treatment, the diameters of the aggregates nearly all increased but remained in the “nano range”, ranging from tens to hundreds of nanometer increments. The percentage increment is more significant for the mixed solvent with 0.05 THF volume compared to the 0.01 counterpart, indicating that the organic solvent may reduce the kinetic energy barrier that prevents these smaller hydrophobic aggregates from coalescing into bigger, thermodynamically more stable ones. Based on these observations, we suspect that heating induced a phase transformation for TPENI-Ph(OMe)₃ and TPE nano-aggregates, leading to ACQ and a different AIE color, respectively. To back the phase transformation hypothesis, we first examined the DSC results for the solid-state samples of the four TPE derivatives (Figure 3G,H; Figure S10), while all four molecules in both as-synthesized and fine-ground forms exhibit sharp endothermic peaks characteristic of crystals melting, only TPENI-Ph(OMe)₃ possesses a strong exothermic peak around 200°C.
Based on the above experimental evidence, we therefore propose, for TPE and TPENI-Ph(OMe)₃, that the AIE nano-aggregates generated in situ at room temperature are locked in a kinetically favored but thermodynamically unstable state. According to the DSC traces and SEM images, the state may arise from an amorphous (glass) phase in which intermolecular packing is less than optimal and favors AIE with high efficiency. However, supplying the state with energy (heating) or lowering the kinetic barrier (with solvent) may quickly lead to a phase transition to an ordered, thermodynamically stable state, where presumably the ideal intermolecular packing reduces or entirely quenches the AIE shown in Scheme 2, in which a kinetic AIE (k-AIE) state is converted to a thermodynamic AIE (t-AIE) state or an ACQ state. For TPENI-Ph and TPENI-Ph(OMe), however, minor variations in substituent groups only result in one observable AIE state that is resistant to heating or solvent treatment; it is also possible that there is a different aggregation state with an exceedingly high kinetic barrier beyond the experimental condition and therefore further investigation is warranted. The current work clearly demonstrates that some organic AIE systems are complicated with multiple phase transitions, and the differentiation between “k-AIE” and “t-AIE” could be important in both theoretical understanding and practical applications.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (21975238, 22103077), and the startup fund from University of Science and Technology of China (KY2340000139).

**DATA AVAILABILITY STATEMENT**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**CONFLICT OF INTEREST**

The authors declare that they have no conflict of interest.

**ORCID**

Xianchong Nie https://orcid.org/0000-0002-0068-433X
Guoqing Zhang https://orcid.org/0000-0001-5796-8547

**REFERENCES**

1. Y. Hong, J. W. Lam, B. Z. Tang, Chem. Soc. Rev. 2011, 40, 5361.
2. A. C. Sedgwick, L. Wu, H.-H. Han, S. D. Bull, X.-P. He, T. D. James, J. L. Sessler, B. Z. Tang, H. Tian, J. Yoon, Chem. Soc. Rev. 2018, 47, 8842.
3. X. Ma, J. Wang, H. Tian, Accounts Chem. Res. 2019, 52, 738.
4. X. Wang, H. Shi, H. Ma, W. Ye, L. Song, J. Zan, X. Yao, X. Ou, G. Yang, Z. Zhao. Nat. Photonics. 2021, 15, 187.
5. X. Liu, Y. Duan, B. Liu. Aggregate 2021, 2, 4.
6. Z. Wu, Q. Yao, S.-q. Zang, J. Xie. Natl. Sci. Rev. 2021, 8, nwaa208.
7. T. Wang, Z. Hu, X. Nie, L. Huang, M. Hui, X. Sun, G. Zhang, Nat. Commun. 2021, 12, 1.
8. R. Ghosh, F. C. Spano. Accounts Chem. Rev. 2020, 53, 2201.
9. W. Zhao, Z. He, B. Z. Tang. Nat. Rev. Mater. 2020, 5, 1. https://www.nature.com/articles/s41578-020-0223-z
10. X. Nie, T. Wang, W. Huang, H. Su, B. Chen, X. Zhang, G. Zhang. J. Mater. Chem. C 2021, 9, 15698.
11. S. Suzuki, S. Sasaki, A. S. Sairi, R. Iwai, B. Z. Tang, G. i. Konishi. Angew. Chem. Int. Ed. 2020, 59, 9940.
12. X. Nie, H. Su, T. Wang, H. Miao, B. Chen, G. Zhang, J. Phys. Chem. Lett. 2021, 12, 3099.
13. J. Zhao, Z. Chi, Y. Zhang, Z. Mao, Z. Yang, E. Ubba, Z. Chi. J. Mater. Chem. C. 2018, 6, 6327.
14. S. Liu, G. Feng, B. Z. Tang, B. Liu. Chem. Sci. 2021, 12, 6488.
