Supporting information:

The tight intermolecular packing through supramolecular interactions in crystal of cyano substituented oligo(p-phenylene vinylene): a key factor for aggregation-induced emission

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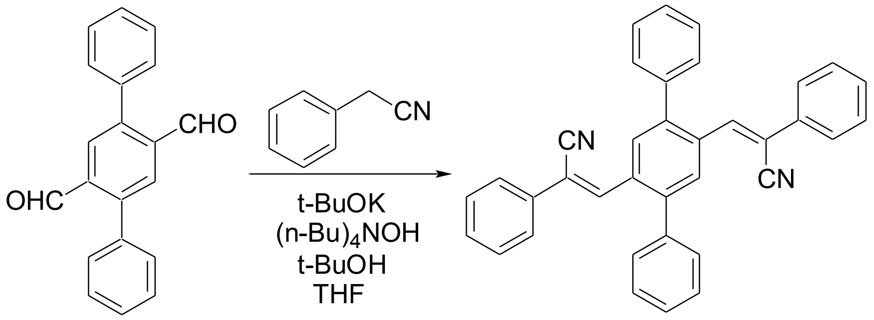
1. General experiments.

Measurement. The NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with chloroform-*d* as solvents and tetramethylsilane (TMS) as the internal standard. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The melting points were determined using a Germany NETZSCH (DSC-204) instrument differential scanning calorimeter at 10 °C/min with nitrogen flushing. The mass spectra were recorded on a Kratos MALDITOF mass system.

Materials. [1,1';4',1"] terphenyl-2',5'-dicarbaldehyde were prepared according to literature procedures[S1]. Potassium tertobutoxide 98% and tetra-butyl ammonium hydroxide (1 M solution in methanol) were purchased from Aldrich and used without further purification unless otherwise noted. THF and tert-butanol was dried and purified by fractional distillation over sodium. Column chromatography was performed using silica gel (200-300 mesh).

2. Synthesis and characterization of CN-DPDSB.

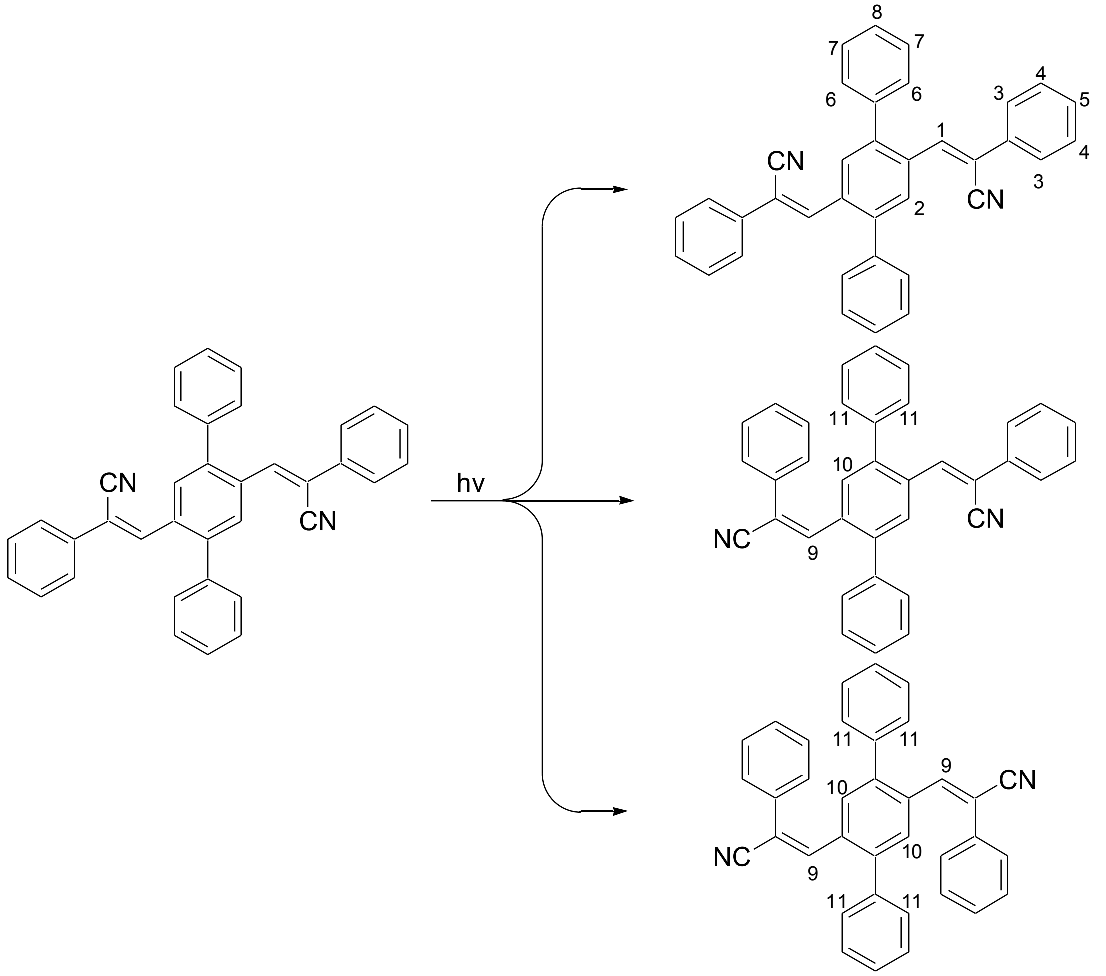


Scheme S1. Synthetic route for CN-DPDSB.

[1,1';4',1"] terphenyl-2',5'-dicarbaldehyde (0.3 mmol) and phenylacetonitrile (0.6 mmol) were dissolved in *tert*-butanol (2 mL) and THF (1 mL) at 40°C under nitrogen atmosphere. Potassium *tert*-butoxide (0.05 mmol) and tetra-n-butylammonium hydroxide (0.05mmol, 1 M solution in methanol) was added quickly, and the mixture was stirred vigorously at 50 °C. After 20 min the mixture was poured into acidified methanol. The precipitate was collected and dissolved in chloroform and then reprecipitated in methanol. The crude product was purified by column chromatography (silica gel, dichloromethane) in the darkness to give the green solid in 70% yield. m.p. 307 °C (DSC); ^{1}H-NMR(500 MHz, 25 °C, $CDCl_3$, TMS, ppm): $\delta = 8.27$ (s, 2H), 7.59 (d, J(HH)=6.714Hz, 4H), 7.57 (s, 2H), 7.53 (d, J(HH)=6.714Hz, 4H), 7.50 (t, J(HH)=7.019Hz, 4H), 7.38-7.46 (m, 8H); ^{13}C NMR (500 MHz, 25 °C, $CDCl_3$, TMS, ppm): $\delta = 141.61$, 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.

3. The ^{1}H-NMR spectra of CN-DPDSB.

The ^{1}H-NMR spectrum of CN-DPDSB is shown in Figure S1, where the position and intensity of the NMR signals provide the proof of the structure of the obtained compound with two *trans*-double bonds. For example, a single peak (1) at 8.27ppm is ascribed to the protons on vinyl bonds. Such a downfield resonance is due to the effect of the strong withdrawing cynao group on vinyl bonds. The chemical shift of the protons on central phenyl is at 7.57ppm (another single peak (2)) and a double peak (3) at 7.59 ppm is ascribed to the protons on end phenyl rings in terphenyl direction. The signal peaks of other photons of *trans*-CN-DPDSB are remarked in Figure S1. After CN-DPDSB in solution was irradiated in daylight for several hours, its ^{1}H-NMR become very complex. In the ^{1}H-NMR of mixed CN-DPDSB solution, the appearance of some new signals in high field except the signals of *trans*-CN-DPDSB show the appearance of the photoisomerization of *trans*-CN-DPDSB and the formation of different conformational isomers such as *cis*-CN-DPDSB (the possible isomers are showed in Scheme S2). For example, in high field of ^{1}H-NMR, a new single peak (10) at 7.17ppm and a new double peak (11) at 6.95 ppm are assigned to the signal of the protons on central phenyl and on end phenyl rings in terphenyl direction in *cis-i*somers of CN-DPDSB, respectively, which could be due to the shielding effect of the pheryl ring in the distyrylbenzene direction in *cis*-isomers. Another new single peak (9) at 8.20ppm is the signals of the protons on vinyl bonds. The peaks at 7.31~7.54 ppm include the signals of the photons of *trans*-CN-DPDSB and other phenyl protons in *cis-i*somers of CN-DPDSB. The higher field resonance of the protons in *cis*-isomers compared with *trans*-CN-DPDSB should be due to more twisted and lower conjugated structure of the *cis*-isomers, which is the same as other OPV[S2]. According to the intensity of the signals relative to *cis*-conformation and that to *trans*-conformation in the ^{1}H-NMR spectrum of CN-DPDSB after irradiation, the content of the *cis*-conformation can be estimated to be 60%. Thus high *cis*-conformation content indicates easy photoisomerization of twisted *trans*-CN-DPDSB in solution.



Scheme S2. Photoisomerization process for *trans*-CN-DPDSB in solution during irradiation in daylight.

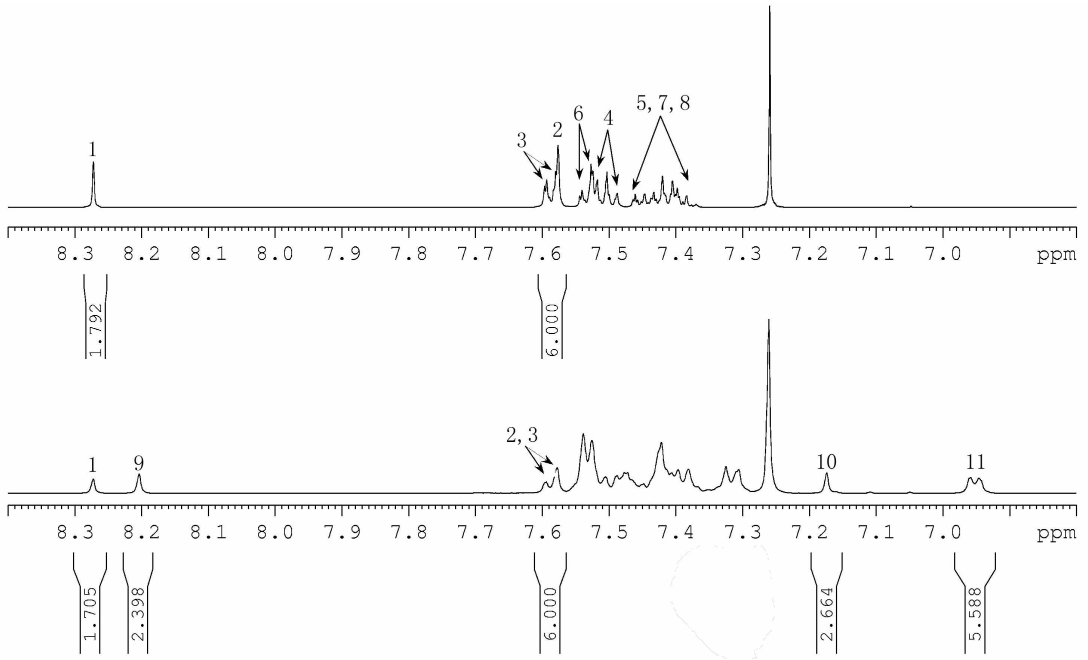


Figure S1. ^{1}H-NMR spectra of *trans*-CN-DPDSB in $CDCl_3$ (up). The spectrum of the irradiated solution of CN-DPDSB is also shown for comparison (down). The numbers correspond to the numbers in Scheme S2.

4. Single crystal X-ray diffraction data of CN-DPDSB.

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 diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-Kα and Control Software using the RAPID AUTO at 293 (±2) °C. The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs,[S3] respectively. 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. Crystal data refinement conditions and experimental details are tabulated in Table S1.

Table S1. Crystal data and structure refinement for CN-DPDSB.

Identification code	CN-DPDSB
Empirical formula	$C_{36}H_{24}N_2$
Formula weight	484.57
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.6450(13) Å.
	b = 27.561(6) Å
	c = 7.6528(15) Å
	alpha = 90 deg.
	beta = 110.83(3) deg.
	gamma = 90 deg.
Volume	1309.9(4) Å^3
Z, Calculated density	2, 1.229 Mg/m^3
Absorption coefficient	0.071 mm^{-1}
F(000)	508
Crystal size	0.452 × 0.165 × 0.067 mm
Theta range for data collection	3.21 to 27.48 deg.
Reflections collected/unique	12667 / 3004 [R(int) = 0.0995]
Completeness to theta=27.48	99.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3004 / 0 / 220
Goodness-of-fit on F^2	0.951
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1057
R indices (all data)	R1 = 0.1663, wR2 = 0.1399

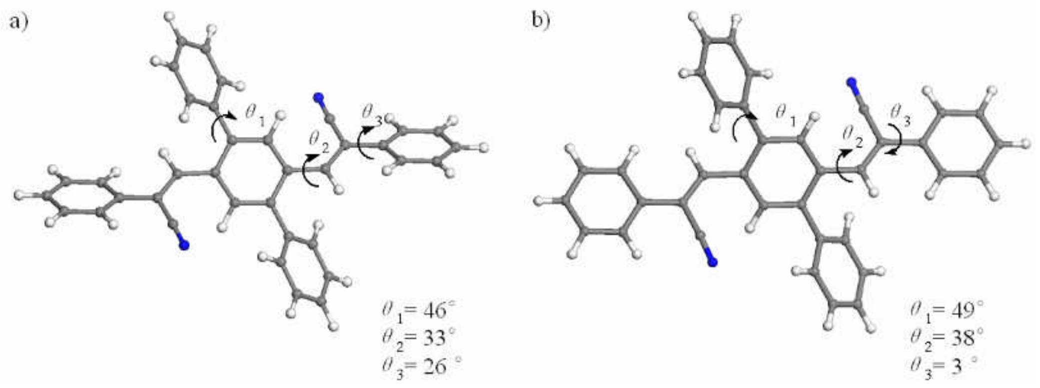


Figure S2. (a) The geometry of CN-DPDSB optimized in the gas phase by using the DFT/B3LYP/6-31G in the Gaussian03 program pockets. (b) The structure of CN-DPDSB in single crystal.

5. Optical properties of CN-DPDSB.

Figure S3 display UV-Vis spectra in THF solution, UV-Vis spectra in film and the PL spectra in film and in crystal of CN-DPDSB. The film of CN-DPDSB shows strong blue fluorescence (λ_{max} = 458 nm, Φ_{fl} = 60%) and the crystal shows more strong blue fluorescence (λ_{max} = 469 nm, Φ_{fl} = 80%).

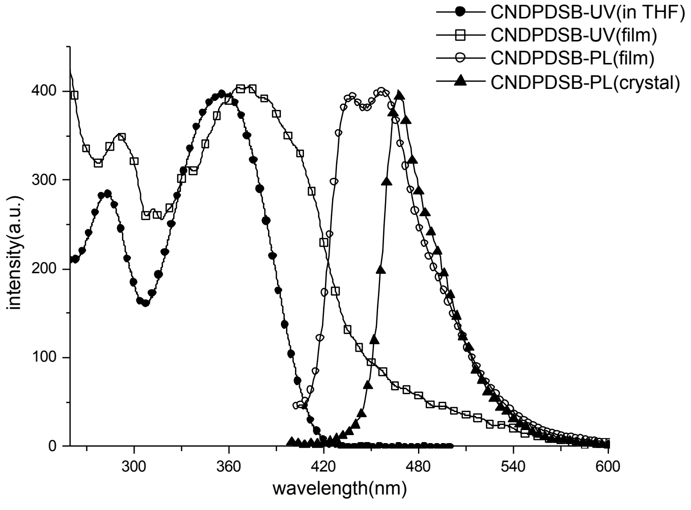


Figure S3. UV-Vis spectra and the PL spectra normalized of CN-DPDSB.

6. Amplified spontaneous emission (ASE) of the quadrate crystal of CN-DPDSB.

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. Because our test is under the room temperature and without any protection, the spectra under intensity pulsed UV laser degenerated very quickly and we can only get few narrowed spectra. The further investigation about the ASE should be down under the inert gas protection. Anyway, the preliminary results of ASE indicate the potential application in organic lasers of the CN-DPDSB single crystal.

Reference:

S1 Z. Q. Xie, B. Yang, L. L. Liu, M. Li, D. Lin, Y. G. Ma, G. Cheng and S. Y. Liu, *J. Phys. Org. Chem.*, 2005, **18**, 962.

S2 (a) F. J. Lange, M. Leuze and M. Hanack, *J. Phys. Org. Chem.*, 2001, **14**, 474. (b) K. Ohsumi, R. Nakagawa, Y. Fukuda, T. Hatanaka, Y. Morinaga, Y. Nihei, K. Ohishi, Y. Suga, Y. Akiyama and T. Tsuji, *J. Med. Chem.*, 1998, **41**, 3022. (c) K. Sandros, M. Sundahl, O. Wennerstrom and U. Norinder, *J. Am. Chem. Soc.*, 1990, **112**, 3082. (d) Z. Q. Xie, B. Yang, L. L. Liu, M. Li, D. Lin, Y. G. Ma, G. Cheng and S. Y. Liu, *J. Phys. Org. Chem.*, 2005, **18**, 962.

S3 SHELXTL Reference Manual, version 5.1, Bruker AXS Inc., Madison, WI, 1998.