# CrystEngComm



**View Article Online** 

# PAPER



Cite this: CrystEngComm, 2016, **18**, 7305

Received 13th April 2016, Accepted 30th May 2016

DOI: 10.1039/c6ce00848h

www.rsc.org/crystengcomm

# Introduction

Solid-state photoreactions are necessarily accompanied by molecular motion, inducing macroscopic mechanical motion in bulk crystals. Molecular machines based on the linkage of microscopic molecular motion to macroscale crystal motion have received substantial attention in the contexts of both basic research and their wide range of potential applications. Such mechanical crystals are amenable to remote operation

# Mechanical motion of molecular crystals induced by [4 + 4] photodimerisation<sup>†</sup>

Hideko Koshima,<sup>\*a</sup> Hidetaka Uchimoto,<sup>b</sup> Takuya Taniguchi,<sup>c</sup> Jun Nakamura,<sup>b</sup> Tsuyoshi Asahi<sup>b</sup> and Toru Asahi<sup>ac</sup>

The photomechanical bending of crystals of a stilbene-type compound substituted with anthracene and indanone groups, (E)-2-(9-anthrylmethylene)-1-indanone (trans-1), was investigated. When a narrow platelike microcrystal was irradiated with ultraviolet (UV) light at 365 nm, the crystal gradually bent away from the light source and finally reached a semicircular shape after more than 10 min. A larger rod-like crystal, approximately 10 mm in length, also exhibited a slight bending motion. The cessation of UV irradiation caused the bent crystals to return very slowly to their straight form. In the crystals, the anthracene planes of two neighbouring trans-1 molecules are arranged in a head-to-tail parallel manner, with a short planeto-plane distance of only 3.72 Å. The <sup>1</sup>H nuclear magnetic resonance spectra of *trans*-1 crystals before and after UV irradiation revealed the intermolecular [4 + 4] photodimerisation of the two anthracene planes, while the trans-to-cis photoisomerisation was not significant. The UV-vis absorption spectra of the trans-1 powder crystals, obtained using a diffuse reflectance spectrophotometer, showed a gradual increase in absorbance between 200 and 500 nm with increasing UV irradiation time, reaching a maximum after 1 h. Thermal back-monomerisation was very slow in the dark, not recovering the initial spectrum even after 25 days. The fluorescence spectra at 570 nm, derived from the anthracene excimer, decreased in intensity with increasing UV irradiation time due to a decrease in the amount of anthracene chromophore via photodimerisation. In situ X-ray measurements revealed that the bending of the crystals was caused by slight elongation of the *b* axis of the unit cell, corresponding to the long axis of the rod-like crystals. Calculations revealed that the observed crystal elongation could be explained by an optimised head-to-tail [4 + 4] orientation of the anthracene dimer.

> with light and do not require wire connections. The photomechanical motion involves the direct conversion of light energy to mechanical energy, which is beneficial with regard to energy conversion. Despite the fact that molecular crystals have been commonly thought of as rigid and fragile, in 2007, Irie and coworkers reported reversible bending in rod-like molecular crystals of photochromic diarylethene upon photoirradiation and elucidated the bending mechanism using X-ray crystallographic analyses before and after irradiation, thereby linking molecular-level shape changes to macroscale mechanical motion in crystals.<sup>1</sup> In addition, Bardeen and coworkers demonstrated irreversible and reversible shape changes in rod-like nanocrystals of anthracene carboxylates by photodimerisation.<sup>2</sup> We previously reported several types of photomechanical bending of azobenzenes,<sup>3</sup> salicylideneanilines,<sup>4,5</sup> and furylfulgide<sup>6</sup> crystals. In the past decade, research on photomechanical crystals such as diarylethenes,<sup>7-9</sup> anthracenes,<sup>10,11</sup> azobenzenes,<sup>12</sup> benzylidenedimethylimidazolinone,13 cinnamic acid,14 bispyridylethylene salt,15 and naphthalene diimides<sup>16</sup> has increased rapidly. Recently, reviews<sup>17-20</sup> and a book<sup>21</sup> on photomechanical crystals have

<sup>&</sup>lt;sup>a</sup> Research Organization for Nano & Life Innovation, Waseda University, 513 Wasedatsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan.

E-mail: hkoshima@aoni.waseda.jp

<sup>&</sup>lt;sup>b</sup> Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan <sup>c</sup> Department of Advanced Science and Engineering, Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Movie S1, photomechanical bending of *trans-*1 crystal upon UV irradiation. CCDC reference numbers 1473633, 1473634, 1482558 and 1482559. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ce00848h

also been published. Nevertheless, there is a need for further development of new mechanical crystals with various characteristics in order to achieve their wide application potential as synthetic molecular machinery.<sup>22</sup>

A stilbene-type compound substituted with anthracene and indanone groups, (*E*)-2-(9-anthrylmethylene)-1-indanone (*trans*-1), undergoes *trans*-to-*cis* photoisomerisation in solution. In contrast, intermolecular [4 + 4] photodimerisation of the anthracene chromophore of *trans*-1 occurs in a crystalline state (Scheme 1).<sup>23,24</sup> Herein, we report the bending motion of rod-like *trans*-1 microcrystals upon ultraviolet (UV) irradiation. The possible mechanism behind this bending is also discussed based on *in situ* X-ray measurements and calculations of the optimised anthracene dimer product.

### **Experimental section**

#### Materials

Compound *trans*-1 was synthesised in accordance with the literature by the condensation of 9-anthraldehyde with 1-indanone.<sup>25</sup> Single crystals of *trans*-1 were prepared by slow evaporation of the solution in ethyl acetate as yellow rods [melting point (mp) 188.6–190.3 °C]. Microcrystals of *trans*-1 were prepared by sublimation of crystalline powder in a small aluminium pan covered with a glass plate. *Cis*-1 was prepared by photoirradiation (380 <  $\lambda$  < 740 nm) of *trans*-1 in acetone solution with a xenon lamp. Crystals of *cis*-1 were prepared by recrystallisation from acetone as a yellow block (mp 224.3–229.8 °C).

#### X-ray crystallography

X-ray diffraction (XRD) data for a *trans*-1 single microcrystal were collected using a Rigaku VariMax SaturnCCD724 diffractometer equipped with a monochromatic Cu-K $\alpha$  radiation source ( $\lambda = 1.54187$  Å). A Rigaku R-AXIS RAPID diffractometer with a monochromatic Mo-K $\alpha$  radiation source ( $\lambda = 0.71069$  Å) was also employed. Crystal structures were solved using direct methods and expanded using Fourier techniques. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were not refined. Hydrogen atoms attached to carbon atoms were located in the calculated positions. Calculations were performed using Rigaku crystal structure software packages.<sup>26</sup>



**Scheme 1** [4 + 4] Photodimerisation of (*E*)-2-(9-anthrylmethylene)-1-indanone (*trans*-1) in the crystals.

#### Spectrophotometry

UV-vis diffuse reflectance spectra of *trans*-1 powder crystals were measured using a Perkin Elmer Lambda 650 spectrophotometer. UV light irradiation was conducted using a Keyence UV-LED UV-400 lamp (365 nm, 40 mW cm<sup>-2</sup>) and an Asahi Spectra MAX-302 xenon lamp with a 260 nm band pass filter. Fluorescence spectra of *trans*-1 crystals were measured by using a Hitachi F-4500 fluorospectrophotometer.

#### Observation of photomechanical motion

Rod-like single crystals of *trans*-1 were mounted on the tips of glass needles. Any photomechanical motion upon UV light irradiation was observed and recorded with a Keyence VHX-5000 digital high-speed microscope. UV irradiation was performed using a Keyence UV-LED UV-400 lamp (365 nm, 40 mW cm<sup>-2</sup>) and an Asahi Spectra MAX-302 xenon lamp with a 260 nm band pass filter.

## Results and discussion

#### Photomechanical motion

Narrow plate-like microcrystals of *trans*-1 were obtained by sublimation on a glass plate (Fig. S1a, ESI<sup>†</sup>). The XRD diffractograms of the microcrystals contained four peaks, which were assigned to 002, 102, 204, and 306 reflections based on crystallographic data. The major top surface was identified as the (102) face, and the minor one as the (001) face (Fig. S1b, ESI<sup>†</sup>). The longitudinal direction was denoted along the *b* axis based on comparisons with rod-like bulk single crystals.

Fig. 1a shows a piece of a narrow plate-like microcrystal of *trans*-1 (511  $\mu$ m long × 4.5  $\mu$ m wide × 0.5  $\mu$ m thick) grown from the surface of another crystal on a glass plate by sublimation at 140 °C for 6 h. The lower portion of the microcrystal was fixed, while the upper portion was free to move. When the microcrystal was irradiated from the right at 365 nm with a UV-LED lamp (40 mW cm<sup>-2</sup>), the crystal gradually bent away from the light to reach a tip displacement angle of 28° after 4 min (Fig. 1b), reaching more than 180° after 13 min (Fig. 1c and Movie S1, ESI†).



Fig. 1 Bending of a narrow plate-like *trans*-1 microcrystal is shown (a) before and after UV irradiation from the right for (b) 4 and (c) 13 min. The scale bar is 100  $\mu$ m.

Rod-like single crystals of *trans*-1 approximately 10 mm in length were obtained by slow evaporation of an ethyl acetate solution. A piece of the crystal ( $8.20 \times 0.40 \times 0.36 \text{ mm}^3$ ) was submitted for X-ray crystallographic analysis; the top surfaces were assigned as the (001) and (100) faces along the longitudinal direction along the *b* axis. Fig. 2a shows the frontal (001) face with one end fixed to a glass needle with an adhesive. When the (100) face was irradiated from the right at 365 nm, the crystal gradually bent away from the light to reach a maximum tip displacement angle of 3° after 5 min (Fig. 2b). Further irradiation did not increase the bend angle.

We checked the relationship between the bending angle and the thickness by irradiating several different sizes of plate-like *trans*-1 crystals. As a result, it was revealed that the logarithm of the bending angle was inversely and linearly proportional to the logarithm of the crystal thickness (Fig. S2†).

The reversibility of the bending was also examined. A narrow plate-like crystal (2700 × 67 × 15  $\mu$ m<sup>3</sup>) gradually bent upon UV irradiation to reach a maximum tip displacement angle of 14° after 20 min (Fig. 3, panels a and b). Subsequent cessation of UV irradiation did not result in recovery from the bent state, even after one day (Fig. 3c). Prolonged storage of the crystal in the dark resulted in a partial return of the bend angle to 4° (Fig. 3d). This slow return to a straight shape is likely to have been due to very slow thermal backmonomerisation from the anthracene dimer 2 to the *trans*-1 molecule. Furthermore, when a narrow plate-like microcrystal of *trans*-1 (426.3 × 5.1 × 0.5  $\mu$ m<sup>3</sup>) was alternately irradiated from the right and the left four times for a total of 15 min in order to prevent bending, the length of the crystal increased by 0.5% (Fig. S3, ESI†).

#### Crystal structure and photomechanical motion relationship

X-ray crystallographic analysis of *trans*-1 was performed using a microcrystal ( $130 \times 41 \times 16 \ \mu m^3$ ) at 20 °C.<sup>27</sup> This crystal belongs to the orthorhombic system and space group *Pbca*. Its ORTEP diagram is shown in Fig. 4a. The *trans*-1 molecule has a torsional conformation with a dihedral angle between the anthracene plane and the indanone plane of 71.65°. The



**Fig. 2** The frontal (001) face of the rod-like *trans*-**1** single crystal (a) before and (b) after UV irradiation from the right. The scale bar is 2 mm.



Fig. 3 Reversible bending of a narrow plate-like *trans*-1 microcrystal (a) before and (b) upon UV irradiation from the left for 20 min, and then straightening after cessation of UV irradiation for (c) one day and (d) 12 days. The scale bar is 500  $\mu$ m.

two *trans*-1 molecules are arranged in a parallel head-to-tail manner with some slip of the anthracene planes (Fig. 4, panels b and c). The plane-to-plane distance is only 3.72 Å, suggesting that the occurrence of intermolecular [4 + 4] photodimerisation affords the head-to-tail anthracene dimer 2 by UV irradiation.

The <sup>1</sup>H nuclear magnetic resonance (NMR) spectra of powdered *trans*-1 crystals were measured in CDCl<sub>3</sub> after they had been irradiated at 365 nm for 4 h. The spectrum of *trans*-1 contained two singlet peaks at 2.84 and 4.82 ppm (integration ratio 2:1) and aromatic proton signals at 6.7–7.1 ppm. These data indicate that the anthracene dimer 2 was produced *via* intermolecular [4 + 4] cycloaddition (Fig. S4, ESI†), consistent with a previous report.<sup>23</sup> However, the characteristic singlet peak of the *cis*-1 isomer at 4.24 ppm was not observed after UV irradiation, indicating almost no occurrence of *trans*-to-*cis* photoisomerisation. The yield of [4 + 4] cycloadduct 2 was estimated to be 4% from the hydrogen integration. Irradiation at 365 nm for longer than 4 h did not increase the yield, and irradiation at 400 and 420 nm gave lower yields of 2.

The UV-vis absorption spectra of the powdered *trans*-1 crystals measured by diffuse reflectance spectrophotometry at 20 °C revealed a broad absorption peak between 200 and 500 nm (Fig. 5a). The peak intensity increased upon UV



**Fig. 4** Crystal structure of *trans*-**1**. (a) ORTEP drawing at the 50% probability level. Head-to-tail parallel arrangements of anthracene planes are shown on the (b) (010), (c) (100), and (d) (001) faces. The red arrow indicates the direction of the anisotropic elongation of the crystal along the *b* axis. Hydrogen atoms in (b–d) are omitted for clarity.



**Fig. 5** UV-vis diffuse reflectance spectra of *trans*-**1** in the powder crystals: (a) UV irradiation at 365 nm, and then (b) in the dark after cessation of UV irradiation.

irradiation at 365 nm, reaching a steady state after 60 min. The observed changes in the absorption spectra of the *trans*-isomer are attributable not to the *trans*-to-*cis* isomerisation, but to [4 + 4] photodimerisation.<sup>28</sup> The cessation of UV irradiation did not completely recover the initial spectrum even after 25 days, showing very slow thermal backmonomerisation to the *trans*-isomer (Fig. 5b). Such slow spectral changes upon UV irradiation and after the cessation of irradiation of *trans*-1 in the crystalline state can reasonably explain the slow bend and return motion of the rod-like crystals, as shown in Fig. 1–3.

For reference, the absorption spectra of the *trans*-1 and *cis*-1 isomers were measured in acetonitrile solution (Fig. S5, ESI<sup>†</sup>) and were similar to those reported in the literature.<sup>24</sup> Photoisomerisation to the *cis*-isomer proceeded smoothly in solution. UV irradiation of the *trans*-1 isomer for only 2 min was nearly sufficient to complete the isomerisation, demonstrating a different photochemical behaviour from that observed in the crystalline state.

The fluorescence spectra of powdered *trans*-1 crystals, with excitation at 360 nm, contained a fluorescence peak at 570 nm, derived from the anthracene excimer (Fig. 6a).<sup>29</sup> UV irradiation (365 nm, 40 mW cm<sup>-2</sup>) decreased the fluorescence intensity to 50% and 20% after 15 and 60 min, respectively, due to a decrease in the relative concentration of the anthracene chromophore by [4 + 4] photodimerisation in the crystalline state. The image in Fig. 6b shows the faint yellow/ green fluorescence emitted from the irradiated spot.

The bending motion of the *trans*-1 plate-like crystals to the opposite side of the UV light source indicates that the irradiated surface expands along the long axis of the crystals, which corresponds to the *b* axis. To confirm the mechanism responsible for this motion, *in situ* X-ray crystallographic



**Fig. 6** (a) Fluorescence spectra of *trans*-**1** in the powder crystals ( $\lambda_{ex}$  = 360 nm) before and under UV irradiation at 365 nm. (b) Photograph of the *trans*-**1** single crystal after UV irradiation.

analyses were preformed before and after UV irradiation. First, the same microcrystal of *trans*-1 (130 × 41 × 16  $\mu$ m<sup>3</sup>), the crystal structure of which was determined as shown in Fig. 4,<sup>27</sup> was homogeneously irradiated at 365 nm (40 mW cm<sup>-2</sup>) under slow rotation (10 rpm). Any changes in the unit cell dimensions were intermittently measured. The lengths of the *a* and *b* axes of the unit cell gradually increased with increasing irradiation time by +0.24% and +0.71%, respectively, after 160 min, while that of the *c* axis decreased (-0.41%) (Fig. S6, ESI†). However, the cell parameters obtained by the crystallographic analysis without UV irradiation almost returned to their initial values (*a*, -0.03%; *b*, +0.01%; *c*, -0.30%).<sup>27</sup>

In order to make clear the reason for the return to the initial unit cell lengths during X-ray measurement for two days, we checked the changes in the cell parameters of another crystal  $(0.8 \times 0.2 \times 0.1 \text{ mm}^3)$  under continuous UV irradiation during X-ray measurement.<sup>27</sup> The crystal was first irradiated with UV light for 180 min; the cell parameters changed (a, +0.12%; b,+0.35%; c, -0.02%). Subsequently, the crystal was submitted to crystallographic analysis under continuous UV irradiation; the X-ray measurement was completed after 8 h. The cell parameters partially returned to their initial values (a, -0.03%; b,0.12%; c, -0.25%) even upon keeping the crystal under UV irradiation. These results suggest that the back-monomerization of the cycloadduct might be caused by exposure to X-ray radiation. Similar cleavage of the cycloadduct by X-ray exposure during crystallographic measurement was previously reported.<sup>30</sup> Further study is required to elucidate the mechanism.

The molecular geometry of the head-to-tail anthracene dimer 2 was optimised by molecular mechanics calculations using the universal force field algorithm in Avogadro.<sup>31</sup> The distance between the two end hydrogen atoms H3 and H4 of the optimised dimer 2 was estimated to be 20.10 Å (Fig. 7b), while that between the two end hydrogen atoms H1 and H2 of the head-to-tail parallel stacking of the two *trans*-1 molecules from the crystal structure was 19.94 Å (Fig. 7a). This suggests that the crystal length elongates along the *b* axis *via* [4 + 4] photodimerisation.

Fig. 7(panels c and d) shows a possible mechanism of bending of the *trans*-1 crystal. On the (100) face, the head-to-tail parallel stacking of the two *trans*-1 molecules is arranged in a zigzag manner to form a columnar structure along the b



Fig. 7 Molecular conformations of (a) the head-to-tail parallel stacking of the two *trans*-1 molecules and (b) the optimised dimer 2 molecule on the (100) face. The direction of the dimer 2 molecule was also optimised by least-squares for minimising atom displacement accompanied by intermolecular [4 + 4] photodimerisation. Schematic illustration of the photomechanical bending of the *trans*-1 crystal (c) before and (d) after UV irradiation.

axis (Fig. 7c). When the (001) face of a narrow plate-like crystal is irradiated with UV light, the length of the crystal along the longitudinal direction, *i.e.*, along the *b* axis, increases at the irradiated surface while the back surface of the crystal does not change due to the lack of light penetration. This causes the crystal to bend away from the light source (Fig. 7d).

# Conclusions

Upon UV irradiation, a narrow plate-like microcrystal of a stilbene-type compound substituted with anthracene and indanone groups (trans-1) gradually bent away from the light source, attaining a semicircular shape. A larger rod-like crystal, approximately 10 mm in length, also exhibited a slight bending motion. The cessation of UV irradiation resulted in a very slow return of the bent crystals to their original straight forms. In the crystals, the anthracene planes of two neighbouring trans-1 molecules are arranged in a head-to-tail parallel manner, with a short plane-to-plane distance of only 3.72 Å. <sup>1</sup>H NMR measurements revealed that intermolecular [4 + 4] photodimerisation of the two anthracene planes mainly occurred, while trans-to-cis photoisomerisation was not significant. In situ X-ray measurements revealed that the bending motion of the crystals was caused by slight elongation of the *b* axis of the unit cell, corresponding to the long axis of the rod-like crystals. Molecular geometry calculations revealed that this crystal elongation could be explained by the optimised geometry of the head-to-tail anthracene dimer.

# Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research in a Priority Area "New Frontiers in Photochromism" (471) of the Ministry of Education, Culture, Sports, Science and Technology and a Grant-in-Aid for Scientific Research (B) (22350063) of the Japan Society for the Promotion of Sciences. This work was also supported by the High-Tech Research Center (TWIns) and the Leading Graduate Program in Science and Engineering, Waseda University.

## Notes and references

- 1 S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778–781.
- 2 (a) R. O. Al-Kaysi, A. Müller and M. C. J. Bardeen, J. Am. Chem. Soc., 2006, 128, 15938–15939; (b) R. O. Al-Kaysi and C. J. Bardeen, Adv. Mater., 2007, 19, 1276–1280.
- 3 (a) H. Koshima, N. Ojima and H. Uchimoto, J. Am. Chem. Soc., 2009, 131, 6890–6891; (b) H. Koshima and N. Ojima, Dyes Pigm., 2012, 92, 798–801.
- 4 H. Koshima, K. Takechi, H. Uchimoto, M. Shiro and D. Hashizume, *Chem. Commun.*, 2011, 47, 11423–11425.
- 5 H. Koshima, R. Matsuo, M. Matsudomi, Y. Uemura and M. Shiro, *Cryst. Growth Des.*, 2013, 13, 4330–4337.
- 6 H. Koshima, H. Nakaya, H. Uchimoto and N. Ojima, *Chem. Lett.*, 2012, **41**, 107–109.
- 7 (a) L. Kuroki, S. Takami, K. Yoza, M. Morimoto and M. Irie, *Photochem. Photobiol. Sci.*, 2010, 9, 221–225; (b) M. Morimoto and M. Irie, *J. Am. Chem. Soc.*, 2010, 132, 14172–14178; (c) F. Terao, M. Morimoto and M. Irie, *Angew. Chem., Int. Ed.*, 2012, 51, 901–904.
- 8 K. Uchida, S. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma and B. L. Feringa, *Chem. Commun.*, 2008, 326–328.
- 9 (a) S. Kobatake, H. Hasegawa and K. Miyamura, Cryst. Growth Des., 2011, 11, 1223–1229; (b) D. Kitagawa, H. Nishi and S. Kobatake, Angew. Chem., Int. Ed., 2013, 52, 9320–9322; (c) D. Kitagawa and S. Kobatake, J. Phys. Chem. C, 2013, 117, 20887–20892; (d) D. Kitagawa and S. Kobatake, Photochem. Photobiol. Sci., 2014, 13, 764–769.
- 10 (a) L. Zhu, A. Agarwal, J. Kai, R. O. Al-Kaysi, F. S. Tham, T. Ghaddar, L. Mueller and C. J. Bardeen, *J. Mater. Chem.*, 2011, 21, 6258–6268; (b) L. Zhu, R. O. Al-Kaysi and C. J. Bardeen, *J. Am. Chem. Soc.*, 2011, 133, 12569–12575.
- 11 T. Kim, M. K. Al-Muhanna, S. D. Al-Suwaidan, R. O. Al-Kaysi and C. J. Bardeen, *Angew. Chem., Int. Ed.*, 2013, 52, 6889–6893.
- 12 (a) O. S. Bushuyev, T. A. Singleton and C. J. Barrett, Adv. Mater., 2013, 25, 1796–8000; (b) O. S. Bushuyev, A. Tomberg, T. Friščić and C. J. Barrett, J. Am. Chem. Soc., 2013, 135, 12556–12559; (c) O. S. Bushuyev, T. C. Corkery, C. J. Barret and T. Friščić, Chem. Sci., 2014, 5, 3158–3164.
- 13 P. Naumov, J. Kowalik, K. M. Solntsev, A. Baldridge, J.-S. Moon, C. Kranz and L. M. Tolbert, *J. Am. Chem. Soc.*, 2010, 132, 5845–5857.

- 14 T. Kim, L. Zhu, L. J. Mueller and C. J. Bardeen, *CrystEngComm*, 2012, 14, 7792–7799.
- 15 J.-K. Sun, W. Li, C. Chen, C.-X. Ren, D.-M. Pan and J. Zhang, Angew. Chem., Int. Ed., 2013, 52, 6653–6657.
- 16 Y. Matsunaga, K. Goto, K. Kubono, K. Sako and T. Shinmyozu, *Chem. Eur. J.*, 2014, **20**, 7309–7316.
- 17 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, 114, 12174–12277.
- 18 T. Kim, L. Zhu, R. O. Al-Kaysi and C. J. Bardeen, *ChemPhysChem*, 2014, 15, 400–414.
- 19 P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath and E. Boldyreva, *Chem. Rev.*, 2015, 115, 12440–12490.
- 20 J. M. Abendroth, O. S. Bushuyev, P. S. Weiss and C. J. Barrett, *ACS Nano*, 2015, 9, 7746–7768.
- 21 New Frontiers in Photochromism, ed. M. Irie, Y. Yokoyama and T. Seki, Springer, Tokyo, 2013, ch. 1 and 2.
- 22 M. A. Garcia-Garibay, Angew. Chem., Int. Ed., 2007, 46, 8945-8947.
- 23 Y. Mori and K. Maeda, Acta Crystallogr., Sect. B: Struct. Sci., 1994, 50, 106–112.

- 24 J. Harada, M. Harakawa, S. Sugiyama and K. Ogawa, *CrystEngComm*, 2009, **11**, 1235–1239.
- 25 A. Russell and W. B. Happoldt Jr., J. Am. Chem. Soc., 1942, 64, 1101–1103.
- 26 CrystalStructure 2014, version 4.1., Rigaku Corporation, Tokyo, Japan.
- 27 X-Ray diffraction analyses of *trans*-1 crystals before and after UV irradiation were carried out at 20 °C. The crystal data were deposited in the ESI<sup>†</sup>.
- 28 B. Hans-Dieter, B. Hans-Christian and L. Vratislav, J. Photochem. Photobiol., A, 1996, 97, 25–32.
- 29 A. Chandross and J. Ferguson, J. Chem. Phys., 1966, 45, 3564–3567.
- 30 (a) A. Mori, N. Kato, H. Takeshita, Y. Kurahashi and M. Ito, J. Chem. Soc., Chem. Commun., 1994, 869–870; (b) H. Uekusa and Y. Ohashi, Mol. Cryst. Liq. Cryst., 1996, 279, 285–289; (c) A. Mori, T. Nakamura, K. Kudo, T. Takeshita and N. Kato, Mol. Cryst. Liq. Cryst., 2002, 389, 65–71.
- 31 M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch,E. Zurek and G. R. Hutchison, *J. Cheminf.*, 2012, 4, 17.