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Chiral BINOL-Bridged Imidazole Dimer Possessing Sub-Millisecond Fast Photochromism

Cite this: DOI: 10.1039/x0xx00000x

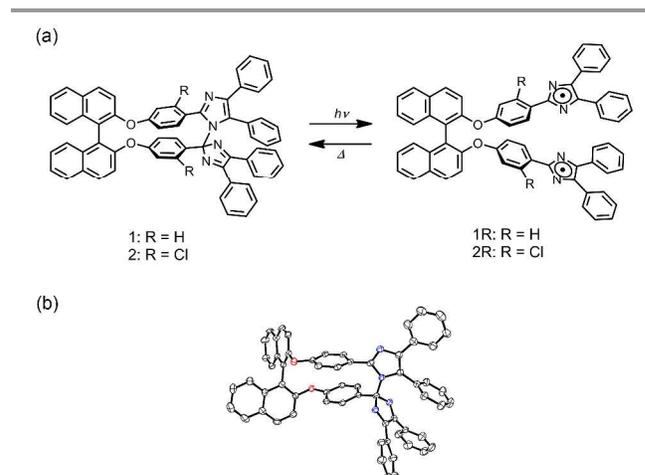
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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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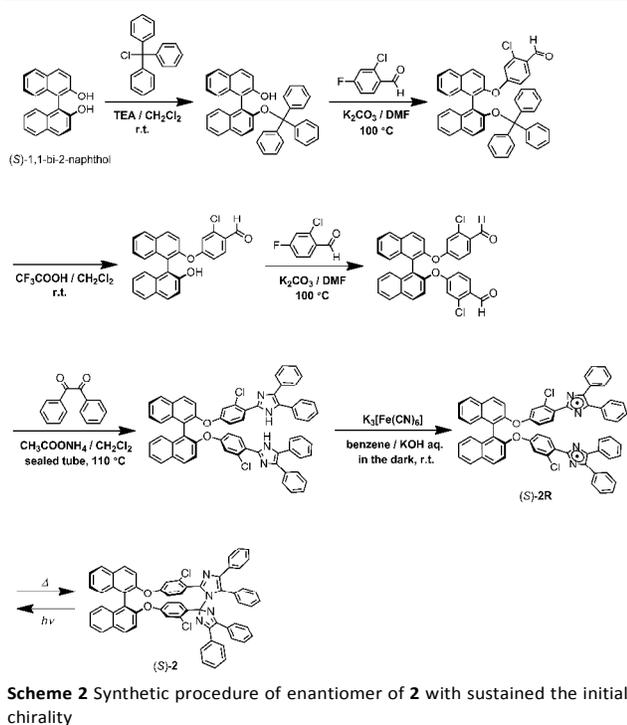
We developed a chiral 1,1'-bi-2-naphthol-bridged imidazole dimer possessing 100 μ s fast photochromism and high fatigue resistance. It offers great opportunities for the practical applications to a fast photoresponsive chiral dopant, invisible security materials and optical trigger molecules to induce the dynamic structural change of biological matters.

Chirality in chemistry fields is usually used to describe molecular structures that are not superimposed in the mirror image and has been widely accepted in asymmetric syntheses,^{1,2} phase transitions of chiral nematic liquid crystals,³⁻⁵ and chiroptical sensors.⁶⁻⁸ In recent two decades, light-driven phase transitions of liquid crystals and molecular motors as a trigger have been extensively studied by using azobenzene,^{4,5,9-11} diarylethene,¹²⁻¹⁴ and thioxanthene-based alkene derivatives.¹⁵ For example, several researchers have demonstrated that the chiral photoswitch molecules induce the reversible modulation of circularly dichroism (CD) signals and the pitch of helical structures,¹⁴ the inversion of the helicity of chiral nematic phases,¹³ and the rotation of a micrometer-scale glass rod through the phase transition of cholesteric liquid crystals.¹⁵ However, since the photochromic reactions of azobenzene and diarylethene derivatives are generally slow except several azo and diarylethene derivatives,¹⁶⁻¹⁸ the repetition rate to induce photochromism was limited. Recently, we have developed a series of bridged imidazole dimers, which act as milliseconds to sub-seconds fast photochromic switches.¹⁹⁻²² The combination of fast photochromic switches and chiral properties would achieve fast photoswitches of chiral molecules, which would be promising for the fast photoresponsive chiral dopants. Here, we developed a new type of photochromic bridged imidazole dimer which acts as a hundred of μ s fast molecular switch with the high durability and the sustained chirality. We applied 1,1'-bi-2-naphthol (BINOL) as a linker to bind two imidazoles, which gives a chiral property to the bridged imidazole dimer (compound **1** in Scheme



Scheme 1 (a) Photochromism of **1** and **2**. (b) ORTEP representation of the molecular structure of **1** with thermal ellipsoid at 50% probability obtained by X-ray crystallographic analysis.²³

1a). Besides this, we incorporate chloro groups to the *o*-position of phenyl rings at the 2-position of the imidazole rings to accelerate the photochromic reaction and to improve fatigue resistance (compound **2** in Scheme 1a). It has been known that *o*-chlorohexaarylbiimidazole (*o*-Cl-HABI) shows the faster thermal back reaction (tens-of-seconds) and the high durability as compared to HABI possibly because of the distortion of the molecular structure or the heavy atom effect caused by the chloro group.²² We expect that the effect of the chloro group is applicable for the bridged imidazole dimers as well. Since stable fast photochromic molecules with sustained chirality can induce cooperative motions and volume changes spontaneously, these chiral photochromic molecules will open up novel application fields such as fast photoresponsive chiral dopants for optical gates and filters, security information systems with chirality and a



trigger to probe dynamic motions of biological matters such as unfolding of proteins and the isomerization of DNAs.^{24,25}

It is noteworthy that the enantiomers of **1** and **2** can be synthesized from the enantiomer of BINOL without any optical resolutions. The chiral synthesis of **2** is shown in Scheme 2. The incorporation of a bulky group such as a trityl group into BINOL (the first step) enables to sustain the chirality of BINOL at even more than 100 °C. In the case of the previous study of the naphthalene bridged imidazole dimer,²⁶ the optical resolution was required for the enantiomer of the product because the product was obtained as the racemate. The detail of the syntheses of the enantiomers of **1** and **2** are shown in the supporting information.

Scheme 1a illustrates the photochromism of **1** and **2**. The irradiation of UV light to **1** and **2** breaks the C–N bond between the imidazole rings and radical species **1R** and **2R** are generated, which are the origin of the colouration. The radical species spontaneously recombines to the initial dimer by the thermal reaction at room temperature without the irradiation with visible light. Scheme 1b shows the ORTEP representation of the molecular structure of **1** obtained by X-ray crystallographic analysis. The detail of each photochromism is revealed by steady-state UV-vis absorption and laser flash photolysis measurements.

Fig. 1a shows the steady-state UV-vis absorption spectra and the transient absorption spectra of **1** and **2**. The blue vertical lines indicate the theoretical absorption spectra for **2** and **2R** calculated by the conventional TDDFT MPW1PW91/6-31+G(d)/M062X/6-31G(d) and UMPW1PW91/6-31+G(d)/UM062X/6-31G(d) methods, respectively. It clearly shows that the spectra of **1** and **2** are almost identical irrespective of the substitution of the chloro groups. The steady-

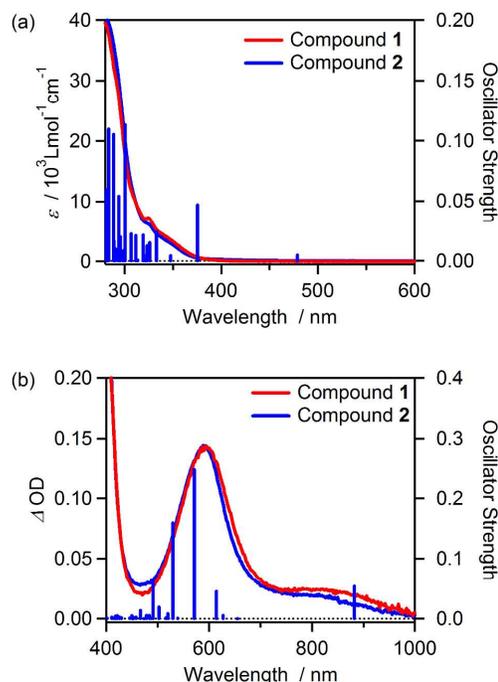


Fig. 1 (a) Steady-state UV-vis absorption spectra and (b) transient absorption spectra of the racemates **1** (red) and **2** (blue) in degassed benzene (excitation wavelength, 355 nm; pulse width, 5 ns; power 4 mJ/pulse; the concentrations of **1** and **2** are 2.1×10^{-5} and 2.2×10^{-4} M, respectively). Blue vertical lines indicate the theoretical absorption spectra for **2** and **2R**.

state UV-vis absorption spectra of **1** and **2** are very similar with each other, which increase in their absorbance below ~370 nm and have a small sharp peak at ~330 nm. The transient absorption spectra of the coloured species of **2** are similar to that of **1** as well as steady-state UV-vis absorption spectra (Fig. 1b). The transient absorption spectra show a relatively sharp absorption at 590 nm as compared to those of the [2.2]paracyclophane bridged imidazole dimers, which have a broad transient absorption at the near IR region due to the interaction between the two imidazole radical chromophores.^{21,22} It suggests that the interaction between the two imidazole chromophores of **1R** and **2R** is weak mostly because of the larger degree of freedom in **1R** and **2R** as compared to those of the [2.2]paracyclophane bridged imidazole dimers. The TDDFT calculations indicate that the peak at 590 nm is due to the transition from the BINOL moiety to the 4 π -imidazole ring through the phenyl ring at the 2-position of the imidazole ring. (Fig. S35). While the transient absorption spectra of the coloured species of **1** and **2** are very similar with each other, the striking difference appears in their decay profiles. Fig. 2 shows the decay profiles of **1R** and **2R** generated upon a UV light pulse observed at 400 nm at different temperature (excitation wavelength: 355 nm, Intensity: 4 mJ/pulse). The decays are well fitted with a single exponential function and the half-life of **2R** at 25 °C is 100 μ s, which is more than 100 times faster than that of **1R** (38 ms). We conducted the temperature dependence of the decay profiles of the coloured species and obtained the

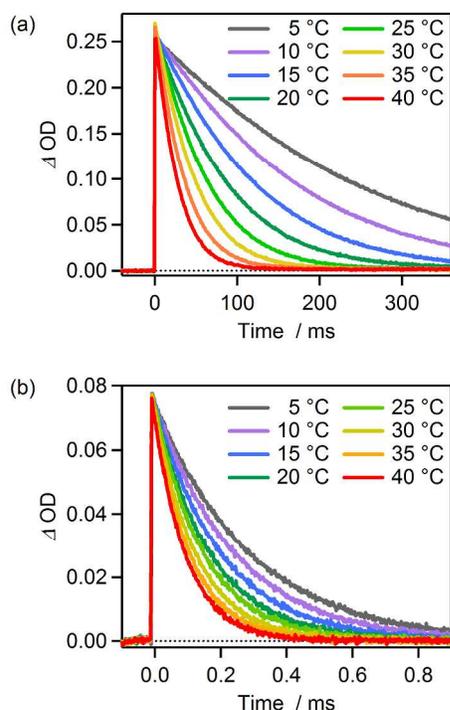


Fig. 2 Decay profiles of (a) **1R** and (b) **2R** monitored at 400 nm in degassed benzene (2.1×10^{-5} and 2.3×10^{-5} M for **1** and **2**, respectively). The measurements were performed in the temperature range from 5 to 40 °C.

Table 1 Decolouration half-lives at 298 K, and activation parameters of **1R** and **2R** in degassed benzene.

Compound	ΔH^\ddagger / kJ mol^{-1}	ΔS^\ddagger / $\text{J K}^{-1} \text{mol}^{-1}$	ΔG^\ddagger / kJ mol^{-1}	$\tau_{1/2}$ / ms
1R	43.5	-74.9	65.8	38.0
2R	19.7	-105.4	51.1	0.10

activation parameters (Table 1) by using the Eyring plots (Figs.

S29 and S30). Compound **2R** shows a smaller ΔG^\ddagger value and it explains the acceleration of the decolouration rate of **2R**, which is well consistent with the relationship between HABI and *o*-Cl-HABI.²⁷ As similar to them, the origin of the acceleration is most probably because of the distortion of the molecular structure and/or the heavy atom effect due to the chloro group.

Fig. 3a shows the CD spectra of (*R*)- and (*S*)-**2** before 355 nm laser pulse irradiation and after 10,000 laser shots. We observe the symmetrical Cotton effects depending on the (*R*)- and (*S*)- chirality below 400 nm, which is due to the BINOL moiety of the imidazole dimer. Though 1,1'-binaphthyl is known to photoracemize through the rotation of the intraannular C–C bond upon UV light irradiation,^{28,29} the chirality of the BINOL moiety of **2** sustains after many cycles of the photochromic reaction. Interestingly, the CD spectroscopy and the chiral HPLC analysis (Fig. 3b) revealed that **2** is robust and is not racemized even after 10,000 shots of ns laser pulses (5 ns and 4 mJ/pulse). In addition, we examined fatigue resistance of **2** through the steady-state UV-vis absorption spectra (Fig. S31). While the absorption spectrum of **1** changes after 10,000 shots of ns laser pulses, that of **2** is almost identical even after 15,000 shots of ns laser pulses. It shows that the durability of **2** is greatly improved compared with that of **1**. Thus **2** has high fatigue resistance and is suitable for the practical application to a fast photochromic chiral dopant.

In conclusion, we developed a chiral BINOL-bridged imidazole dimer which acts as a hundred of μs fast molecular switch with the high fatigue resistance. We found that the substitution of the chloro groups to the *o*-position of the phenyl rings at the 2-position of the imidazole rings drastically accelerated the photochromic reaction and improved fatigue resistance. In addition to these interesting molecular features, the present synthetic procedure for the enantiomer of **2** is simple, not costly and sustains the initial chirality of the starting material. It offers great opportunities for the practical applications to a fast photoresponsive chiral dopant, invisible security materials and optical-trigger molecules to induce the dynamic structural change of biological matters.

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

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization data. See DOI: 10.1039/c000000x/

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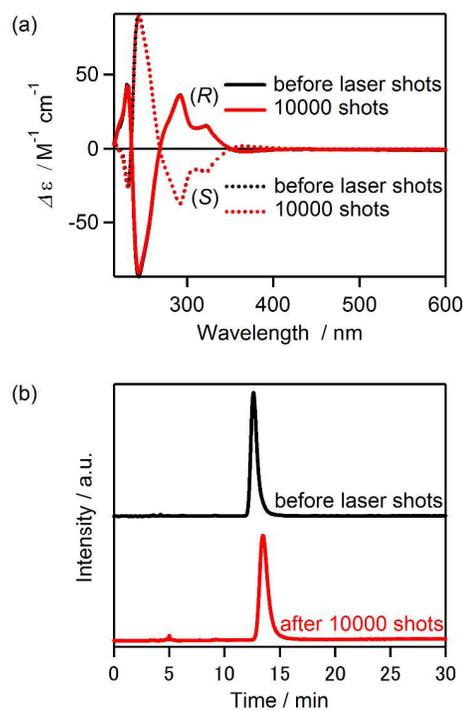
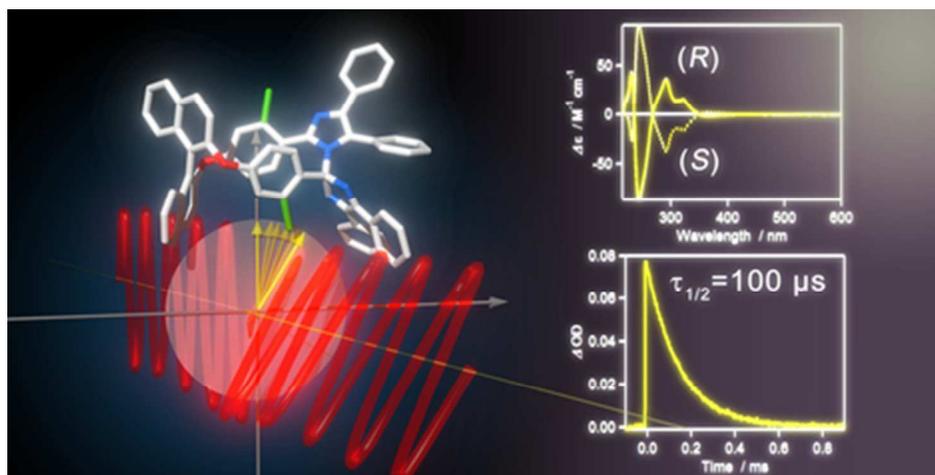


Fig. 3 (a) CD spectra of (*R*)-**2** (solid lines) and (*S*)-**2** (dashed lines) in acetonitrile (3.3×10^{-5} M) at room temperature. The red and black lines indicate the spectra before laser shots and those after laser shots, respectively. (b) Chiral HPLC chromatograms of (*S*)-**2** before (black) and after 10,000 shots (red) of nanosecond laser pulses (355 nm; pulse width, 5 ns; power 4 mJ/pulse) at 25 °C. Both optical purities are 99% ee.

- Crystallographic data for **1**: $C_{60}H_{40}N_4O_2$, $M_r=872.98$; triclinic; space group $P\bar{1}$; $a=10.8574(15)$, $b=14.598(2)$, $c=15.654(2)$ Å; $\alpha=90.116(2)$, $\beta=105.115(2)$, $\gamma=110.614(2)^\circ$; $V=2229.8(5)$ Å³; $\rho_{\text{calcd}}=1.300$ g cm⁻³; $Z=2$; $R_1=0.0565$ [$I > 2.0\sigma(I)$], $wR_2=0.1105$ (all data), GOF=1.023 (data/restrain/params=8830/0/613). CCDC 996722 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
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