

Electronic Supplementary Information

**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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Figures, Tables, and Schemes

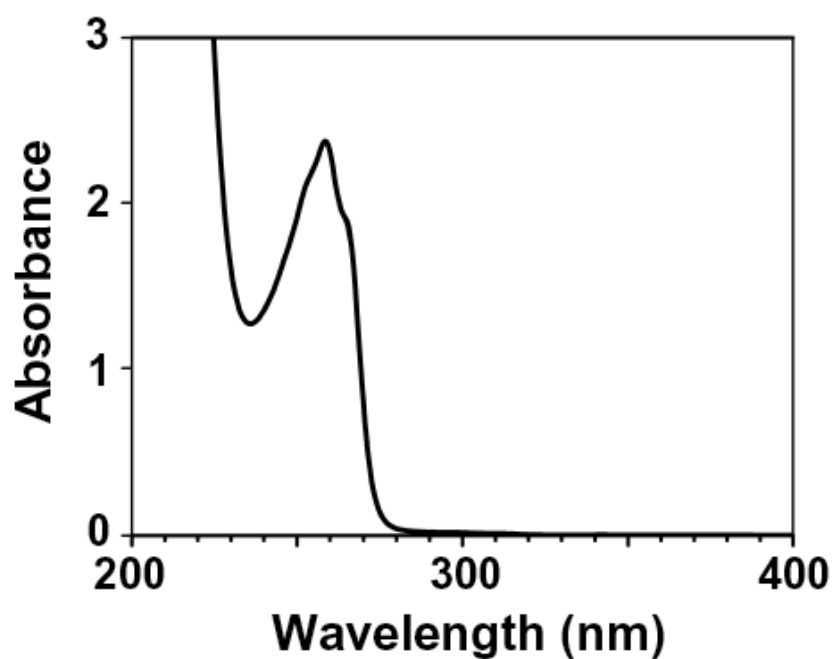


Figure S1. The absorption spectrum of *rctt*-tpcb (3.6 mM) in CH₃CN recorded using a quartz cuvette with 1 mm optical path length.

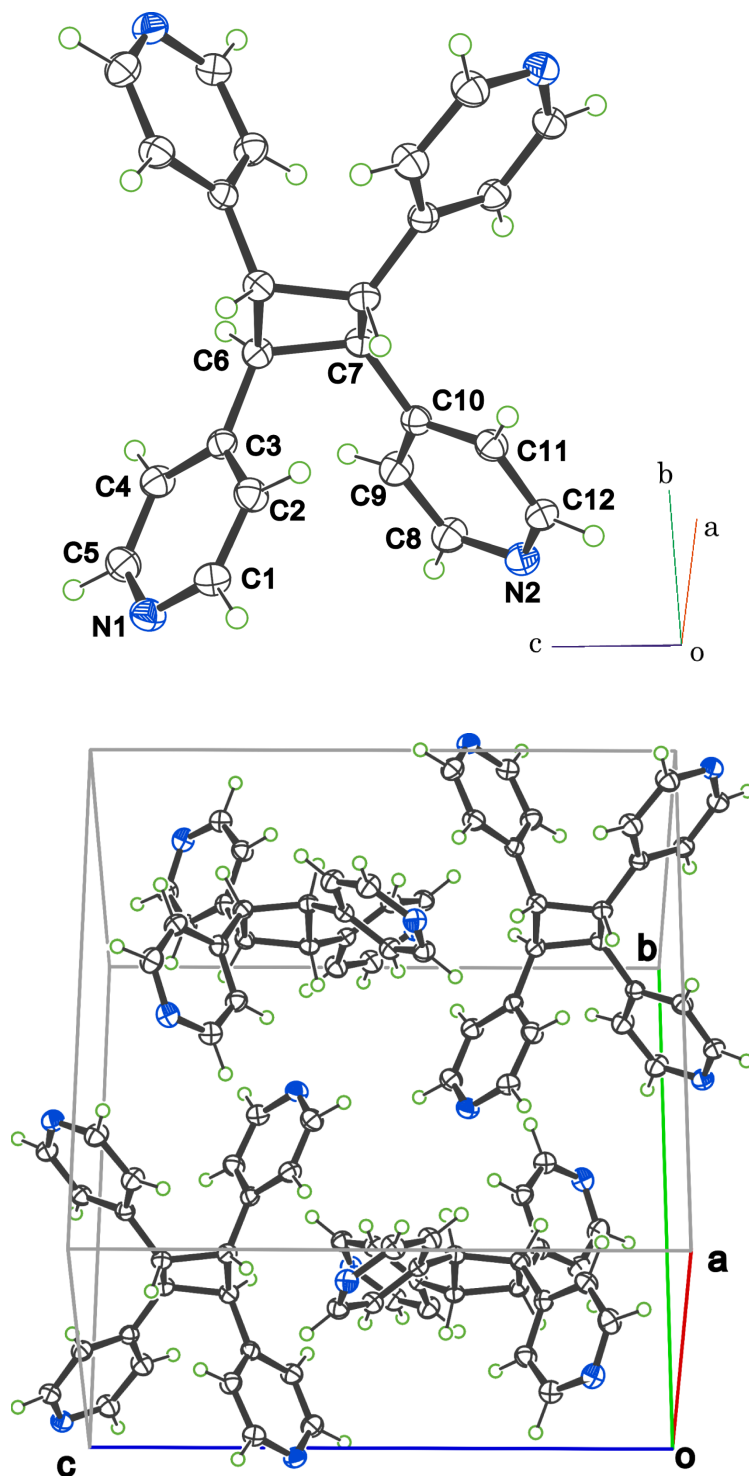


Figure S2. ORTEP diagrams of *rctt-tpcb* showing the atom-numbering scheme (a), and a unit cell packing (b), with thermal ellipsoids drawn at the 50 % probability level. H atoms were placed at calculated positions and refined as a riding model.

Table S1. Selected bond lengths (Å) of *rctt*-tpcb.

N1	-	C1	1.340(2)
C7	-	C10	1.499(2)
C9	-	C10	1.390(2)
C10	-	C11	1.392(2)
N2	-	C12	1.339(2)
C11	-	C12	1.392(2)
C1	-	C2	1.386(2)
C2	-	C3	1.396(2)
C3	-	C4	1.395(2)
N1	-	C5	1.339(2)
C4	-	C5	1.390(2)
C3	-	C6	1.5082(19)
C6	-	C6 ⁱ	1.569(3)
C6	-	C7	1.574(2)
C7	-	C7 ⁱ	1.542(3)
N2	-	C8	1.346(2)
C8	-	C9	1.386(2)

i) 1.5-x, 1.5-y, z

Table S2. Selected bond angles (°) of *rctt*-tpcb.

C5	-	N1	-	C1	115.68(14)
C8	-	C9	-	C10	119.87(15)
C12	-	C11	-	C10	119.19(14)
C9	-	C10	-	C11	116.93(13)
N2	-	C12	-	C11	124.31(14)
N1	-	C1	-	C2	124.32(15)
C4	-	C3	-	C2	116.31(13)
C1	-	C2	-	C3	119.73(15)
C5	-	C4	-	C3	119.69(14)
N1	-	C5	-	C4	124.24(16)
C4	-	C3	-	C6	121.08(13)
C2	-	C3	-	C6	122.60(13)
C3	-	C6	-	C6 ⁱ	114.14(14)
C10	-	C7	-	C6	120.04(12)
C7	-	C7 ⁱ	-	C6	89.67(7)
C3	-	C6	-	C7	117.48(12)
C6	-	C6 ⁱ	-	C7	88.69(7)
C10	-	C7	-	C7 ⁱ	121.49(13)
C9	-	C10	-	C7	119.79(13)
C11	-	C10	-	C7	123.23(13)
C12	-	N2	-	C8	115.90(13)
N2	-	C8	-	C9	123.76(15)

i) 1.5-x, 1.5-y, z

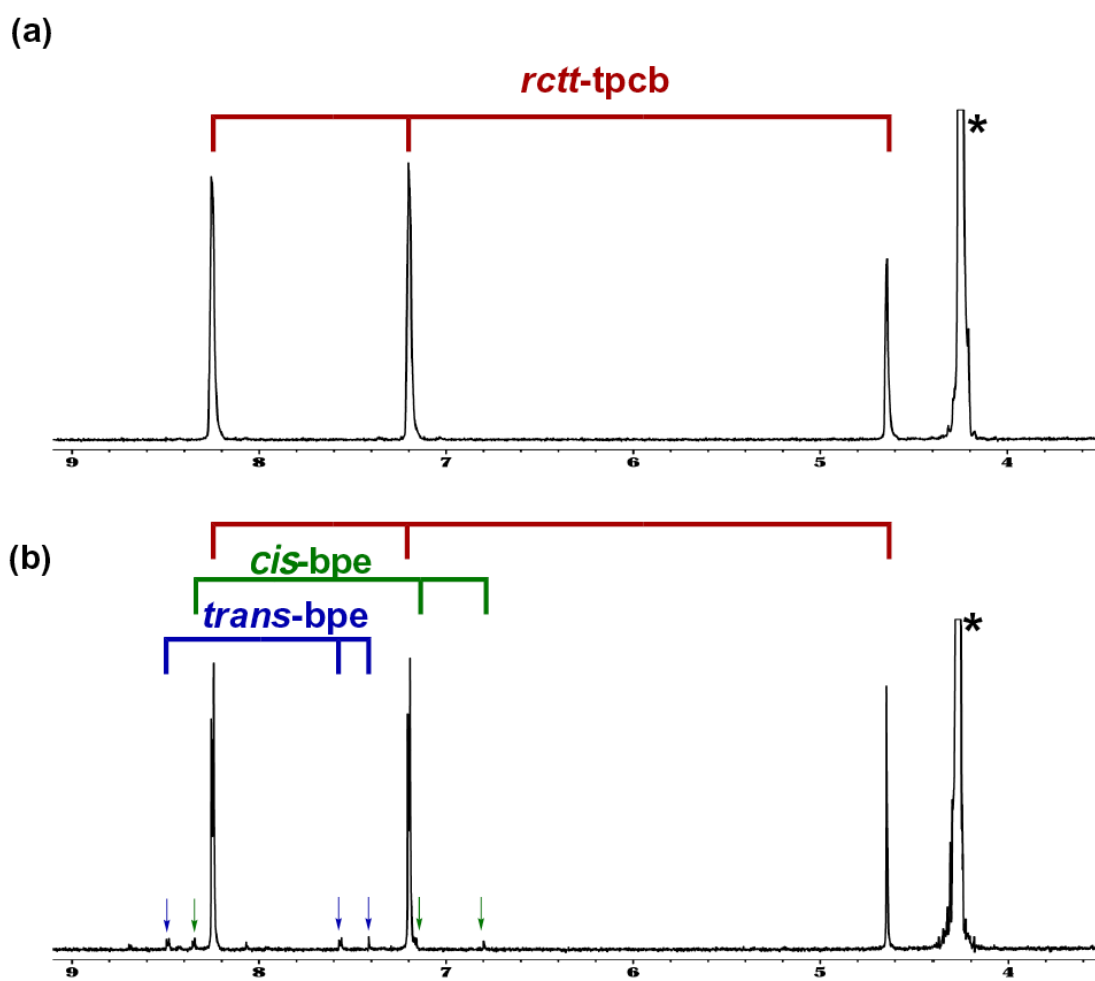


Figure S3. ^1H NMR spectrum of an authentic sample of *rctt-tpcb* before (top) and after (bottom) irradiated at 266 nm in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (50 v/v%). Solvent peaks are denoted by the asterisk.

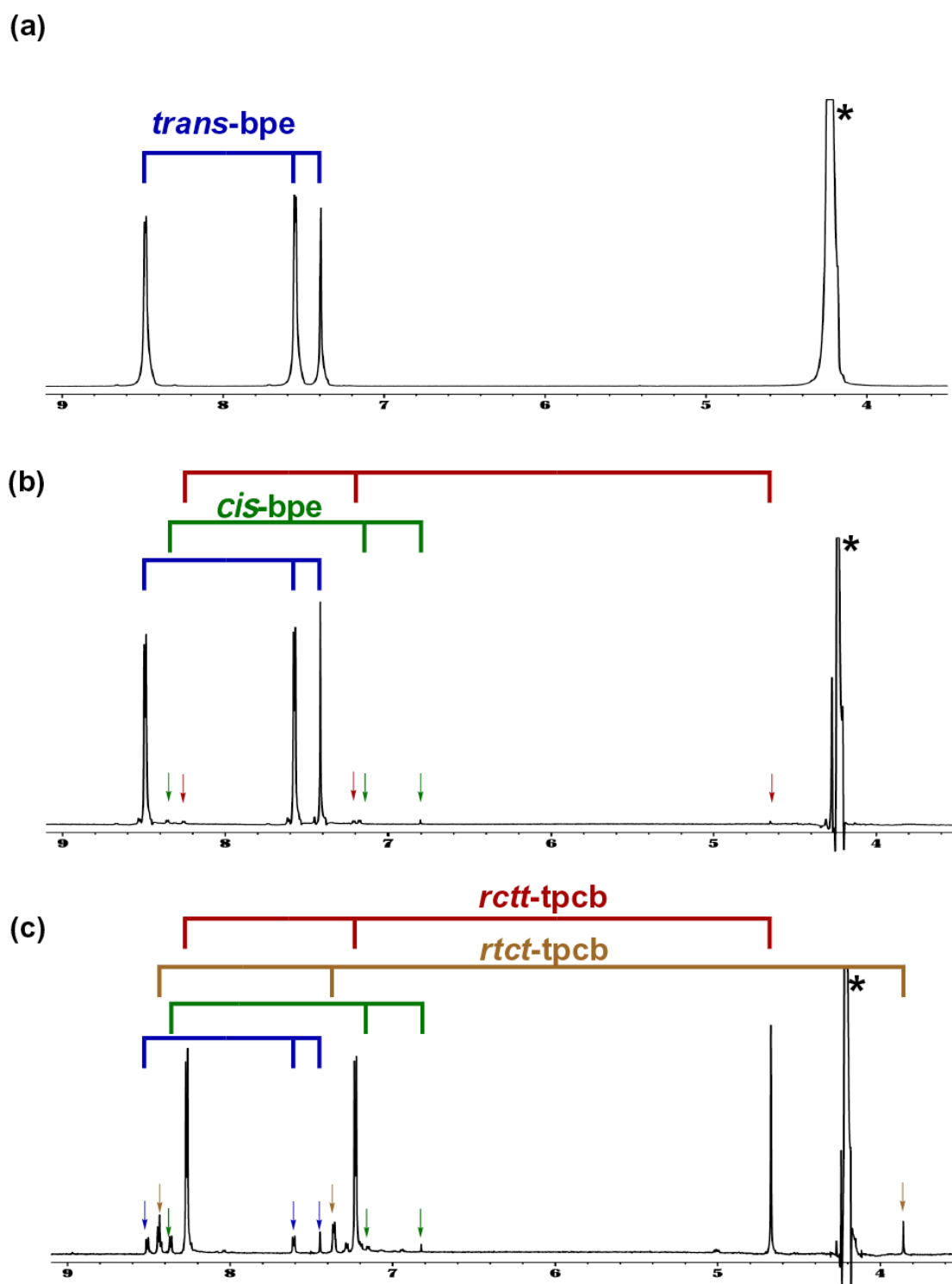
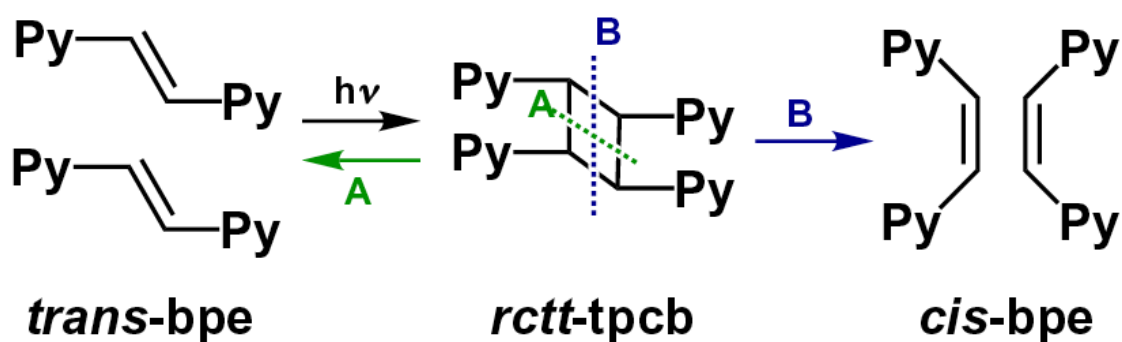


Figure S4. ^1H NMR spectrum of the reaction solution ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (50 v/v%)) before (a) and after (b) irradiated by 266 nm Nd:YAG laser pulse, and after irradiated by 355 nm laser pulse (c). Solvent peaks are denoted by the asterisk.

Table S3. Comparison of the product ratio excited by 3rd and 4th harmonic generation Nd:YAG laser pulse.

Ext. wavelength	<i>trans</i> -bpe (%)	<i>cis</i> -bpe (%)	<i>rctt</i> -tpcb (%)	<i>rtct</i> -tpcb (%)
355 nm	6	4	77	13
266 nm	98	1	1	0



Scheme S1. Schematic representation of relationship between two patterns of symmetric *rctt*-tpcb ring cleavage and the resulting geometries of bpe isomers: Cleavage along the dotted line **A** and **B** yield two *trans*-bpe and two *cis*-bpe, respectively. Py = pyridyl ring.