



A real-time dynamic holographic material using a fast photochromic molecule

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SUBJECT AREAS:

PHYSICAL CHEMISTRY

IMAGING

OPTICAL MATERIALS AND
DEVICES

ORGANIC CHEMISTRY

Received

15 June 2012

Accepted

18 October 2012

Published

8 November 2012

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We have developed a real-time, dynamic holographic material that exhibits rapid colouration upon irradiation with UV light and successive fast thermal bleaching within tens of milliseconds at room temperature. Photochromic polymer films were prepared by a simple solution-casting method from the benzene solution of the mixture of the photochromic molecule, poly(ethyl acrylate), and poly(phenoxyethyl acrylate). The real-time control of holographic images using the photochromic polymer film yields a speed equivalent to the time resolution of the human eye. This new type of dynamic holographic material based on fast photochromism opens up an exciting new area of research in the future development of a large dynamic 3D display.

Recently, 3D display technology has attracted much attention due to the spread of 3D televisions. A real-time, dynamic, 3D display can be achieved using holograms, which can reconstruct vast amounts of information and can produce 3D images that appear similar to how humans see the original objects. Hence, holography has attracted much attention as a next-generation 3D display technology that requires no special eyewear¹⁻⁸. However, no commercial use of holographic 3D display technology has been developed to date because of serious issues that have not yet been solved. The major problem to be solved in the production of a practical holographic 3D display is the development of large size photoresponsive materials that can update holographic images in real time. Photorefractive polymeric materials are one member of a class of candidates that make it possible to refresh images every few seconds⁷⁻⁹. However, the photorefractive effect requires the application of a high voltage to record light-based information. In contrast, photochromic materials can store light-based information without applying a voltage. Photochromic materials are a well-known class of molecules that change their colour upon irradiation with light; the photogenerated species can be reversed to the initial species either thermally or by subsequent irradiation with a specific wavelength of light¹⁰. In addition, large size photochromic polymer films can be easily prepared from a polymer solution containing photochromic molecules by a simple solution-casting method. In this study, we prepared and analysed a real-time dynamic holographic material using a fast photochromic polymer film with unique photoresponsive characteristics.

Holograms, which are recordings of the interference patterns in two- or three-dimensional media, are a key technology for the development of future 3D displays¹. The interference pattern can be formed when the reference beam, a point source of light of fixed wavelength, encounters light of the same fixed wavelength arriving from the object. When the hologram is illuminated by the reference beam alone, the diffraction pattern recreates the wavefronts of light from the original object, and an image indistinguishable from the original object is recreated. True real-time updatable holographic displays will become feasible after the development of an ideal photoresponsive material. The refractive index or transmittance of such a material can be modulated only when it is irradiated with light, and they recover rapidly to the initial values after the cessation of irradiation. The use of photochromic^{2-5,11,12} and photorefractive^{7,13} materials in the development of real-time dynamic holographic recording media have been reported, but no ideal photoresponsive materials have been developed to date. Real-time dynamic holography should be able to update 3D images without a time lag between the movement of the objects and the movement of the recreated 3D images. Recently, Peyghambarian et al. successfully developed a quasi-real-time dynamic holographic display that can refresh images every two seconds⁸. They employed photorefractive polymeric materials in an updatable holographic 3D display. However, the refresh rate is not sufficient to display 3D images at a rate that is comfortable for the human eye. The improvement of the refresh rate using a revolutionary new photoresponsive material has been desired.

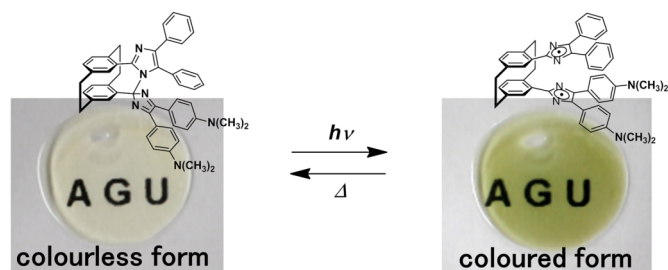


Figure 1 | Chemical structure and photochromic reaction of the [2.2]PC-bridged imidazole dimer. Insets shows the colour change of the polymer film (thickness: 170 μm).

We recently developed a unique series of photochromic [2.2]PC-bridged imidazole dimers with a [2.2]paracyclophane ([2.2]PC) moiety that couples two diphenylimidazole groups. The dimers exhibit instantaneous colouration upon exposure to UV light and rapid fading in the dark^{14–16}. Upon UV light irradiation, the C–N bond between the two imidazole rings of the [2.2]PC-bridged imidazole dimer is homolytically cleaved to give a pair of imidazolyl radicals, and the colour of the solution changes from colourless to blue. In contrast to any other currently available photochromic molecules, the [2.2]PC-bridged imidazole dimers have high quantum yields close to unity for the bond-cleavage reactions, enabling the visible inspection of the colouration upon UV light irradiation, even with their fast thermal bleaching rate. The coloured species of the [2.2]PC-bridged imidazole dimer has a first-order decay with a half-life of tens of milliseconds, which is favourable for detection by the human eye. Thermally reversible photochromic molecules offer the opportunity to change and reset the molecular properties by simply turning a light source on and off. Photochromic molecules exhibiting such intense photocolouration and fast thermal bleaching performance could be promising materials for fast light modulator applications.

Hence, we expected that the use of the fast photochromic polymer film as a dynamically updatable holographic recording medium would enable the real-time updating of object information. Here, we describe the development of a fast photochromic polymer for use in a real-time dynamic holographic material that can be easily prepared by a simple casting method from a solution of the photochromic polymer. The real-time control of 2D holographic images using the photochromic polymer film yields a speed equivalent to the time resolution of the human eye.

Results

The newly designed photochromic [2.2]PC-bridged imidazole dimer with increased photosensitivity to blue light, as shown in Figure 1, was developed to perform holographic recording with blue recording beams at 405 nm. Photochromic polymer films of good optical quality with a thickness of approximately 170 μm were prepared by a simple solution-casting method from the benzene solution of the mixture of the photochromic molecule, poly(ethyl acrylate), and poly(phenoxethyl acrylate) at a ratio of 1:1:2 wt%. Figure 2b shows the decay profile of the coloured species obtained by a nanosecond transient spectroscopy for the photochromic film. The half-life of the coloured species in the polymer matrix is 17 ms at room temperature. It should be emphasised that the original colourless state is fully recovered within 100 ms after the cessation of the irradiation, even in the polymer matrix, at room temperature. Thus, the photochromic film doped with the [2.2]PC-bridged imidazole dimer can potentially be applied to real-time image processing at video frame rates.

The recording of the real-time holographic grating was carried out using the photochromic film as the recording medium. Real-time holographic properties were investigated by measuring the changes in the growth and decay rates of the diffraction efficiency with optical switching of the writing beams. Two s-polarised beams at 405 nm with equal intensities of 18 mW were employed as the writing beams. The polarisation direction dependence of the writing beam on the

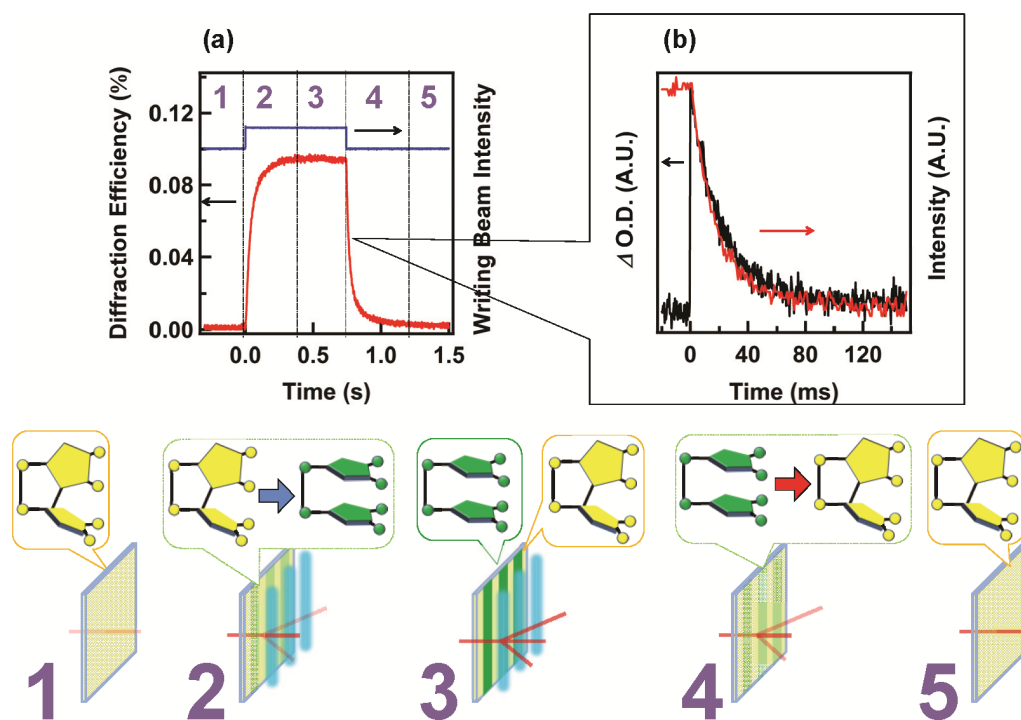


Figure 2 | (a) Real-time diffraction efficiency profiles for the first-order diffracted light of the photochromic polymer film (red line) with the switching of the writing beams (blue line) at room temperature. (b) Decay profile of the first-order diffracted light intensity (red line) and that of the coloured species of the photochromic polymer film (black line), monitored at 670 nm after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 3 mJ/pulse).

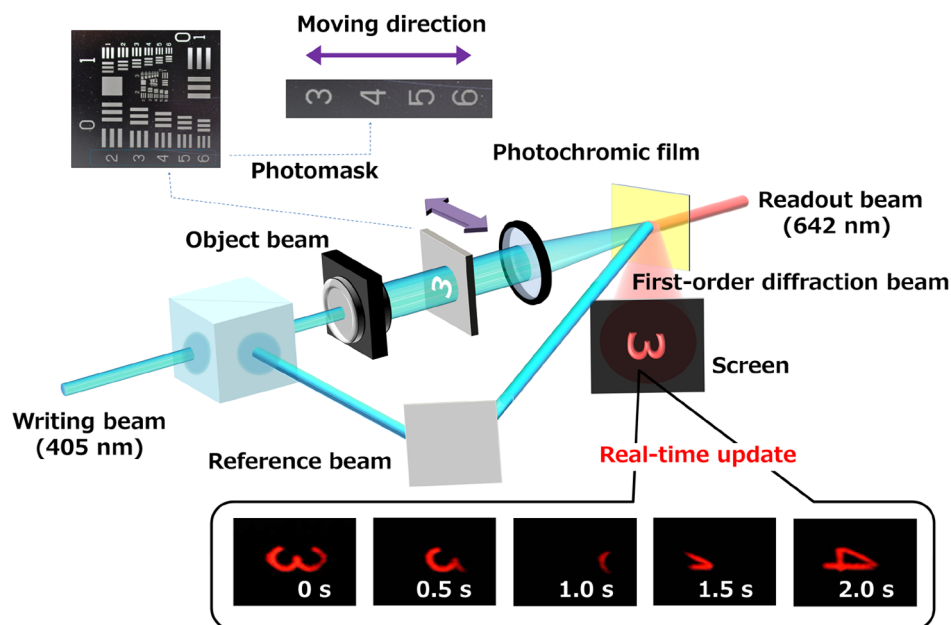


Figure 3 | Optical setup for the real-time holographic recording and the real-time development of the 2D holographic images.

diffraction intensity of the holographic grating is negligibly small in our holographic system. Two polarised beams obtained with a beam splitter at an equal light intensity were interfered on the photochromic film with an interbeam angle of 7° . Their overlap gave rise to an interference pattern that resulted in the spatial variation in the concentration of the coloured form of the photochromic molecule in the photochromic polymer. The formation of the holographic grating was monitored through the first-order diffraction signal using a 1.4 mW 642 nm light beam. The diffraction efficiency was defined as the ratio of the first-order diffracted light intensity to the intensity of the transmitted laser beam at normal incidence through the unexposed film before the recording of the holograms. Figure 2a shows the real-time diffraction efficiency profiles. The diffraction efficiency instantly increases in response to the irradiation of the writing beam, and it remains unaltered after an exposure time of 300 ms. The intensity of the diffracted light fades away soon after cutting off the writing beams. The reason for the low diffraction efficiencies can be explained as follows. The photoconversion efficiency from the colourless to the coloured forms of the photochromic molecules would decrease in the penetration depth of the excitation light inside of the photochromic polymer film. The extinction coefficient of the colourless form of the photochromic molecule at 405 nm is large ($1.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and most of the incident photons are absorbed only by the surface within a thickness of a few μm . In addition, the extinction coefficient of the coloured form at 405 nm is larger than that of the colourless form (Figures S7 and S8). That is to say, the photochromic reaction occurs only in the surface region of the polymer film upon irradiation with a 405 nm light beam, and the colourless form remains unchanged inside of the photochromic polymer film. Hence, the grating thickness is very thin. For this reason, the recorded grating in this photochromic polymer film is not the Bragg-type but the Raman-Nath type showing the multiple diffracted lights. Indeed the second-order diffracted light can be observed for the photochromic polymer film. We have also considered that the hologram is a mixed type of amplitude and phase types. Phase modulation of the wavefront permits diffraction efficiencies of about 6% for thin amplitude type of holograms, leading to low diffraction efficiency. Moreover, the photochromic molecule exhibits instantaneous colouration upon exposure to UV light and rapid fading in the dark. Thus the concentration of the coloured form is relatively low in the photostationary state under continuous

irradiation with a 405 nm light beam, leading to low diffraction efficiency. It should be noted that the decay profile of the intensity for the diffracted light completely coincides with the decolouration profile of the coloured species generated by the photochromic reaction in the same polymer film (Figure 2b). This result clearly indicates that the photoinduced changes in the diffraction efficiency are caused by the photochemical changes in the photochromic molecule. Thus, by employing a thermally reversible fast photochromic molecule, we have succeeded in achieving real-time control of the writing and erasing of a holographic grating.

We also attempted the real-time control of a 2D holographic image using the same photochromic film. The optical setup for the real-time holographic recording is shown in Figure 3. The Gaussian beam from a blue laser was split to form the reference and object beams. Information for a moving object (1951 USAF resolution test chart, negative type) was recorded on the photochromic film by interfering the s-polarised reference and object beams. The intensity of the two s-polarised beams at 405 nm with equal intensities of 18 mW was employed as the writing beams. The real-time development of the holograms was read out using a 140 mW 642 nm light beam. The first-order diffracted beam from the photochromic film was projected onto a screen. As shown in Figure 3, the changes in the image of the first-order diffracted beam were followed by the movement of the object without a time lag. It is worth noting that the diffracted images are clear and that no afterimage was observed, as expected from the fast formation and disappearance of the holographic grating shown in Figure 2. Supplementary Movie S1 shows the real-time development of a 2D holographic image projected on a screen.

Discussion

The fast photochromic molecules offer the opportunity to change and reset the molecular properties by simply turning a light source on and off. Photochromic molecules exhibiting such intense photocolouration and fast thermal bleaching performance were proved to be promising materials for modulating the refractive index and transmittance of a material only where it is irradiated with light. This fast response to the exposure of light enables to record and update the interference patterns of the reference beam and the object beam required for real-time dynamic holographic recording media. Photochromic materials have high resolution and high exposure



sensitivity and can be used as a holographic display without applying a voltage. Moreover, the preparation of a photochromic recording medium is simple compared to that of a photorefractive recording medium. We developed a fast photochromic polymer composed of a fast photochromic molecule, poly(ethyl acrylate), and poly(phenoxethyl acrylate) with unique photoresponsive characteristics, and we achieved real-time dynamic holographic recording with the photochromic polymer film, which can be easily prepared by a simple solution-casting method. The maximum diffraction efficiency of our holographic material is reached when the material is exposed for approximately 300 ms with an intensity of 36 mW (approximately 12 mW/mm²) at room temperature. The intensity of the diffracted light fades away soon after cutting off the writing beams. As can be found from Figure 2b, the time taken to erase the holographic grating is less than 100 ms. In the case of other photochromic materials such as azobenzene³, the intensity of the diffraction beam attained a maximum value about 1 s after the irradiation of the writing beams (25 mW/mm²). However, when the writing beams were turned off, the time taken to erase the holographic grating is more than 3 s. In the case of photorefractive materials⁸, upon irradiation of the pulsed laser at a repetition rate of 50 Hz (the light energy at the sample location was 650 mJ/cm²), the intensity of the diffraction beam attained a maximum value about 30 s after starting the laser irradiation. The holographic grating fades away after a few minutes by natural decay, or it can be erased by recording the new 3D images. When recording a new image, the new interference pattern erases the old pattern, resulting in the formation of a new diffraction structure.

The recording sensitivity of a medium has been employed to evaluate holographic materials^{17–20}. The recording sensitivity (*S*) is defined as the slope of square root of the diffraction efficiency as a function of time at the very initial stage of hologram formation, divided by the product of the writing beam intensity and the thickness of the medium. It can be calculated by the formula:

$$S = \frac{\partial \sqrt{\eta}}{\partial t} \frac{1}{I_0 d}$$

where η is the diffraction efficiency, I_0 is the writing beam intensity, and d is the thickness of the medium. The sensitivity depends mainly on the writing time and the corresponding refractive-index modulation. The value of $\frac{\partial \sqrt{\eta}}{\partial t}$ was estimated from the slope of square root of the diffraction efficiency as a function of time at the very initial stage of the hologram formation. In our experimental condition, $\frac{\partial \sqrt{\eta}}{\partial t}$ was 1.05 s⁻¹, the thickness of the photochromic film was approximately 170 μ m, and the two s-polarised beams at 405 nm with equal intensities of approximately 0.6 W/cm² were employed as the writing beams. The estimated *S* value of the photochromic film is 51 cm/J. The holographic materials of silver halides exhibit excellent holographic properties. They are sensitized in the spectral range below 1000 nm, allowing also realization of multi-color holographic recording. The sensitivity values >1100 cm/J were reported for the silver halides. The holographic sensitivities of inorganic photorefractive crystals are between tens and hundreds cm/J. In the case of other photochromic molecules, the *S* values are a few hundreds cm/J¹⁹. Though our holographic material shows a lower recording sensitivity compared with other holographic materials, the faster erasing time makes the material highly attractive for real-time dynamic holographic materials. This new type of holographic material based on the fast photochromism opens up an exciting new area of research in the future development of a large dynamic 3D display.

Methods

Materials. All chemicals were purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Chemical Industry Co., Ltd. (TCI) and used as received without further

purification, unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2 mm E.Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (60 N). [2.2]Pracyclopheane-4,13-dicarbaldehyde was prepared from [2.2]paracyclopheane according to a reported procedure¹⁴.

pseudogem-[4-formyl-13-(4,5-diphenyl-1H-imidazol-2-yl)][2.2]paracyclopheane (1). Compound 1 was synthesized from [2.2]paracyclopheane-4,13-dicarbaldehyde as previously reported procedure¹⁵.

pseudogem-[4,5-diphenyl-1H-imidazol-2-yl-4,5-(3,4-N,N-dimethylphenylamino)-1H-imidazol-2-yl][2.2]paracyclopheane (2). In a sealed tube, compound 1 (0.21 g, 0.46 mmol), 4,4'-Bis(dimethylamino)benzil (0.16 g, 0.95 mmol) and ammonium acetate (0.18 g, 2.3 mmol) were stirred at 110 °C in CHCl₃ (1.1 mL) for 20 h. The reaction mixture was cooled to 0 °C and added to hexane. The precipitate was filtered, and washed with hexane and water. The residual precipitate was purified by silica gel column chromatography using CH₂Cl₂/ethyl acetate (1/1 v/v) as an eluent to afford compound 2 as pale yellow powder. ¹H NMR (500 MHz, DMSO-*d*₆) δ : 11.61 (s, 1H), 11.28 (s, 1H), 7.29 (d, *J* = 6.7 Hz, 2H), 7.21–7.07 (m, 14H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.60 (t, *J* = 7.9 Hz, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 8.6 Hz, 2H), 4.56–4.47 (m, 2H), 3.17–2.95 (m, 6H), 2.88 (s, 6H), 2.81 (s, 6H); FAB-MS: *m/z* 730 [M+H]⁺.

pseudogem-DPI-BDMADPI[2.2]PC. All manipulations were carried out with the exclusion of light. Under nitrogen atmosphere, compound 2 (0.27 g, 0.37 mmol) was dissolved in benzene (95 mL). A solution of potassium ferricyanide (6.7 g, 20 mmol) and KOH (2.1 g, 37 mmol) in water (95 mL) was added dropwise, and the reaction mixture was vigorously stirred at room temperature for 20 min. The aqueous layer was separated, and was extracted with benzene. The combined organic layer was washed with water, and then dried over sodium sulfate. The solvent was removed under reduced pressure. The product was purified by silica gel column chromatography on silica gel (neutralized by treatment with triethylamine) using ethyl acetate/hexane (1/1 v/v) as an eluent, and recrystallized from hexane/CH₂Cl₂ to afford pseudogem-DPI-BDMADPI[2.2]PC as yellow needle crystal. ¹H NMR (500 MHz, DMSO-*d*₆) δ : 7.39 (t, *J* = 4.6 Hz, 1H), 7.20–6.94 (m, 14H), 6.80 (s, 1H), 6.68–6.64 (m, 4H), 6.54 (d, *J* = 9.2 Hz, 2H), 6.49–6.42 (m, 2H), 4.44–4.36 (m, 1H), 3.26–2.90 (m, 19H); ¹³C-NMR (125 MHz, CDCl₃) δ : 168.25, 164.91, 151.67, 151.55, 146.94, 143.42, 141.25, 140.61, 139.26, 138.07, 137.34, 137.09, 135.89, 135.47, 134.78, 134.68, 134.31, 133.40, 132.75, 132.50, 132.37, 132.20, 131.52, 131.38, 128.33, 128.29, 127.90, 127.88, 127.87, 127.69, 126.84, 125.83, 119.15, 118.95, 111.15, 110.52, 110.31, 40.07, 40.04, 35.32, 35.23, 34.45, 34.14; HRMS (*m/z*): [M+H]⁺ calcd. for C₅₀H₄₄N₆, 729.3700; found, 729.6996.

Measurement of UV-visible absorption spectra. UV-visible absorption spectra were recorded on a Shimadzu UV-3150. UV-Vis absorption spectra of pseudogem-DPI-BDMADPI[2.2]PC in degassed benzene (2.1 × 10⁻⁵ M) and the polymer matrix (25 wt%) are shown in Figures S4 and S5.

Experimental detail for laser flash photolysis. Laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer. A Continuum Minilite II Q-switched Nd:YAG laser with the third harmonic at 355 nm (pulse width, 5 ns; power, 3mJ/pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a spectrometer (Unisoku MD200). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments.

Experimental detail for the real-time hologram. Two s-polarised beams at 405 nm with equal intensities of 18 mW from a CrystaLaser DPSS blue laser (DL-405-050-S) were employed as the writing beams. The recording of the real-time holographic grating and the real-time control of a 2D holographic image were monitored through the first-order diffraction signal using a 1.4 mW 642 nm light beam and 140 mW 642 nm light beam, respectively, from an Omicron LuxX642 diode laser. Optical setups are shown in Figures S9 and S10.

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Acknowledgments

The present research was supported partly by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), a Grant-in-Aid for Scientific Research (A) (22245025) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Author contributions

J. A. designed the study, and N. I. prepared the polymer film and performed the hologram experiments. T. K. synthesised the compounds. J. A. and N. I. analysed data and wrote the paper.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Ishii, N., Kato, T. & Abe, J. A real-time dynamic holographic material using a fast photochromic molecule. *Sci. Rep.* **2**, 819; DOI:10.1038/srep00819 (2012).