Solvation-Enhanced Intermolecular Charge Transfer Interaction in Organic Cocrystals: Enlarged C–C Surface Close Contact in Mixed Packing between PTZ and TCNB

Jing Wang, † Aisen Li, †‡ Shuping Xu, † Chongping Song, † Yijia Geng, † Ling Ye, † Houyu Zhang, † and Weiqing Xu*†

† State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry and ‡ College of Physics, Jilin University, Changchun 130012, P. R. China

ABSTRACT: The mixed π–π packing of the donor (D) and acceptor (A) molecules is the highlighting feature of the intermolecular interactions following charge transfer (CT) issues in organic cocrystal systems. There is an inverse relationship between the D–A interplanar distance and the intermolecular CT interaction. However, the D–A C–C surface close contact (relative areas) on the intermolecular CT interactions in organic cocrystal systems is rarely investigated. Herein, we designed and constructed a novel cocrystal and its solvate cocrystal. The structural and electrostatic potential analyses suggest that the solvation destroys the N–H···N hydrogen bond interaction between phenothiazine (PTZ) and 1,2,4,5-tetracyanobenzene (TCNB), which causes the TCNB molecules to have a 90° rotation along the normal axis of the PTZ plane. Thus, the D–A C–C surface close contact is enlarged, strengthening the intermolecular π–π stacking interactions and intermolecular CT interaction between PTZ and TCNB, which are further evidenced by the absorption and Raman spectroscopic analyses. This study provides rare evidence of the enlarged C–C surface close contact in the mixed packing between D and A that greatly contributes to the intermolecular CT interaction in a D–A cocrystal system. It also provides a deeper understanding of the role of solvation in the structure–property relationship of organic cocrystal materials.

INTRODUCTION

The weak intermolecular interactions of noncovalent bonds are important driving forces to assemble the organic cocrystals with two or more competent molecules and/or ionic compounds. 1–4 For instance, π–π stacking, 5–7 halogen bonds, 8,9 hydrogen bonds, 10,11 and charge transfer (CT). 12,13 Methods based on the tuning of intermolecular interaction for organic cocrystals are advantageous in regulating the structure, simplifying operation, and reducing cost. 14,15 The organic charge transfer cocrystals (OCTCs) are derived from the ordered assembly and aggregation of donor (D) and acceptor (A) molecules via the intermolecular CT interactions. 1,2,6 Meanwhile, the D and A molecules are piled up in the separated (⋯DDD⋯AAAA⋯) and alternated (⋯DADA⋯ DADA⋯) stack mode. 16–19 The transport of electrons in an OCTC can be enhanced due to the intermolecular CT interaction, 7 which makes them gain growing attention in the applications of electricity functional materials 20–28 and novel optical materials. 29–37

In fact, the intermolecular CT interaction of the cocrystal is relevant to the highest occupied molecular orbital (HOMO) of D molecule and the lowest unoccupied molecular orbital (LUMO) of A molecule. 1,2 Hence, the degree of charge transfer (DCT) is defined as the numbers of CT from D to A molecules during the process of crystallization. It depends on the electronic coupling between the HOMO of D and the LUMO of A, which can be evaluated by calculating the changes of the bond length. 3 It is also reported that the DCT can be determined by the Raman frequency shift. 5 The CT transition of the OCTC can be characterized by the ultraviolet–visible (uv–vis) absorption 2,38,39 and fluorescence spectroscopies 32,40,41 based on the electron transition from D to A while the D–A crystal absorbs external light radiation.

So far, the intermolecular CT interaction of OCTC is adjusted and controlled mainly by two methods. One is based on the selection of chemical components during the synthesis of CT materials. The D and A molecules are extremely important for tuning the CT interaction in a cocrystal. When the A molecule is fixed, the DCT can be tuned by adjusting the HOMO of D. 30,42,43 Similarly, the tunable DCT of OCTC can be realized by tuning the LUMO of A while the D molecule is fixed. 30,44 Besides, the DCT of the cocrystal can be adjusted by different stoichiometric ratios of D and A. For these synthetic methods, the D–A mixed packing distances will be shortened...
with the DCT increasing. The second method for tuning the intermolecular CT interaction is the high-pressure method. The D−A interplanar mixed packing distances become narrower during the compression process, leading to the enhancement of the intermolecular CT interaction and the red-shifts of the spectral bands. In certain cases, the D−A mixed packing distance is inversely proportional to the intermolecular CT interaction.

Solvent molecules as one of the building components are also fully considered into the structures of OCTC. Hu et al. reported a cocrystal, perylene−TCNB, and they studied the changes of its structure, color, and dramatic shape, while the aromatic solvents (tetrahydrofuran, THF) were accommodated. Owing to the doping of the solvent molecules, the intermolecular D/A distance was enlarged, causing the CT interaction to decrease. Zhang et al. also reported that the assembly of chlorobenzene into the structure of coronene−2,3,5,6-tetrafluoro−7,7,8,8-tetracyanoquinodimethane can depress the short-contact interactions and enlarge the D/A distance. However, the solvation-enhanced intermolecular CT interaction in an OCTC is rarely reported. Luckily, in the present work, we observed such a phenomenon in two novel phenothiazine (PTZ)−TCNB cocrystals. In these two OCTCs (PT and PT-S), PTZ acts as D while TCNB acts as A, and both of them feature strong near-infrared optical absorption properties. The role of acetonitrile on the π−π stacking interaction but also enhanced intermolecular D/A CT interaction, which is different from previous publications that the weakened CT interactions were observed once the additional solvents were attended.

RESULTS/DISCUSSION

Crystal Structure and Growth of Cocrystal PT and PT-S. To determine the effect of solvation on the intermolecular CT interaction in the D−A organic cocrystal, we designed and synthesized the novel cocrystal PT and its solvate cocrystal PT-S. PTZ and TCNB organic molecules of the PT or PT-S cocrystal are assembled together by the π−π interaction and CT interaction between the donor and the acceptor (Scheme 1). Acetonitrile joins in the stacking structure of the PTZ and TCNB organic molecules as a ratio of 1:1:1 in the PT-S cocrystal (Scheme 1b).

The single-crystal x-ray diffraction (SXRD) results show that the PT belongs to the monoclinic space-group P1 with the cell parameters of \( a = 16.1392 \) \( \text{Å} \), \( b = 7.0421 \) \( \text{Å} \), \( c = 33.352 \) \( \text{Å} \), \( \alpha = 90^\circ \), \( \beta = 93.830^\circ \), and \( \gamma = 90^\circ \). The PT-S is assigned to the triclinic space-group p1 with the cell parameters of \( a = 7.3820 \) \( \text{Å} \), \( b = 8.0065 \) \( \text{Å} \), \( c = 19.177 \) \( \text{Å} \), \( \alpha = 83.907^\circ \), \( \beta = 80.546^\circ \), and \( \gamma = 70.6490^\circ \) (Supporting Information of Table S1). Their π−π packing arrangements are exhibited in Figure 1A,B. The PTZ and TCNB molecules present an alternate stacking mode (⋯D−A−D−A⋯) along the b-axis with the centroid−centroid distance \( (d_{c−c}) \) of 3.8705 and 3.6843 Å for the cocrystal PT (Figure 1A), but along the a-axis with the shorter \( d_{c−c} \) distance of 3.8245, 3.6125, 3.6784, and 3.5446 Å for the cocrystal PT-S (Figure 1B). The growth morphologies of PT and PT-S are computed by materials studio software and shown in Figure 1C,D. The cocrystal PT grows along the [010] direction (Figure 1C) and the cocrystal PT-S grows along the [100] direction (Figure 1D). They keep growing along the⋯D−A−D−A⋯stacking direction. The optical images of PT and PT-S are shown in Figure 1E,F. PTZ and TCNB organic molecules are assembled into an ultralong cocrystal wire along the [010] direction. In the cocrystal PT, the crystal grows along the [100] direction.

Solvation-Enhanced Intermolecular CT between PTZ and TCNB. The colors of cocrystal PT and PT-S exhibit significant changes (black) compared to their pristine components (Figure 2A). The color changes indicate that the intermolecular CT interaction between PTZ and TCNB are generated in this cocrystal. To assess the intermolecular CT interaction between D and A in the cocrystal PT and PT-S, the UV−vis absorption spectra as well as Raman spectra of PTZ, TCNB, PT, and PT-S crystals were analyzed. Figure 2B shows the UV−vis absorption spectra of the PTZ THF solution, the TCNB acetonitrile solution, and the PT and PT-S solid crystals. The absorption peaks of the TCNB acetonitrile solution are located at 304 and 317 nm, and the absorption band of PTZ THF solution is situated in a range of 280−380 nm. When PTZ and TCNB molecules are assembled as a cocrystal via the CT interaction, absorption edge displays an obvious red shift and covers the whole wavelength range of UV−vis−NIR. The absorption edge of PT-S (∼860 nm) is located at higher wavenumbers than that of PT (∼800 nm). Our results prove that the solvent accommodation enhances the intermolecular CT transition from PTZ to TCNB.

The in situ Raman spectra of the PTZ power, the TCNB power, the PT solid crystal, and PT-S solid crystal were also investigated at the 633 nm excitation line (Figure 2C). The Raman vibrational bands of C≡N are located at 2230−2600 cm\(^{-1}\) in TCNB, PT, and PT-S. To clearly understand and identify these peaks, we simulated and assigned the Raman bands of the C≡N in TCNB, PT, and PT-S as shown in Figures S1, S2, and Table S2. Four vibration−rotation Raman bands of C≡N are observed (peak 1, peak 2, peak 3, and peak 4) (Figures S1 and S2). In each Raman band, the four cyano groups of the TCNB molecule show different vibration−rotation modes and intensities. One of the four cyano groups is attributed to the strong stretching vibration of C≡N, whereas the other three belong to the weak stretching or whirling vibrations of C≡N (Table S2). In the experiment, the four overlapping C≡N Raman bands of the TCNB power are observed at 2250, 2242, 2239, and 2239 cm\(^{-1}\), respectively (Figure 2D). When TCNB and PTZ form a cocrystal PT, these four bands shift to lower wavenumbers (2246, 2241, 2237, and 2237 cm\(^{-1}\)) (Figure 2D), indicating the formation of intermolecular CT interaction between the two molecules. Similarly, when the acetonitrile is accommodated into the
structure of the PT-S cocrystal, four overlapping Raman peaks of C≡N also shift to the lower wavenumbers (2240, 2237, 2235, and 2235 cm\(^{-1}\)) (Figure 2D). The relatively lower wavenumber shifts of these four bands indicate stronger intermolecular CT interaction in PT-S than in PT. Based on the structural analysis, we infer that the enhanced CT interaction may come from the shorter \(d_{cc}\) distance (Figure 1A,B).

The DCT of PT-S and PT is calculated as about 0.075\(e^2\) and 0.031\(e^2\) according to the Mulliken population analysis, respectively. The theoretical molecular orbitals of the HOMO and LUMO in PT and PT-S were performed based on the SXRD data. Figure S3A,B exhibit the theoretical molecular orbitals of the HOMO and LUMO of the two cocrystals. The electron clouds of the crystal HOMO mainly cover PTZ, whereas the electron clouds of the crystal LUMO are contributed from TCNB, which certifies the existence of the CT transition in the PT-S cocrystal. The energy levels of the HOMO and LUMO in PT and PT-S confirm that the solvation reduces the bandgap of the cocrystal, strengthening the intermolecular CT interaction.

**Figure 1.** Stacking structure of the (A) PT viewed along the [100] and (B) PT-S viewed along the [010] directions, respectively. The numbers are the closest centroid–centroid distances between PTZ and TCNB. The simulated growth morphology of (C) PT and (D) PT-S. The optical images of (E) PT (magnification × 10) and (F) PT-S (magnification × 5). The scale bars are 0.10 mm.

**Figure 2.** (A) Photos, (B) Uv–vis absorption spectra, and (C) Raman spectra of PTZ, TCNB, PT, and PT-S. (D) Histograms of the four Raman vibrational wavenumbers of C≡N in TCNB, PT, and PT-S.

---

**Solvation Effect on Intermolecular Hydrogen Bond Interactions in Cocrystals.** To clarify the mechanism of solvation-enhanced intermolecular CT between PTZ and TCNB, we analyzed the solvation effect on intermolecular hydrogen bond interactions in cocrystals. In PT, PTZ (D) owns a dihedral angle of 157° and exhibits a \(\pi\)–\(\pi\) stacking structure with TCNB (A) (Figure S4A). A strong N–H···N hydrogen bond with the bond length of 2.3063 Å between PTZ and TCNB is identifiable (Figure 3A). The dihedral angle of PTZ is reduced to 150° in the PT-S (Figure 3B). The N atom from acetonitrile displays a stronger N–H···N (bond length is 2.257 Å) interaction with PTZ (Figure S4B) rather than TCNB. Interestingly, compared with the structure of PT, TCNB in PT-S shows the rotation angle of 90° parallel to the plane of PTZ in the absence of the N–H···N hydrogen bonds between TCNB and PTZ (Figure 3B).

The Hirshfeld surface of the PTZ molecule in PT and PT-S is mapped with \(d_{\text{norm}}\) (Figure 3C,D) using CrystalExplorer 3.1 software, where the red color indicates that the sum of the hydrogen bond d is shorter than the van der Waals radii, and the blue one is opposite. In Figure 3C, the red region...
on the PTZ surface shows that the N−H bond is connected with the N atom from the cyano group of TCNB in PT.

In contrast, in PT-S (Figure 3D), the acetonitrile molecule presents a stronger N−H···N interaction with PTZ instead of TCNB. The intermolecular hydrogen bond interactions in the crystal structures of PT and PT-S are summarized in Figures S5, S6 and Table S3, respectively. The major intermolecular interaction between TCNB and its adjacent PTZ (Figure S5A) is the C−H···N bond (the N atom is from TCNB and the C−H is from the adjacent PTZ). The distances of the C−H···N bonds in PT (2.6613−3.2883 Å) become shorter relative to those in PT-S (2.6816−3.5544 Å) (Table S3). The C−H···N hydrogen bond interactions also exist between the adjacent TCNB molecules, and their distance in PT (2.6320 Å) is shorter than that in PT-S (2.7906 Å). Each of the adjacent TCNB in PT is packed in the same plane. However, they are parallel to each other with an interplanar distance of 1.6932 Å in PT-S. Moreover, one acetonitrile is fixed in the lattice by the C−H···N with the adjacent TCNB, PTZ, and acetonitrile (Figure S6C and Table S3) in PT-S.

The C−H bonds from acetonitrile are connected to N from TCNB with the distance of 2.8751, 3.3952, 3.1741, and 3.1609 Å. The C−H bonds from PTZ are connected with the N atoms from acetonitrile with the distance of 3.0972 and 2.9834 Å. Also, the distance of the C−H···N between every two adjacent acetonitrile molecules is 2.9396 Å. The analyses of intermolecular interactions reveal that owing to the introduction of acetonitrile, the hydrogen-bond quantity increases and the short-contact distance between D and A is enlarged.

To further confirm the above conclusion, we performed the ESP analyses of PT and PT-S. The sum of surface close contact C−···C in PT (12.2%) displays 1.1%, which is lower than that in PT-S (13.3%), demonstrating that acetonitrile enhances the π−π interaction between PTZ and TCNB (Figure 5A,B).

Thus, the D/A stacking structure rearrangement is identified. With the increase of the π−π interaction, the intermolecular CT transition from PTZ (D) to TCNB (A) can be improved, and the electron density around the TCNB increases as well, leading to the lower wavenumber shifts of the Raman bands.

CONCLUSIONS

Cocrystal PT and its solvate product PT-S with the near-infrared absorption feature were successfully achieved and their intermolecular CT transition from PTZ to TCNB were improved. The intermolecular charge transfer properties were studied. Compared with the PT, acetonitrile accommodation changes the structure of the cocrystal, modifies the type of hydrogen bonds, and increases the distance of the intermolecular CT transition from PTZ to TCNB.

Figure 3. N−H···N interaction in the structure of PT (A) and PT-S (B) and the Hirshfeld surfaces of PT (C) and PT-S (D).

Figure 4. Electrostatic potential of the TCNB molecule is mapped on the Hirshfeld surface in the PT (A) and PT-S (B), respectively. The fingerprint plots of N−H and N−N interaction in PT (C, E) and PT-S (D, F).

Figure 5. Surface patches identified with C−C surface patches close contact in the PT (A) and PT-S (B).
hydrogen bond. As a result, the PT-S shows that the enhanced intermolecular charge transfer interaction resulted from the largely overlaid π–π stacking between phenothiazine and 1,2,4,5-tetracyanobenzene. The absorption edge for PT-S is located at 850 nm, which is at a shorter wavelength (800 nm) for PT. Raman analysis discloses that the C≡N vibrational peaks of PT-S shift to lower wavenumbers compared to those of PT. Both experimental data and theoretical analysis results suggest that the solvation effect leads to enhancement of the intermolecular charge transfer interaction between phenothiazine and 1,2,4,5-tetracyanobenzene. This study provides a unique example of the intermolecular charge transfer interaction that can be enhanced by means of the solvent accommodation, which is of significance for a deeper understanding of the organic charge transfer cocrystal functional materials and provides a reference for the design and preparation of the organic charge transfer cocrystal.

**EXPERIMENTAL AND THEORETICAL METHODS**

**Materials.** Phenothiazine (PTZ) (99%) and 1,2,4,5-tetracyanobenzene (TCNB) were purchased from Sigma Company (98%). Tetrahydrofuran (THF) and acetonitrile (HPLC, ≥99.9%) were obtained from Aladdin Company. All of them were directly used without further purification.

**Synthesis of Cocrystal PT and Solvate Cocrystal PT-S.** 2.0 mL of THF was used to dissolve the mixtures of PTZ power (0.0199 g) and TCNB power (0.0178 g) in a glass vial, and then the solvate was evaporated slowly at room temperature for 1 week. Finally, the black block cocrystals (PT) were obtained in the solution (Scheme 1a). To achieve the solvate cocrystal (PT-S) (Scheme 1b), 10 mM of the PTZ THF solution and 10 mM TCNB acetonitrile solution were first prepared. The PTZ THF solution was mixed rapidly with the TCNB acetonitrile solution and the mixtures were subjected to ultrasonic treatment for 2 min. Finally, the mixture solution was evaporated slowly for 1 week to achieve several bigger black block solvate cocrystals PT-S.

**X-ray Crystal Structure Determination.** The single-crystal x-ray diffraction (SXRD) data of PT and PT-S were collected at 293 K on the R-Axis RAPID diffractometer (Japan) with the Cu Kα radiation source (wavelength is 1.542 Å). The two crystal structures were solved by SHELXT with direct methods. All of the nonhydrogen atoms were located by SHELXTX directly and refined anisotropically by SHELX2018 with least squares methods. All of the hydrogens on N atoms were identified from Q-maps and refined with Uiso(H) = 1.5Uiso(O). The hydrogens on C atoms were added with the riding model. The revised data have been deposited with the Cambridge Crystallographic Data Center (CCDC) (accession codes CCDC 1882967 and 1882968). The stacking structure and intermolecular interactions of the cocrystal were analyzed via diamond software.

**Characterization.** Ultraviolet–visible (UV–vis) absorption spectra of PTZ THF solution and TCNB acetonitrile solution were recorded on a US4000 UV–vis spectrometer (Ocean Optics). The solid UV–vis absorption spectra of PT and PT-S were recorded using the U-4100 UV–vis–NIR spectrophotometer (Hitachi, Japan). The Raman spectra of PTZ, TCNB, PT, and PT-S were obtained on a LabRAM Aramis Raman spectrometer (Horiba Jobin Yvon) equipped with a 633 nm excitation line. The optical images of PT and PT-S were captured by a T64000 Raman confocal microscope system and the distances were measured by an object micrometer 0.01 mm × 100.

**Theoretical Simulation.** Combined with the SXRD crystal data, the Hirshfeld surfaces, electrostatic potential, and molecular orbital were simulated by CrystalExplorer 3.1. The Hirshfeld surfaces and the electrostatic potential (ESP) were mapped with a density functional theory (DFT), at the 6-31G(d, p) basis set using the Gaussian 09 program package. The TCNB crystal data come from CCDC no 1268166. The DCT of the cocrystal was calculated by the Mulliken population analysis. The growth morphologies of PT and PT-S were simulated by materials studio software. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01083.

**Crystal data and structure refinement; fingerprint plots of PT and PT-S, simulation and identification for the Raman bands of C≡N in TCNB, PT, and PT-S; energy level and molecular orbital of the HOMO and LUMO in the PT and PT-S; intermolecular interaction information of cocrystal PT and PT-S (PDF)**

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: xuwq@jlu.edu.cn.

**ORCID**

Shuping Xu: 0000-0002-6216-6175
Houyu Zhang: 0000-0003-0360-6035
Weiqing Xu: 0000-0002-1947-317X

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Authors gratefully thank the support from the National Natural Science Foundation of China via 12175087, 12175088 and the China Postdoctoral Science Foundation (Grant Nos 21573087, 21573092, and 91441105). The authors declare no competing financial interest.

**REFERENCES**

(1) Sun, L.; Zhu, W. G.; Yang, F. X.; Li, B. L.; Ren, X. C.; Zhang, X. T.; Hu, W. P. Molecular cocrystals: design, charge-transfer and optoelectronic functionality. *Phys. Chem. Chem. Phys.* 2018, 20, 6009–6023.

(2) Jiang, H.; Hu, P.; Ye, J.; Zhang, K. K.; Long, Y.; Hu, W. P.; Kloc, C. Tuning of the degree of charge transfer and the electronic properties in organic binary compounds by crystal engineering: a perspective. *J. Mater. Chem. C* 2018, 6, 1884–1902.

(3) Mandal, T.; Dey, A.; Pathak, S.; Islam, M. M.; Konar, S.; Castro, J. O.; Seth, S. K.; Ray, P. P.; Frontera, A.; Mukhopadhyay, S. Structures, photoresponse properties and DNA binding abilities of 4-(4-pyridyl)-2-pyridone salts. *RSC Adv.* 2019, 9, 9663–9677.

(4) Mandal, T.; Pathak, S.; Dey, A.; Islam, M. M.; Seth, S. K.; Masum, A. A.; Castro, J. O.; Ray, P. P.; Frontera, A.; Mukhopadhyay, S. Structures, photoresponse properties, and biological activity of...
(5) Bora, P.; Saikia, B.; Sarma, B. Regulation of π−π stacking interactions in small molecule cocrysals and/or salts for physicochemical property modulation. *Cryst. Growth Des.* 2018, 18, 1448–1458.

(6) Riwar, L. J.; Trapp, N.; Kuhn, B.; Diederich, F. Substituent effects in parallel-displaced π−π stacking interactions: distance matters. *Angew. Chem., Int. Ed.* 2017, 56, 11252–11257.

(7) Sangtani, E.; Mandal, S. K.; Sreelakshmi, A. S.; Munshi, P.; Gonnade, R. G. Salts and cocrysals of furosemide with pyridines: differences in π-stacking and color polymor. *Cryst. Growth Des.* 2017, 17, 3071–3087.

(8) Li, A. S.; Wang, J.; Liu, Y. J.; Xu, S. P.; Chu, N.; Geng, Y. J.; Li, B.; Xu, B.; Cui, H. N.; Xu, W. Q. Remarkable pressure-induced emission enhancement based on intermolecular charge transfer in halogen bond-driven dual-component co-crysals. *Phys. Chem. Chem. Phys.* 2018, 20, 30297–30303.

(9) Topić, F.; Rissanen, K. Systematic construction of ternary cocrysals by orthogonal and robust hydrogen and halogen bonds. *J. Am. Chem. Soc.* 2016, 138, 6610–6616.

(10) Sokolov, A. N.; Frisicic, T.; MacGillivray, L. R. Enforced face-to-face stacking of organic semiconductor building blocks within hydrogen-bonded molecular cocrysals. *J. Am. Chem. Soc.* 2006, 128, 2806–2807.

(11) Harris, K. D. M.; Stainton, N. M.; Callan, A. M.; Howie, R. A. Crystal engineering of hydrogen-bonded co-crysals between cyanyric acid and ‘diamide’ molecules. *J. Mater. Chem.* 1993, 3, 947–952.

(12) Zhu, W.; Zheng, R. H.; Fu, X. L.; Fu, H. B.; Shi, Q.; Zhen, Y. G.; Dong, H. L.; Hu, W. P. Revealing the charge-transfer interactions in self-assembled organic cocrysals: two-dimensional photonic applications. *Angew. Chem., Int. Ed.* 2015, 54, 6785–6789.

(13) Sun, Y. Q.; Lei, Y. L.; Dong, H. L.; Zhen, Y. G.; Hu, W. P. Solvatomechanical bending of organic charge transfer cocrysal. *J. Am. Chem. Soc.* 2018, 140, 6186–6189.

(14) Sutton, A. L.; Abrahams, B. F.; D’Alessandro, D. M.; Elliott, R. W.; Hudson, T. A.; Robson, R.; Usov, P. M. Structural and optical investigations of charge transfer complexes involving the F$_2$TCNQ dianion. *CrystEngComm* 2014, 16, 5234–5243.

(15) Vermeulen, D.; Zhu, L. Y.; Goetz, K. P.; Hu, P.; Jiang, H.; Day, C. S.; Jurcescu, O. D.; Coropceanu, V.; Kloc, C.; McNei, L. E. Charge transport properties of Perylene-TCNQ crystals: the effect of stoichiometry. *J. Phys. Chem. C* 2014, 118, 24688–24696.

(16) Khorasani, S.; Fernandes, M. A. A Synthetic co-crysatal prepared by cooperative single-crystal-to-single-crystal solid-state diels–alder reaction. *Chem. Commun.* 2017, 53, 4969–4972.

(17) Tahara, K.; Fujita, T.; Sonoda, M.; Shiro, M.; Tobe, Y. Donors and acceptors based on triangular dehydrobenzo [12] annulenes: formation of a triple-layered rosette structure by a charge-transfer complex. *J. Am. Chem. Soc.* 2008, 130, 14339–14345.

(18) Usman, R.; Khan, A.; Sun, H.; Wang, M. L. Study of charge transfer interaction modes in the mixed donor-acceptor cocrysals of pyrene derivatives and TCNQ: a combined structural, thermal, spectroscopic, and Hirshfeld surfaces analysis. *J. Solid State Chem.* 2018, 266, 112–120.

(19) Liu, G. F.; Liu, J.; Ye, X.; Nie, L.; Gu, P.; Tao, X. T.; Zhang, Q. C. Self-healing behavior in a thermo-mechanically responsive cocrysatal during a reversible phase transition. *Angew. Chem., Int. Ed.* 2017, 56, 198–202.

(20) Zhang, J.; Xu, W.; Sheng, P.; Zhao, G. Y.; Zhu, D. B. Organic donor-acceptor complexes as novel organic semiconductors. *Acc. Chem. Res.* 2017, 50, 1654–1662.

(21) Qin, Y.; Zhang, J.; Zheng, Y. Y.; Geng, H.; Zhao, G. Y.; Xu, W.; Hu, W. P.; Shuai, Z. G.; Zhu, D. B. Charge-transfer complex crystal based on extended-π-conjugated acceptor and sulfur-bridged annulene: charge transfer interaction and remarkable high ambipolar transport characteristics. *Adv. Mater.* 2014, 26, 4093–4099.
(39) Wang, Y.; Zhu, W. G.; Du, W. N.; Liu, X. F.; Zhang, X. T.; Dong, H. L.; Hu, W. P. Cocrystals strategy towards novel materials for near-infrared photothermal conversion and imaging. Angew. Chem., Int. Ed. 2018, 57, 3963–396.

(40) Sun, Y. Q.; Lei, Y. L.; Sun, X. H.; Lee, S. T.; Liao, L. S. Charge-transfer emission of mixed organic cocrystal microtubes over the whole composition range. Chem. Mater. 2015, 27, 1157–1163.

(41) Khan, A.; Wang, M. L.; Usman, R.; Sun, H.; Du, M.; Xu, C. X. Molecular marriage via charge transfer interaction in organic charge transfer co-crystals toward solid-state fluorescence modulation. Cryst. Growth Des. 2017, 17, 1251–1257.

(42) Hu, P.; Li, H. N.; Li, Y. X.; Jiang, H.; Kloc, C. Single-crystal growth, structures, charge transfer and transport properties of anthracene-F4TCNQ and tetracene-F4TCNQ charge-transfer compounds. CrystEngComm 2017, 19, 618–624.

(43) Hu, P.; Wang, S. C.; Chaturvedi, A.; Wei, F. X.; Zhu, X. T.; Zhang, X. T.; Li, R. J.; Li, Y. X.; Jiang, H.; Long, Y.; Kloc, C. Impact of C-H···X (X = F, N) and π-π interactions on tuning the degree of charge transfer in F6TNAP-based organic binary compound single crystals. Cryst. Growth Des. 2018, 18, 1776–1785.

(44) Hu, P.; Du, K. Z.; Wei, F. X.; Jiang, H.; Kloc, C. Crystal growth, HOMO-LUMO engineering, and charge transfer degree in perylene FxTCNQ (x = 1, 2, 4) organic charge transfer binary compounds. Cryst. Growth Des. 2016, 16, 3019–3027.

(45) Ono, T.; Tsukiyama, Y.; Taema, A.; Sato, H.; Kiyooka, H.; Yamada, Y.; Nagahashi, A.; Nishiyama, M.; I.; Y.; A.; Otawa, Y.; Abe, M.; Hisaeda, Y. Piezofluorochromism in charge-transfer inclusion crystals: the influence of high pressure versus mechanical grinding. ChemPhotoChem 2018, 2, 416–420.

(46) Liu, Y. J.; Zeng, Q. X.; Zou, B.; Liu, Y.; Xu, B.; Tian, W. J. Piezochromic luminescence of donor–acceptor cocrystals: distinct responses to anisotropic grinding and isotropic compression. Angew. Chem., Int. Ed. 2018, 57, 15670–15674.

(47) Wu, X. J.; Wang, M. L.; Du, M.; Lu, J.; Chen, J. X.; Khan, A.; Usman, R.; Wei, X.; Feng, Q.; Xu, C. X. Reversible accommodation and desorption of aromatics on a charge transfer cocrystal involving an anthracene derivative and TCNQ. Cryst. Growth Des. 2015, 15, 434–441.

(48) Zhang, J.; Liu, G. F.; Zhou, Y. C.; Long, G. K.; Gu, P. Y.; Zhang, Q. C. Solvent accommodation: functionalities can be tailored through co-crystallization based on 1:1 coronene-F4TCNQ charge-transfer complex. ACS Appl. Mater. Interfaces 2017, 9, 1183–1188.

(49) Seth, S. K. The importance of CH···X (X = O, II) interaction of a new mixed ligand Cu(II) coordination polymer: structure, hirshfeld surface and theoretical studies. Crystals 2018, 8, 455.

(50) Seth, S. K.; Bauzá, A.; Frontera, A. Screening polymorphism in a Ni(II) metal–organic framework: experimental observations, Hirshfield surface analyses and DFT studies. CrystEngComm 2018, 20, 746–754.

(51) Wolff, S. K.; Grimwood, D. J.; McKinnon; Wolff, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer 3.1; University of Western Australia, 2012.

(52) Spackman, M. A.; Jayatilaka, D. Hirshfeld surface analysis. CrystEngComm 2009, 11, 19–32.

(53) Spackman, M. A.; McKinnon, J. J.; Jayatilaka, D. Electrostatic potentials mapped on Hirshfeld surfaces provide direct insight into intermolecular interactions in crystals. CrystEngComm 2008, 10, 377–388.

(54) Zhuo, M. P.; Tao, Y. C.; Wang, X. D.; Wu, Y. C.; Chen, S.; Liao, L. S.; Jiang, L. 2D organic photonics: an asymmetric optical waveguide in selfassembled halogen-bonded cocrystals. Angew. Chem., Int. Ed. 2018, 57, 11300–11304.

(55) George, M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.