A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201810149
Angew. Chem. 10.1002/ange.201810149

Link to VoR: http://dx.doi.org/10.1002/anie.201810149
http://dx.doi.org/10.1002/ange.201810149

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Piezochromic Luminescence of Donor−Acceptor Co-crystal: Distinct Responses to Anisotropic Grinding and Isotropic Compression

Yingjie Liu,[a] Qingxin Zeng,[b] Bo Zou*,[b] Yu Liu,[a] Bin Xu*, [a] and Wenjing Tian[a]

Piezochromic luminescent materials that exhibit distinct luminescence responses to different types of mechanical stresses have been emerging as a kind of new important materials which are rarely investigated. Here, we report a donor−acceptor (D-A) charge-transfer (CT) co-crystal, which show a distinct hypochromatic and bathochromatic shifts upon anisotropic grinding and isotropic compression, respectively. Detailed spectroscopic and structural analyses revealed that the hypochromatic shifted emission under grinding is attributable to a structural reorganization from loosely segregated-stack to mixed-stack, while the bathochromatic shifted emission originates from the closer proximity to the formation of the tight packing structure. The study presents a very rare evidence of distinct luminescent response to anisotropic grinding and isotropic compression on the basis of structural rearrangement in a D-A co-crystal, and thus enriches the insight of the piezochromic luminescence.

Piezochromic luminescent materials with multi-color switching are recently attracted enormous research interest due to their appealing applications in advanced photonics, such as optical recording, security ink, memory and sensors.[1] Various piezochromic materials based on organic molecules, metal complexes, and polymers have been devised showing actively controllable luminescence characteristics response to external mechanical stimuli, such as grinding, shearing, tension or hydrostatic pressure.[2] However, there are only few reports on materials that show the switchable luminescence responses to different types of mechanical forces.[3] For example, Zhang and co-workers demonstrated a boron diketonate crystal exhibiting a blue-shifted emission under tension, but a red-shifted emission under grinding and compressing.[3b] Yamaguchi et al. reported a tetrathiazolylthiophene fluorophore which displays distinct luminescent responses to grinding and compressing.[3a] But in these cases, when treated by grinding, the original crystals convert into amorphous powders, so that it is difficult to establish the relationship between the fluorescent properties and molecular packing structure of the grinded solids.

In recent years, big progress has been made[4] in the study of supramolecular assembly whose main driving forces are noncovalent interactions, such as π-π interactions, hydrogen and halogen bonds, charge-transfer (CT) interactions, electrostatic interactions and host − guest Interactions, etc. The organic co-crystal,[5] in which π-conjugated components can self-assemble in long term ordered structure based on the supramolecular interactions is one of the most important supramolecular assemblies. It is a promising way to forecast the presence of multiple phases of co-crystal itself and its fluorescence changes during the structural alteration.[6] Organic co-crystals with typical mixed or segregated stacking of donor (D) and acceptor (A) molecules show unique physicochemical properties since the intermolecular D-A pairs give rise to the distinct band energies originated from localized frontier molecular orbitals (FMOs).[7] In these D-A co-crystals, the Coulombic interactions induced from the large energetic offset between D and A lead to the intended loosely packed stacking structure, which is benefit for a stimuli responsive feature.[6a] For instance, Park et al. reported that the luminescence of a crystalline donor–acceptor mixture film had blue shift from 658nm to 472nm due to the structural transformation from the mixed phase into demixed phase under solvent vapor annealing, and then recover to the original color under grinding or thermal stimuli.[6a] It is expected that a piezochromic system can be achieved by using appropriate donor and acceptor pairs in which there is a moderate intermolecular interactions design for a flexible packed structure. However, up to now there is nearly no reports on the organic D-A co-crystals with distinct responses to different mechanical stimuli.

Herein we report the distinct luminescent responses to anisotropic grinding and isotropic compression from a D-A co-crystal, called CT-R, in which 1, 4-bis-p-cyanostyrylbenzene (CNDSB) severs as donor (D) and TCNB as acceptor (A). It shows a unique enhanced hypochromatic shifted emission under grinding, but a remarkable bathochromic shifted emission under hydrostatic pressure. An in-depth understanding of luminescence switch has been elucidated through a precise correlation of the chemical, structural, optical and thermal properties

1, 4-bis-p-cyanostyrylbenzene (CNDSB) was readily synthesized by the Wittig-Horner reaction[8] (Scheme S1). Because of their simple and rigid molecular structure, CNDSB and TCNB together hold strong crystallization tendency. Red CT-R co-crystals with block-like shape (Figure 1) were obtained by solvent evaporation process, where CNDSB and TCNB were mixed with a molar ratio of 4:3 in a dichloromethane solution. Compared with the individual component CNDSB and TCNB, CT-R showed a new, broad bathochromic-shifted absorption at around 490 nm (Figure S1a). The red emission of co-crystal peaked at 643 nm (Figure S1b), which is also greatly red-shift compared with that of CNDSB and TCNB crystals. In addition, the CT-R co-crystal showed high solid-state photoluminescence quantum yield (PLQY) (Φ_F) up to 13.0% (Table S1). This redshifted absorption and emission features indicate existence

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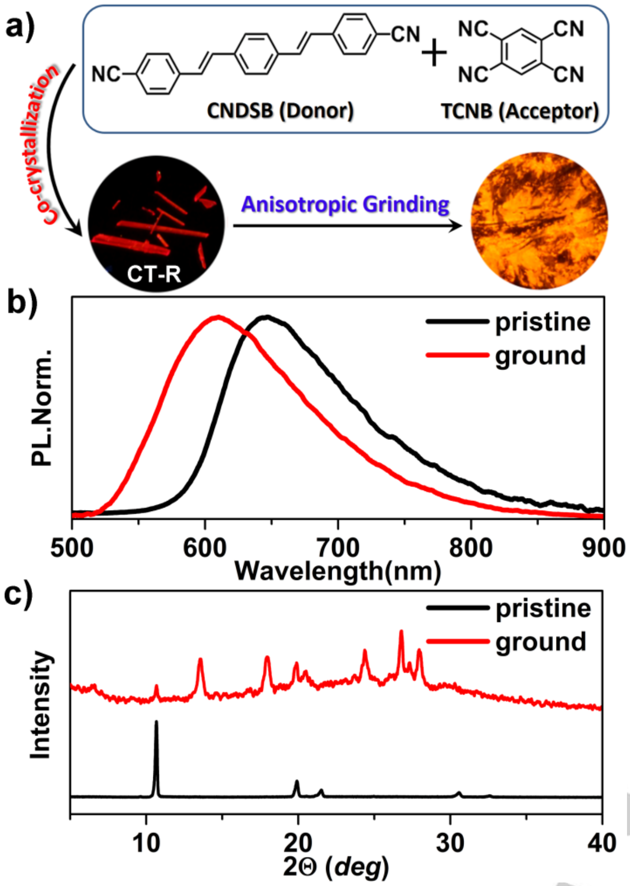

Figure 1. a) Molecular structure of the resulting CT-R co-crystal. b) Fluorescence images, c) corresponding fluorescence spectra and PXRD patterns of CT-R co-crystal before and after ground.

of CT excitations between CNDSB and TCNB, where CNDSB molecules act as the donors (D) and TCNB as the acceptors (A).[6a, 9] This is consistent with the slightly longer fluorescence lifetime of the red emission in CT-R co-crystal (17.5 ns, Figure S3) against that of the yellow emission in CNDSB crystal (13.1ns). The radiation rate constant (k_r) of CT-R are calculated to be 7.48×10^{6} s^{-1}, and it is very near to the typical value of a CT complex.[9b, 10] This relatively slow radiation implies its CT transition nature, further confirmed by electron spin resonance (ESR) measurements (Figure S3). A sharp signal was observed centered at the magnetic field of 3506 G, indicating the presence of unpaired electrons in the co-crystals.[11] The g-factor calculated from the ESR theory is 2.0042, which is similar to the value of free electron (2.0023). These behaviors disclose the CT interactions between CNDSB and TCNB.

To our surprise, the emission of pristine co-crystals exhibited obviously hypochromatic shift after grinding the samples (Figure 1). The ground powders showed bright orange fluorescence with an increased PLQY up to 22% and a 33 nm spectral shift to 610 nm. The powder X-ray diffraction (PXRD) curve of the pristine sample had sharp and high diffraction peaks (Figure 1c), indicating a well-ordered crystalline structure of CT-R crystals. The ground powders, however, showed a number of broad and strong diffraction peaks. Although some resolvable peaks of the ground sample were consistent with those of the pristine sample, the relative intensity was greatly reduced. It is worthy to note that the new diffraction peak position of the obtained ground sample is completely different from that of the pristine crystalline sample. It suggests that the initial molecular arrangements in the co-crystal have been destructed and may be undergoing reorganization to new crystallization state during the grinding processes.

In addition, the switchable fluorescence feature can also occur by the thermal stimulus. By heating the crystals at 145˚C for 12h in an oven and cooling down to room temperature, the red-emitting sample turned into orange-emitting solids (see Figure S4 a, b). The heated samples exhibited a broad emission band peaked at about 575 nm which is blue-shifted by about 68 nm compared with that of the pristine crystals. Moreover, the heated samples possessed a sharp PXRD signal (Figure S4c), which matched well with that of ground sample. From the differential scanning calorimetry (DSC) curves (Figure S5), there showed a transition around 145 °C prior to melting at 293 °C, implying that there should have a crystallization processes during thermal treatments.[12]

On the other hand, CT-R co-crystal showed a significant bathochromic shift in both emission and absorption under hydrostatic pressure (Figure 2). The high-pressure experiments were performed by using a diamond anvil cell (DAC) with silicone oil as a pressure-transmitting medium. During the compression process, the absorption spectra were gradually red-shifted from around 490 nm to 640 nm and simultaneously the red single crystal progressively became dark red. Besides, the fluorescence maximum peak was gradually red-shifted and its intensity gradually decreased, and eventually to a near infrared emission at 744 nm when the pressure reached at 5.08 GPa. The large wavelength difference of 104 nm in the red shift was observed. It should be noted that both of the absorption and fluorescence spectra can recover to the original absorption and emission band, respectively, when the hydrostatic pressure was

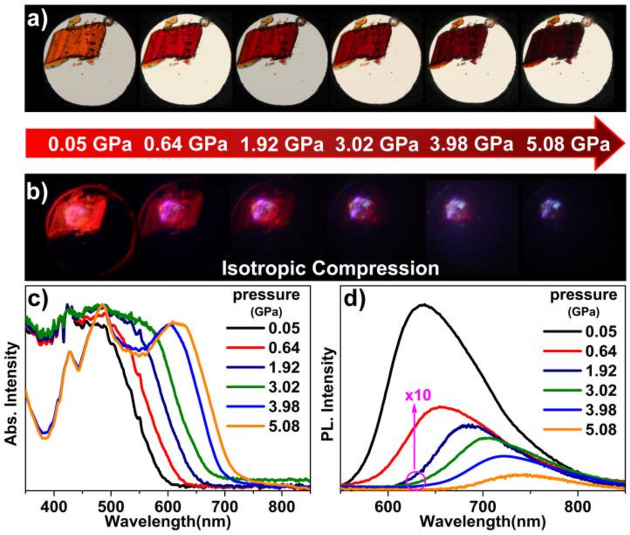

Figure 2. a, b) Visible and fluorescence images of a single crystal of CT-R under different hydrostatic pressures. c, d) Corresponding absorption and fluorescence spectra. The value of the four curves in the magenta circle is magnified tenfold.

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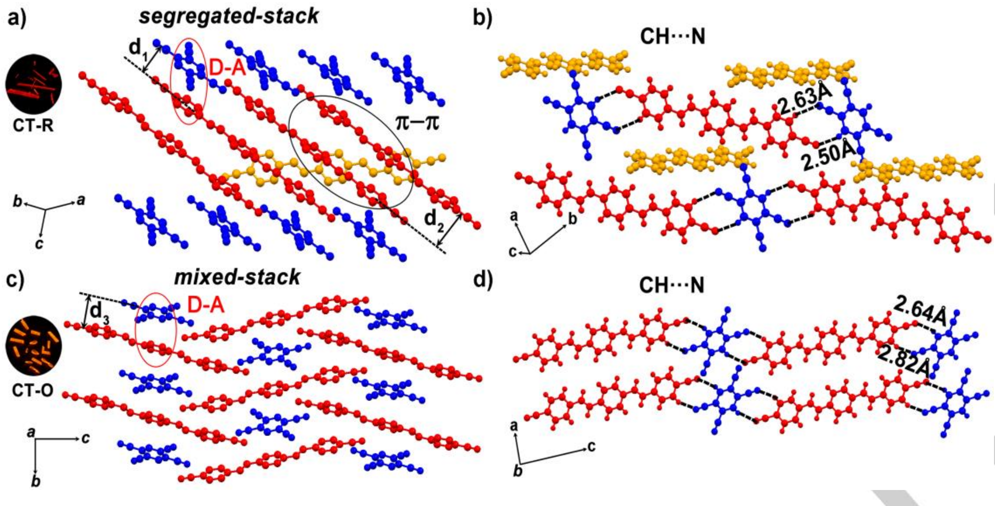

Figure 3. Single crystal under UV light (365 nm) and stacking modes of a) CT-R and c) CT-O. Hydrogen atoms are omitted for clarity. d_1 = 3.44 Å, d_2 = 3.33 Å, d_3 = 3.54 Å. C-H···N intermolecular interactions in b) CT-R and d) CT-O.

returned to ambient pressure (Figure S6). The unique restorability in the luminescence behavior implies that the molecular packing mode in CT-R crystal would not change substantially during the high-pressure experiment processes.[13] Therefore, these observations of CT-R co-crystals under the different mechanical force stimuli suggest that this unique piezochromic behavior may come from the different nature.

The luminescent materials that show such distinct luminescence responses to anisotropic grinding and isotropic compression are rarely presented, although some materials have been reported to show the switchable luminescence under the external mechanical force stimuli. First, the observed unique piezochromism feature in the CT-R co-crystal is quite different from the previous reports about the single component luminescent materials,[3] where the luminescence comes from the two-component CT complex. In addition, the grinding induced luminescence of CT-R shows not only enhanced solid state efficiency, but also a hypochromatic shift to the short-wavelength region, whereas the compression induced luminescence tends to a bathochromic shifted and weakened emission. These observations give us a greatest opportunity to enrich the understanding of the mechanism of piezochromic behavior based on organic luminescent materials.

Surprisingly, further mixing CNDSB and TCNB with a molar ratio of 1:1 in a dichloromethane solution, bright orange emitting crystals with high PLQY (26.2%), named CT-O, were obtained by solvent evaporation process. The emission of CT-O was located at around 600 nm (Figure S7), which is close to that of ground sample of CT-R crystals. More importantly, the PXRD pattern of CT-O is fully consistent with ground samples of CT-R, demonstrating that the obtained ground samples adopt a same molecular arrangement as those of the CT-O polymorph (Figure S9). Moreover, upon grinding the CT-R crystals, the Raman peaks (Figure S10) located at the wavenumber range of 1150-1650 cm^{-1} slightly shifted towards high frequency vibration, and finally coincided with the Raman spectrum of CT-O. The comparisons in both PXRD and Raman spectra before and after grinding the co-crystals suggest that CT-R undergoes a molecular rearrangement process to a packing structure analogous to CT-O under grinding, which also agreed with thermal analysis.

The structural analysis of two polymorphs of co-crystal could give insights into the nature of the emission in the crystalline state and its piezochromic luminescence behavior. CT-R held the triclinic crystal system and P -1 space group, while CT-O was crystallizing in the monoclinic crystal system and space group P 21/n.[14] They crystallized in different stoichiometric packing ratios of CNDSB (D) and TCNB (A), which is 4:3 for CT-R and 1:1 for CT-O, respectively. CT-R exhibited the segregated stacking mode (Figure 3a), which was consists of segregated D and A molecular columns with an intermolecular D–D distance of 3.44 Å and D–A distance of 3.33 Å, thus giving rise to moderate π-π and CT interactions, respectively. The two types of C-H···N hydrogen bonds (Figure 3b and Figure S11 and S12), as self-assembly driving forces along distinct directions, make molecules aggregate and expand to form linear molecular chains. In sharp contrast, CT-O possessed the mixed stacking mode and consisted of a longer

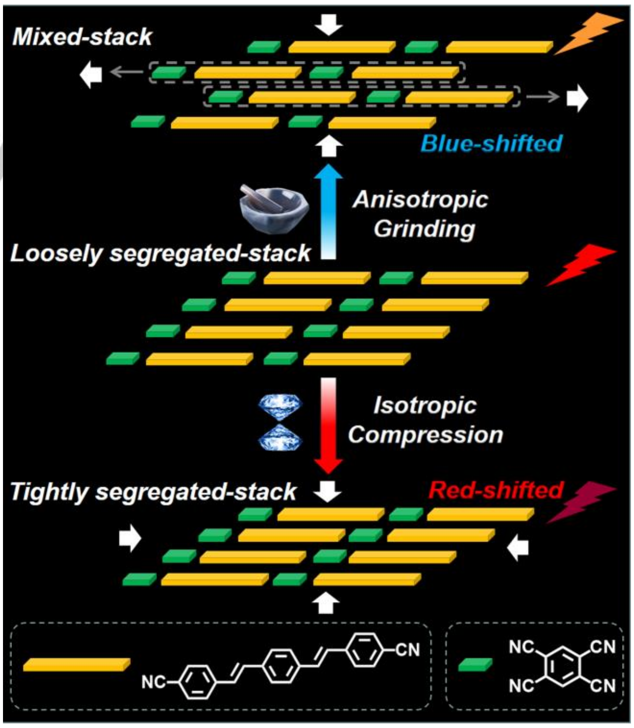

Figure 4. Transition modeling schematic of molecular stacking mode in CT-R co-crystal under different mechanical force stimuli.

D-A intermolecular distance of 3.54 Å along b axis (Figure 3c). There are almost no π-π interactions between adjacent CNDSB molecules, whereas the two types of intermolecular C-H⋯N interactions (Figure 3d, Figure S13 and S14) result in unique mixed alterative molecular columns. These relatively weak intermolecular interactions and the intended loosely packed molecular arrangement are necessary for a stimuli responsive feature.

Putting all the experimental data together enable us to draw a clear overall picture of the unique piezochromic luminescent behavior of CT-R co-crystal (Figure 4). Upon the grinding, the loosely stacking molecular columns in CT-R may happen to slide along the molecular stretching orientation since the strong and directional C-H⋯N interactions within the molecular chains, where the slide direction between adjacent molecular columns could be opposite due to the anisotropic shear force. A structural reorganization thus can be realized from the segregated-stack to the mixed-stack, resulting in the weaken π-π and CT interactions among CNDSB and TCNB. Accordingly, the observed enhanced and blue shifted emission of the ground samples possibly originated from integrating of the weaken exciton coupling between the pairs of neighboring CNDSB and CT transition strength. On the other hand, the hydrostatic pressure induces molecules to form tighter packing structure,[3a, 13] which was demonstrated through the optimized lattice parameters of CT-R under the external stress calculated by the CASTEP module (Table S4 and S5). The interfacial distance between the mean planes of D-A molecules (d_1) and D-D molecules (d_2) becomes much shorter from 3.44 Å to 3.03 Å and 3.33 Å to 2.95 Å, respectively. It suggests that the hydrogen bonded lattice is deformed, which reduces the void space among the adjacent moieties. As a result of the closer proximity, the enhanced π-π and CT interactions is formed without changing segregated stacking mode, which is likely the origin of the red-shifted emission under isotropic compression.

In summary, we have successfully demonstrated the distinct luminescent responsive feature to anisotropic grinding and isotropic compression based on a donor-acceptor co-crystal CT-R. The intermolecular CT, π-π, C-H⋯N interactions are the driving forces for self-assembly and result in the loosely segregated packing mode. Grinding of the crystals leads to a structural rearrangement from segregated-stack to mixed-stack in which π-π and CT interactions are weakened and hence results in a blue-shifted and enhanced emission. In contrast, the hydrostatic pressure leads to a remarkable red-shifted emission, originating from the closer arrangement and enhanced π-π and CT interactions. These structural deformations of the non-covalent interaction network upon mechanical stress were fully confirmed by both experimental and theoretical studies. Hence, the clear distinction of piezochromic luminescent responses through the structural reorganization is achieved using the co-crystal approach by changing the solid state and the types of the mechanical forces. Furthermore, we anticipate that the rational molecular design and crystal engineering strategy presented here might not only provide important insight for the supramolecular control of intermolecular interaction by external stimuli, but the discrimination between anisotropic grinding and isotropic compression would also accelerate and enrich the chemistry of the piezochromism.

Acknowledgements

This work was supported by the Natural Science Foundation of China (51773080, 21674041, 51573068, 21725304), Program for Changbaishan Scholars of Jilin Province, Jilin Province project (20160101305JC), and the “Talents Cultivation Program“ of Jilin University.

Keywords: anisotropic grinding • donor−acceptor co-crystal • isotropic compression • molecular rearrangement • piezochromic materials

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[14] CCDC 1836790 (CT-R), 1567482 (CT-O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Structure solution and refinement were conducted using SHELX-97 and Olex2 1.2.

Entry for the Table of Contents

COMMUNICATION

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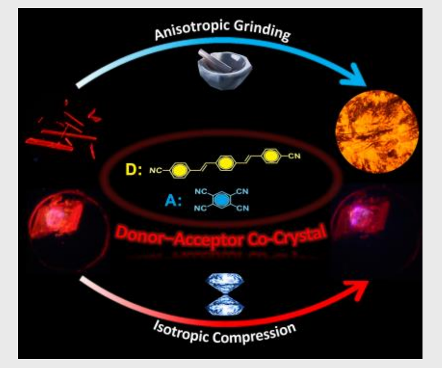

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