

Photoswitching of intramolecular chiral stack in a helical tetrathiazole†

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 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

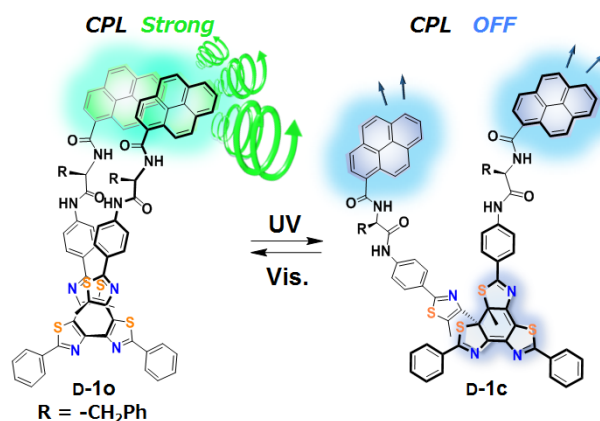
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On-off photoswitching of circularly polarized luminescence was achieved with a pyrene-bearing helical tetrathiazole, in which two pyrene fluorophores stack in a chiral fashion (folded state). The pyrene-excimer based CPL was reversibly controlled by a geometrical change of tetrathiazole on the photoisomerization.

Light is one of the external stimuli to trigger a change in the physicochemical properties of molecules in a noninvasive manner, promising a wide range of applications. Chiroptical photoswitches are of particular interest in terms of advanced informational technologies.¹ Circularly polarized luminescence (CPL) has been attracting much interest as an important chiroptical phenomenon which offers potential applications in sensors, display and optical storage.² Meanwhile, the chiroptical photoswitches have often been demonstrated by the stereoselective isomerization of photochromic molecules, changing circular dichroism (CD) and optical rotatory dispersion (ORD).¹ Akagi and co-workers reported the reversible changes of CPL intensity in films of chirally aggregated conjugated polymers bearing photoresponsive dithienylethenes.³ A photo-generated isomer of dithienylethene with an intense visible absorption band efficiently quenched the emission from π -conjugated polymers in the aggregates. However, dynamic photoswitching of CPL in solution with a unimolecular system has still remained one of the important challenges in the development of chiroptical photoswitches.

Here we report a chiroptical photoswitch which dynamically modulates CPL emission using a photochromic tetrathiazole⁴ scaffold. In the previous work, we reported that the tetrathiazole folds into a one-turn helical conformation with photochromic reactivity by multiple intramolecular interactions.^{4b} The

phenylthiazole units at both ends of tetrathiazole form π - π stacking in a helical manner. In the present study, pyrene fluorophores are introduced in these positions via a chiral spacer of phenylalanine (D- or L-**1o**, Fig. 1). The chiral spacer is expected to control the handedness of helix, twisting the pyrene-stack in a one-handed direction. Chiral excimers of pyrenes have been reported to exhibit relatively strong CPL with $|g_{\text{lum}}|$ value of 1%,^{5,6} which is given by the equation $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of the left- and right-handed circularly polarized emissions, respectively. The off-on photoswitching of fluorophore-stacking have been demonstrated with trans-cis isomerizations of thioindigo⁷ and overcrowded alkene.⁸ On the other hand, the light-induced geometrical changes of most diarylethenes and their aromatic derivatives are rather small, which supports their photo-reactivity in crystals.⁹ Unlike conventional diarylethenes, the photochromism in tetrathiazoles gives rise to a large structural change from an open- to a ring-closed photoisomer, driving the fluorophores to change their position and orientation with the dynamic sp^2/sp^3 interconversion on the reacting carbon atoms (Fig. 1).



The tetrathiazole **1o** was synthesized from a NH₂-functionalized tetrathiazole by a condensation with Boc-

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† Electronic Supplementary Information (ESI) available: Detailed experimental methods and additional data. See DOI: 10.1039/x0xx00000x

phenylalanine, a deprotection of Boc-group followed by a condensation with 1-pyrenecarboxylic acid (see the ESI[†] for details). The conformational behavior of **1o** in solution was characterized with variable temperature (vt) ¹H NMR. The compound **1o** gave an NMR profile with a broadened peak pattern at 30 °C because of the limited solubility in 1,1,2,2-tetrachloroethane-*d*₂ at high concentration (> 10⁻³ M). Each peak assignment was determined based on the homonuclear ¹H-¹H correlation spectroscopy (COSY, Fig. S3[†]). The two methyl groups at the ends of tetrathiazole moiety gave a singlet peak at 2.05 ppm (Fig. S2[†]). The methyl signal at a very upfield chemical shift indicated the folded helical conformation of **1o** as shown in Fig. 1, wherein the ring-current effects of the facing thiazolyl rings operate on these methyl groups.^{4c} As shown in Fig. 2, amide-N-H signals (H₃ and H₅) showed a continuous upfield-shift with peak sharpening upon heating to 100 °C, indicating that these protons participate in hydrogen bonding interactions. Meanwhile, the protons H₁ and H₂ representative for pyrene-protons exhibited a down-field shift with increasing temperature. The pyrene rings seem, thus, to stack so closely that significant ring-current effect operates on their protons.^{4b,c} Furthermore, the nuclear Overhauser effect correlation spectroscopy (NOESY) measurement figured out the through space interactions in the pyrene-protons region above 7.7 ppm (Fig. S3[†]). We also performed a conformational search for *D*-**1o** with the MMFF94s force field using the CONFLEX program.¹⁰ The calculation study identified that the helical conformation with the stacking of pyrene units was the most stable conformer, which is more stable than a conformer with non-stacked pyrene moieties by 6 kcalmol⁻¹ (Fig. S4[†]). These ¹H NMR and computational simulation results well supported that **1o** adopts the folded conformation with the pyrene-stack as shown in Fig 1.

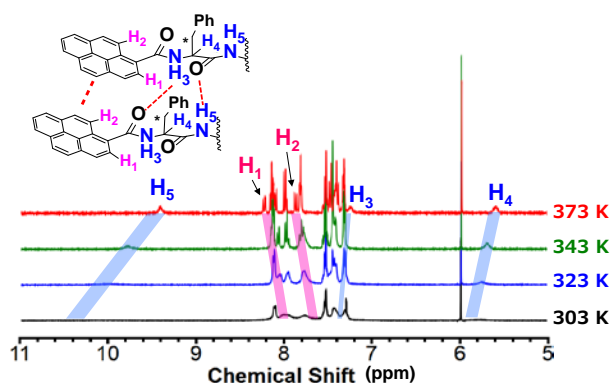


Fig. 2 Vt ¹H NMR spectra of *L*-**1o** in the low magnetic field region (in 1,1,2,2-tetrachloroethane-*d*₂) with the part of the chemical structure of *L*-**1o**.

Fig. 3 summarizes the optical response of **1o** with respect to UV light ($\lambda = 365$ nm) irradiation. The absorption of pyrene-amide moiety was overlapped with that of tetrathiazole framework below 400 nm, leading to the slight red-shift of absorption peak relative to the unsubstituted tetra(2-phenylthiazole) (Fig. 3a) with an increase in the molar absorption coefficient (ϵ) from 4.5×10^4 to 9.8×10^4 M⁻¹cm⁻¹.^{4a} CD spectra of **1o** enantiomers gave mirror image profiles in the region of π - π transitions, suggesting the preferential formation of one-

handed helix (Fig. 3b). Although the exciton coupling¹¹ of pyrene units was not clear because of the superimposed signal originating from the main framework of tetrathiazole, the signs of first Cotton effect implied that *D*- and *L*-**1o** possess a right- and left-handed helix, respectively.^{4b}

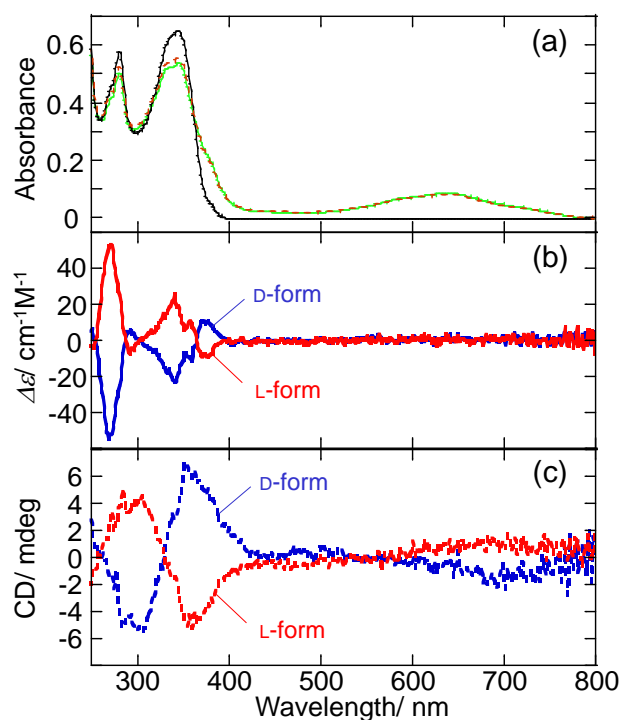


Fig. 3 Absorption(a) and CD(b,c) spectral change of **1** in chloroform (8.7×10^{-6} M). (a) black line: *L*-**1o**; green solid line: *L*-**1c**; orange dashed line: PSS state. (b,c) solid lines: **1o**; dashed lines: PSS state (blue lines: *D*-forms, red lines: *L*-forms).

UV irradiation to **1o** solution resulted in the emergence of absorption band in the visible region due to the formation of **1c**. **1o** showed relatively high coloration performance with a quantum yield (ϕ_{o-c}) of 50%. The decrease in ϕ_{o-c} relative to the unsubstituted tetra(2-phenylthiazole)^{4a} ($\phi_{o-c} = 60\%$) may be attributed to the light absorption of pyrene moieties which might not contribute to the photoisomerization. While the quantum yield of cycloreversion (ϕ_{c-o}) could not be determined, the very high conversion ratio over 99% at the photostationary state (PSS) suggested a suppressed value for ϕ_{c-o} .^{4a} Meanwhile, a drastic change was recorded in the CD spectra, in which broad CD signals at the wavelength of visible absorption band of photoproducts emerged with changing the CD pattern below 400 nm after UV irradiation (Fig. 3c). Chiral induction of helix-handedness in *D*- and *L*-**1o** thus successfully led to a diastereoselective photoreaction which proceed in the conrotatory manner. To determine the diastereo-excess (*de*) in **1c**, the photoproducts were investigated by ¹H NMR and chiral HPLC. In the ¹H NMR, only a set of methyl peaks were observed due to the different electromagnetic environment of the end methyl groups in **1c** (Fig. S5[†]). Since the chiral groups were far from these methyl groups, the diastereomers might give identical chemical shifts. However, the *D*- and *L*-forms of **1o** exhibited a single peak in a chiral HPLC with slightly different retention times, giving an additional peak after the photoreaction corresponding to the formation of single component **1c** (Fig. S6[†]).

Based on the results of ^1H NMR and chiral HPLC analyses **1o** most likely underwent almost absolute diastereoselective photoreaction. The D- and L-**1o** with a right- and left-handed helical geometry, respectively, led to the formation of the (R, S)- and (S, R)-form **1c**,^{4b} respectively (Fig S7[†]).

The tetrathiazole **1o** showed blue-green emission with an apparent quantum yield (ϕ_f) of 4%. The relatively small emission quantum yield should be attributed to the light absorption by the photochrome part which does not lead to fluorescence. The intense and broad band at 500 nm corresponds to an intramolecular pyrene excimer in accordance with a long lifetime of 21 ns (Fig S8[†]). A weak and structured monomer emission band was also observed at 400 nm with a shorter lifetime of 3.6 ns (Fig S8[†]). The intensity of both excimer and emission bands decreased with UV irradiation (Fig. 4a). The isolated **1c** gave the ϕ_f value far less than 0.1%. Both the emission from monomer and excimer decreased in a liner fashion as a function of conversion ratio to the colored form **1c** (Fig. 4b). The quenching of monomer emission should be attributed to an energy transfer mechanism by the increased absorbance in the range of 380–410 nm in **1c** (Fig. 3a).¹² The same mechanism partly explains the quenching in the excimer emission at 500 nm. Although the spectral overlap of excimer emission around 500 nm with absorption in **1c** is not as prominent as that of monomeric emission, the quenching of excimer emission was a little more significant than that of monomer emission (Fig. 4b). This fact might be attributed to the non-negligible contribution of geometrical factor in **1c** (Fig. 1). Furthermore, the two amide-protons showed an upfield-shift from **1o** to **1c** (Fig. S5[†]), indicating the dissociation of intramolecular hydrogen bonding interactions which tether the pyrene units close to each other.¹³

The chiral induction in the helical conformation of **1o** resulted in the emergence of a strong CPL signal corresponding to the pyrene excimer emission (Fig. 4c). The signs of CPL signal coincide with those of the first Cotton effect observed in CD spectra (Fig. 3b). That is, two pyrene rings are arranged preferentially in a P- and M-configuration in the right- and left-handed helix of D- and L-**1o**, respectively. The dissymmetry factor in luminescence was estimated to be $|g_{\text{lum}}| \sim 1\%$ in consistence with previous reports.^{5,6} Along with the decrease in the excimer emission intensity by the photoisomerization, the CPL intensity decreased. Since the CPL measurement was performed at a higher concentration (1.7×10^{-4} M) in comparison to that for absorption spectra (Fig. 3a), the conversion ratio was not enough to achieve the completely off-state (Fig. 4c). The on-off photoswitching behavior was observed around 6 cycles with alternate UV and visible irradiations as shown in Fig. 4d.

In summary, we prepared tetrathiazoles bearing two pyrene fluorophores through chiral spacers as a chiroptical switch, exhibiting diastereoselective photoisomerizations. The on-off switching of intramolecular excimer CPL was demonstrated upon the photoisomerization in a helical tetrathiazole. In addition to the unimolecular behavior, the application of present molecular system to chiral self-assemblies could further enhance the switching effect¹⁴ of supramolecular chiroptical properties.^{2c} Another direction may include a CPL read-out non-destructive

memory system, which would be achieved by chiral rare-earth complexes¹⁵ with photochromic ligands.¹⁶

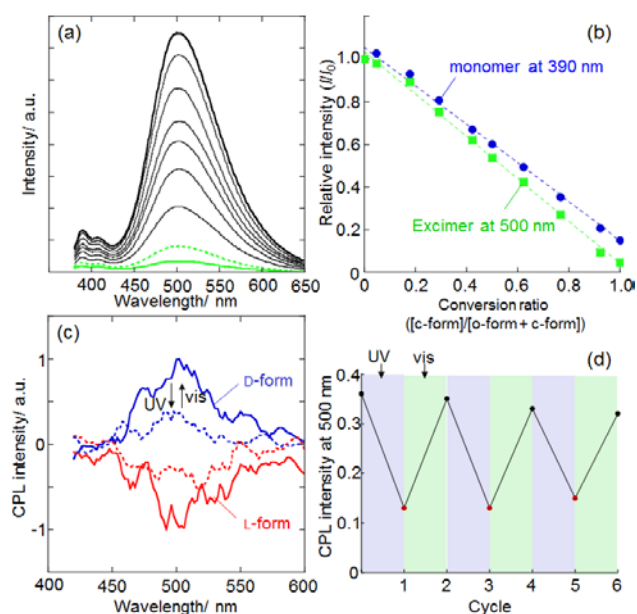


Fig. 4 (a) Fluorescence spectral change of L-**1o** upon UV irradiation in CHCl_3 (4.6×10^{-6} M). Solid thick black line: **1o**-form, solid green line: **1c**-form, dashed green line: at PSS, other traces were measured with the irradiation interval of 5s. (b) Plots of relative emission intensity in monomer (blue, at 390 nm) and excimer (excimer, at 500 nm) emission. I_0 corresponds to the intensity at the conversion of 0. (c) CPL spectra of **1o** in CHCl_3 (1.7×10^{-4} M). D-form: solid blue line; L-form: solid red line; dashed lines: at PSS. (d) Reversible changes of CPL intensity at 500 nm of D-**1o** in chloroform with UV (365 nm) and visible (> 400 nm) irradiations.

This work was partly supported by Grant-in-Aids for Scientific Research (B) (T. N., no. 15H03858), Challenging Exploratory Research (T. N., no. 15K13709) and Scientific Research on Innovative Areas “Photosynergetics” (T. K. no. 26107006) sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan. The authors wish to thank Mr. F. Asanoma and Ms. Y. Nishikawa for their assistance with NMR and mass measurements, respectively.

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