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In situ observation and mechanistic elucidation of metastable colored species in crystalline state photochromism of *trans*-biindenylidenedione†

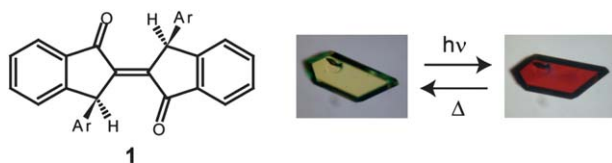
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A metastable colored species from the photochromic reaction of *trans*-biindenylidenedione, which only proceeds in the crystalline state, has been directly observed by *in situ* crystal structure analysis method. The reaction mechanism and observed color change have also been confirmed from the theoretical calculation and the spectral measurement.

Since their discovery, organic photochromic materials have attracted considerable attention due to their potential applications in optical glasses, storage devices, electric displays, and optical switches.¹ Previously, we reported a new organic photochromic compound *trans*-3,3'-diaryl-3*H*,3'*H*-[2,2']biindenylidene-1,1'-dione derivative (**1**).² The initially yellow crystals of this type of compound turn red upon UV irradiation. These irradiated crystals then thermally return to the initial yellow color in the dark.^{2b} Interestingly, the photochromism of these compounds is only seen in the crystalline state and not in solution because a *cis*–*trans* isomerization occurs instead of the photochromic reaction in solution.^{2b} This restriction of the investigation to the crystalline state makes it difficult to investigate the mechanistic aspects of the photochromism. Furthermore, the isolation of the red species is difficult because it readily returns to the initial yellow state when the compound is dissolved. For these reasons, the structure of the metastable red color species has remained unclear.



Of all the techniques used to investigate the solid-state photochromism, single crystal X-ray diffraction analysis is the most powerful and allows the direct observation of the different species generated by the photochromic reaction.³ Herein, we report the direct observation of changes in the crystal structure of 3-methyl-phenyl substituted **1** (denote **1a**) under photoirradiated conditions on a single

crystal and establish the mechanistic aspects of the photochromic reaction.

1a was prepared according to the previously reported method.^{2b} Yellow platelets were obtained by recrystallization and were used for all the single crystal X-ray diffraction measurements. To compare the crystal structures of the initial and irradiated states, the X-ray diffraction measurements and integrations were carried out using identical conditions.⁴

The molecular structure observed for the initial yellow crystal is shown in Fig. 1a. One of the two 3-methyl-phenyl groups was found to be disordered with a minor occupancy of 7.8(4)% as determined by least squares refinement. Introducing this disorder to the model decreased R_1 [$F^2 > 2\sigma(I)$] from 0.0469 to 0.0432 and improved the residual electron density ($\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$, $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$).⁵

After measurement of the initial yellow crystal, the crystal was photoirradiated using a high pressure mercury lamp (SANEI UVF-352S, 350W)⁷ and then the measurement was repeated under continuous photoirradiation.⁸ The photoirradiation induced a color

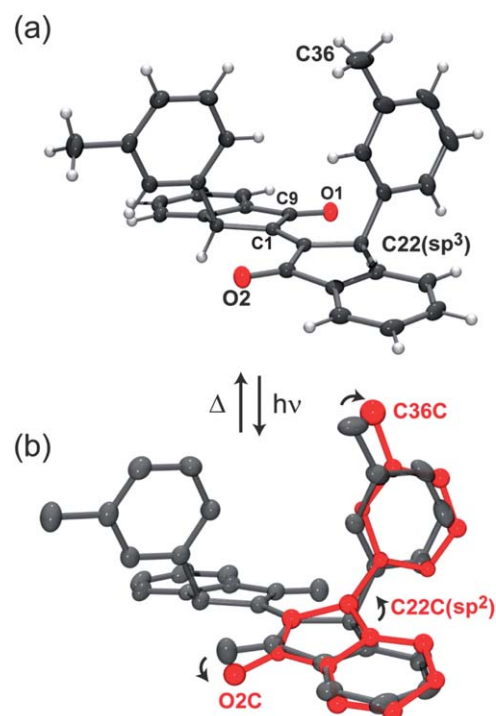


Fig. 1 The molecular structure in (a) the initial yellow crystal (before photoirradiation) and (b) the red crystal (under photoirradiation) with the arrows indicating the structural changes on photoirradiation. The displacement ellipsoids are shown at the 50% probability level and the disorder observed in the 3-methyl-phenyl group was omitted for clarity.

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† Electronic supplementary information (ESI) available: CIF files of crystal structures of the initial yellow crystal, the photoirradiated red crystal and the yellow crystal after storing the red coloured crystal in a dark condition. CCDC reference numbers 784442–784444. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00642d

change from yellow to red and the unit cell parameters were slightly increased ($\Delta a = +0.021(2) \text{ \AA}$, $\Delta b = +0.115(3) \text{ \AA}$, $\Delta c = +0.010(3) \text{ \AA}$, $\Delta\beta = 0.650(4)^\circ$, $\Delta V = +14.0(7) \text{ \AA}^3$) while retaining the same space group.⁹ During the structural refinement, significant residual electron density peaks were observed around C36 (0.88 e \AA^{-3}), C22 (0.62 e \AA^{-3}) and O2 (0.50 e \AA^{-3}) which were not observed in the initial yellow crystal. These peaks were deemed to be due to the presence of the red species. After assigning these peaks, the red molecule generated by photoirradiation was revealed as shown in Fig. 1b. The occupancy of this red color molecule was refined to 13.0(3)% and low levels of residual electron density were achieved ($\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$, $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$).

The most important feature of the structural change from yellow to red is the change in the geometry of C22 from sp^3 to sp^2 (labelled C22 and C22C, respectively, in Fig. 1). This change was confirmed from the sum of the internal bond angles around C22C which was calculated to be 359.6° (almost 360°) and from the planarity around C22C, as all of the atoms bonded to C22C were within 0.05 \AA of the same plane. In addition, the observed residual electron density around C36 and O2 clearly indicates a possible inclination of the indenone ring and 3-methyl-phenyl group (*ca.* 15°), which would be caused by the geometrical change at C22, as shown by the arrows in Fig. 1b. These results indicate C22C has become an sp^2 carbon. The other interesting structural change after photoirradiation was that the length of the C1–C9 bond decreased by $0.026(3) \text{ \AA}$ and the C9–O1 bond increased by $0.018(3) \text{ \AA}$.¹⁰ No disorder was detected in this indenone ring in either the initial structure or the photoirradiated structure, however, the red molecule would overlap the yellow molecule and causes these changes even at an occupancy of only 13%.

Assuming these changes in bond length are due to the C22C carbon being sp^2 , the chemical structure of the red color molecule can be drawn as **2a**, as shown in Fig. 2. In this molecule, in addition to the changes around C22, the bond between C1 and C9 changes from a single to a double bond and the bond between C9 and O1 changes from a double to a single bond. These changes are all consistent with the structural features of the metastable red molecule described above. Further confirmation of this chemical structure (**2a**) comes from IR spectral changes upon photoirradiation.¹¹ Although hydrogen atoms are difficult to observe from X-ray diffraction due to the small scattering factor, the observation of the OH group generated in **2a** aids in the assignment of the new molecule. As shown in the IR spectra (Fig. 3), a new absorption band appeared at 3490 cm^{-1} in the red crystal and this has been assigned to be an O–H stretching vibration mode.

The reaction scheme shown in Fig. 2 can be considered a Norrish Type II reaction and occurs *via* intramolecular hydrogen abstraction. In the Norrish Type II reaction, the carbonyl $n\pi^*$ excitation is the driving force resulting in the abstraction of the γ -hydrogen atom and

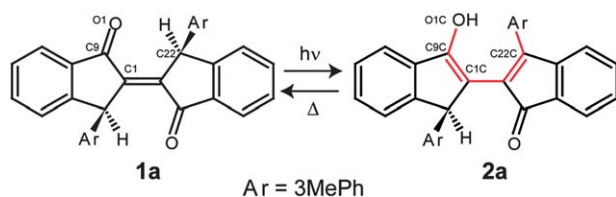


Fig. 2 Chemical diagrams of the initial yellow molecule (**1a**) and red species (**2a**) as determined in this study.

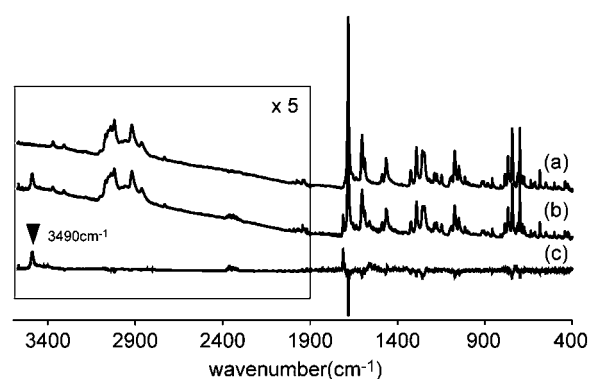


Fig. 3 IR spectra of (a) initial yellow crystal, (b) red crystal obtained by the photoirradiation and (c) difference plot (subtract a from b).

formation of a hydroxy group. Thus the photochromic reaction of **1a** produces **2a**. The biradicals observed in a previous study^{2b} are consistent with the Norrish Type II reaction because it proceeds *via* a biradical intermediate.

The UV spectra of **1a** before and after photoirradiation are shown in Fig. 4. A strong absorption band appears centred at 570 nm and causes the color change from yellow to red. To confirm that the molecular structure of **2a** has an absorption band at 570 nm , the simulated UV/vis spectra were calculated for **1a** and **2a**.¹² A strong absorption band was calculated at 516 nm only for **2a** indicating this interpretation of the spectrum is consistent with the molecular structure described for **2a**.

The red colored single crystal was finally stored in the dark for two days and the diffraction data were collected again. The crystal had returned to yellow and the unit cell parameters had also returned to almost the same values as the initial measurements.¹³ In addition, the residual electron densities observed only in the red crystal had disappeared and the analysed structure was the same as the initial structure from the yellow crystal ($\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$, $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$). This clearly indicates that the observed residual electron densities were due to the presence of the red molecule.

In summary, the metastable red color species generated by the photochromic reaction of **1a** has been directly observed by X-ray diffraction analysis of a photoirradiated single crystal. From the observed structure, the reaction product was determined to be **2a** and the mechanism of the photochromic reaction is consistent with

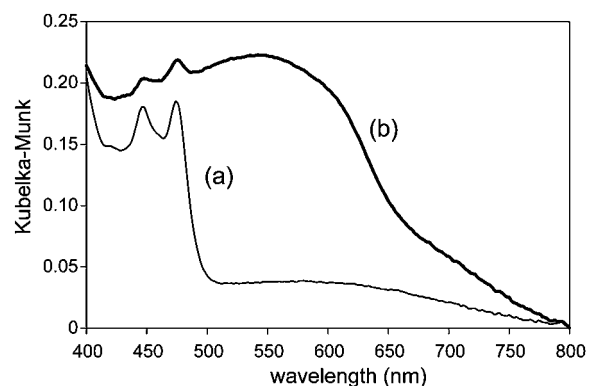


Fig. 4 UV/vis spectra of (a) the initial yellow crystal and (b) the red crystal obtained by photoirradiation.

a Norrish Type II reaction. This conclusion was supported by additional spectral studies. It is important to note that this reaction only proceeds in the crystalline state and that the photoirradiated single crystal X-ray diffraction analysis plays a unique role in the identification of the photochromic reaction.

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- The data collections were carried out at $-180\text{ }^{\circ}\text{C}$ on a Bruker SMART CCD diffractometer (MoK α radiation).
- Crystal structure of the initial yellow crystal: C₃₂H₂₄O₂, $M_r = 440.51$, monoclinic, space group $P2_1/c$, $a = 11.3635(14)\text{ } \text{\AA}$, $b = 14.1791(17)\text{ } \text{\AA}$, $c = 15.1146(18)\text{ } \text{\AA}$, $\beta = 111.006(2)^{\circ}$, $V = 2273.5(5)\text{ } \text{\AA}^3$, $D_{\text{calc}} = 1.287\text{ g cm}^{-3}$, $T = -180\text{ }^{\circ}\text{C}$, no. of unique reflections = 5232, $R_{\text{int}} = 0.0403$ up to $2\theta = 55^{\circ}$, no. of parameters = 328, $R_1 [F^2 > 2\sigma(F^2)] = 0.0432$, $wR_2 (F^2) = 0.1197$, $S = 1.040$ for 5232 reflections. The crystal structure was solved using direct methods in SHELXS-97 (ref. 6) and refined by full-matrix least square on F^2 using SHELXL-97.⁶ In the structural refinement, all non-hydrogen atoms belonging to the major part of the disorder were refined anisotropically and the atoms of the minor part of the disorder were refined isotropically. All hydrogen atoms were located geometrically and refined using a riding model.
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- In some cases, using an absorption edge light may give much larger reaction conversion; however, it did not give better result in this case, so that the photoirradiation was carried out without any optical filters.
- The photoirradiation was carried out at $20\text{ }^{\circ}\text{C}$ on the diffractometer. The distance from light source to crystal was *ca.* 5 cm and the single crystal was rotated during the photoirradiation. After 6 hours of photoirradiation, the crystal was cooled down to $-180\text{ }^{\circ}\text{C}$ (data collection temperature). Because the photochromic reaction thermally returns to the initial state, the photoirradiation was continued during the diffraction measurement in order to keep as many molecules in the red state as possible.
- Crystal structure of the red crystal measured under photoirradiation: C₃₂H₂₄O₂, $M_r = 440.51$, monoclinic, space group $P2_1/c$, $a = 11.3843(15)\text{ } \text{\AA}$, $b = 14.2937(19)\text{ } \text{\AA}$, $c = 15.125(2)\text{ } \text{\AA}$, $\beta = 111.656(3)^{\circ}$, $V = 2287.5(5)\text{ } \text{\AA}^3$, $D_{\text{calc}} = 1.279\text{ g cm}^{-3}$, $T = -180\text{ }^{\circ}\text{C}$, no. of unique reflections = 5280, $R_{\text{int}} = 0.0554$ up to $2\theta = 55^{\circ}$, no. of parameters = 376, $R_1 [F^2 > 2\sigma(F^2)] = 0.0471$, $wR_2 (F^2) = 0.1308$, $S = 1.018$ for 5280 reflections.
- Bond lengths have only been discussed for the part without disorder, as the bond length precision for disordered parts is always low. Among the bond length of non-disordered part, only C1–C9 and C9–O1 had changes in their bond lengths larger than 3σ .
- A KBr pellet (0.5 wt%) of **1a** was prepared and used for FTIR spectral measurement (Bio-Rad Excalibur FTS 3000). The photoirradiation was carried out using a high-pressure mercury lamp.
- The computational calculations were carried out using SPARTAN'08 (Wavefunction, Inc.). The molecular structures obtained by the X-ray diffraction analysis were used for the calculations with generated hydrogen atoms in suitable positions. A single point energy calculation using DFT (B3LYP with a 6-31G* basis set) followed by the time-dependent DFT calculations provided the simulation UV/vis spectra. The geometry optimization of **2a** induced a large conformational change due to the rotation around the central single bond. Because such optimized molecular conformation does not correspond to the actual molecular conformation in the crystal, the calculations were carried out without geometry optimization.
- Crystal structure of the yellow crystal after storing the red crystal in a dark condition for two days: C₃₂H₂₄O₂, $M_r = 440.51$, monoclinic, space group $P2_1/c$, $a = 11.3564(14)\text{ } \text{\AA}$, $b = 14.1618(17)\text{ } \text{\AA}$, $c = 15.1141(18)\text{ } \text{\AA}$, $\beta = 111.017(2)^{\circ}$, $V = 2269.0(5)\text{ } \text{\AA}^3$, $D_{\text{calc}} = 1.290\text{ g cm}^{-3}$, $T = -180\text{ }^{\circ}\text{C}$, no. of unique reflections = 5244, $R_{\text{int}} = 0.0451$ up to $2\theta = 55^{\circ}$, no. of parameters = 328, $R_1 [F^2 > 2\sigma(F^2)] = 0.0439$, $wR_2 (F^2) = 0.1189$, $S = 1.021$ for 5244 reflections.