

# Supramolecular Interactions Induced Fluorescence in Crystal: Anomalous Emission of 2,5-Diphenyl-1,4-distyrylbenzene with All *cis* Double Bonds

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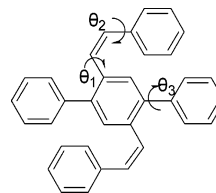
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The optical and electronic properties of poly(*p*-phenylene vinylene)s (PPVs) have been widely investigated due to their applications in light-emitting diodes (LEDs)<sup>1</sup> and lasers.<sup>2</sup> The presence of *cis*/*trans*-vinylene units in PPVs and their photochemical isomerization attract special attention because a *cis*-isomer generally shows weak luminescence and is regarded as *cis*-defect.<sup>3</sup> Although great efforts have been made on the investigation of relationships that exist between the *cis*-/*trans*-conformation in a polymer chain and the resulting luminescent properties,<sup>4</sup> the understanding of these dependencies is still incomplete, which is partially due to a lack of more definite structural information for polymer systems. In this context, oligomers as model compounds for corresponding polymers and active materials have been paid special attention.<sup>5</sup> A large number of oligo-PPVs (OPVs) are synthesized and investigated, and some of their single-crystal structures are reported.<sup>6</sup> Up to now, the reported single-crystal structures of OPVs are all *trans*-isomers, and no single crystal of the *cis*-isomer is obtained and determined

Chart 1. Molecular Structure of *cis*-DPDSB



probably due to their lower thermal stability. In recent synthesis of a model compound of poly[(2,5-diphenyl-*p*-phenylene)vinylene] (DP-PPV),<sup>7</sup> 2,5-diphenyl-1,4-distyrylbenzene (DPDSB) utilizing a 2-fold Wittig reaction, we find accidentally that the obtained DPDSB has two *cis* double bonds (*cis*-DPDSB) in its molecule. The single crystal of *cis*-DPDSB is easily obtained by recrystallization, and surprisingly, *cis*-DPDSB shows strong fluorescence in crystal.

*cis*-DPDSB is an OPV trimer with two *cis* double bonds (Chart 1). The FT-IR spectrum of this material shows no absorption band at about 960 cm<sup>-1</sup> (out-of-plane bending mode of C–H in *trans*-vinylene<sup>8</sup>), and the <sup>1</sup>H NMR spectrum shows the chemical shift of vinyne protons appearing in about 6.5 ppm with a large coupling constant of 12 Hz (characteristic chemical shift and coupling constant of vinyne protons in the *cis*-configuration<sup>9</sup>), which indicates that the double bonds in this material are *cis*-conformation. It is further unequivocally confirmed by a single-crystal X-ray diffraction study.

The structure of *cis*-DPDSB and its packing arrangement in single crystal is shown in Figure 1. A noteworthy feature of this molecule in crystal is its torsion conformation, which is similar to what is obtained from geometry optimization for the *cis*-DPDSB molecule in the gas phase. The torsion angles between the double bond and two adjacent phenyl rings are 43.1° ( $\theta_1$ ) and 38.3° ( $\theta_2$ ), respectively. The torsion angle between the central phenyl ring and the adjacent phenyl ring (along the *p*-terphenyl direction) is 52.4° ( $\theta_3$ ), which is larger than that in *p*-terphenyl (38.4°<sup>10</sup>). And it must be noticed that all end phenyl rings that connect to the double bond (for example, ring A shown in Figure 1b) is inserted

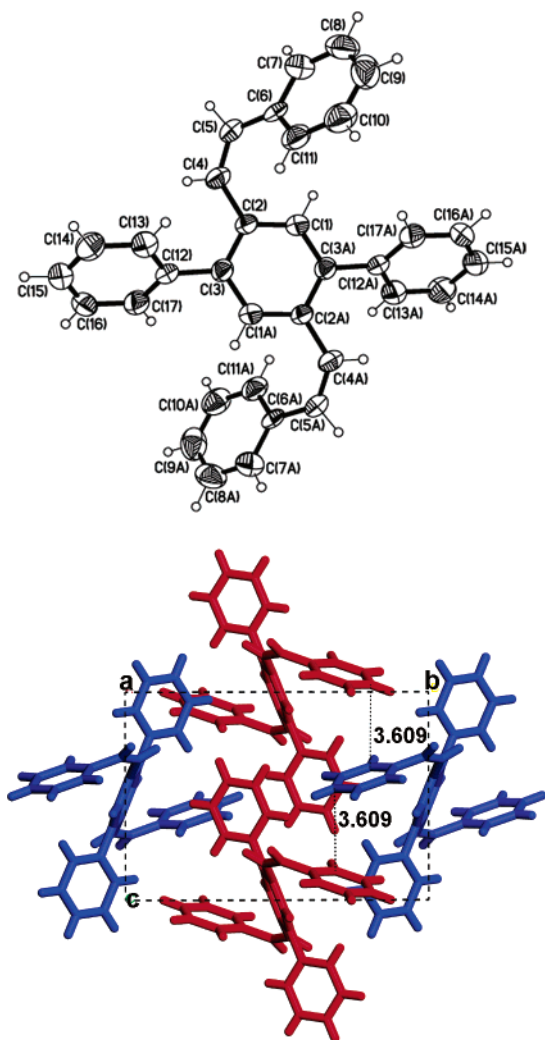
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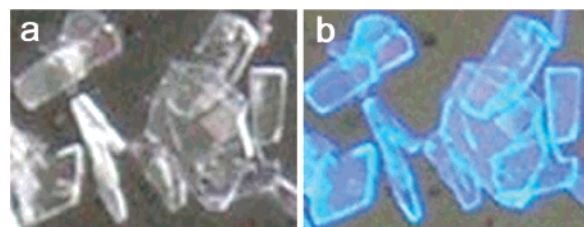
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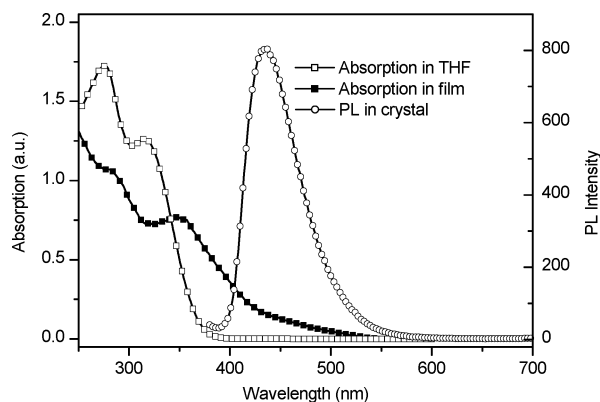
**Figure 1.** Left: ORTEP drawing of *cis*-DPDSB. The ellipsoid probability is 25%. Right: Packing arrangement of *cis*-DPDSB, viewed down the **a** axis. The phenyl ring A that connects to the double bond is inserted between ring B and ring C of the two adjacent molecules.

between the two adjacent rings (shown as ring B and C) of other molecules and the distance between phenyl ring A and ring B (or ring C) is 3.609 Å, which means some intramolecular motions, *c.a.* twisting of double bond and twisting of the end phenyl ring that connect to double bonds, are not free.

The absorption spectrum of *cis*-DPDSB in dilute tetrahydrofuran (THF) solution with an absorption band at 315.5 nm is shown in Figure 3. The molar absorption coefficient of this material is  $21900 \text{ M}^{-1} \text{ cm}^{-1}$  ( $\lambda = 315.5 \text{ nm}$ ), which is smaller than the trans-isomer we have prepared ( $48500 \text{ M}^{-1} \text{ cm}^{-1}$  at 354 nm, see Supporting Information). It is the torsion conformation of *cis*-DPDSB that induces a large blue shift in the absorption spectrum and the small molar absorption coefficient. Uncommonly, there is almost no fluorescence in THF solution, while strong fluorescence of *cis*-DPDSB in crystal with the emission band at about 436 nm is observed (Figure 2 and Figure 3). In solution the intramolecular motions around the double bonds in the excited state are free due to the low viscosity, which cause the complicated photochemical processes, *c.a.* *cis*–*trans* isomerization and photocyclization to 7,14-diphenyl-dibenzo-



**Figure 2.** The pictures of *cis*-DPDSB crystals under natural light (a) and an ultraviolet lamp (360 nm) (b). The white edge is due to light diffraction.

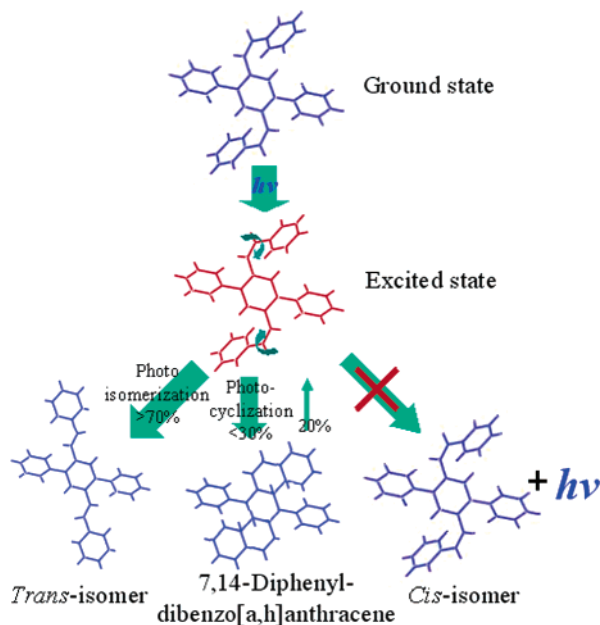


**Figure 3.** The absorption spectra in THF solution and in film, and PL spectrum in crystal of *cis*-DPDSB.

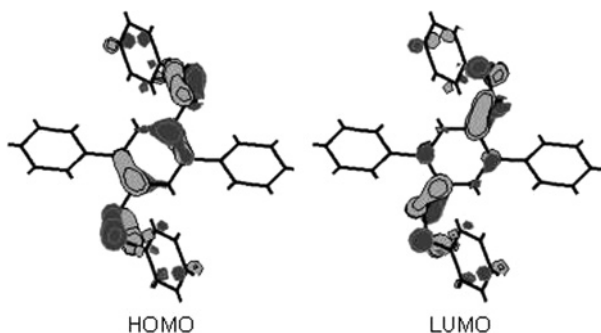
[a,h]anthracene, to occur easily.<sup>11</sup> In our experiment, *cis*-DPDSB/THF solution shows almost no fluorescence initially, but after it is exposed under ultraviolet lamp (315 nm) for several seconds the fluorescence increases dramatically. Evidently the photochemical processes occur and the trans-isomer plays the role of the following emission. Thus, the reason for *cis*-DPDSB showing no fluorescence in solution is that such complicated photochemical processes compete with the luminescence process (as shown in Figure 4).<sup>11</sup> While in crystal intramolecular motions, especially the twisting of double bond and twisting of the end ring of the distyrylbenzene segment, are limited due to the interaction between phenyl ring A and ring B (or ring C) for the relatively short distance (3.609 Å). And that is to say the energy barrier from the *cis*-isomer to *trans*-isomer/7,14-diphenyl-dibenzo[a,h]anthracene is increased dramatically so that such photochemical processes become impossible. Thus, the excited state cannot be decayed by isomerization or photocyclization and then the emission process occurs. Generally, *trans*-OPVs have several photoluminescence (PL) bands, while *cis*-DPDSB has only one PL band with relatively narrow bandwidth and relatively large Stokes shift in crystal (as shown in Figure 3, there is an absorption band at 350 nm in the solid state). So this material may be a promising candidate for further optimization as good laser material in pure blue emission band.

To determine which chromophores, distyrylbenzene or terphenyl, actually emits here, the frontier orbital of *cis*-DPDSB is inspected (B3LYP/6-31G). As shown in Figure 5, the HOMO and LUMO are completely localized on the distyrylbenzene segment, which indicates that the main

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**Figure 4.** Schematic of photochemical and emission processes of *cis*-DPDSB in solution. *cis*-DPDSB shows no emission in solution because the photo isomerization and photocyclization processes compete with the luminescence process due to the molecule being free. The solution of the resulting compounds might be more complex for the photochemical processes can occur only at one C–C double bond or both C–C double bonds. The percentages of photochemical processes are based on the results of stilbene (see ref 11).



**Figure 5.** Frontier molecular orbital of *cis*-DPDSB.

contribution in fluorescence is distyrylbenzene, not terphenyl. The same result can be concluded from the molecular structure: the terphenyl has too large torsion angle ( $52.4^\circ$ ) between the rings to form a conjugated system, while the conjugated degree of the central ring and the double bonds is influenced slightly. It has been reported that the emission of the *p*-terphenyl film is at 370 nm,<sup>12</sup> which is largely different compared to the observed emission at 436 nm. In addition, since the effective conjugation of *cis*-DPDSB must be shorter than distyrylbenzene (trans-isomer) for its torsion conformation, it is reasonable that the emission band of *cis*-

DPDSB crystal at 436 nm blue-shifted to distyrylbenzene crystal (trans-isomer) at 468 nm.<sup>6d</sup> All of the above suggest that the distyrylbenzene segment is the main chromophore in this molecule.

The melting point of *cis*-DPDSB determined by DSC experiment is 192.5 °C. And the up and down scans in DSC experiments are repeated accurately for the first three times. In fact, several milligrams of *cis*-DPDSB powder is heated at 180 °C under ambient pressure (in argon) for 36 h, and no difference is observed by FT-IR before and after the heat treatment, which confirms the excellent thermal stability of *cis*-DPDSB.

The multilayer OLEDs with the structure of ITO/NPB (50 nm)/*cis*-DPDSB (5 nm)/BCP (10 nm)/Alq<sub>3</sub> (35 nm)/LiF (0.5 nm)/Al are fabricated by thermal deposition in a vacuum chamber, where NPB (*N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine) acts as a hole-transporting layer, BCP (bathocuprine) as the exciton-blocking layer, and Alq<sub>3</sub> (tris(8-hydroxyquinolino) aluminum) as the electron-transporting layer. *cis*-DPDSB exhibits blue emission at a peak of 440 nm with CIE coordinates of  $x = 0.18$  and  $y = 0.18$  in the pure blue spectral region. The devices exhibit a turn-on voltage of 6 V with maximum luminance efficiency of 0.75 cd/A (0.34 lm/W) and luminance of 800 cd/m<sup>2</sup>, respectively.

To summarize, we have synthesized *cis*-DPDSB and determined its structure in crystal by X-ray diffraction. Anomalous, *cis*-DPDSB has strong fluorescence in the solid state, which is probably attributed to the lattice effect that limits the twisting vibration of the double bonds and the twisting of the end phenyl ring that connect to the double bond to lessen the possibility of *cis*–*trans* isomerization and photocyclization to 7,14-diphenyl-dibenzo[a,h]anthracene. In this way, the supramolecular interaction-induced emission of *cis*-DPDSB makes it maybe useful as LED and laser material because the organics are normally used as solid state in devices. And the high melting point and excellent thermal stability of this material make it possible to obtain a stable device.

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**Supporting Information Available:** General experimental procedure, synthesis and characterization, crystal structure determination, calculation of molecular simulation of *cis*-DPDSB, and OLEDs fabrications. Photochemical processes and X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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