A Highly Luminescent Organic Crystal with the Well-Balanced Charge Transport Property: the Role of Cyano-Substitution in the Terminal Phenyl Unit of Distyrylbenzene

Huan Wang,^{,†} Fenglong Sun,[†] Yang Zhao,[†] Ping Lu,^{*,‡} Baohui Wang,[†] Huaiyuan Wang^{*,†}*

[†] College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing, 163318, PR China.

[‡] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, PR China.

Corresponding authors: wanghuan83214@gmail.com (H. Wang); lup@jlu.edu.cn (P. Lu); wanghyjiji@163.com (H. Y. Wang)

ABSTRACT: 1,4-bis(2-cyano styryl)benzene (2-CSB) crystal with cyano substituent groups introduced to the terminal phenyl rings of distyrylbenzene (DSB) has been prepared and its luminescence efficiency could be as high as ~55%. Based on the analyses of cyclic voltammetry and crystal structure, cyano substituents not only lower the LUMO level but also result in a change of the packing mode from the herringbone arrangement to the face-to-face slipped π

stacking motif. Then field-effect transistors (FETs) based on high-quality 2-CSB crystals grown by the physical vapor transport method have been fabricated and the highest hole and electron mobilities were measured as 0.66 and 0.29 cm²/Vs, which enhanced the corresponding values of DSB crystal by up to one and two orders of magnitude, respectively. 2-CSB crystal simultaneously combined the high luminescence and the well-balanced mobility is expected to be of interest for the fundamental research of organic light-emitting devices.

Keywords: cyano-substituted distyrylbenzene crystal, high luminescence efficiency, C–H···N hydrogen bond interaction, face-to-face slipped π stacking motif, well-balanced charge transport property

1. Introduction:

Organic crystals constructed by π -conjugated molecules provide an ideal system for investigating structure–property relationships among organic semiconductors [1,2]. In the meanwhile, the superiorities of organic crystals such as high thermal stability and high carrier mobility make them attractive candidates for optoelectronic devices such as optically pumped lasers [3,4], field-effect transistors (FETs) [5,6], electroluminescence [7,8], and photovoltaic cells [9,10]. To achieve organic bright lighting devices even electrically pumped ‘injection lasers’ under the high current density up to several kA·cm⁻² without luminescence efficiency roll-off [11,12], the efficient light emission and well-balanced high carrier mobility constructed into an organic crystal should be the prior considered strategy.

Distyrylbenzene (DSB) as a simple model compound of poly(p-phenylenevinylene) (PPV) derivatives remains the linear conjugated core and has the herringbone-type crystal structure; but presents a large electron injection barrier. DSB derivatives commonly have the high

luminescence efficiency and tunable color emission, which can be realized by introducing the substituents of methyl [13–15], cyano [16–20], or phenyl [21–24] to modulate the molecular stacking modes in the crystals. Structure–property relationships of functionalized DSB have been discussed in a recent review [25]. However, non-balanced carrier transport existed in most of these crystals that the electron mobility was at least one order of magnitude lower than the hole mobility. Simultaneously, less of cofacial π orbital overlap resulted in both hole and electron mobility usually smaller than 10^{-1} cm²/Vs due to molecular twisted configuration or substituent steric effect enlarging the intermolecular distance. Therefore, enhancing the electron injection into molecule and constructing the π stacking structure to provide more efficient orbital overlap are significant. It has been verified that fluoro- and cyano-groups in DSB derivatives can effectively improve the electron mobility [26] and thereby achieve the balanced carrier transport [27]. To the best of our knowledge, in these reported crystals the cyano-substituted positions are all in the vinylene unit of DSB derivatives. Notably, in some molecular systems of cyano-substitution in the vinylene unit [28,29], polymorphs with different intermolecular stacking modes can be easily formed in which the face-to-face π stacking lack due to the molecular twisted configuration will result to a poor charge-transport performance in the crystal. Recently, DSB derivatives with cyano substituted in the terminal phenyls and similar stilbene compounds for fluorescence and optoelectronic applications have been explored [30–33]; but the effect of cyano-substitution in the terminal phenyl unit on the charge transport characteristic has not been investigated yet. Based on some crystal structure analyses, these intrinsically linear cyano substituents have no influence on the rigid and planar configuration of conjugated molecules and can be easy to form the stronger intermolecular interactions by the halogen bonds or hydrogen bonds which is also the advantage compared with other electron-withdrawing groups. In

additions, the molecular design combined with cyano-substitution in the terminal phenyl unit and high-mobility conjugated unit as the central core can be as a strategy to develop highly balanced-charge-transport organic crystalline materials.

In this work, 1,4-bis(2-cyano styryl)benzene (2-CSB) that cyano substituents are added on the terminal phenyl rings of DSB is considered because firstly, cyano as the electron-withdrawing functional groups can effectively reduce the lowest unoccupied molecular orbital (LUMO) level which remarkably enhances the electron affinity [34]; and secondly, nitrogen atoms on the cyano can form the C–H...N hydrogen bond interactions with the hydrogen atoms on the phenyl rings of the adjacent molecules which induce the intermolecular π overlap stacks in the crystal [35]. To obtain the high quality 2-CSB crystal suitable for the FET device fabrication, physical vapor transport (PVT) method is adopted which can provide the very smooth crystal surface with high purity [36]. The structural determination of 2-CSB crystal grown from vapor depends on the comparison of microcrystals experimental diffraction pattern to the single crystal data of the crystal grown from solution as mentioned in the previously published work [37]. The highest mobilities deduced from the FETs measurements for hole and electron are 0.66 and 0.29 cm²/Vs, respectively. It is noteworthy that the level of the hole/electronic mobility of cyano-substitution in the terminal phenyl unit (2-CSB) compared with those in the vinylene unit [26,38] generally has one or two orders of magnitude enhancement. It indicated that 2-CSB crystal has the well-balanced bipolar carrier-transport characteristics. On the basis of crystal structure analysis, C–H...N hydrogen bonds induce 2-CSB molecules to be packed in a face-to-face slipped π stacking motif and the π – π interaction distance is about 3.5 Å, which may thus be responsible for the high mobility. In addition, the substitution of cyano groups lowers the LUMO level and is efficient for electron injection into molecules. The primary results will guide us to design and

prepare the highly balanced-charge-transport organic crystals for the promising optoelectronic applications from the perspective of structure–property relationships.

2. Experimental section:

Crystal growth: The slice-like crystal of 2-CSB was grown by the PVT method using argon as the gas. The sublimation temperature of material was controlled as 210 °C and the gas flow rate was 40 mL/min. After 12 h of stable growth, the slice-like crystal can be prepared, hanging inside the growth tube. The thicker crystal for crystallographic structure determination was grown in the mixture of chloroform and methanol.

Fluorescence spectra were recorded using RF-5301PC spectrophotometers. Crystalline state PL efficiencies were measured with integrating spheres [39]. Electrochemical measurements were performed with a BAS 100W Bioanalytical System, a glass-carbon disk electrode was used as the working electrode, a Pt wire as the counter electrode, Ag/AgCl as the reference electrode and Bu₄NClO₄ (0.1 M) in acetonitrile as electrolyte. The scan rate was equal to 0.1 V/s for measuring the cyclic voltammetry (CV) curve of samples. The measurements were calibrated using ferrocene (Fc) as the standard, and the levels were determined according to the onset potentials ($E_{\text{Fc/Fc}^+}^{\text{red}} = 0.08 \text{ eV}$, $E_{\text{Fc/Fc}^+}^{\text{ox}} = 0.23 \text{ eV}$). The atomic force microscope (AFM) images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIa operating in the tapping mode. Si cantilever tips (TESP) with the resonance frequency of approximately 300 kHz and the spring constant of about 40 N·m⁻¹ were used. The wide-angle X-ray diffraction was detected with a Rigaku X-ray diffractometer (D/Max-rA, using Cu-K α radiation of wavelength 1.542 Å).

Crystal FET fabrications: A 100-nm-thick SiO₂ layer on a highly doped silicon wafer was used as an insulator. A 100-nm-thick poly(methylmethacrylate) (PMMA) layer was spin coated from

a toluene solution (30 mg/mL) onto the wafer. After the PMMA deposition, the substrates were maintained overnight in an oven at 70 °C and were subsequently annealed at 100 °C for 3 h under a N₂ atmosphere. Next, the crystal was carefully placed on the substrate. The 200-nm-thick top-contact gold or calcium electrodes were thermally evaporated on the crystal surface at a rate of 0.1–0.2 nm/s through a shadow mask under a background pressure of 1×10⁻⁶ mbar. The channel length and width were checked with an optical microscope. The FET measurements were carried out using semiconductor parameter analyzer HP4155C (Agilent Technologies) in a glovebox without exposing the substrate to air.

3. Results and discussion:

3.1 Electrochemical property

Cyclic voltammetry (CV) was employed to investigate the electrochemical behaviors of DSB and 2-CSB. The HOMO and LUMO levels could be estimated through CV curves. As shown in Figure 1a, the reduction-onset potentials (E^{red}) of DSB and 2-CSB are -2.47 and -1.86 V, respectively; and then the LUMO levels of DSB and 2-CSB can be calculated to be ~2.3 and ~2.9 eV, respectively, according to the fomular ($\text{LUMO} = eE^{\text{red}} - E^{\text{red}}_{\text{Fc/Fc}^+} + 4.8 \text{ eV}$ [vs. Ag/Ag⁺]). Therefore, cyano substituents as the electron-withdrawing functional groups can effectively enhance electron affinity of the distyrylbenzenes, which also has been verified in the previous work [34]. Similarly, the oxidation-onset potentials (E^{ox}) of DSB and 2-CSB are 0.75 and 1.12 V, respectively; the HOMO levels of DSB and 2-CSB are calculated to be ~5.3 and ~5.7 eV, respectively, according to the fomular ($\text{HOMO} = eE^{\text{ox}} - E^{\text{ox}}_{\text{Fc/Fc}^+} + 4.8 \text{ eV}$ [vs. Ag/Ag⁺]). Figure 1b shows the energy level diagrams of these two molecules.

Figure 1. (a) Cyclic voltammograms of DSB and 2-CSB; (b) Summary of the data collected for DSB and 2-CSB, where the dashed and solid lines show the LUMO and HOMO levels, respectively.

3.2 Crystal structure analysis

In the DSB crystal structure (Figure 2a), the molecules are recognized as the herringbone arrangement [13,40]. The arenes of the adjacent molecules adopt an edge-to-face geometry with a center-to-center distance of ~ 4.76 Å and a dihedral angle of $\sim 60^\circ$ in the *ab* plane. The experimentally determined cell parameters of 2-CSB single crystal grown in the mixture of chloroform and methanol as the same as recently reported are $a = 3.913$ Å; $b = 6.966$ Å; $c = 15.611$ Å; $\alpha = 95.798^\circ$; $\beta = 93.445^\circ$; $\gamma = 92.199^\circ$ [35]. As shown in Figure 2b, three types of C–H $\cdots$ N interactions (I, II and III) exist between 2-CSB molecules. The H $\cdots$ N distances of three interactions I, II and III are 2.67(7), 2.92(6) and 2.63(4) Å; and the C–H $\cdots$ N angles are 129.7° , 119.0° and 157.8° , respectively. The analysis data of C–H $\cdots$ N hydrogen bonds are summarized in the Table 1. It is noteworthy that intermolecular C–H $\cdots$ N interactions construct the molecular clusters along the *a* axis, in which each 2-CSB molecule preserves the same orientation and has a

face-to-face slipped π stacking motif. The intermolecular distance between neighboring molecules is about 3.5 Å.

Figure 2. (a) DSB molecular packing in the crystal: “herringbone” arrangement of molecules in the ab plane with intermolecular arene-arene interactions; (b) 2-CSB molecular packing in the crystal: π overlap stacks between molecules along the a axis.

Table 1. C–H $\cdots$ N hydrogen bonds in the 2-CSB crystal.

C–H $\cdots$ N hydrogen bond ^a	I	II	III
$d/\text{\AA}$ (H $\cdots$ N)	2.67(7)	2.92(6)	2.63(4)
$\theta/^\circ$ (angle of C–H $\cdots$ N)	129.7	119.0	157.8

^aDistances are reported in angstroms, and the angles are reported in degrees.

3.3 Optical Property

Figure 3 shows the emission spectra and optical photographs of DSB and 2-CSB crystals, respectively. In our previous work [41], DSB crystal grown from vapor with a high PL efficiency of ~65% has three emission peaks of 444, 467 and 500 nm, corresponding to 0–0, 0–1 and 0–2 transition emissions, respectively. 2-CSB crystals prepared by different growth method both

have one main emission peak at around 490 nm; and their crystalline state PL efficiencies measured in an integrating sphere are both as high as ~55%. It indicates that introducing cyano substituents to the terminal phenyl rings of DSB tunes the emitting color but maintains a high luminescence efficiency in the crystal of distyrylbenzene derivative system. Meanwhile, the crystals have the slice-like shapes but the thickness of the crystal grown from vapor is much thinner than that grown from solution because the crystal growth at relative high temperature by the PVT method is more easily along the direction of stronger intermolecular interaction, which has been also discussed in our previous work [41]. As above mentioned, the C–H···N interactions in the *ab* plane are stronger than that along the *c* axis in the 2-CSB crystal.

Figure 3. The emission spectra of DSB and 2-CSB crystals grown from solution (Mixture of chloroform and methanol) and vapor (Argon atmosphere), respectively. The corresponding optical photographs under UV light are shown in the right side, and the scale bar is 1 millimeter.

3.4 Structure Determination of 2-CSB crystal grown from vapor

The thickness of the slice-like crystal grown from vapor was only about several micrometers, which is helpful for obtaining a better FET device performance. However, the crystal is too thin to generate enough diffraction data for its structure determination. Previously, the molecular

stacking structure of the relatively thicker crystal grown in the mixture of chloroform and methanol has been determined. Herein, we compared the wide-angle X-ray diffraction (XRD) patterns of the crystals grown from solution and vapor to certify their similar structure (Figure 4) that this method has been also referred in our early work [37]. In the experiment, the crystal grown from vapor was trituated into microcrystals to give more diffraction peaks. By comparing the experimental diffraction pattern and the calculated one (based on the single crystal data of the crystal grown from solution), it can be easily seen that almost all of the diffraction peak positions are consistent, which means that the crystals grown in different conditions (argon gas and mixture solution) possess the same molecular stacking structure.

Figure 4. Wide-angle X-ray diffraction pattern of the slice-like crystal (grown from vapor) trituated into micro crystals and calculated diffraction pattern based on the single crystal data (grown from solution).

Tapping-mode AFM has been used to observe the flat area of 2-CSB crystal surface with a scanning range of $20 \times 20 \mu\text{m}^2$. From the AFM height image shown in Figure 5, step-like morphology has been found. According to the cross-section analysis, the average height of one step is about 1.8 nm. Figure 6 shows the XRD pattern on one slice-like crystal. In the experiment,

the crystal was flatted parallel to the glass substrate. As can be seen, the diffraction peaks occur equidistantly with varying angle degree, so the crystal has good ordered layer structures. According to the Bragg equation ($2d\sin\theta=n\lambda$), the strong diffraction peak at 11.1° corresponds to (002) crystal plane and the thickness of one 2-CSB molecular layer is calculated to be $\sim 15.9 \text{ \AA}$, which corresponds to the height of one step in the AFM image. The AFM image and XRD pattern of DSB crystal are shown in Figure S1 in the supporting information.

Figure 5. AFM height image ($20 \mu\text{m} \times 20 \mu\text{m}$) of the slice-like 2-CSB crystal and the sectional analysis of the AFM image (the thickness of one step is around 1.8 nm).

Figure 6. Experimental wide-angle X-ray diffraction pattern of one slice-like crystal grown from vapor (in the test the crystal was flatted parallel to the glass substrate).

The calculated layer thickness corresponded well with the step height observed by AFM, but was generally ~ 0.2 nm smaller than the AFM results, due to the systematic error of the instrument in the process of scanning the AFM images. Obviously, the results of AFM morphology and XRD pattern suggest that the slice-like crystal grown by the PVT method has a layer-by-layer structure and each layer corresponds to a molecular monolayer. The thickness of one layer is in good agreement with the dimension of the unit cell parameter c ($15.611 \text{ \AA}$), which indicates that the layer-by-layer growth in the crystal is along the c axis and the crystal surface corresponds to the ab plane of unit cell. Thus, the long axes of the 2-CSB molecules form an angle of 60° with respect to the crystal surface. On the basis of the crystal structure, we draw the molecular stacking mode in the molecular layer, as shown in Figure 7. As can be seen, all of the molecules are packed in the same orientation along the a axis, in which intermolecular π overlap stacks will benefit for the carrier transport in the 2-CSB crystal-based field-effect transistors.

Figure 7. Oriented alignment of the molecules in the crystal: the height of the molecular layer ($15.9 \text{ \AA}$) from AFM and XRD results corresponds to the length of 2-CSB molecule along the c axis direction vector; and the angle of the molecular long axis with ab plane is 60° shown in the right side.

3.5 Field-effect mobility measurement of 2-CSB crystal

The slice-like 2-CSB crystal grown from vapor has the very smooth surface that is important for the performance of organic single crystal FETs because of the conductive channel locating within the first few molecular layers of the surface area. The top-contact hole- and electron-transport FETs based on the 2-CSB crystal were constructed, respectively. The capacitance of gate dielectric (SiO₂/ 100 nm + PMMA/ 100 nm) was about 13.8 nF/cm². Gold and calcium electrodes were chosen for the hole- and electron-carrier injections, considering the HOMO and LUMO levels of ~5.7 and ~2.9 eV, respectively. Figure 8a–d shows the output and transfer characteristics of our best devices. The hole and electron mobilities extracted from saturation regions were as high as 0.66 and 0.29 cm²/Vs, respectively. The average hole and electron mobilities estimated from 20 devices were about 0.36 and 0.15 cm²/Vs, respectively (Figure 8e–f). As comparison, the measured hole and electron mobilities of DSB crystal in our fabricated devices were ~0.02 and ~0.003 cm²/Vs, respectively (see Figure S2 in the supporting information). As can be seen, the cyano substituted 2-CSB comparing to unsubstituted DSB enhanced the hole and electron mobility by up to one and two orders of magnitude, respectively. Since the substitution of electron-withdrawing functional groups lowers the DSB's LUMO level matched with calcium's work function (~2.9 eV), electron injection into 2-CSB would be more efficient. Meanwhile, π stacking structure induced by intermolecular C–H···N interactions facilitates the carrier transport. It is also the reason that 2-CSB crystal can keep a higher hole mobility although its HOMO level is a little lower than DSB's.

Figure 8. Output characteristics (a, c) and transfer characteristics (b, d) of OFETs based on 2-CSB crystals with symmetric gold and calcium electrodes, respectively. Histogram of hole (e) and electron (f) mobility calculated from 20 devices. The inserts in figure (b, d) are the device top-view photographs. Channel length (L) and width (W) were determined by optical microscopy: $L/W=100/500\text{ }\mu\text{m}$ (b); $L/W=100/900\text{ }\mu\text{m}$ (d).

Here, it is noteworthy that the hole and electron mobilities measured by FETs are both along the a axis of 2-CSB crystal, which is the direction of maximum carrier mobility. As shown in Figure 9, the predominant orientation of the crystal growth corresponds to the long strip-shape direction of the crystal (crystallographic a axis) because the intermolecular C–H $\cdots$ N interactions

induce π overlap stacks with π - π distance of ~ 3.5 Å to form the channel of facilitating carrier transport along this direction.

Figure 9. Schematic view of 2-CSB molecules arrangement along the a axis which is the predominant orientation of the crystal growth, corresponding to the long strip-shape direction of the crystal shown in the picture.

4. Conclusion:

In summary, we prepared the crystal with cyano-substitution in the terminal phenyl unit of distyrylbenzene (2-CSB) by the PVT method, determined its crystal structure and fabricated crystal-based FETs. The introduction of cyano substituents as electron-withdrawing groups lowers the LUMO level and is efficient to electron injection into 2-CSB. Meanwhile, the C-H $\cdots$ N interactions construct the intermolecular π stacking structure along the a axis in the crystal, which enhance π orbital overlap and facilitate carrier transport. The highest hole and electron mobilities of 2-CSB crystal are 0.66 and 0.29 cm²/Vs, respectively. Therefore, 2-CSB

crystal with a high PL efficiency of ~55% and well-balanced carrier mobility would be promising for the development of organic light-emitting diodes (OLEDs) and light-emitting organic field-effect transistors (LE-OFETs).

Supporting Information. AFM image and XRD pattern of DSB crystal; the DSB crystal-based field-effect transistors; and the cif files of DSB and 2-CSB crystals (CCDC 921998, 979756).

Acknowledgment

We are grateful for financial support from the Youth Science Foundation of Heilongjiang Province (QC2014C046), University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2015073) and National Science Foundation of China (Grant No. 51175066).

References

- [1] H. Moon, R. Zeis, E.-J. Borkent, C. Besnard, A.J. Lovinger, T. Siegrist, C. Kloc, Z.N. Bao, Synthesis, crystal structure, and transistor performance of tetracene derivatives, *J. Am. Chem. Soc.* 126 (2004) 15322–15323.
- [2] Z.Q. Xie, B. Yang, F. Li, G. Cheng, L.L. Liu, G.D. Yang, H. Xu, L. Ye, M. Hanif, S.Y. Liu, D.G. Ma, Y.G. Ma, Cross dipole stacking in the crystal of distyrylbenzene derivative: the approach toward high solid-state luminescence efficiency, *J. Am. Chem. Soc.* 127 (2005) 14152–14153.
- [3] H. Yanagi, T. Ohara, T. Morikawa, Self-waveguided gain-narrowing of blue light emission from epitaxially oriented *p*-sexiphenyl crystals, *Adv. Mater.* 13 (2001) 1452–1455.

[4] M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, T. Koyama, Y. Taniguchi, Improved crystal-growth and emission gain-narrowing of thiophene/phenylene co-oligomers, *Adv. Mater.* 15 (2003) 213–217.

[5] V.C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R.L. Willett, T. Someya, M.E. Gershenson, J.A. Rogers, Elastomeric transistor stamps: reversible probing of charge transport in organic crystals, *Science* 303 (2004) 1644–1646.

[6] A.L. Briseno, S.C.B. Mannsfeld, M.M. Ling, S. Liu, R.J. Tseng, C. Reese, M.E. Roberts, Y. Yang, F. Wudl, Z.N. Bao, Patterning organic single-crystal transistor arrays, *Nature* 444 (2006) 913–917.

[7] X.J. Li, Y.X. Xu, F. Li, Y.G. Ma, Organic light-emitting diodes based on an ambipolar single crystal, *Org. Electron.* 13 (2012) 762–766.

[8] R. Ding, J. Feng, X.L. Zhang, W. Zhou, H.H. Fang, Y.F. Liu, Q.D. Chen, H.Y. Wang, H.B. Sun, Fabrication and characterization of organic single crystal-based light-emitting devices with improved contact between the metallic electrodes and crystal, *Adv. Funct. Mater.* 24 (2014) 7085–7092.

[9] R.J. Tseng, R. Chan, V.C. Tung, Y. Yang, Anisotropy in organic single-crystal photovoltaic characteristics, *Adv. Mater.* 20 (2008) 435–438.

[10] Y.J. Zhang, H.L. Dong, Q.X. Tang, S. Ferdous, F. Liu, S.C.B. Mannsfeld, W.P. Hu, A.L. Briseno, Organic single-crystalline p-n junction nanoribbons, *J. Am. Chem. Soc.* 132 (2010) 11580–11584.

- [11] T. Takenobu, S.Z. Bisri, T. Takahashi, M. Yahiro, C. Adachi, Y. Iwasa, High current density in light-emitting transistors of organic single crystals, *Phys. Rev. Lett.* 100 (2008) 066601.
- [12] K. Sawabe, M. Imakawa, M. Nakano, T. Yamao, S. Hotta, Y. Iwasa, T. Takenobu, Current-confinement structure and extremely high current density in organic light-emitting transistors, *Adv. Mater.* 24 (2012) 6141–6146.
- [13] S. Varghese, S.K. Park, S. Casado, R.C. Fischer, R. Resel, B.M. n-Medina, R. Wannemacher, S. Y. Park, J. Gierschner, Stimulated emission properties of sterically modified distyrylbenzene-based H-aggregate single crystals, *J. Phys. Chem. Lett.* 4 (2013) 1597–1602.
- [14] R. Kabe, H. Nakanotani, T. Sakanoue, M. Yahiro, C. Adachi, Effect of molecular morphology on amplified spontaneous emission of bis-styrylbenzene derivatives, *Adv. Mater.* 21 (2009) 4034–4038.
- [15] Z.Q. Xie, W.J. Xie, F. Li, L.L. Liu, H. Wang, Y.G. Ma, Controlling supramolecular microstructure to realize highly efficient nondoped deep blue organic light-emitting devices: the role of diphenyl substituents in distyrylbenzene derivatives, *J. Phys. Chem. C* 112 (2008) 9066–9071.
- [16] Y.P. Li, F. Li, H.Y. Zhang, Z.Q. Xie, W.J. Xie, H. Xu, B. Li, F.Z. Shen, L. Ye, M. Hanif, D.G. Ma, Y.G. Ma, Tight intermolecular packing through supramolecular interactions in crystals of cyano substituted oligo(*para*-phenylene vinylene): a key factor for aggregation-induced emission, *Chem. Commun.* (2007) 231–233.

- [17] Y.J. Zhang, G.L. Zhuang, M. Ouyang, B. Hu, Q.B. Song, J.W. Sun, C. Zhang, C. Gu, Y.X. Xu, Y.G. Ma, Mechanochromic and thermochromic fluorescent properties of cyanostilbene derivatives, *Dyes Pigments* 98 (2013) 486–492.
- [18] H. Wang, F. Li, I. Ravia, B.R. Gao, Y.P. Li, V. Medvedev, H.B. Sun, N. Tessler, Y.G. Ma, Cyano-substituted oligo(*p*-phenylene vinylene) single crystals: a promising laser material, *Adv. Funct. Mater.* 21 (2011) 3770–3777.
- [19] S. Varghese, S.-J. Yoon, E.M. Calzado, S. Casado, P.G. Boj, M.A. Díaz-García, R. Resel, R. Fischer, B. Milián-Medina, R. Wannemacher, S.Y. Park, J. Gierschner, Stimulated resonance raman scattering and laser oscillation in highly emissive distyrylbenzene-based molecular crystals, *Adv. Mater.* 24 (2012) 6473–6478.
- [20] S.-J. Yoon, S. Varghese, S.K. Park, R. Wannemacher, J. Gierschner, S.Y. Park, Color-tuned, highly emissive dicyanodistyrylbenzene single crystals: manipulating intermolecular stacking interactions for spontaneous and stimulated emission characteristics, *Adv. Optical Mater.* 1 (2013) 232–237.
- [21] H. Nakanotani, M. Saito, H. Nakamura, C. Adachi, Tuning of threshold voltage by interfacial carrier doping in organic single crystal ambipolar light-emitting transistors and their bright electroluminescence, *Appl. Phys. Lett.* 95 (2009) 103307.
- [22] H. Nakanotani, M. Saito, H. Nakamura, C. Adachi, Highly balanced ambipolar mobilities with intense electroluminescence in field-effect transistors based on organic single crystal oligo(*p*-phenylenevinylene) derivatives, *Appl. Phys. Lett.* 95 (2009) 033308.

[23] Z.Q. Xie, B. Yang, W.J. Xie, L.L. Liu, F.Z. Shen, H. Wang, X.Y. Yang, Z.M. Wang, Y.P. Li, M. Hanif, G.D. Yang, L. Ye, Y.G. Ma, A class of nonplanar conjugated compounds with aggregation-induced emission: structural and optical properties of 2,5-diphenyl-1,4-distyrylbenzene derivatives with all cis double bonds, *J. Phys. Chem. B* 110 (2006) 20993–21000.

[24] Z.Q. Xie, B. Yang, G. Cheng, L.L. Liu, F. He, F.Z. Shen, Y.G. Ma, S.Y. Liu, Supramolecular interactions induced fluorescence in crystal: anomalous emission of 2,5-diphenyl-1,4-distyrylbenzene with all cis double bonds, *Chem. Mater.* 17 (2005) 1287–1289.

[25] J. Gierschner, S.Y. Park, Luminescent distyrylbenzenes: tailoring molecular structure and crystalline morphology, *J. Mater. Chem. C* 1 (2013) 5818–5832.

[26] S.K. Park, J.H. Kim, S.-J. Yoon, O.K. Kwon, B.-K. An, S.Y. Park, High-performance *n*-type organic transistor with a solution processed and exfoliation-transferred two-dimensional crystalline layered film, *Chem. Mater.* 24 (2012) 3263–3268.

[27] J. Deng, J. Tang, Y.X. Xu, L.Q. Liu, Y. Wang, Z.Q. Xie, Y.G. Ma, Cyano-substituted oligo(*p*-phenylene vinylene) single-crystal with balanced hole and electron injection and transport for ambipolar field-effect transistors, *Phys. Chem. Chem. Phys.* 17 (2015) 3421–3425.

[28] Y.X. Xu, H.Y. Zhang, F. Li, F.Z. Shen, H. Wang, X.J. Li, Y. Yu, Y.G. Ma, Supramolecular interaction-induced self-assembly of organic molecules into ultra-long tubular crystals with wave guiding and amplified spontaneous emission, *J. Mater. Chem.* 22 (2012) 1592–1597.

- [29] S.J. Yoon, J.W. Chung, J. Gierschner, K.S. Kim, M.G. Choi, D. Kim, S.Y. Park, Multistimuli two-color luminescence switching via different slip-stacking of highly fluorescent molecular sheets, *J. Am. Chem. Soc.* 132 (2010) 13675–13683.
- [30] D.P. Yan, A. Delori, G.O. Lloyd, T. Friščić, G.M. Day, W. Jones, J. Lu, M. Wei, D.G. Evans, X. Duan, A cocrystal strategy to tune the luminescent properties of stilbene-type organic solid-state materials, *Angew. Chem. Int. Ed.* 50 (2011) 12483–12486.
- [31] D.P. Yan, J. Lu, J. Ma, M. Wei, D.G. Evans, X. Duan, Reversibly thermochromic, fluorescent ultrathin films with a supramolecular architecture, *Angew. Chem. Int. Ed.* 50 (2011) 720–723.
- [32] D.P. Yan, D.G. Evans, Molecular crystalline materials with tunable luminescent properties: from polymorphs to multi-component solids, *Mater. Horiz.* 1 (2014) 46–57.
- [33] D.P. Yan, Micro-/nanostructured multicomponent molecular materials: design, assembly, and functionality, *Chem. Eur. J.* 21 (2015) 4880–4896.
- [34] M.S. Liu, X.Z. Jiang, S. Liu, P. Herguth, A.K.-Y. Jen, Effect of cyano substituents on electron affinity and electron-transporting properties of conjugated polymers, *Macromolecules* 35 (2002) 3532–3538.
- [35] G.L. Fan, D.P. Yan, Positional isomers of cyanostilbene: two-component molecular assembly and multiple-stimuli responsive luminescence, *Sci. Rep.* 4 (2014) 4933.
- [36] H. Wang, Z.Q. Xie, B. Yang, F.Z. Shen, Y.P. Li, Y.G. Ma, Several slice-like organic crystals grown by the physical vapor transport method: combining atomic force microscopy and

X-ray diffraction to explore the characteristics of crystal formation, *CrystEngComm* 10 (2008) 1252–1257.

[37] Z.Q. Xie, H. Wang, F. Li, W.J. Xie, L.L. Liu, B. Yang, L. Ye, Y.G. Ma, Crystal structure of a highly luminescent slice crystal grown in the vapor phase: a new polymorph of 2,5-diphenyl-1,4-distyrylbenzene, *Cryst. Growth Des.* 7 (2007) 2512–2516.

[38] S.K. Park, S. Varghese, J.H. Kim, S.-J. Yoon, O.K. Kwon, B.-K. An, J. Gierschner, S.Y. Park, Tailor-made highly luminescent and ambipolar transporting organic mixed stacked charge-transfer crystals: an isometric donor–acceptor approach, *J. Am. Chem. Soc.* 135 (2013) 4757–4764.

[39] Y. Kawamura, H. Sasabe, C. Adachi, Simple accurate system for measuring absolute photoluminescence quantum efficiency in organic solid-state thin film, *Jpn. J. Appl. Phys. Part 1* 43 (2004) 7729–7730.

[40] C.C. Wu, M.C. DeLong, Z.V. Vardeny, J.P. Ferraris, Structural and optical studies of distyrylbenzene single crystals, *Synth. Met.* 137 (2003) 939–941.

[41] H. Wang, F. Li, B.R. Gao, Z.Q. Xie, S.J. Liu, C.L. Wang, D.H. Hu, F.Z. Shen, Y.X. Xu, H. Shang, Q.D. Chen, Y.G. Ma, H.B. Sun, Doped organic crystals with high efficiency, color-tunable emission toward laser application, *Cryst. Growth Des.* 9 (2009) 4945–4950.

Graphical Abstract

Cyano substituted distyrylbenzene derivative (2-CSB) crystal has the high luminescence efficiency of ~55% and well-balanced charge transport characteristics with the hole and electron mobility of 0.66 and 0.29 cm²/Vs, respectively. The introduction of cyano substituents lowers the LUMO level and is efficient to electron injection into 2-CSB. Meanwhile, intermolecular C–H···N interactions construct the face-to-face slipped π stacking motif facilitating carrier transport.