

Synthesis, Optical Properties and Fluorescence Cell Imaging of Novel Mixed Fluorinated Subphthalocyanines

Shutong Zhou¹, Xiaojuan Lv², Minghui Li¹, Zijian Gao¹, Shengnan Tu¹, Shanshan Qiao¹, Mengjia Mo¹, Xu Tang³, Yemei, Wang^{1*}, Shasha Sun^{1*}

¹School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212013, China

²School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

³Institute for Advanced Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

*Correspondence: wangym@just.edu.cn, Tel.: +86-15365996930; sunshasha@just.edu.cn;

Supplementary Materials

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i. Experimental Section

General information: Unless noted, all reagents or solvents were obtained from commercial suppliers and used without further purification. All air sensitive experiments were performed in N₂ atmosphere through Schlenk technology. ¹H, ¹³C, ¹⁹F and ¹¹B NMR spectra were recorded on a JNM-ECZ400S/L1 spectrometer (operating as 400 MHz for ¹H, 100 MHz for ¹³C, 376 MHz for ¹⁹F and 128 MHz for ¹¹B) using the residual solvent as the internal reference for ¹H (δ = 7.26 ppm in CDCl₃), ¹³C (δ = 76.8 ppm in CDCl₃), and CF₃COOH as the external reference for ¹⁹F (δ = -76.5 ppm). ¹H and ¹⁹F NMR spectra were acquired with Single Plus Experiment (SPE) with a pulse length of 3.06 μ s and a recycle delay of 5 s. ¹³C NMR spectra were acquired with Single Plus Experiment (SPE) with a pulse length of 3.30 μ s and a recycle delay of 2 s. ¹¹B NMR spectra were acquired with Single Plus Experiment (SPE) with a pulse length of 3.33 μ s and a recycle delay of 2 s. Mass spectra were conducted at Thermo Scientific Q Exactive Focus LC-MS/MS (APCI). A Hitachi F-4600 fluorescence spectrophotometer was used to measure fluorescence spectrum. An Edinburgh FLS-980 spectrometer was used to determine fluorescence quantum yield. The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Thermo Scientific Nicolet iS50 spectrometer in the spectral range of 4000–400 cm⁻¹ with 16 scans and a resolution of 8 cm⁻¹. Melting point of samples were recorded on a melting point tester of Tianfen-RY-51. Preparative separations were performed using silica gel column chromatography (Shanghai test Silica Gel 60N, spherical, neutral, 300-400 mesh). Thin-layer chromatography (TLC) was performed with aluminum sheet silica gel 60 F₂₅₄ (Merck).

X-ray Analysis: Single crystal of **6** was obtained by the slow diffusion of n-hexane into a CH₂Cl₂ solution of them. X-ray crystallographic data for **6** (CCDC: 2220751) was recorded at 296 K on a Bruker APEX DUO diffractometer using graphite-monochromate Mo-K α radiation from the corresponding set of confocal optics. The structures were solved by a direct method (SHELXT)^[s1] and refined using a full-matrix least squares technique (SHELXL)^[s2, s3].

Cyclic voltammetry: The cyclic voltammetry was conducted in a solution of 0.1 M TBAP in dry-CH₂Cl₂ with a scan rate of 0.1 V s⁻¹ in an argon-filled cell. A glassy carbon electrode and a platinum wire were used as a working and a counter electrode, respectively. A saturated Calomel electrode (SCE) was used as reference electrodes.

Computational methods: Gaussian 9 software packages were used to carry out density functional theory (DFT) and time-dependent DFT (TDDFT) calculations using a B3LYP functional with a 6-31G(d) basis sets.

Cell culture: For cell culture, cells were seeded in cell culture plates using Dulbecco's modified Eagle's medium (DMEM) with 10% fetal bovine serum (FBS) and incubated at 37% under a humidified atmosphere with 5% CO₂ for 24 h to reach 80% confluence.

ii. HRMS Spectra

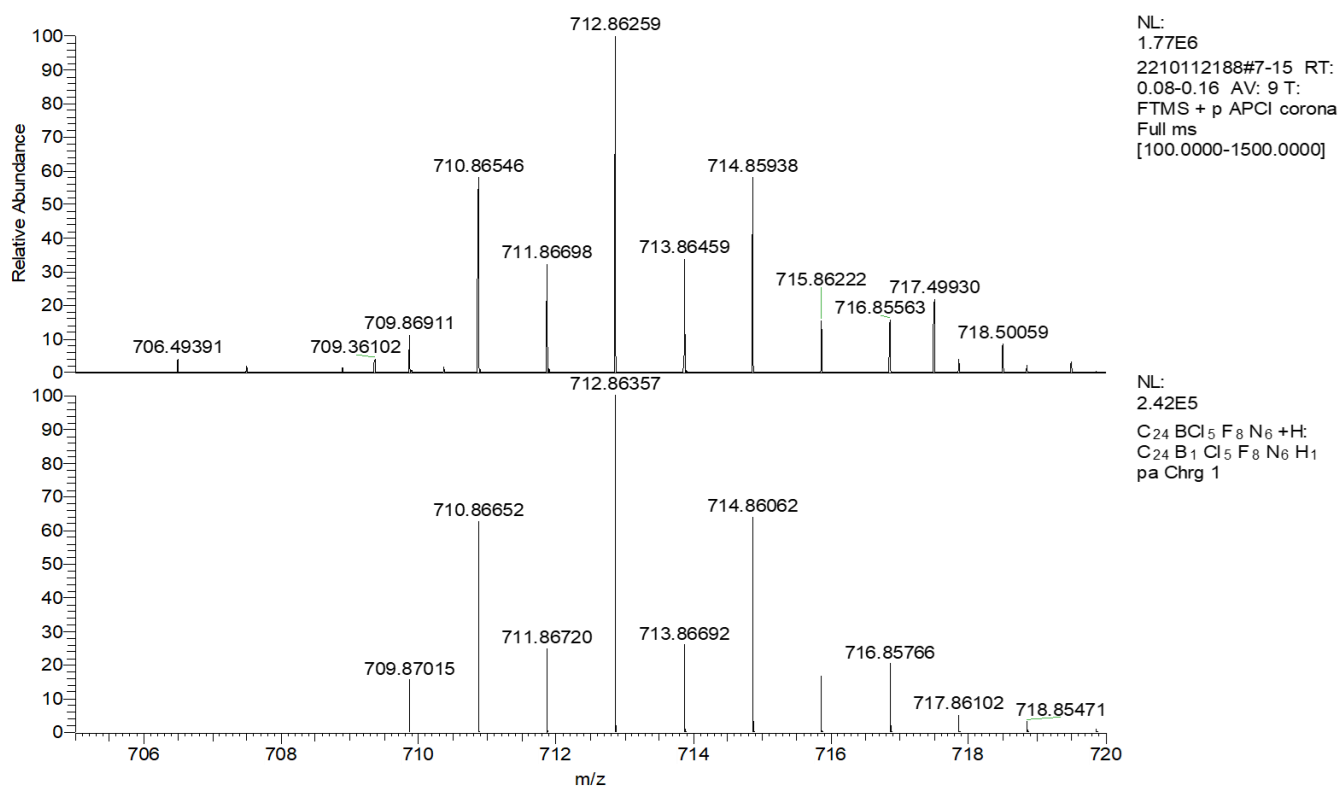


Figure S1. HR-APCI-MS spectrum of 5.

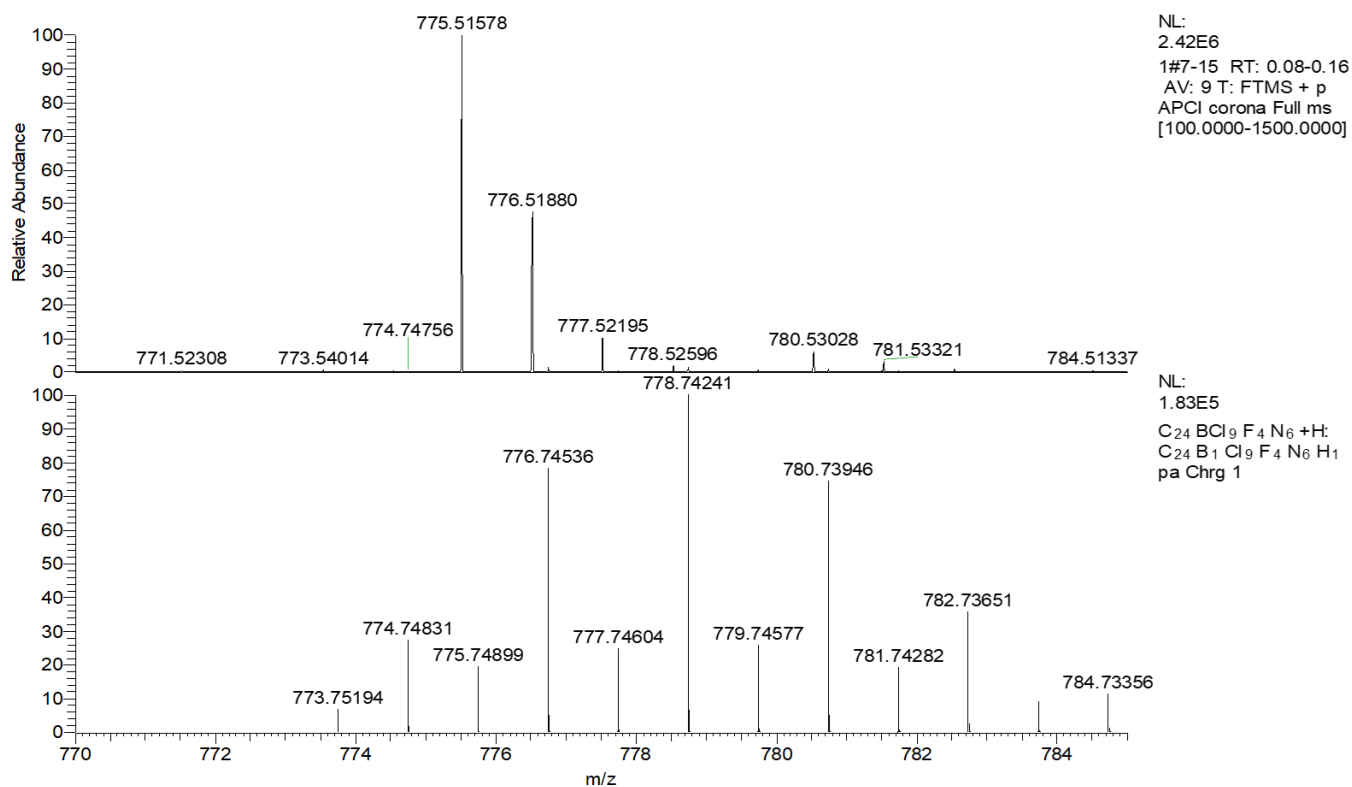


Figure S2. HR-APCI-MS spectrum of 6.

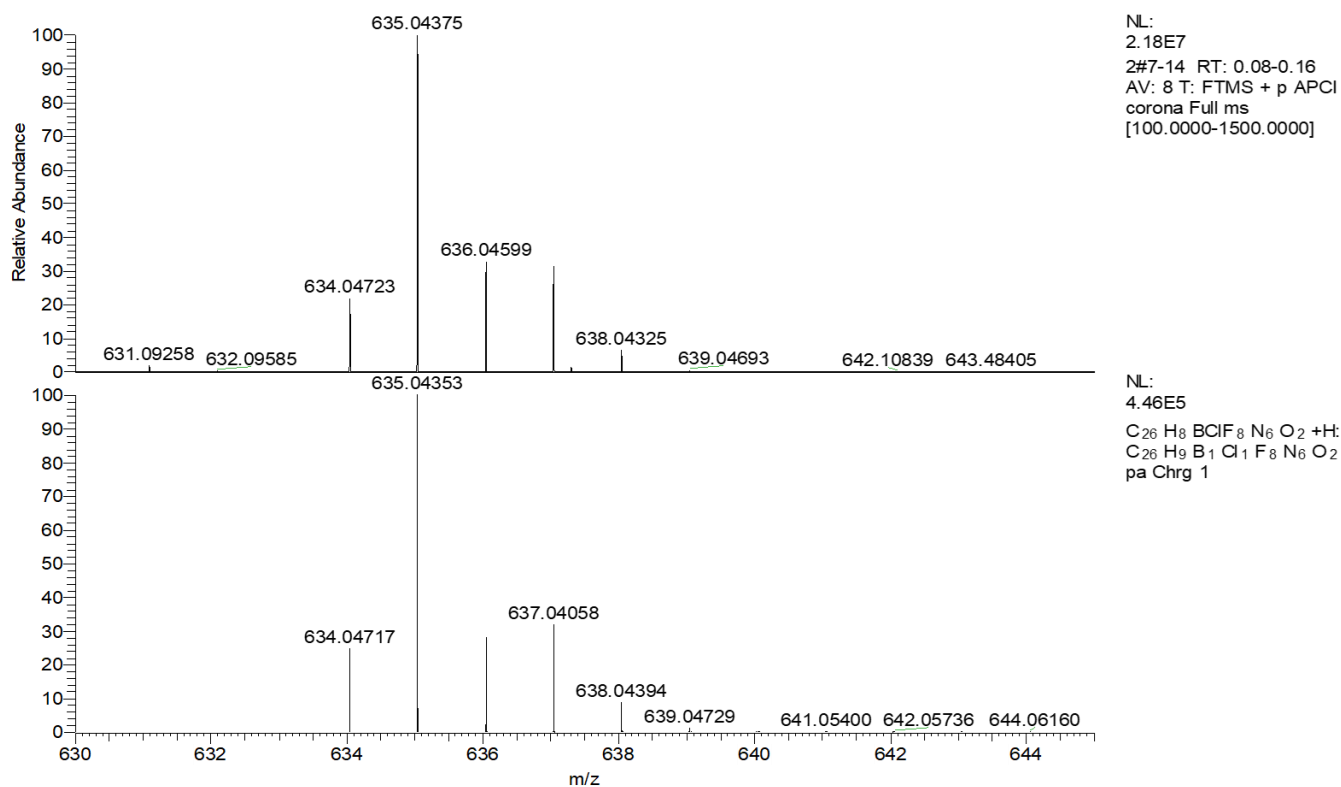


Figure S3. HR-APCI-MS spectrum of 7.

iii. NMR Spectra

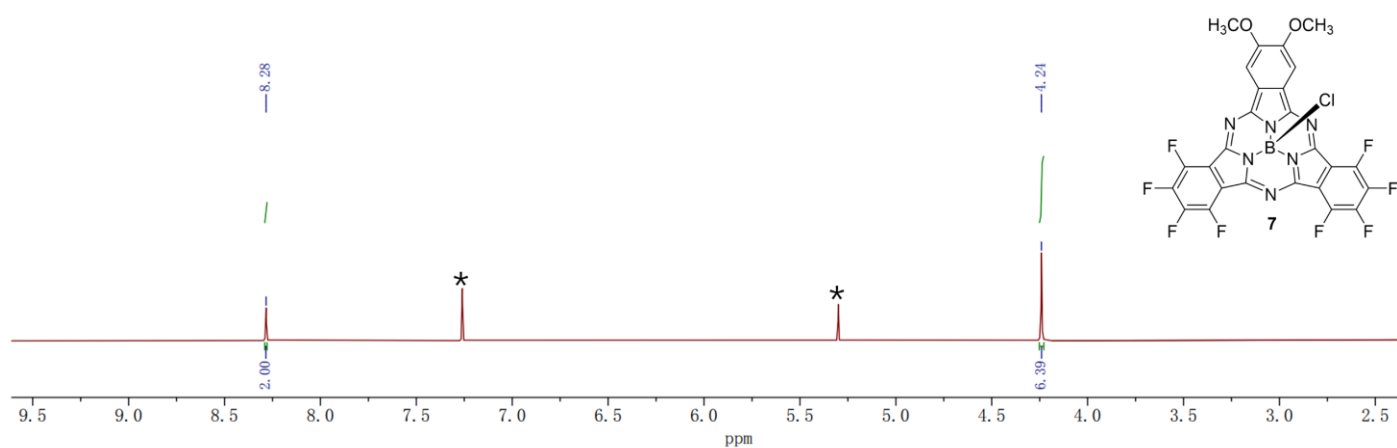


Figure S4. ¹H NMR spectrum of 7 in CDCl₃ (* residual solvent).

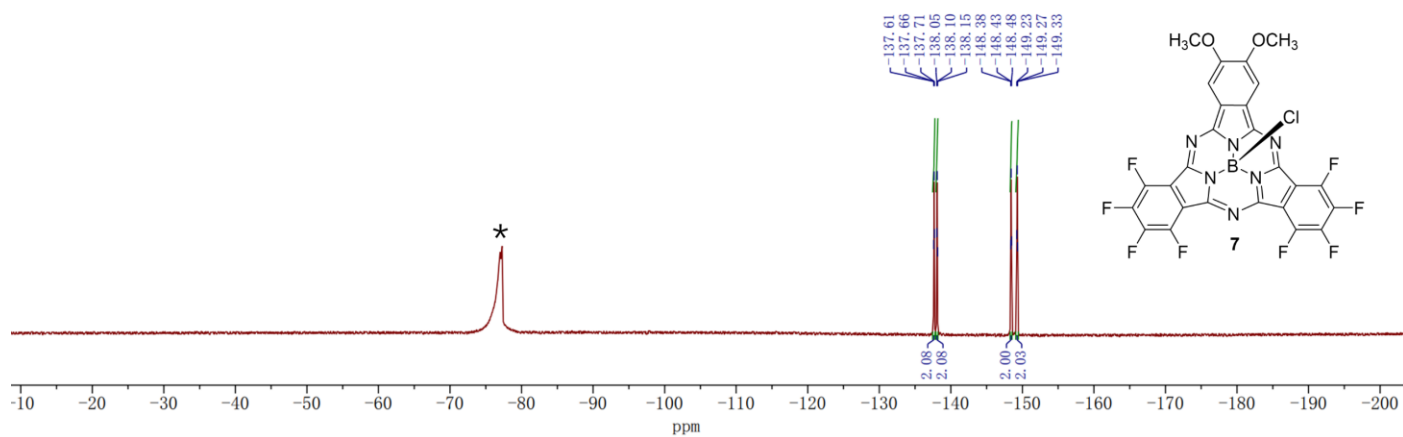


Figure S5. ¹⁹F NMR spectrum of 7 in CDCl₃ (* CF₃COOH as reference).

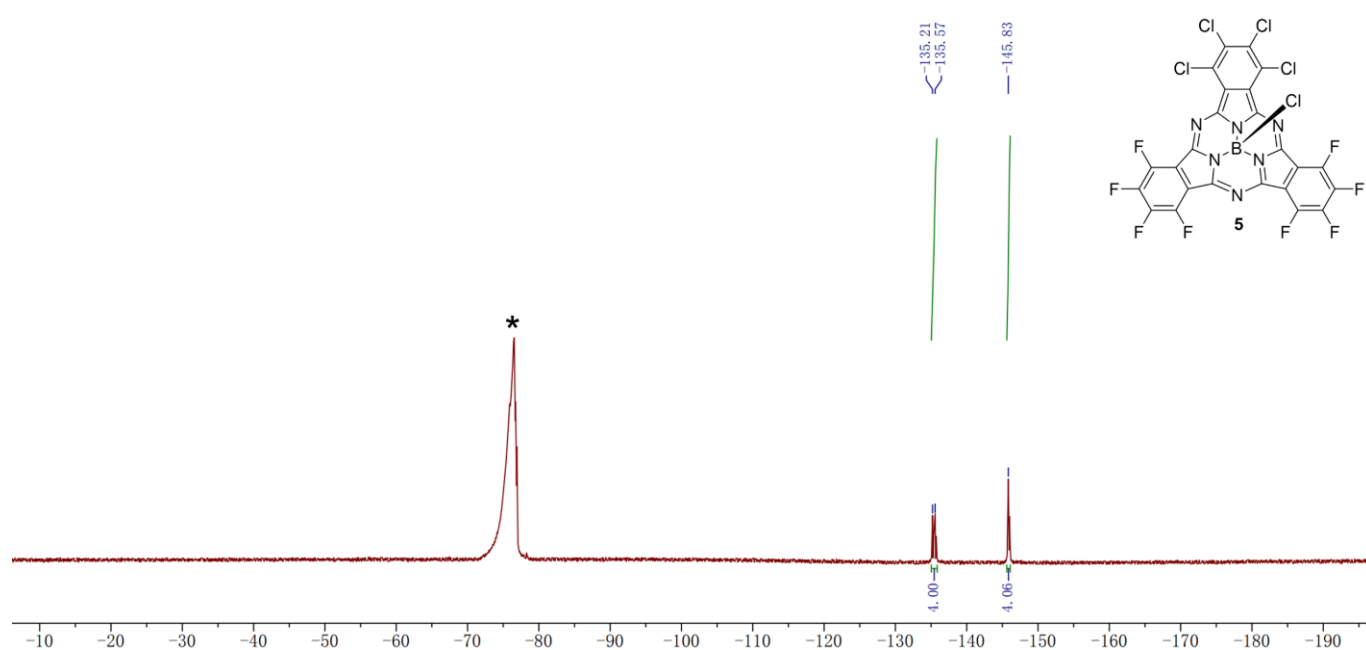


Figure S6. ¹⁹F NMR spectrum of 5 in CDCl₃ (* CF₃COOH as reference).

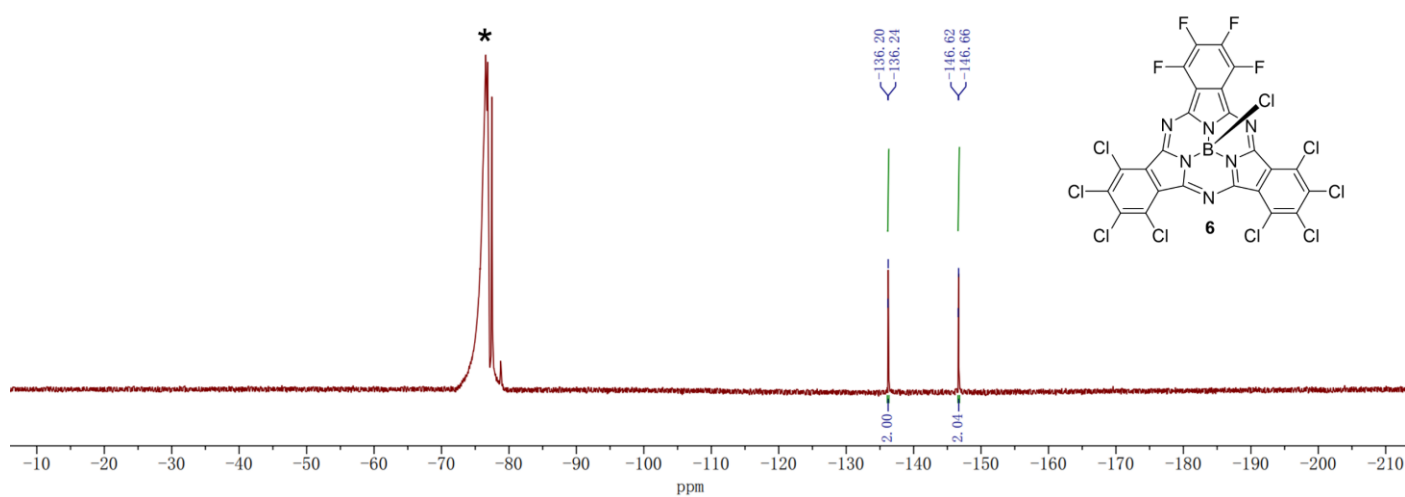


Figure S7. ^{19}F NMR spectrum of **6** in CDCl_3 (* CF_3COOH as reference).

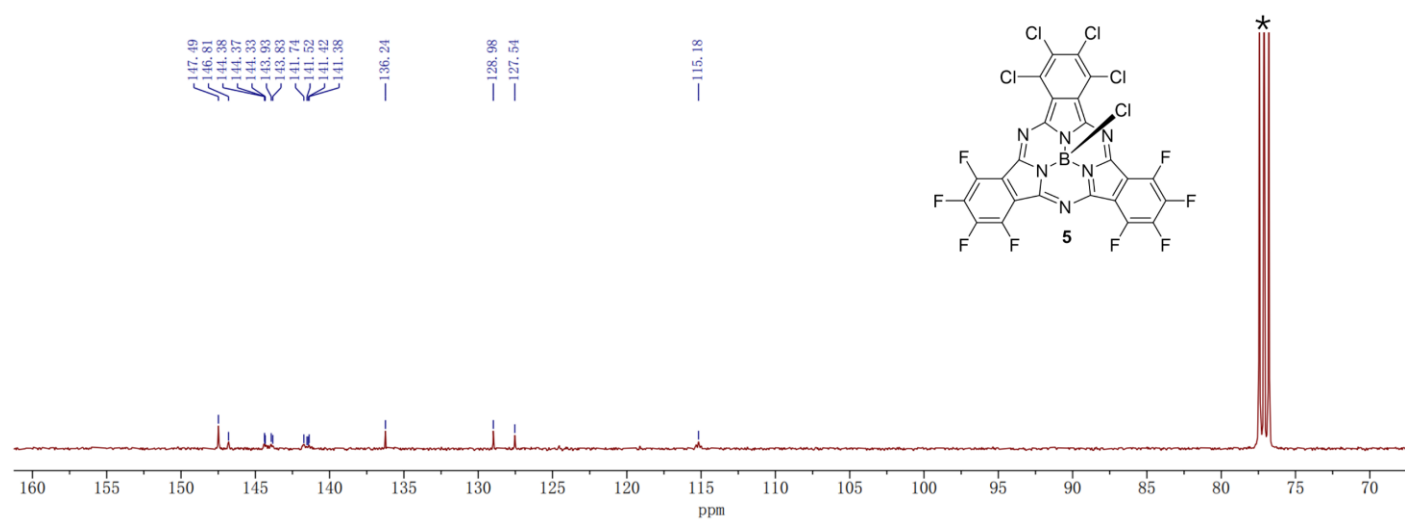


Figure S8. ^{13}C NMR spectrum of **5** in CDCl_3 (* residual solvent).

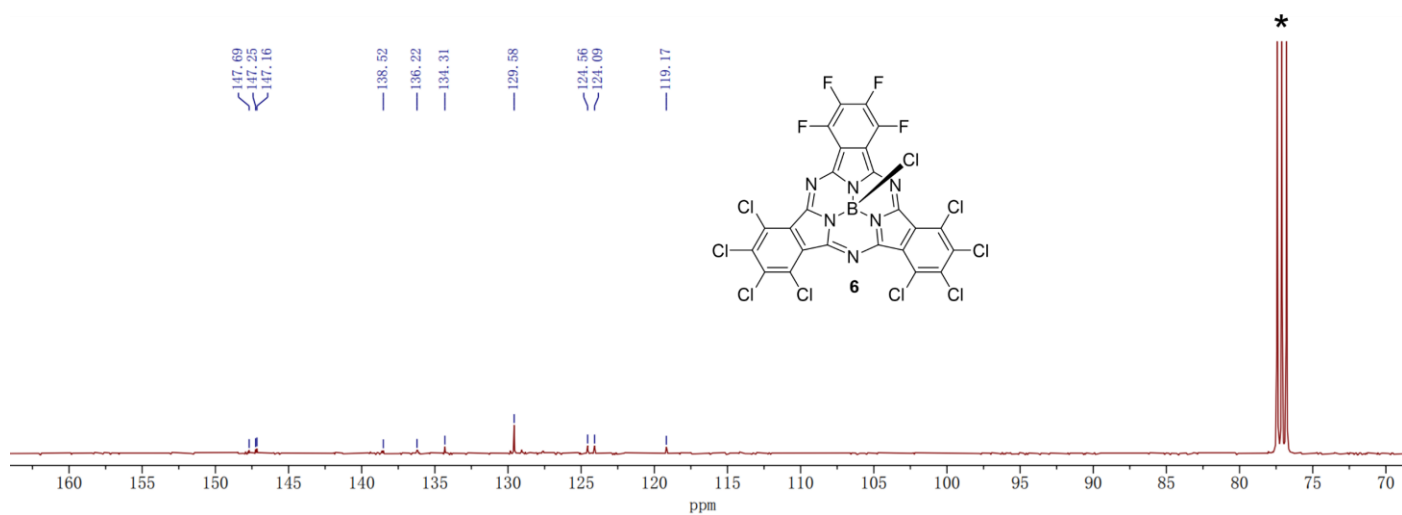


Figure S9. ¹³C NMR spectrum of **6** in CDCl₃ (* residual solvent).

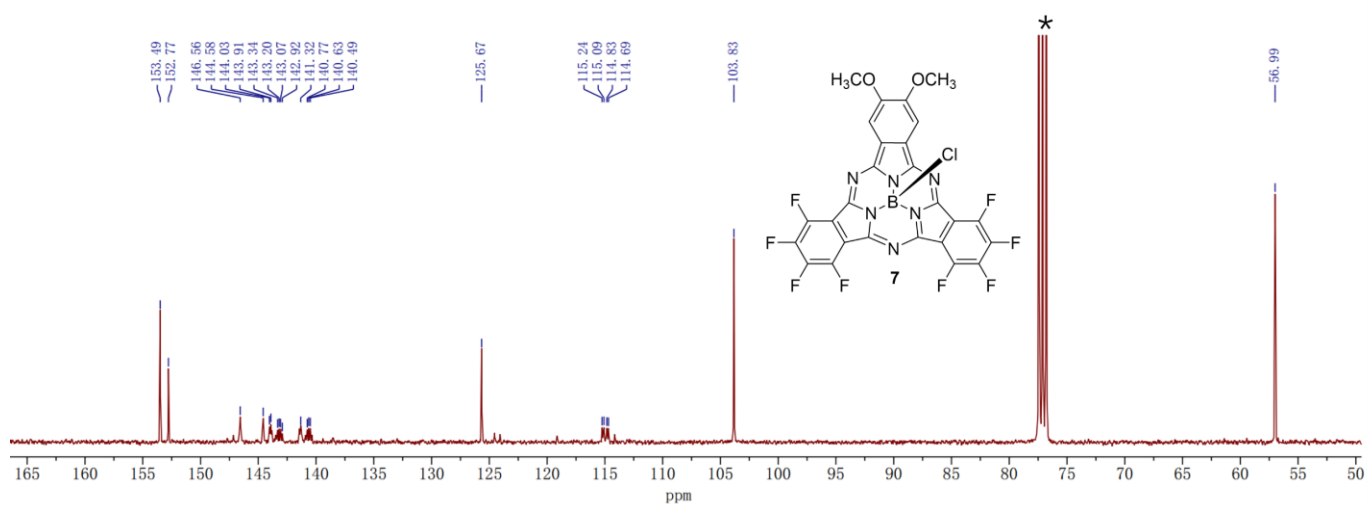


Figure S10. ¹³C NMR spectrum of **7** in CDCl₃ (* residual solvent).

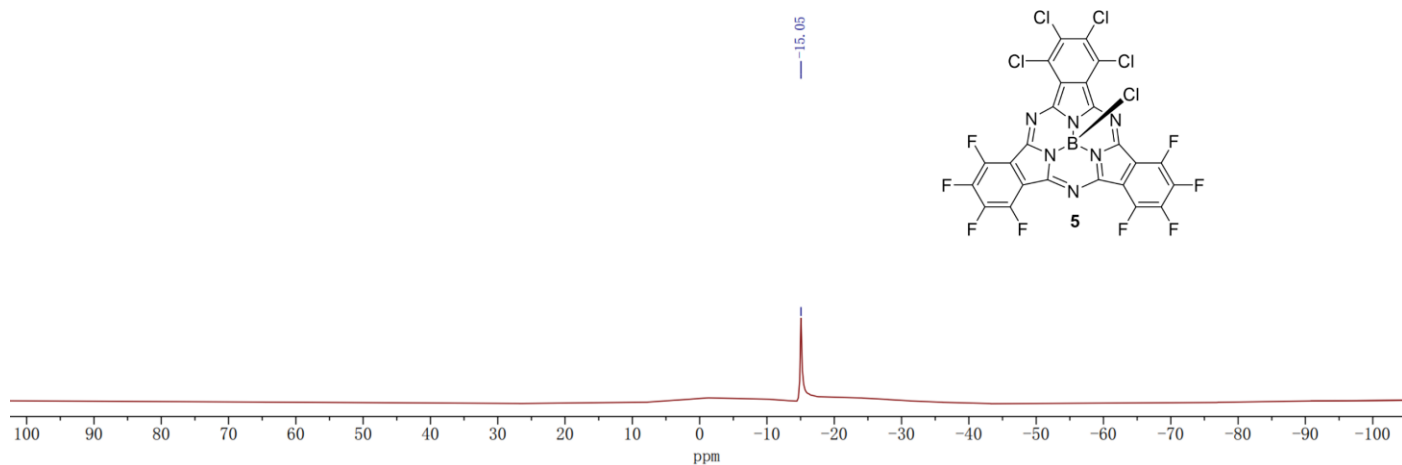


Figure S11. ^{11}B NMR spectrum of **5** in CDCl_3 (* residual solvent).

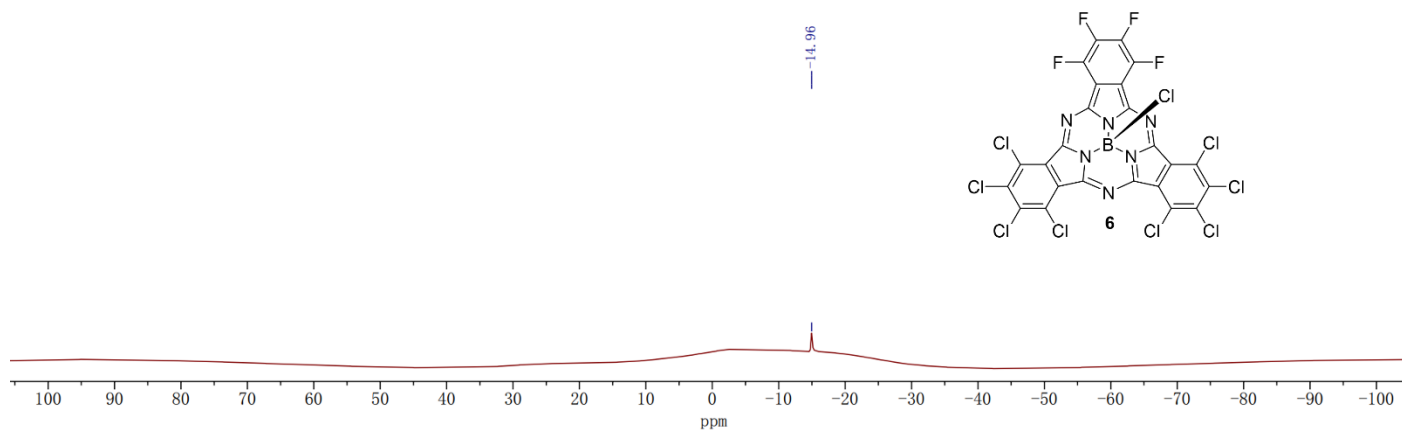


Figure S12. ^{11}B NMR spectrum of **6** in CDCl_3 .

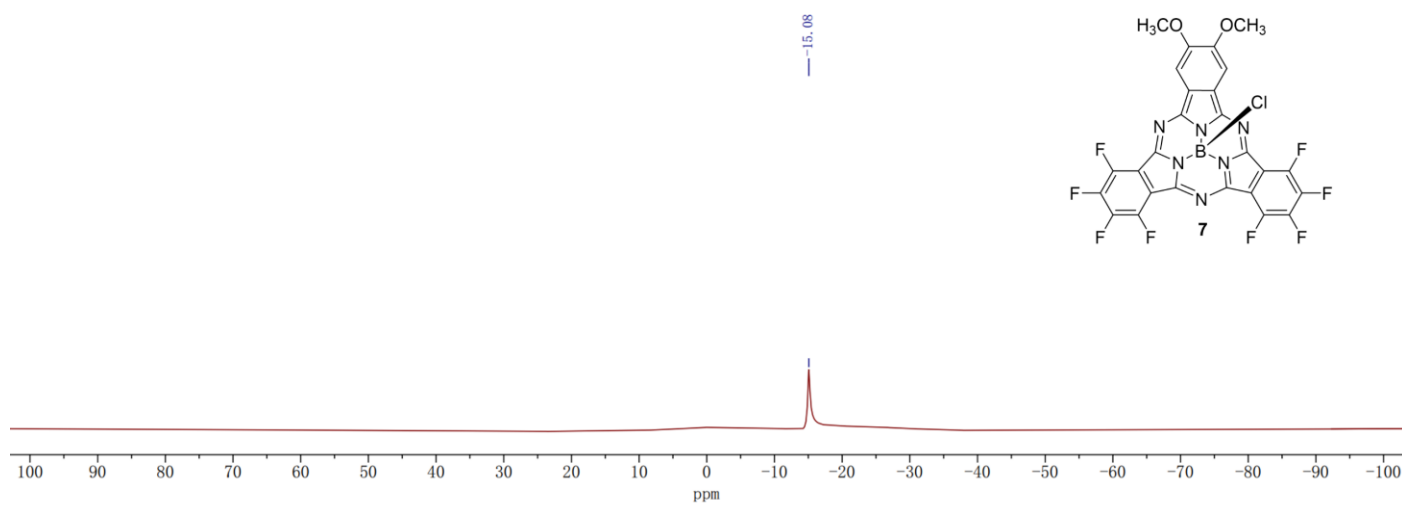


Figure S13. ^{11}B NMR spectrum of **7** in CDCl_3 (* residual solvent).

iv. IR Spectra

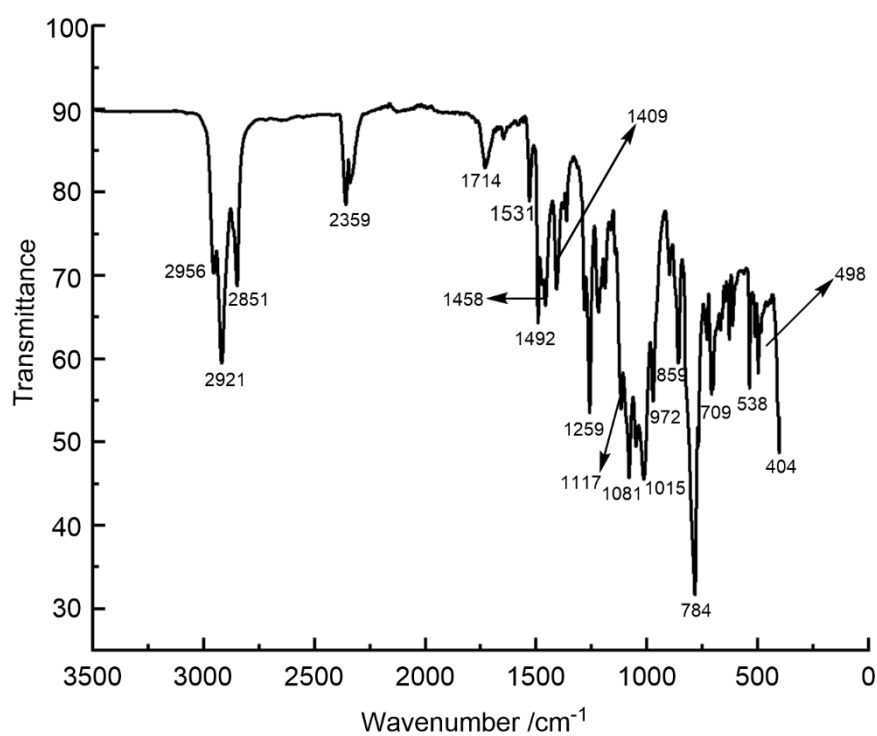


Figure S14. IR spectra of 5 in CH₂Cl₂.

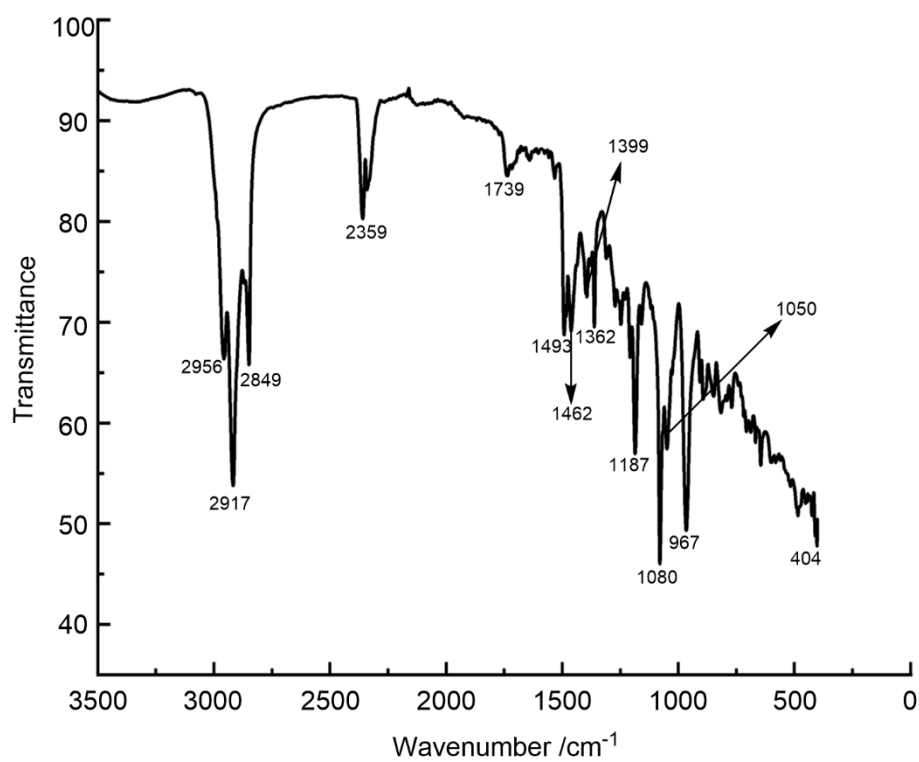


Figure S15. IR spectra of 6 in CH₂Cl₂.

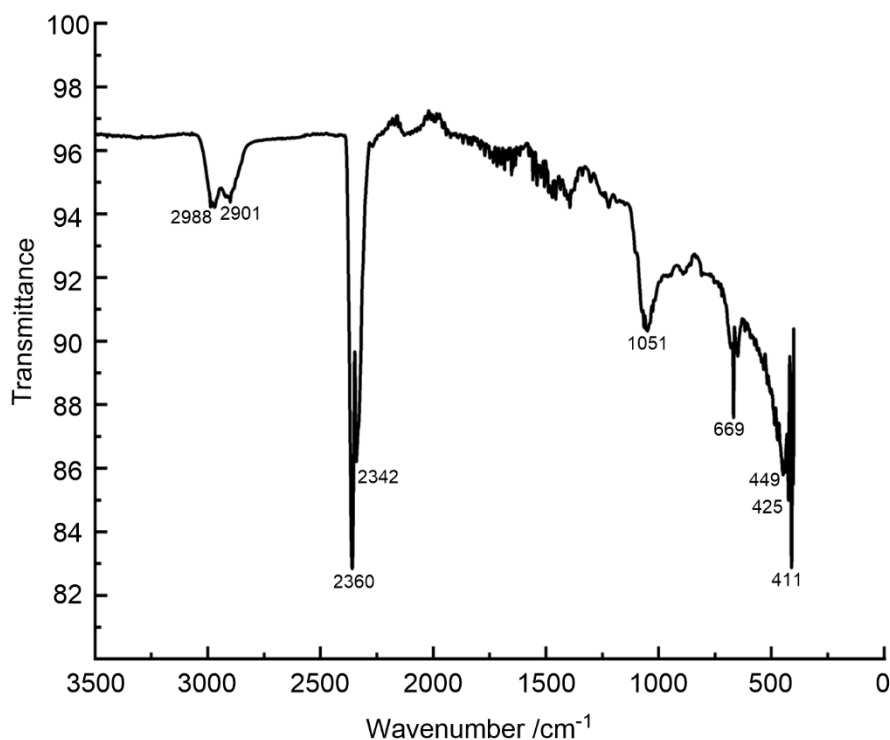


Figure S16. IR spectra of **7** in CH₂Cl₂.

v. Crystallographic data

Table S1. Crystal data and structure refinement.

Moiety formula	C ₂₄ BCl ₉ F ₄ N ₆	F (000)	804
Formula weight	1643.26	θ (°) for data collection	2.611 to 27.450
Temperature (K)	300	Index ranges	$-9 \leq h \leq 9$, $-17 \leq k \leq 16$, $-20 \leq l \leq 20$
Wavelength (Å)	0.71073	Reflection collected	54438
Crystal system	Triclinic	Unique reflections	6922 ($R_{\text{int}} = 0.0922$)
Space group	<i>P</i> -1	Completeness	0.999
Unit cell dimensions	$a = 7.296(2)$ Å, $\alpha = 102.695(9)$	Absorption correction	multi-scan
	$b = 13.497(4)$ Å, $\beta = 95.706(11)$	Max. and min. transmission	0.7456, 0.6600
	$c = 16.141(5)$ Å, $\gamma = 98.457(9)$	Data/restraints/parameters	6922 / 86 / 452
Volume (Å ³)	1519.3(8)	Goodness-of-fit on F^2	1.013
<i>Z</i>	1	Final <i>R</i> indices [$I > 2\sigma(I)$]	0.0534
Density (calcd.) (g/cm ³)	1.796	wR_2 indices (all data)	0.1205
μ (cm ⁻¹)	0.973	Large diff. peak and hole	0.430, -0.326
Crystal size (mm ³)	0.16 x 0.15 x 0.13	CCDC no.	2220751

Table S2. The length (Å) of C-F bonds and C-Cl bonds from the monocrystal of **6**.

C1–F1	C2–F2	C3–F3	C4–F4	C5–Cl1	C6–Cl2
1.343	1.338	1.351	1.347	1.709	1.726
C7–Cl3	C8–Cl4	C9–Cl5	C10–Cl6	C11–Cl7	C12–Cl8
1.718	1.717	1.709	1.719	1.716	1.711

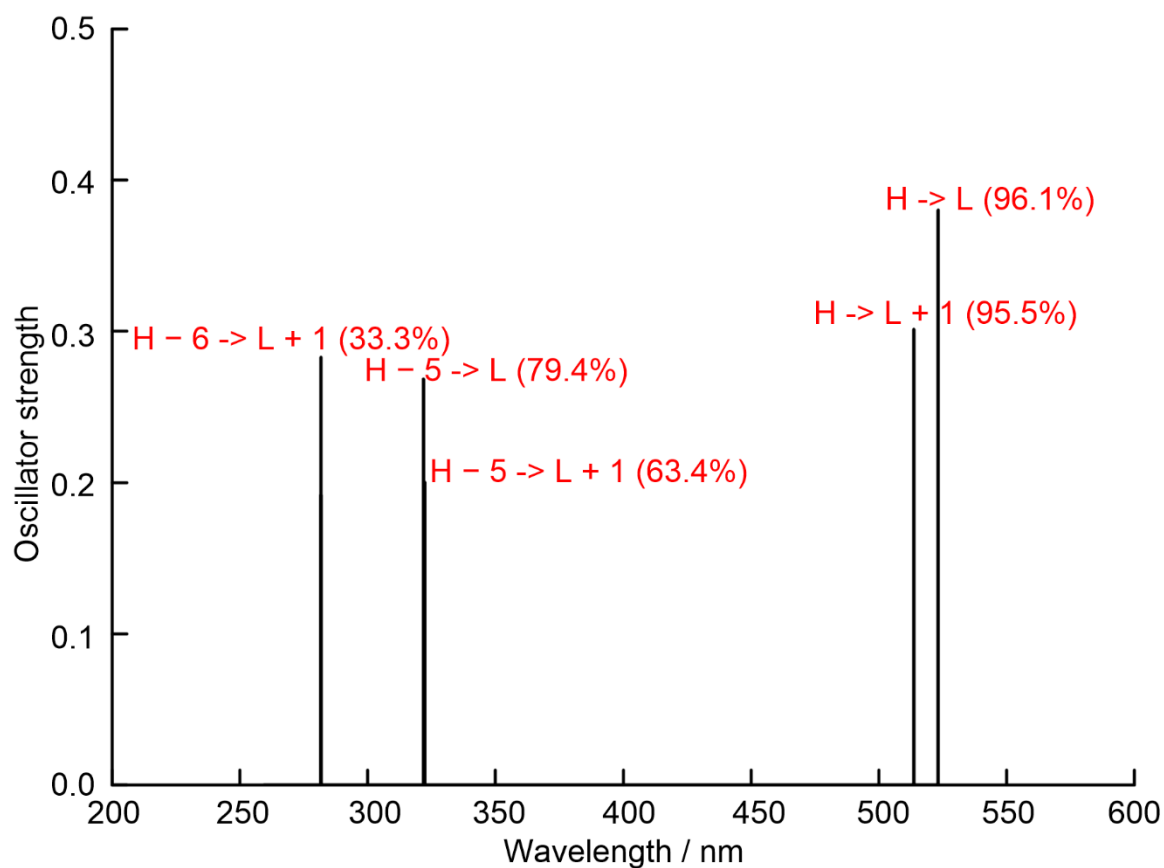


Figure S17. Vertical excitation energy of compound 5 calculated based on TDDFT.

Table S3. Selected transition energies, oscillator strengths, and major contributors of 5 calculated by TDDFT methods at the B3LYP/6-31G(d) level.

$\lambda(\text{nm})$	f^a	Major contribution (weight%) ^b
523.27	0.38010	H -> L (96.1%)
513.60	0.30130	H -> L + 1 (95.5%)
322.36	0.20020	H - 5 -> L + 1 (63.4%), H - 4 -> L (14.8%), H - 3 -> L+1 (10.1%), H - 6 -> L + 1 (6.8%)
321.74	0.26820	H - 5 -> L (79.4%), H - 6 -> L (6.4%), H - 4 -> L + 1 (6.1%)
281.71	0.28207	H - 6 -> L + 1 (33.3%), H - 7 -> L (25.4%), H - 7 -> L + 1 (9.1%), H - 6 -> L (7.7%)

^a : Oscillator strength. ^b: H and L denote the HOMO and LUMO, respectively.

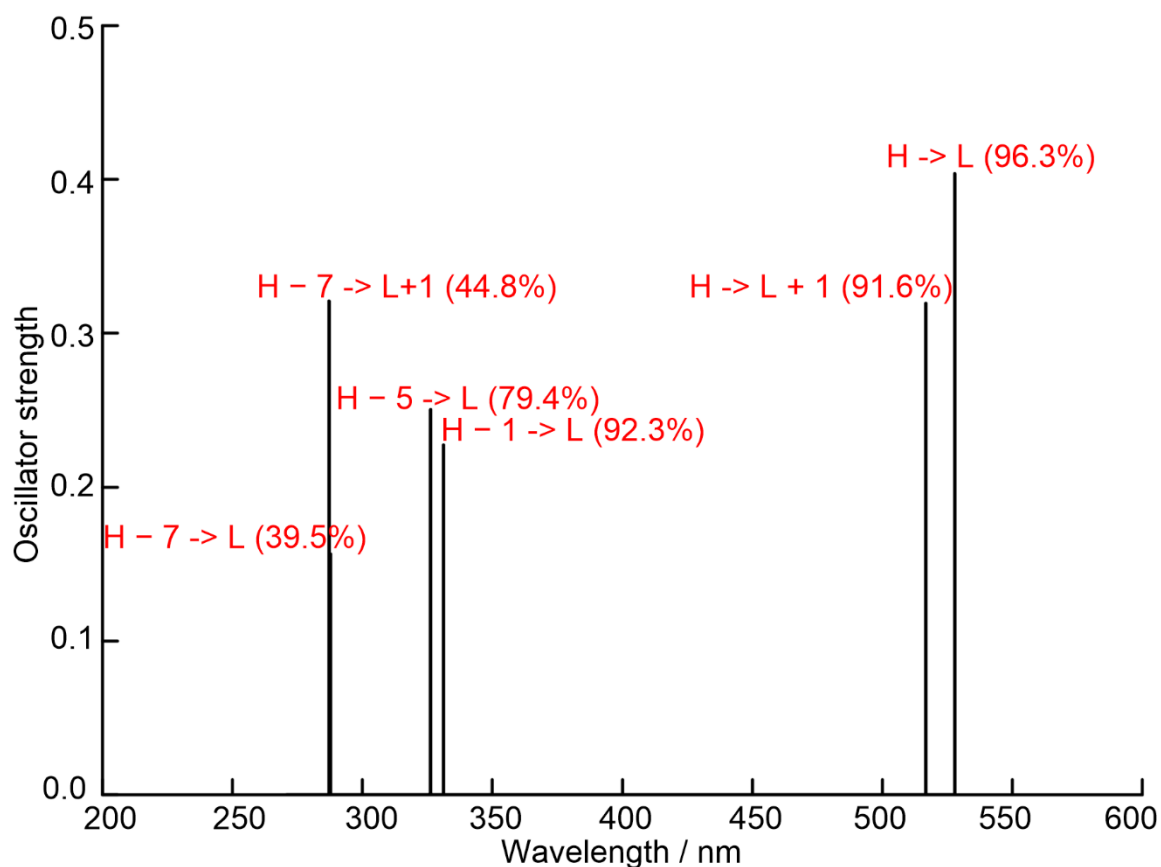


Figure S18. Vertical excitation energy of compound **6** calculated based on TDDFT.

Table S4. Selected transition energies, oscillator strengths, and major contributors of **6** calculated by TDDFT methods at the B3LYP/6-31G(d) level.

$\lambda(\text{nm})$	f^a	Major contribution (weight%) ^b
528	0.40380	H -> L (96.3%)
517	0.31960	H -> L + 1 (91.6%)
331	0.22720	H - 1 -> L (92.3%)
326	0.25050	H - 5 -> L (79.4%), H - 3 -> L + 1 (6.8%)
288	0.15660	H - 7 -> L (39.5%), H - 6 -> L + 1 (32.3%), H - 11 -> L (8.6%)
287	0.32090	H - 7 -> L+1 (44.8%), H - 6 -> L (19.6%), H - 8 -> L + 1 (7.2%), H - 11 -> L + 1 (5.9%), H - 5 -> L + 1 (5.1%)

^a: Oscillator strength. ^b: H and L denote the HOMO and LUMO, respectively.

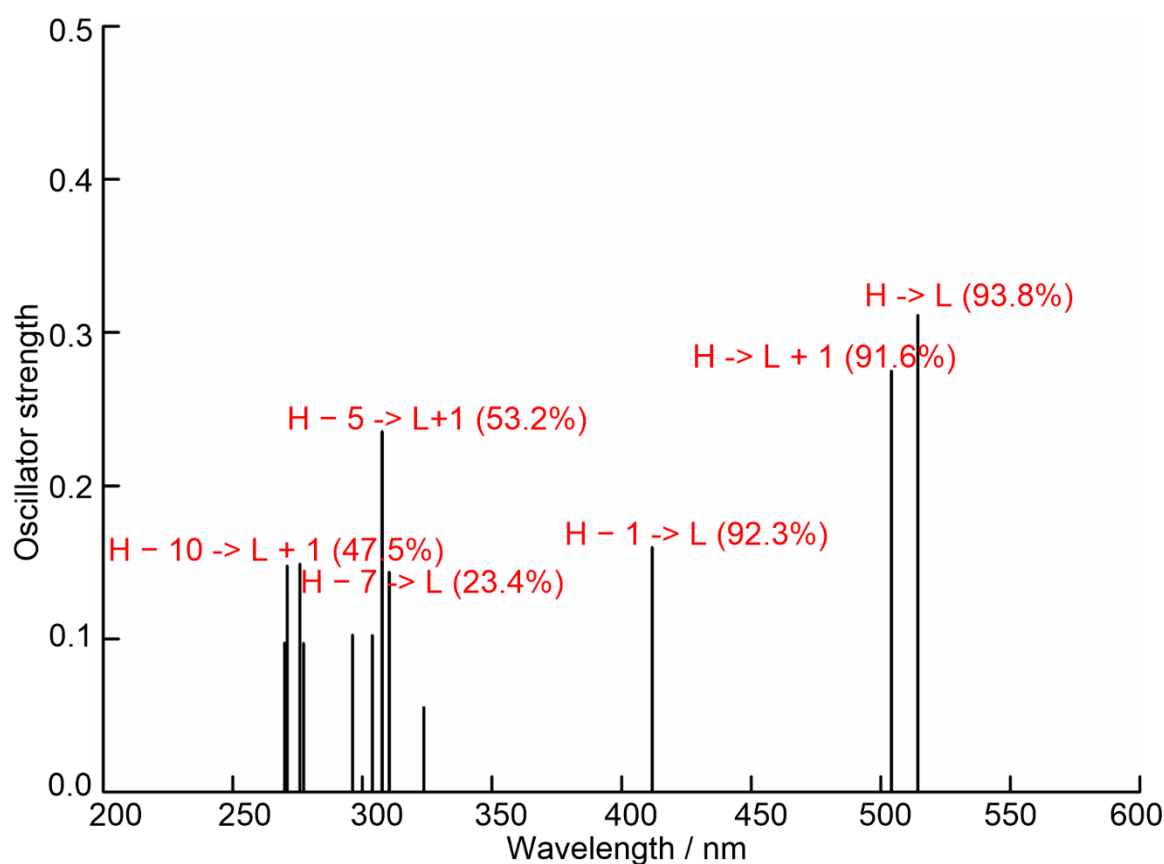


Figure S19. Vertical excitation energy of compound 7 calculated based on TDDFT.

Table S5. Selected transition energies, oscillator strengths, and major contributors of 7 calculated by TDDFT methods at the B3LYP/6-31G(d) level.

$\lambda(\text{nm})$	f^a	Major contribution (weight%) ^b
514	0.31140	H -> L (93.8%)
504	0.27510	H -> L + 1 (91.6%)
411	0.15980	H - 1 -> L (92.3%)
308	0.23540	H - 5 -> L+1 (53.2%), H -> L + 4 (15.4%), H -> L + 3 (7.9%), H -> L + 2 (7.7%), H - 4 -> L (5.2%)
276	0.14870	H - 7 -> L (23.4%), H - 6 -> L + 1 (16.7%), H - 7 -> L + 1 (15.3%), H - 8 -> L + 1 (11.1%), H - 10 -> L (9.3%)
271	0.14770	H - 10 -> L + 1 (47.5%), H - 10 -> L (12.1%), H - 6 -> L + 1 (8.2%), H - 1 -> L + 4 (6.0%), H - 1 -> L + 2 (5.2%)

^a : Oscillator strength. ^b: H and L denote the HOMO and LUMO, respectively.

vii. References

1. Sheldrick, G.M. Experimental phasing with SHELXC/D/E: combining chain tracing with density modification. *Acta Crystallographica Section D: Biological Crystallography*. **2010**, *66*, 479-85.
2. Yoshioka, S.; Inokuma, Y.; Hoshino, M.; Sato, T.; Fujita, M. Absolute structure determination of compounds with axial and planar chirality using the crystalline sponge method. *Chemical science*. **2015**, *6*, 3765-8.
3. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallographica Section C: Structural Chemistry*. **2015**, *71*, 3–8.