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Manuscript number: CC-COM-01-2023-000333.R1

View Article Online
DOI: 10.1039/D3CC00333G

Title: Light-Driven Flagella-Like Motion of Coordination Compound Single Crystals

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ARTICLE

Light-Driven Flagella-Like Motion of Coordination Compound Single Crystals

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

DOI: 10.1039/x0xx00000x

Single crystals of coordination complexes showing mechanical motion under the influence of external stimuli are of great interest due to their applications in photoactuators, sensors and probes. The solid-state [2+2] cycloaddition reaction is one of the most prominent chemical reactions for photoresponsive materials in recent years. However, there is a relatively very limited number of compounds reported and most of these compounds have only shown destructive photosensitive effects. Here in our work, we have reported two photoreactive Zn(II) metal complexes with a thiophene based photoreactive linker, 2tpy (4-(2-(thiophen-2-yl)vinyl)pyridine). In addition, under photoirradiation these complexes showed flagella-like bending, firstly bending towards and subsequently bending away from the excitation light source. This is the first report of metal-complexes and solid-state [2+2] cycloaddition reaction, which presents flagella-like motion in single crystals.

Introduction

Stimuli-responsive dynamic single crystals have been discovered to show mechanical motions like bending, curling, jumping, twisting flipping, hopping, breaking, elongation, contraction, and explosion.¹⁻⁴ Most of these reports showed triggering of these materials taking place through external stimuli such as light, heat, and magnetism.^{5,6} Recently, light has been utilized as one of the best stimuli mainly due to its remote action, non-invasive, target manipulation, control over input intensity and wavelength.^{3, 7-12} Most of these reported mechanical motions are caused by the anisotropic strain generation in the single crystals during the photoreaction. Generation of such strain can be activated through various chemical reactions including photo-cycloaddition reactions, cis-trans isomerism, and reversible cyclization reactions.¹³⁻¹⁷ These photo-responsive single crystals gained attention due to their forecast applications as an activator for artificial muscles, smart medical devices, memory devices, sensors, and probes.

The photochemical solid-state [2+2] cycloaddition reaction is a green synthetic procedure to obtain cyclobutane derivatives in quantitative yields. Several studies describe diverse strategies to bring the olefin containing the molecule to satisfy Schmidt's criteria in the crystal lattice.¹⁸ These strategies comprise various noncovalent interactions (π - π , halogen bond, C-H \cdots π interactions, H-bond, and so on) and utilization of coordination bonds.¹⁹⁻²⁴ With significant knowledge of transition metal ions and their geometries, designing photoreactive metal complexes is straightforward. In addition, metal ions also support the preparation of multi-functional materials where the metal ions are known to offer other

properties such as magnetism, and optical properties.²⁵⁻³⁰ So far, a significant number of photo-responsive metal complex crystals have been designed using 4-styrylpyridine (4spy) linker and its fluoro derivatives.^{26, 27, 31, 32} Meanwhile, the isostructural nature of thiophene and benzene is well-known in the literature.³³ By considering this, we have attempted to replace the phenyl group with the thiophene group to obtain the new photoreactive linker, 2tpy (4-(2-(thiophen-2-yl)vinyl)pyridine), which could be utilized for the photo-responsive materials with better properties and applications.

Here, two photoreactive Zn(II) metal complexes, [Zn(3,4-DFBA)₂(2tpy)₂] (**1**), [Zn(2,6-DFBA)₂(2tpy)₂].H₂O (**2**) have been successfully synthesized by using thiophene based photoreactive linker, 2tpy, and difluorinated benzoate co-linker (3,4-DFBA (3,4-DFBA = 3,4-difluorobenzoate); 2,6-DFBA, (2,6-DFBA = 2,6-difluorobenzoate)).³⁴⁻³⁷ These compounds are mononuclear metal complexes with Zn(II) at tetrahedral coordination geometry with the head-to-tail alignment of the 2tpy linker. UV irradiation of these compounds showed ~100% and ~50% photo reactivity in **1** and **2**, respectively. In addition, both of these compounds showed an interesting flagella-like bending behaviour (towards followed by away from the light source).³⁸ To the best of our knowledge, this is the first report of such two-sided bending during the [2+2] photochemical reactions for metal-complexes. Furthermore, during the photoirradiation of thin crystals of **2**, these crystals have shown ca. 4% increase in length along with reversible bending of the crystals. This reversible bending behaviour has been explained through numerical simulation.

Electronic Supplementary Information (ESI) available: This includes, PDF file shows a detailed description of the experimental methods, characterization techniques such as NMR, SEM, TGA, detailed description of the videos, numerical simulations and so on. SI also include videos of **1** and **2** under photoexcitation. For further details see DOI: 10.1039/x0xx00000x

Results and discussion

Structural analysis of $[\text{Zn}(\text{3,4-DFBA})_2(\text{2tpy})_2]$, **1:** Light yellow coloured platy needle shaped single crystals of $[\text{Zn}(\text{3,4-DFBA})_2(\text{2tpy})_2]$, **1** were obtained by slow evaporation of the mixture of MeOH and EtOH solution containing 1:2:1 ratio of $\text{Zn}(\text{NO}_3)_2$, 3,4-DFBA and 2tpy. This metal complex was crystallized in monoclinic space group $P2_1/n$ with $Z = 2$ which is elucidated from single crystal XRD (SXRD), and the asymmetric unit constitutes half of the formula of the compound. The Zn(II) atom adopted tetrahedral coordination geometry by coordination with the pyridyl groups of two 2tpy ligands and monodentate coordination of 3,4-DFBA (Fig. 1a). Detailed analysis of crystal structure of this compound showed that both the 2tpy linkers of **1** are well aligned with its neighbour linker in *head-to-tail* (HT) manner (Fig. 1b). This HT alignment is stabilized by π - π interactions between thiophene and pyridyl group. The centre of inversion is also located between these olefin groups of HT aligned 2tpy linkers shown in Fig. 1b. The separation between the centres of the olefin groups is 3.97 Å,

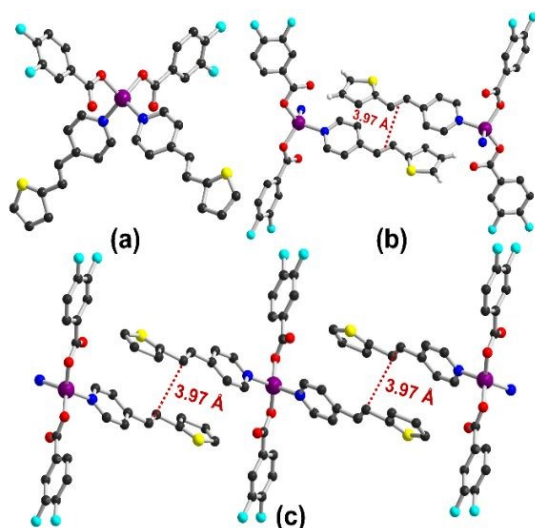


Figure 1. (a) Tetrahedral coordination geometry of Zn(II) atom in **1**. (b) Head-to-tail alignment in **1**. (c) Extended head-to-tail alignment. Most of the H-atoms are omitted for clarity. Colour code: C = black, N = blue, O = red, H = white, F = cyan, S = yellow, Zn = purple.

and it falls within Schmidt's topochemical criteria.¹⁸ Thus, this compound is expected to undergo a quantitative photoreaction, leading to the polymerization of metal complex into 1D coordination polymer (CP) (Fig. 1c).

The photo-reactivity of **1** was investigated through ^1H NMR, by UV irradiating the powdered sample using LUZCHEM photoreactor. The formation of photoproduct was evidenced by shifting of pyridyl protons from 8.52 ppm to 8.37 ppm and decrease in the intensity of olefin protons at 7.75 ppm and 6.94 ppm respectively. At the same time cyclo-butane peaks at 4.83 ppm and 4.40 ppm started to appear (Fig. 2). To understand the reaction kinetics of this photoreaction, ^1H NMR studies have been performed by taking out the sample from photoreactor at regular intervals of time and dissolve this UV irradiated powder in $\text{DMSO-}d_6$ solvent. As expected from SXRD data, 2tpy linker

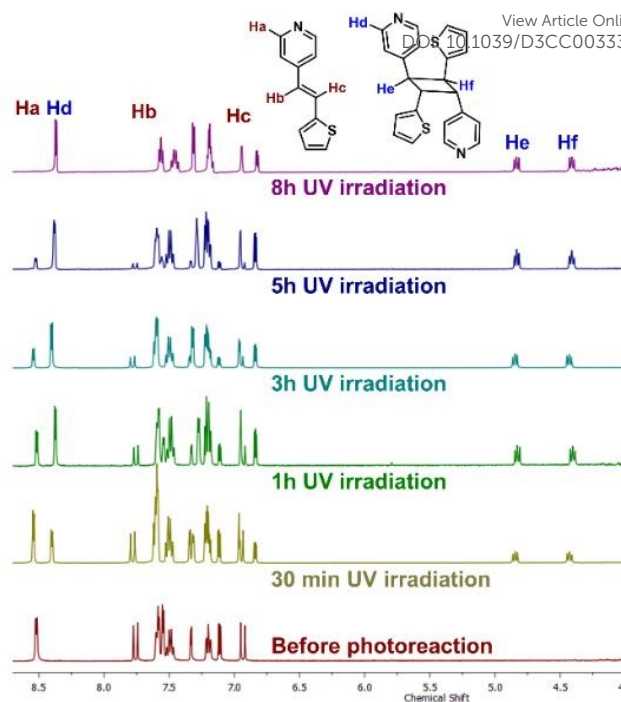


Figure 2. Time dependent photoreaction of **1**.

has shown quantitative photo reactivity with the conversion of 2tpy to *rctt*-ptcb (*rctt*-1,3-bis(4'-pyridyl)-2,4-bis(2-thiophene)cyclobutane), also confirmed from the time dimerization plot as shown in Fig. S1 in SI. This photoreaction has also been supported by HRMS data (Fig. S2 in SI). In addition, thermal stability of the compound has been increased after this photoreaction of **1** (Fig. S3 in SI).

Structural analysis of $[\text{Zn}(\text{2,6-DFBA})_2(\text{2tpy})_2]\cdot\text{H}_2\text{O}$, **2:** Pale yellow coloured long thin platy shaped single crystals of **2** (Fig. 3(a)) were synthesized by using similar synthetic procedure as **1**, using 2,6-DFBA instead of 3,4-DFBA. This compound is crystallized in triclinic *P*-1 space group with *Z* = 2, confirmed from SXRD. The asymmetric unit constitutes double the formula of the compound. The coordination of the Zn(II) atom is bound by two 2tpy ligands, and the oxygen of 2,6-DFBA in monodentate manner. Hence, Zn(II) metal adopts tetrahedral geometry as shown in Fig. 3a. Although Zn(II) adopts the tetrahedral geometry similar to **1**, only one 2tpy linker in **2** is aligned with its neighbouring 2tpy linkers in HT manner, as

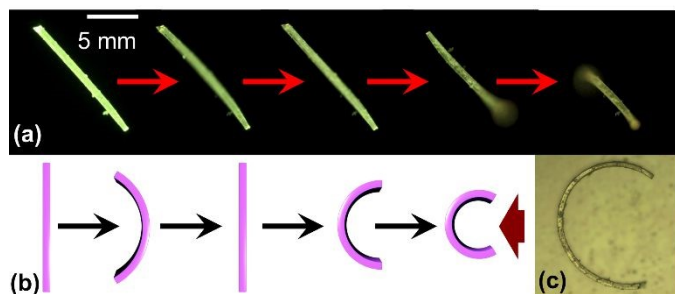


Figure 4. (a) Fluorescence images showing the mechanical motions of **1** when exposed to UV light (from top) under fluorescence microscope. (b) Schematic side view showing the forward and backward bending of the single crystals that is observed under UV irradiation and wine colour arrow showing the direction of the light corresponding to the crystal. (c) Optical image showing the shape of the bent crystal after the complete photoreaction at normal light.

shown in Fig. 3b. The separation between the centres of aligned olefin groups is 3.68 Å as shown in Fig. 3b (within Schmidt's criteria).¹⁸ This change in 3D packing behaviour compared to **1** could be driven by the non-covalent interactions (Fig. S5 in SI). Thus, this compound has shown only ~50% of [2+2] cycloaddition reaction upon UV irradiation (Fig. S6 and S7 in SI). Hence, this compound is expected to form dimers after the photoreaction.

As designed, UV irradiation of single crystals of both the compounds has shown an interesting mechanical motion along with photoreactivity. To monitor these mechanical motions, these crystals are exposed to UV ($\lambda = 390$ nm) by using fluorescence microscope which is attached with a high-resolution camera. When these thin-platy single crystals of **1** are irradiated, initially the central part of the crystals bend towards the light with a lower distance, and upon further irradiation, these crystals bent back, such as the central part of the platy crystal moved away from the light and the edges of the crystals move close to the exposed light as shown in Fig. 4 (see SEM images in Fig. S8 and videos in SI). The crystal of **2** also underwent a similar type of mechanical motion, but in addition, these crystals have shown flipping (see videos in the SI). Up to our knowledge, this flagella-like motion of single crystals is reported for the first time in coordination complexes or solid-state [2+2] photo-cycloaddition reactions.^{7, 38} It is observed that the PL intensity of the crystals were decreased during the photoreaction, thus, PL measurements were performed, which is in line with our observation (see Fig. S9, SI). Time resolved fluorescence has been measured which also presented lowering

of fluorescence lifetime after the photoreaction (Table S2 and Fig. S10-S13, SI). DOI: 10.1039/D3CC00333G

In both cases of **1** and **2**, the extent of mechanical bending is highly dependent on the thickness of the crystals. Thinner crystals have shown significantly faster bending along with larger bending motion. As the thickness of the crystals increased, the extent of this bending gets reduced along with slower bending behaviour. Upon UV irradiation of thinner

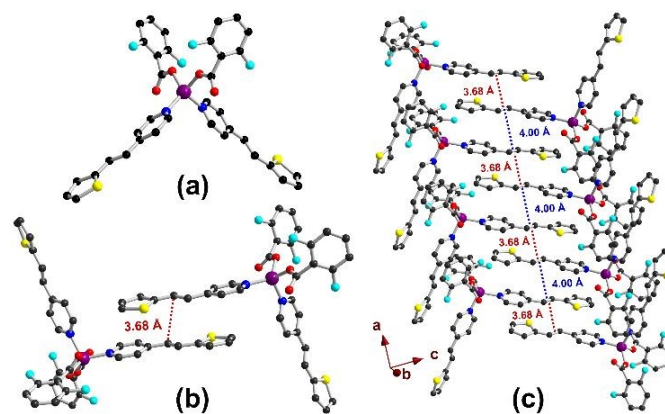


Figure 3. (a) Tetrahedral coordination geometry of Zn(II) atom in **2**. (b) Head-to-tail alignment of 2tpy and distance between olefin pair. (c) Extended head-to-tail alignment in **2** and the alignment of these olefins are along *a*-axis. H-atoms are omitted for clarity. Colour code: C = black, N = blue, O = red, H = white, F = cyan, S = yellow, Zn = purple.

crystals (crystal thickness: ~10-15 μm) of **2**, these crystals couldn't show flagella-like motion. However, they have shown reversible bending, as shown in Fig. 5. Along with this reversible bending, a significant increment in the length of the crystals (ca. 4%) has been observed. This may be due to the different molecular packing and the percentage of a photoreaction in the case of **2** compared to **1**. To further understand this reversible bending behaviour, face indexing of the crystals were performed which showed that the crystals are elongated along *a*-axis (Fig. 3c and S14 in SI).^{10, 39, 40} This is in line with the molecular packing and the alignment of the photoreactive 2tpy linkers. Thus, the increment of the single crystal length during the photoreaction of these compounds is understood to be due to the anisotropic expansion of the crystals, especially along the *a*-axis. Such kind of photoinduced elongation of the single crystals due to solid-state [2+2] photoreaction is scarce.¹³

To further evaluate the mechanism of these mechanical motions, possible change in unit cell volume of the crystals has been attempted using XRD measurements. However, due to the poor quality of XRD after the photoreaction, this anisotropic volume change couldn't be evaluated. Thus, we have assessed the change in unit cell volume through the change in density of the crystals has been estimated using floatation method (see Table S3, SI). These measurements showed that the volume of the crystals got increased by 2.93% and 1.94% in the case of **1** and **2**, respectively during the photoreaction. This volume expansion in **1** and **2** into their photoproduct facilitates the conversion of the accumulated strain energy into kinetic energy.²⁶ As observed above, the elongation of **2** is observed to be 4% which suggests the possible lowering of other dimensions (anisotropic strain accumulation during the photoreaction).^{31, 32, 41}

To understand the reversible bending of thin crystals of **2** (Fig. 5), numerical simulations has been performed with the finite element method. These numerical simulations suggest that during the early stage of the photoreaction, a non-homogeneous photoreaction in different layers of crystals causes the bending of crystals.⁴² Further, with sufficient exposure time, the photoreaction becomes more homogeneous among different layers and the crystal returns towards its initial position (see SI for more details).

Conclusions

To sum up, we have successfully presented photo driven flagella-type motion from two long platy single crystals of photoreactive metal complexes due to [2+2] photoreaction. To the best of our knowledge, this is the first paper presenting flagella-like motion of crystals due to [2+2] photoreaction or metal complexes. The photoreaction of these compounds has been confirmed through ¹H NMR and other characterizations. In addition, these mechanical motions are morphology driven, where the thinner crystals showed better motion with larger distances, whereas thicker crystals showed slower and minimal motions. Thin crystals of **2** have shown reversible bending behaviour along with elongation of the crystal ca. 4% along the α -axis, while the volume of the crystals increased by only ~1.94 %. This proves that the mechanical bending behaviour is due to anisotropic cell volume expansion and strain creation during the photoreaction. The mechanism has been modelled through numerical simulations. Such kind of flagella-like motion and elongation of the crystals can be utilized in various novel applications such as actuators, photo-switches, sensors, to name a few.

Conflicts of interest

There are no conflicts to declare.

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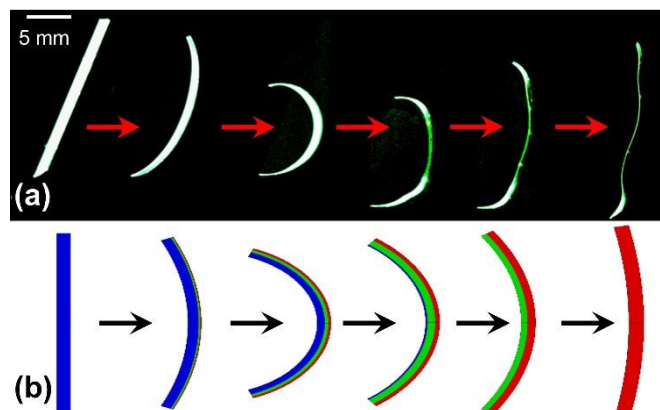


Figure 5. (a) Fluorescence images showing the mechanical motions of thin crystals of **2** when exposed to UV. (b) Schematic view showing the reversible bending that is numerically simulated.

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DOI: 10.1039/D3CC00333G