JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 16 Jun 2019

Downloaded from http://pubs.acs.org on June 16, 2019

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Spiro-functionalized Diphenylethenes: Suppression of a Reversible Photocyclization Contributes to the AIE Effect

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Supporting Information Placeholder

ABSTRACT: Many aggregation-induced emission (AIE) materials are featured by the diphenylethene (DPE) moiety which exhibits rich photophysical and photochemical activities. The understanding of these activities behind AIE is essential to guide the design of fluorescent materials with improved performance. Herein by fusing a flexible DPE with a rigid spiro scaffold, we report a class of novel deep-blue material with solid-state fluorescent quantum yield (Φ_F) up to 99.8%. Along with the AIE phenomenon, we identified a reversible photocyclization (PC) on DPE with visible chromism, which is, on the contrary, popularized in solutions but blocked by aggregation. We studied the steric and electronic effects of structural perturbation and concluded that the PC is a key process behind the RIMs (restriction of intramolecular motions) mechanism for these materials. Mitigation of the PC leads to enhanced fluorescence in solutions and loss of the AIE characteristics.

Solid-state luminescent materials have attracted attentions because of their applications in lasing, LED display, chemical sensing, biological imaging and so on.[1] In many cases, fluorophores that emit strongly in dilute solutions become faint or even non-emissive in the solid state, where the formation of molecule aggregates causes self-quenching.[2] In a reverse manner, AIE-active materials fluoresce weakly when molecularly dissolved, but become much more emissive in the solid state.[3] Many AIE luminogens (AIEgens) have flexible rotors, such as aryl rings featuring a modular pattern of the diarylethene (DAE) moiety (Fig. 1).[4] The structural design has paved the way for solid-state emitters as well as fluorogenic materials,[5] but frequently with limited tunability on the luminescence color and leaving much rooms for improving the solid-state Φ_F (Fig. S1). One suspected reason is that some non-radiative pathways popularized in solutions might be not fully blocked in the solid state. One solution to this issue is thus to modulate the state-dependent elemental relaxation processes.[6]

Albeit the AIE effect can be generally attributed to suppression of non-radiative pathways by aggregation, the working mechanism for specific AIEgens remains to be addressed.[7] As for DPE-featured AIEgens, intramolecular motions such as rotation of Ph, torsion/twisting of C=C[8] and puckering of the central ring,[9] formation of through-space aromatic-dimer at excited states,[10] and photochemical *E*/Z isomerization[11] or cyclization[12] *via* conical intersections, have been suggested to be decisive factors in the fluorescence light-up process (Fig. 1A).[13] Specifically, the PC-mediated photochemical deactivation was proposed as the dominant relaxation pathway in the prototypical tetraphenylethene derivatives (TPEs),[14] but lack of experimental evidences due to the

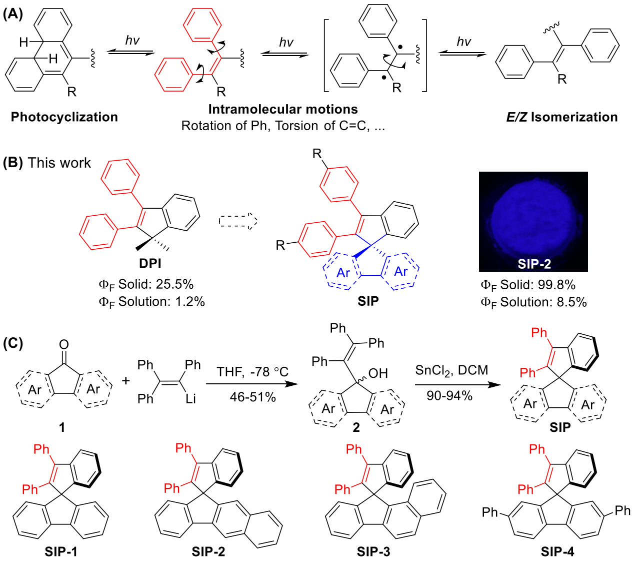

Figure 1. (A) Photophysical and photochemical processes of the DPE moiety. (B) Hydrocarbons **DPI** and **SIPs** studied in this work. (C) Synthesis of **SIPs**.

reversible nature of PC in an ultrafast process.[15] In other aspects, DAEs have been known as photochromic materials *via* the PC chemistry.[16]

In the way searching for deep-blue emitters, we found that hydrocarbon **DPI** (Fig. 1B) is AIE-active and exhibits deep-blue emission with 25.5% Φ_F in the solid state (Table 1, Fig. S2-4). To boost the solid-state photoluminescence (PL) further, we envision that structural modulation by a rigid spiro scaffold to substitute the dimethyl unit would help restricting the conformation of excited fluorophores, and thereby modulate the relaxation processes.[17] Meanwhile the sp^3-hybridized spiro avoids extension of the π-system to a significant degree.[18] For the first time, **SIPs** with different spiro scaffolds were efficiently synthesized by modifying the classic synthesis from Clarkson (Fig. 1C).[19] We evaluated a series of **SIPs** and found an optimal one, **SIP-2**, showing solid-state Φ_F = 99.8%. Its CIE coordinate is moreover close to the European Broadcasting Union standard blue (0.15, 0.06).

Table 1 summarizes the photophysical properties of **DPI** and **SIPs** in solution and solid states. Their UV-*vis* and PL remained unsubtle to solvent effects ($\lambda_{ex}/\lambda_{em}$ = 310/420~5 nm) from non-polar to polar solvents (Fig. S5-6), indicative of relatively rigid conformations at the ground and excited states (Fig. S7). Due to the π-conjugation break in the spiro linkage, **SIPs** retain a deep-blue emission of λ_{em}~420 nm, an impressing blue-shifted color to the prototypical TPE of λ_{em}~460 nm.

The **SIPs** are a new class of AIEgens with deep-blue emission (Fig. S8-11). Their Φ_F values increased significantly in the powder form, ranging from 30.8% to 99.8%, nearly 4-16 times higher than the corresponding ones in dilute solutions (Table 1). The Φ_F values are also much higher than that of **DPI** (Φ_F = 25.5%), showing the intriguing effect exerted by the spiro bridge. The solid-state PL slightly blue-shifted from the corresponding ones in THF solutions, and all belong to deep-blue colors. Viewing from the fluorescence lifetime study, the relaxation pathways of **SIPs** after photoexcitation are highly physical-state-dependent (Fig. S12). These features appear hence to be unique AIE characteristics for **SIPs**, as compared to many spiro compounds suffering from the ACQ.[17] Regarding the PL properties, **SIPs** are comparable to reported spiro-based materials.[20]

We attributed the AIE properties primarily to the flexible DPE moiety. Interestingly, in contrast to the similar solution Φ_F, the regioisomeric spiro-scaffolds result in a large difference on the solid-state Φ_F (**SIP-2**, 99.8% *vs* **SIP-3**, 30.8%). The efficient structural modulation attracts interests on the working mechanism underlying the AIE phenomenon.

Along with the AIE process, we further identified a state-dependent PC process in **DPI** and **SIPs** (Fig. 2A). Upon prolonged light excitation, the **SIP-2** solutions, for example, displayed visible change from colorless to orange-yellow peaked at 475 nm (Fig. 2B). When the irradiation was removed, the solution restored and decolorized within minutes. The colorization-decolorization cycle could be repeated in degassed solutions (Fig. S13). The color was less intensive under air, and was not visible in O_2-purged solutions. By refering to other DAE photoswitches, the emerging absorption at 475 nm was ascribed to the photocyclized π-extending **SIP-2H,** which was tracked and identified by ^{1}H-NMR (Fig. S14-15). The isolation of **SIP-2Ox** as the only product in the air/oxygen-exposing groups supported the formation of **SIP-2H** intermediate. To sum up, **SIP-2** readily undergoes the PC to yield **SIP-2H** in solutions which is thermally reversible, and the **SIP-2H** can be easily oxidized to form the ring-closed **SIP-2Ox**.

On the contrary, the PC-based photochromism is highly suppressed in the solid state (Fig. 2C). NMR analysis showed trival formation (<1%) of **SIP-2Ox** after 8 h irradiation of the powder (Fig. 2D); while a THF-fumed sample was used, the color change is almost instant and intense. Meanwhile the irradiated areas showed diminished fluorescence (Fig. 2C). Similar to the AIE, the PC-based photochromism is state-dependent: the PC is highly suppressed in the solid states, but popularized in diluted solutions.

To evaluate the PC sensitivity on the molecule state, we firstly studied the concentration effect in solutions. As indicated by molecular dynamic simulations and ultrafast spectroscopyical results on TPEs,[14] the photo-catalyzed forward cyclization, in general, accomplishes within pico-seconds after photon absorption, as prohibits a correlation study of the PC dynamics in respond to its physical state. Anyway, we could monitor the spontaneous ring-opening process of **SIP-2H** by following the absorption decay at 475 nm (Fig. 2E). The monoexponential fitting analysis yields a half-life time of 370 s, 415 s and 523 s for [**SIP-2**] = 0.2, 5 and 10 mM, respectively (Fig. S16). The positive correlation implies that the ring-opening step is comparably suppressed in a higher concentration, a phenomenon similar to concentration-caused fluorescence quenching. According to the general principles of microscopic reversibility, the monomolecular cyclization step is reasonably impacted by the physical state as well.

We further examined the AIE and PC behaviors of **SIP-2** in a series of colloidal solutions made by re-precipitation (Fig. 2F). The PL and absorption intensity of **SIP-2** had negligible change from 0% to 50% water fraction (f_w). With a further increase of f_w, the evident Tyndall effect approved the formation of aggregates. In accordance with the AIE, the PL increased progressively when aggregation occurred. On the exact contrary, the absorption at 475 nm declined swiftly (after a light irradiation of 3 min), and became colorless when f_w reached 70 vol% (middle). As in Fig. 2G, there is a negative correlation between the PL and the PC-based photochromism in these colloids. Similar phenomenon were observed for other **SIPs** (Fig. S17-19). It thus can be hypothesized that the occurrence of PC deactivates the excited states of **SIPs**, leading to faint emission in dilute solutions; while the deactivation of the photochemical PC by molecule aggregation boosts the emission in the solid state.[21]

Table 1. Photophysical properties of SIPs at different states

Name	λ_{ex}	λ_{em} [nm] (Φ_F %)		τ [ns] (k_r [10^8 s^{-1}], k_{nr} [10^8 s^{-1}])^a		CIE (x, y)	E_g^{opt} [eV]^b
	THF	THF	Powder	THF	Powder	Film	
DPI	280	415 (1.2)	406 (25.5)	2.41 (0.01, 4.13)	1.60 (1.59, 4.66)	(0.152, 0.048)	3.58
SIP-1	310	425 (7.6)	415 (59.8)	2.25 (0.34, 4.10)	3.22 (1.86, 1.24)	(0.153, 0.058)	3.41
SIP-2	316	424 (8.5)	416 (99.8)	1.80 (0.47, 5.08)	2.65 (3.77, 0.01)	(0.154, 0.056)	3.35
SIP-3	310	420 (7.1)	415 (30.8)	1.82 (0.39, 5.10)	2.32 (1.33, 2.09)	(0.154, 0.055)	3.43
SIP-4	310	424 (7.5)	419 (57.2)	1.54 (0.48, 6.01)	2.09 (2.74, 2.04)	(0.153, 0.057)	3.43

$^a k_r$: radiative decay rate; k_{nr} : nonradiative decay rate. ^{b}Calculated from UV adsorption.

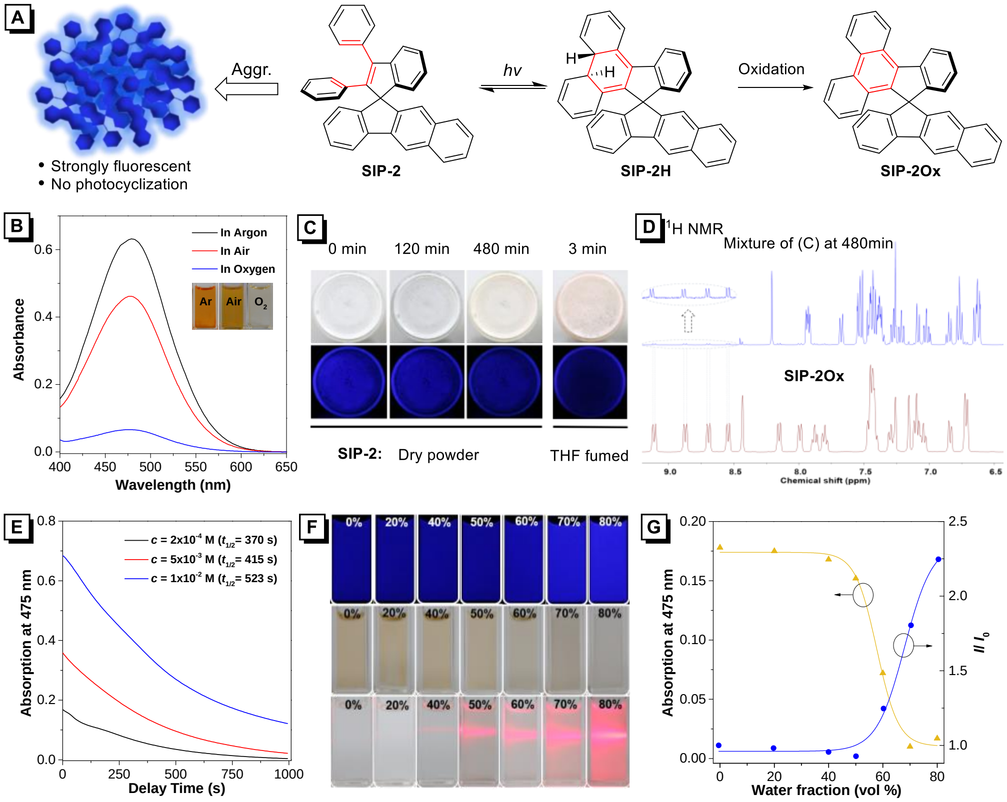

Figure 2. (A) AIE and PC processes of **SIP-2** in the dissolved and aggregated states. (B) UV-*vis* absorption of **SIP-2** in THF (1×10^{-2} M) upon irradiation (313 nm, 8 W) under argon, air and oxygen. (C) Photochromism for the dry, and THF-fumed **SIP-2** powders. (D) ^{1}H NMR showing trace **SIP-2Ox** after 480 min irradiation of the dry sample. (E) Decay of absorption at 475 nm (**SIP-2H**) after irradiation for 3 min on samples of different **[SIP-2]**, at 20 ºC. (F) Photographs of **SIP-2** colloids (showing fractions of water f_w in THF) after the light irradiation. (G) Plots of relative PL intensity (I/I_0) and absorption at 475 nm *vs* the f_w; [**SIP-2**] = 2×10^{-4} M, λ_{ex}: 316 nm, I_0 = intensity at f_w = 0%.

The next question is that to what extent the photochemical PC process is bound to the AIE effect. The non-radiative decay *via* the cyclized intermediate is energetically barrierless in solutions for TPEs,[14a, 14c] which is also likely the same case here for **SIPs**. Therefore, the key is to understand the suppression effects of aggregation on the photochemical cyclization. In fact, many DAEs are PC-active in the solid state. There are, however, only empirical rules for predicting the photochromism activities.[22] As appoved by powder XRD analysis, the **SIP** powders as prepared are largely in crystalline states (Fig. S20). Accordingly, we scrutinized the crystalline structures of **SIPs** (Fig. 3 and S21). The DPEs of **SIPs** all show an antiparallel conformation favorable for the cyclization, but the distances (*d*) between the photocyclization reactive carbon atoms vary largely, depending on the spiro structure (Fig. 3, left). The large *d* for **SIP-1/3** suggests a less propensity to the PC pathway in the crystalline,[22] as is consistent with the observation that **SIP-1/3** are much more photochromism-resistant than **SIP-2/4** (Fig. S22). The case is different for **SIP-2/4** having both favorable orientations and intramolecular distances (*d* ~ 3.40 Å) for the PC (comparing to *d* ~ 3.21 Å in computated S_1, Fig. S7). In the crystalline packing, both DPE rotors are obviously constrained by the benzofluorene unit from adjacent molecules *via* multiple C-H···π and π-π interactions (Fig. 3, middle). As indicated by the free-motion space for the DPE, **SIP-2/4** had a low probability for the PC. From the perspectives of RIMs theory, the conformational restriction by aggregation likely contributes to the AIE effect *via* deactivating the photochemical cyclization.

Notably, it is not right to relate the AIE effect solely to the suppression of the photochemical processes. Comparably, in all **SIPs** with aggregation-caused suppression of the PC, the ultrahigh PL performance of **SIP-2** is likely associated with the rigid crystalline packing too, manifested by the rich and regular C-H···π and π-π interactions between the spiro backbones (Fig. 3, right).

Furthermore, structural mitigation of the PC activity leads to loss of the AIE characteristics (Fig. 4). The absence of PC is observed in **SIP-5** with bulky naphthalene, and **SIP-6** with CN substitution which deviate the reacting sites away upon photo-activation (Fig. S7, Table S1). In comparison to **SIP-2**, both showed enhanced emission in solutions (**SIP-5**, 39.1%; **SIP-6**, 94.5%), which can be ascribed to the deactivation of the PC-mediated pathways. In addition likely due to the loss of the PC activity, the ring-closed **SIP-2Ox** is also not AIE-active (Fig. S25).

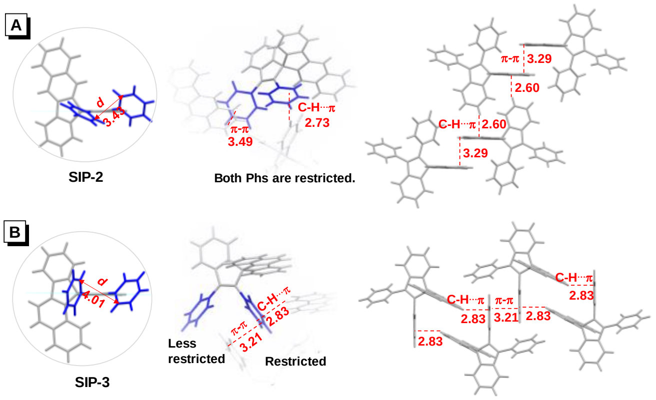

Figure 3. Crystalline structures of **SIP-2/3** showing parameters for the PC and AIE.

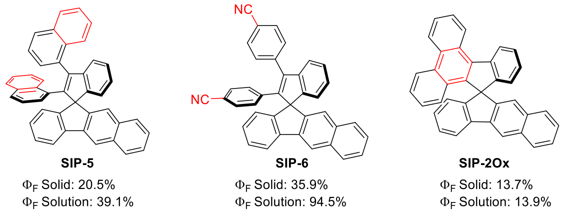

Figure 4. Mitigation of the **PC** activity in **SIP-2** leading to loss of the AIE characteristics.

In summary, by simply merging a DPE moiety with a spiro-scaffold, we introduced a new class of AIEgens (**DPI** and **SIPs**) with strong deep-blue emission in the solid state. We disclosed a dominant role of the photochemical cyclization in the non-radiative pathways in dilute solutions, and the suppression of the PC is bound to the boosted emission in the solid state. During the structural modulation of PL properties, the unique spiro functionalities are highlighted, by steric, electronic and other effects on the PC activity, leading to ultrahigh emission efficiency with a good control on the color shift. The PC-engaged working mechanism for AIE which has been argued for TPEs, might work for other unprecedent AIEgens and lead to the design of fluorescent materials with enhanced performance and applicability.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge on the ACS Publications website.
Synthesis description, characterization details

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors thank the National Natural Science Foundation of China (51573040), Hunan Provincial NSFC (2018JJ1008).

REFERENCES

(1) (a) Ostroverkhova, O. Organic optoelectronic materials: mechanisms and applications. *Chem. Rev.* **2016**, *116*, 13279-13412. (b) Terai, T.; Nagano, T. Fluorescent probes for bioimaging applications. *Curr. Opin. Chem. Biol.* **2008**, *12*, 515-521.
(2) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*. 3rd ed.; Springer: New York, **2006**.
(3) (a) He, Z.; Ke, C.; Tang, B. Z. Journey of aggregation-induced emission research. *ACS Omega* **2018**, *3*, 3267-3277. (b) 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*, 11718-940.
(4) (a) Zhuang, Z.; Bu, F.; Luo, W.; Peng, H.; Chen, S.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. Steric, conjugation and electronic impacts on the photoluminescence and electroluminescence properties of luminogens based on phosphindole oxide. *J. Mater. Chem. C* **2017**, *5*, 1836-1842. (b) Yuan, C.; Saito, S.; Camacho, C.; Kowalczyk, T.; Irle, S.; Yamaguchi, S. Hybridization of a flexible cyclooctatetraene core and rigid aceneimide wings for multiluminescent flapping π systems. *Chem. Eur. J.* **2014**, *20*, 2193-2200. (c) Shen, P.; Zhuang, Z.; Zhao, Z.; Tang, B. Z. AIEgens based on main group heterocycles. *J. Mater. Chem. C* **2018**, *6*, 11835-11852. (d) Han, T.; Zhang, Y.; Feng, X.; Lin, Z.; Tong, B.; Shi, J.; Zhi, J.; Dong, Y. Reversible and hydrogen bonding-assisted piezochromic luminescence for solid-state tetraaryl-buta-1,3-diene. *Chem. Commun.* **2013**, *49*, 7049-7051. (e) Guo, J.; Hu, S.; Luo, W.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. A novel aggregation-induced emission platform from 2,3-diphenylbenzo[b]thiophene S, S-dioxide. *Chem. Commun.* **2017**, *53*, 1463-1466. (f) Chen, M.; Li, L.; Nie, H.; Tong, J.; Yan, L.; Xu, B.; Sun, J. Z.; Tian, W.; Zhao, Z.; Qin, A.; Tang, B. Z. Tetraphenylpyrazine-based AIEgens: facile preparation and tunable light emission. *Chem. Sci.* **2015**, *6*, 1932-1937. (g) Cai, Y.; Qin, A.; Tang, B. Z. Siloles in optoelectronic devices. *J. Mater. Chem. C* **2017**, *5*, 7375-7389. (h) Bu, F.; Wang, E.; Peng, Q.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. Structural and theoretical insights into the AIE attributes of phosphindole oxide: the balance between rigidity and flexibility. *Chem. Eur. J.* **2015**, *21*, 4440-4449.
(5) Xie, S.; Wong, A. Y. H.; Chen, S.; Tang, B. Z. Fluorogenic detection and characterization of proteins by aggregation-induced emission methods. *Chem. Eur. J.* **2019**, *25*, 5824-5847.
(6) Zhao, Z.; Wang, Z.; Lu, P.; Chan, C. Y.; Liu, D.; Lam, J. W.; Sung, H. H.; Williams, I. D.; Ma, Y.; Tang, B. Z. Structural modulation of solid-state emission of 2,5-bis(trialkylsilylethynyl)-3,4-diphenylsiloles. *Angew. Chem. Int. Ed.* **2009**, *48*, 7608-7611.
(7) (a) Chen, Y.; Lam, J. W. Y.; Kwok, R. T. K.; Liu, B.; Tang, B. Z. Aggregation-induced emission: fundamental understanding and future developments. *Mater. Horiz.* **2019**, *6*, 428-433. (b) 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. (c) Zhang, T.; Peng, Q.; Quan, C.; Nie, H.; Niu, Y.; Xie, Y.; Zhao, Z.; Tang, B. Z.; Shuai, Z. Using the isotope effect to probe an aggregation induced emission mechanism: theoretical prediction and experimental validation. *Chem. Sci.* **2016,** *7*, 5573-5580. (d) Tian, G.; Sun, D.; Zhang, Y.; Yu, X. Franck–condon blockade and aggregation-modulated conductance in molecular devices using aggregation-induced emission-active molecules. *Angew. Chem. Int. Ed.* **2019**, *58*, 5951-5956. (e) Kokado, K.; Sada, K. Consideration of molecular structure in the excited state to design new luminogens with aggregation-induced emission. *Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201814462.
(8) Kokado, K.; Machida, T.; Iwasa, T.; Taketsugu, T.; Sada, K. Twist of C═C bond plays a crucial role in the quenching of AIE-active tetraphenylethene derivatives in solution. *J. Phys. Chem. C* **2017**, *122*, 245-251.
(9) Shustova, N. B.; Ong, T. C.; Cozzolino A. F.; Michaelis, V. K.; Griffin, R. G.; Dinca, M. Phenyl ring dynamics in a tetraphenylethylene-bridged metal–organic framework: implications for the mechanism of aggregation-induced emission. *J. Am. Chem. Soc.* **2012**, *134*, 15061−15070.
(10) Sturala, J.; Etherington, M. K.; Bismillah, A. N.; Higginbotham, H. F.; Trewby, W.; Aguilar, J. A.; Bromley, E. H. C.; Avestro, A.-J.; Monkman, A. P.; McGonigal, P. R. Excited-state aromatic interactions in the aggregation-induced emission of molecular rotors. *J. Am. Chem. Soc.* **2017**, *139*, 17882-17889. (b) Zhang H, Zheng X, Xie N, He, Z.; Liu, J.; Leung, N. L. C.; Niu, Y.; Huang, X.; Wong, K. S.; Kwok, R. T. K.; Sung, H. H. Y.; Williams, I. D.; Qin, A.; Lam, J. W. Y.; Tang, B. Z. Why do simple molecules with "isolated" phenyl rings emit visible light? *J. Am. Chem. Soc.* **2017**, *139*, 16264-16272.
(11) (a) Le Bras, L.; Adamo, C.; Perrier, A. Modeling the modulation of emission behavior in E/Z isomers of dipyrrolyldiphenylethene: from molecules to nanoaggregates. *J. Phys. Chem. C* **2017**, *121*, 25603-25616. (b) Yang, Z.; Qin, W.; Leung, N. L. C.; Arseneault, M.; Lam, J. W. Y.; Liang, G.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. A mechanistic study of AIE processes of TPE luminogens: intramolecular rotation vs. configurational isomerization. *J. Mater. Chem. C* **2016**, *4*, 99-107.

(12) Cai, Y.; Du, L.; Samedov, K.; Gu, X.; Qi, F.; Sung, H. H. Y.; Patrick, B. O.; Yan, Z.; Jiang, X.; Zhang, H.; Lam, J. W. Y.; Williams, I. D.; Lee Phillips, D.; Qin, A.; Tang, B. Z. Deciphering the working mechanism of aggregation-induced emission of tetraphenylethylene derivatives by ultrafast spectroscopy. *Chem. Sci.* **2018**, *9*, 4662-4670.

(13) Duan, Y. C.; Wu, Y.; Jin, J. L.; Gu, D. M.; Geng, Y.; Zhang, M.; Su, Z. M. Influence of aggregation on the structure and fluorescent properties of a tetraphenylethylene derivative: a theoretical study. *Chemphyschem* **2017**, *18*, 755-762.

(14) (a) 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. (b) Cai, Y.; Samedov, K.; Dolinar, B. S.; Albright, H.; Song, Z.; Zhang, C.; Tang, B. Z.; West, R. AEE-active cyclic tetraphenylsilole derivatives with ~100% solid-state fluorescence quantum efficiency. *Dalton Trans.* **2015**, *44*, 12970-12975. (c) Prlj, A.; Doslic, N.; Corminboeuf, C. How does tetraphenylethylene relax from its excited states? *Phys. Chem. Chem. Phys.* **2016**, *18*, 11606-11609.

(15) Snyder, J. A.; Bragg, A. E. Ultrafast pump-repump-probe photochemical hole burning as a probe of excited-state reaction pathway branching. *J. Phys. Chem. Lett.* **2018**, *9*, 5847-5854.

(16) (a) Tian, H.; Yang, S. Recent progresses on diarylethene based photochromic switches. *Chem. Soc. Rev.* **2004**, *33*, 85-97. (b) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem. Rev.* **2014**, *114*, 12174-12277.

(17) (a) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. Spiro compounds for organic optoelectronics. *Chem. Rev.* **2007**, *107*, 1011-1065. (b) Poriel, C.; Rault-Berthelot, J. Dihydroindenofluorene positional isomers. *Acc. Chem. Res.* **2018**, *51*, 1818-1830. (c) Minkin, V. I. Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic compounds. *Chem. Rev.* **2004**, *104*, 2751-2776.

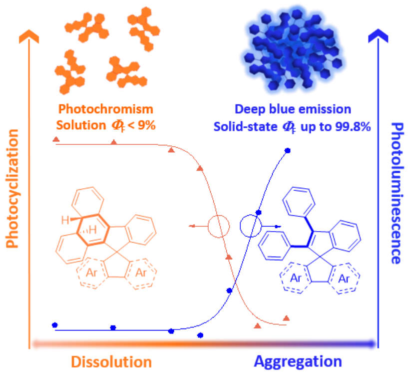
(18) (a) Nakagawa, T.; Miyasaka, Y.; Yokoyama, Y. Photochromism of a spiro-functionalized diarylethene derivative: multi-colour fluorescence modulation with a photon-quantitative photocyclization reactivity. *Chem. Commun.* **2018**, *54*, 3207-3210. (b) Furukawa, S.; Hayashi, K.; Yamagishi, K.; Saito, M. Synthesis and properties of spiro-type heterasumanenes containing group 14 elements as bridging atoms. *Mater. Chem. Front.* **2018**, *2*, 929-934.

(19) Clarkson, R. G.; Gomberg, M. Spirans with four aromatic radicals on the spiro carbon atom. *J. Am. Chem. Soc.* **1930**, *52*, 2881-2891.

(20) (a) Huang, J.; Yang, X.; Wang, J.; Zhong, C.; Wang, L.; Qin, J.; Li, Z. New tetraphenylethene-based efficient blue luminophors: aggregation induced emission and partially controllable emitting color. *J. Mater. Chem.* **2012**, *22*, 2478-2484. (b) Méhes, G.; Nomura, H.; Zhang, Q.; Nakagawa, T.; Adachi, C. Enhanced electroluminescence efficiency in a spiro-acridine derivative through thermally activated delayed fluorescence. *Angew. Chem. Int. Ed.* **2012**, *51*, 11311-11315. (c) Sicard, L. J.; Li, H.-C.; Wang, Q.; Liu, X.-Y.; Jeannin, O.; Rault-Berthelot, J.; Liao, L.-S.; Jiang, Z.-Q.; Poriel, C. C1-linked spirobifluorene dimers: pure hydrocarbon hosts for high-performance blue phosphorescent OLEDs. *Angew. Chem. Int. Ed.* **2019**, *58*, 3848-3853. (d) Xue, M.-M.; Xie, Y.-M.; Cui, L.-S.; Liu, X.-Y.; Yuan, X.-D.; Li, Y.-X.; Jiang, Z.-Q.; Liao, L.-S. The control of conjugation lengths and steric hindrance to modulate aggregation-induced emission with high electroluminescence properties and interesting optical properties. *Chem. Eur. J.* **2016**, *22*, 916-924. (e) Belikov, M. Y.; Ievlev, M. Y.; Belikova, I. V.; Ershov, O. V.; Tafeenko, V. A.; Surazhskaya, M. D. Directed synthesis of new spiro-fused photochromes of diarylethene series. *Chem. Heterocycl. Compd.* **2015**, *51*, 518-525. (f) Wang, Y.; Liu, W.; Qu, Z.; Tan, H.; Liu, Y.; Xie, G.; Zhu, W. Spirotriphenylamine based star-shaped D-A molecules meeting AIE chromophore for both efficient solution-processed doped and nondoped blue organic light-emitting diodes. *Dyes Pigm.* **2017**, *143*, 173-182.

(21) (a) Wu, Y.; Yan, C.; Li, D.; Yuan, C.; Sun, J.; Zhou, S.; Zhang, H.-L.; Shao, X. Migratory shift in oxidative cyclodehydrogenation reaction of tetraphenylethylenes containing electron-rich THDTAP moiety. *Chem. Asian J.* **2019**, *14*, 1860-1869. (b) Zhu, L.; Wang, R.; Tan, L.; Liang, X.; Zhong, C.; Wu, F. Aggregation-induced emission and aggregation-promoted photo-oxidation in thiophene-substituted tetraphenylethylene derivative. *Chem. Asian J.* **2016**, *11*, 2932-2937. (c) He, Z.; Shan, L.; Mei, J.; Wang, H.; Lam, J. W. Y.; Sung, H. H. Y.; Williams, I. D.; Gu, X.; Miao, Q.; Tang, B. Z. Aggregation-induced emission and aggregation-promoted photochromism of bis(diphenylmethylene)dihydroacenes. *Chem. Sci.* **2015**, *6*, 3538-3543. (d) Gu, X.; Wang, H.; Roose, J.; He, Z.; Zhou, Y.; Yan, Y.; Cai, Y.; Shi, H.; Zhang, Y.; Sung, H. H.; Lam, J. W.; Miao, Q.; Zhao, Y.; Wong, K. S.; Williams, I. D.; Tang, B. Z. A luminescent nitrogen-containing polycyclic aromatic hydrocarbon synthesized by photocyclodehydrogenation with unprecedented regioselectivity. *Chem. Eur. J.* **2015**, *21*, 17973-1780.

(22) ‘In thiophene-type DAE, *d* > 4.20 Å suggests a low activity in the PC’ in Kobatake, S.; Kuma, S.; Irie, M. Single-crystalline photochromism of diarylethene dimers bridged by a spiro structure. *J. Phys. Org. Chem.* **2007**, *20*, 960-967.


Photochromism
Solution Φ_f < 9%
Deep blue emission
Solid-state Φ_f up to 99.8%
Photocyclization
Photoluminescence
H
H
Ar
Ar
Ar
Ar
Dissolution
Aggregation