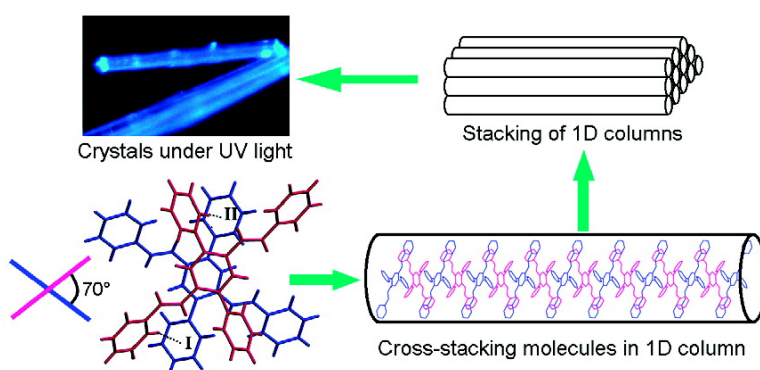


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Cross Dipole Stacking in the Crystal of Distyrylbenzene Derivative: The Approach toward High Solid-State Luminescence Efficiency

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Poly(*p*-phenylene vinylene) (PPV)-type polymers and oligomers have attracted more attention as luminescent materials due to their applications in organic light-emitting diodes (OLEDs)^{1–4} and lasers.^{5–7} However, H-aggregation that exists widely in such π -conjugated compounds dramatically decreases the luminescence quantum yield upon going from dilute blends or solutions to films.^{8–11} The most efficient configuration to prevent any decrease in luminescence efficiency, prefigured by theoretical investigations in the clusters of conjugated molecules, is to adjust the long axes of adjacent chains to be perpendicular in condensed media.^{12–14} In such a cross stacking, the luminescence emission will be close to the single molecular emission for the strong oscillator strength in the transition between the ground state and the lowest excited state. This type of cross-packing mode has been expected in some liquid crystal molecules, but the accurate crystal structure has not been determined.^{15,16} In our continued effort to inspect the packing mode of distyrylbenzene (DSB) derivatives,^{17,18} we were surprised to find that 2,5-diphenyl-1,4-distyrylbenzene with two *trans* double bonds (*trans*-DPDSB) tends to adopt a stable cross-stacking mode in crystalline state. The following experiments demonstrate that this material exhibits excellent thermal stability, charge-transfer ability, attractive OLEDs performance, and the amplified spontaneous emission (ASE) in the needlelike crystalline state. Herein we report the cross-stacking structure and the attractive luminescence properties of *trans*-DPDSB.

trans-DPDSB was synthesized by Wittig reaction and was fully characterized by NMR, FT-IR, elemental analysis, and differential scanning calorimeter (DSC) methods. Single crystals of *trans*-DPDSB were prepared by vaporizing a mixture of chloroform and methanol (1:2) slowly. The crystal data reveal that there are two crystallographically independent conformations of *trans*-DPDSB (Figure 1).

As shown in Figure 2, the most attractive structural feature of the crystal packing is that the molecules are packed into one-dimensional molecular columns along the *b* axis. They overlap upon the central phenyl rings, and one molecule is rotated relative to the other by an angle of 70° about an axis that passes through the centers of both molecules. For the excited transition dipoles of PPV-type conjugated molecules along their long axis, the observed molecular packing in *trans*-DPDSB single crystal is the first example of the cross dipole stacking of conjugated molecules in solid states, which may enhance the solid-state fluorescence prefigured by theoretical analysis.^{12,13} As shown in Figure 3, in

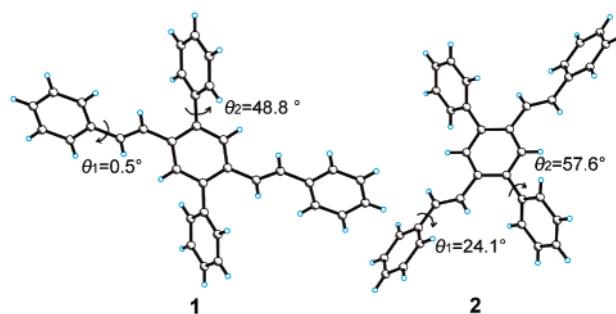


Figure 1. Different conformational structures of *trans*-DPDSB in crystal.

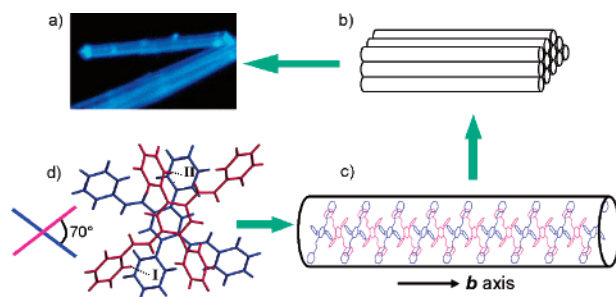


Figure 2. (a) Crystals of *trans*-DPDSB under UV light (365 nm). (b) Stacking of 1D molecular columns. (c) Cross-stacking molecules in 1D molecular column. (d) Schematic of the aromatic CH/ π hydrogen bonds between two adjacent molecules. Interaction distances for I and II are 3.08 and 2.67 Å respectively. Conformation 1 is drawn in blue and 2 in red.

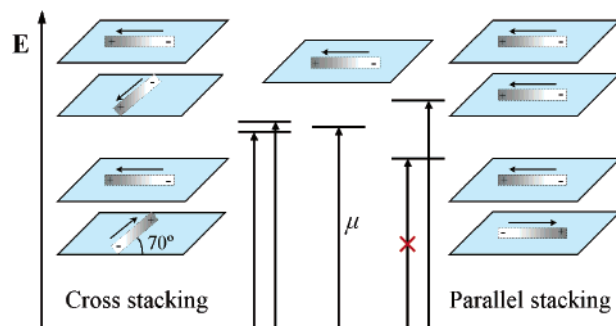


Figure 3. Splitting of the optically allowed transitions of a single chain (sketched in the middle) in a cross-stacking configuration (*trans*-DPDSB) and a parallel-stacking configuration (H-aggregate).

the parallel-stacking dimer, the lowest excited state corresponds to the destructive combination of the transition dipole moment of the individual chains, and it is optically forbidden. However, in the cross-stacking dimer, the energy splitting between the lowest two excited states of the dimer is reduced, and a progressive transfer

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of intensity from the second excited state to the lowest excited state occurs. This promotes a finite transition dipole moment between the ground state and the lowest excited state of the clusters, which is highly beneficial for the light-emission properties. Additionally, the overlapped central phenyl rings along one-dimensional molecular columns (*b* axis) can act as a channel for electron transport, producing high carrier mobility. Actually, the single crystal of *trans*-DPDSB exhibits very strong pure blue emission, when excited under an ultraviolet lamp (365 nm) (shown in Figure 2a). OLED studies have demonstrated good electron-transporting property of *trans*-DPDSB films (see Supporting Information).

The distance between the central rings of adjacent molecules is 4.1 Å (*b*/2), which means there is no face-to-face π - π interaction. As shown in Figure 2d, there are two different types of aromatic CH/ π hydrogen bonds between the adjacent two molecules in each column, where two carbon atoms of conformation **2** act as proton donors and the two phenyl substituents of conformation **1** act as acceptors. The interaction distance and the angle of C-H- π center for interaction **I** are 3.08 Å and 154°, and for interaction **II** are 2.67 Å and 157°, respectively. Considering that the enthalpy of aromatic CH/ π hydrogen bonds 6.5–10.3 kJ/mol for one unit^{19–22} but 10.3 kJ/mol seems to be the best value,²² we believe that such CH/ π interactions are the key driving force for the cross-stacking mode. At the same time the attractive force of such CH/ π intermolecular interactions induces the different molecular conformations in the crystal. The distyrylbenzene segment of conformation **1** is planar, and that of conformation **2** is torsional (Figure 1). In detail, the torsional angle θ_1 in conformation **1** is 0.5°, while in conformation **2** the aromatic CH/ π hydrogen bond **I** raises the torsional angle to 24.1°. A similar influence by the aromatic CH/ π hydrogen bond **II** on the torsional angle of *p*-terphenyl segment can be observed.

trans-DPDSB shows excellent thermal stability (melting point of 251–254 °C determined by DSC), good electron-transporting property, and strong pure blue emission in solids, rendering it as good OLED material. The achieved maximum luminescence and luminous efficiency of *trans*-DPDSB-based OLEDs with a simple device structure are 2100 cd m⁻² and 1.53 cd A⁻¹, respectively, which are much higher than that of the device using *p*-bis(*p*-styrylstyryl)benzene as the emitting layer.²³ The big difference in performance can be attributed to the different stacking modes between *trans*-DPDSB (cross stacking) and *p*-bis(*p*-styrylstyryl)benzene (H-aggregate). Interestingly, *trans*-DPDSB tends to form transparent and needlelike crystals, and from Figure 2a, the tip of needlelike single crystal shows stronger fluorescence than the body surface of the crystal, indicating a natural self-wave-guided structure of this crystal.^{24,25} Therefore, obtained needlelike *trans*-DPDSB crystals with strong fluorescence emission and self-wave-guided structure are expected as ideal gain media for optically pumped solid-state lasers.^{26,27} The ASE with threshold power of about 0.68 mJ/pulse and the initial broad blue emission collapsing into the intense and narrow blue band from needlelike *trans*-DPDSB single crystals with the increase of pumping intensity have been observed in primary experiments for optically pumped lasers.

To summarize, we are the first to obtain the cross stacking of *trans*-DPDSB, where the aromatic CH/ π hydrogen bonds act as the driving force. The crystal of *trans*-DPDSB has excellent thermal stability, good electron-transporting property, and strong pure blue emission, which make this material, a promising candidate for OLED and laser. The primary experiments on OLED and laser imply the potential applications of this material, and further investigation is presently underway.

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Supporting Information Available: Complete ref 27; synthesis and characterization, crystal structure determination, photoluminescence properties, OLED fabrication, ASE experiment of *trans*-DPDSB; 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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