Tight intermolecular packing through supramolecular interactions in crystals of cyano substituted oligo(*para*-phenylene vinylene): a key factor for aggregation-induced emission†

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Strong supramolecular interactions, which induced tight packing and rigid molecules in crystals of cyano substituent oligo(*para*-phenylene vinylene) (CN-DPDSB), are the key factor for the high luminescence efficiency of its crystals; opposite to its isolated molecules in solution which have very low luminescence efficiency.

Most conjugated molecules with a planar and rigid structure show high fluorescence in their dilute solutions but become weakly luminescent in the solid state due to the formation of less emissive species such as excimers.[1] However, the ideal luminescent material must possess high solid-state luminescence efficiency, because organic devices such as organic light-emitting diodes (OLEDs) and lasers are only able to function in a film or crystalline state. Consequently increasing attention has been paid to enhancing the solid-state efficiency of luminescent materials. Tang and co-workers[2–4] and Park and co-workers[5] in the past few years have reported several material systems that have aggregation-induced emission (AIE) properties. The common structural characteristics of these AIE active isolated molecules are twisted in conformation, *e.g.* silacyclopentadienes (siloles), and 1-cyano-*trans*-1,2-bis-(4′-methylbiphenyl)-ethylene (CN-MBE). The origin of the AIE phenomenon is assumed to be related to the effects of intramolecular planarization or specific aggregation (H- or J-aggregation) in the solid state.[5,6] However, recent studies on the crystals of silole derivatives and another AIE active molecule, *cis*-2,5-diphenyl-1,4-distyrylbenzene (*cis*-DPDSB), reveal that their twisted configurations are maintained in the solid state, and suggest that the AIE phenomenon is caused by restricted intramolecular vibrational and rotational motions in the aggregated solid.[2–4,7,8] These intramolecular vibrational and rotational motions, which behave strongly in these twisted conjugated molecules, lead to the fast nonradiative relaxation and reduced fluorescence quantum yield in solutions. Therefore the rigorous restriction of these free motions in the solid state is an approach to increase the fluorescence emission of AIE active materials. If molecular rigidity is beneficial to the high fluorescence efficiency of a single molecule, then tight intermolecular packing through intermolecular interaction to enhance the molecular rigidity is an important factor in highly luminescent solids of these twisted AIE molecules. Herein, we report the crystal structure of an AIE active molecule, cyano substituted oligo(*para*-phenylene vinylene) (CN-DPDSB) (Fig. 1), its supramolecular interaction-induced close stacking, and extremely strong fluorescence emission in the solid state.

CN-DPDSB was synthesized by a typical Knoevenagel condensation.[9] A single crystal of CN-DPDSB was prepared by vaporizing a mixture of dichloromethane and methanol slowly at room temperature under rigorous exclusion of light. The crystal data reveal that CN-DPDSB has a *trans*-conformation in the molecule with relatively large torsional angles of the double bond and its adjacent phenyl rings (Fig. 1(b) and ESI†). CN-DPDSB shows almost no fluorescence ($\Phi_{\mathrm{fl}} \sim 1\%$) in THF solution,[10] but its crystal shows very strong fluorescence in the blue spectral region ($\lambda_{\mathrm{max}} = 469$ nm) with an efficiency Φ_{fl} up to 80% (Φ_{fl} in the solid state is obtained in a calibrated integrating sphere),[11] which exhibits a typical AIE behavior.

The structure of CN-DPDSB and the optimized geometry of isolated CN-DPDSB are shown in Fig. 1(a), which demonstrates a twisted configuration of CN-DPDSB in the gas phase or dilute solution due to the bulky cyano group substituents on the vinyl bond and phenyl groups on the central phenyl ring.[12] The origin of nonfluorescence of CN-DPDSB in solution is related to such a twisted configuration and the corresponding intramolecular

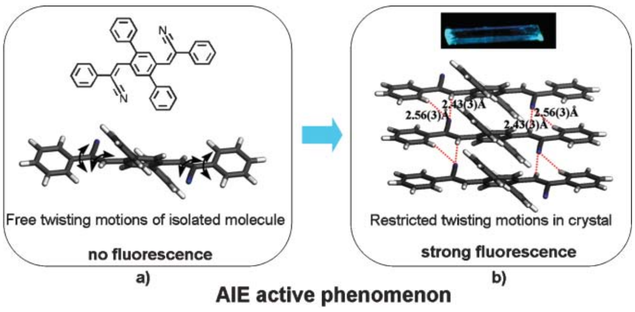

Fig. 1 (a) Molecular structure of CN-DPDSB (top) and the geometry of isolated CN-DPDSB (bottom). (b) Crystal of CN-DPDSB under UV light (top) and CN-DPDSB structure fixed under C–H···N hydrogen-bonding interactions in a crystal (bottom).

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† Electronic supplementary information (ESI) available: Synthesis, ^{1}H-NMR spectrum, the optimized geometry in the gas phase, crystal structure determination, photoluminescence properties, ASE experiment of CN-DPDSB. See DOI: 10.1039/b612732k

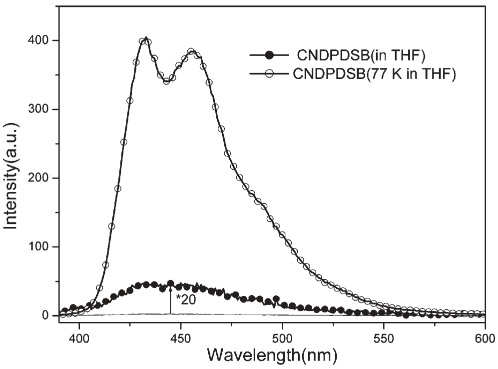

Fig. 2 The PL spectra of CN-DPDSB at room temperature and 77 K in dilute THF solution (5×10^{-6} mol L^{-1}).

motions around the double bonds, such as the twisting and probably the out-of-plane bending modes.[13] These intramolecular motions cause the complicated photochemical processes *e.g. cis–trans* isomerization to occur easily and thus lead to low fluorescence efficiency.[14–18] The easy photoisomerization can be clearly validated using the ^{1}H-NMR spectrum‡ by monitoring the CN-DPDSB solution after exposure to daylight for several hours (see ESI†). In a frozen glass state, such as dilute THF solution (5×10^{-6} mol L^{-1}) at 77 K, the non-fluorescent CN-DPDSB becomes strongly fluorescent and the intensity of the PL (photoluminescence) is ~100-fold higher than that at room temperature (Fig. 2). This is due to the enhanced potential barrier for the intramolecular motions around the double bonds in such a very rigid media at low temperature,[13] which prevents the occurrence of the photoisomerization. The observed strong emission in crystals of CN-DPDSB may have the same origin as its strong emission at low temperature due to suppressed intramolecular motions through strong supramolecular interactions in crystal packing.§

The CN-DPDSB molecule lies about an inversion centre in a single crystal. Its packing arrangement is shown in Fig. 3. We found the most important feature in the crystal is that a cyano group interacts with two hydrogen atoms of the neighboring molecule to form two C–H···N hydrogen bonds, and then a network is formed in the crystal as shown in Fig. 3(a). The interaction distances of the two hydrogen bonds (H···N) are 2.43(3) and 2.56(3) Å, and the angles of C–H···N are 155(2) and 158(2)°, respectively, which means that these supramolecular interactions are relatively strong.[19,20] It is the C–H···N hydrogen bonds that fix the double bond and the peripheral phenyl ring, and prevent the free twisting motions around the double bonds. Assisted by the strong supramolecular interactions, the molecule becomes more rigid, although with a non-planar configuration. In other words, the photoisomerization process around the double bonds becomes impossible, which ensures light radiation from the torsional molecules. Different from general fluorescence quenching of many planar molecules due to parallel molecular stacking with strong π–π interactions,[1,18,21,22] the twisted structure of CN-DPDSB prevents face-to-face π–π stacking interactions along the long molecular axis by the bulky cyano and phenyl substituents (Fig. 3(c)). Thus the strong supramolecular interactions induce tight packing and rigid molecules, without parallel stacking, making the crystal show very strong fluorescence.

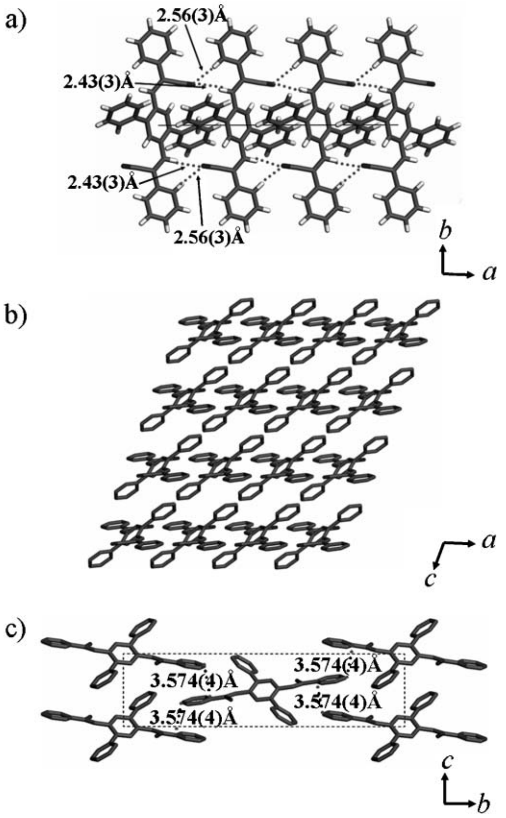

Fig. 3 Molecular packing diagram of CN-DPDSB under hydrogen–nitrogen interactions viewed along (a) the *ab* plane, (b) the *ac* plane, (c) the *bc* plane. The shortest distance between neighboring molecules in (c) is 3.574(4) Å between atom C6 and C9 in glide related molecules.

Under the key driving force of C–H···N hydrogen-bonding interactions, CN-DPDSB tends to form transparent and platelet crystals (Fig. 1(b)). The picture of a CN-DPDSB single crystal under a UV lamp shows stronger emission in the tip than that of the body surface, which indicates there should be self-waveguided emission.[23,24] Thus an optically pumped solid-state laser is expected for this crystal.[25–28] The full widths at half maximum (FWHMs) of the spectrum produced by the UV laser with an energy of 0.6 mJ pulse^{-1} is only 6 nm, which is much less than that

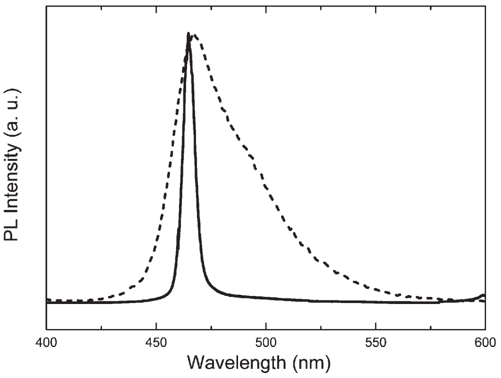

Fig. 4 The PL spectrum of a CN-DPDSB single crystal exposed under the pulsed UV laser (solid curve). The conventional PL spectrum exposed under a Xe lamp light through the monochromator is shown for comparison (dashed curve).

of the normal PL (exposed under the Xe lamp light through the monochromator) spectrum of 40 nm (Fig. 4). The narrowed spectrum is thought to be amplified spontaneous emission (ASE).¶ The preliminary results of ASE indicate the potential application of the CN-DPDSB single crystal in organic lasers.[29–31]

To summarize, we have demonstrated the supramolecular interaction-induced strong emission of AIE active molecule CN-DPDSB in the solid state, which makes this material a promising candidate for OLEDs and lasers. The primary laser experiments have been done, and further investigation is presently underway.

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Notes and references

‡ *Characterization data for CN-DPDSB*: mp 307 °C (DSC); ^{1}H-NMR (500 MHz, 25 °C, CDCl$_3$, TMS, ppm): δ = 8.27 (s, 2H), 7.59 (d, J(HH) = 6.714 Hz, 4H), 7.57 (s, 2H), 7.53 (d, J(HH) = 6.714 Hz, 4H), 7.50 (t, J(HH) = 7.019 Hz, 4H), 7.38–7.46 (m, 8H); ^{13}C NMR (500 MHz, 25 °C, CDCl$_3$, TMS, ppm): δ = 141.61, 141.22, 138.86, 133.90, 133.53, 130.57, 130.13, 129.43, 129.15, 128.69, 128.28, 126.10, 117.93, 114.04; MALDI-TOF MS: m/z = 485.9 ([M + H]$^+$), Calcd. for $C_{36}H_{24}N_2$: 484.2.

§ *Crystal data*: CN-DPDSB: $C_{36}H_{24}N_2$, M_r = 484.57, Monoclinic, space group $P2(1)/n$, a = 6.6450(13), b = 27.561(6), c = 7.6528(15) Å, β = 110.83(3)°, V = 1309.9(4) Å^3, Z = 2, μ = 0.071 mm^{-1}, ρ_{calc} = 1.229 Mg m^{-3}, F(000) = 508. 3004 reflections measured, 12 667 unique (R_{int} = 0.0995). Structure diffraction intensities were collected on a Rigaku RAXIS-PRID diffractometer using the ω-scan technique with graphite-monochromated MoKα (c = 0.071073 Å) ratio. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs.[32] The space groups were determined from the systematic absences and their correctness was confined by successful solution and refinement of structures. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were added in idealized position and refined with isotropic displacement. CCDC 616163. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612732k

¶ *Amplified spontaneous emission (ASE) experiment*: The pumping condition is as the following: The excitation source is the third harmonic (355 nm) of a Nd:YAG (yttrium-aluminum-garnet) laser with a repetition rate of 10 Hz and pulse duration of about 10 ns. The intensity of the pump is 0.6 mJ/pulse. The beam is focused using a cylindrical lens into a stripe whose shape is adjusted to 6.1 mm × 0.25 mm by a slit. The pump stripe is parallel to the long axis of the crystals. The emission is detected using a charge coupled device (CCD) spectrograph. The sample is one single crystal that is glued onto a crystal substrate. The size of this crystal is about 1.5 mm long and 0.2 mm wide.

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