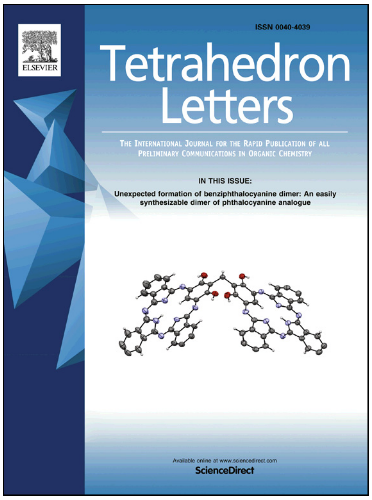

Relationship between mechanochromic behavior and crystal structures in donor-π-acceptor compounds consisted of aromatic rings with ester moiety as an acceptor

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PII: S0040-4039(17)30949-8
DOI: http://dx.doi.org/10.1016/j.tetlet.2017.07.085
Reference: TETL 49167

To appear in: *Tetrahedron Letters*

Received Date: 20 June 2017
Revised Date: 20 July 2017
Accepted Date: 25 July 2017

Please cite this article as: Matsumoto, S., Moteki, J., Ito, Y., Akazome, M., Relationship between mechanochromic behavior and crystal structures in donor-π-acceptor compounds consisted of aromatic rings with ester moiety as an acceptor, *Tetrahedron Letters* (2017), doi: http://dx.doi.org/10.1016/j.tetlet.2017.07.085

Tetrahedron Letters
journal homepage: www.elsevier.com

Relationship between mechanochromic behavior and crystal structures in donor-π-acceptor compounds consisted of aromatic rings with ester moiety as an acceptor

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

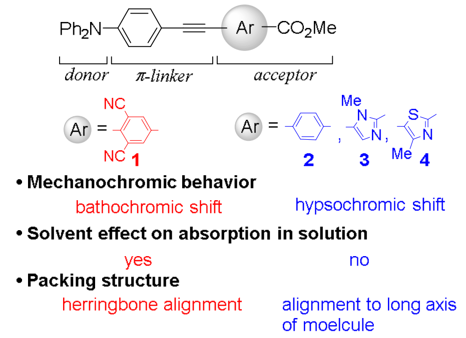
Keywords:
Mechanochromism
Donor-π-acceptor compounds
Crystal structure
Bathochromic shift
Hypsochromic shift

ABSTRACT

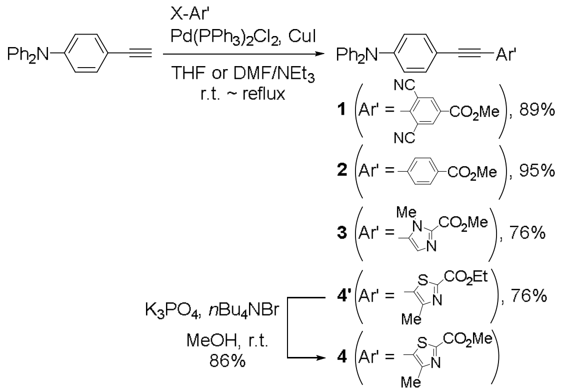
We investigated the mechanochromic behavior of donor-π-acceptor compounds which consisted of diphenylaminophenylacetylene as a donor-π moiety and (hetero)aromatic ring bearing ester as an acceptor. The compounds with dicyanobenzoic ester gave the bathochromic shift by grinding, whereas the compounds consisted of the ester with benzene, imidazole, and thiazole rings showed the hypsochromic shift. From single-crystal X-ray analysis, we revealed that the compound with bathochromic shift gave the herringbone alignment with *H*-aggregate-like π-stacking in the crystal structure. On the contrary, the compounds with hypsochromic shift showed the structure with the alignment of long axis of the molecule in crystal structure.

Organic compounds possess a variety of functional properties such as medicinal, optical, and electronic ones. Especially, π-conjugated materials are utilized for the sensing of light. Recently, mechanochromic phenomena focus on the scientific investigation in the light of their fluorescence properties.[1] The mechanochromic materials can be reverted to original colors by recrystallization, vapor exposure, heating, and so on. Such a reversible mechanochromic performance can be obtained by changing the molecular conformations and packing structures when the molecular structure is not destroyed during grinding.[2] Plenty of mechanochromic materials have been reported with various structural features.[3] However, the control of the direction of the wavelength change is still a challenging problem. During our investigation on the donor-π-acceptor materials for dye-sensitized solar cells,[4] we found that the mechanochromism of the compounds consisted of diphenylamine, phenylethynyl, and (hetero)aromatic ring with ester moiety as a donor, π-linker, and acceptor, respectively. Herein, we report the bathochromic and hypsochromic shift of donor-π-acceptor compounds (**1**-**4**) (Scheme 1) by grinding. The compounds had the resembled features on the absorption in the solution and on the crystal structures according to the mechanochromic property.

The compounds were synthesized by Sonogashira coupling reaction with *p*-(diphenylamino)phenylacetylene[5] and the corresponding aryl halide (Scheme 2). We uniformed methyl esters to avoid the differences derived from the ester moiety. Transformation of ester moiety was required in the synthesis of **4**. The conversion of ethyl ester to methyl ester was achieved by the transesterification reported by Cepanec and co-workers.[6]



Scheme 1. Structure and features of the reported compounds.



Scheme 2. Synthesis of compounds (**1**-**4**).

The mechanochromism was examined by ground with an agate mortar. The yellow color of the crystals of **1** changed into a bright-red color by grinding (Figure 1a (inset)).[7] This change was supported by the spectral change in solid-state diffused reflection-absorption spectra. Before grinding, the maximum absorption peak (λ_{max}) was observed at 444 nm (Figure 1a). Absorbance at a longer wavelength was increased by grinding. As a result, a bathochromic shift was observed. On the contrary, the hypsochromic shifts were observed in **2**, **3**, and **4**. In the case of **2**, λ_{max} of shorter wavelength at 424 nm with a small peak at 536 nm appeared from the ground solid of **2**, whereas the crystals showed λ_{max} at 448 nm (Figure 1b). The decrease of the absorption at a longer wavelength was observed in the case of the crystals of **3** and **4** with the hypsochromic shift of λ_{max} (Figure 1c, d). The peak tops of the spectra included in the shoulder peaks were concerned with visualized color based on the Griffiths's color circle.[8] λ_{max} of **1** was observed at 444 nm before grinding. The complementary color at that wavelength is estimated as a yellow color on the Griffiths's color circle. After grinding, λ_{max} was kept at 444 nm, but the shoulder peak at 522 nm appeared, whose complementary color is a red color. In the case of **2**, the change of λ_{max} from 448 nm to 424 nm was observed. The border line between yellow and yellowish-green in the Griffiths's color circle is 435 nm. Thus, the slight color change of **2** in visual contact was observed (Figure 1b (inset)). The color of **3** before grinding is a faint orange, which was supported by the complementary color of the shoulder peak of **3** (464 nm). Furthermore, the color of ground **3** was pale yellow. Actually, λ_{max} of ground **3** was observed at 394 nm in nearly ultra violet region. As the same manner, the color of **4** was changed from orange to yellow, whose complementary colors included the shoulder or peak of absorption of **4** (522 nm for former-ground sample and 452 nm for ground sample).[9] All compounds could be obtained the pre-ground color by recrystallization from *n*-hexane and $CHCl_3$.

To get the information about the change of the crystal structure, we conducted a power X-ray diffraction analysis on the compounds before and after grinding (Figure S1). As the results, all diffraction patterns after grinding were shown to have broadened peaks compared with the diffraction patterns before grinding, which would be caused by a decrease of the crystallinity. We could not obtain the amorphous patterns with entire broadening of the peaks, even after hard grinding. However, the conditions of the solid should be changed from a highly-ordered crystalline state to amorphous-like diffused one, and those differences would be the reason for the mechanochromic phenomenon.

All of the crystal structures could be revealed by a single-crystal X-ray analysis (Figure 2), whose crystal was obtained by the recrystallization from *n*-hexane and $CHCl_3$.[10] Although the molecules of **2**, **3**, and **4** aligned toward a long axis of the molecule (Figure 2b, 2c, and 2d, respectively), the herringbone packing in **1** was found in its crystal structure with *ca.* 80° deviation (Figure 2a). It seems to be a clear contrast in the mechanochromic behavior.

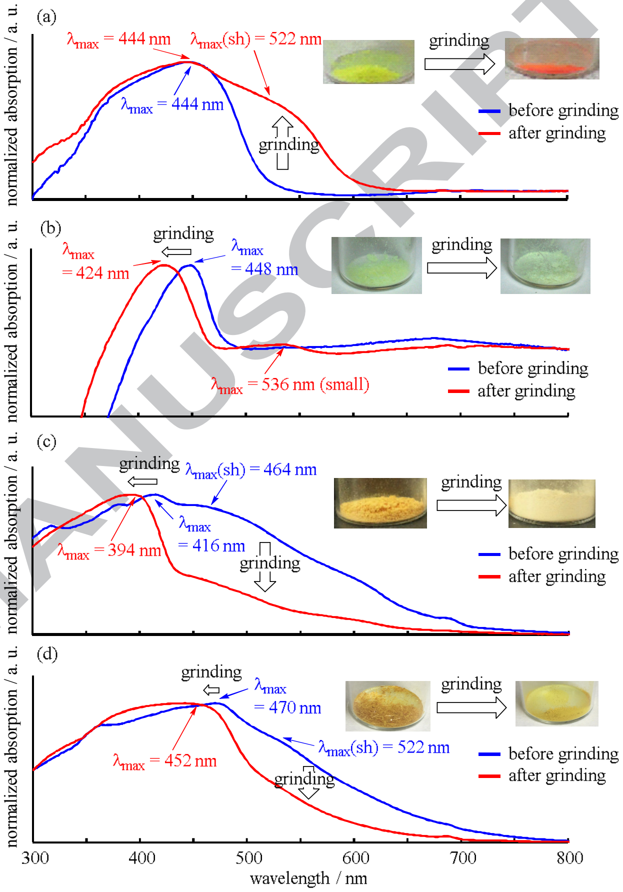


Figure 1. Solid-state diffused absorption-diffraction spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4** before and after grinding (blue and red lines, respectively). Insets were photographs of the solids before and after grinding.

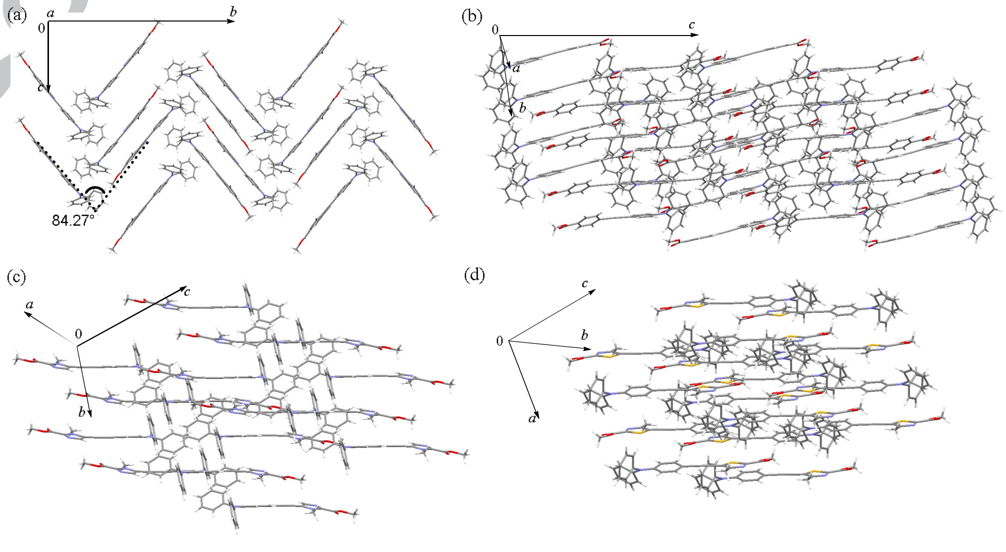


Figure 2. Packing structure of (a) **1**, (b) **2**, (c) **3**, and (d) **4** by single-crystal X-ray analysis represented in 2×2×2 cells.

Focused on the π-stacking interaction, two molecules of **1** were constructed as a dimer by stacking on a π-conjugated skeleton with short contacts between C atoms on dicyanobenzoate moiety and phenylacetylene moiety with 3.381 and 3.327 Å (depicted as **A** and **B** in Figure S4a) within the sum of van der Waals radii (3.54 Å = 1.77 Å (C(arom.)) + 1.77 Å (C(sp^2))[11]; two molecules were aligned alternately. Furthermore, each dimer was contacted with the interaction between the cyano group and carbon on methoxycarbonyl group (3.161 and 3.399 Å) (depicted as **C** and **D** in Figure S4a) cut in the sum of van der Waals radii (3.32 Å = 1.77 Å (C(arom.)) + 1.55 Å (N(sp^2)). The alignment of each dimer also situated alternately. The distances between π-planes in the dimer and between the dimers was estimated as 3.305 and 3.325 Å, respectively. In the crystal of **2**, there were two geometrically different isomers in crystal of **2**. The short contact with π-π interaction was observed in ester moieties (depicted as **A** in Figure S4b). The distance was within the sum of van der Waals radii (3.27 Å = 1.77 Å (C(arom.)) + 1.50 Å (O(sp^2)). However, there is no efficient π-stacking for the π-planes of **2**. Overlap of the π-planes was only observed between two molecules with a distance of 3.559 Å, which was longer than those of **1**, and the alignment of the molecules situated alternately. In the case of **3** and **4**, there was no short contact of each atoms between the π-planes (Figure S4c and S4d). In addition, the distances between neighboring π-planes for **3** and **4** were longer than those of **1**. In the crystal of **3**, continuous overlap of π-planes at a distance of 3.687 Å was observed with a similar direction in each molecule (Figure S4c). In the crystal of **4**, one overlap of π-planes at a distance of 3.799 Å was observed with alternated alignment of each molecule. And another overlap of π-planes was shown too long distance (5.592 Å).

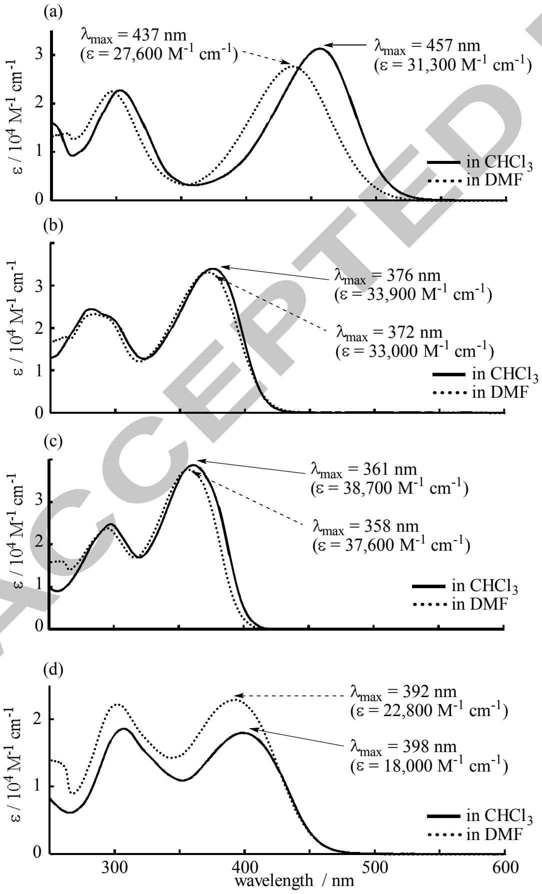
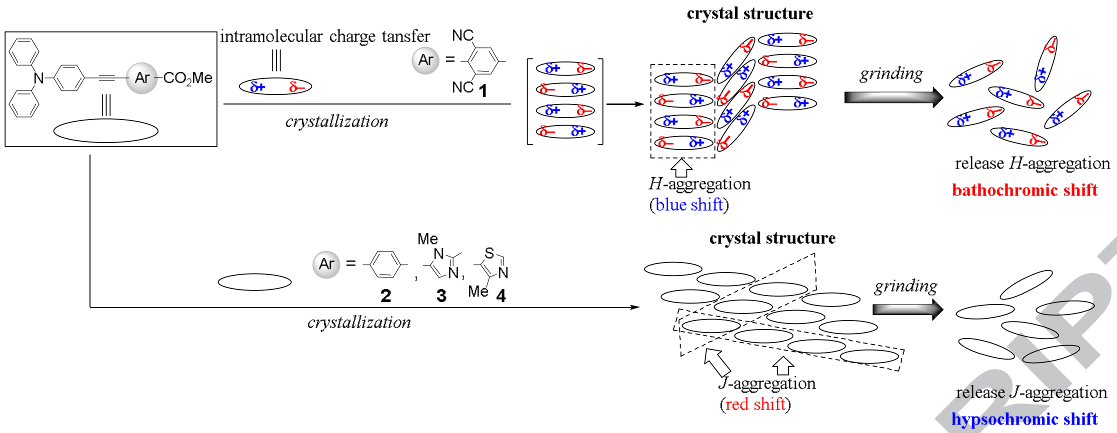


Figure 3. The UV-Vis spectra (3.0× 10^{-5} M) of (a) **1**, (b) **2**, (c) **3**, and (d) **4** in $CHCl_3$ (plane line) and in DMF (dashed line).

The absorption properties in the solution also showed a clear contrast against the mechanochromic change of each compound. We measured UV-Vis spectra of **1**, **2**, **3**, and **4** in $CHCl_3$ and DMF (Figure 3), and the solvent effect was observed in **1**. The polar DMF solution gave shorter λ_{max} than that in $CHCl_3$. From the DFT calculation, the absorption would be derived from intramolecular charge transfer transition because of separation of HOMO and LLUMO orbitals (Figure S6a). Based on the negative solvatochromism, it suggested that **1** possesses a polar structure in the ground state.[12] On the other hand, little changes of λ_{max} were obtained in the case of **2**, **3**, and **4**. Those absorptions were attributed to π-π* transition based on the DFT calculation (Figure S6b-d). By comparing to λ_{max} in the crystalline state (Figure 1, before grinding) and the solution (Figure 3), the difference between **1** and **2**, **3**, and **4** was also revealed. λ_{max} (448, 416, and 470 nm) of **2**, **3**, and **4** in the solid state were observed at longer wavelengths against the solution (372-376, 358-361, and 392-398 nm), respectively. However, λ_{max} (444 nm) in the solid state of **1** was shorter wavelength than that in $CHCl_3$ (457 nm).

We would like to represent the plausible mechanism based on the obtained results, although the reason for the mechanochromism of those compounds is still unclear because of no detailed information about the aggregated structure after grinding. In the case of **1**, the single molecule has partially charge-separated structure derived from intramolecular charge transfer. The crystal packing is constructed by the π-stacking with the alternated alignment of each molecule to cancel their charge separation. It is supported that the π-stacking interactions give shorter distances than those of **2**, **3**, and **4**. Such structure is called *H*-aggregated structure. The compound with *H*-aggregate is well known to change the absorption peak with blue shift.[13] Therefore, shorter λ_{max} in the solid state was observed against the solution. Furthermore, the crystal structure depicted in Figure 2a and 3a is obtained by the aid of interactions at diphenylaminophenyl moiety (Figure S5a), whose motif is promising to give CH-π interactions.[14] By grinding the crystals, the *H*-aggregated structure can be destroyed, and the absorption peak changes with bathochromic shift (Scheme 3). On the other hand, the compounds of **2**, **3**, and **4** have no restriction with their charge separation when making the crystal structures. Therefore, they are preferable to construct the crystal structures in keeping with alignment of their long axis of single molecule. It is conceivable that the situation of the closest packing the rectangular parallelepiped. As the result, the packing depicted in Figure 2b-d and Figure S4b-d will be obtained with the interaction at diphenylaminophenyl moiety (also see Figure S5b-d). The alignment of the long axis resembles the structure with *J*-aggregation, which is known to give a red shift in the absorption spectrum.[13] Therefore, longer λ_{max} in the solid state was observed against the solution. By grinding the crystals, the (partial) release of the feature derived from *J*-aggregated motif gives the hypsochromic shift (Scheme 3). In view of the structure of **2** and **4** represented in Figure 3b and 3d, the *H*-aggregated-like structure was found to be a dimeric one. However, such *H*-aggregation motifs were unconnected from each other. It is suggested that the aggregated band is observed by the interaction between more than three molecules.[15] Therefore, the absorption of longer wavelengths would be observed in the crystalline state of **2** and **4**.

In summary, we synthesized the donor-π-acceptor compounds (**1**-**4**) with diphenylaminophenylacetylene as a donor-π moiety. Each compound showed the mechanochromism, but the direction of mechanochromic behavior was different. Furthermore, we revealed that **1** with bathochromic shift by grinding possesses the herringbone packing with the *H*-aggregate-like π-stacking interaction. On the contrary, the crystal structures of **2**-**4** with hypsochromic shift by grinding obtained the alignment toward a long axis of the molecules. Furthermore, the absorption which changes to longer wavelengths in the solid state was also observed by comparing the absorption peak in the solution, which would be derived from *J*-aggregated interaction. We now investigate in the mechanochromism of the compounds with other acceptor moieties, and will report in due course.



Scheme 3 Proposed mechanism of the formation of crystal packing and of the color change by the mechanical grinding.

Supplementary data

Supplementary data associated with this article can be found in the online version at

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10. Crystal data for **1**: $C_{30}H_{19}N_3O_2$, monoclinic, $P2_1/n$, a = 8.7940(7) Å, b = 27.059(2) Å, c = 9.9703(8) Å; β = 105.0460(10) °, V = 2291.2(3) Å^3, Z = 4, R = 0.0428, wR_2 = 0.1149, T = 173 K (CCDC 1554374); Crystal data for **2**: $C_{28}H_{21}NO_2$, triclinic, P-1, a = 9.7690(11) Å, b = 9.7883(11) Å, c = 23.930(3) Å, α = 81.529(2)°, β = 80.5720(10)°, γ= 69.2500(10)°, V = 2101.0(4) Å^3, Z = 4, R = 0.0466, wR_2 = 0.1428, T = 173 K (CCDC 1554375); Crystal data for **3**: $C_{26}H_{21}N_3O_2$, triclinic, P-1, a = 7.7989(7) Å, b = 9.4503(8) Å, c = 14.6987(12) Å, α = 91.5780(10) °, β = 103.1870(10)°, γ= 104.6570(10)°, V = 1016.24(15) Å^3, Z = 2, R = 0.0453, wR_2 = 0.1183, T = 173 K (CCDC 1554376); Crystal data for **4**: $C_{26}H_{20}N_2O_2S$, triclinic, P-1, a = 8.850(2) Å, b = 11.022(3) Å, c = 11.549(3) Å, α = 76.819(3) °, β = 86.764(3)°, γ= 85.685(3)°, V = 1092.9(5) Å^3, Z = 2, R = 0.0484, wR_2 = 0.1381, T = 173 K (CCDC 1554377). Crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publication. The data are obtainable free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.
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Relationship between Mechanochromic Behavior and Crystal Structures in Donor-π-acceptor Compounds Consisted of Aromatic Rings with Ester Moiety as an Acceptor

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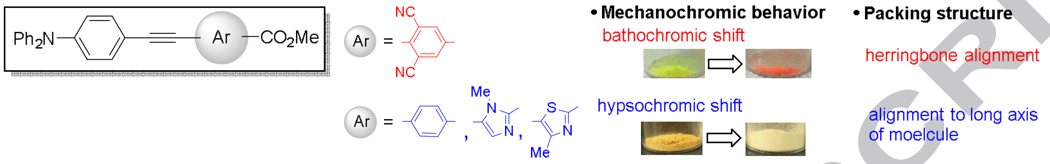

Title: **Relationship between mechanochromic behavior and crystal structures in donor-π-acceptor compounds consisted of aromatic rings with ester moiety as an acceptor**

Highlights:

1. Each mechanochromism with bathochromic and hypsochromic shifts was observed.
2. Two types of the alignment were obtained from crystal structure.
3. Relation between the mechanochromism and the solvent effect was found.
4. The mechanism of the mechanochromism was proposed.