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Shedding light on the origin of the-solid state luminescence enhancement in butterfly molecules

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short-range exciton coupling, fluorescence.

Different molecular strategies have been carefully evaluated to produce Solid-State Luminescence Enhancement (SLE) in compounds that show dark states in solution. A set of α -phenylstyrylarene derivatives with a butterfly-shape has been designed and synthesised for the first time with the aim of improving the solid-state fluorescence emission of their parent styrylarene compounds. Although these butterfly molecules are not fluorescent in solution, one of them (1,2,4,5-tetra(α -phenylstyryl)benzene) exhibited a fluorescence quantum yield as high

as 68% in a drop cast sample and 31% in its crystalline form. In contrast, 1,3,5-tris(α phenylstyryl)benzene and 4,6-bis(α -phenylstyryl)pyrimidine did not show SLE. A range of fluorescence spectroscopy experiments and Density Functional Theory calculations were carried out to unravel the origin of the different photophysical behaviour of these compounds in the solid state. The results indicate that the rational strategy to control the SLE effect in luminogens depends on a delicate balance between molecular properties and inter-/intramolecular interactions in the solid state.

1. Introduction

Solid-State Luminescence Enhancement (SLE) is an amazing phenomenon that has attracted a great deal of attention due to its potential use in the development of new functional materials in which the luminescence properties depend on a range of factors beyond the chemical formula.^[1,2] Aggregation-Induced Emission (AIE) is also used as a synonym of SLE although the concept of 'molecular aggregation' is more frequently associated with solution phases.^[2] Considerable effort is currently being made to obtain SLE luminogens and to unravel the mechanisms responsible for fluorescence 'on/off' switching between solution and solid state, such as exciton coupling effects,^[3-7] restriction of intramolecular motions (RIM),^[8-10] blocking of Z/E-photoisomerisation,^[11] and restricted access to conical intersections (RACI),^[2,12,13] amongst others. The control of the supramolecular structure is therefore key to obtaining SLE luminogens because short- and long-range intermolecular interactions determine solid-state photophysical properties. Accordingly, the type of solid phase (powder, crystal, drop cast, etc.), the procedure used to obtain it (drop casting, spin coating, etc.) and some external physical stimuli (mechanoluminescence) are also critical aspects to be considered in the design of lightemitting solid materials.^[14-16]

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A number of bulky chemical groups with sterically congested structures, such as tetraphenylethylene (TPE), *cis*, *cis*-1,2,3,4-tetraphenylbutadiene, tetraphenylpyrazine (TPP) and hexaphenylsilole (HPS), are commonly used to obtain SLE luminogens.^[8-10,14,17-19] In general, the incorporation of these moieties has a huge impact on the fluorescence emission wavelength and quantum yield. In the electronically excited state of these compounds, the molecular motions of their phenyl rotors and carbon skeleton vibrations consume the excess energy and result in dark states in solution. However, the intermolecular interactions of these bulky moieties with neighbouring molecules can restrict their molecular motions and yield bright states in solid state. The understanding of the so-called RIM mechanism has allowed the development of a large family of SLE luminogens containing TPE, HPS or other sterically congested groups with twisted phenyl rings.^[8-10,14,17-19] Although the RIM mechanism has been successfully employed to explain the fluorescence enhancement observed in a large variety of luminogens, a thorough description of the SLE effect should involve a global study of the potential energy surface.^[12,13] In this sense, other mechanisms such as RACI or the blocking of Z/E-photoisomerisation have also been associated with the fluorescence enhancement observed in the solid state or in molecular aggregates formed in solution.^[2,11-13,20,21] The main drawback of this global treatment is the considerable increase in the computational cost associated with calculations of the electronic excited states.^[12,13] Intermolecular forces are also important factors that determine the photophysical properties of a bulk material. For instance, many conventional fluorophores have planar and π -conjugated structures that favour the establishment of π - π stacking interactions in the solid state, which are typically associated with fluorescence quenching effects. Nevertheless, this is not a general rule because there are diverse examples of planar π -conjugated molecules that exhibit SLE due to different mechanisms such as exciton coupling.^[6,7] Diverse SLE luminogens with sterically congested structures, such as butterfly-like or propeller-like shapes, have been designed to reduce intermolecular stacking

interactions.^[9,22-24] In these cases, the effect of the intramolecular interactions on the photophysical properties of the material could gain importance and should also be considered. Styrylarenes are a well-known family of compounds^[25-30] but only a few studies on their solidstate photophysical properties have been reported to date.^[2,11,20,31] Interestingly, SLE and AIE (in solvent mixtures) have been reported for some compounds belonging to this family with two and three styryl branches (compounds 4, 5 and some 1,4-di(styryl)benzenes) but, to our knowledge, fluorescence enhancement has not previously been reported for tetra(styryl)benzenes in the solid state.^[2,11,19,20] In compound **6** some rocking movements occur in the phenyl rings (associated with high Huang-Rhys factors) and these are not totally restricted in the solid state and hence SLE is not observed.^[11] The new molecular structures designed here (1-3) contain the styrylarene core (in blue in Scheme 1) but also incorporate new phenyl rotors to generate triphenylethylene moieties (in red in Scheme 1). The presence of several triphenylethylene moieties in the same molecule leads to butterfly-like structures that resemble some TPE derivatives for which SLE has been reported.^[10] The modification of the molecular structure of π -conjugated fluorophores by introducing additional molecular rotors, e.g., phenyl rings, has proven to be a suitable strategy to produce luminogens with high fluorescence quantum yields in the solid state by tuning the balance between the loss of planarity of the molecule, the restriction of intramolecular movements and hindering of π - π stacking interactions.^[8-10] Different spectroscopic experiments have been conducted to investigate the solid-state photophysical properties and to analyse the modifications of these photophysical properties with respect to those reported for the parent styrylarene compounds (4, 6 and 7). In addition, Density Functional Theory (DFT) provided valuable information to interpret the mechanisms responsible for SLE in this type of butterfly molecule.

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2. Results and discussion

2.1. Synthesis and molecular structure.

The synthesis of compounds **1** and **2** was based on the Horner-Wadsworth-Emmons (HWE) reaction for the formation of double bonds, a methodology extensively developed by some of us since 1999 with slight modifications.^[25] The main advantage of this methodology is that the HWE reaction usually requires an easy workup in a catalyst-free approach. However, compound **3** was prepared according to the procedure reported by Gramage-Doria *et al.*^[32] through a general ruthenium(II)-catalysed methodology for the arylation of alkenylic C–H bonds. More detailed characterisation data for the compounds are provided in the Supporting Information (SI).

Good quality crystals suitable for single crystal X-ray diffraction analysis were obtained for compounds **2** and **3** by vapour diffusion from CHCl₃/EtOH and CHCl₃/CH₃CN solvent systems, respectively. A view of the molecular structure of **2** and **3** is shown in **Figure 1**, **2** and **3**. For compound **2**, two crystallographically independent molecules are observed, i.e., **2a** (centrosymmetric) and **2b** (see **Figure 1**). In both cases, there are no classical hydrogen bonds or strong π - π stacking interactions, as evidenced by the large intermolecular distances (*ca*. 5.0– 5.9 Å). Nevertheless, the highly twisted conformation of the molecules, especially in **2b**, promotes a larger number of inter- and intramolecular interactions by C–H··· π hydrogen bonds. For instance, **2b** exhibits three C–H··· π intramolecular interactions that could explain its overcrowded arrangement in relation to **2a** (see **Figure 2**).

Although short-range π - π stacking interactions were not found for compound **2**, the presence of parallel stacking π - π and C–H··· π interactions at longer distances contributes to the three-dimensional structure observed in the crystal in a similar way to that observed in a large number of proteins (see the view of the 3D structure of **2** along the *c* axis in **Figure S1**).^[33]

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The crystal packing in compound **3** is due to three types of interactions, i.e., a nonclassical hydrogen bond between C31–H31…N2 atoms that promotes a dimeric arrangement (**Figure 3A**) and π - π stacking (**Figure 3B**) and C–H… π (**Figure 3C**) interactions. In addition, molecule **3** exhibits one intramolecular interaction between a hydrogen of the pyrimidine ring and the closest phenyl ring of the α -phenylstyryl branch (see **Figure S2**).

2.2 Photophysics in solution.

The experimental UV-vis absorption spectra of the studied compounds were recorded in THF solution (see Figure 4). Intense bands were observed at 313 and 331 nm for compounds 1 and 2, respectively. The UV-vis spectrum of compound 3 shows a less prominent band centred at 337 nm and a weak peak at around 300 nm. These bands were assigned by performing full geometry optimisations to predict the most stable conformations in THF solution and calculating the vertical electronic transitions at the TD-M06-2X/6-31G* level of theory. Molecular structures in which the diphenylethylene branches are pointing outward in relation to the central benzene/pyrimidine plane were modelled for all of the compounds in solution (see Figure 5; some selected geometrical parameters calculated for these compounds are also collected in Tables S1–S4). The geometries computed for 2 and 3 in solution closely resemble their X-ray crystal structures (Figure S3 and Tables S2-S4 for a comparison of some geometrical parameters calculated in solution with the experimental data in solid state). For compound 2, in which two crystallographically independent molecules were observed, our theoretical calculations predicted that conformation 2b is 7.8 kcal/mol more stable than 2a in THF solution at 298.15 K. The largest deviations between the calculated and the experimental structures were found for **2b**, in which two dihedral angles belonging to the same α -phenylstyryl branch are markedly modified, with variations of 22° and 49° on going from solution to solid state, $|\Delta \tau_{s-c}|$. In molecule 2a, two dihedral angles also belonging to the same α -phenylstyryl

branch showed significant variations ($|\Delta \tau_{s-c}|$ of 18° and 20°). Smaller differences were observed between the calculated structure of 3 and its crystal structure ($|\Delta \tau_{s-c}| < 10^\circ$). These results can be related to the more overcrowded crystal structures of **2a** and **2b** when compared to **3**.

In general, the wavelengths calculated for the lowest-lying electronic transitions (λ_{abs}^{calc}) match well with the experimental absorption maxima (λ_{abs}^{exp}) , with $|\Delta\lambda| = \lambda_{abs}^{calc} - \lambda_{abs}^{exp} \leq$ **21** *nm* in all cases (see **Table 1**). As reported for other 1,3,5-tris(styryl)benzenes,^[11,20,34] some degeneracy was observed in the frontier molecular orbitals of compound 1 (see Figure 5). In consequence, two electronic transitions ($S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$) with close energy and oscillator strength were found for this compound. Three electronic transitions $(S_0 \rightarrow S_1, S_0 \rightarrow S_2 \text{ and } S_1, S_0 \rightarrow S_2 \text{ and } S_1 \rightarrow S_2 \text{ and } S_2 \rightarrow S_2 \text{ and } S_1 \rightarrow S_2 \text{ and } S_2 \rightarrow S_2 \text{ and } S_2 \rightarrow S_2 \rightarrow S_2 \text{ and } S_2 \rightarrow S_2 \rightarrow S_2 \rightarrow S_2 \text{ and } S_2 \rightarrow S_2$ $S_0 \rightarrow S_3$) involving the HOMO-1 to LUMO+1 frontier orbitals were assigned to the broad absorption band of compound 2 centred at 331 nm. It is worth noting that while the frontier orbitals are completely delocalised over the whole structure of 2a, they become localised along two α -phenylstyryl branches in diagonal positions in **2b**. This result could mean that molecule **2a** would act as a chromophore as a whole, while only two α -phenylstyryl branches in **2b** would be involved in the photoexcitation. A similar observation, namely the planarization of two diagonal styryl branches upon photoexcitation, was previously reported for the parent compound **6**.^[11] In the case of compound **3**, the lowest-lying electronic transition was assigned to a HOMO \rightarrow LUMO transition (contribution of 89%) and these molecular orbitals were fully delocalised.

Fluorescence emission spectra recorded for the studied compounds in THF solution are shown in **Figure 4**. An unstructured band centred at 424 nm was found for compound **1**. In the case of **2**, a broad emission band with a weak vibronic structure was recorded, i.e., two peaks at 467 nm and 488 nm can be distinguished. This result is in contrast to the clear vibronic structure observed in the fluorescence emission spectra of the parent styrylarene compounds **4**

and 6.^[11] A vibronic structure is also clearly discerned in the emission spectrum of 3, with two peaks at 400 and 421 nm. The calculated emission energies for the $S_1 \rightarrow S_0$ transition are collected in Table 2. The best match is found for compound 2 while the larger discrepancies for compounds **1** and **3** are within the range of expected deviations.^[24,35,36] In order to get some insight in this issue, the molecular orbitals of the first excited state have been represented in the Figure S4. As can be seen, while the molecular orbitals in the ground state of compound 3 are delocalised on all the molecule, there is a significant redistribution of the charge in the excited state. Thus, we could postulate that M06-2X overestimates the intramolecular charge transfer in the excited state (and the energetic stabilization of the S₁ state in a polar solvent) in the case of compound 3 justifying the large deviation between the experimental a calculated emissions. It is worth noting that the presence of additional phenyl rotors in compounds 1-3 produces a substantial drop in the fluorescence quantum yield ($\Phi_{\rm F}$) in solution when compared to their parent styrylarene compounds, i.e., the Φ_F values measured for compounds 1–3 in THF solution was < 1%, in contrast to the values reported for **4** and **6** (60% and 57%) (see **Table 2**).^[20,11] A low quantum yield (albeit higher than that recorded for 3) was also obtained for compound 7 (6%) by Achelle et al.^[29] In addition, the oscillator strength, f, calculated for the lowest-lying electronic transition of compound 3 (0.63) is lower than those calculated for equivalent transitions in 1, 2a and 2b (≥ 0.82). Hence, a lower radiative rate constant (k_r) is expected for 3 than for 1 and 2 on considering the Strickler–Berg relation, which establishes that k_r is directly related to f.^[37,38] This issue is key because the fluorescence quantum yield of a compound depends on the balance between the radiative and non-radiative (k_{nr}) rate constants. SLE is a phenomenon that originates from restrictions of the non-radiative pathways in the solid state, which in turn lead to k_r becoming comparable or higher than k_{nr} . Therefore, although nonradiative pathways were partially blocked, a low value of k_r could prevent the appearance of

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the SLE phenomenon. This issue will be considered again in the analysis of the photophysical properties of **3** in the solid state.

Different comparative analyses of the molecular properties were performed in order to gain insights into the low luminescence experienced by compounds **1–3** upon photoexcitation (see **Figure 6** and **Tables S1–S4**). Compounds **1** and **3** undergo large changes in one α -phenylstyryl branch on varying diverse dihedral angles, $|\Delta \tau_{S1-S0}|$, with values up to almost 40°. In the case of molecules **2a** and **2b**, the main changes occurred in the dihedral angles belonging to two α -phenylstyryl branches located along a diagonal axis ($|\Delta \tau_{S1-S0}| \leq 25^\circ$). The rotational barriers calculated for the phenyl rotors indicate that these rings can be twisted with a relatively low energy consumption (for instance, ~2 kcal mol⁻¹ or less for torsions of 30°, see **Figure 6**). This fact, which is probably due to the poor conjugation of the α -phenylstyryl moieties, could help to dissipate the excess energy from the photoexcitation processes and yield dark states in solution. It is worth mentioning that although there is an increase in the co-planarity between the central arene ring and some ethylene moieties upon photoexcitation (see **Figure S5**), the peripheral phenyl rotors remain twisted with respect to the central unit. This contrasts with the behaviour of compounds **4** and **6**, in which a planarization of one styryl branch (in **4**) or two (diagonal) styryl branches (in **6**) was observed upon photoexcitation.^[11]

The reorganisation energy (λ) and Huang–Rhys (HR) factors are also key parameters that provide valuable information on the dynamics of the electronic relaxation of excited states. The decomposition of the reorganisation energy into contributions from each normal mode, *i*, enable us to determine the main vibrations involved in the electronic relaxations.

$$\lambda = \sum_{i=1}^{n} \lambda_i \tag{1}$$

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Graphical representations of λ_i vs. normal mode wavenumber (ω_i) calculated for the studied compounds are shown in **Figures 7** and **S9**. Several vibrational modes in the low energy region (< 200 cm⁻¹) make a significant contribution to the total reorganisation energy of the three compounds, as already reported for molecules such as TPE and HPS.^[39,40] These out-of-plane modes correspond to twisting or wagging vibrations, which can help to dissipate the absorbed energy and lead to dark states in solution (see **Figure S6**). C–C stretching modes in the high energy region (1600–1750 cm⁻¹) could also contribute to the non-radiative deactivation. The dimensionless HR factors account for the displacement of the equilibrium positions of the nuclei upon photoexcitation and quantify the strength of the electron-vibrational coupling. These factors can be calculated from the reorganisation energy of each vibrational mode according to

$$\mathbf{S}_{i} = \frac{\lambda_{i}}{\hbar\omega_{i}} \tag{2}$$

All of the compounds show large HR factors associated with the normal mode in the low energy region (see **Figure 7** and **S7** and **Table S5**). Some HR factors calculated for compounds **1** and **3** are particularly high, e.g., those associated with wagging and twisting modes of the phenyl rotors of **1** at 20 cm⁻¹ ($S_i = 34$) and 34 cm⁻¹ ($S_i = 13$), which are comparable to the HR factor values reported for related compounds such as *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene and 1,1,4,4-tetraphenyl-butadiene.^[41] It must be remembered that the largest structural changes upon photoexcitation were also calculated for **1** and **3** while less extensive modifications were found for the overcrowded structures of **2a** and **2b**. Although somewhat lower HR factor values were obtained for **2a** and **2b**, a large number of significantly high HR factors ($S_i > 5$) was obtained for these compounds in comparison with the tris(α -phenylstyryl)

derivative. In general, these results highlight the high efficiency of the non-radiative deactivation pathways in compounds 1-3 and are consistent with the low fluorescence quantum yields measured for all of the compounds in solution.

2.3 Photophysics in the solid state

The emission and excitation spectra obtained for compounds 1–3 in powder form are shown in **Figure 8**. More detailed information on the fluorescence excitation and emission wavelength maxima, and quantum yields of the studied compounds (and the related compounds **4–6**) in different solid forms (crystal, drop cast and powder) are collected in **Table 3**. The difference in optical properties observed between the dropcast, powder and crystal could be a consequence of the existence of different morphologies between crystalline and amorphous zones in the different solid states. At present, we are carrying out studies to help understand this fact better.

Compound **2** shows green fluorescence emission with CIE chromaticity coordinates of (0.11, 0.49), in contrast with the blue emission of **1** and **3** (see **Figure 8c** and **Table 3**). There was an increase in the fluorescence quantum yield for compound **2** from < 1% in THF solution to 31% in the crystalline state or 68% in a drop cast sample when the solid sample was prepared by drop casting method (from a 5 mM solution in 1:1 mixture of acetonitrile:THF). On the contrary, SLE effect was not observed for compounds **1** and **3**. This result could be due to the absence of close π - π stacking interactions observed in the crystal structure of compound **2**. This type of intermolecular interaction, which is commonly associated with fluorescence quenching effects, is generally hampered in bulky molecular structures such as propeller-shaped and butterfly-shaped molecules.^[19] In addition, the SLE effect observed for compound **2** can be related to the large number of inter- and intramolecular interactions by C–H··· π hydrogen bonds that were found in the crystal structure (see **Figure 2** and **S1**). Recently, Yu et al. demonstrated

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that C-H $\cdots\pi$ intramolecular interactions restrict the molecular motions and lead to an SLE effect in bis(α-phenylstyryl)benzene derivatives.^[42] Similar conclusions have been reported for luminescent molecules in which C-H··· π intermolecular interactions are established in the crystal structure.^[43,44] In contrast, the fluorescence quantum yield reported for the parent compound 6 decreases from THF solution (57%) to the solid state (1.7%).^[11] Transmission electron micrographs showed narrow lattice fringes (with a periodicity of tenths of nanometers) for this compound in the solid state. Discotic conjugated molecules tend to form columnar mesophases through π - π stacking interactions and these lattice fringes are generally associated with the intracolumnar periodicity. Thus, a shorter intracolumnar periodicity was found for the supramolecular structure of compound 6 (with d-spacing of 0.21 nm) than in 4 and 5 (with dspacing of 0.88–0.92 nm and 0.70 nm, respectively).^[11,20] Accordingly, noticeable spectral differences were found for compound 6 in the solid state ($\lambda_{em}^{exp} = 547$ nm, in powder), with respect to THF solution ($\lambda_{em}^{exp} = 461 \text{ nm}$).^[11] On the contrary, closer emission spectra in the solid state and solution were obtained for compound 2 ($\lambda_{em}^{exp} = 509$ nm, in the crystal; $\lambda_{em}^{exp} =$ 467, 488 nm in THF solution) than for 6. This fact illustrates the role of those intermolecular interactions in the distinct photophysical behaviour of compounds 2 and 6 in the solid state.

Unfortunately, a thorough analysis on the inter- and intramolecular interactions could not be carry out for compound **1** since its crystal structure was not obtained. Nevertheless, it must be highlighted some spectral differences and similarities between **1** and its parent compound **4**. As mentioned, the fluorescence quantum yield of compound **4** in THF solution (60%) is significantly higher than the value of Φ_F measured for **1** (< 1%).^[20] In the solid state, no significant variations of Φ_F were found for both compounds (< 1% for **1**; 50-51% for **4**) with respect to THF solution.^[20] In the case of compound **1**, the fluorescence emission spectra in the solid state (λ_{em}^{exp} = 421 nm in powder) is very close to that in THF solution (λ_{em}^{exp} = 424 nm). For

compound **4**, the spectral differences found between the solid state and solution are small but slightly larger than for **1** ($\lambda_{em}^{exp} = 448$ nm, in powder; $\lambda_{em}^{exp} = 399$, 420 nm in THF solution). This fact suggests weak electronic coupling between neighbouring molecules in the solid state of compound **1**. In a similar way to this compound, weak fluorescence emission was also observed for **3** in the solid state. Within the series of compounds **1** – **3**, the lowest radiative rate constant, k_r , in solution is expected for **3**, as discussed in the previous section. In the solid state, the non-radiative rate constant, k_{nr} , could also increase due to the π - π stacking intermolecular interactions observed in its crystal structure (see **Figure 3**). k_r could also be affected by π - π stacking intermolecular interactions but the low fluorescence quantum yield measured in the solid state indicates that the radiative decay is not an efficient mechanism in comparison with the non-radiative deactivation.

In addition to the analysis based on the restriction of intramolecular movements, a parallel study was performed on the effect that intermolecular interactions have on the photophysical properties of the crystal considering the short-range exciton coupling. According to Spano and Hestand,^{16,71} the charge-transfer produced by wave function overlap between neighbouring molecules with short intermolecular distances creates an effective short-range exciton coupling that can induce J- or H-like behaviour, which resembles the photophysical effects of the classical Coulombic exciton-coupling produced in molecular aggregates. This photophysical behaviour can be estimated from the sign of the charge transfer intermolecular coupling, $J_{CT} \alpha - (t_h t_e)$, where $t_h t_e$ is the product of the hole and electron transfer integrals between neighbouring chromophores. H-type behaviour is expected when the sign of the product $t_h t_e$ is negative and, hence, $J_{CT} > 0$, while J-behaviour occurs when $t_h t_e > 0$ and $J_{CT} < 0$. The values of the electron and hole transfer integrals are provided in **Table 4** along with the product $t_h t_e$ calculated for different dimers extracted from the crystal X-ray structure. The dimer bb corresponds to two neighbouring molecules of **2b** while ab is formed by a molecule of **2a**

and a neighbouring molecule of **2b** (**Figure S8**). A, B and C are dimers of the molecule **3** and are shown in **Figure 3**. According to the results collected in **Table 4**, a significantly high value of the product $t_h t_e$ was only found for dimer C.^[6,7] Therefore, a short-range exciton coupling could be produced in that dimer and this could lead to H-type behaviour in the crystal of compound **3**. This result is also consistent with the low fluorescence quantum yield measured for **3** in the solid state, since a lowering of the radiative rate constant is associated with H-type behaviour.

3. Conclusions

A set of butterfly-shaped α -phenylstyrylarenes (1–3) have been synthesised for the first time with the aim of improving the solid-state fluorescence emission of their parent styrylarene compounds (4, 6 and 7). All of the α -phenylstyrylarene derivatives showed poor fluorescence emission in solution but the fluorescence quantum yield increased markedly for compound 2 in the solid form ($\Phi_F = 31\%$ in the crystalline state and $\Phi_F = 68\%$ in a drop cast sample). SLE was only observed for compound 2 and this was associated with the lack of close π - π stacking interactions in the crystal structure as well as the existence of diverse inter- and intramolecular C–H··· π interactions, which restrict the molecular motions and lead to a fluorescence enhancement. In contrast, in compound 3 π - π stacking intermolecular interactions are established in the crystal and these are typically associated with fluorescence quenching effects. In addition, a short-range exciton coupling could be produced in the crystal of compound 3 and this led to an H-type behaviour and lowering of the radiative rate constant. Both results are consistent with the low fluorescence quantum yield measured for 3 in the solid state. An indepth study on the origin of the poor fluorescence emission of compound 1 in the solid form could not be carried out because the crystal structure was not available. Accepted Manuscript

In this work we have tried to shed light on the origin of the SLE phenomenon in butterfly molecules. The inclusion of bulky chemical groups with sterically congested structures, such as TPE, TPP and HPS, or triphenylethylene in our case, is an interesting strategy to obtain luminescence enhancement in the solid state, but this outcome is not guaranteed. Only the thorough study of the effects of diverse phenomena such as RIM, exciton coupling, RACI and photoisomerisation, amongst others, on the radiative and non-radiative constants allow conclusions to be drawn about the origin of SLE phenomena. The analysis of inter- and intramolecular interactions in the crystal structure can assist in this task and is an essential strategy for the rational design of highly luminescent compounds.

4. Experimental Section

Synthesis. Compounds **1** and **2** were prepared following a standard methodology by the HWE reaction between the commercial benzophenone and the corresponding phosphonate core in the presence of potassium *tert*-butoxide (see SI, **Scheme S1**). Compound **3** was synthesised according to the procedure reported by Gramage-Doria *et al.*^[32] Specific details concerning preparation of **1**, **2** and **3** and their characterisation are provided in the SI (**Figure S9–S12**).

Crystallography. Details of the crystallographic data collection and refinement parameters are given in **Table S6**. The measurements were performed on a Bruker-Apex-II CCD diffractometer with graphite monochromated Mo-K_{α} (λ = 0.71073 Å) radiation at 100 K. The structures were solved by direct methods and refined using SHELXL-2016/4 software employing full-matrix least-squares methods on F².^[45] Lorentz, polarisation and multiscan absorption corrections were applied with SADABS.^[46] All non-H atoms were refined anisotropically; some hydrogen atoms were located and refined isotropically and others were placed in idealised positions and treated using riding models. All calculations were carried out with PLATON^[47] and graphics were drawn with MERCURY.^[48] The CIF files have been

deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1971518 (2) and 1971517 (3). Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spectroscopy. Unless otherwise stated, spectra were acquired in THF at 20 °C with a sample concentration of 1 µM. Quartz cuvettes (Hellma Analytics) of 10 mm were employed for all absorption and emission measurements on liquid samples. UV-Vis absorption spectra were acquired on a V-750 (Jasco) spectrophotometer at a scan rate of 600 nm min⁻¹. A Peltier accessory was employed to control the temperature of the spectrophotometer measuring cell. Fluorescence emission spectra in solution were acquired on an FS5 (Edinburgh Instruments) spectrofluorometer equipped with a 150 W Xe lamp as light source and a PMT (photomultiplier tube) detector (R928P model). The temperature was controlled using a Peltier accessory (temperature-controlled cuvette holder, TLC 50, Quantum Northwest). Fluorescence emission spectra in the solid state were recorded on the FS5 spectrofluorometer using an integrating sphere. Fluorescence quantum yield and chromaticity calculations were carried out using the F980 Software from Edinburgh Instruments.

Computational Details. The theoretical calculations were performed using the Density Functional Theory (DFT) on the Gaussian 09 package (version D.01)^[49] at the M06-2X/6-31G* level of theory.^[50] This functional has proven to be suitable for the calculation of photophysical properties of related styrylbenzenes.^[11,20,27,34] Full geometry optimisations of the ground (S₀) and first excited (S₁) states were carried and vibrational frequencies were calculated to check the absence of imaginary frequencies. The initial molecular geometries were those from X-ray diffraction of compounds **2** and **3**. In the absence of experimental geometry data, a conformational analysis was carried out on compound **1**. The effect of the solvent was included by the polarisable continuum model (PCM) as implemented in the Gaussian package.^[51-53]

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Vertical electronic transitions and geometry optimisation of the excited electronic states were computed using Time-Dependent DFT calculations (TD-M06-2X/6-31G*) in solution. The fluorescence emission energy from the first excited state was calculated at the same level of theory as $E_{em}(S_1) = E_{S1}(G_{S1}) - E_{S0}(G_{S1})$, where $E_{S1}(G_{S1})$ is the energy of the S₁ state in its equilibrium geometry (G_{S1}), in the state-specific solvation approach,^[54] while $E_{S0}(G_{S1})$ corresponds to the energy of the S₀ state at the S₁ state geometry (G_{S1}) and with the static solvation from the excited state.^[55] The contribution of each normal mode to the reorganisation energy was calculated using the programme DUSHIN developed by Reimers.^[56] The electronic coupling was calculated at the M06-2X/6-31G* level for dimers extracted from the crystal structure. The calculations were carried out using the projective method implemented in the J-from-g03 programme.^[57,58]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] Y. Chen, J. W. Y. Lam, R. T. K. Kwok, B. Liu, B. Z. Tang, *Mater. Horiz.* 2019, 6, 428–433.
- [2] J. Shi, L. E. Aguilar Suarez, S.-J. Yoon, S. Varghese, C. Serpa, S. Y. Park, L. Lüer, D. Roca-Sanjuán, B. Milián-Medina, J. Gierschner, J. Phys. Chem. C 2017, 121, 23166–23183.
- [3] E. G. McRae, M. Kasha, J. Chem. Phys. 1958, 28, 721-722.
- [4] M. Kasha, Radiat. Res. 1963, 20, 55-71.
- [5] M. Kasha, H. R. Rawls, M. Ashraf El-Bayoumi, Pure Appl. Chem. 1965, 11, 371-392.
- [6] N. J. Hestand, F. C. Spano, Acc. Chem. Res. 2017, 50, 341-350.
- [7] N. J. Hestand, F. C. Spano, Chem. Rev. 2018, 118, 7069-7163.
- [8] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, Chem. Rev. 2015, 115, 11718–11940.
- [9] Y. Hong, J. W. Y. Lam and B. Z. Tang, Chem. Soc. Rev. 2011, 40, 5361–5388.
- [10] Y. Hong, J. W. Y. Lam and B. Z. Tang, Chem. Commun. 2009, 4332–4353.
- [11] R. Domínguez, M. Moral, M. P. Fernández-Liencres, T. Peña-Ruiz, J. Tolosa, J. Canales-Vázquez, J. C. García-Martínez, A. Navarro, A. Garzón-Ruiz, *Chem. Eur. J.* 2020, 26, 3373–3384.
- [12] R. Crespo-Otero, Q. Li, L. Blancafort, Chem. Asian J. 2019, 14, 700-714.
- [13] X.-L. Peng, S. Ruiz-Barragán, Z.-S. Li, Q.-S. Li, L. Blancafort, J. Mater. Chem. C
 2016, 4, 2802–2810.

10.1002/chem.202002920

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- [14] M. Jiang, X. Gu, R. T. K. Kwok, Y. Li, H. H. Y. Sung, X. Zheng, Y. Zhang, J. W. Y. Lam, I. D. Williams, X. Huang, K. S. Wong, B. Z. Tang, *Adv. Funct. Mater.* 2017, 28, 1704589.
- [15] Y. Yu, C. Wang, Y. Wei, Y. Fan, J. Yang, J. Wang, M. Han, Q. Li, Z. Li, Adv. Optical Mater. 2019, 7, 1900505.
- [16] N. Zerby, O. Malka, S. Bhattacharya, N. N. Kadamannil, M. Baranov, R. Jelinek, Adv. Optical Mater. 2019, 7, 1900232.
- [17] J. Chen, B. Xu, X. Ouyang, B. Z. Tang, Y. Cao, J. Phys. Chem. A 2004, 108, 7522–7526.
- [18] M. Chen, L. Li, H. Nie, J. Tong, L. Yan, B. Xu, J. Z. Sun, W. Tian, Z. Zhao, A. Qin,
 B. Z. Tang, *Chem. Sci.* 2015, *6*, 1932–1937.
- [19] Z. Zhao, B. He, B. Z. Tang, Chem. Sci. 2015, 6, 5347–5365.
- [20] A. Garzón, M. P. Fernández-Liencres, M. Moral, T. Peña-Ruiz, A. Navarro, J. Tolosa,
 J. Canales-Vázquez, D. Hermida-Merino, I. Bravo, J. Albaladejo, J. C. García-Martínez,
 J. Phys. Chem. C 2017, 121, 4720–4733.
- [21] A. Garzón, A. Navarro, D. López, J. Perles, E. M. García-Frutos, J. Phys. Chem. C 2017, 121, 27071–27081.
- [22] X. Yin, J. Z. Low, K. J. Fallon, D. W. Paley, L. M. Campos, *Chem. Sci.* 2019, 10, 10733–10739.
- [23] H. Tong, Y. Hong, Y. Dong, Y. Ren, M. Häussler, J. W. Y. Lam, K. S. Wong, B. Z.
 Tang, J. Phys. Chem. B 2007, 111, 8, 2000–2007.
- [24] M. P. Fernández-Liencres, T. Peña-Ruiz, J. M. Granadino-Roldán, M. Moral, A. Valenzuela-Pereira, A. Garzón-Ruiz, A. Navarro, J. Phys. Chem. C 2018, 122, 12002–12014.

- [25] J. C. García-Martínez, E. Díez-Barra, J. Rodríguez-López, Curr. Org. Synth. 2008, 5, 267–290.
- [26] E. Díez-Barra, J. C. García-Martínez, S. Merino, R. del Rey, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, J. Org. Chem. 2001, 66, 5664–5670.
- [27] M. Moral, R. Domínguez, M. P. Fernández-Liencres, A. Garzón-Ruiz, J. C. García-Martínez, A. Navarro, J. Chem. Phys. 2019, 150, 064309.
- [28] P. Ehlers, A. Hakobyan, A. Neubauer, S. Lochbrunner, P. Langer, *Adv. Synth. Catal.* **2013**, *355*, 1849–1858.
- [29] S. Achelle, I. Nouira, B. Pfaffinger, Y. Ramondenc, N. Plé, J. Rodríguez-López, J. Org. Chem. 2009, 74, 3711–3717.
- [30] H. Zhang, F. Rominger, U. H. F. Bunz, J. Freudenberg, Chem. Eur. J. 2019, 25, 11218–11222.
- [31] C. Coya, A. de Andrés, R. Gómez, C. Seoane, J. L. Segura, J. Lumines 2008, 128, 761–764.
- [32] R. Gramage-Doria, S. Achelle, C. Bruneau, F. Robin-le Guen, V. Dorcet, T. Roisnel, J. Org. Chem. 2018, 83, 1462–1477.
- [33] M. Nishio, Y. Umezawa, J. Fantini, M.S. Weiss, P. Chakrabarti, *Phys. Chem. Chem. Phys.* 2014, 16, 12648–12683.
- [34] M. Moral, J. Tolosa, J. Canales-Vázquez, J. Carlos Sancho-García, A. Garzón-Ruiz, J. C. García-Martínez, J. Phys. Chem. C 2019, 123, 11179–11188.
- [35] T. Zhang, H. Ma, Y. Niu, W. Li, D.Wang, Q. Peng, Z. Shuai, W. Liang, J. Phys. Chem. C 2015, 119, 5040–5047.
- [36] Q. Wu, T. Zhang, Q. Peng, D. Wang, Z.Shuai, Phys. Chem. Chem. Phys. 2014, 16, 5545–5552.
- [37] J. P. Vikesland, S. J. Strickler, J. Chem. Phys. 1974, 60, 660-663.

- [38] M. Fecková, P. le Poul, F. Robin-le Guen, T. Roisnel, O. Pytela, M. Klikar, F. Bureš,
 S. Achelle, *J. Org. Chem.* 2018, *83*, 11712–11726.
- [39] N. L. C. Leung, N. Xie, W. Yuan, Y. Liu, Q. Wu, Q. Peng, Q. Miao, J. W. Y. Lam, B.
 Z. Tang, *Chem. Eur. J.* 2014, 20, 15349–15353.
- [40] T. Zhang, Y. Jiang, Y. Niu, D. Wang, Q. Peng, Z. Shuai, J. Phys. Chem. A 2014, 118, 9094–9104.
- [41] Q. Peng, Y. Yi, Z. Shuai, J. Shao, J. Am. Chem. Soc. 2007, 129, 9333–9339.
- [42] B. Yu, D. Liu, Y. Wang, T. Zhang, Y.-M. Zhang, M. Li, S. X.-A. Zhang, *Phys. Chem. Chem. Phys.* 2018, 20, 23851–23855.
- [43] Z. Xie, T. Yu, J. Chen, E. Ubba, L. Wang, Z. Mao, T. Su, Y. Zhang, M. P. Aldred, Z. Chi, *Chem. Sci.* 2018, *9*, 5787–5794.
- [44] M. Islam, Z. Hu, Q. Wang, C. Redshaw, X. Feng, *Mater. Chem. Front.* 2019, *3*, 762–781.
- [45] Sheldrick GM. SHELXL-2016/4. University of Göttingen. Germany. 2016.
- [46] Sheldrick GM. SADABS 2.10. 2003.
- [47] Spek AL. PLATON. A multipurpose crystallographic tool. Utrecht University. Utrecht. The Netherlands. 2003.
- [48] Cambridge Crystallographic Data Centre. MERCURY 3.9. Cambridge. England.2001-2016.
- [49] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R.

Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven,
K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd,
E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K.
Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam,
M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O.
Farkas, J. B. Foresman, D. J. Fox, Gaussian. Inc. Wallingford CT, 2009.

- [50] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [51] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 2003, 24, 669-681.
- [52] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 2005, 105, 2999–3094.
- [53] R. Cammi, S. Corni, B. Mennucci, J. Tomasi, J. Chem. Phys. 2005, 122, 104513.
- [54] R. Improta, J. Chem. Phys. 2006, 125, 054103.
- [55] G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, V. Barone. J. Chem. Phys. 2006, 124, 094107.
- [56] J. R. Reimers, J. Chem. Phys. 2001, 115, 9103-9109.
- [57] B. Baumeier, J. Kirkpatrick, D. Andrienko, Phys. Chem. Chem. Phys. 2010, 12, 11103–11113.
- [58] J. Kirkpatrick, Int. J. Quantum Chem. 2008, 108, 51-56.





Scheme 1. Chemical structures of synthesized compounds (1–3) along with some related compounds (4–7). As an example, the styrylarene core of compound 1 is shown in blue while a triphenylethylene subunit is highlighted in red.



Figure 1. Distribution in the crystal structure of compound 2 and geometrical structures (view through the central ring) of the two conformers found (2a and 2b).

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Figure 2. Intramolecular interactions in molecule 2b.



Figure 3. Detail views of the C-H··N (A), π - π stacking (B) and C-H··· π (C) intermolecular interactions in compound **3**.



Figure 4. Absorption spectra and fluorescence emission spectra of compounds 1, 2, and 3 in THF (sample concentrations were 1 μ M).



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Figure 5. Energy levels and shapes of frontier molecular orbitals calculated for **1**, **2a**, **2b** and **3** (isocontour plots (0.02 au)).

Figure 6. Left: Selected dihedral angles calculated for the ground (grey) and excited state (black) in THF solution for compounds **2a** (a) and **3** (b). The number of the dihedral angle (τ) is represented in the ordinate axis while its value is shown in the abscissa axis. The dihedral angle numbering is shown in **Tables S2-S4**. The vertical discontinuous lines are used to delimit the dihedral angles of each α -phenylstyryl branch in the molecule. The arrows represent the largest changes upon excitation. **Right:** Relative energy barrier as a function of the rotational angle of phenyl rotors calculated for compounds **2a** (a) and **3** (b).





Figure 7. (a) Reorganization energy and (b) Huang-Rhys factors *versus* normal mode wavenumbers calculated for **2b**. (c) Atomic displacements of the two vibrational modes for which the highest Huang-Rhys factors were obtained.



Figure 8. Compounds **1**, **2** and **3** in powder: Excitation (a) and fluorescence emission (b) spectra. CIE1976 chromaticity diagrams (c) and picture under ultraviolet light (d).

Table 1. Absorption maximum wavelength (λ_{abs}^{exp}) , logarithm of the molar absorption coefficient (ε), wavelengths calculated for the vertical electronic transitions (λ_{abs}^{calc}), oscillator strengths (f) and main components of the transitions (% contribution). Experiments and calculations were carried out in THF solution.

Compd	λ ^{exp} [nm(eV)]	log(ε) [mM ⁻¹ cm ⁻¹]	λ ^{calc} [nm(eV)]	f	Transition	Contribution (>20%)
4	313(3.96)	4.76	292(4.25)	0.844	$S_0 \rightarrow S_1$	H-1→L(28); H→L+1(24)
1			291(4.26)	0.822	$S_0 \rightarrow S_2$	H→L(34)
	331(3.75)	4.71	347(3.58)	1.316	$S_0 \rightarrow S_1$	H→L(84)
2a			332(3.73)	0.805	$S_0 \rightarrow S_2$	H-1→L(88)
			321(3.87)	0.643	$S_0 \rightarrow S_3$	H→L+1(83)
	331(3.75)	4.71	335(3.70)	0.957	$S_0 \rightarrow S_1$	H→L(84)
2b			304(4.08)	0.174	$S_0 \rightarrow S_2$	H→L+1(77)
			297(4.18)	0.836	$S_0 \rightarrow S_3$	H-1→L(74)
2	337(3.68)	4.37	320(3.88)	0.633	$S_0 \rightarrow S_1$	H→L(89)
3	~300(4.13)	4.37	282(4.40)	0.405	$S_0 \rightarrow S_2$	H-1→L(68); H→L+1(29)
4 ^{a)}	329 (3.77)	4.99	_	_	_	_
5 ^{b)}	356 (3.48)	4.77	_	_	_	_
6 ^{b)}	350 (3.54)	4.99	_	_	_	_

^{a)} From reference [20]. ^{a)} From reference [11]

Table 2. Fluorescence excitation and emission wavelength maxima $(\lambda_{ex}^{exp} \text{ and } \lambda_{em}^{exp})$ along with the wavelength calculated for the S₁ \rightarrow S₀ transition (λ_{em}^{calc}) . Experiments and calculations were carried out in THF solution.

Compound	λ_{ex}^{exp} [nm(eV)]	$\lambda_{em}^{exp}[nm(eV)]$	Φ _F [%]	λ_{em}^{calc} [nm(eV)]	
1	318(3.89)	424(2.92)	< 1	516(2.40)	
2a	340(3.65)	467(2.65)	< 1	502(2.47)	
		488(2.54)			
2b	340(3.65)	467(2.65)	< 1	477(2.60)	
		488(2.54)			
3	329(3.77)	400(3.10)	< 1	510(2.43)	
		421(2.94)			
4 ^{a)}	_	399 (3.11)	60	_	
		420 (2.95)			
5 ^{b)}	_	439 (2.82)	< 1	_	
6 ^{b)}	_	461 (2.69)	57	_	

^{a)} From reference [20]. ^{a)} From reference [11]

Table 3. Fluorescence excitation and emission wavelength maxima (λ_{ex}^{exp} and λ_{em}^{exp}), quantum yield (Φ_F) and CIE1976 chromaticity coordinates determined for compounds **1–3** in the solid state.

Compound [sample state]	λ ^{exp} [nm (eV)]	λ ^{exp} [nm (eV)]	Φ _F [%]	CIE1976	
1 [crystal]	-	-			
1 [powder]	407 (3.04)	421 (2.94)	< 1	(0.15, 0.35)	
1 [drop cast] ^{a)}	348 (3.56)	434 (2.86)	< 1		
2 [crystal]	441 (2.81)	509 (2.44)	31		
2 [powder]	435 (2.85)	503 (2.46)	29	(0.11, 0.49)	
2 [drop cast] ^{a)}	398 (3.12)	488 (2.54)	68		
3 [crystal]	383 (3.24)	443 (2.79)	< 1		
3 [powder]	381 (3.25)	439 (2.82)	< 1	(0.16, 0.35)	
3 [drop cast] ^{a)}	330 (3.76)	438 (2.83)	< 1		
4 ^{b)} [powder]	419 (2.96)	448 (2.77)	50	(0.15, 0.10)	
4 ^{b)} [drop cast] ^{c)}	365 (3.40)	439 (2.82)	51	-	
5 ^{d)} [powder]	_	529 (2.34)	5.5	_	
6 ^{d)} [powder]	_	547 (2.27)	1.7	_	

^{a)} Sample obtained by drop casting from a 5 mM solution of compound in a 1:1 acetonitrile:THF solvent mixture. ^{b)} From reference [20]. ^{c)} Sample obtained by drop casting from a concentrated THF solution. ^{d)} From reference [11]

Table 4. Electron and hole transfer integrals (t_e and t_h , respectively) along with the product $t_h t_e$ and sign estimated for the charge transfer intermolecular coupling, J_{CT}

	Compound	Dimer	<i>t_h</i> [meV]	<i>t</i> e [meV]	t _h t _e [meV²]	Sign of J _{CT}
	•	ab	-2.68	-0.50	1.3	$J_{CT} < 0$
	2	bb	-59.07	10.52	-621.3	$J_{CT}>0$
		А	-4.56	-4.06	18.5	$J_{CT} < 0$
	2	В	-0.68	-4.25	2.9	$J_{CT} < 0$
	3	С	-48.63	98.96	-4812.5	$J_{CT} > 0$



A new set of butterfly-shaped α -phenylstyrylarene derivatives has been synthesised with the aim of improving the solid-state fluorescence emission of their parent styrylarene compounds. X-ray diffraction, fluorescence spectroscopy and Density Functional Theory calculations were carried out to unravel the origin of the different photophysical behaviour of these compounds in the solid state.

Keyword phenylstyrylarene derivatives, π - π stacking, solid-state luminescence enhancement,

short-range exciton coupling, fluorescence.

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Shedding light on the origin of the-solid state luminescence enhancement in butterfly molecules

