

Electronic Supplementary Information for:

Synthesis of helically twisted [1+1]macrocycles assisted by amidinium-carboxylate salt bridges and control of their chiroptical properties

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1. Characterization of [1+1]Macrocycles (2)

1.1. ESI-Mass Spectra

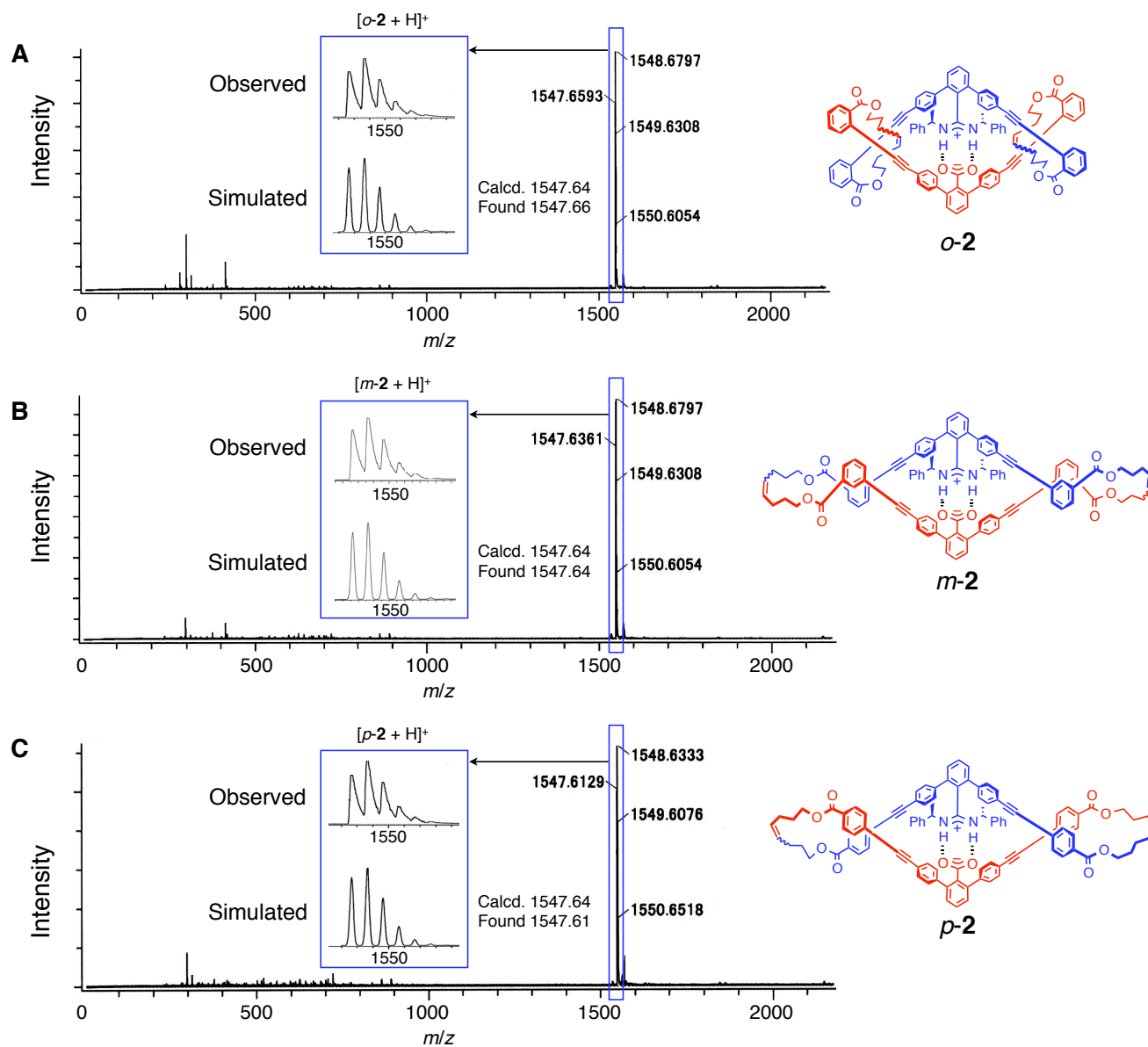


Figure S1. Positive mode ESI-MS spectra of (A) *o-2*, (B) *m-2*, and (C) *p-2* in CHCl₃/MeOH (1/1, v/v).

1.2. RCM Reaction of the Carboxylic Acid (*o*-1b) Using 1st Generation Grubbs' Catalyst

Experimental Procedure: A solution of the carboxylic acid *o*-1b (6.98 mg, 10.0 μmol) in dry toluene (100 mL) was deoxygenated by freeze-pump-thaw cycles for 3 times. To this was added the 1st generation Grubbs' catalyst (3.00 mg, 3.50 μmol), and the reaction mixture was stirred at ambient temperature for 24 h under Ar. The mixture was subjected to ESI-MS analysis.

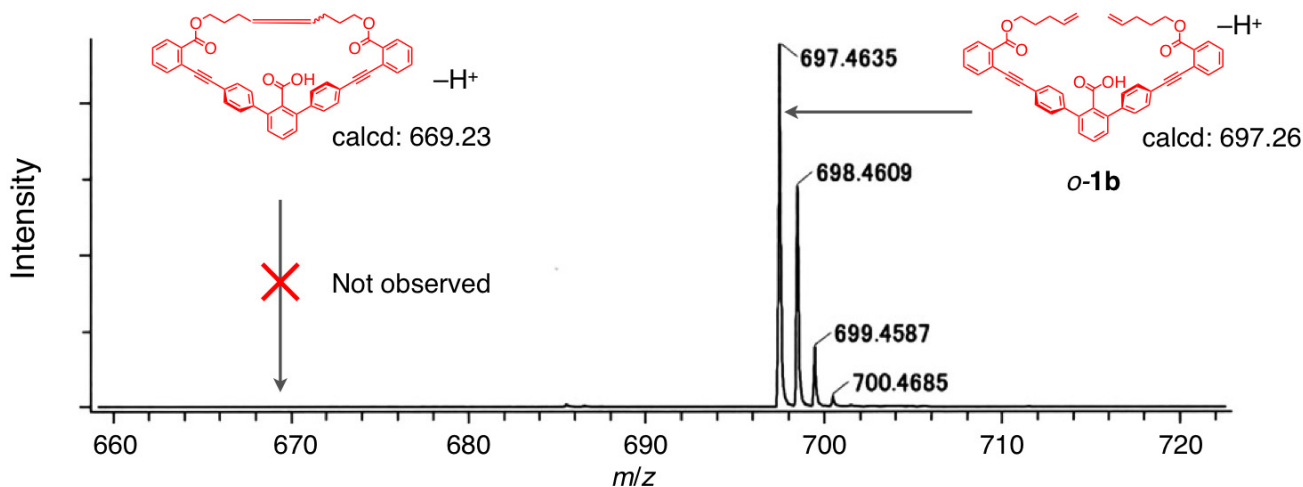


Figure S2. ESI-MS spectrum of the crude products after the reaction of *o*-1b with the 1st generation Grubbs' catalyst.

1.3. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) Spectra of *p*-[1+1]Macrocycle (*p*-2) with Different *cis/trans* Ratios

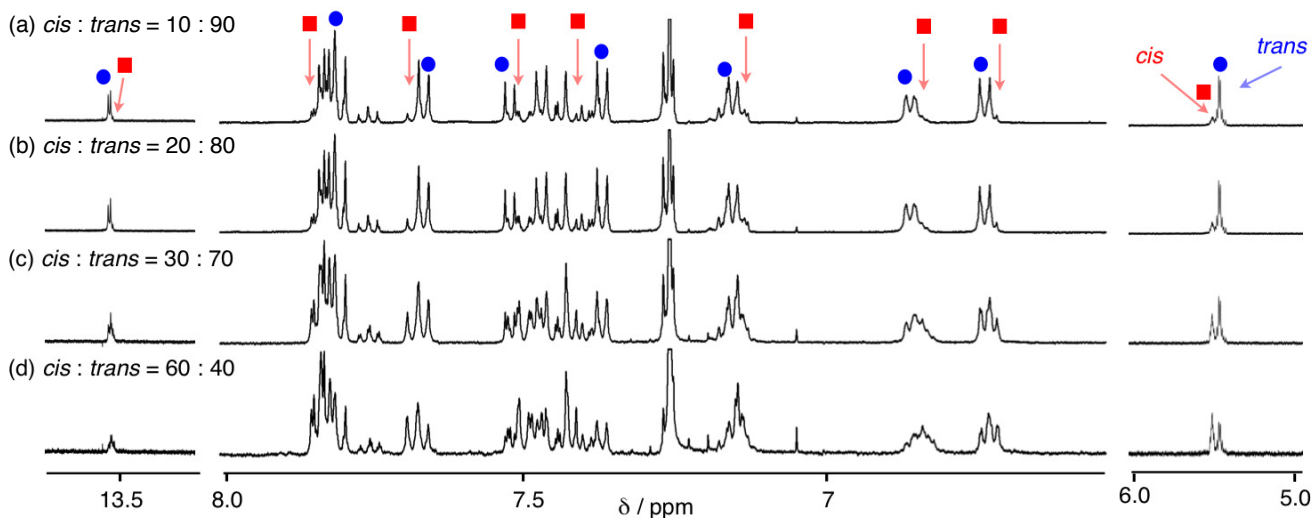


Figure S3. Partial ^1H NMR spectra (500 MHz, 1.0 mM, 25 $^\circ\text{C}$) of *p*-2 with different *cis/trans* ratios in CDCl_3 .

1.4. CD Spectra of *m*-[1+1]Macrocycles (*m*-2)

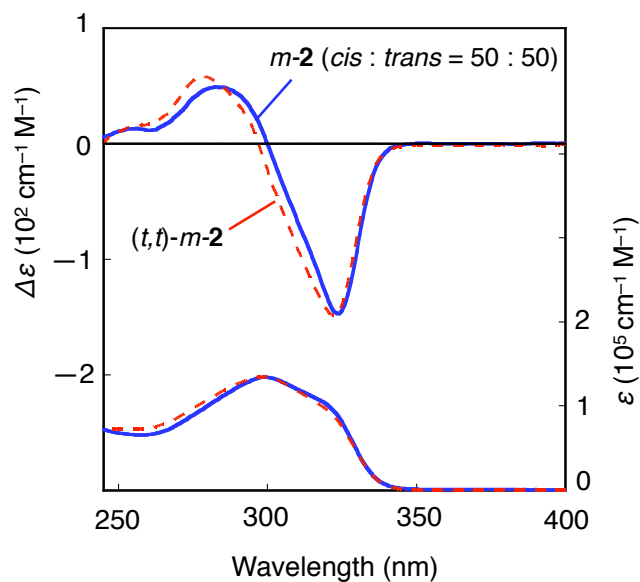
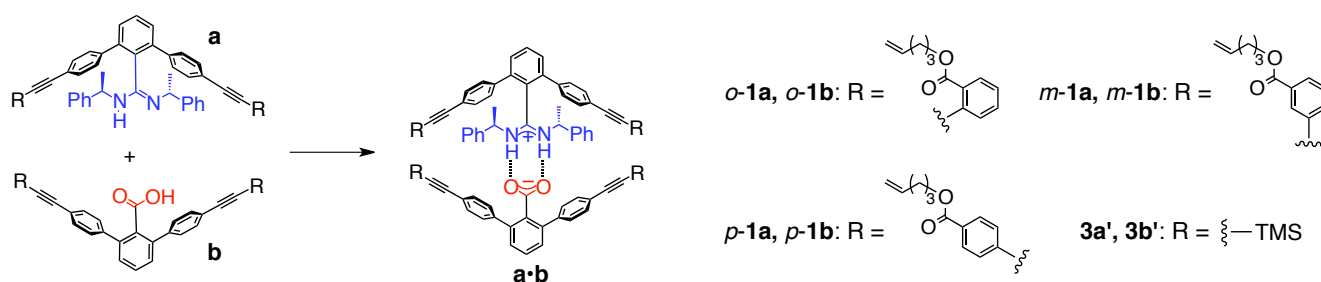
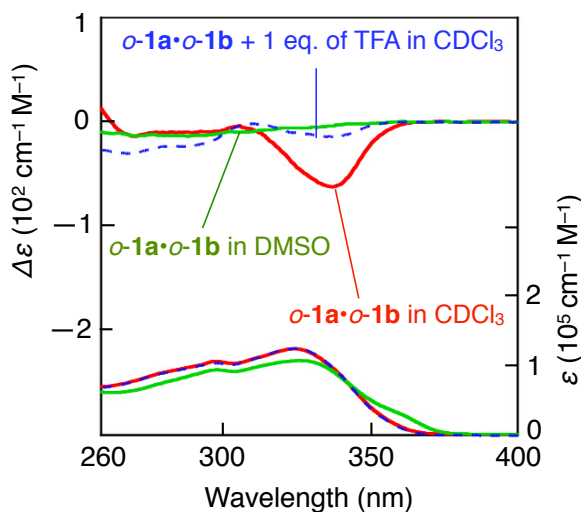


Figure S4. CD and absorption spectra of the (*trans, trans*)-*m*-[1+1]macrocycle ($(t,t)\text{-}m\text{-}2$) and as prepared *m*-[1+1]macrocycle (*m*-2) (*trans* : *cis* = 50 : 50) in CDCl_3 (0.1 mM) at 20 °C.

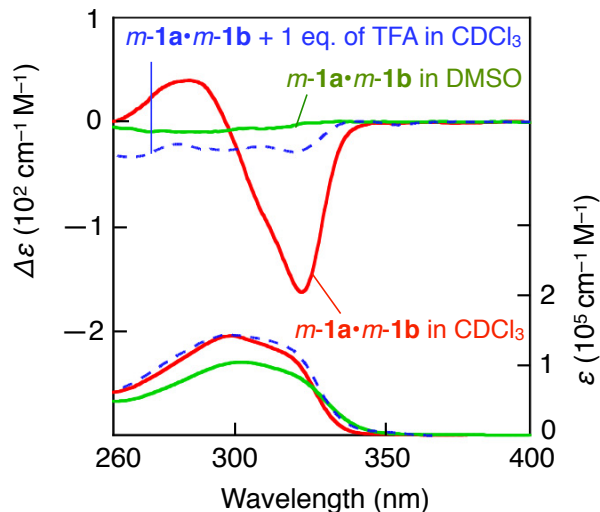
2. CD and Absorption Spectra of Models



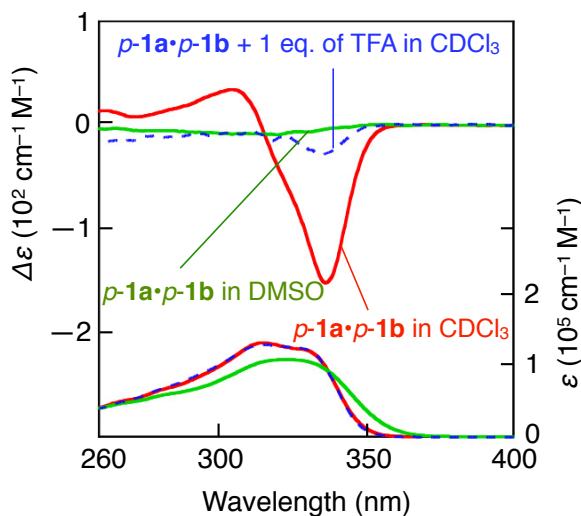
A: $o\text{-1a}\cdot o\text{-1b}$



B: $m\text{-1a}\cdot m\text{-1b}$



C: $p\text{-1a}\cdot p\text{-1b}$



D: $3a'\cdot 3b'$

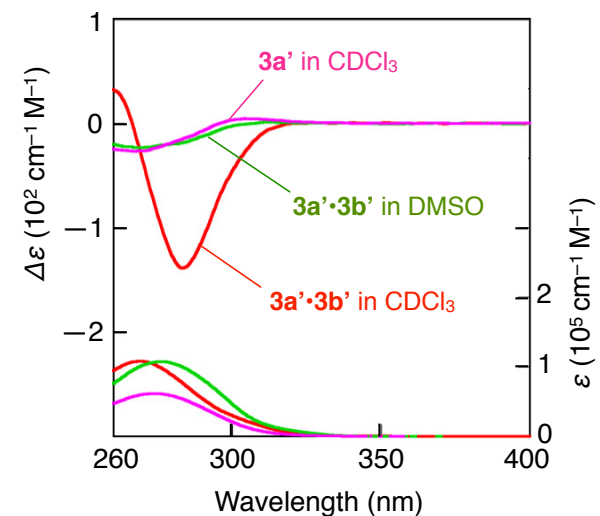


Figure S5. CD and absorption spectra of (A) $o\text{-1a}\cdot o\text{-1b}$, (B) $m\text{-1a}\cdot m\text{-1b}$, and (C) $p\text{-1a}\cdot p\text{-1b}$ in CHCl_3 (0.1 mM) (red) and DMSO (0.1 mM) (green) at 20 °C and after the addition of 1 equiv. of TFA in CHCl_3 (0.1 mM) at 20 °C (dashed blue). (D) CD and absorption spectra of $3a'$ (0.1 mM) in CDCl_3 and $3a'\cdot 3b'$ (0.1 mM) in CDCl_3 and DMSO at 25 °C.^{S2}

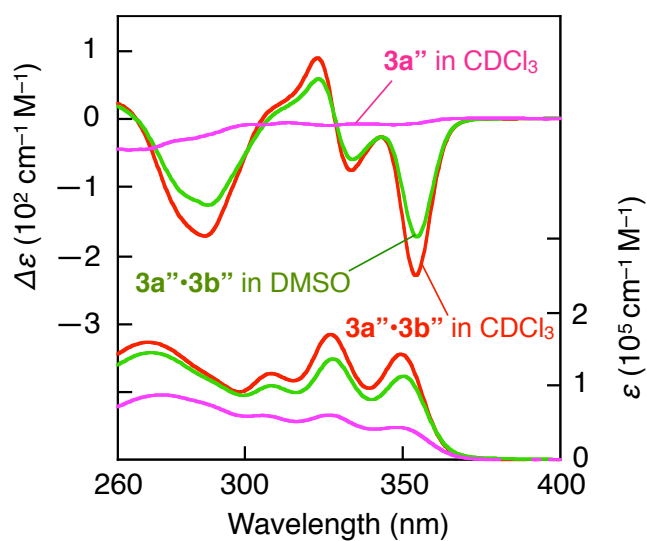
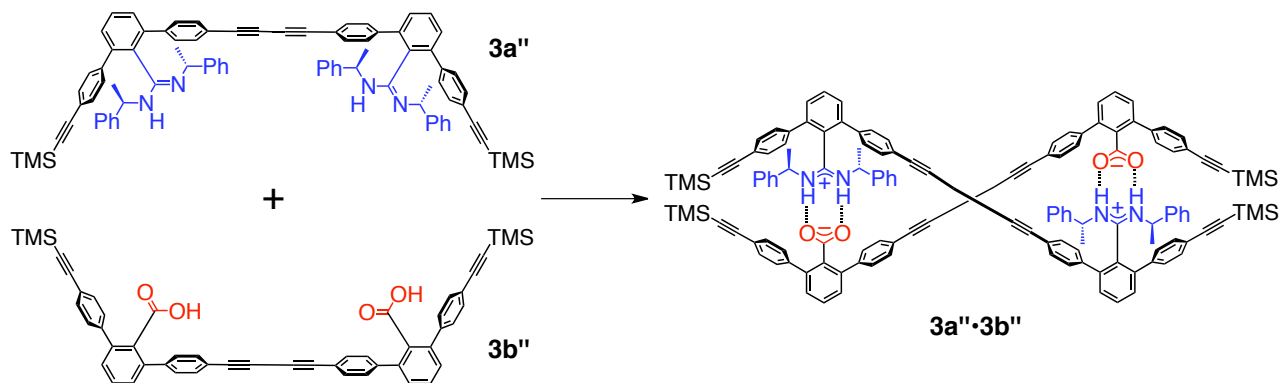


Figure S6. CD and absorption spectra of **3a''** (0.1 mM) in CDCl_3 and **3a''·3b''** (0.1 mM) in CDCl_3 and DMSO at 25 °C.^{S2}

3. CD and Absorption Spectral Changes of [1+1]Macrocycles in Diluted Acidic Solution

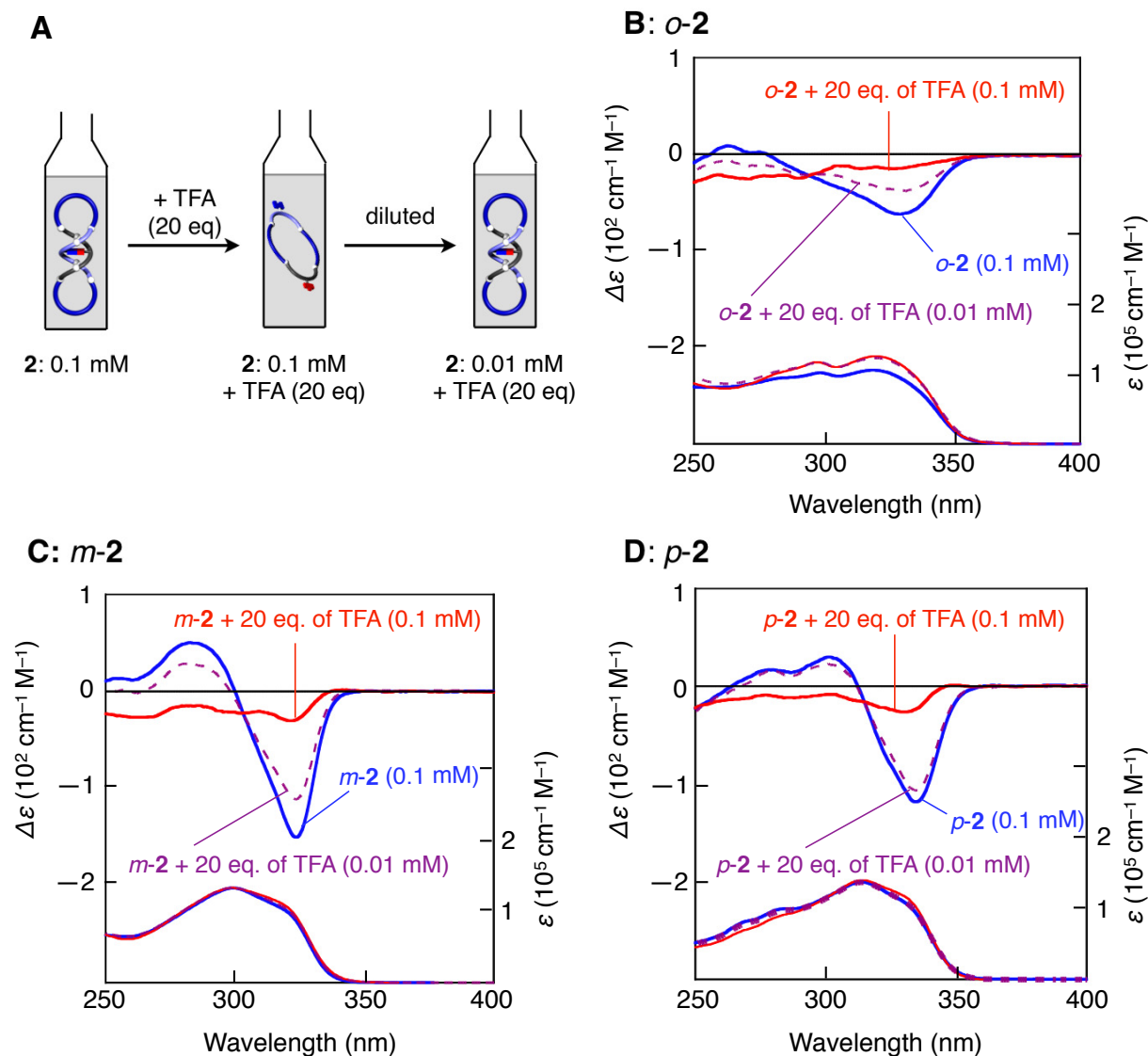


Figure S7. (A) Structural changes of macrocycles upon the addition of TFA followed by dilution. CD and absorption spectra of (B) *o*-2, (C) *m*-2, and (D) *p*-2 in CHCl₃ (0.1 mM) at 20 °C before (blue) and after the addition of 20 equiv. of TFA (red) followed by dilution with CHCl₃ (0.01 mM) (dashed violet).

4. Time-Dependent CD, Absorption and Fluorescence Spectra of [1+1]Macrocycles in the Presence of $\text{Zn}(\text{ClO}_4)_2$

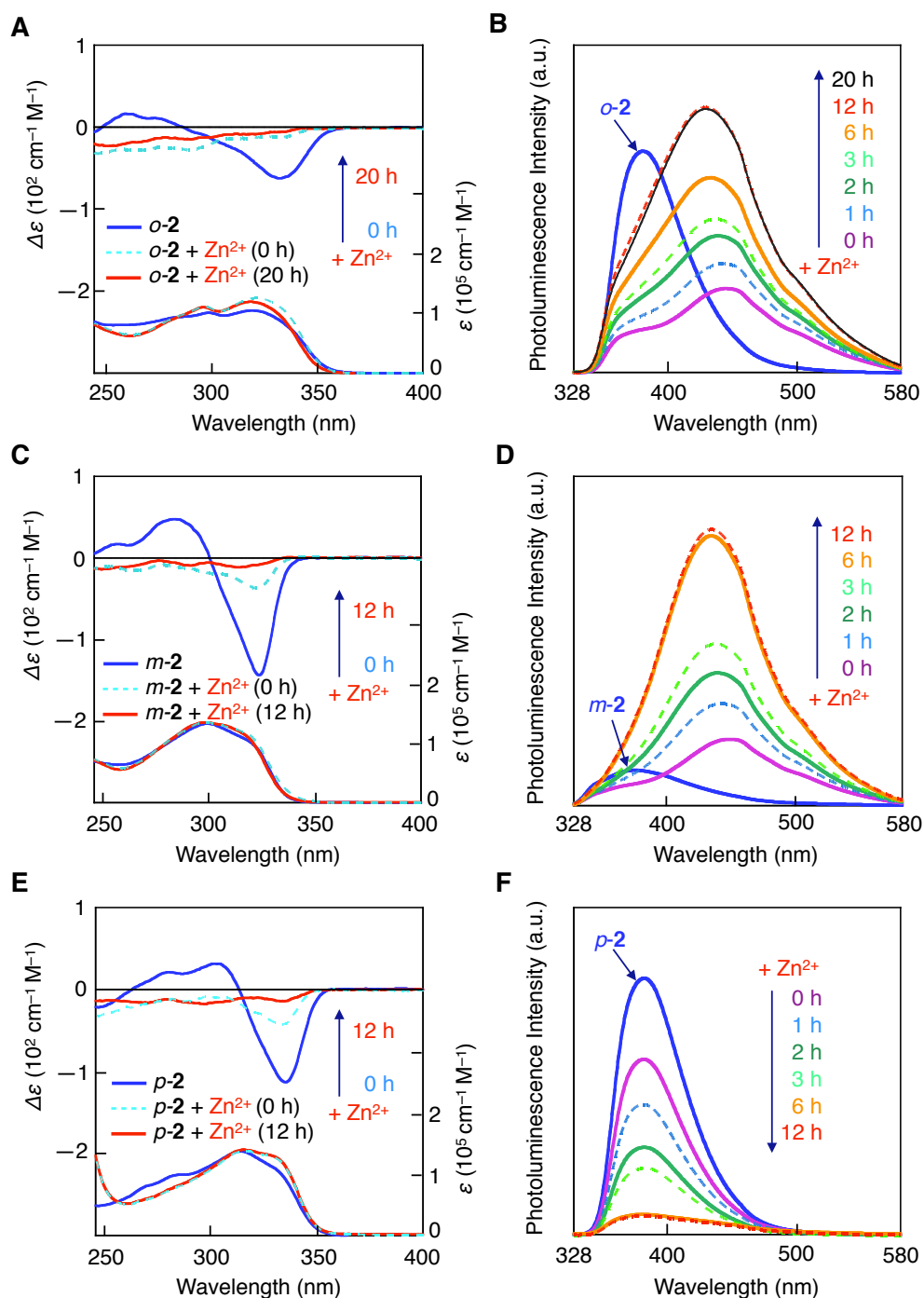
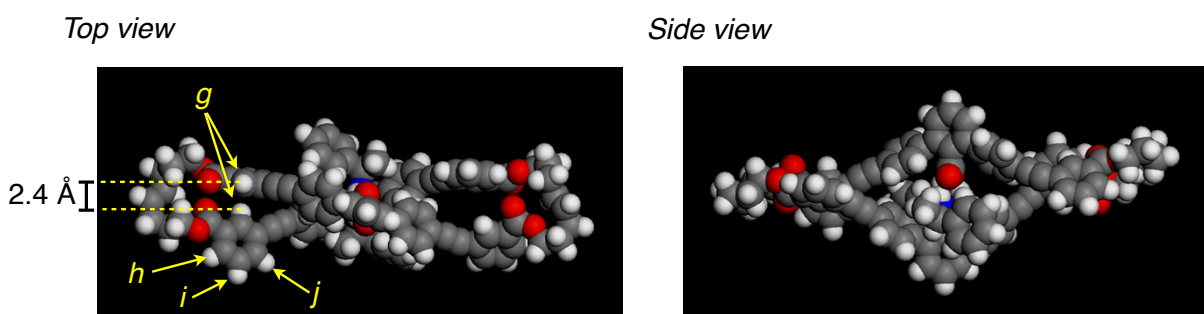


Figure S8. Time-dependent CD, absorption (A, C, E), and fluorescence spectra (B, D, F) of *o*-2 (A, B) ($\lambda_{\text{ex}} = 313 \text{ nm}$), *m*-2 (C, D) ($\lambda_{\text{ex}} = 300 \text{ nm}$), and *p*-2 (E, F) ($\lambda_{\text{ex}} = 313 \text{ nm}$) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (10/1, 0.01 mM) at ambient temperature before (blue) and after the addition of 2 equiv. of $\text{Zn}(\text{ClO}_4)_2$.

5. Molecular-Mechanics Calculations of *trans-trans* and *cis-cis* Isomers of *m*-[1+1]Macrocyclic (*m*-2)

The molecular mechanics (MM)-calculations of the *trans-trans* and *cis-cis* isomers of the *m*-[1+1]macrocyclic (*m*-2) were performed on a Windows XP PC using the Compass Force Field as implemented in the Material Studio package (Version 4.1; Accelrys Inc.). The initial structures of the *trans-trans* and *cis-cis* isomers with a right-handed helical macrocyclic conformation were constructed based on the crystal structure of a double helical dimer comprising complementary amidine and carboxylic acid dimers linked by diacetylene residues bound together through salt bridges.^{S2} The energy minimization was conducted using the Smart Minimizer of the Discover module using the Compass Force Field until the root-mean-square (r.m.s.) value became less than 0.1 kcal mol⁻¹ Å⁻¹. The optimized structures indicate that the (*trans, trans*)-*m*-[1+1]macrocyclic appears to have a more highly strain structure than that of the (*cis, cis*)-isomer, resulting in the upfield shifts of the *m*-linked aromatic proton resonances, in particular *g* due to the ring current effect as observed in the ¹H NMR spectra (*d* and *e* in Fig. 2B).

A: *Trans-trans* isomer of *m*-[1+1]macrocyclic (*m*-2)



B: *Cis-cis* isomer of *m*-[1+1]macrocyclic (*m*-2)

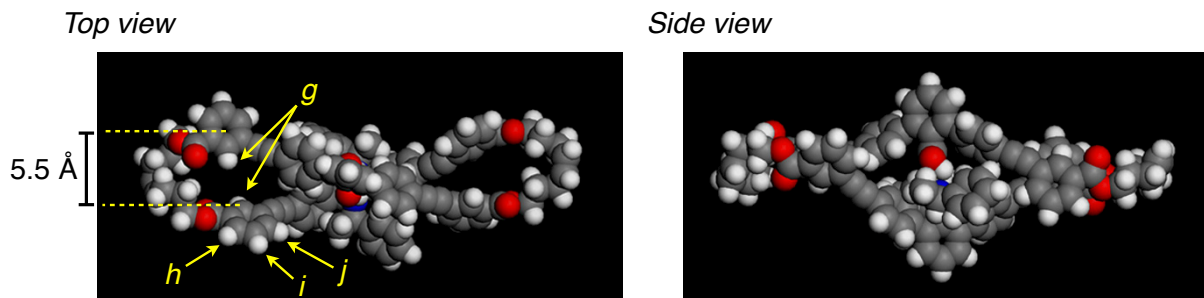


Figure S9. Space-filling drawings of the calculated structures of (A) *trans-trans* and (B) *cis-cis* isomers of the *m*-[1+1]macrocyclic. Hydrogen (white), carbon (gray), nitrogen (blue), and oxygen (red).

6. Supporting References

- (S1) T. Maeda, Y. Furusho, S.-i. Sakurai, J. Kumaki, K. Okoshi and E. Yashima, *J. Am. Chem. Soc.*, **2008**, *130*, 7938–7945.
- (S2) Y. Tanaka, H. Katagiri, Y. Furusho and E. Yashima, *Angew. Chem., Int. Ed.*, **2005**, *44*, 3867–3870.