ELECTRONIC SUPPLEMENTARY INFORMATION

Protonation-induced red-coloured circularly polarized luminescence of [5]carbohelicene fused by benzimidazole

Hayato Sakai,*[a] Takako Kubota,[a] Junpei Yuasa,*[bc] Yasuyuki Araki,[d] Tomo Sakanoue,[e] Taishi Takenobu,[e] Takehiko Wada,[d] Tsuyoshi Kawai,*[b] and Taku Hasobe*[a]

[a]*Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama, Kanagawa 223-8522 Japan*
[b]*Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192 Japan*
[c]*PRESTO, Japan Science and Technology Agency, Kawaguchi, 332-0012 Japan*
[d]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan*
[e]*Department of Applied Physics, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo 169-8555 Japan*

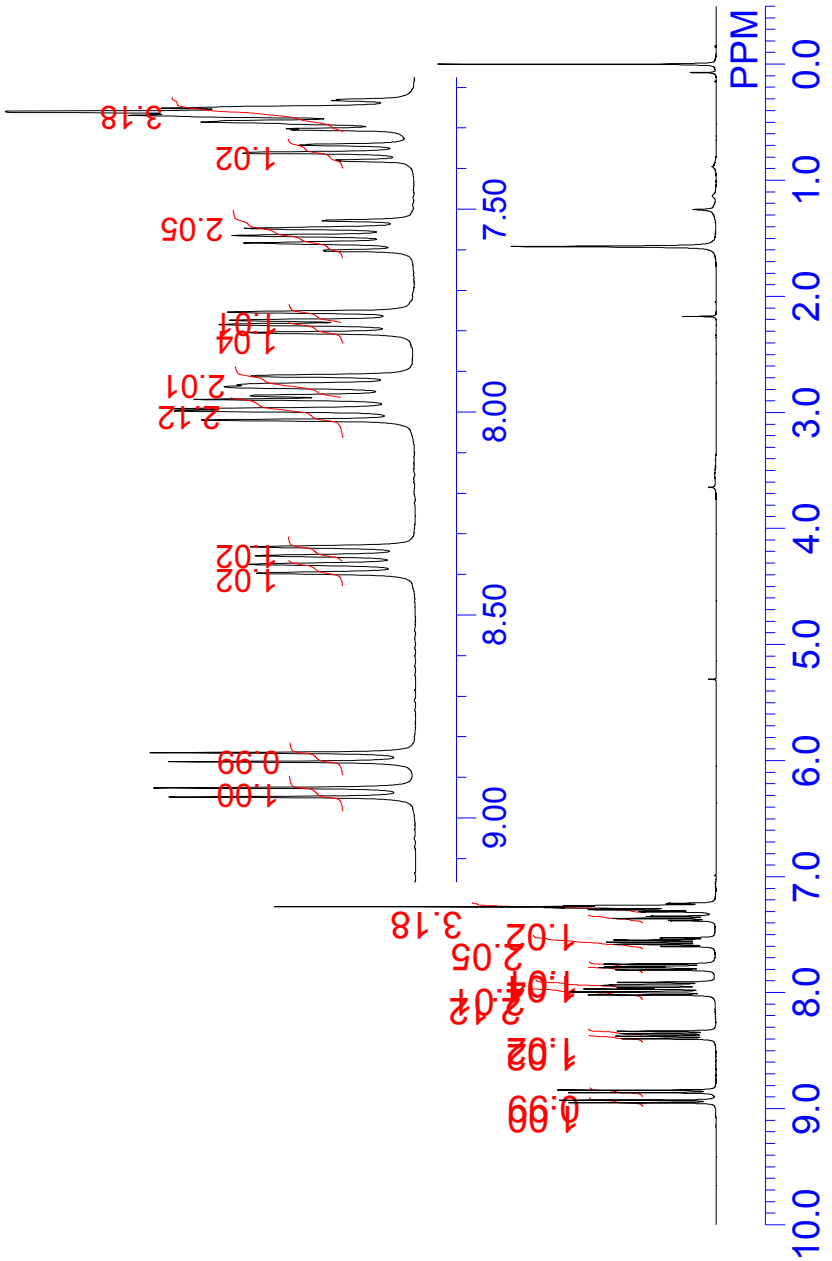


Fig. S1 ^{1}H NMR spectrum of [5]HeliBI.

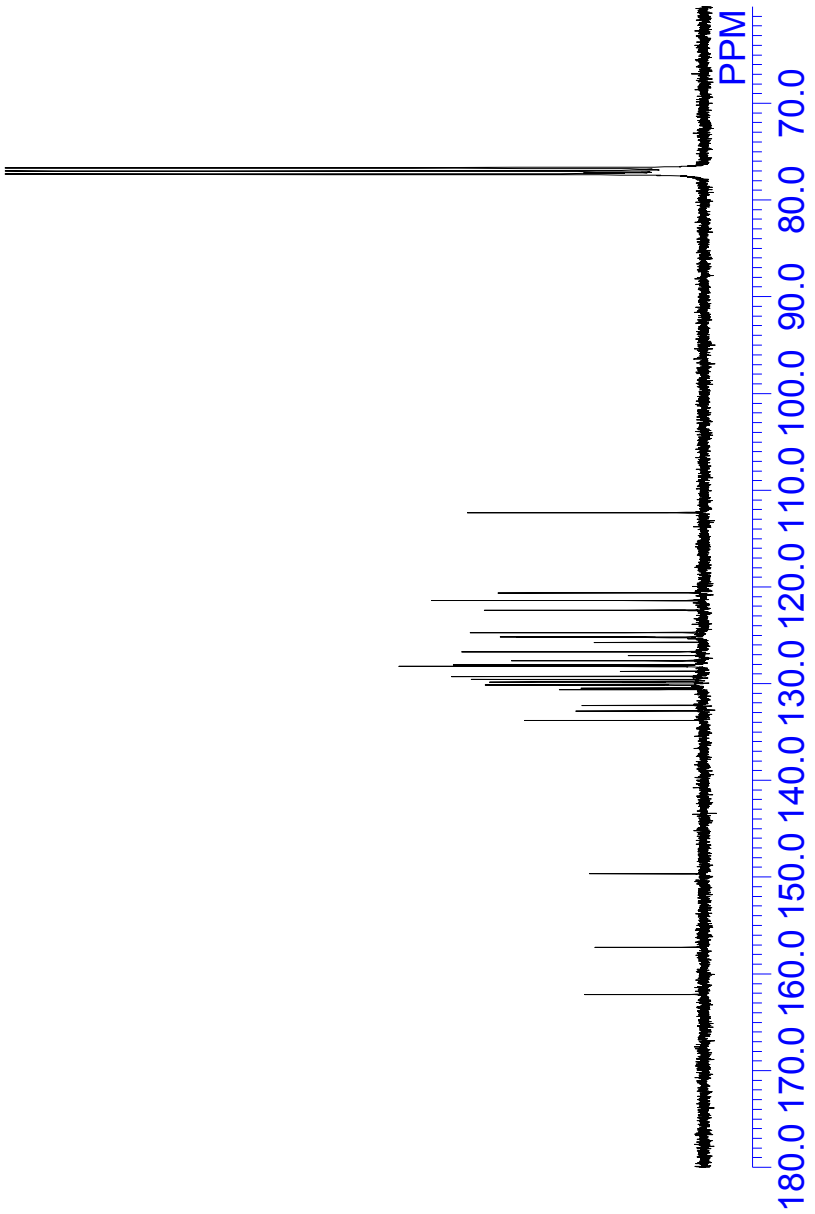


Fig. S2 ^{13}C NMR spectrum of [5]HeliBI.

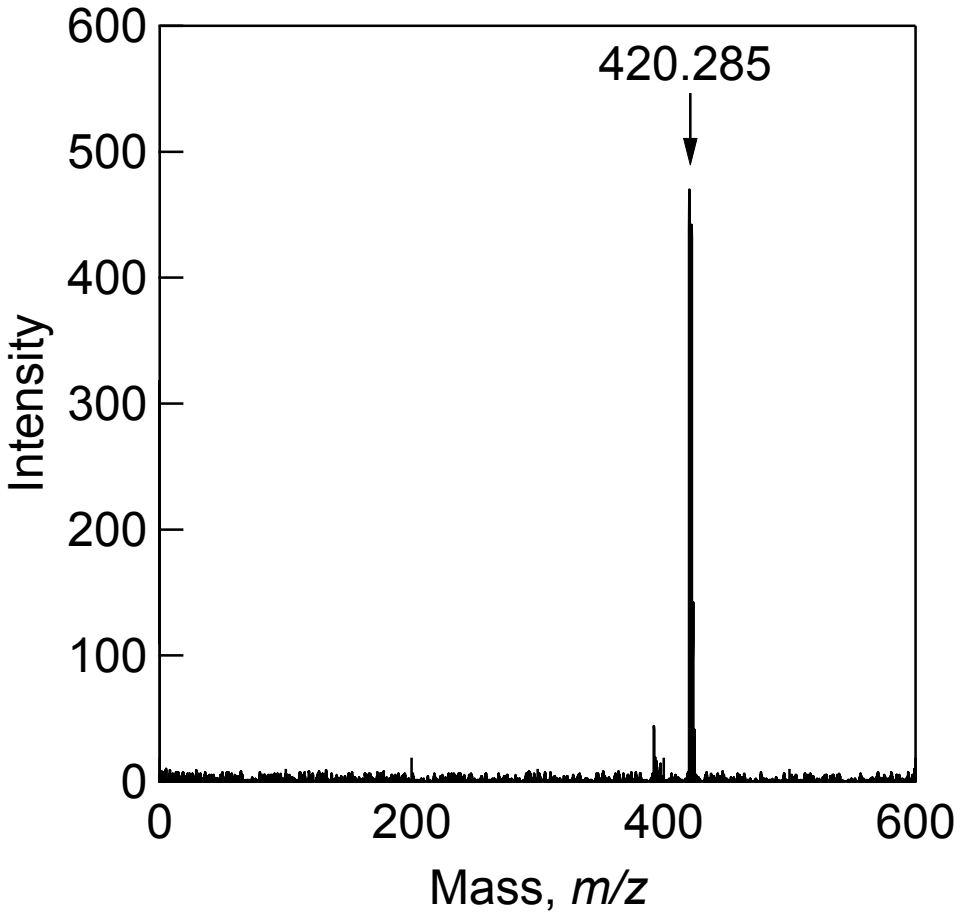


Fig. S3 High-resolution MALDI-TOF MS spectral profile of [5]HeliBI.

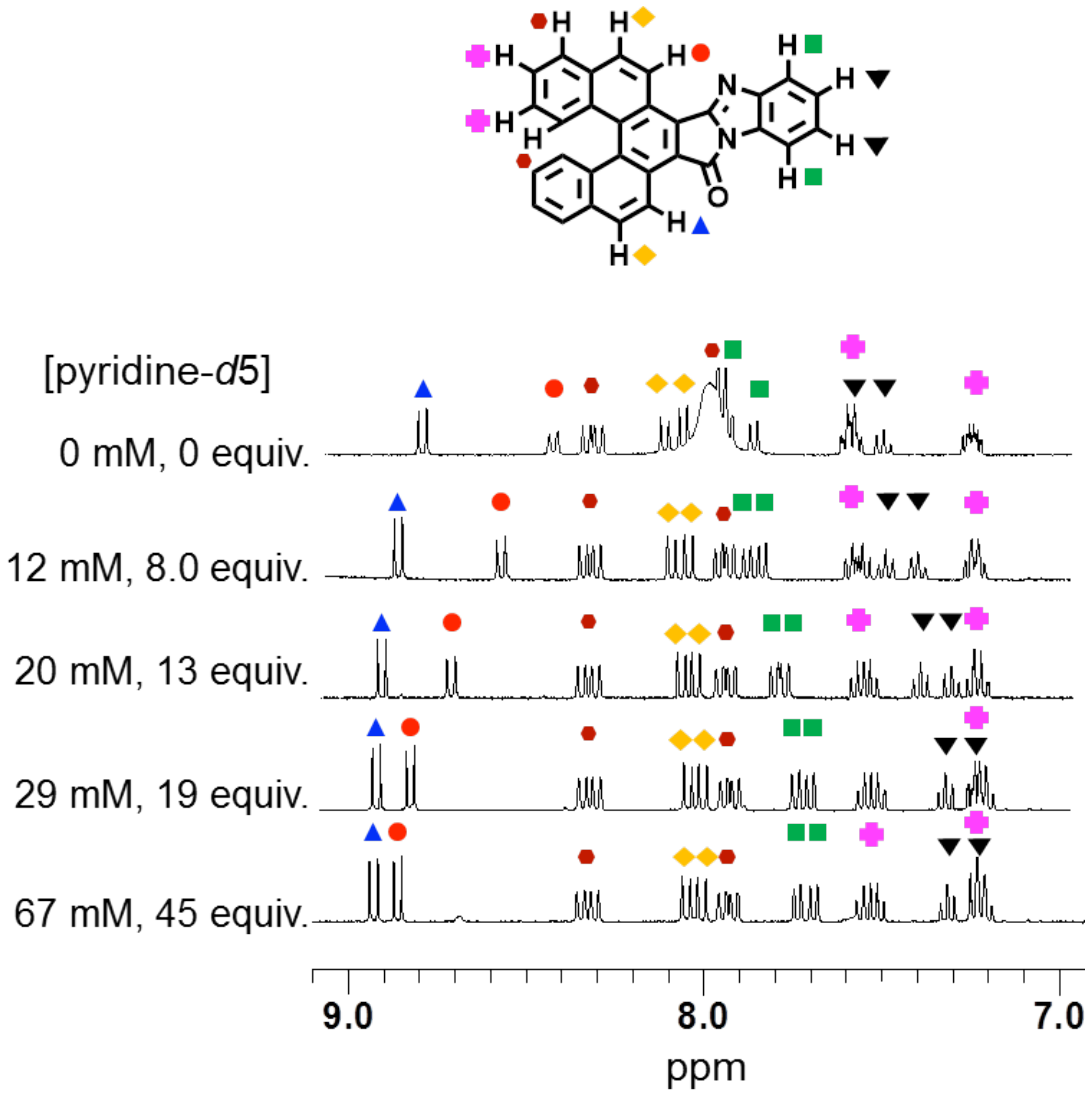


Fig. S4 ^{1}H NMR spectral changes of [5]HeliBI (1.5 mM) and TFA-*d* (66 mM) upon addition of pyridine-*d*5 (0-67 mM) in CD_2Cl_2.

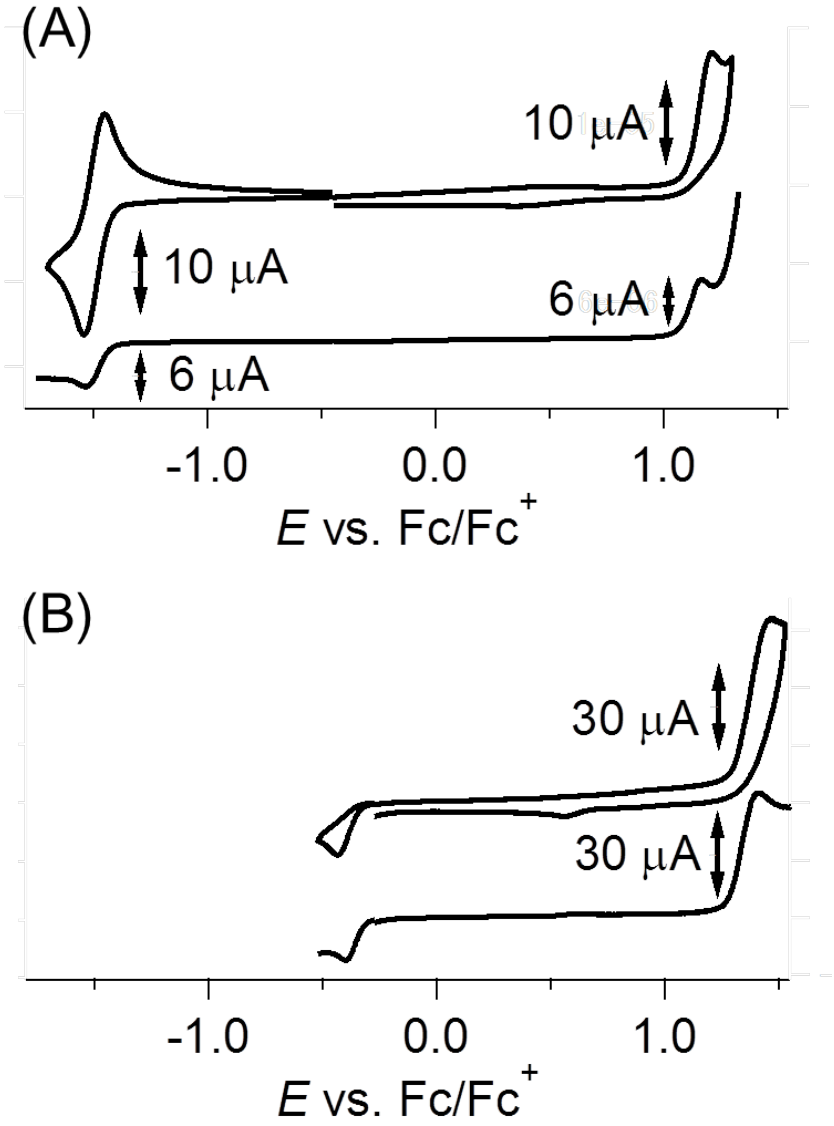
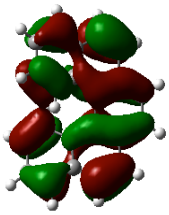
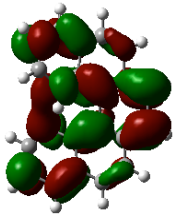
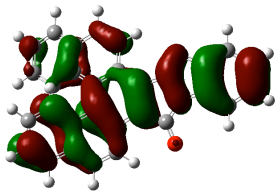
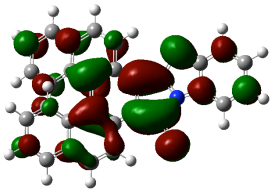


Fig. S5 Cyclic and differential pulse voltammograms of (A) [5]HeliBI in CH_2Cl_2, (B) H^+-[5]HeliBI in CH_2Cl_2 with 0.1 M $^nBu_4NPF_6$ as supporting electrolyte. Scan rates: 0.1 V s^{-1} for CV and 0.01 V s^{-1} for DPV.

Table S1. Molecular orbitals and energy levels calculated by DFT method (B3LYP/6-31+G(d) level).

Helicene	HOMO	LUMO	*ΔE*
[5]Heli	 -5.49 eV	 -1.29 eV	4.20 eV
[5]HeliBI	 -5.73 eV	 -3.30 eV	2.43 eV

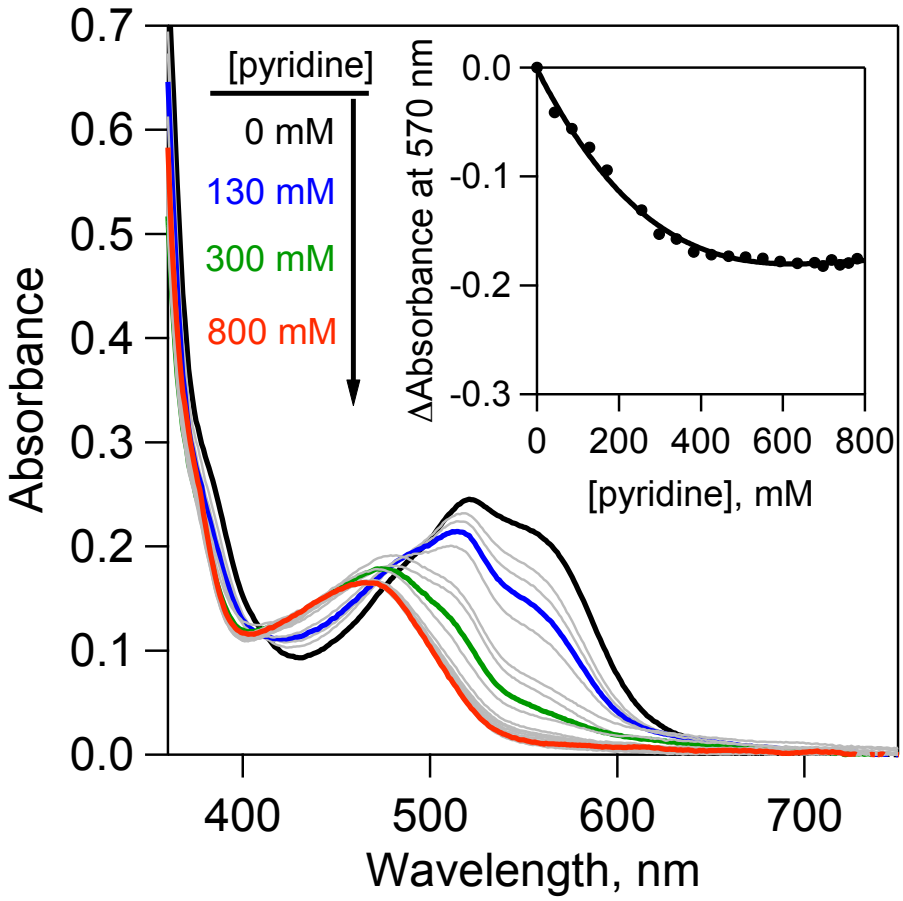


Fig. S6 Absorption spectral changes of [5]HeliBI (20 μM) and TFA (910 mM) upon addition of pyridine (0-800 mM) in CH_2Cl_2. The inserted figure indicates *Δ*Absorption profiles at 570 nm.

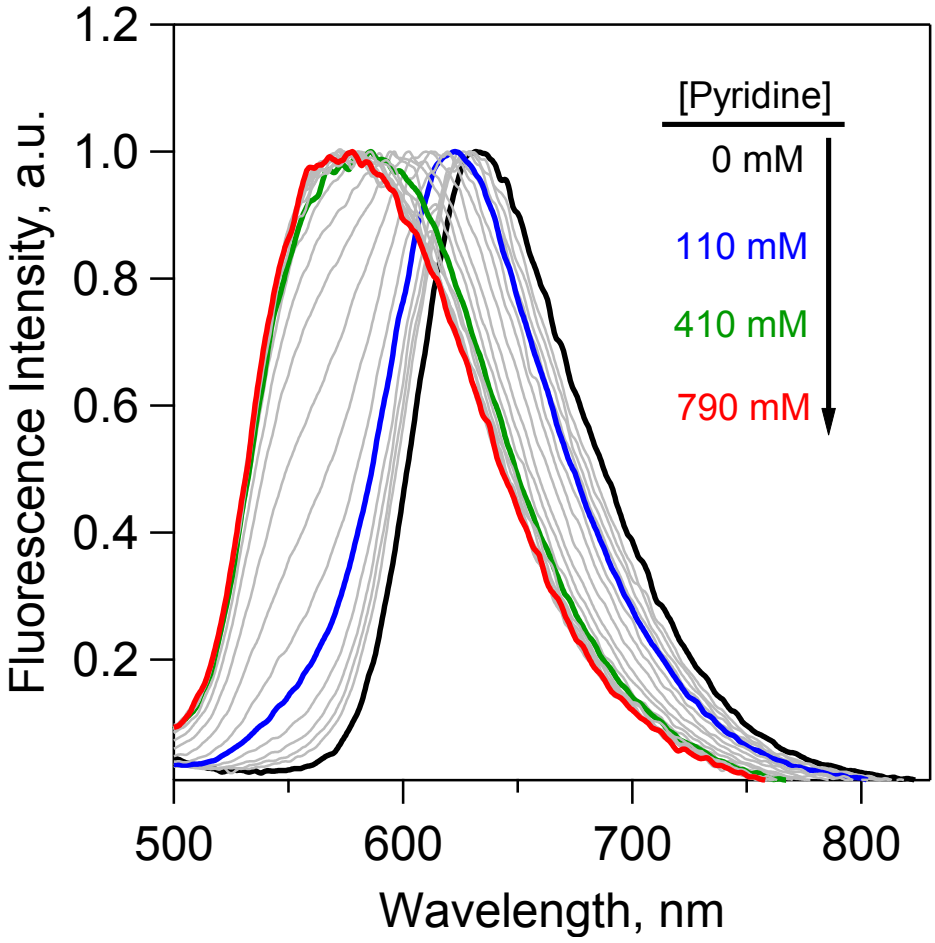


Fig. S7 Fluorescence spectral changes of [5]HeliBI (20 μM) and TFA (790 mM) upon addition of pyridine (0-790 mM) in CH_2Cl_2. Excitation wavelength is 355 nm.

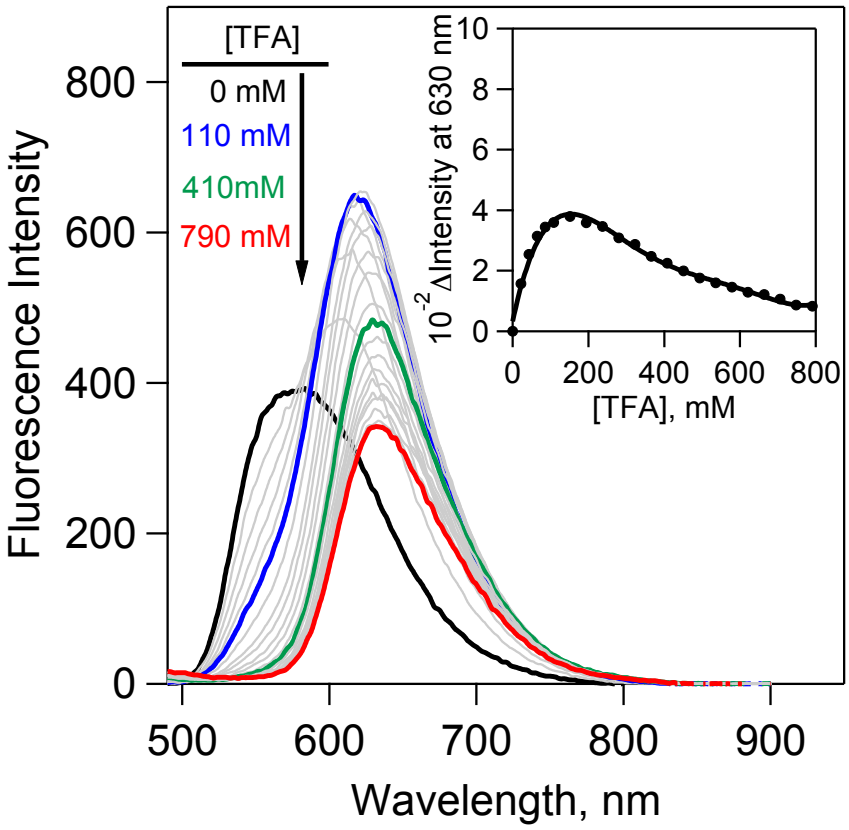


Fig. S8 Fluorescence spectral changes of [5]HeliBI (20 μM) upon addition of TFA (790 mM) in CH_2Cl_2. The inserted figure indicates *Δ*intensity profiles at 630 nm. Excitation wavelength is 355 nm.

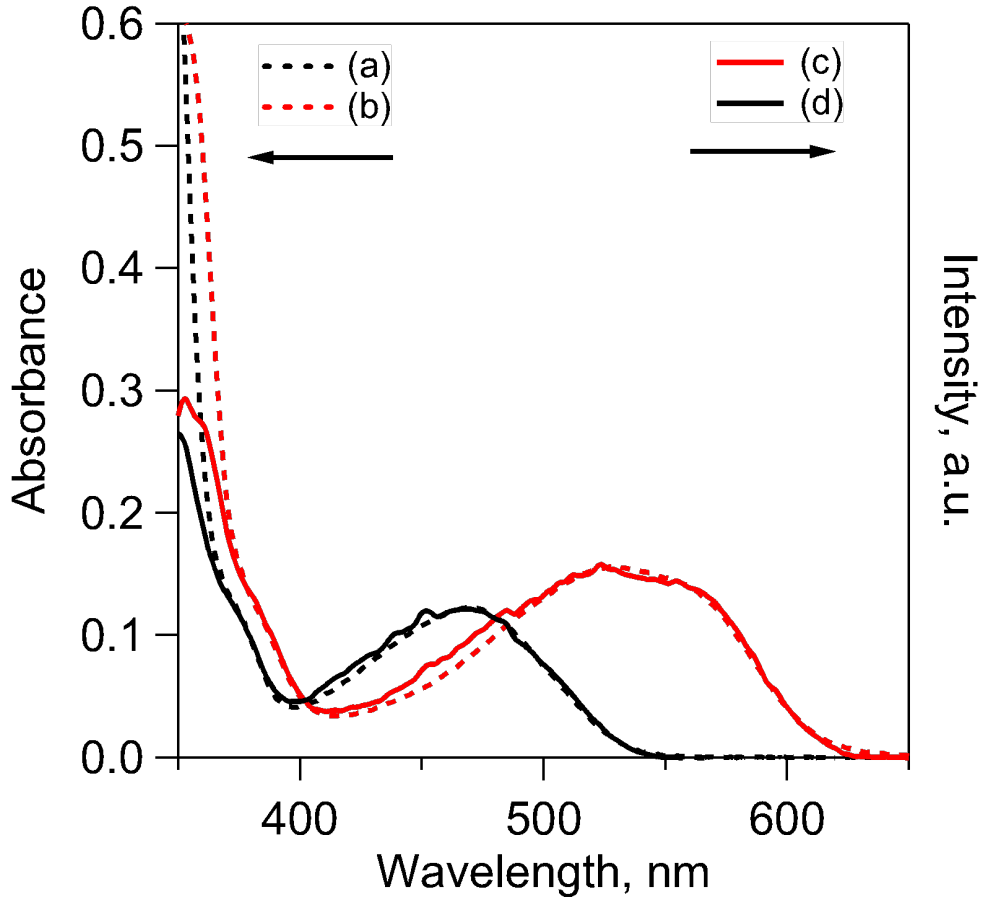


Fig. S9 UV-vis spectra of (a) [5]HeliBI (20 μM) in CH_2Cl_2 and (b) H^+-[5]HeliBI (20 μM) in CH_2Cl_2, and fluorescence excitation spectra of (c) [5]HeliBI (20 μM) in CH_2Cl_2 and (d) H^+-[5]HeliBI (20 μM) in CH_2Cl_2. Excitation wavelength is 355 nm.

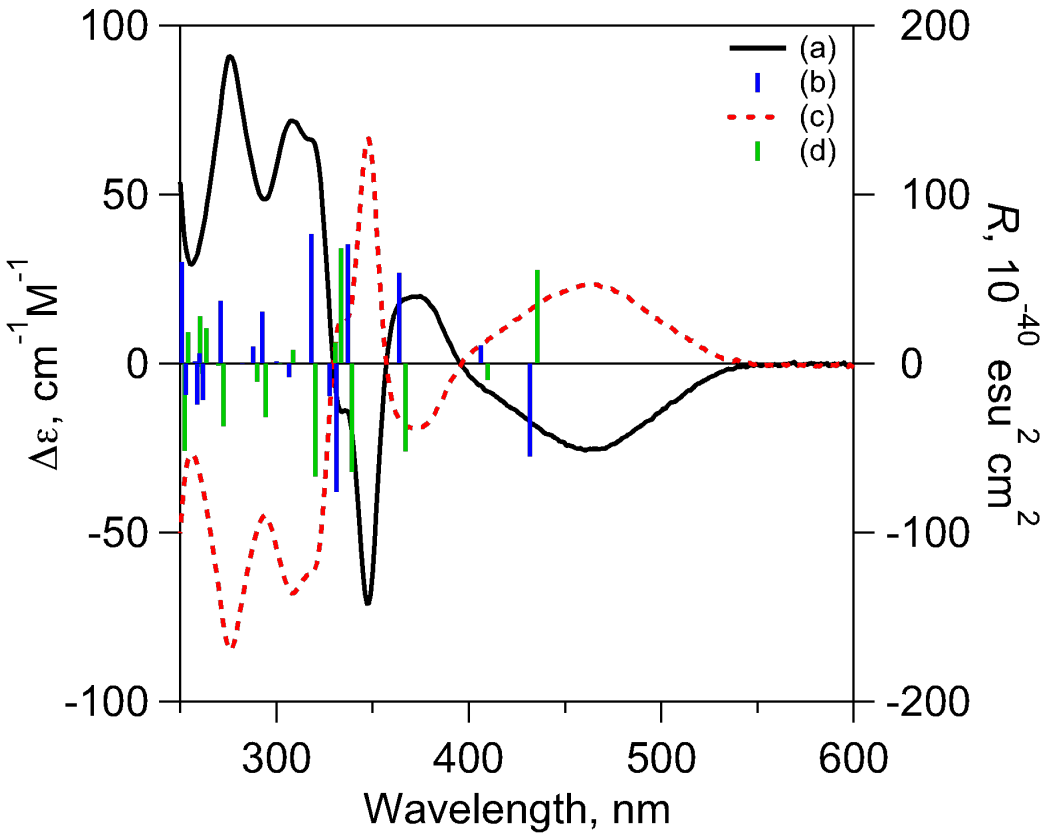


Fig. S10 (a) CD spectrum of (+)-(*P*)-[5]HeliBI in CH_2Cl_2, (b) simulated CD spectrum of (+)-(*P*)-[5]HeliBI, (c) CD spectrum of (−)-(*M*)-[5]HeliBI in CH_2Cl_2, and (d) simulated CD spectrum of (−)-(*M*)-[5]HeliBI in CH_2Cl_2. TDDFT calculations were performed by Gaussian suite of programs at the B3LYP level of theory and the 6-311+G(d,p) basis set.