

# Pulsed Nd:YAG laser induced high throughput stereospecific [2 + 2] cycloaddition of highly organized 1,2-bis(4-pyridyl)ethylene in a supramolecular scaffold†‡

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**The 3rd harmonic generation in a Nd:YAG pulsed laser induces the high throughput [2 + 2] cycloaddition of 1,2-bis(4-pyridyl)ethylene that assemble itself tightly into a face-to-face manner around the Yb<sup>3+</sup> octaqua complex via hydrogen bonds, without damaging the cyclobutyl ring-containing products.**

The intermolecular photochemical [2 + 2] cycloaddition of olefins is a highly effective approach for the preparation of the corresponding cyclobutane containing molecules that are practically inaccessible by solution phase reaction. Intermolecular photocycloaddition occurs most efficiently and selectively in the crystalline state because participating C=C bonds must be aligned in parallel orientations with distances shorter than 4.2 Å,<sup>1,2</sup> and a variety of frameworks have been devised to satisfy these criteria.<sup>3–9</sup> For a *trans* substituted olefin, such as *trans*-1,2-bis(4-pyridyl)ethylene (*trans*-bpe), the stereospecificity of the resulting cyclobutyl ring is determined by the relative positions of the participating

olefins: the parallel and anti-parallel arrangements yield the chair (*rcct* isomer) and saddle (*rtct* isomer) conformations, respectively.<sup>10</sup> Recently, we demonstrated the stereospecific solid-state photocycloaddition of *trans*-bpe to obtain the *rcct* isomer of tetrapyr-idylcyclobutane (*rcct*-tpcb) by irradiation at 365 nm (full width at half maximum = 9 nm) (Fig. 1).<sup>11</sup> In this reaction, we capitalized on the water molecules in the first coordination sphere of Yb<sup>3+</sup> to assemble *trans*-bpe via hydrogen bond interactions between water and the pyridine nitrogen. In the resulting supramolecular complex, [Yb(OH<sub>2</sub>)<sub>8</sub>](bpe)<sub>7.5</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (**1**), *trans*-bpe molecules are aligned parallel in a face-to-face manner through the π–π stacking interactions of the chromophores, forming infinite columnar stacks with the distance between the centers of adjacent C=C bonds smaller than 3.7 Å. We also found that a catalytic cycloaddition occurred in a solution containing *trans*-bpe and Yb<sup>3+</sup>, indicating that the tight and regular arrangement of *trans*-bpe is maintained in the solution phase as well. Then, the resulting cyclobutyl ring containing products are readily discharged from the water coordination sphere and replaced by bulk *trans*-bpe to complete the catalytic cycle.

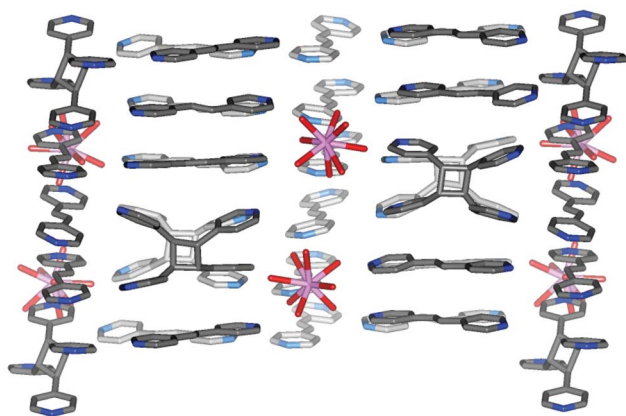
Despite the importance of intermolecular photocycloaddition in synthetic organic chemistry, little progress has been made in understanding the excitation wavelength dependence of the product yields that would lead to a significant improvement in the reaction efficiency. This is partly due to the lack of a prototypical complex that exhibits photocycloaddition of the π-interacted C=C bonds in solution, allowing product isolation and characterization.

Herein we report the excitation wavelength dependence of the intermolecular photocycloaddition of *trans*-bpe observed in solution by virtue of the supramolecular assembly, and demonstrate the drastic enhancement of the product yield by pulsed Nd:YAG laser excitation. Because it is critical to avoid the complication of photochemical *trans*–*cis* isomerization to assess the net yield of the photocycloaddition product, narrowly spaced stacks of *trans*-bpe, formed around [Yb(OH)<sub>8</sub>]<sup>3+</sup>, provide an ideal reaction field by preventing rotation of the aryl moieties around the C–C bond following the excitation of an electron localized on

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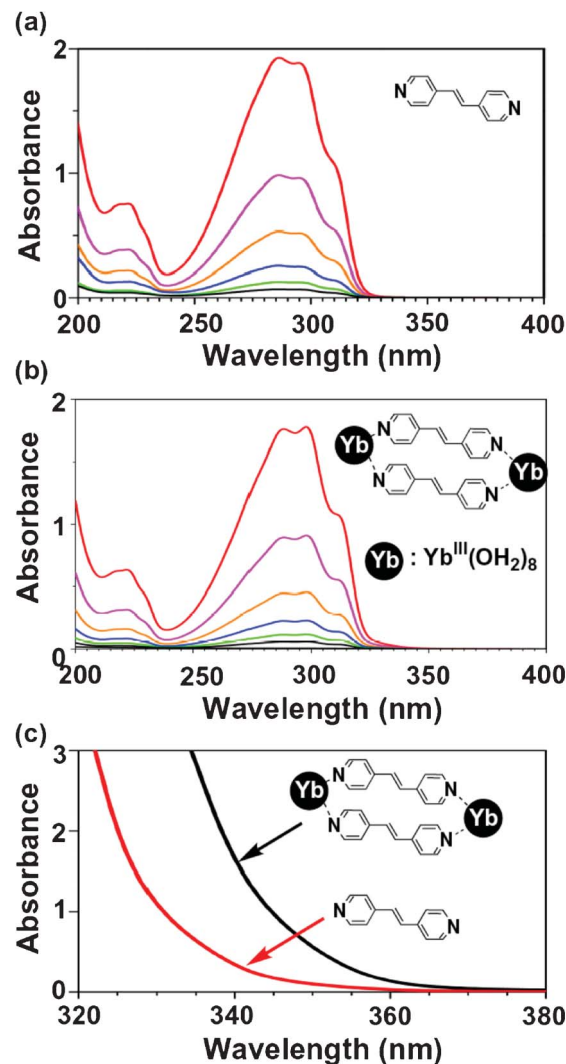
‡ The percent yields of all the products (*trans*-bpe, *cis*-bpe, *rcct*-tpcb and *rtct*-tpcb) were calculated using a ratio of the <sup>1</sup>H NMR peak heights of a solution after irradiation by a Xe lamp (1 mW s<sup>−1</sup> at 298 nm) through a diffraction grating and a 5 nm aperture. A flow cell experiment was conducted by pumping a solution (net volume of 1.63 mL) into a quartz flow cell (0.025 mm thickness) at a rate of 0.005 mL min<sup>−1</sup> while irradiating with a Xe lamp. For laser excitation, a nanosecond pulsed laser system LFP-100 (Tokyo Instruments, Inc.) was employed as a light source. An original sample of *rcct*-tpcb was prepared by the mechanochemical grinding of Yb(SO<sub>3</sub>CF<sub>3</sub>)<sub>3</sub> (15 mg, 24 μmol), *trans*-bpe (33 mg, 181 μmol) and distilled water (50 μL), followed by UV irradiation at 365 nm. The product was isolated by extraction with chloroform and recrystallized from acetonitrile to obtain colorless prismatic crystals. X-ray diffraction data collection for *rcct*-tpcb: a single crystal was mounted on a goniometer using a loop; intensity data were collected at 113 K on a RIGAKU Saturn 70 CCD system; structure solution and refinement were carried out by using a SHELXS-97 and a SHELXL. Crystal data for *rcct*-tpcb: C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>, orthorhombic, Pccn, *a* = 9.3776(5), *b* = 13.9561(9), *c* = 14.0544(8), α = 90, β = 90, γ = 90, *V* = 1839.37(19) Å<sup>3</sup>, *Z* = 4, *R*<sub>1</sub> = 0.0603 [*I* > 2σ(*I*)], *wR*<sub>2</sub> = 0.1938 (all reflections), GOF = 1.141, 15224 reflections measured, 2102 unique (*R*<sub>int</sub> = 0.0410).



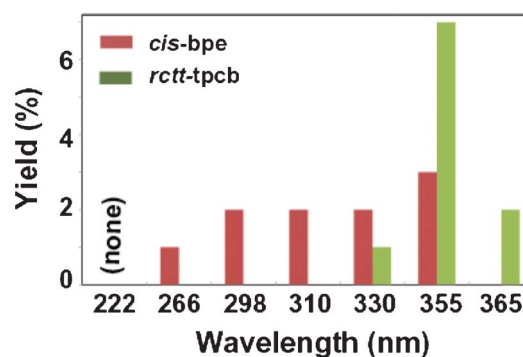
**Fig. 1** Perspective view of the crystal structure of complex **1** along the crystallographic *b*-axis after UV irradiation, showing partial structural conversion due to the formation of *rctt*-tpcb. Yb: pink, C: gray, N: blue, O: red. Hydrogen atoms and counter anions are omitted for clarity. See ref. 11 for details.

the C=C bond.<sup>12</sup> We discovered that the absorption band of stacked *trans*-bpe shifted toward longer wavelengths due to the strong  $\pi$ - $\pi$  stacking interactions.<sup>13</sup> When the solution undergoes continuous UV irradiation, a cyclobutyl ring in *rctt*-tpcb cleaves symmetrically into two *cis*- or *trans*-bpe (see the ESI† Scheme S1). We also show that the 3rd harmonic generation (355 nm) in a pulsed Nd:YAG laser can selectively excite *trans*-bpe without damaging *rctt*-tpcb, which is transparent to that wavelength (see the ESI† Fig. S1).

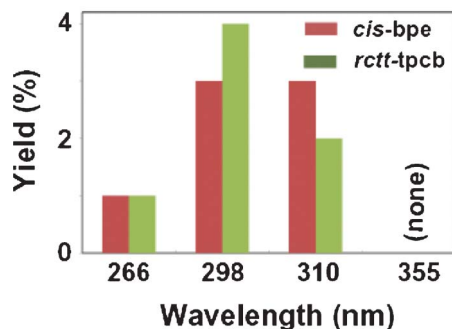
In the absence of metal ions the  $\pi \rightarrow \pi^*$  transition of *trans*-bpe was observed at 240–370 nm ( $\lambda_{\text{max}} = 288$  nm) in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (50v/v%) and the absorbance increased linearly in the range of 0.78–25.0 mM (Fig. 2a). The absorption spectrum of *trans*-bpe in the presence of  $\text{Yb}^{3+}$  has red-shifted by *ca.* 10 nm ( $\lambda_{\text{max}} = 298$  nm), presumably due to the presence of extensive  $\pi$ -interactions among the chromophores (Fig. 2b and 2c).<sup>13</sup> Subsequently, the excitation wavelength-dependence of the product ratio was compared by irradiating the local absorption maxima belong to *trans*-bpe (222, 298, 310 and 330 nm) and to *rctt*-tpcb (266 nm) in addition to the characteristic absorption band arising from  $\pi$ -interacted *trans*-bpe (355 and 365 nm), as observed in a solution containing *trans*-bpe and  $\text{Yb}(\text{CF}_3\text{SO}_3)_3$  (Fig. 3).<sup>‡</sup> When excited at 310 nm or shorter wavelengths only *cis*-bpe was detected, except at 222 nm where no photochemical product was detected. The *rctt*-tpcb isomer was first observed at a 330 nm irradiation and the yield peaked at 355 nm before it became the only product at 365 nm, where this molecule can hardly absorb light, suggesting that *cis*-bpe was primarily formed by the excitation of *rctt*-tpcb and the subsequent symmetric cleavage of the cyclobutyl ring in addition to the isomerization of *trans*-bpe in the bulk solution. The credibility of such a reaction pathway was confirmed by irradiation of an authentic sample of *rctt*-tpcb at 266 nm that produced 3.9 and 3.5% of *cis*- and *trans*-bpe, respectively (see the ESI† Fig. S2 and S3, Table S1 and S2). For the purpose of avoiding further excitation of *rctt*-tpcb in a batch process, we employed a cuvette flow cell.<sup>‡</sup> In this experiment we established that excitation at 266, 298, and 310 nm produced *rctt*-tpcb, although the yield was disappointingly low



**Fig. 2** Absorption spectra of (a) *trans*-bpe (red (25.0 mM), pink (12.5 mM), orange (6.25 mM), blue (3.13 mM), green (1.56 mM), black (0.78 mM)) and (b) *trans*-bpe with  $\text{Yb}^{3+}$  (the molar ratio of  $\text{Yb}^{3+}$  : *trans*-bpe is 1 : 8). Red-shift of the absorption spectrum (c) pronounced at higher concentrations: *trans*-bpe (100 mM) with  $\text{Yb}^{3+}$  (12.5 mM). Optical path length: 0.025 mm for (a) and (b), 1.0 mm for (c).



**Fig. 3** Excitation wavelength dependence of the yields of *rctt*-tpcb and *cis*-bpe obtained in a batch process using a solution containing *trans*-bpe (7.3 mg, 0.04 mmol) and  $\text{Yb}(\text{CF}_3\text{SO}_3)_3$  (3.1 mg, 0.005 mmol).



**Fig. 4** Excitation wavelength dependence of the yields of *rctt*-tpcb and *cis*-bpe obtained in a cuvette flow-cell process using a solution containing *trans*-bpe (29.7 mg, 0.163 mmol) and Yb(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (12.4 mg, 0.02 mmol).

(Fig. 4). Because an insufficient photon flux density was considered responsible for the poor yield, we employed the 3rd harmonic generation (355 nm) in a high power Nd:YAG laser pulse (10 mW per pulse, 10 ns, 10 Hz) in combination with a flow cell system that improved the yield of *rctt*-tpcb to 77% (23.0 mg, 0.063 mmol) while *cis*- and *trans*-bpe were held at 4.0 (1.2 mg, 0.007 mmol) and 6.0% (1.8 mg, 0.010 mmol), respectively, during a mere 3.6 ms of the overall irradiation period (see the ESI,<sup>†</sup> Fig. S4 and Table S3).<sup>‡</sup> However, evidence shows that the high photon flux density alone is not the only determining factor for the conversion rate. When we used the 4th harmonic generation (266 nm) of a Nd:YAG laser pulse (5 mW per pulse, 10 ns, 10 Hz), *trans*-bpe produced only 1% of *rctt*-tpcb and *cis*-bpe each, suggesting that the high photon flux density is not sufficient unless excited at an appropriate wavelength to achieve a high conversion efficiency. The isolated yields of the products in a batch process under Nd:YAG laser pulse excitation were also verified and approximately 62% of *trans*-bpe was converted to tpcb with an *rctt*/*rtct* ratio of 87 : 13.

In conclusion, when *trans*-bpe are stacked tightly in a face-to-face manner and rotation of the aryl moieties is practically impossible, [2 + 2] cycloaddition becomes its primary photo-

chemical reaction. When a light source with a wavelength shorter than 355 nm is used the resulting cycloaddition product, *rctt*-tpcb, undergoes further excitation and cyclobutyl ring cleavage occurs. This inconvenience can be circumvented if irradiated in the narrow range between 355 and 365 nm, where the absorbance of *rctt*-tpcb is very low, with a high power pulsed laser. A further investigation into the wavelength dependence of the cyclobutyl ring cleavage might lead to the development of a supramolecular system that exhibits reversible cyclobutyl ring formation and cleavage controlled by an external light.

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