

To unravel the factor to dominantly impact the emission energy of crystal diphenyldibenzofulvene derivatives

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Abstract

Aggregation-induced emission luminogens (AIEgens) have been regarded as one of the significant prospects for organic light-emitting diodes, sensors, biological therapies, etc. owing to their intense emission in aggregated states. The expanded π -conjugated molecule conformations supposedly acquire the emission with a lower energy, however the optical performance of AIEgens in aggregated states defies this empirical assumption. The unexpected photophysical characteristics of AIEgens make it more challenging to design molecular conformations. Herein, to unveil the crucial factors dominating the optical performance of AIEgens, a series of diphenyldibenzofulvene (DPDBF) derivatives in crystals are utilized. We revealed that the emission energy of DPDBF derivatives in crystals is attributed to the tight connection with the conformation of the planar π -conjugated segment, but not the conformation torsion of phenyl blades or the intermolecular coupling, after systematically analyzing the impact factors, including molecular conformation parameters and intermolecular coupling, and further proved with the calculation results. Although the energy gap between the HOMO and LUMO is somewhat reduced by the expanded π -conjugated molecular conformation of the aforementioned DPDBF derivatives, the Stokes shift effect, which is primarily influenced by the conformation of the planar π -conjugated moiety, can realize to adjust the emission energy in a much more effective manner.

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Aggregation-induced emission luminogens (AIEgens) have been regarded as one of the significant prospects for organic light-emitting diodes, sensors, biological therapies, etc. owing to their intense emission in aggregated states. The expanded π -conjugated molecule conformations supposedly acquire the emission with a lower energy, however the optical performance of AIEgens in aggregated states defies this empirical assumption. The unexpected photophysical characteristics of AIEgens make it more challenging to design molecular conformations. Herein, to unveil the crucial factors dominating the optical performance of AIEgens, a series of diphenyldibenzofulvene (DPDBF) derivatives in crystals are utilized. We revealed that the emission energy of DPDBF derivatives in crystals is attributed to the tight connection with the conformation of the planar π -conjugated segment, but not the conformation torsion of phenyl blades or the intermolecular coupling, after systematically analyzing the impact factors, including molecular conformation parameters and intermolecular coupling, and further proved with the calculation results. Although the energy gap between the HOMO and LUMO is somewhat reduced by the expanded π -conjugated molecular conformation of the aforementioned DPDBF derivatives, the Stokes shift effect, which is primarily influenced by the conformation of the planar π -conjugated moiety, can realize to adjust the emission energy in a much more effective manner.

1. Introduction

Since 2001, Tang et al. precisely conceptualized the aggregation-induced emission (AIE) phenomena in which the organic compounds present faint emissions in dissolved states but intense emissions in aggregated solid-states.^[1] AIE luminogens (AIEgens) have been extensively developed and widely utilized in a variety of applications, including organic light-emitting diodes,^[2–9] sensors,^[10–14] and biological therapies,^[15–21] owing to the competitive strength to dissolve the challenge of aggregation-caused quenching (ACQ) behavior of conventional fluorescent dyes. Generally, the AIEgens are typically built in the π -conjugated molecular architectures with a lot of branching groups to prevent fluorescence quenching in aggregated states.^[22–25] Additionally, the expanded π -conjugated molecular structures are commonly believed to produce the emission with a longer wavelength (lower energy), which can be used to modify the emission wavelength of AIEgens.^[26–29] The optical behaviors of π -conjugated AIEgens, however, are considerably more complex and do not simply follow this empirical principle. As a result, it demonstrates the significance of thoroughly understanding the emission mechanism of AIEgens and developing trustworthy theories to guide molecular design. So far, great effort has been donated to investigate the photophysical properties of AIEgens experimentally and theoretically, including the investigations concerning the typical AIEgens diphenyldibenzofulvene (DPDBF) and its derivatives.^[30–33] According to empirical evidence, the photophysical characteristics of DPDBF derivatives customarily follow the typical AIE behavior that is attributed to the propeller-like molecular conformations offer sufficient steric space to prevent emission quenching.^[29–33] The significantly increased emission of DPDBF derivatives during the transformation from dissolved states to aggregated solid-states has been explained theoretically using the constrained rotation of the middle ethylenic C=C bond and low-frequency twisting of the phenyl groups.^[34] However, it continues to call for the endeavor to better reveal the fundamental characteristics affecting the optical performance of DPDBF derivatives in aggregated states, which benefits tailoring the emission of materials for application-specific requirements. In recent decade years, a lot of crystals of DPDBF derivatives have been synthesized, even a portion of the materials obtaining the polymorphs.^[30–32] Thus, systematically discussing the photophysical properties of crystal materials of DPDBF derivatives allows for the classification of the intrinsic factors to optical performances and promotes the molecular structure design of AIEgens.

The extra-high pressure technology is very useful for analyzing the optical performance of DPDBF derivatives in crystals. This technology has been widely used to study the piezochromic luminescence of perovskites,^[35,36] and some intriguing phenomena, such as pressure-induced emission (PIE), have been observed.^[37] Aside from that, the external pressure stimulus adds to more evidence for the intramolecular and intermolecular coupling. For example, the 9-(3-(1,2,2-triphenylvinyl)-phenyl)anthracene (mTPE-AN) crystal is built on

discrete π - π anthracene (AN) stacking with tetraphenylethylene (TPE) as spacer.^[38] According to the investigation, the emission signal of mTPE-AN at ambient pressure originates from the emission center of the discrete AN dimer whose π - π face-to-face stacking distance is around 3.527 Å. However, at the extra-high pressure, it forces the π - π stacking of AN dimers to be disrupted. Thus, the pressure-induced blue-shift of emission is due to the transfer of the emission center from the disrupted AN dimer section to TPE moiety. Another example, the 9,10-bis((E)-2-(pyrid-2-yl)anthracene (BP2VA) powder shows a continued shift of emission center from green (528 nm) to red (652 nm) in the range of 0–7.9 GPa.^[39] Under ambient pressure, the three polymorphs of BP2VA crystals exhibit tight π - π stacking at distances between 3.38–3.65 Å. Furthermore, the photophysical properties of a series of BP2VA crystals at ambient pressure suggest a relationship between the increased π - π stacking area and the emission with a continued bathochromic-shift. Accordingly, the enhanced π - π interaction between adjacent AN moieties correctly explain the pressure-induced bathochromic-shift of emission of BP2VA powder. Additionally, some studies have highlighted the piezochromic luminescence of AIEgens in the near-infrared range and the AIE-to-ACQ transformation.^[40–42] These studies appear to confirm a general principle that the piezochromic luminescence of AIEgens under increasing pressure mostly exhibits an initially enhanced emission tendency and then follows a gradually decayed tendency. It is associated with the AIEgens that have flexible molecular conformations. The initial increase in emission intensity is caused by the enhanced steric hindrance due to the pressure-induced larger compaction to the flexible molecular conformations.^[42] With further increased pressure, the stimulated intramolecular and intermolecular couplings originated from the progressively closing distance of the π - π stacking and hydrogen bonds reasonably cause a continuous bathochromic-shift of emission, along with a decay of emission intensity. Nevertheless, the piezochromic luminescence of materials that experience the obvious π - π face-to-face stacking and closing distance to surrounding molecules exhibits a continuously decaying emission intensity and a shift in the emission center with increasing pressure but does not appear an initial increase window of emission intensity.^[40]

Herein, we cautiously examined the photophysical characteristics of a wide diversity of DPDBF derivatives in crystals (**S1**–**S5**) to elucidate the inherent components contributing to the emission energy of AIEgens. The attributes considered include bond angles (θ_1 – θ_4 , θ_7), twisted angles (θ_5 and θ_6), bond lengths (r_1 – r_4), and the hydrogen bonds with near distances. Contrary to previous research on DPDBF derivatives draws the conclusion that the rotation/stretching of the ethylenic $C_1=C_2$ bond and the twisted angles play critical roles in the greatly increased emission during the transition from the dissolved state to aggregated solid-state, we reveal a novel factor that the parameter (θ_1) has a significantly greater influence than the other aforementioned components on the emission energy of crystals **S1**–**S5**. Meanwhile, the intermolecular coupling in the crystals at ambient pressure is also taken into account as a minor impact factor that contributes to the modest overlap of disordered π - π stacking. In addition, calculations are performed to examine the photophysical characteristics of crystals, further confirming that the parameter θ_1 in the planar π -conjugated moiety tightly associates with the Stokes shift of the emission of DPDBF derivatives in crystals realizing to efficiently adjust the emission energy.

2. Results and discussion

2.1. Luminescence of DPDBF derivatives

Understanding the optical characteristics of crystals of DPDBF derivatives that produce unexpectedly emission colors does not just follow the empirical principle that the expanded π -conjugated structures of AIEgens cause longer wavelength (lower energy) emission.^[30–33] Inspiringly, it is done mostly by discussing about the main components that have an effect on the emission, such as molecule conformation, π - π stacking, and partial hydrogen bonds in the crystal structures. In order to achieve this goal, a variety of DPDBF derivatives are used to construct the crystals **S1**–**S5**. Thereinto, the crystal **S1** was formed using THF, while the crystals **S2**–**S5** are generated using a mixture of dichloromethane and petroleum ether (1:4) (supporting information).

For **S1**, the middle ethylenic $C_1=C_2$ bond connects one fluorene and one phenyl blade at two sides, forming the propeller-shaped molecular structure. The planar π -conjugated moiety is characterized by the combina-

tion of two fluorine and middle $C_1=C_2$ bond components which are situated on the same planar plane with a little conformation torsion (ϑ_1 2.50). The twisted angle of ϑ_6 is used to describe the molecular conformation torsion of the phenyl blade to the planar moiety. Figure 1 depicts the analogous schematic diagram of DPDBF with the planar π -conjugated moiety and phenyl blades. Here, the distance of the ethylenic $C_1=C_2$ bond is 1.326 , ϑ_1 is 105.20, r_1 and r_2 are 1.474 and 1.484 , respectively. However, the 87.80 of ϑ_6 implies the almost perpendicular twist of the phenyl blade to the planar π -conjugated moiety. The π - π interaction is strictly limited with $\vartheta_7=69.30$ and $r_4=5.226$, according to the dimer structure of **S1** (Figure 2A, Table 1), which is derived from the monoclinic $I 2/c$ crystal structure ($a = 19.1364(15)$, $b = 7.2252(4)$, $c = 21.8109(15)$, $\beta = 109.875(8)^\circ$, $V = 2836.0(4) \text{ \AA}^3$) at ambient pressure (Figure S3). The hydrogen bonds in the crystal between the C-H of the phenyl blade and the planar moiety of an adjacent molecule are, as depicted in Figure 2A, 3.211 and 3.283 , respectively. The function of close hydrogen bonds would be to enhance the steric hindrance in molecular stacking and intermolecular coupling.^[1,30,31,40,43] Therefore, to provide further evidence about the influence of π - π interaction and hydrogen bonds on the emission, the piezochromic luminescence of **S1** in the range of 1.0 atm–12.7 GPa is characterized. The **S1** shows an almost undetectable emission at ambient pressure. With the characterization pressure increased in the 1.0 atm–1.0 GPa range, **S1** gains the significantly enhanced emission with green color centered at ~ 500 nm, and then the emission intensity follows a slight consecutive increase tendency in the 1.0–2.5 GPa range without the shifting of emission center. By further raising the measurement pressure in the 2.5–12.7 GPa range, the emission intensity gradually decays accompanied by a bathochromic-shift of the emission center from 500 to 560 nm (Figure 3A-D). The related UV-Vis spectra of **S1** in the 1.0 atm–12.7 GPa range show the absorption with obviously expended edge to the lower energy (Figure 3E). Therefore, the increased measurement pressure in the 1.0 atm–2.5 GPa range promotes blocking the non-radiative transition and causes the improved radiative transition, but it does not alter the energy gap of S_1 - S_0 de-excitation transition. Apart from the applied pressure larger than 2.5 GPa, the declined energy gap of S_1 - S_0 de-excitation transition of **S1** can be discerned due to the progressively enhanced intermolecular coupling and the possible conformation-induced intramolecular coupling.^[44]

Compared to **S1** , the single molecular conformation of **S2** expands a more phenyl blade, allowing it to still crystallize in the monoclinic $P 2_1/n$ space group ($a = 9.682(5)$, $b = 9.310(5)$, $c = 20.443(10)$, $\beta = 102.48(3)^\circ$, $V = 1799.18(162) \text{ \AA}^3$). In contrast, **S2** gains the emission with a shorter wavelength (centered at 485 nm) at ambient pressure. Meanwhile, the significant characteristics from the planar π -conjugated moiety (planar torsion ϑ_1 4.50) are 104.80 of ϑ_1 , 1.493 of r_1 and 1.491 of r_2 . In terms of the conformation torsion of two phenyl blades, the ϑ_5 and ϑ_6 are 80.30 and 74.00, respectively. **S2** obviously possesses a longer ethylenic $C_1=C_2$ bond (1.348) and slightly less twisted phenyl blades than **S1** . The result implies that the torsion of phenyl blades should not dominate the emission colors of DPDBF derivatives in crystals because of the conflict with the general expectation that the less twisted phenyl blade improves to decline the emission energy.^[31, 40] In addition, the dimer structure of **S2** also demonstrates the poor π - π face-to-face stacking with $\vartheta_7 = 74.00$ and $r_4 = 6.959$. The C-H... π hydrogen bond with a close distance of 2.916 derives from the intermolecular interaction between the adjacent fluorine groups (Figure 2B). To further estimate the influence of intermolecular coupling, the piezochromic luminescence of **S2** is shown in Figure S4. The emission intensity follows the initial increase in the 1.0 atm–1.0 GPa range, then it performs a successfully weakening tendency in the 1.0–18.4 GPa range. Focusing on the emission wavelength, the crystal **S2** does not appear the distinguished shift of emission (centered at ~ 485 nm) in the 1.0 atm–2.5 GPa range. Only when the applied pressure is larger than 2.5 GPa, a shift of the emission center appears. Hence, the intermolecular coupling is also wiped from the list of main factors to significantly affect the emission color of **S2** in crystals at ambient pressure. Simultaneously, the energy gap of S_1 - S_0 de-excitation transition of **S2** is compressed after the applied pressure up to 2.5 GPa.

The molecular conformation of **S3** comprises a planar π -conjugated moiety and two phenyl blades, similar to **S2** , where one phenyl blades is functionalized with the methoxyl group. In the planar π -conjugated moiety (conformation torsion ϑ_1 3.10) of **S3** , it presents the 104.90 of ϑ_1 , 1.495 of r_1 , and 1.493 of r_2 . The ethylenic $C_1=C_2$ bond of **S3** is slightly elongated to 1.351 (r_3) compared to that of **S2** (1.348), which is attributed to the expanded π -conjugated conformation. The phenyl blades of **S3** are also severely twisted to

the planar moiety with 69.50 of ϑ_5 and 69.30 of ϑ_6 , respectively. In terms of the dimer of **S3** (Figure 1C), it is analogous to that of **S1** with poor π - π face-to-face stacking. Clearly, the molecular stacking of **S3** is much more compacted than that of **S1** with 4.999 of r_2 and 75.30 of ϑ_7 , as well as the shorter C-H[?][?][?] π hydrogen bond (2.918). For this configuration, **S3** crystalizes in a much lower symmetric triclinic P -1 space group (a =9.1555(10), b =9.7905(11), c =11.2758(10) , α =107.229(9)°, β =94.415(8)°, γ =93.320(9)°, V = 959.05(18) $\text{\AA}^3$). Thus, the intermolecular coupling of **S3** should be stronger than that of **S1** . In generally, the enhanced coupling among molecules is expected to cause lower energy emission.^[45,46] Beyond that, the expanded π -conjugated molecular structure of **S3** is also commonly believed as the reason of lower emission energy due to the potentially declined energy gap of S_1 - S_0 de-excitation transition.^[47,48] However, the result does not follow the expectations, such as, at ambient pressure the crystal **S3** reversely achieves the intense blue emission centered at ~475 nm under UV irradiance with a shorter emission wavelength (higher energy) compared to that of **S1** (500 nm). The compact stacking structure (Figure 2C, S3C and S5) of **S3** adequately implies that there is no enhanced tendency of emission intensity in the initially enhanced pressure range due to the close distance among molecules leads to intense hydrogen bonds and the strong steric hindrance to block the non-radiative transition.^[40] Obviously, we can conclude that the closer molecular stacking without valid π - π stacking could not cause the lower emission energy. To gain the lower energy emission of **S3** , a pressure larger than 3.0 GPa should be applied. Up to now, according to the analyses of the **S1** –**S3** crystals, it is identified that some crucial factors must be underestimated in the evaluation system to expect the emission energy.

The crystals **S4** and **S5** are the polymorphs of 9-[di(4-methoxyphenyl)methylene]-9h-fluorene whose space groups of crystal systems are monoclinic $P2_1/n$ and orthorhombic $Pba2$ (**S4** : a =13.7817(5), b =10.1241(3), c =4.4309(5), β =90.170(3)°, V =2013.50(12) $\text{\AA}^3$; **S5** : a =20.2749(7), b =20.5378(7), c =9.7640(4) , V = 4065.7(3) $\text{\AA}^3$), respectively. For **S4** , the propeller-shaped molecular conformation appears with the torsion of phenyl blades with twisted angles ϑ_5 (74.50) and ϑ_6 (58.20). The planar moiety (conformation torsion ϑ_1 3.60) has relatively longer ethylenic $C_1=C_2$ bond (1.354), smaller ϑ_1 (104.80), and the longer r_1 (1.494) and r_2 (1.495), compared to that of **S1** –**S3** . In addition, the overlapping area of π - π stacking is also small and the close C-H[?][?][?] π hydrogen bonds are around 2.808 (Figure 2D). The intermolecular coupling is described by the parameters r_4 and ϑ_7 are 6.302 and 55.60, respectively. The piezochromic luminescence of **S4** indicates that the emission color is irrespective to the applied pressure in 1.0 atm–3.1 GPa range (Figure 4C and 4D), and the emission intensity is also very stable in this range, both of which are interpreted to be due to the relatively compact stacking structure. Corresponding UV-Vis absorption spectra address a slow shift of absorption edge. Further increase the applied pressure in the 5.6–18.4 GPa range, the emission follows the tendency with a gradually declining emission intensity and a bathochromic-shift of the emission center, along with the appearance of another absorption band centered around 520 nm. As a result, intermolecular coupling should not be the crucial factor affecting the emission color of **S4** at ambient pressure. Contrastively, the phenyl blades in crystal **S5** 's molecular conformation have slightly less torsion, measuring 64.30 of ϑ_5 and 49.40 of ϑ_6 . While the planar moiety (conformation torsion ϑ_1 10.70) shows a longer ethylenic $C_1=C_2$ bond (1.355) and ϑ_1 (105.20), and the related shorter r_1 (1.492) and r_2 (1.489). To evaluate the intermolecular coupling impact, the dimer is constructed on the close C-H[?][?][?] π hydrogen bonds with 3.155–3.190 , and the π - π stacking displays the limited overlapping area. The piezochromic luminescence of **S5** displays a steep increase of emission intensity in 1.0 atm–2.1 GPa without the valiance of emission color, and followed by a progressive decline in emission with a bathochromic-shift of emission in 2.1–16.2 GPa. The corresponding absorption spectra also perform a continuous bathochromic-shift of the absorption edge. As a result, in context of the disordered π - π stacking mode at ambient pressure and the stable emission color in the range of 1.0 atm–2.1 GPa, it can be put forward the conclusion that the intermolecular coupling of **S5** is unlikely to be the primary factor to cause the lower energy of emission which is responsible for the larger ϑ_1 but not the slightly less twisted phenyl blades compared to that of **S4** .

After systematically discussing the optical performance of **S1** –**S5** , the ϑ_1 is precisely attached as the crucial factor to impact the emission energy of DPDBF derivatives in crystal, more important than the other factors including the π - π stacking, C-H[?][?][?] π hydrogen bonds and the torsion angle of phenyl blades.

From an experimental point of view, the propeller-shaped molecular conformation and the stacking mode with disordered π - π stacking are the substantial contributors to cause the weak intermolecular coupling-induced charge transfer. The optical properties of DPDBF derivatives are principally derived from single molecular conformations.

2.2 Theoretic calculation and discussion

To theoretically elucidate the optical performance of the **S1**–**S5**, the calculations were performed by hybrid quantum mechanics and molecular mechanics (QM/MM) approach with pbe1pbe/6-31G(d,p) level of theory for QM and mechanics/uff level of theory for MM in the Gaussian 16 package.^[49,50] As shown in Figure S6, the aggregate structures approached by QM/MM (supporting information) find that the local minima of S_0 and the visualized molecular orbitals principally contribute to the amplitude of the S_0 - S_1 transition. The S_0 - S_1 excitation transitions of **S1**–**S4** are all primarily contributed from their HOMO to LUMO transitions occupying by larger than 90% of amplitude, while that of **S5** consists of two main contributions including 31.5% amplitude from HOMO to LUMO transition and 67.1% amplitude from HOMO-1 to LUMO transition. The calculated emission wavelengths are consistent well with the experimental data. It states the detected emission signal derived from the de-excitation transitions of S_1 - S_0 of **S2**–**S5** and the corresponding emission decay curves further substantiate it with the fitted lifetimes in nano-second scale (Figure S7). At ambient pressure, the fitted lifetimes of **S2**–**S5** monitored at the maximum emission wavelength are 11.3, 28.5, 12.9 and 4.4 ns, respectively. Unfortunately, the faint emission of **S1** at ambient pressure hinders the measurement of the emission decay curve and quantum yield value. The pressure-dependent emission decay curves of **S1** and **S5** reveal that the fitted lifetime values are matching well with the change tendencies of corresponding piezochromic luminescence (Figure 5). This result also confirms the nano-second scale of lifetimes of **S1** (0.4–1.6 ns) in 1.0–12.7 GPa and **S5** (0.4–4.4 ns) in 1 atm–14.3 GPa. Therefore, the pressure-induced bathochromic-shifts of emission of **S1** and **S5** could not be derived from phosphorescence of the de-excitation transition of triplet states. The quantum yield values of **S2**–**S5** at ambient pressure are 13.2, 22.1, 47.0 and 44.3, respectively. According to the calculated and experimental results, **S1** and **S5** harvest the emission with lower energy compared to that of **S2**–**S4**. Particularly, **S1** has the smallest π -conjugated molecular conformation among the listed DPDBF derivatives. To barely consider the energy gaps between calculated HOMO to LUMO of **S1**–**S5**, the expanded π -conjugated molecular conformations indeed lead to a decrease in the energy gap, which gradually diminishes from 4.684 eV of **S1** to 3.977 eV of **S5** (Figure 6A). Extraordinarily, **S1** performs the significantly larger Stokes shift with $\lambda_{\text{ex}} = 334$ nm (S_0 - S_1 transition, 29940 cm^{-1}) and $\lambda_{\text{em}} = 523$ nm (S_1 - S_0 transition, 19120 cm^{-1}) with a 10820 cm^{-1} of calculated energy lost. As a result, the emission energy of the list of DPDBF derivatives in crystals is mostly influenced by the Stokes shift effect and minorly affected by the energy gap between HOMO to LUMO. However, the torsion of phenyl blades has been frequently mentioned in the emission mechanism of AIEgens. According to this theory, the torsion angle of phenyl blades has been approximately bridged to the energy of the de-excitation transition of S_1 - S_0 transition in which the less twisted angle equals the less emission energy.^[30–33] In fact, it can be noticed that the propeller-shaped molecular conformations of DPDBF derivatives do not form the slightly twisted phenyl blades at ambient pressure. In spite of the relatively much less twisted phenyl blades of **S5** with 64.30 of θ_5 and 49.40 of θ_6 , the torsion-induced intramolecular charge transfer may not significantly affect the emission energy. In addition, the π - π face-to-face stacking in DPDBF crystals is always disordered without obviously overlapped areas. Benefitting from the systematical analysis of the list of DPDBF derivatives, we successfully realized that the Stokes shift effect can be achieved to adjust the emission energy in a much more efficient way than expanding the π -conjugated conformation, which is dominantly impacted by the conformation of planar π -conjugated moiety in this material system.

Simultaneously, other material systems of AIEgens can achieve low energy emissions while experiencing intense intermolecular or intramolecular π - π face-to-face interactions. For instance, in investigations of AIEgens including dpTPAAZ,^[51] BPMT,^[40] and 2TPAT-AN,^[52] the intermolecular coupling is emphasized to endow the materials with high-efficiency near-infrared emissions and restricted non-radiative decay rates though the intermolecular charge transfer. This strategy is helpful to conquer the challenge of the energy gap law. Because it successfully avoids the contradiction between the declined charge-transfer emissive state

and the following lower radiative transition rate. Moreover, such materials can consist of one pure organic component or multi-components.^[25,53] For studies involving intramolecular π - π face-to-face interactions, it also reduces the emission energy through space coupling to realize charge transfer.^[54] However, in the above-mentioned cases, the molecular stackings all exist the obvious π - π face-to-face stacking. Clearly, the abundant molecular conformations of AIEgens, in particular, can have a significant influence by varied factors on the resulting optical performance. Finally, Figure 6B is depicted to systematically sum the intrinsic connection among the listed DPDBF derivatives to display the essential components, and the parameter ϑ_1 can be utilized to approximately expect the emission energy of DPDBF derivatives.

3. Conclusion

After systematically discussing the photophysical properties of DPDBF derivatives in crystals, a novel parameter (ϑ_1) in the planar π -conjugated moiety is precisely assigned as the crucial factor to impact the emission energy, while factors related to the torsion angles of phenyl blades, π - π face-to-face interactions, and hydrogen bonds are treated as minor factors. According to the calculation result, the molecular conformations of DPDBF derivatives with larger ϑ_1 value harvest the obviously enhanced Stokes shift to more efficiently decline the emission energy than through expanding the π -conjugated structures. This investigation can be utilized as one of the typical examples of AIEgens to guide the molecular design whose molecular conformations consist of a planar π -conjugated segment and the stacking structures do not exist the strong intramolecular and intermolecular π - π face-to-face interactions.

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Conflict of Interests

The authors declare no conflict of interests.

Supporting Information

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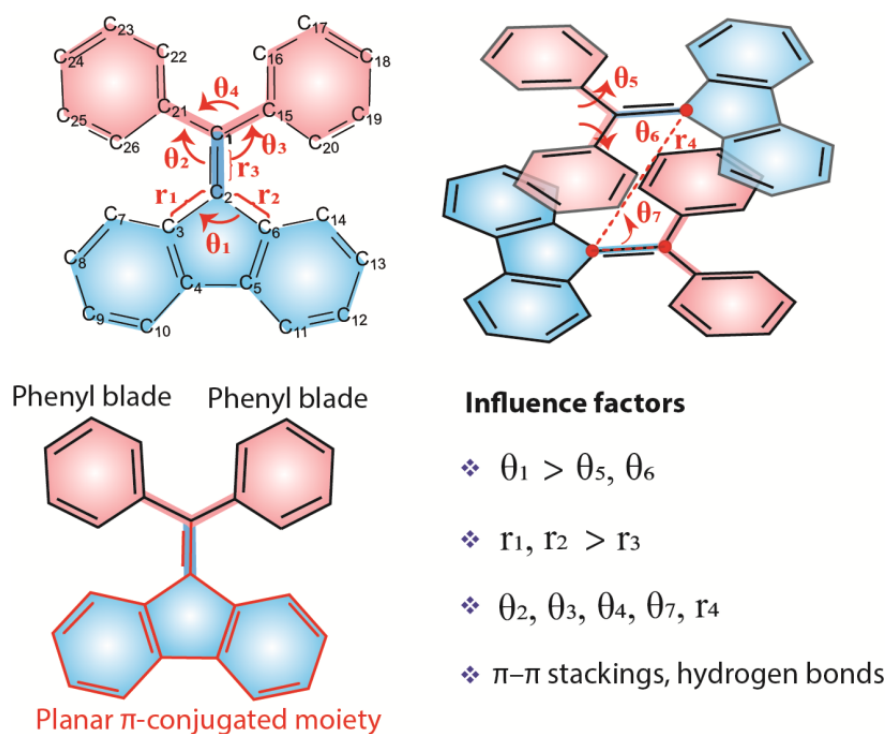


Figure 1. Schematic diagrams to display the discussed factors, named planar π -conjugated moiety, and phenyl blades.

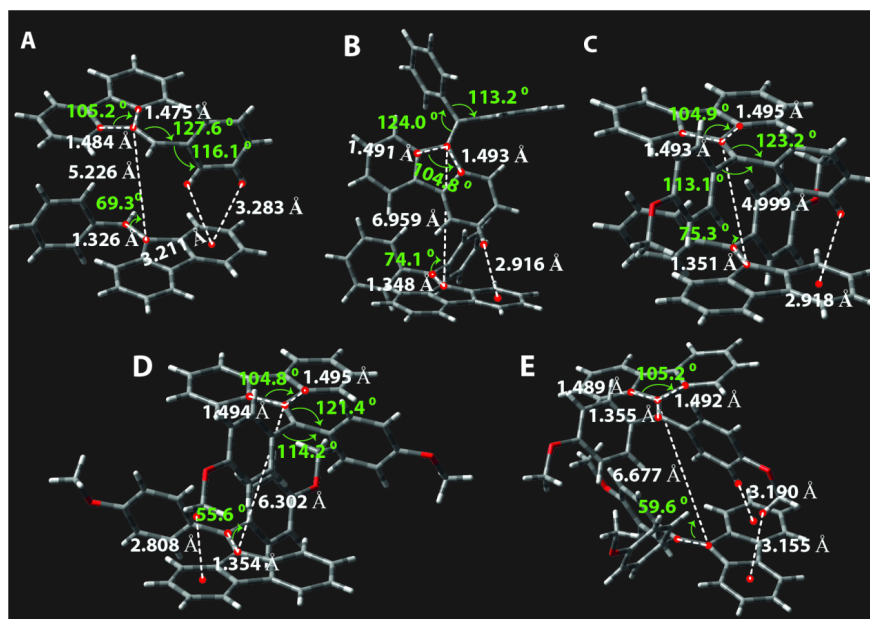


Figure 2. Dimer structures of (A) S1 , (B) S2 , (C) S3 , (D) S4 , and (E) S5 extracted from the crystal structures.

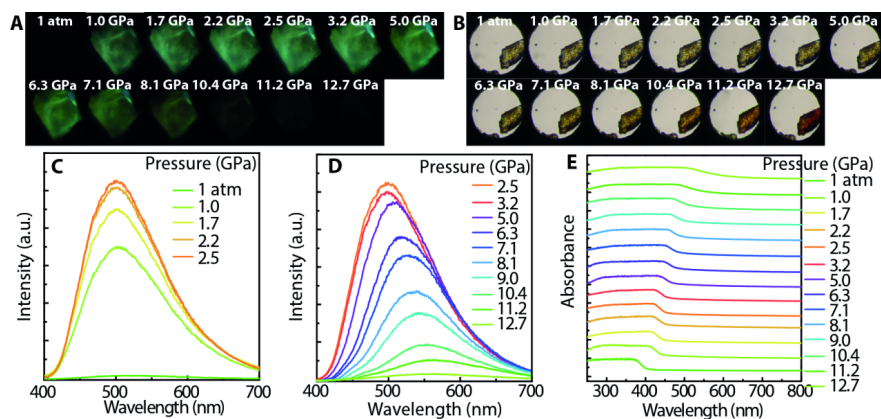


Figure 3. Photos of crystal S1 (A) under UV irradiance and (B) daylight applied with varied pressure, along with the corresponding (C) and (D) emission spectra and (E) UV-Vis absorption spectra.

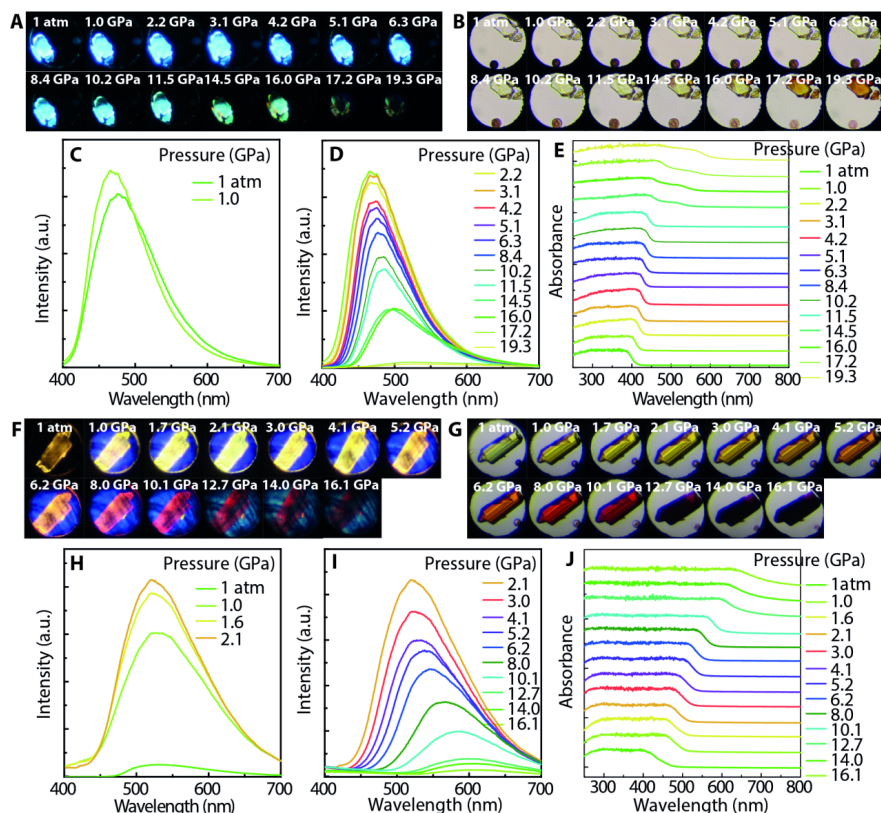


Figure 4. Photos of crystal S4 (A) under UV irradiance and (B) daylight applied with varied pressure, along with the corresponding (C) and (D) emission spectra and (E) UV-Vis absorption spectra. Photos of crystal S5 (F) under UV irradiance and (G) daylight applied with varied pressure, along with the corresponding (H) and (I) emission spectra and (J) UV-Vis absorption spectra.

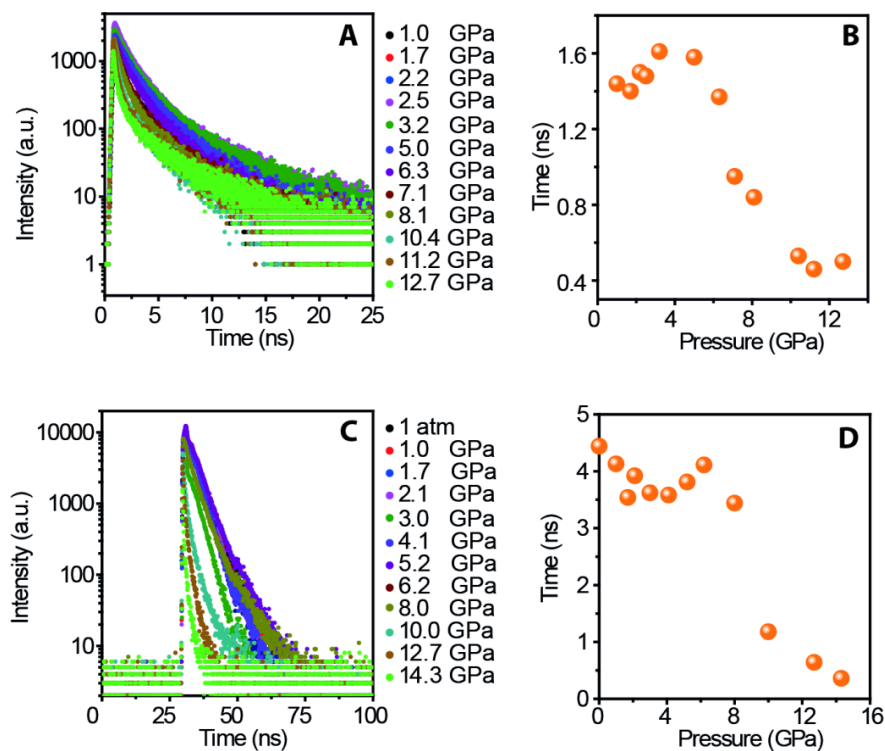


Figure 5. (A) Pressure-dependent emission decay curves and (B) the corresponding fitted lifetime values of S_1 . (C) Pressure-dependent emission decay curves and (D) the corresponding fitted lifetime values of S_5 .

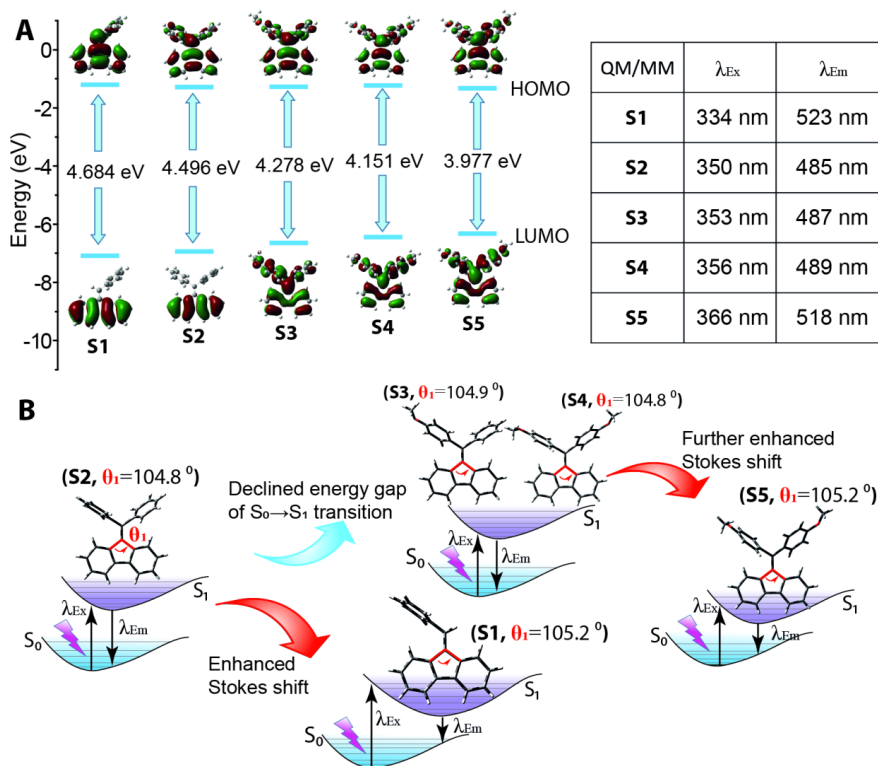


Figure 6. (A) Visualized HOMO and LUMO molecular orbitals of **S1**–**S5**, and (B) corresponding schematic diagram of the energy transfer mechanism, illustrated with the table to present the wavelengths of (λ_{Ex}) calculated S_0 - S_1 and (λ_{Em}) S_1 - S_0 transitions.

Table 1. Important parameters of the dimers of **S1**, **S2**, **S3**, **S4** and **S5**.

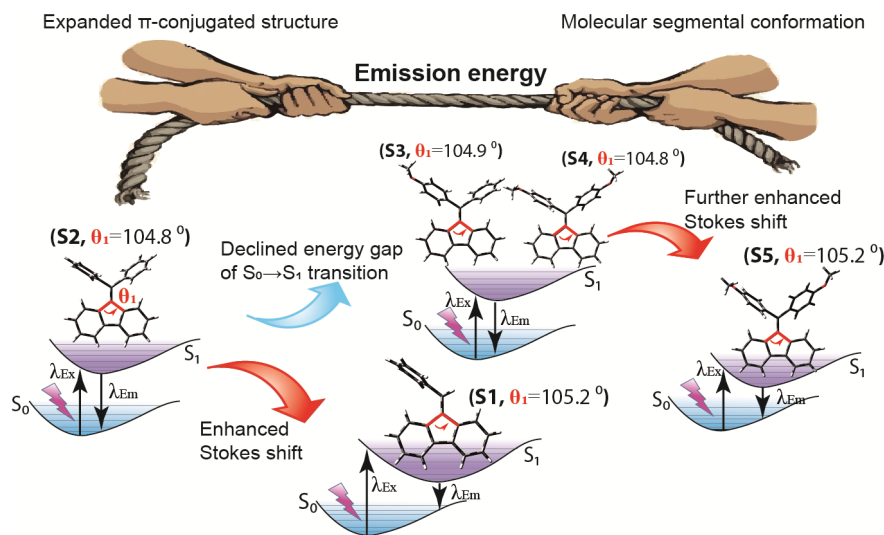
	ϑ_1 (°)	ϑ_2 (°)	ϑ_3 (°)	ϑ_4 (°)	ϑ_5 (°)	ϑ_6 (°)	ϑ_7 (°)	r_1 (°)	r_2 (°)	r_3 (°)	r_4 (°)
S1	105.2		127.6			87.8	69.3	1.475	1.484	1.326	5.226
S2	104.8	124.0	122.8	113.2	80.3	74.0	74.1	1.493	1.491	1.348	6.959
S3	104.9	123.6	123.2	113.1	69.5	69.3	75.3	1.495	1.493	1.351	4.999
S4	104.8	121.4	124.3	114.2	74.5	58.2	55.6	1.494	1.495	1.354	6.302
S5	105.2	121.3	123.9	114.7	64.3	49.4	59.6	1.492	1.489	1.355	6.677

Unveil the crucial factors dominating the optical performance of a series of diphenyldibenzofulvene (DPDBF) derivatives by combined systematically analyzing the impact factors, including molecular conformation parameters and intermolecular coupling, with the calculations.

Keywords aggregation-induced emission, diphenyldibenzofulvene derivatives, planar π -conjugated segment, Stokes shift

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To unravel the factor to dominantly impact the emission energy of crystal diphenyldibenzofulvene derivatives



Supporting Information

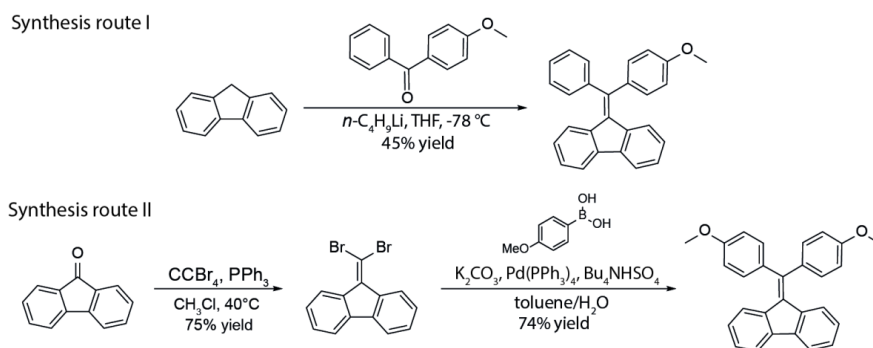
To unravel the factor to dominantly impact the emission energy of crystal diphenyldibenzofulvene derivatives

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MATERIALS AND METHOD

1.1 Materials

Tetrahydrofuran (THF, Sigma-Aldrich, 99.9%), fluorine (Energy Chemical, 98%), methoxybenzophenone (Meyer, 98%), *n*-C₄H₉Li (Energy Chemical), diphenyldibenzofulvene (Beijing Warwick Chemical Co., Ltd., 95%), 9-Benzylidene-fluorene (Shanghai Bepharma Science & Technology Co., Ltd., 97%), 9-fluorenone (J&K, 98%), triphenylphosphine (Energy Chemical, 98%), 4-methoxyphenylboronic acid (Meyer, 97%), Tetrakis(triphenylphosphine)palladium (Bide Pharmatech Ltd., 98%), tetrabutyl-ammonium hydrogen sulfate (Meyer, 99%). All reactions were conducted under an atmosphere of dry nitrogen with oven-dried glassware or vacuum line techniques. All anhydrous solvents were purchased from Sigma-Aldrich and directly used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification.



Scheme S1. Synthesis routes of I and II to produce 9-(4-Methoxyphenylphenylmethylene)-9H-Fluorene and 9-[di(4-methoxyphenyl)methylene]-9H-fluorene, respectively.

1.2 Preparation of 9-(4-methoxyphenylphenylmethylene)-9H-fluorene

The synthesis was consistent with the previous publication, as presented in synthesis route I of Scheme S1.^[1] A solution of fluorene (4.0 g, 24 mmol) in 100 mL THF was added to *n*-BuLi (20 mL, 48 mmol) in hexane at -78 °C under nitrogen protection. After stirring for 2 h at -78 °C, the solution of methoxybenzophenone (4.3 g, 20 mmol) in 30 mL of THF was added to the mixture. The resulting mixture was slowly warmed to room temperature and stirred for 10 h. After the complete reaction, the solution was concentrated by a rotary evaporator, and then the crude product was further purified by a silica gel CC using hexane/chloroform (1:1 v/v) to provide 9-(4-methoxyphenylphenylmethylene)-9H-fluorene as powdery solid in 45% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74–7.68 (m, 2H), 7.41 (s, 3H), 7.37 (d, *J* = 3.7 Hz, 2H), 7.3–7.29 (m, 2H), 7.23 (s, 2H), 6.94 (d, *J* = 12.0 Hz, 4H), 6.84 (s, 1H), 3.88 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.88, 145.65, 143.37, 140.43, 139.03, 135.39, 133.87, 131.66, 130.15, 128.83, 128.36, 127.52, 127.46, 126.45, 126.41, 124.84, 124.80, 119.34, 119.31, 114.19, 77.45, 77.14, 76.82, 55.42.

1.3 Preparation of 9-[di(4-methoxyphenyl)methylene]-9H-fluorene

It was prepared according to the literature procedures.^[2,3] A solution of 9-fluorenone (3.6 g, 20 mmol), carbon tetrabromide (13.27 g, 40 mmol), and triphenylphosphine (20.98 g, 80 mmol) in 100 ml dichloromethane was stirred at 40 for 24 h. After cooling to room temperature, the reaction mixture was concentrated in a vacuum and purified by silica-gel CC using hexane to provide 9-(dibromomethylene)-9H-fluorene as yellow solid (5.04 g, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.59 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H).

A solution of 9-(dibromomethylene)-9H-fluorene (1 g, 3 mmol), 4-methoxyphenylboronic acid (1.14 g, 7.5 mmol), Pd(PPh₃)₄ (0.35 g, 0.3 mmol), K₂CO₃ (1.24 g, 9 mmol) and tetrabutyl-ammonium hydrogen sulfate (0.1 g, 0.3 mmol) in water (30 ml) and toluene (60 ml) was stirred at 90 for 12 h under nitrogen. The solvent was removed in a vacuum, and the crude reaction mixture was purified by silica-gel CC to provide 9-[di(4-methoxyphenyl)methylene]-9H-fluorene (0.87 g, 74% yield) as light yellow solid (petroleum ether/dichloromethane = 3:2). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 7.85 (d, *J* = 7.6 Hz, 2H), 7.25 (q, *J*

= 7.0 Hz, 6H), 7.05–6.97 (m, 6H), 6.66 (d, J = 8.0 Hz, 2H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, chloroform- d) δ (ppm): 160.05, 140.34, 139.35, 135.71, 132.12, 127.33, 126.43, 124.72, 119.40, 114.18, 55.46.

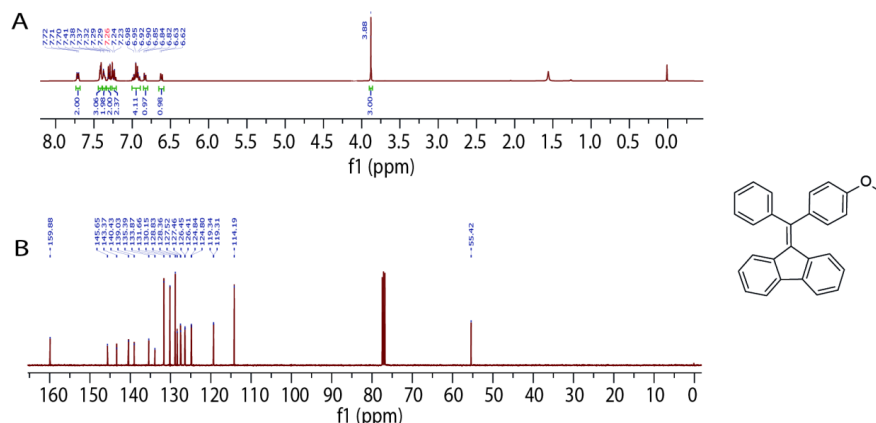


Figure S1. (A) ^1H and (B) ^{13}C NMR spectra of 9-(4-Methoxyphenylphenylmethylene)-9H-Fluorene.

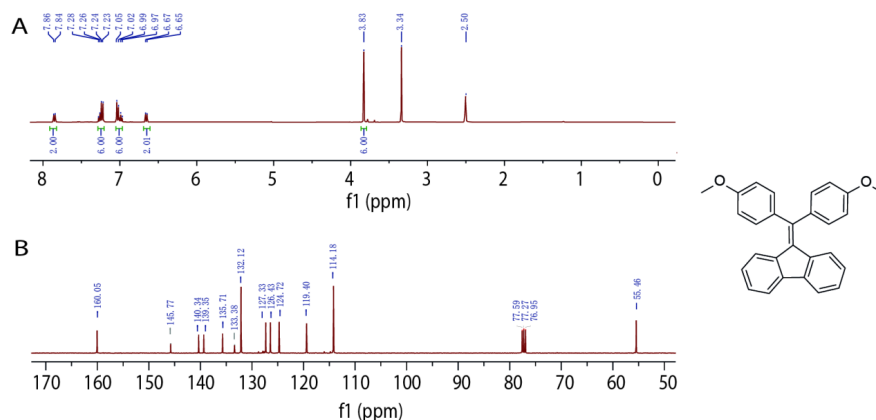


Figure S2. (A) ^1H and (B) ^{13}C NMR spectra of 9-[di(4-methoxyphenyl)methylene]-9h-fluorene.

Characterization details

JEOL JNM-ECA400 spectrometer was utilized to record the ^1H and ^{13}C NMR spectra coupling with Delta 5.3.1 data collector. Single crystal X-ray diffractions were carried out with graphite monochromated Mo radiation ($\lambda = 0.71073 \text{ \AA}$) on an Oxford Diffraction Gemini *E* Ultra diffractometer. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif (CCDC 2251135-2251138 for **S1-S5** except **S2**, which is taken directly from the above website). The time-resolution emission curves were obtained by the HORIBA Deltaflex lifetime fluorometer. In situ high pressure, the emission spectra were measured by using a 355 nm laser excitation line at 10 mW. Absorption spectra were measured based on a deuterium-halogen light source to record the signal in the 300–800 nm range. In emission and absorption spectra experiments, the fiber spectrometer was an Ocean Optics QE6500 spectrometer. High-pressure experiments were conducted by using a symmetrical diamond anvil cell (DAC). A T301 stainless steel gasket was preindented to 45 μm in thickness, then a 150 μm diameter center hole was dilled as the sample chamber. A small ruby ball was loaded into the sample chamber along with the samples for pressure calibration using the ruby fluorescence method. Silicone oil was used as a pressure-transmitting medium for the experiments of emission and absorption.

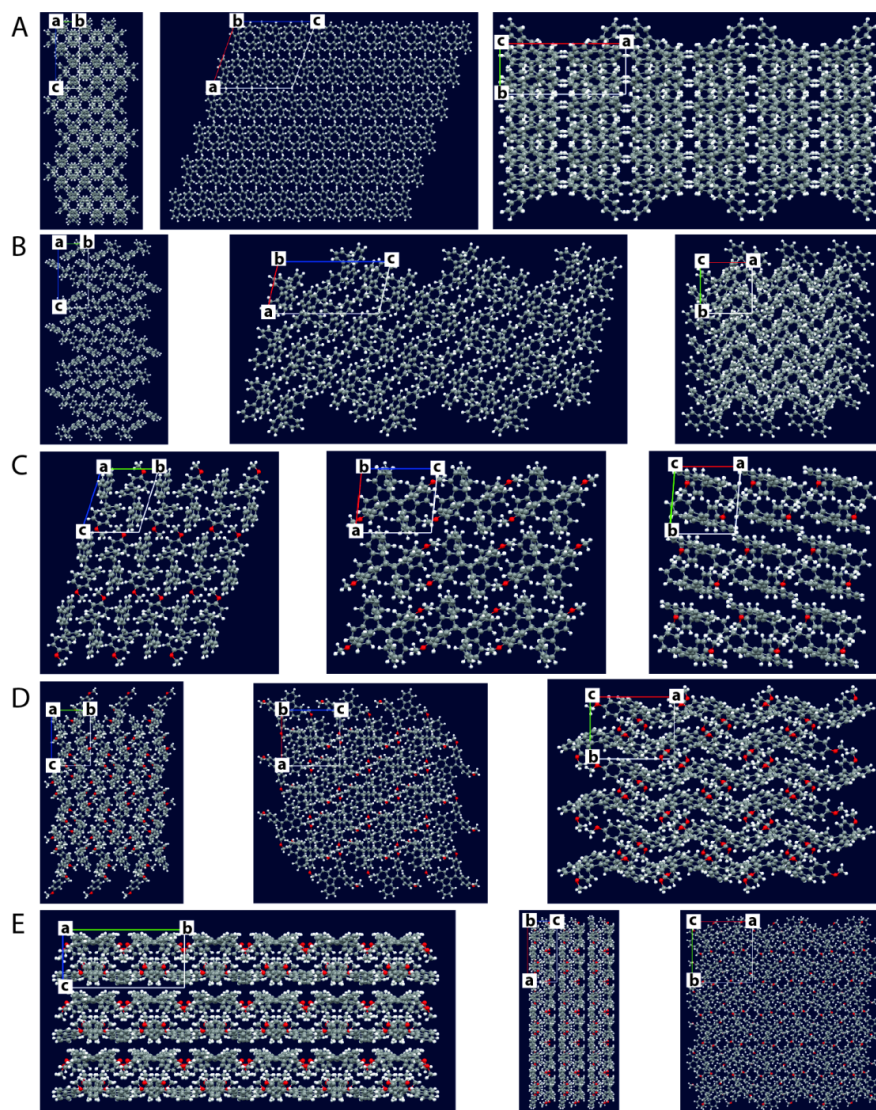


Figure S3. Molecular stacks within the crystals of (A) **S1** , (B) **S2** , (C) **S3** , (D) **S4** , and (E) **S5** (*a*, *b*, and *c* axis directions).

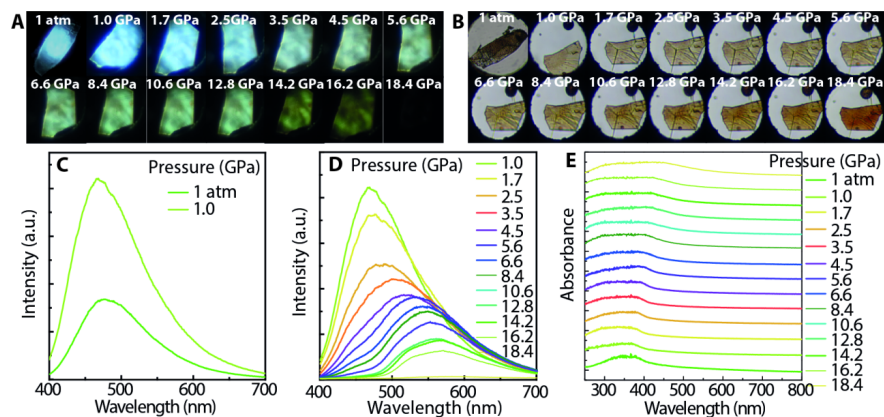


Figure S4. Photos of crystal **S2** (A) under UV irradiance and (B) daylight applied with varied pressure, along with the corresponding (C) and (D) emission spectra and (E) UV-Vis absorption spectra.

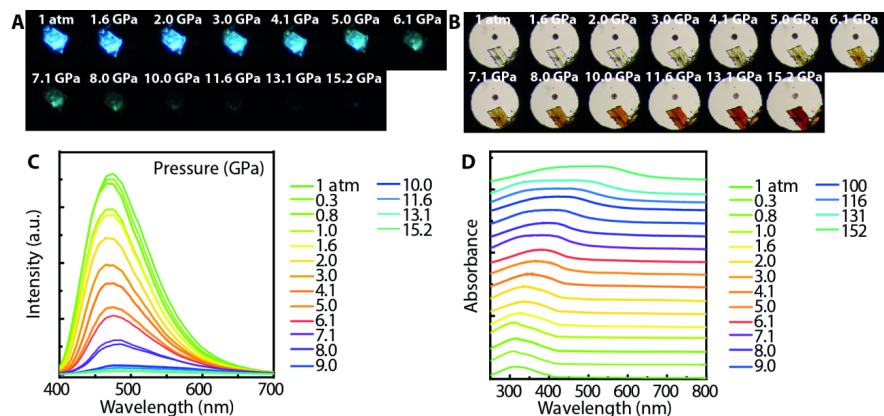


Figure S5. Photos of crystal **S3** (A) under UV irradiance and (B) daylight applied with varied pressure, along with the corresponding (C) emission spectra and (D) UV-Vis absorption spectra.

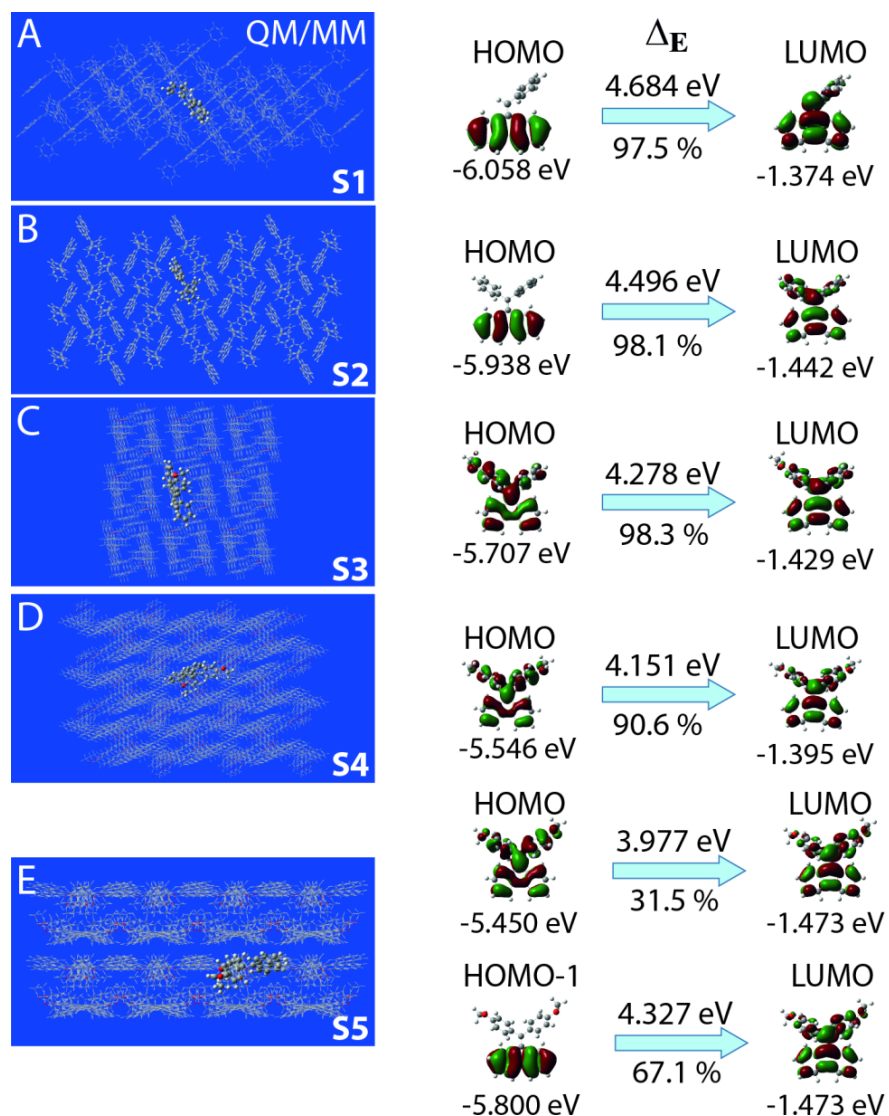


Figure S6. Aggregate structures approached by QM/MM to find the local minima of S_0 and the visualized molecular orbitals principally contributing to the amplitude of S_0-S_1 transition of (A) **S1** , (B) **S2** , (C) **S3** , (D) **S4** , and (E) **S5** .

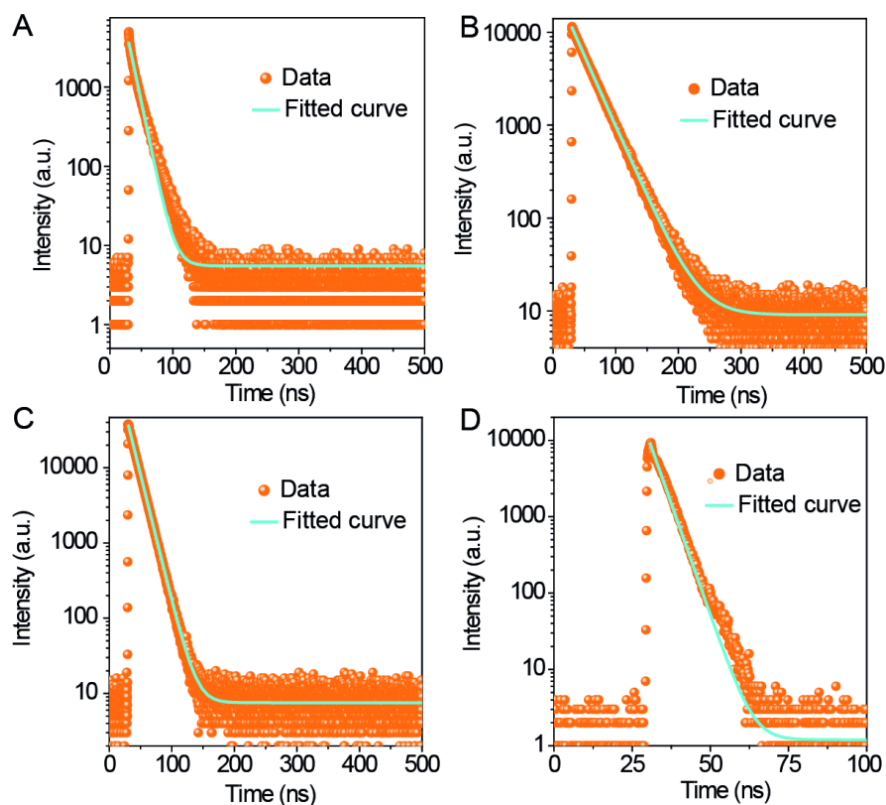


Figure S7. Emission decay curves of crystal (A) **S2** , (B) **S3** , (C) **S4** , and (D) **S5** , all monitored at the maximum emission wavelengths.

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