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# Mechano- and Photoresponsive Behavior of a Bis(cyanostyryl)benzene Fluorophore

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**Abstract:** The mechanoresponsive behaviour and photochemical response of a new bis(cyanostyryl)benzene fluorophore (CSB-5) were investigated. Green fluorescence with  $\lambda_{em,max}$  of 507 nm was found for CSB-5 in chloroform solution, mirroring the behaviour of a previously reported similar dye (CSB-6). On the other hand, crystalline samples of CSB-5 exhibited orange fluorescence with  $\lambda_{em,max}$  of 620 nm, attributable to excimer emission. Although the emission color change was not clearly noticeable by naked eye, CSB-5 exhibited mechanochromic luminescence, due to transformation into the amorphous state upon grinding the crystalline powder. Interestingly, rubbed films of CSB-5 prepared on glass substrates exhibited a pronounced emission color change from orange to green when exposed to UV light. This response is the result of a photochemical reaction that occurs in the amorphous state and which causes a decrease of the excimer emission sites so that the emission color changes from excimer to monomer. The crystalline material did not display such a photoinduced emission color change and the difference in photochemical reactivity between crystalline and amorphous states was exploited to pattern the emission color of rubbed films.

## Introduction

Organic emitting materials that exhibit emission color changes in response to their surrounding environment or upon exposure to external stimuli are fundamentally interesting and useful for practical applications. Typical phenomena include thermo-chromic,<sup>[1]</sup> solvatochromic,<sup>[2]</sup> and vapochromic emission

characteristics.<sup>[3]</sup> Photo-triggered fluorescence switching of photochromic materials is also a long-standing subject of interest.<sup>[4]</sup> In the last decade, the phenomenon of mechanochromic emission, that is reversible emission color change of solid material induced by mechanical stimuli such as grinding, have attracted a great deal of attention.<sup>[5]</sup> The phenomenon is often induced by a change of the intermolecular interactions, which is caused by altering the molecular arrangement in the solid state through mechanical force. Not only a variety of simple molecular systems, but mechanochromic luminescent supramolecular systems and self-assembled dyad molecule with dual sensitivity of photo- and mechanochromism have also been reported.<sup>[6]</sup>

Nakano and coworkers recently reported two series of mechanochromic luminescent materials<sup>[7,8]</sup> and demonstrated with a series of diarylaminobenzaldehyde-based amorphous molecular materials that the mechanical induction of large conformational changes of excited molecules can give rise to mechanoresponsive luminescence.<sup>[7]</sup> A series of mono-substituted pyrenes was used to show that mechanochromic emission can be caused by formation of defects by grinding the crystalline samples that allows the excimer formation.<sup>[8]</sup>

Molecular materials based on bis(cyanostyryl)benzene chromophores have also been widely exploited as basis for mechanoresponsive effects, because these molecules can adopt a range of solid state structures that give rise to multicolor emission. In a series of studies, the Weder group blended small amounts of bis(cyanostyryl)benzene derivatives with polymers and showed that tensile deformation leads to a break-up of dye aggregates and thus a change from excimer-dominated to monomer-rich emission.<sup>[9]</sup> The same group also reported that certain bis(cyanostyryl)benzene derivatives show stimuli-responsive luminescent properties in absence of a polymer matrix.<sup>[10]</sup> Park and co-workers reported that a bis(cyanostyryl)benzene derivative exhibits two-color fluorescence switching in response to pressure, heat, and solvent vapor.<sup>[11]</sup> Sagara, Weder, and co-workers later reported that another derivative, CSB-6 (Chart 1), can adopt a variety of polymorphs, depending upon the crystallization method, and exhibit multi-color emission, depending its morphology.<sup>[12]</sup> Based on comparison with other bis(cyanostyryl)benzene derivatives led to the conclusion that the 4-methylphenoxyethylene groups attached to the ends of the bis(cyanostyryl)benzene core are important to control the molecular packing in the crystalline state and support the formation of a variety of polymorphs. It stands to reason that the modification of such appended groups should allow creating other emitting materials with interesting structures and properties.

Here we report the investigation of the new bis(cyanostyryl)-benzene derivative CSB-5, in which the length of the methylene chain in the terminal groups was changed relative to CSB-6 (Chart

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1). Although CSB-5 only displayed one crystalline phase, the compound was found to exhibit mechanochromic luminescence due to the formation of an amorphous state upon grinding. In addition, a pronounced emission color change was observed when an amorphous rubbed film was exposed to blue light, which appears to result from a photochemical reaction that causes a decrease of the excimer emission sites so that the emission color changes from excimer to monomer.

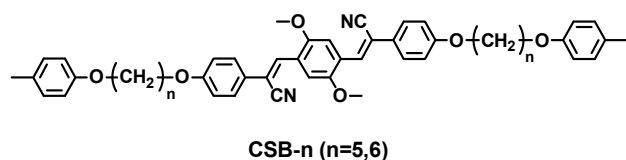
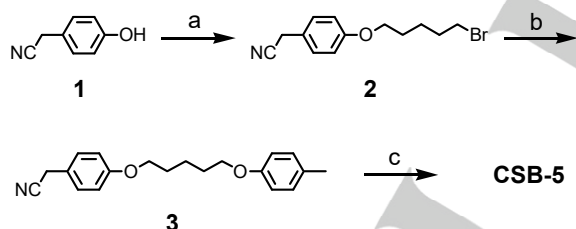


Chart 1. Chemical structures of bis(cyanostyryl)benzene derivatives studied.

## Results and Discussion

### Synthesis of CSB-5 and optical properties in solution

CSB-5 was synthesized by adapting the procedure reported for the synthesis of CSB-6<sup>[12]</sup> using 1,5-dibromopentane instead of 1,6-dibromohexane. Scheme 1 shows the synthetic route of CSB-5 through three steps from 4-hydroxybenzylcyanide (**1**). The overall yield of CSB-5 based on **1** was ca. 10%. CSB-5 was purified by recrystallization from 1,4-dioxane, obtained in the form of thin orange needles, and characterized to satisfaction by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis.



Scheme 1. Synthesis of CSB-5. a: 1,5-dibromopentane, K<sub>2</sub>CO<sub>3</sub>, DMF. b: 4-methylphenol, K<sub>2</sub>CO<sub>3</sub>, DMF. c: t-C<sub>4</sub>H<sub>9</sub>OK, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NOH, t-C<sub>4</sub>H<sub>9</sub>OH, THF.

CSB-5 was further characterized by single-crystal X-ray crystallography. Figure 1 shows the molecular structure of CSB-5, obtained from a single crystal that was prepared by a vapor diffusion technique using chloroform and hexane as good and poor solvents, respectively. The molecule placed on the inversion center of the crystal and hence the molecule has an inversion symmetry. The methylene chains in CSB-5 molecule took all trans-zigzag conformations, and therefore, the molecule has a planar structure in the crystalline state.

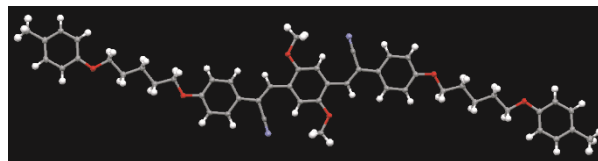
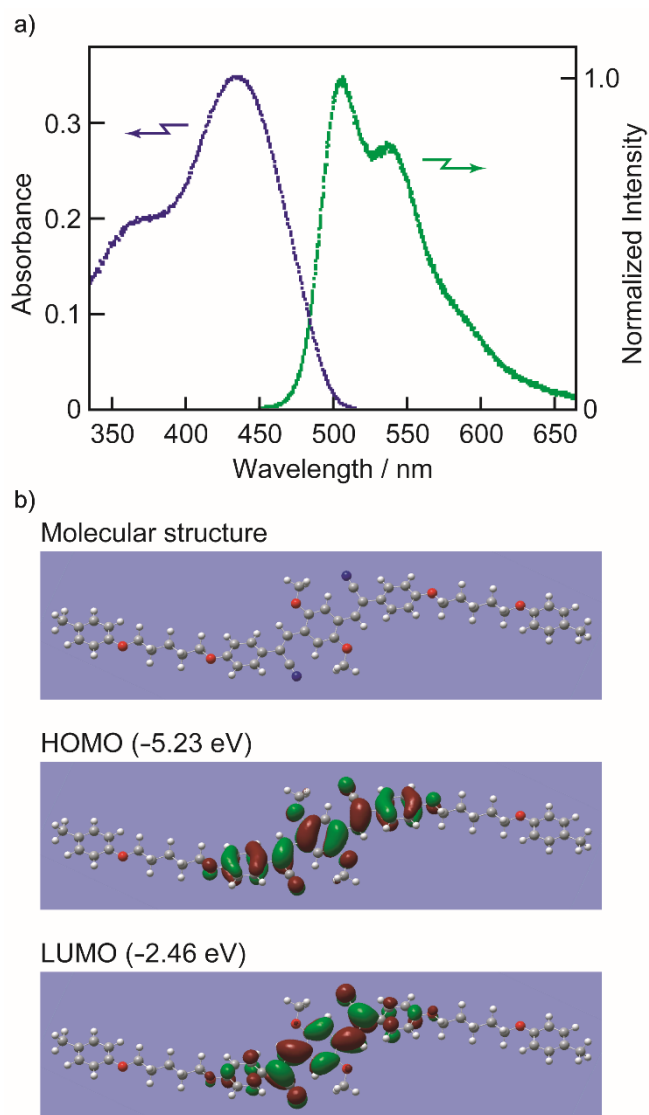


Figure 1. Molecular structure of CSB-5 in a single crystal.

Electronic absorption and emission spectra of CSB-5 in chloroform are shown in Figure 2 together with the result of DFT calculations. The electronic absorption spectrum (dark blue plots of Figure 2a) shows an absorption band around 433 nm, with a shoulder around 360 nm. The spectrum is almost identical to that of CSB-6 in a corresponding solution. DFT calculations of CSB-5 indicate that both HOMO and LUMO exist predominantly at the central bis(cyanostyryl)benzene core of the molecule (Figure 2b), consistent with the fact that the absorption spectrum of CSB-5 is virtually identical to that of CSB-6 and the notion that the length of the methylene chain does not impact the solution properties. The absorption band around 433 nm is attributable to the HOMO–LUMO transition. The emission spectrum of CSB-5 in solution (green plots of Figure 2a) shows a band with a maximum at 507 nm and clear vibrational structure. Since the fluorescence life time was 1.4 ns as described below, the emission, which is again virtually identical with that of CSB-6, is attributable to monomeric fluorescence. Thus, the electronic absorption and emission properties in solution are as expected independent of the methylene chain length.



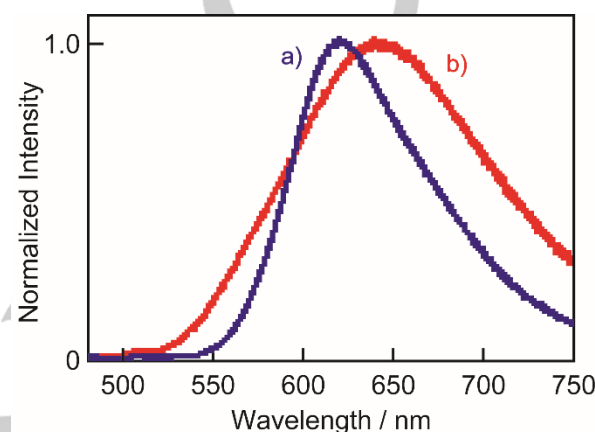
**Figure 2.** a) Electronic absorption and emission spectrum of CSB-5 in chloroform ( $1.0 \times 10^{-5}$  mol L $^{-1}$ ,  $\lambda_{\text{ex}}$ : 400 nm). b) Optimized molecular structure together with HOMO and LUMO surfaces of CSB-5 obtained by DFT calculation based on B3LYP/6-31G(d,p).

#### Photoluminescence properties of CSB-5 in the solid states

CSB-5 was also found to fluoresce brightly in solid form. Figure 3a shows the emission spectrum of CSB-5 recrystallized from 1,4-dioxane. The broad emission band features a maximum around 620 nm, i.e., at a wavelength that is considerably red-shifted from the emission maximum observed in solution. The emission is dominated by excimer formation, which is supported by the longer fluorescence lifetime of 18 ns as described below (Table 1). In contrast to CSB-6, which exhibits several polymorphs with a variety of emission color depending on the crystallization method, only one crystalline form was obtained when CSB-5 was crystallized from different kinds of solvents. Thus, the difference of the methylene chain length indeed affects the molecular

arrangement in the crystalline state and as will be shown in the following, also the stimuli-responsive luminescent properties.

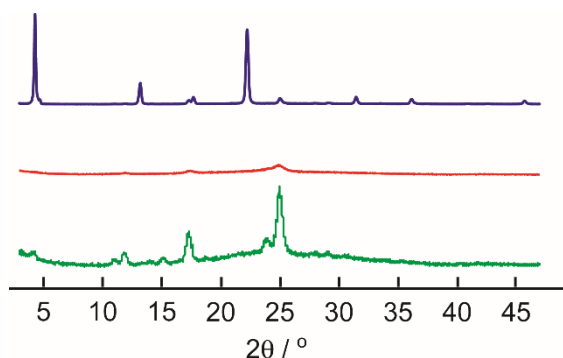
Although the emission color change was not clearly noticeable by naked eye, the CSB-5 was found to exhibit mechanochromic luminescence. As Figure 3b shows, ground samples display a broader emission band, with the emission peak shifted to a longer wavelength ( $\lambda_{\text{em,max}}$ : 640 nm) compared to the crystalline state. When the ground sample was immersed in a few drops of THF, the spectrum gradually recovered to the original. The recovery of the spectrum was also induced by annealing of the ground sample at 100 °C for 1 min.



**Figure 3.** Emission spectrum of CSB-5 a) in the crystalline state (dark blue) and b) after grinding (red) state.  $\lambda_{\text{ex}}$ : 400 nm.

Figure 4 shows the X-ray diffraction (XRD) patterns of CSB-5. While several strong and sharp peaks can be observed for the crystallized sample, the peaks almost completely disappeared upon grinding, suggesting that an amorphous state was formed by grinding. When the ground sample was immersed in a few drops of THF, the sharp peaks again appeared. The difference in relative intensities of the peaks would be ascribed to their different morphology between needles and powder. Axis of needle-like crystals are parallel to the substrate surface, whereas those of powder can be oriented in any directions. Thus we concluded that the immersed sample returned to the original crystalline form.

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**Figure 4.** XRD patterns of CSB-5 in the crystallized form (dark blue, top), after grinding a sample (red, middle), and after immersing the sample (green, bottom).

In order to gain further information on the electronic properties of CSB-5, fluorescence lifetime measurements were performed; the fluorescence decay profiles are shown in Figure S1 and results are summarized in Table 1. In dilute chloroform solution, the fluorescence lifetime was 1.4 ns, suggesting that the emission in solution can be attributed to monomeric fluorescence of CSB-5. On the other hand, the lifetime was considerably longer (18 ns) for the crystalline sample, suggesting that the emission of the crystalline state was due to excimer emission. It is noted that the fluorescence decay of the crystalline sample is well described by a single-exponential decay. As described below, the CSB-5 molecules stack face to face with slips. Thus, the excimer can immediately be formed with the neighboring molecule after the first singlet excited state of a first CSB-5 molecule is populated by absorption of a photon. The crystal structure with  $Z=1$  suggests that only one kind of excimer site exists in the crystal, resulting in a fluorescence decay with single component. In contrast, the ground sample displayed a much more complex emission decay profile that could only be well fitted with a tri-exponential decay function. The result suggests the formation of a variety of excimer sites upon grinding the crystal.

**Table 1.** Fluorescence lifetimes of CSB-5 together with ratio of the component in parenthesis.

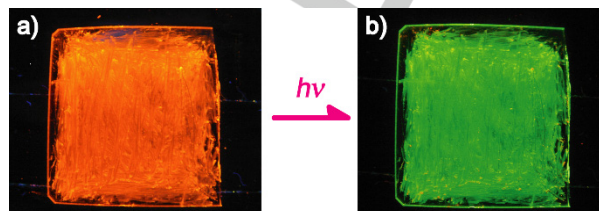
Chloroform solution <sup>[a]</sup>	Recrystallized sample <sup>[b]</sup>	Ground sample <sup>[b]</sup>
1.4 ns (1.00)	18 ns (1.00)	1.0 ns (0.14)
		5.7 ns (0.13)
		15 ns (0.73)

$\lambda_{\text{ex}}$ : 405 nm. [a] monitored at 500 nm. [b] monitored at 620 nm.

#### Photoinduced emission color change of CSB-5 in the solid states

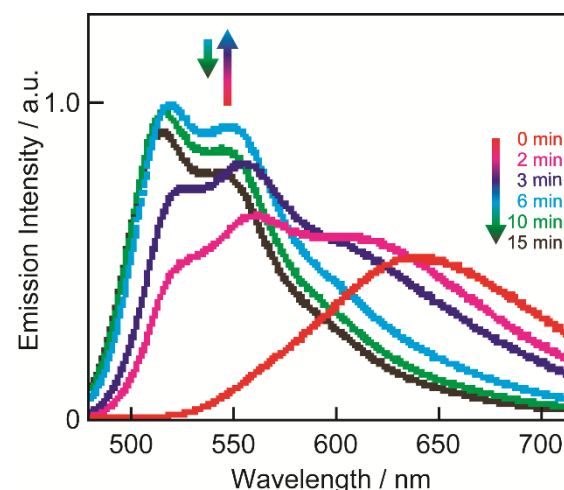
During the investigation of the luminescence and mechanochromic properties of CSB-5, a drastic emission color

change of the rubbed films prepared on glass substrates was observed upon irradiation with 450 nm-light. As shown in Figure 5, the orange emission of the rubbed film gradually changed upon irradiation with 450 nm-LED light and the emission color turned to green within several minutes.



**Figure 5.** Pictures showing the fluorescence of a rubbed film of CSB-5 under illumination with 365 nm-UV light a) before irradiation and b) after 10 min irradiation with a 450 nm-LED light (ca. 32 mW cm<sup>-2</sup>).

This drastic emission color change is also evident from Figure 6, which shows the spectral changes of the rubbed film upon irradiation with 450 nm-light. Before irradiation, the emission band was observed around 640 nm attributable to excimer emission, suggesting that the rubbed film was in the amorphous state. Upon irradiation of the rubbed film, the intensity of the emission band around 640 nm gradually decreased, while a band around 510 nm formed and increased over the course of 6 min irradiation with 450 nm-light with an intensity of 15 mW cm<sup>-2</sup>. Further irradiation only caused a moderate reduction of the emission intensity. The spectrum after 6 min irradiation was similar to that of CSB-5 in solution (Figure 2). Fluorescence decay profile for the film after 10 min irradiation (Figure S1d) could be fitted with tri-exponential decay function, their lifetimes with the ratio of the component in parenthesis being 0.96 ns (0.54), 2.1 ns (0.44), and 6.9 ns (0.02). These results suggest that the green emission of irradiated sample was mainly due to monomeric fluorescence of CSB-5.

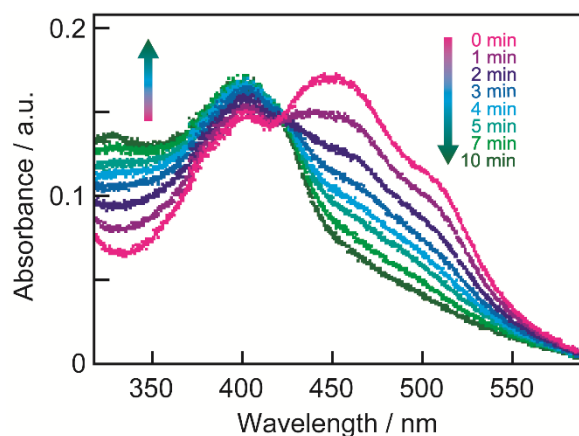


**Figure 6.** Emission spectral change of the rubbed film of CSB-5 upon irradiation with 450 nm-light (ca. 15 mW cm<sup>-2</sup>).  $\lambda_{\text{ex}}$ : 400 nm.



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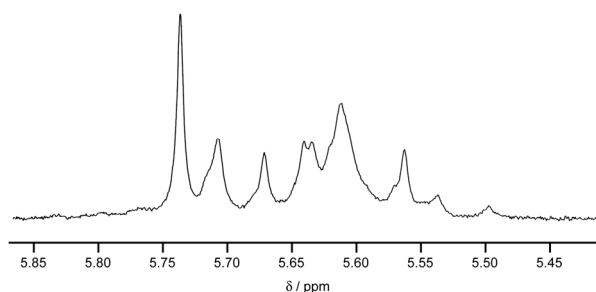
Several cyanostyrylbenzene derivatives have been reported to exhibit photochemical reactions such as [2+2] photocycloaddition, E-Z photoisomerization, and photocyclization,<sup>[13]</sup> and the here-observed photoinduced change of the emission color of rubbed CSB-5 films might be due to photochemical reactions. In fact, a change of the electronic absorption spectrum that was observed upon irradiating the rubbed sample with 450 nm light, as shown in Figure 7, supports this conclusion. The absorption band in the wavelength region above ca. 430 nm decreased and simultaneously the band in shorter wavelength region increased upon irradiation with 450 nm-LED light.



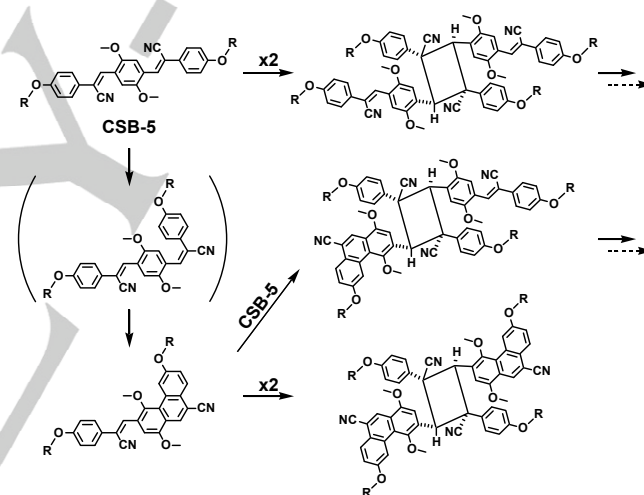
**Figure 7.** Electronic absorption spectral change of a rubbed film of CSB-5 upon irradiation with 450 nm-light (ca. 3 mW cm<sup>-2</sup>).

Although we could not isolate the products of this photochemical reaction to determine their exact molecular structure, mass spectrometry, FT-IR and <sup>1</sup>H NMR spectra provided some information about the photochemical products in the sample film. Mass spectrometry of the irradiated sample suggested the formation of dimers (*m/z*: around 1577 [M+Na<sup>+</sup>]), trimers (*m/z*: around 2354 [M+Na<sup>+</sup>]), and tetramer (*m/z*: around 3131 [M+Na<sup>+</sup>]) of CSB-5 (Figure S2). With regard to FT-IR spectra of the sample, the absorption band attributable to the C≡N stretching vibration mode at 2209 cm<sup>-1</sup> changed upon irradiation, and a new band growing on the higher wavenumber side could be observed as a shoulder (Figure S3). In addition, the <sup>1</sup>H NMR spectrum of the mixture in CDCl<sub>3</sub> (Figure S4) shows new signals in the region of 5.45 - 5.80 ppm (Figure 8), suggesting the production of some cyclobutane derivatives. Thus, a [2+2] photocycloaddition is likely taking place upon irradiating the amorphous form of CSB-5 with blue light. In addition to the [2+2] photocycloaddition reaction, cyanostyrylbenzene derivatives can isomerize to form the Z-isomer and cyclize to form phenanthrenes upon irradiation,<sup>[13]</sup> and therefore a variety of photochemical products might be produced as shown in Scheme 2 due to two reactive ethene sites existing in each CSB-5 molecule. For example, not only dimers but oligomers can be produced. In addition, [2+2] photocycloaddition of photochemically produced phenanthrene isomer is also possible at the remaining ethene moiety. These reactions might cause the complicated <sup>1</sup>H NMR spectrum even in the region of

5.45 - 5.80 ppm (Figure 8). Longer and more intense light irradiation resulted in more complicated NMR spectrum presumably because further photochemical reactions and/or photo-degradations of the molecules also took place.



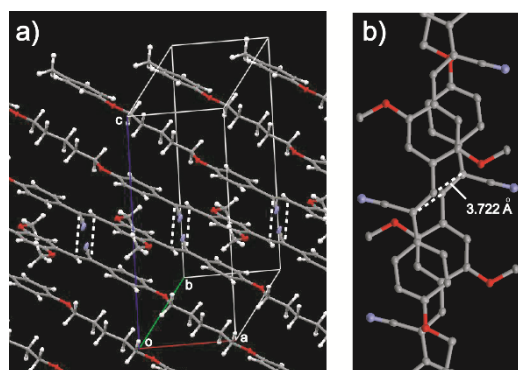
**Figure 8.** Partial <sup>1</sup>H NMR spectrum of the material produced by irradiation of the rubbed film of CSB-5 with 450 nm-LED light (32 mW cm<sup>-2</sup>) for 10 min. Solvent: CDCl<sub>3</sub>.



**Scheme 2.** Possible photochemical reactions of CSB-5 taking place upon irradiating the rubbed film with blue light.

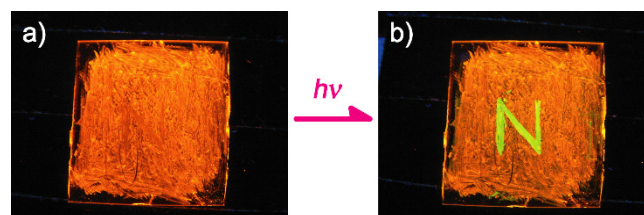
The photoinduced emission color change observed for the rubbed film could be explained as follows. The rubbed film in the amorphous state exhibits excimer emission around 640 nm. Upon irradiation of the film with 450 nm-light, several kinds of photochemical reactions took place. As a result, the excimer emission sites of CSB-5 decreased and hence the monomer emission from remaining CSB-5 molecules increased with increasing irradiation time. However, excess irradiation decreased the concentration of CSB-5 molecules in the solid, resulting in reduction of monomeric emission intensity. Similar photoinduced emission spectral changes due to photochemical reactions that caused a decrease of the excimer emission were reported for diphenylpolyene crystals and pyrene-conjugated DNA analogues.<sup>[14]</sup>

Figure 9 shows the crystal structure of a CSB-5 single crystal obtained by means of vapor diffusion technique as described above. It was found that the CSB-5 molecules stacked face to face with slips to form a columnar structure. In this crystal, the intermolecular distance between reaction points for [2+2] photocycloaddition, i.e., carbon atoms at ethene moiety as indicated by white broken lines in Figure 9, was found to be 3.722 Å. The distance was smaller than 4.2 Å required for topochemical [2+2] photocycloaddition of olefins in the crystalline state, as suggested by Schmidt's rule.<sup>[15]</sup> However, the emission color of the crystalline sample did not change upon irradiation with blue light for more than 30 min. This result suggests that the photochemical reactions did not take place in the crystalline state, even though the distance between reaction points would a priori allow a [2+2] photocycloaddition reaction. It is thus thought that the structural change induced by photochemical reactions is quite large, due to somewhat large and rigid structure of CSB-5, so that this transformation might be prohibited in the crystalline state. On the other hand, such photochemical reactions became easier to take place in the amorphous state due to the increased free volume, resulting in photoinduced change in emission color. Recently, similar mechanically induced change in photochemical reactivity in solid-state for bisamide-substituted diacetylene has been reported.<sup>[16]</sup>



**Figure 9.** a) Crystal structure of CSB-5. b) Overlap of CSB-5 molecules viewed from normal to the molecular plane.

Finally, we have demonstrated the emission patterning using the phenomenon of the photoinduced emission color change. The sample film of CSB-5 was prepared by rubbing the CSB-5 powder onto a transparent glass substrate, followed by annealing the film at 100 °C for 1 min. The resulting film was confirmed to be in the crystalline state by the emission spectrum. Then, the character "N" was written into the film using a toothpick, giving rise to a latent, invisible pattern (Figure 10a) that can be "developed" by irradiating the sample with 450 nm-LED light for a few minutes (Figure 10b). Figure 10 shows the fluorescence images of the films before and after irradiation. The character "N" was obviously recognizable for the irradiated film after irradiation while the pattern was scarcely recognizable before irradiation. The present patterning was caused by the difference of photochemical reactivity between crystalline and amorphous states.



**Figure 10.** Pictures showing the fluorescence of a patterned film of CSB-5 under illumination with 365 nm-UV light a) before irradiation and b) after 3 min irradiation with a 450 nm-LED light (ca. 32 mW cm<sup>-2</sup>). The area shown in (b) as "N" had been rubbed with a toothpick.

## Conclusions

A new bis(cyanostyryl)benzene fluorophore, CSB-5, whose peripheral substituents differ only slightly from those of the previously reported derivative CSB-6, was synthesized and investigated. The electronic absorption and fluorescence spectra of CSB-5 in chloroform solution are almost identical to those of CSB-6, suggesting that the molecular electronic properties are hardly influenced by such modifications, due to the fact that the HOMOs and LUMOs are localized at the bis(cyanostyryl)benzene core. However, the molecular packing in the crystalline state was significantly changed, which also impacted the emitting properties in the solid state. In contrast to CSB-6, which exhibits multi-color emission, only one crystalline state with orange emission was obtained for CSB-5. Although the emission color change was not clearly noticeable by naked eye, CSB-5 exhibits mechanochromic luminescence, due to transformation into the amorphous state upon grinding the crystalline powder. Rubbed films of CSB-5 prepared on glass substrates exhibited a pronounced emission color change from orange to green when exposed to UV light. This response appears to be the result of a photochemical reaction that occurs in the amorphous state and which appears to involve [2+2] photocycloaddition reactions. This reaction could not be observed in the crystalline state, even though the distance between the reaction points for dimerization was short enough, maybe due to the large and rigid structure of CSB-5 that needed large structural change for dimerization. Using the difference of photochemical reactivity between crystalline and amorphous states, we could demonstrate emission patterning of the rubbed film.

## Experimental Section

### Synthesis of 4-(5-bromopentyloxy)benzylcyanide (2)

A DMF solution (150 mL) of 4-hydroxybenzylcyanide (1, 3.00 g, 22.5 mmol) and 1,5-dibromopentane (20.8 g, 90.5 mmol) to which potassium carbonate (7.77 g, 56.2 mmol) had been added was stirred at 60 °C for 3 h. The resulting mixture was cooled to room temperature and washed with saturated aqueous ammonium chloride and subsequently sodium chloride solutions. After the organic phase was dried over magnesium sulfate, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a hexane and ethyl acetate mixture to afford **2** as a yellow viscous liquid. Yield: 4.24 g (66.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 1.57-1.67 (m, 2H), 1.79-1.85 (m, 2H),

1.91-1.98 (m, 2H), 3.45 (t,  $J = 6.8$  Hz, 2H), 3.69 (s, 2H), 3.97 (t,  $J = 6.4$  Hz, 2H), 6.88 (d,  $J = 8.8$  Hz, 2H), 7.23 (d,  $J = 8.8$  Hz, 2H).

### Synthesis of 4-(5-(4-methylphenoxy)pentyl)benzylcyanide (3)

A DMF solution (150 mL) of **2** (2.51 g, 8.90 mmol) and 4-methylphenol (1.06 g, 9.80 mmol) to which potassium carbonate (3.08 g, 22.3 mmol) had been added was stirred at 60 °C for 24 h. The resulting mixture was washed with saturated aqueous ammonium chloride and subsequently sodium chloride solutions. After the organic phase was dried over magnesium sulfate, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a hexane and ethyl acetate mixture to afford **3** as a colorless powder. Yield: 650 mg (23.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 1.62-1.68 (m, 2H), 1.81-1.88 (m, 4H), 2.28 (s, 3H), 3.68 (s, 2H), 3.95-4.00 (q,  $J = 6.5$  Hz, 4H), 6.80 (d,  $J = 8.4$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 7.22 (d,  $J = 8.8$  Hz, 2H).

### Synthesis of 1,4-bis(2-cyano-2-(4-[5-(4-methylphenoxy)pentyl]phenyl)ethenyl)-2,5-dimethoxybenzene (CSB-5)

*t*-Butylalcohol (100 mL) was added to an anhydrous THF solution (20 mL) of **3** (650 mg, 2.10 mmol) and 2,5-dimethoxybenzene-1,4-dicarboxyaldehyde (188 mg, 0.968 mmol). A 10% methanol solution of tetrabutylammonium hydroxide (100 mL) and a THF solution of potassium *t*-butoxide (ca. 1 mol L<sup>-1</sup>, 0.2 mL) were successively added and the reaction mixture was stirred at 50 °C for 1 h. The reaction mixture was cooled to room temperature, methanol (ca. 100 mL) was added, and the resulting precipitate was filtered off. The solid was washed several times with methanol containing a small amount of acetic acid and finally several times with pure methanol. Recrystallization using chloroform / hexane afforded CSB-5. Yield: 524 mg (64.2%). CSB-5 was purified by recrystallization from 1,4-dioxane to give thin orange needles. m.p.: 183.2-183.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 1.63-1.71 (m, 4H), 1.82-1.93 (m, 8H), 2.29 (s, 6H), 3.95 (s, 6H), 3.98 (t,  $J = 6.5$  Hz, 4H), 4.04 (t,  $J = 6.5$  Hz, 4H), 6.81 (d,  $J = 8.6$  Hz, 4H), 6.96 (d,  $J = 9.2$  Hz, 4H), 7.08 (d,  $J = 8.3$  Hz, 4H), 7.64 (d,  $J = 8.9$  Hz, 4H), 7.87 (s, 2H), 7.89 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 20.52, 22.82, 29.04, 29.16, 56.46, 67.88, 68.11, 110.32, 111.65, 114.49, 115.07, 118.64, 125.54, 127.13, 127.58, 129.90, 129.95, 133.80, 151.97, 157.00, 160.13. MALDI-TOF-MS: *m/z* found 799.54 [M+Na]<sup>+</sup>, calcd for C<sub>50</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub>+Na: 799.37. EA: Found: C, 76.92; H, 6.68; N, 3.57%. Calcd for C<sub>50</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub>: C, 77.29; H, 6.75; N, 3.61%.

### X-Ray Crystallography

A single crystal of CSB-5 for X-ray crystallography was obtained by a vapor diffusion method using chloroform solution of CSB-5 with hexane as a poor solvent vapor. X-Ray structure analysis was performed using a single crystal with dimensions of approximately 0.30 x 0.04 x 0.01 mm<sup>3</sup> on a Rigaku VariMax RAPID Imaging Plate diffractometer with confocal mirror-monochromated Mo-K $\alpha$  (0.71075 Å) radiation. A total of 14004 independent reflections was obtained of which 3687 were unique. The structure was solved by direct methods and refined by full matrix least square method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located at their calculated position. They were included in the calculations but were not refined. Crystallographic data were as follows: C<sub>50</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub>, M=776.97, triclinic, space group *P*-1, *a*=6.7139(3), *b*=8.0077(3), *c*=19.7131(9) Å,  $\alpha$ =88.713(6),  $\beta$ =80.597(6),  $\gamma$ =75.391(5)°, *V*=1011.60(8) Å<sup>3</sup>, *Z*=1, *D*<sub>c</sub>=1.275 g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ )=0.831 cm<sup>-1</sup>, *T*=-170 °C, *R*<sub>1</sub>[*I*>2 $\sigma$ (*I*)]=0.0503, *wR*<sub>2</sub>=0.1297. Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC 1889471).

### DFT Calculation

Optimized molecular structure together with its HOMO and LUMO surfaces of CSB-5 were calculated based on density-function theory at B3LYP/6-31G(d,p) level performed with the Gaussian 09.<sup>[17]</sup>

### Photoinduced Emission Color Change of Rubbed Film

The sample film for investigating the photoinduced emission color change was prepared by rubbing the CSB-5 powder onto a transparent glass substrate. The resulting rubbed film was irradiated with 450 nm-LED light (LHP-LED-450, Prizmatix) at ambient atmosphere.

### Measurement and Apparatus

Electronic absorption and fluorescence spectra for solution and solid samples were measured using a U-3500 spectrophotometer (HITACHI Ltd.) and a FP-8300 spectrofluorometer (JASCO Co), respectively, at ambient atmosphere. To determine the fluorescence life times, fluorescence decay profiles were monitored by conventional time-correlated single photon counting method by means of Quantaaurus-Tau (Hamamatsu Photonics). XRD patterns of solid samples were acquired on a Multi Flex-120NP X-ray diffractometer (RIGAKU Co.) with a scan rate of 1 deg min<sup>-1</sup> upon Cu-K $\alpha$  (1.542 Å) radiation. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded using an AB SCIEX TOF/TOF 5800. FT-IR spectra of the samples scraped from the rubbed films before and after irradiation were measured with an FT/IR-4100 spectrometer (JASCO Co). <sup>1</sup>H NMR spectra of CDCl<sub>3</sub> solutions of CSB-5 and the photoirradiated sample were performed by means of JNM-ECA 500 (JEOL Ltd.).

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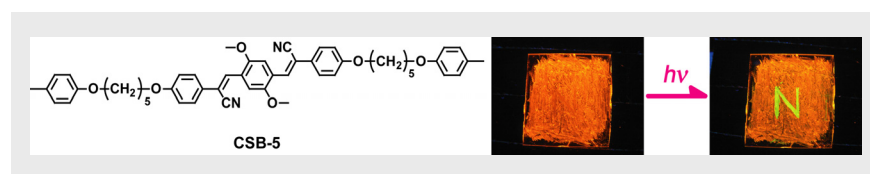


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**Mechano- and Photoresponsive  
Behavior of a  
Bis(cyanostyryl)benzene Fluorophore**

**Emission patterning:** Rubbed films of a new bis(cyanostyryl)benzene derivative (CSB-5) exhibit a pronounced photoinduced emission color change. This effect is the result of photochemical reactions that only take place in the amorphous state, which can be mechanically accessed.