DOI: 10.1002/anie.201306746

Reversible C–C Bond Formation

Reversible Single-Crystal-to-Single-Crystal Photochemical Formation and Thermal Cleavage of a Cyclobutane Ring**

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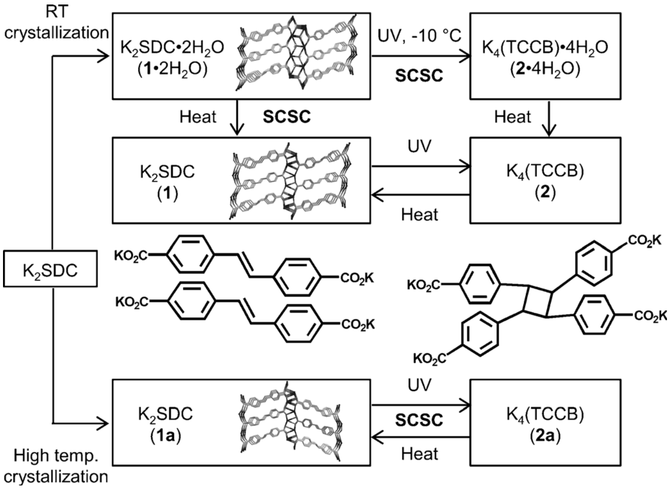
Abstract: *A [2+2] cycloaddition reaction has been observed in a number of solids. The cyclobutane ring in a photodimerized material can be cleaved into olefins by UV light and heat. The high thermal stability of the metal–organic salt K_2SDC ($H_2SDC = 4,4'$-stilbenedicarboxylic acid) has been successfully utilized to investigate the reversible cleavage of a cyclobutane ring. The two polymorphs of K_2SDC undergo reversible cyclobutane formation by UV light and cleavage by heat in cycles. Of these, one polymorph retains its single-crystal nature during the reversible processes. Polymorphs are known to show different physical properties and chemical reactivities. This work reveals that the retention of single-crystal nature is strongly associated with the packing of molecules, which is controlled by kinetics and thermodynamics. The photoemissive nature of the products makes this as a promising material for photoswitches and optical data storage devices.*

Only a few photoreactive organic molecules exhibit photoreactivity in a reversible manner in the single-crystal state.[1] In this respect, diarylethene is one of the most successful systems.[2] Such reversible photoreactive systems find potential applications in photoswitching, optical recording, and sensing.[3] Although cyclobutane rings formed by a [2+2] cycloaddition reaction have been intensively investigated,[4] no thermally reversible cleavage of the cyclobutane ring with high selectivity was achieved because of the thermal instability at high temperatures.[5] Herein we report, to the best of our knowledge, the first reversible single-crystal-to-single-crystal (SCSC) [2+2] photocycloaddition and thermal-cleavage reactions.[6] First of all, to improve thermal stability in the crystalline state, we prepared a potassium salt, K_2SDC, from *trans*-4,4′-stilbenedicarboxylic acid (H_2SDC; Scheme 1).[7]



Scheme 1. Details of the structural transformations in the K_2SDC system under different experimental conditions.

Secondly, to retain the single crystal nature during the whole process, we prepared dehydrated single crystals. In sharp contrast, when the dehydrated crystals were prepared from the hydrated crystals, these did not show a reversible SCSC [2+2] cycloaddition/thermal-cleavage reaction, although the reversible [2+2] cycloaddition/thermal-cleavage reaction occurred in powder crystalline state. The difference in the single-crystal stability between those two dehydrated crystals is attributed to the crystal packing: the high-temperature synthesis produced a herringbone structure of K_2SDC in anhydrous form, whereas the dehydration of a hydrated crystal produced a parallel molecular arrangement. Another salient feature is that the photoemissive properties strongly depend on the crystal packing: compared with the herringbone structure, the parallel structure is more emissive. Even though the same chemical components were used, we could prepare a different photoreactive material by controlling the temperature.

By controlling the recrystallization temperatures of K_2SDC in the range of 25–80 °C, we obtained two types of products, which have parallel or herringbone arrangement of the SDC ligands (Scheme 1). Room-temperature recrystalli-

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[**] J.J.V. sincerely thanks the Ministry of Education Singapore for financial support through NUS FRC Grant R-143-000-562-112. M.K. gratefully acknowledges financial support from BK21 Plus (10Z20130000023) and Basic Research (Project No. 2011-0009930) through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST). The X-ray diffraction study with synchrotron radiation was performed at the Pohang Accelerator Laboratory (Beamline 2D) supported by POSTECH (Proposal No. 2012-3rd-2D-003). We thank Prof. Sungjee Kim and Sekyu Hwang (POSTECH) for assisting with solid-state fluorescence emission spectroscopic measurements. We would like to thank Prof. Edward R. T. Tiekink for correcting the English in this manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306746.

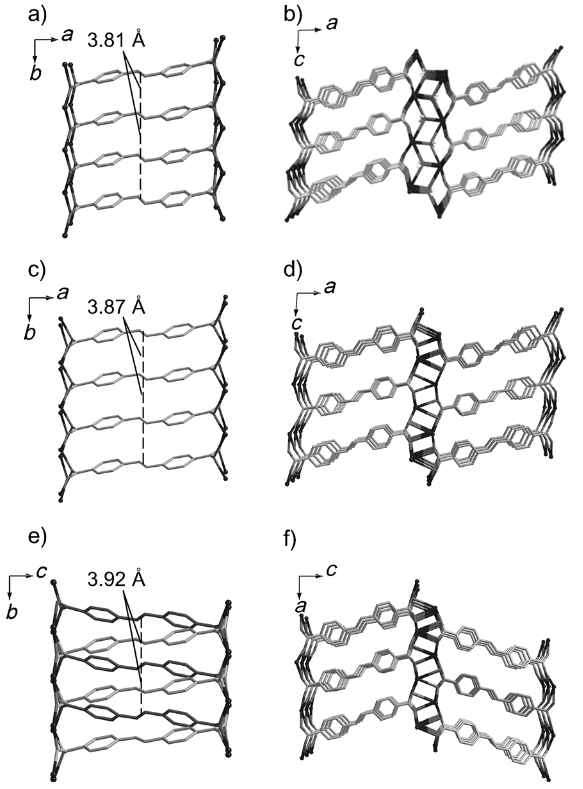

Figure 1. a) Infinite ladder structure along the *b*-axis in $\mathbf{1}\cdot 2\,H_2O$. b) Parallel orientation between two adjacent ladders in $\mathbf{1}\cdot 2\,H_2O$. c) Infinite ladder structure along the *b*-axis in **1**, which was obtained from $\mathbf{1}\cdot 2\,H_2O$ by dehydration in a SCSC manner. d) Parallel orientation between two adjacent ladders in **1**. e) Infinite ladder structure along the *b*-axis in **1a**. The major disordered component is shown in dark gray and the minor disordered component is shown in light gray. Their occupancy factors are 0.877 and 0.123, respectively. f) Herringbone arrangement between two adjacent ladders in **1a**. Only the major component is shown for clarity.[10]

zation produced a hydrated salt, $K_2SDC\cdot 2H_2O$ ($\mathbf{1}\cdot 2H_2O$). In $\mathbf{1}\cdot 2H_2O$, SDC ligands stack along the *b*-axis to form a ladder structure parallel to the adjacent ladders (Figure 1a,b). The distance of 3.81 Å between the reaction sites of C=C bonds in the rungs is suitable for a cycloaddition reaction in the solid state.[4a] Compound $\mathbf{1}\cdot 2H_2O$ undergoes dehydration at 70 °C to produce K_2SDC (**1**) in an SCSC fashion (Figure 1c,d). The dehydrated salt, **1**, has a parallel structure similar to that of $\mathbf{1}\cdot 2H_2O$. On the other hand, high-temperature recrystallization at 60–80 °C produced the anhydrous salt, K_2SDC (**1a**) directly. Species **1a** has the same ladder structure as in $\mathbf{1}\cdot 2H_2O$ or **1**, but has a herringbone arrangement of the ladders rather than parallel as observed in $\mathbf{1}\cdot 2H_2O$ or **1** (Figure 1e,f). Species **1a** is severely disordered into two components (87.7:12.3 %). Although **1** and **1a** have the same composition, their packing structures are different, and thus they are polymorphs.[8] The structural difference generated by temperature control is expected to show different physical properties.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses revealed that both **1** and **1a** are highly stable up to about 500 °C. Such a high thermal stability prompted us to investigate [2+2] cycloaddition and the thermal-cleavage reaction. Thanks to the parallel alignment of SDC^{2-} rungs suitable for [2+2] cycloaddition reaction, we successfully observed that the UV irradiation of single crystals of $\mathbf{1}\cdot 2H_2O$ induced [2+2] cycloaddition in an SCSC manner at −10 °C for 1 h, leading to the formation of $K_4TCCB\cdot 4H_2O$ ($\mathbf{2}\cdot 4H_2O$, where H_4TCCB = tetrakis-1,2,3,4-(4′-carboxyphenyl)cyclobutane). Both SDC^{2-} and $TCCB^{4-}$ were found in the asymmetric unit and each occupancy factor was refined to 0.152 and 0.848, respectively. Furthermore, ^{1}H NMR data revealed that the [2+2] cycloaddition reaction in $\mathbf{1}\cdot 2H_2O$ resulted in the formation of K_4TCCB ($\mathbf{2}\cdot 4H_2O$) in 84.4 % conversion as confirmed by the integration of the olefin and cyclobutane protons (Figure 2). UV irradiation for 2 h reached the maximum conversion of 85.4 %, and a complete photoconversion could not be achieved by prolonged irradiation. Indeed, this maximum conversion is in excellent agreement with the theoretical maximum yield of 82–87 % predicted by the recurrence relations in the infinitely parallel arrangement of the double bonds.[9] We examined the [2+2] cycloaddition reaction of **1** under UV irradiation at room temperature by ^{1}H NMR spectroscopy. **1** underwent circa 59.0 % conversion to K_4TCCB (**2**) in 1 h, while 6 h UV irradiation was required to reach the maximum conversion of 82.4 %.

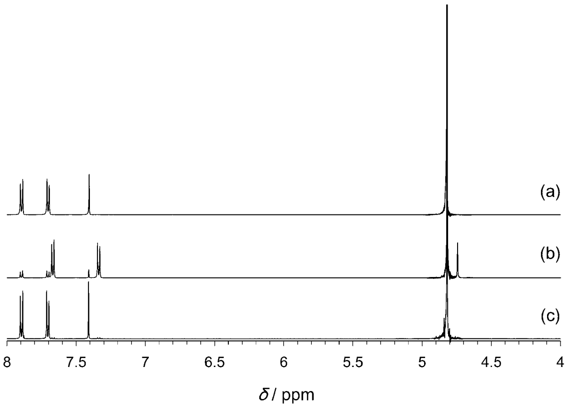

Figure 2. Overlay plot of ^{1}H NMR (500 MHz, D_2O) spectra (offset for clarity) showing photodimerization and thermal cleavage reactions of K_2SDC and its reversibility. a) $\mathbf{1}\cdot 2H_2O$. b) $\mathbf{2}\cdot 4H_2O$ after the UV irradiation of $\mathbf{1}\cdot 2H_2O$, showing about 84.4 % photodimerization from SDC^{2-} to $TCCB^{4-}$. c) **1** after heating of $\mathbf{2}\cdot 4H_2O$, showing about 97 % reversibility.

TG-DSC analyses were also carried out for **2**. Owing to its high thermal stability, DSC of **2** showed a prominent exothermic peak at about 264 °C in the range of 209–295 °C (Supporting Information, Figure S1 d) that is attributable to the thermal cleavage of cyclobutane rings. Indeed, heating **2** at 250 °C for 15 h resulted in selective formation of *trans*-isomer of **1**, which was confirmed by ^{1}H NMR spectroscopy (Figure 2c). Alkali metal salts of organic compounds having higher thermal stability appear to be suitable materials for observing reversible formation and cleavage of cyclobutane rings. In our earlier report, we found that the cyclobutane rings in a coordination polymeric sheet thermally cleaved in

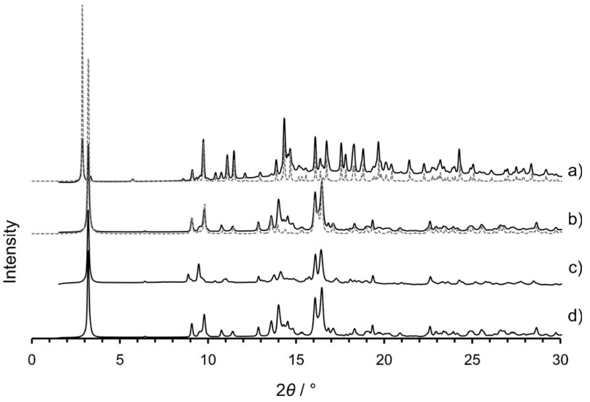

Figure 3. Overlay plots (offset for clarity) of the observed (——) and simulated (-----) PXRD patterns ($\lambda = 0.9000$ Å). a) Observed from $\mathbf{1}{\cdot}2\,H_2O$ (——), simulated from single-crystal XRD data of $\mathbf{1}{\cdot}2\,H_2O$ (-----). b) Observed from **1** obtained by heating of $\mathbf{1}{\cdot}2\,H_2O$ (——), Simulated from single-crystal XRD data of **1** (-----). c) Observed from **2** obtained by UV irradiation of **1** (——). d) Observed from **1** obtained by heating of **2** at 250 °C for 15 h (——).

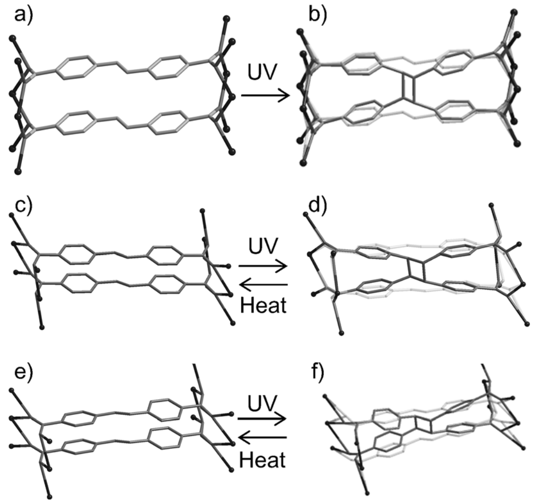

Figure 4. Structural transformation in an SCSC manner. a) SDC^{2-} monomer in $\mathbf{1}{\cdot}2\,H_2O$. b) The coexistence of photoreacted dimer (dark lines) and unreacted monomer (pale lines) in $\mathbf{2}{\cdot}4\,H_2O$. Their occupancy factors are 0.848 and 0.152, respectively. c) SDC^{2-} monomer of major component in **1a** (the occupancy factor is 0.877). d) The coexistence of photoreacted dimer (dark lines) and unreacted monomer (pale lines) in major component in **2a**. Their occupancy factors are 0.573 and 0.292, respectively. e) SDC^{2-} monomer of minor component in **1a** (the occupancy factor is 0.123). f) The coexistence of photoreacted dimer (dark lines) and unreacted monomer (pale lines) in minor component in **2a**. Their occupancy factors are 0.090 and 0.045, respectively.

two different ways to yield a mixture of *cis* and *trans* products.[5b] This is the first reversible formation and cleavage of cyclobutane rings present in a coordination polymer.

The reversible photodimerization/thermal cleavage of **1** was investigated by powder X-ray Diffraction (PXRD) techniques as well as ^{1}H NMR spectroscopy (Figure 3). However, SCSC transformation could not be observed from **1** to **2** after the UV irradiation experiments. This is probably attributed to the fragility of the parallel structure.

Crystals of **1a** underwent a [2+2] cycloaddition reaction as confirmed by ^{1}H NMR spectroscopy that is due to the arrangement of SDC^{2-} rungs similar to that in $\mathbf{1}{\cdot}2\,H_2O$ or **1**, though **1a** is severely disordered and it has a herringbone structure unlike $\mathbf{1}{\cdot}2\,H_2O$ or **1**. Crystals of **1a** underwent about 75.5 % conversion into K_4TCCB (**2a**) under UV irradiation at room temperature for 1 h (Supporting Information). The final photoconversion reached to 85.1 % in 3 h of UV irradiation, also showing an excellent agreement with the theoretical maximum yield. Furthermore, while **1** was not able to retain its single-crystal nature during photodimerization, the SCSC transformation from **1a** to **2a** under UV light at room temperature (Figure 4) was successfully observed. The single-crystal structure determination of **2a** clearly revealed the formation of cyclobutane ring. The conversion ratio was further determined from both the sets of disordered components in the crystal structure of **2a**. The occupancies of the dimer and monomer at the site of major and minor components were determined to be 0.573/0.292 and 0.090/0.045, respectively. Therefore a photochemical conversion of 66.3 % was observed crystallographically in an SCSC manner for this chosen crystal. Furthermore, surprisingly the thermal cleavage of a cyclobutane ring was also achieved in an SCSC fashion by heating of **2a** at 250 °C for 15 h. The crystal structure of **1a** converted from **2a** has the same structure of **1a**, as confirmed by single-crystal X-ray crystallography.[10] It means that the reversible reaction of photodimerization/selective thermal cleavage has been achieved in an SCSC manner. The herringbone structure of K_2SDC and/or the disorder in **1a** obtained by high temperature crystallization enabled the single crystal to maintain its integrity even under harsh conditions.

The reversible SCSC transformation of photodimerization and thermal cleavage inspired us to investigate their photoemissive properties (Figure 5). All of the solids exhibit different blue photoluminescence (PL) under UV light (Supporting Information). The solid-state PL spectra of all

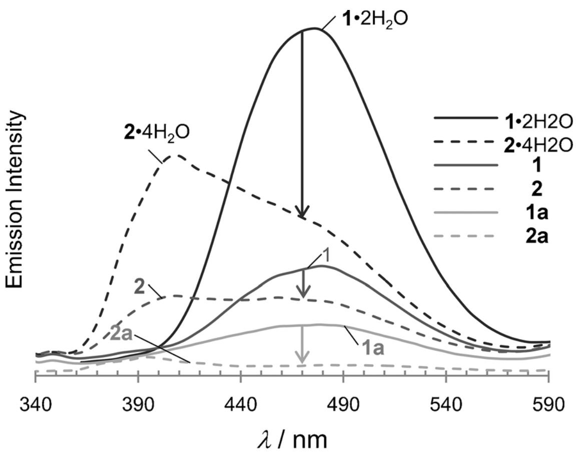

Figure 5. Fluorescence spectra of $\mathbf{1}{\cdot}2\,H_2O$, $\mathbf{2}{\cdot}4\,H_2O$, **1**, **2**, **1a**, and **2a**. Excitation wavelength is at 330 nm. The decreasing rate of emission intensity at 475 nm: 44.1 % ($\mathbf{2}{\cdot}4\,H_2O$ to $\mathbf{1}{\cdot}2\,H_2O$), 69.3 % (**2** to **1**), 20.5 % (**2a** to **1a**).

samples were measured and found to be distinctive. As expected, while the spectra of K_2SDCs, $\mathbf{1}{\cdot}2\,H_2O$, **1**, and **1a** showed a large broad peak around the blue-light-emitting region (ca. 475 nm), the spectra of all K_4TCCBs, $\mathbf{2}{\cdot}4\,H_2O$, **2**, and **2a** showed a broad peak around the violet light emitting region (ca. 400 nm) that is due to the localization of π electrons. Also it is noteworthy that the emission intensities of all the solids around 470 nm decreased drastically. The difference of emission intensities before and after UV irradiation is important for the application as in optical recording. The decrease in intensity around 475 nm from **1a** to **2a** is 20.5 %, whereas from **1** to **2** is 69.3 %. This indicates that the control of recrystallization temperature has an effect not only on the structure packing and single crystal stability, but also on the physical properties.

In summary, this study has demonstrated that varying the temperature in the synthesis produced two polymorphs of simple alkali metal salts of organic compounds having distinct packing with different physical properties. In particular, the high-temperature recrystallization overcomes the difficulty in sustaining its single-crystal nature during the photochemical formation and thermal cleavage. Our preliminary results on the photoemissive properties of the photodimerized and thermally cleaved products appear to support that this system can be extended to design materials for practical applications in optical recording, photoswitching, and sensing.

Received: August 1, 2013
Revised: November 4, 2013

Keywords: C–C bond cleavage · coordination polymers · cycloaddition · polymorphism · solid-state reactions

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[10] CCDC 934677, 934678, 934679, 934680, 934681, and 934682 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.