

Supporting Information

C-N Linked Donor Type Porphyrin Derivatives: Unrevealed Hole-transporting Materials for Efficient Hybrid Perovskite Solar Cells

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Experimental Procedures

Synthesis of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (**2**)¹

Dipyrromethane **1** (500 mg, 3.42 mmol) was dissolved in 600 mL of dry CH₂Cl₂ previously purged with nitrogen for 10 minutes. Then, after purging the resulting mixture with nitrogen for an additional 10 minutes, the required 3,5-di-*tert*-butylbenzaldehyde (792 mg, 3.63 mmol, 1.06 equiv.) was added. The reactional mixture was purged once more (ca. 10 minutes) and then was added TFA (63 μ L, 0.82 mmol, 0.24 equiv.). The reaction mixture was kept under stirring for 17 hours at room temperature, under nitrogen atmosphere, and protected from light. After this period, DDQ (1 g, 4.41 mmol, 1.3 equiv.) was added, and this mixture was refluxed under air atmosphere for 75 minutes. After reaching room temperature, it was added triethylamine (114 μ L, 0.024 equiv.), and the solvents were removed under reduced pressure. After purification of the crude mixture on a silica chromatography column, using CH₂Cl₂/hexane (1:1) as the eluent, the desired product **2** was obtained in 64% yield (752 mg).

¹H NMR (300 MHz, CDCl₃): δ 10.32 (2H, s, 10-H and 20-H), 9.40 (4H, d, J = 4.6 Hz, β -H), 9.14 (4H, d, J = 4.6 Hz, β -H), 8.15 (4H, d, J = 1.8 Hz, 2',6'-H-Ph), 7.84 (2H, t, J = 1.8 Hz, 4'-H-Ph), 1.58 (36H, s, ^tBu-CH₃), -3.02 (2H, s, *N*-H) ppm. UV-Vis (DMF): λ_{\max} (log ϵ) 407 (5.52), 503 (4.10), 538 (3.74), 576 (3.61), 631 (3.31) nm. MS-ESI(+): m/z 687.7 [M+H]⁺.

Synthesis of [5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin]zinc(II) (**3a**)²

The metallation of the free-base porphyrin **2** (22.4 mg, 0.033 mmol) with zinc(II) acetate dihydrate (14.3 mg, 0.065 mmol, 2 equiv.) was carried out in a CHCl₃/MeOH mixture (3:1, 4mL) at room temperature for 1 h. After this period, it was added CH₂Cl₂, the reaction mixture was washed with water and the solvent was removed under reduced pressure. The Zn(II) complex **3a** was obtained pure in 99% yield (24.8 mg) after crystallization from CH₂Cl₂/*n*-hexane.

¹H NMR (300 MHz, CDCl₃): δ 10.34 (2H, s, 2H,10-H and 20-H), 9.46 (4H, d, J = 4.7 Hz, β -H), 9.21 (4H, d, J = 4.7 Hz, β -H), 8.15 (4H, d, J = 1.8 Hz, 2',6'-H-Ph), 7.84 (2H, t, J = 1.8 Hz, 4'-H-Ph), 1.57 (36H, s, ^tBu-CH₃) ppm. UV-Vis (DMF): λ_{\max} (log ϵ) 415 (5.82), 546.5 (4.03), 583 (3.38) nm. MS-ESI(+): m/z 749.6 [M+H]⁺. HRMS-ESI(+): m/z calcd for C₄₈H₅₃N₄Zn 749.3562: [M+H]⁺; found: 749.3531.

Synthesis [5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) (**3b**)²

The metallation of the free-base porphyrin **2** (18.4 mg, 0.027 mmol) with copper(II) acetate monohydrate (10.7 mg, 0.054 mmol, 2 equiv.) was carried out at 60 °C in a CHCl₃/MeOH mixture (3:1, 4 mL). After 15 minutes, the UV-Vis spectrum and the TLC control confirmed the full conversion of the free-base into the desired metalloporphyrin. After cooling, the reaction

mixture was diluted with CH₂Cl₂ and washed with water. The organic phase was collected, and the solvent was removed under reduced pressure. Compound **3b** was obtained quantitatively (20.4 mg).

UV-Vis (chlorobenzene): λ_{\max} (log ϵ) 405 (4.54), 527 (3.29), 559 (2.78) nm. MS-ESI(+): m/z 748.4 [M+H]⁺. HRMS-ESI(+): m/z calcd for C₄₈H₅₂CuN₄: 747.3461: [M]⁺; found 747.3462.

Bromination of the Zn(II) and Cu(II) complexes 3a and 3b: general procedure³

A solution of each porphyrin complex **3a** and **3b** (ca. 59.7 mg) in CHCl₃ (36 mL) containing a few drops of pyridine (4 drops) was kept in an ice bath at 0°C for 15 minutes. After this period, it was added *N*-bromosuccinimide (2.1 equiv.) and the reaction mixture was kept under stirring at the same temperature (0 °C) for 20 minutes, when the TLC control confirmed the total consumption of the starting porphyrin. Then, it was added acetone (12 mL) to stop the reaction and the solvents were removed under reduced pressure. The residue was diluted in CH₂Cl₂ and the organic layer after being washed with water and extracted with CH₂Cl₂ was separated, and the solvent was removed under reduced pressure. After crystallization from CH₂Cl₂/*n*-hexane, the desired dibrominated complexes **4a** and **4b** were obtained in 82% (59 mg) and 85% (61 mg) yield, respectively.

[5,15-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) 4a

¹H NMR (300 MHz, CDCl₃/CD₃OD): δ 9.62 (4H, d, J = 4.8 Hz, β -H), 8.88 (4H, d, J = 4.8 Hz, β -H), 7.98 (4H, d, J = 1.8 Hz, 2',6'-H-Ph), 7.77 (2H, t, J = 1.8 Hz, 4'-H-Ph), 1.48 (36H, s, ^tBu-CH₃). UV-Vis (DMF): λ_{\max} (log ϵ) 432.5 (5.50), 569 (4.09), 610.5 (3.98) nm. MS-ESI(+): m/z 906.5 [M]⁺. HRMS-ESI(+): m/z calcd for C₄₈H₅₀ZnN₄Br₂: 906.2889 [M]⁺; found 906.2885.

[5,15-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinato]copper(II) 4b

UV-Vis (chlorobenzene): λ_{\max} (log ϵ) 423.5 (4.63), 548 (3.29), 587 (2.92) nm. MS-ESI(+): m/z 905.3 [M]⁺.

Table S1. Summary of the various reactional conditions used to prepare compound **5b** by the reaction of porphyrin **4b** and carbazole.

Entry	Reaction	Reagents	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	Buchwald	Pd(OAc) ₂ , ^t BuONa, 18crown-6, <i>rac</i> -BINAP	Toluene/DMF (2:1)	120	48	39
2	Ullman	<i>N</i> -phenylbenzohydrazide, CuI, Cs ₂ CO ₃	DMSO	120	120	31
3	Nucleophilic substitution	NaAuCl ₄ ·2H ₂ O, PhI(OAc) ₂ ,	CH ₂ Cl ₂	rt	4.5	11

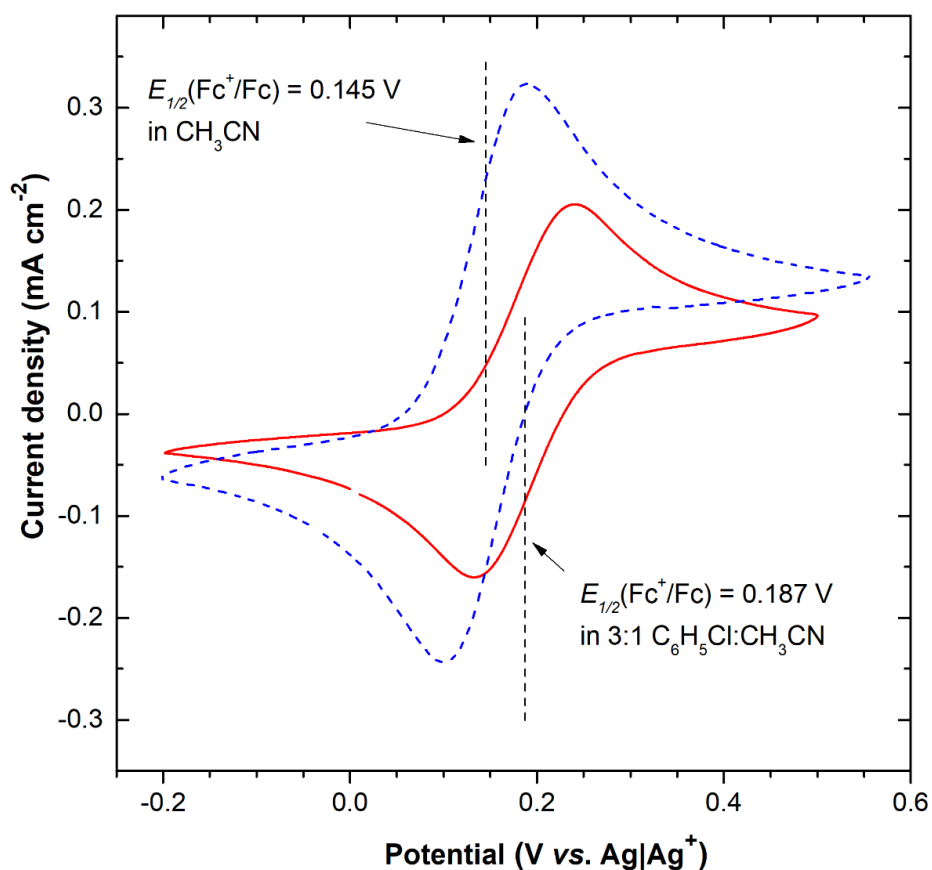


Figure S1. Cyclic voltammogram of the glassy-carbon electrode in 0.75 mM solution of ferrocene + 0.075 M Bu₄NPF₆ in acetonitrile (dashed blue line) and in a 3:1 volume ratio chlorobenzene:acetonitrile mixture (solid red line).

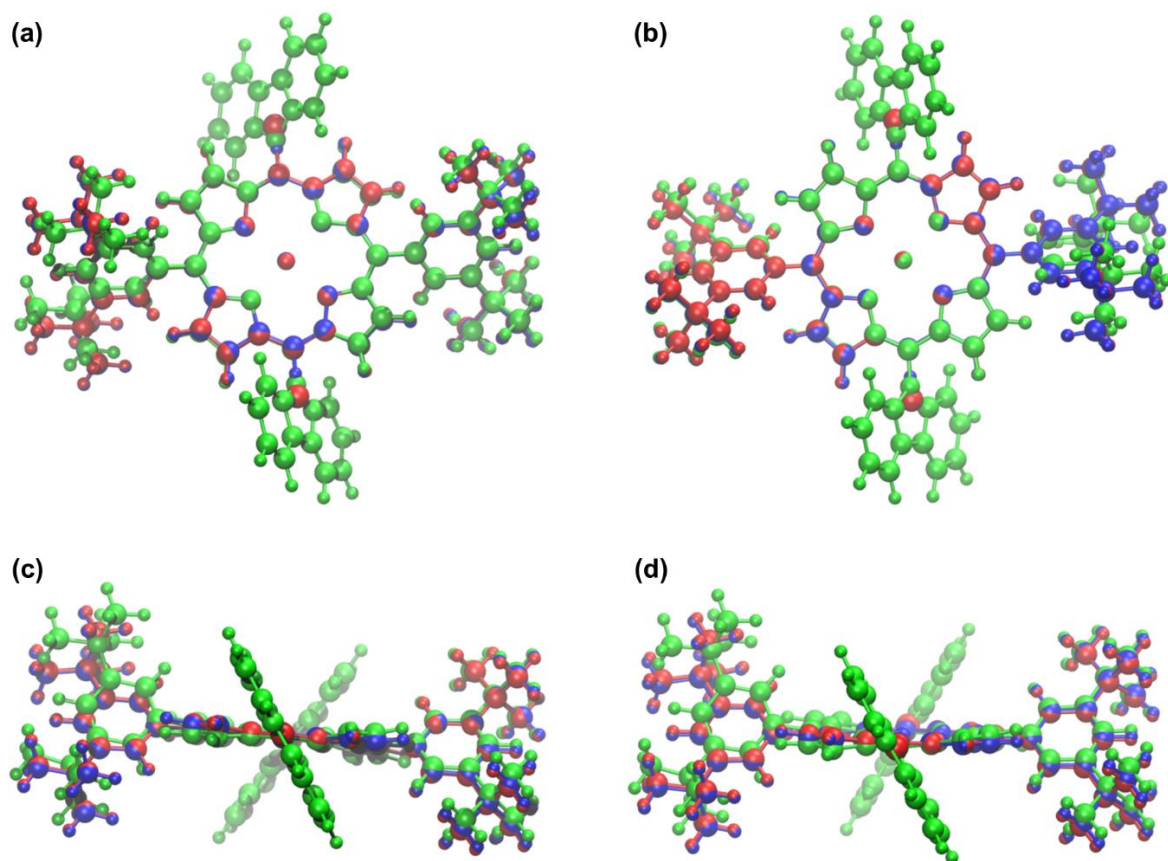


Figure S2. Superimposed geometries for the zinc(II) (a and c) and copper(II) (b and d) complexes: the blue color refers to the structures **3**, red to the structure **4**, and green to the structure **5**.

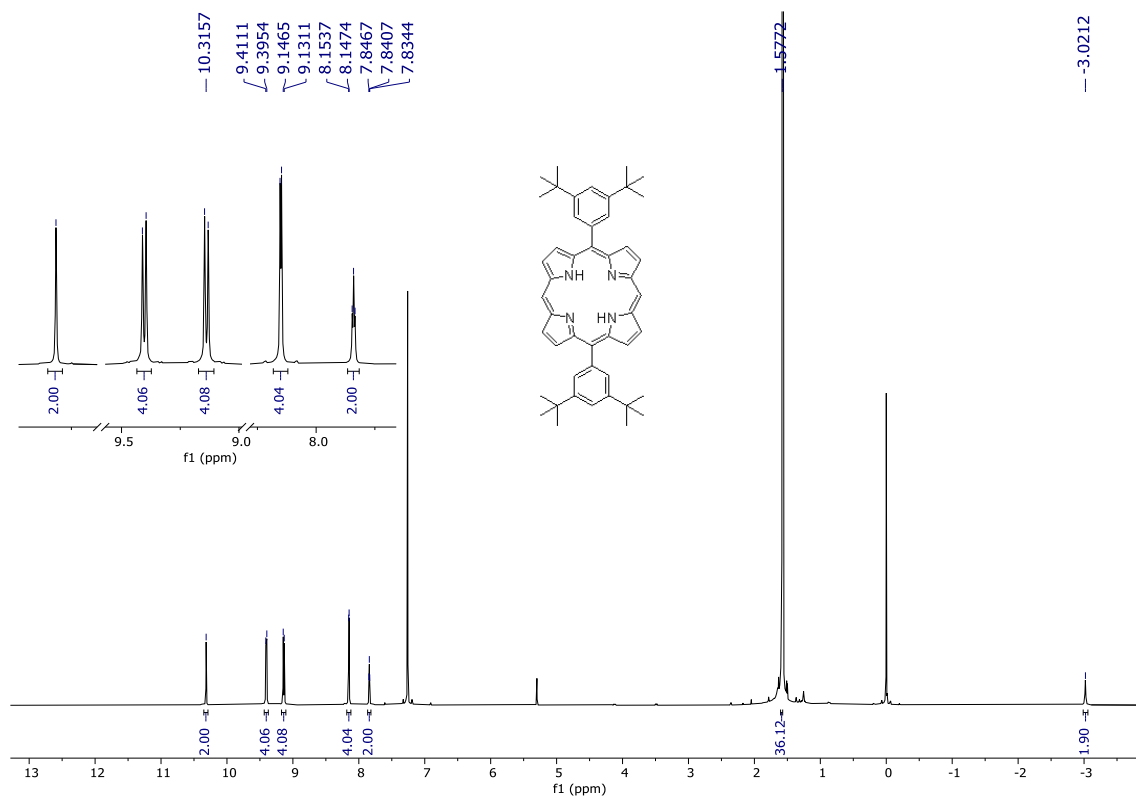


Figure S3. $^1\text{H-NMR}$ spectrum of the compound **2** in CDCl_3 .

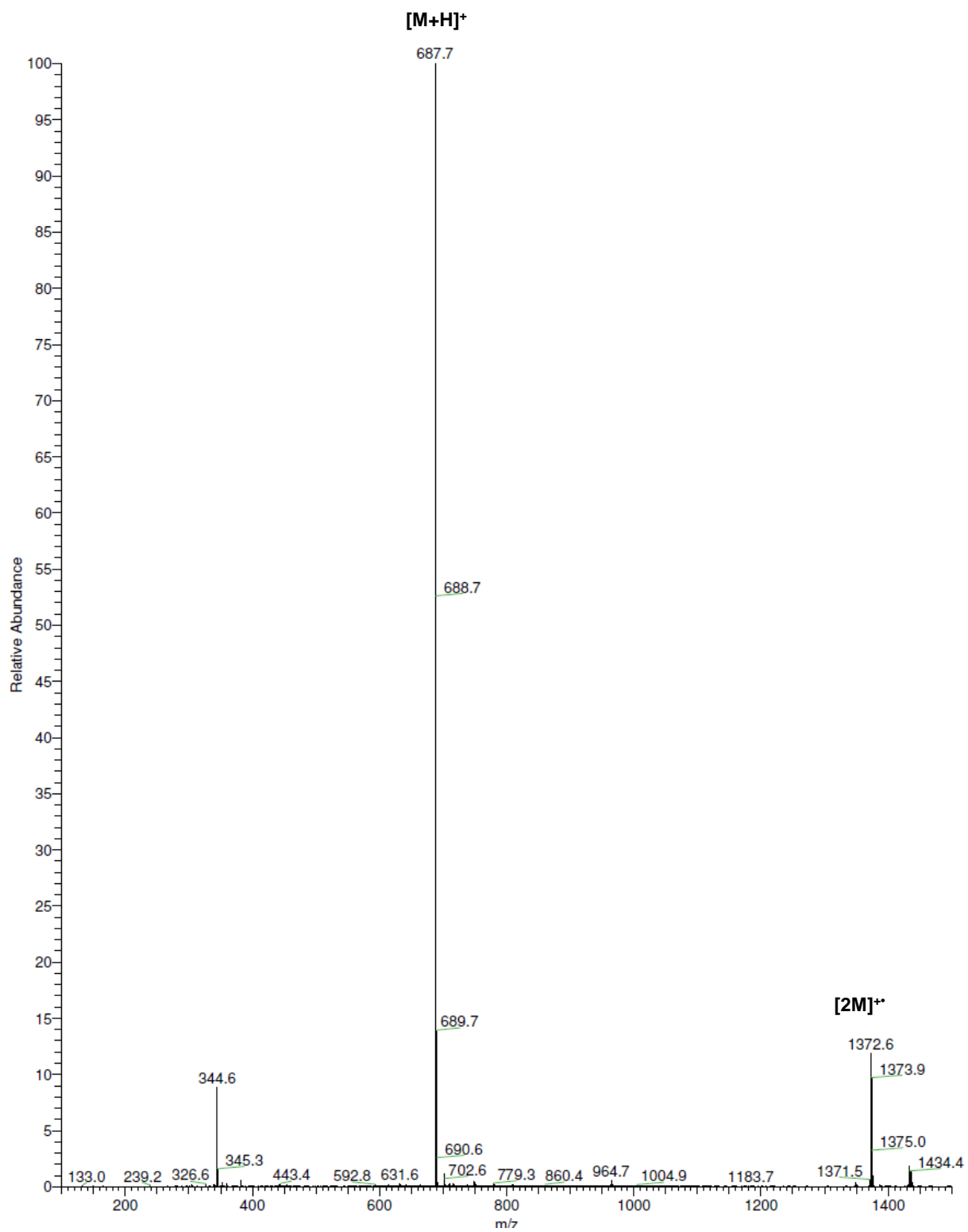


Figure S4. MS-ESI(+) spectrum of compound 2.

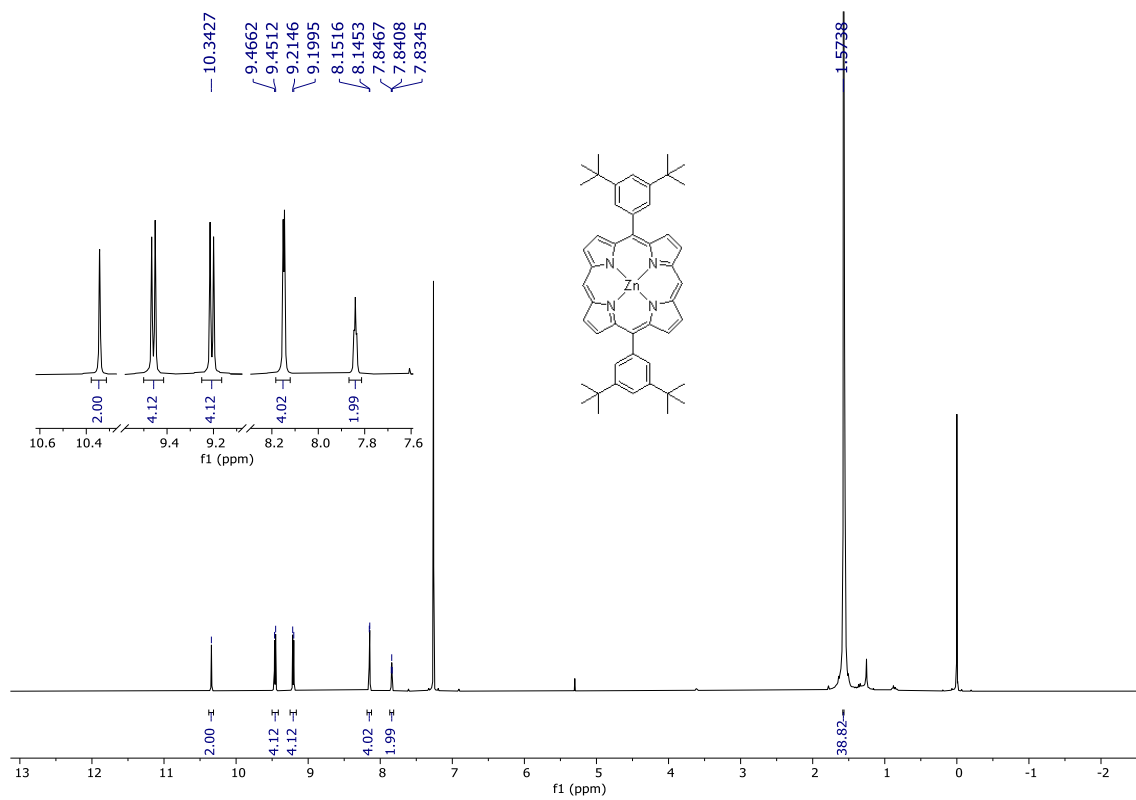


Figure S5. $^1\text{H-NMR}$ spectrum of the compound **3a** in CDCl_3 .

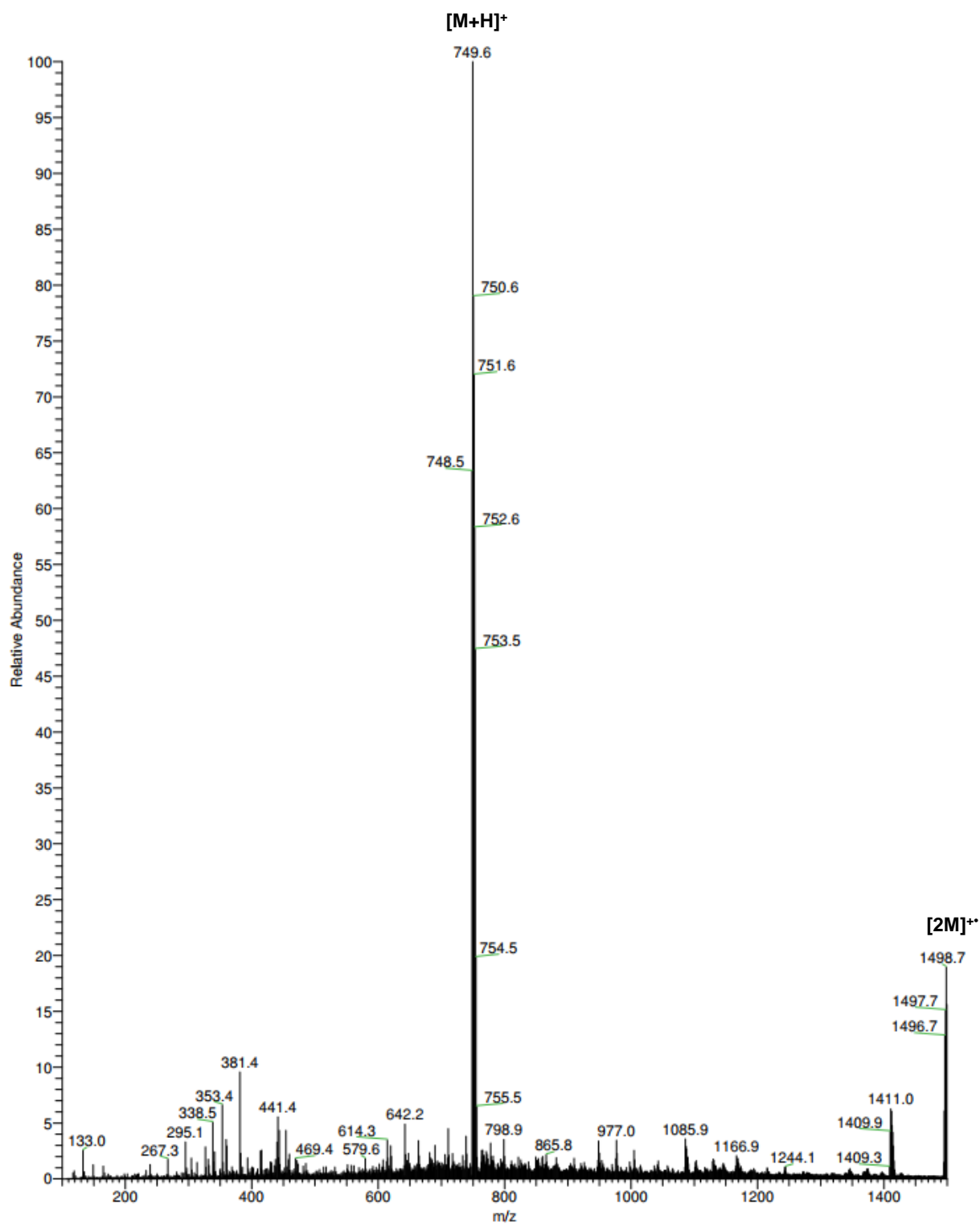


Figure S6. MS-ESI(+) spectrum of compound 3a.

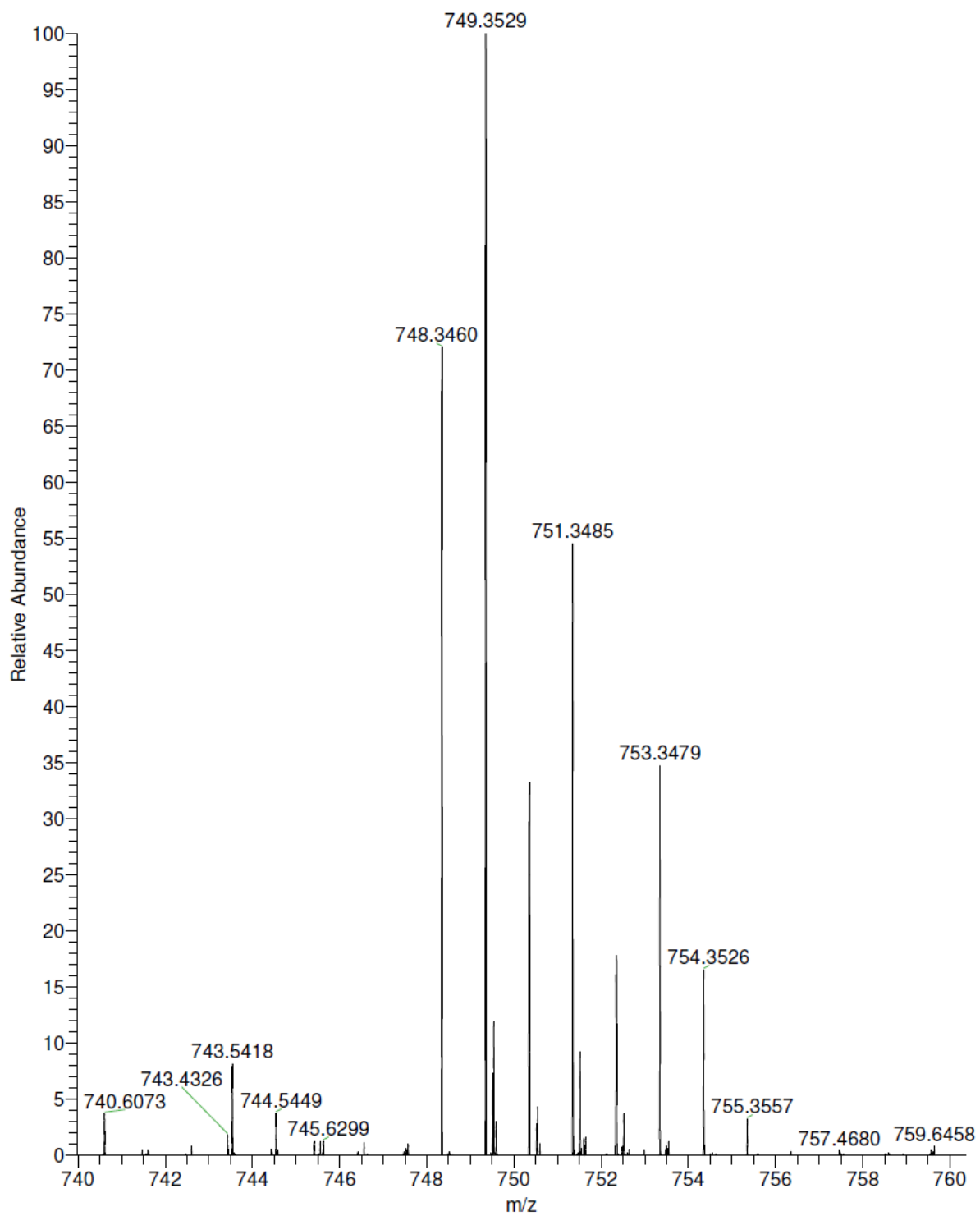


Figure S7. HRMS-ESI(+) spectrum of compound **3a**.

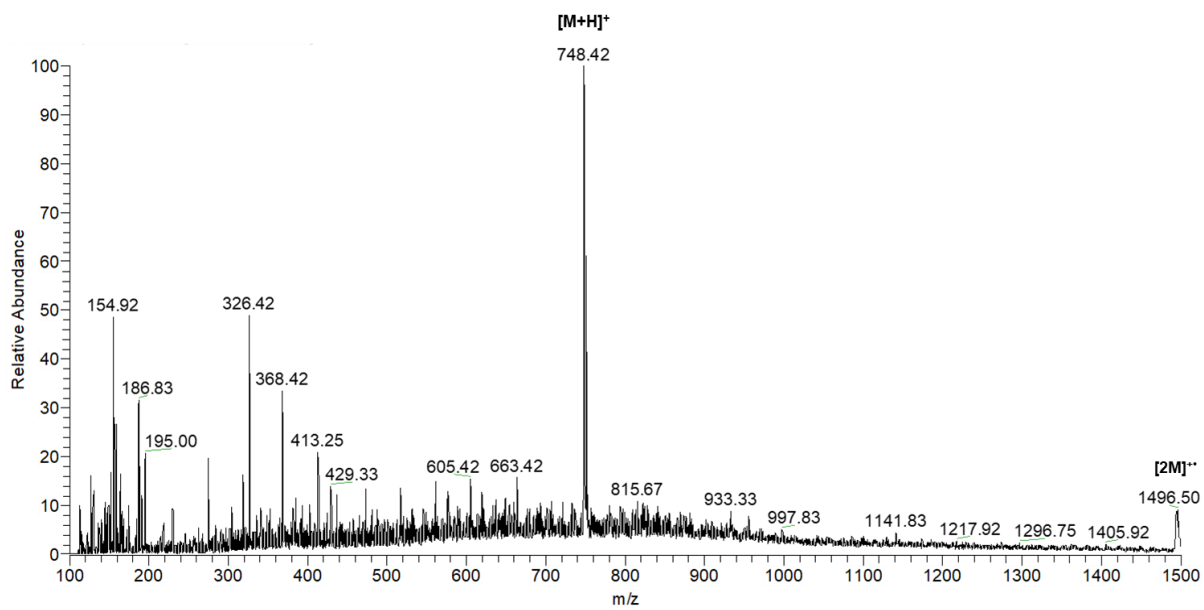


Figure S8. MS-ESI(+) spectrum of compound **3b**.

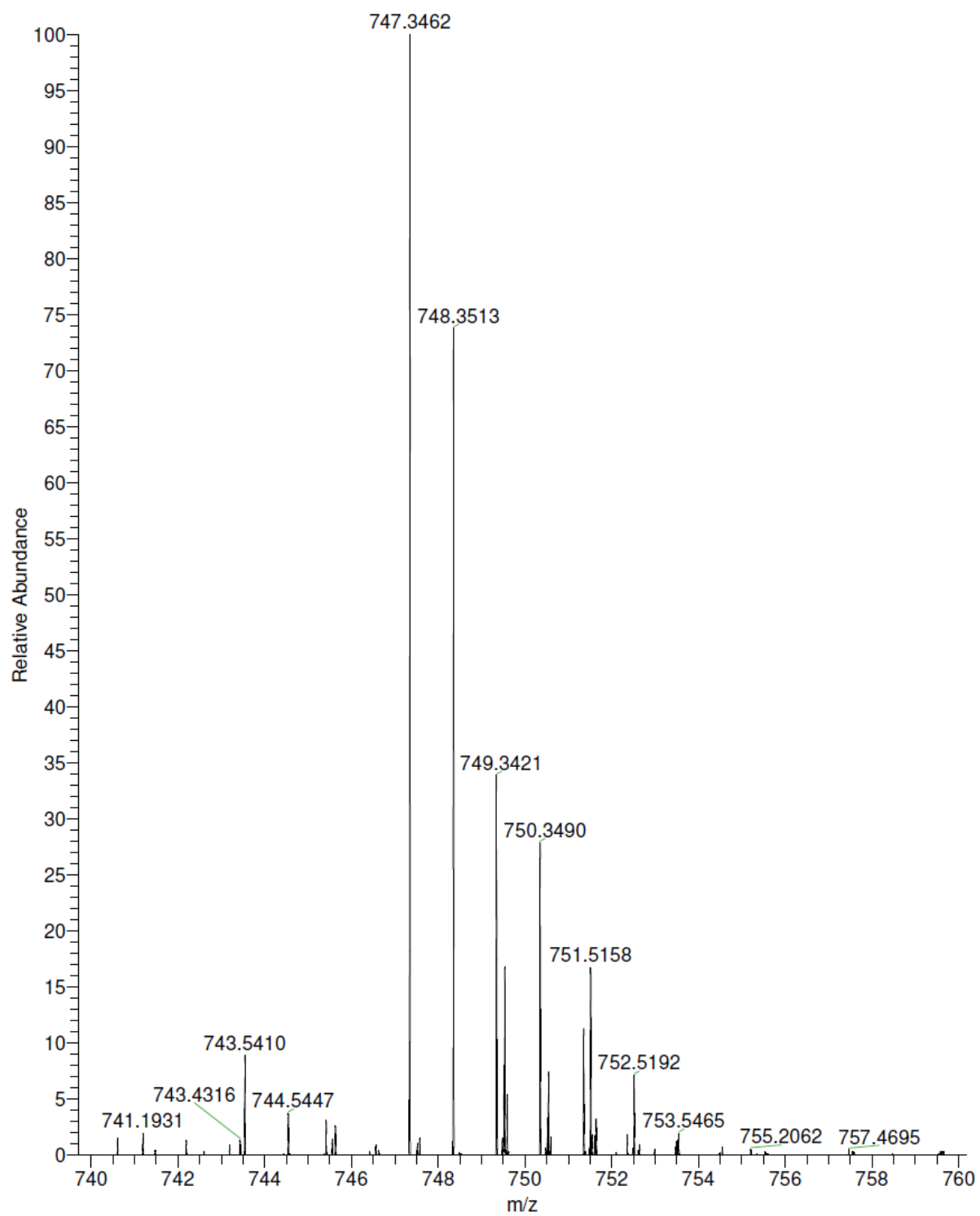


Figure S9. HRMS-ESI(+) spectrum of compound **3b**.

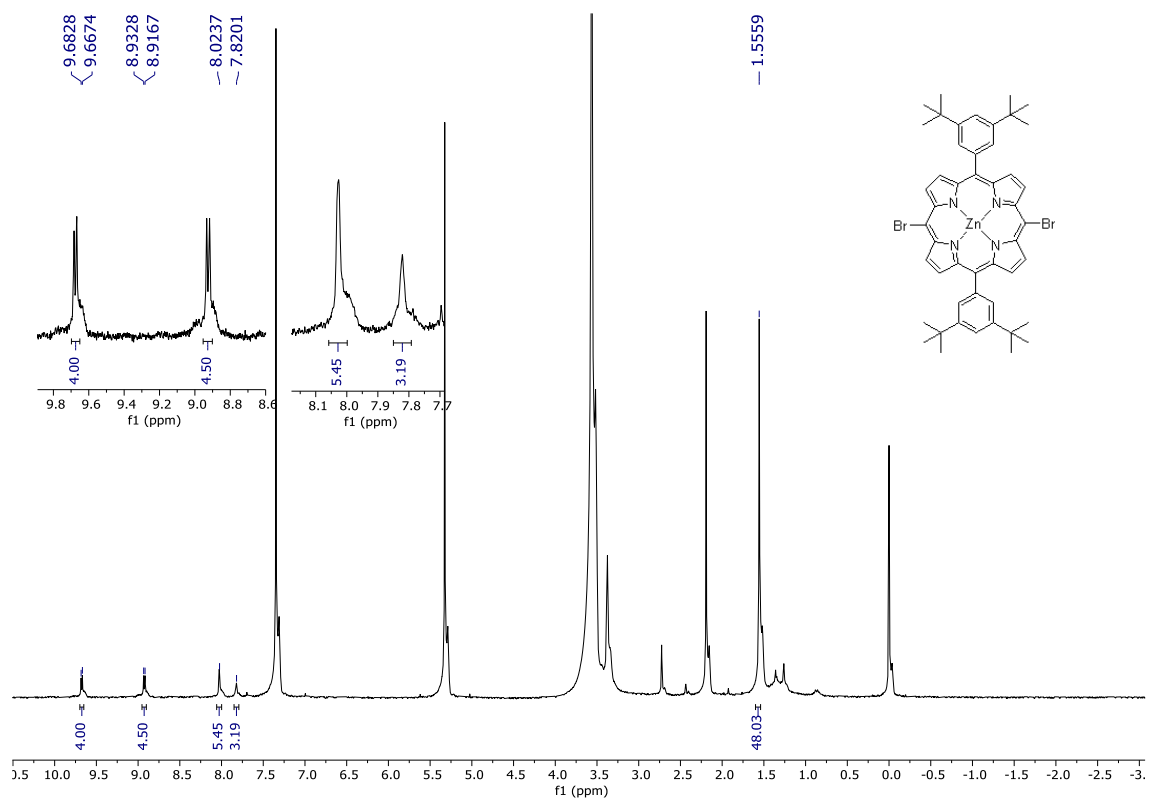


Figure S10. ¹H-NMR spectrum of the compound **4a** in CDCl₃/CD₃OD.

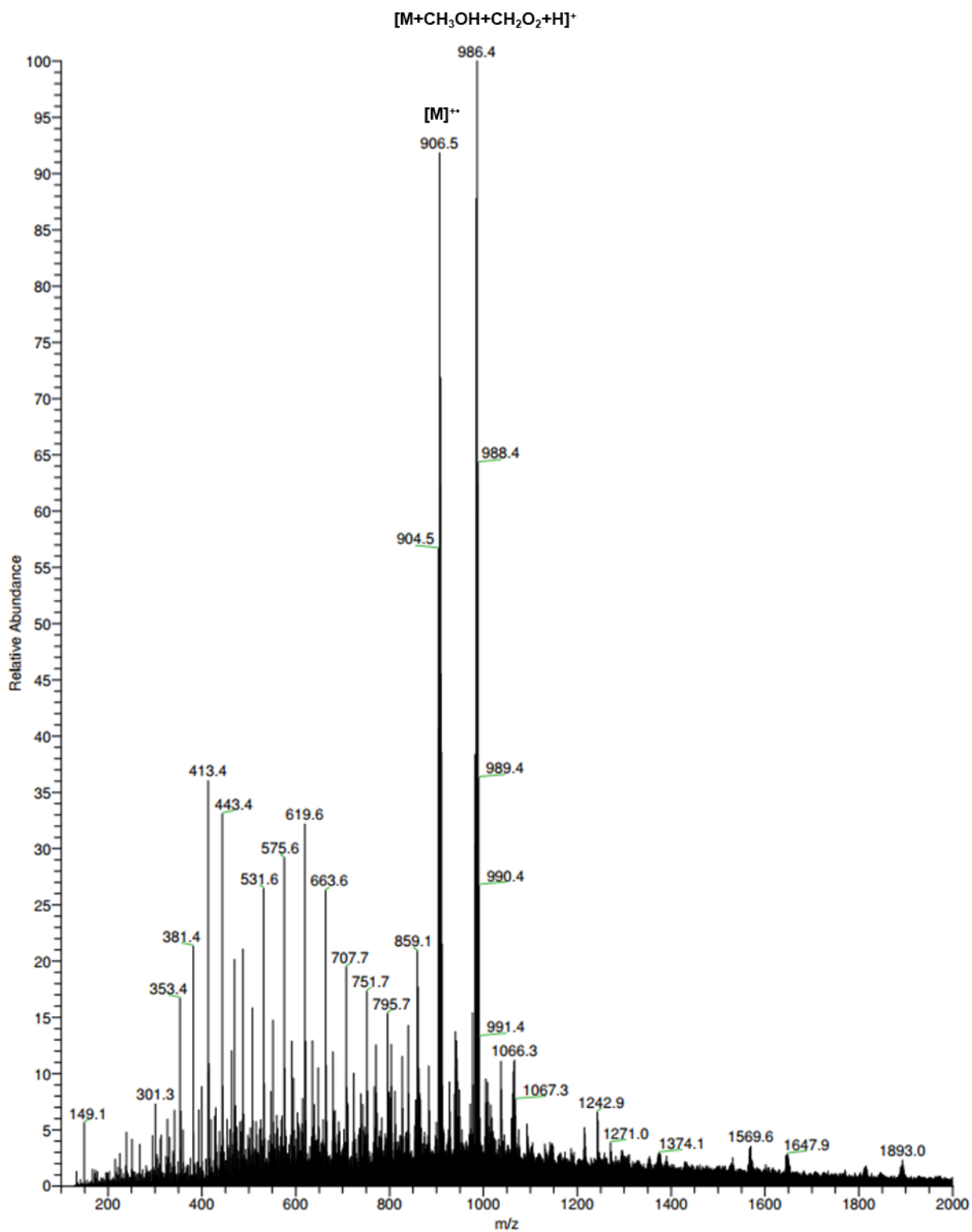


Figure S11. MS-ESI(+) spectrum of compound 4a.

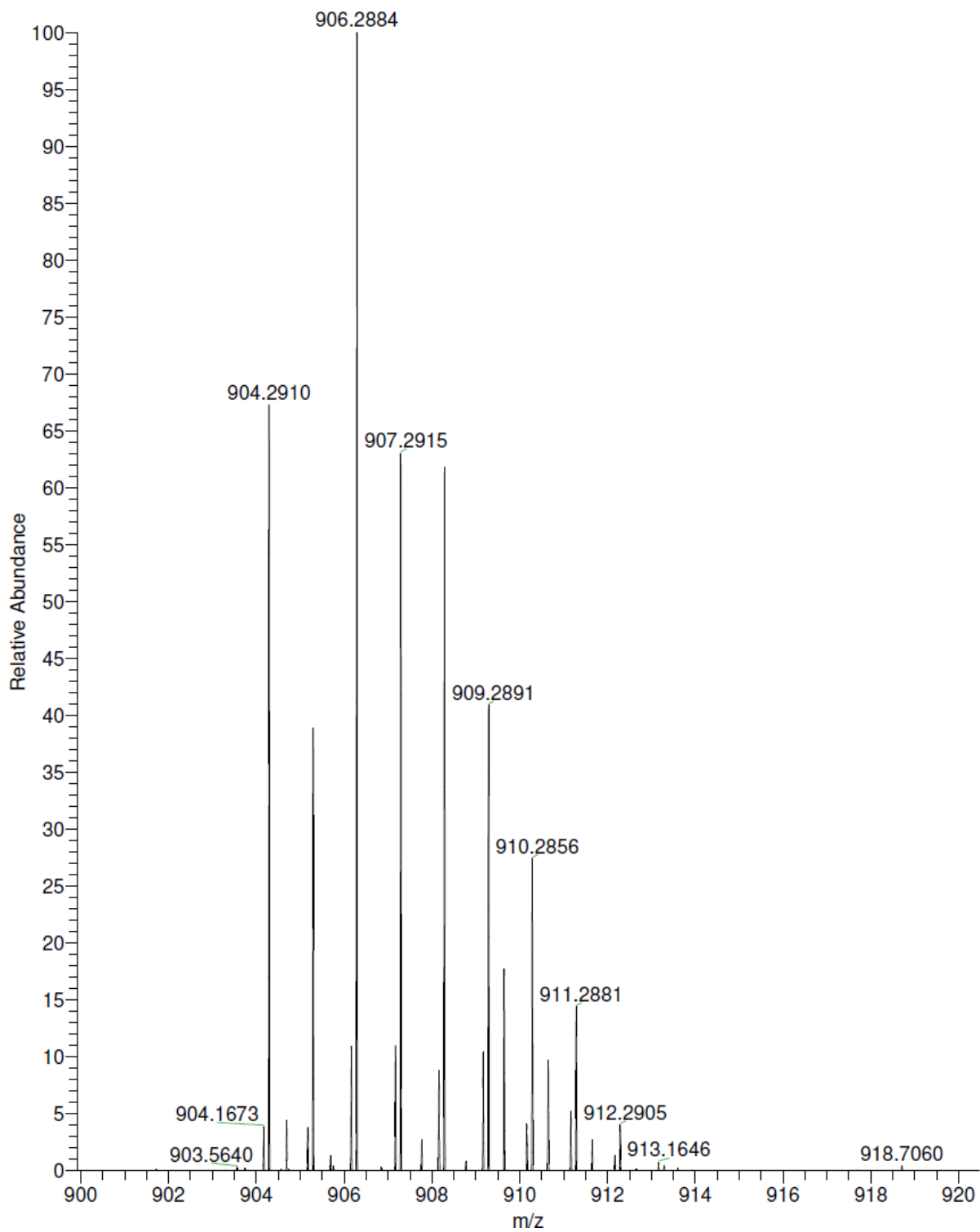


Figure S12. HRMS-ESI(+) spectrum of compound **4a**.

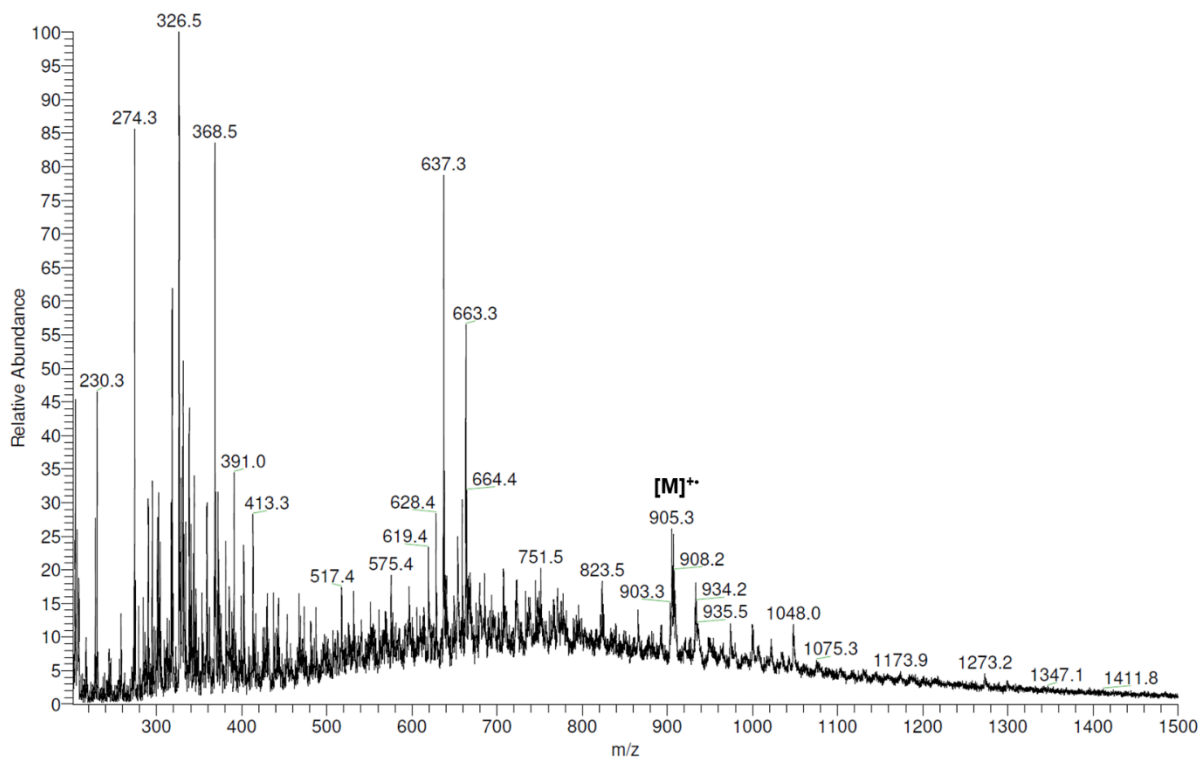


Figure S13. MS-ESI(+) spectrum of compound 4b.

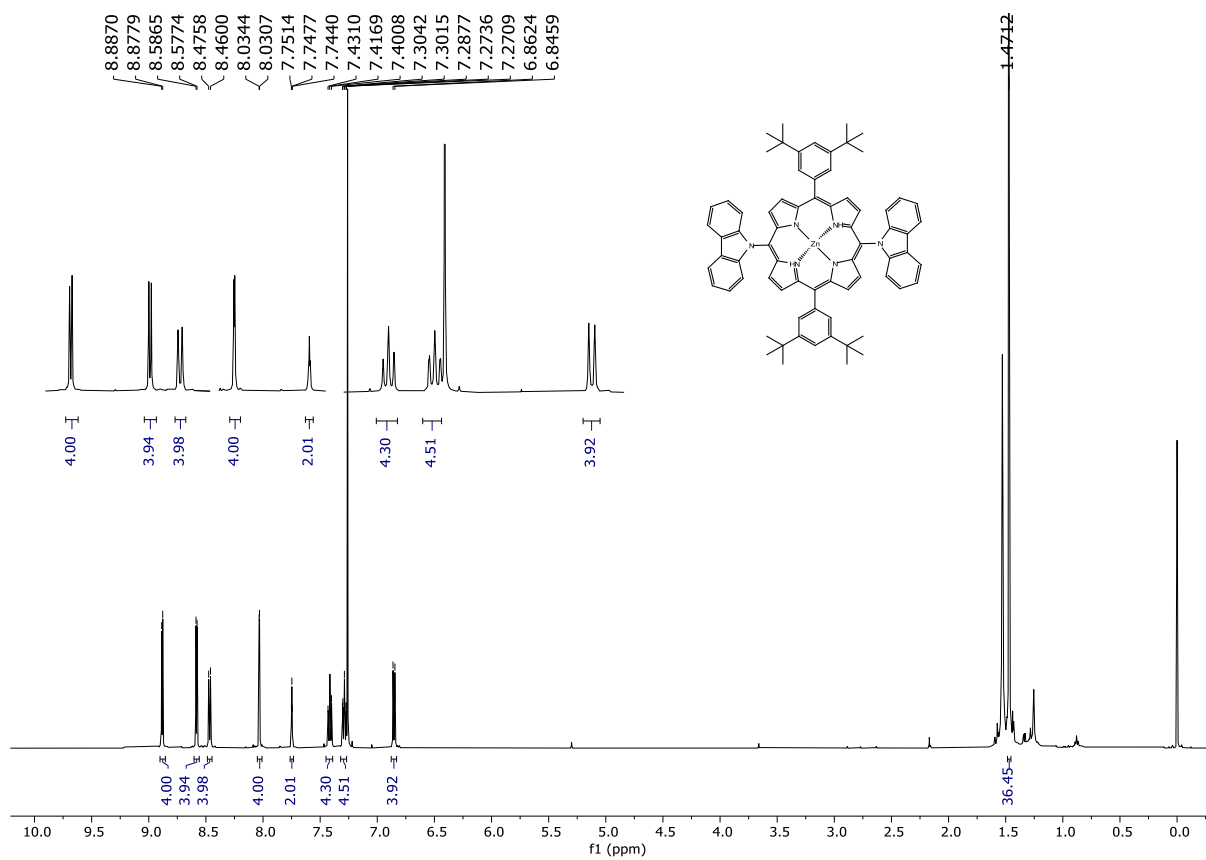


Figure S14. ¹H-NMR spectrum of the compound 5a in CDCl₃.

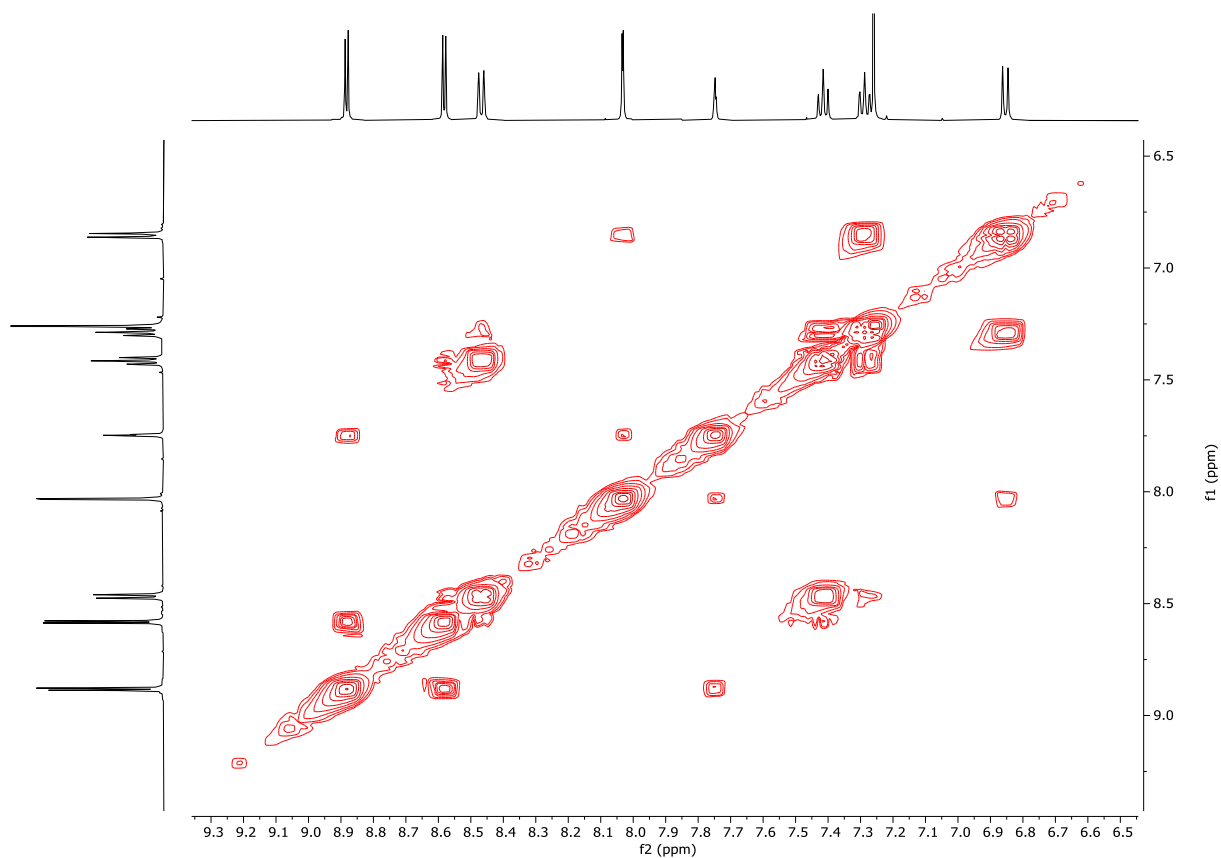


Figure S15. Partial COSY $^1\text{H}/^1\text{H}$ NMR spectrum of compound **5a** in CDCl_3 .

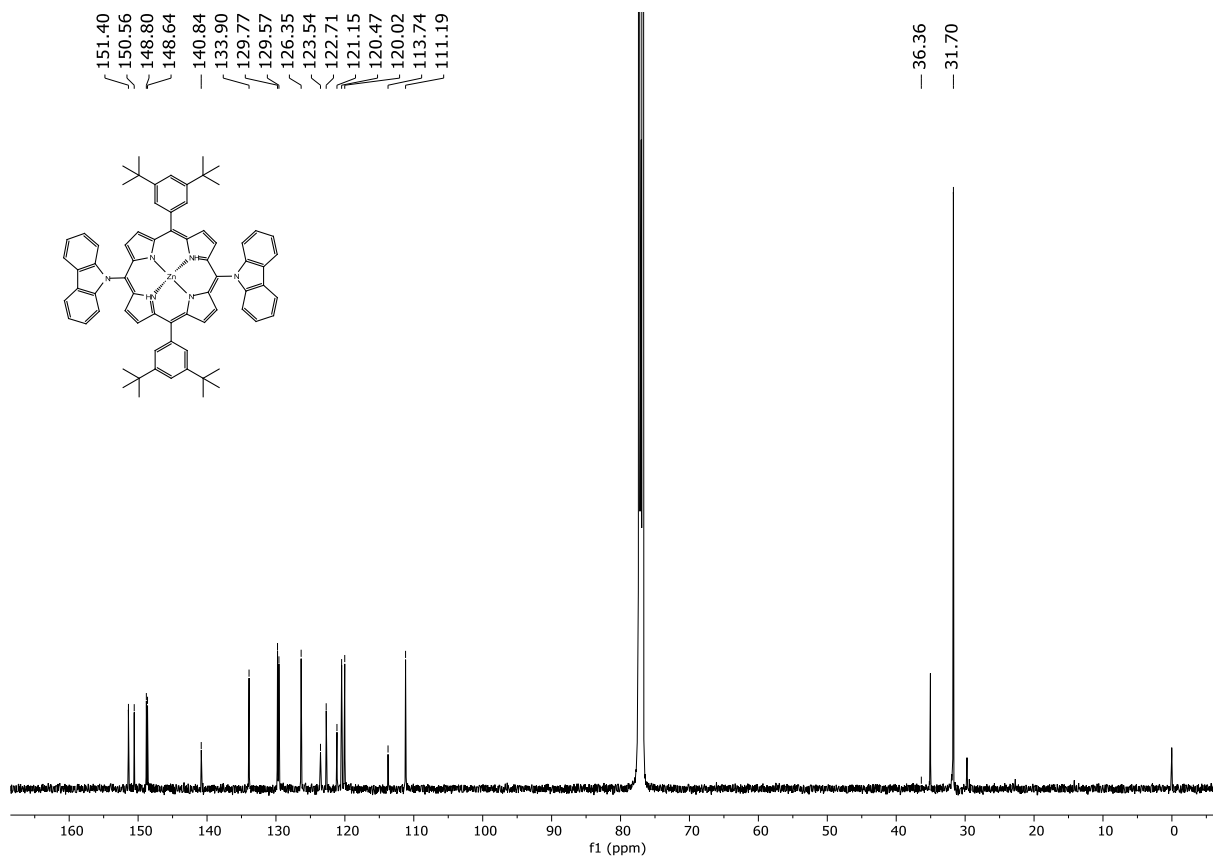


Figure S16. ^{13}C -NMR spectrum of the compound **5a** in CDCl_3 .

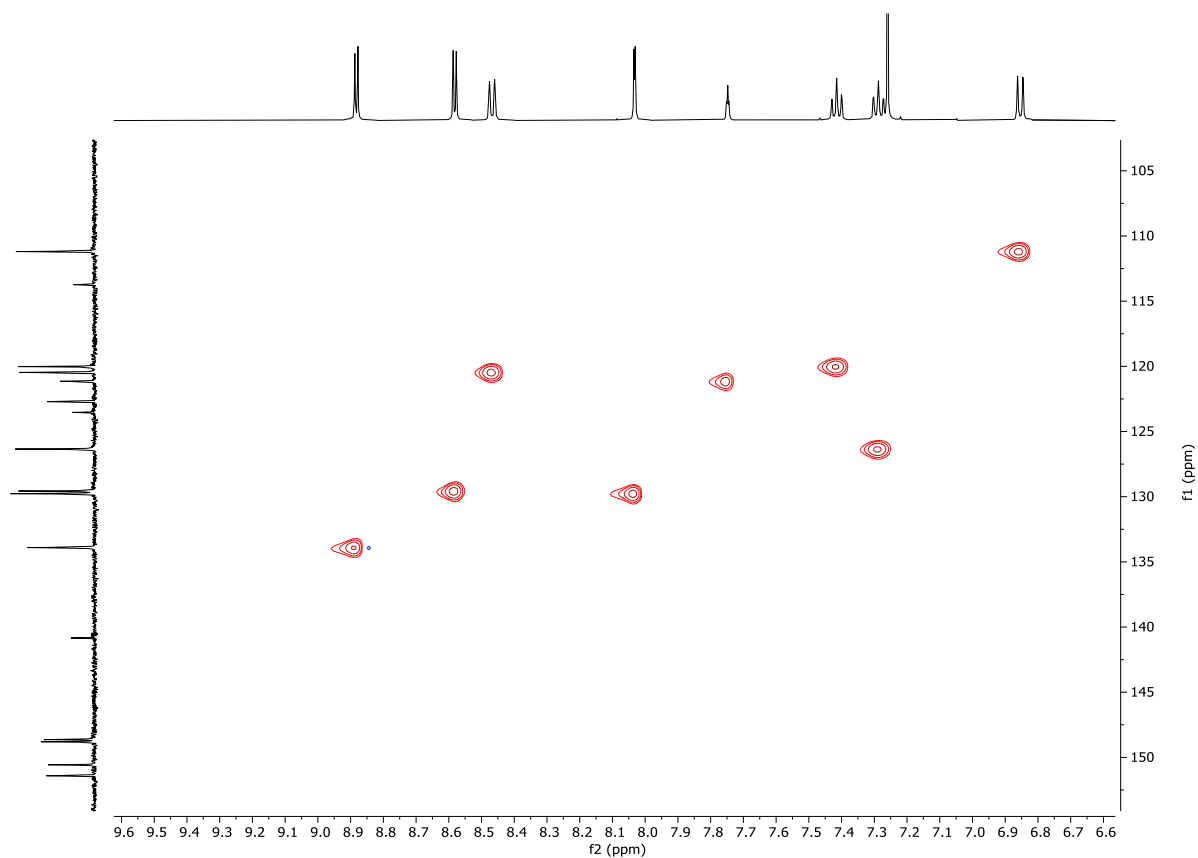


Figure S17. Partial HSQC $^1\text{H}/^{13}\text{C}$ NMR spectrum of compound **5a** in CDCl_3 .

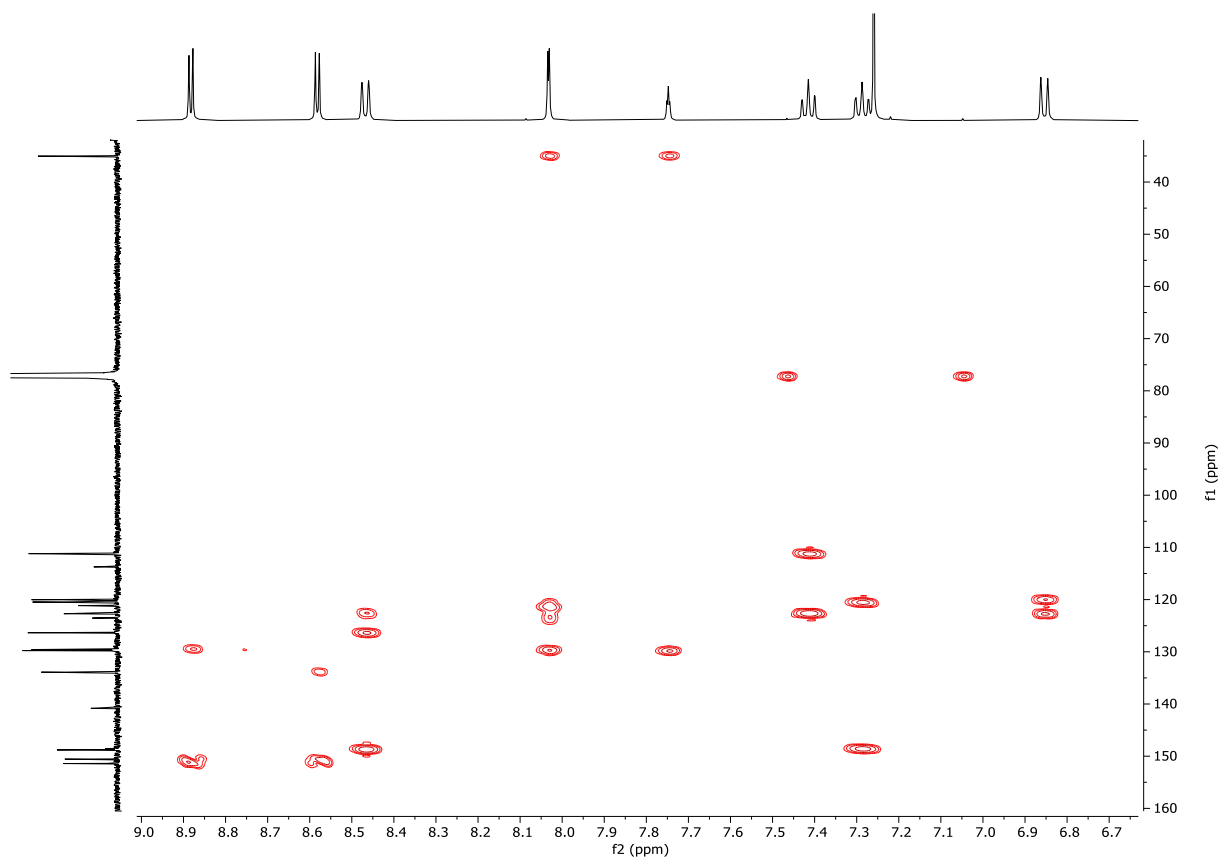


Figure S18. Partial HMBC $^1\text{H}/^{13}\text{C}$ NMR spectrum of compound **5a** in CDCl_3 .

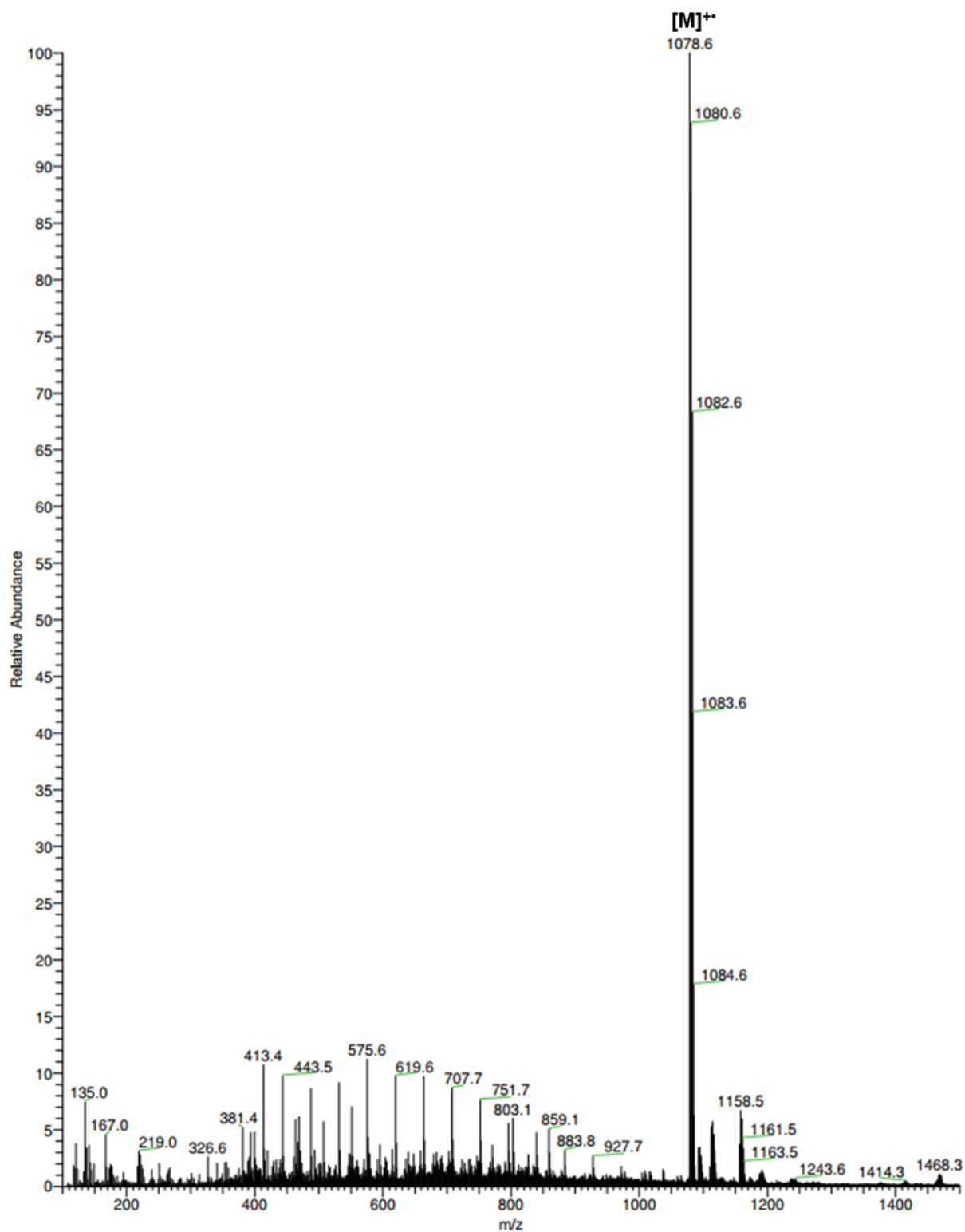


Figure S19. MS-ESI(+) spectrum of compound 5a.

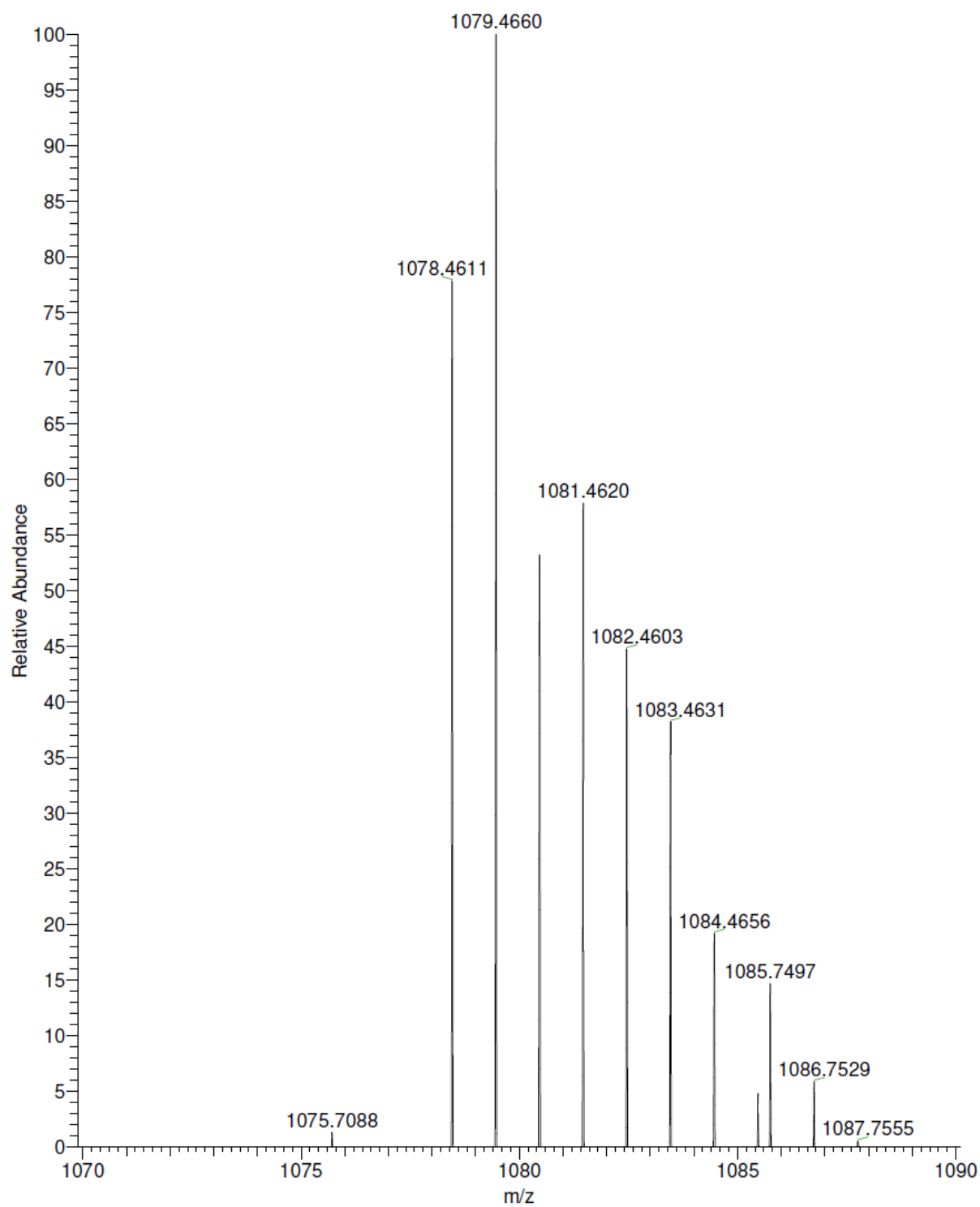


Figure S20. HRMS-ESI(+) spectrum of compound **5a**.

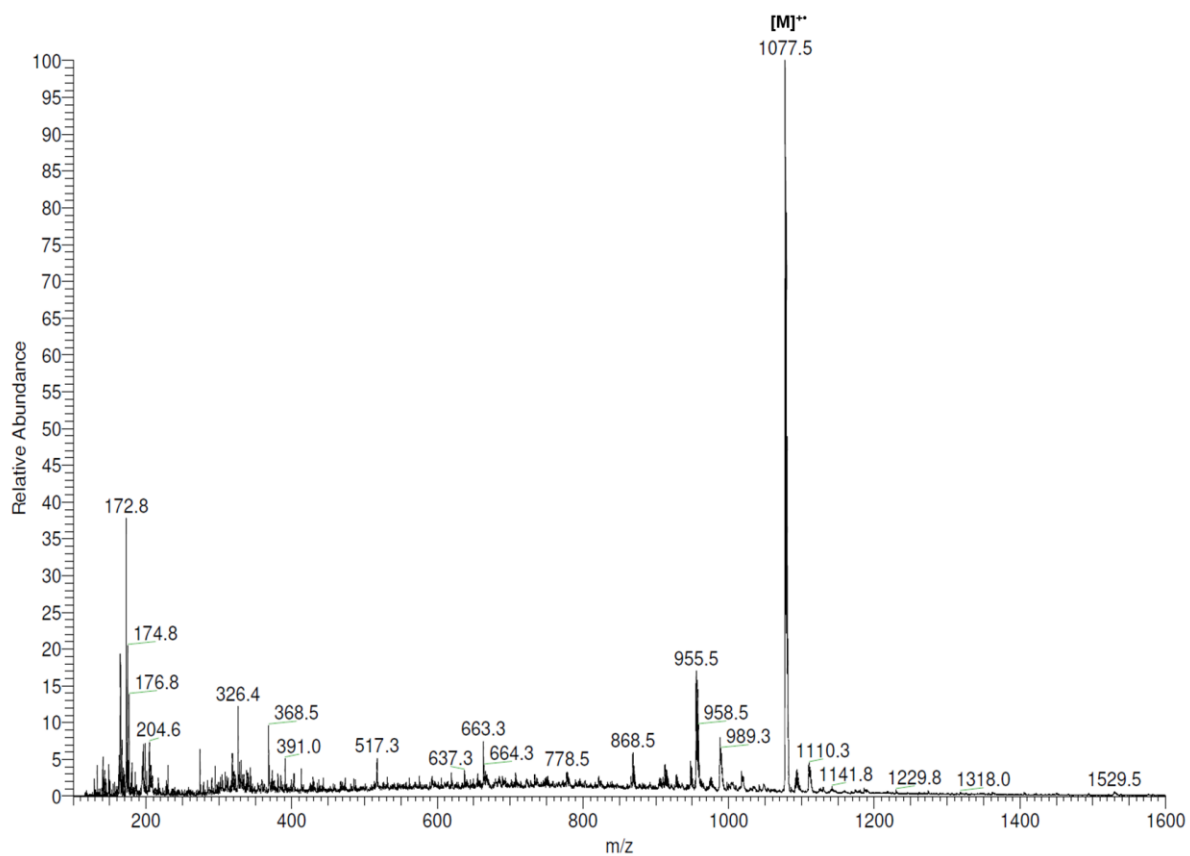


Figure S21. MS-ESI(+) spectrum of compound **5b**.

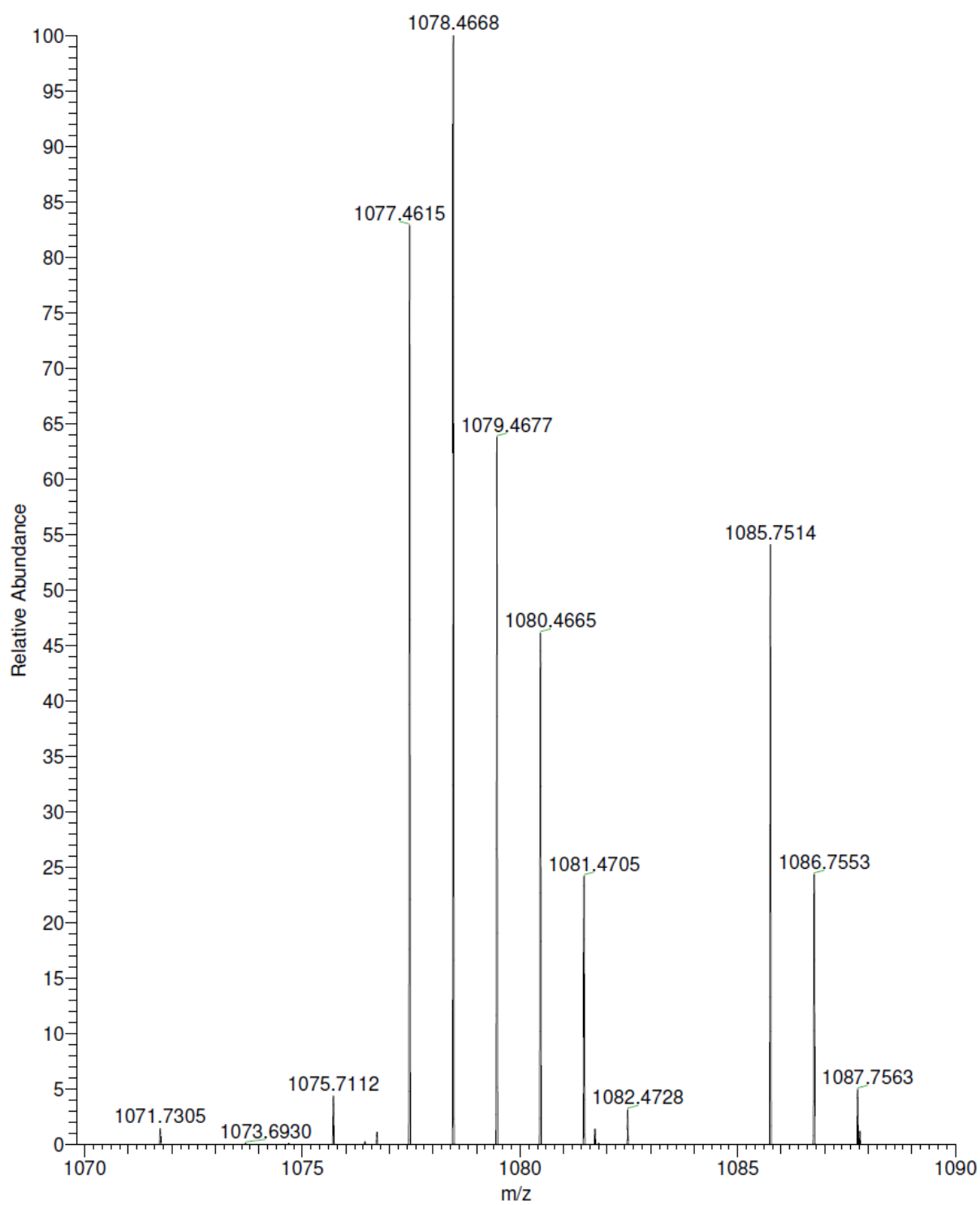


Figure S22. HRMS-ESI(+) spectrum of compound **5b**.

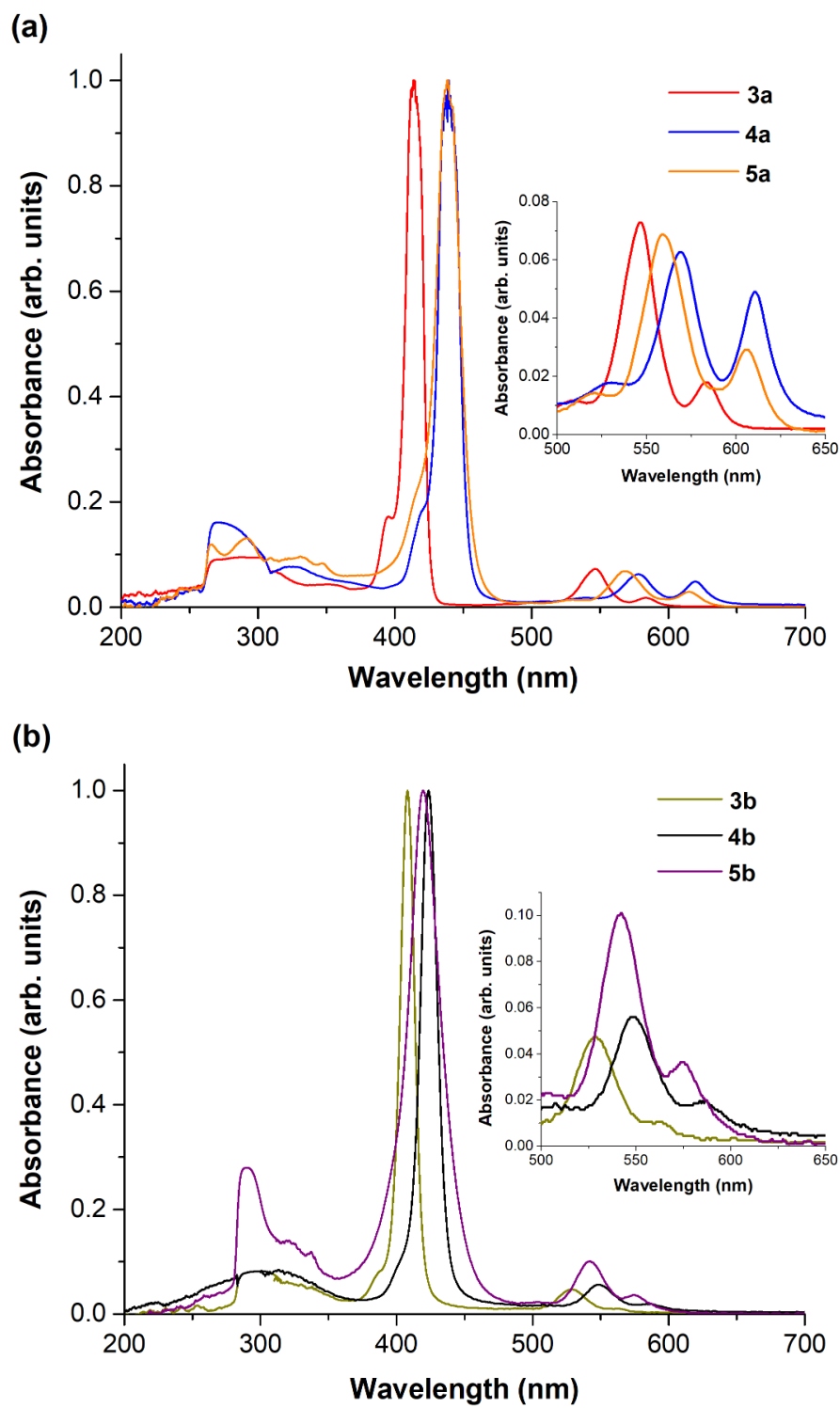


Figure S23. Normalised absorption spectrum of compounds **3a**, **4a** and **5a** (a) in DMF, and compounds **3b**, **4b** and **5b** (b) in chlorobenzene. Inset: magnification of the Q bands region (500-650 nm).

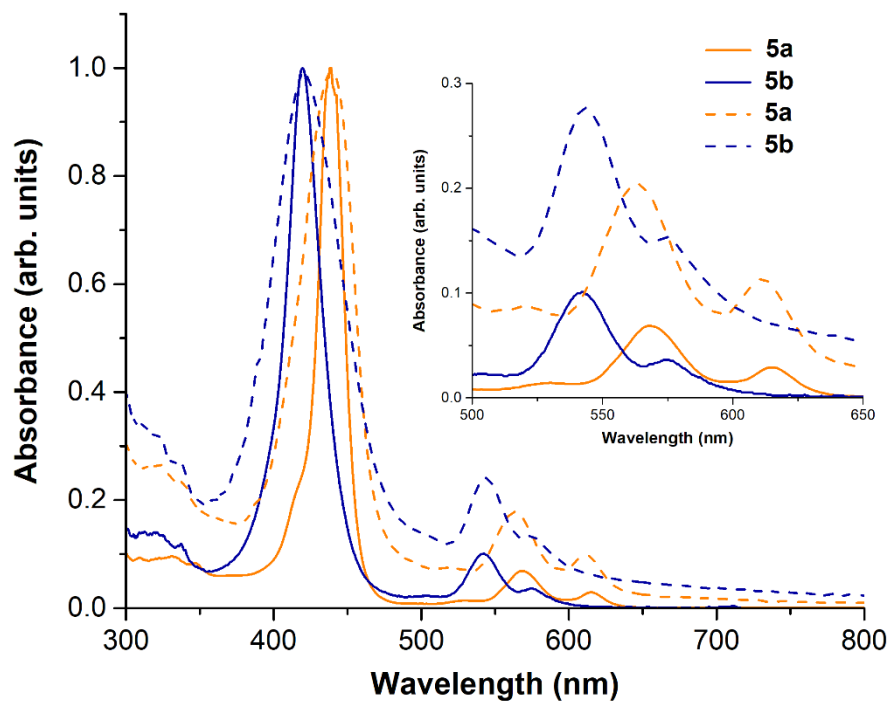


Figure S24. Superimposed normalised absorption spectra of compounds **5a** and **5b** in solution (solid lines), and in spin-coated films on glass substrates (dashed lines). Inset: magnification of the Q bands region (500-650 nm).

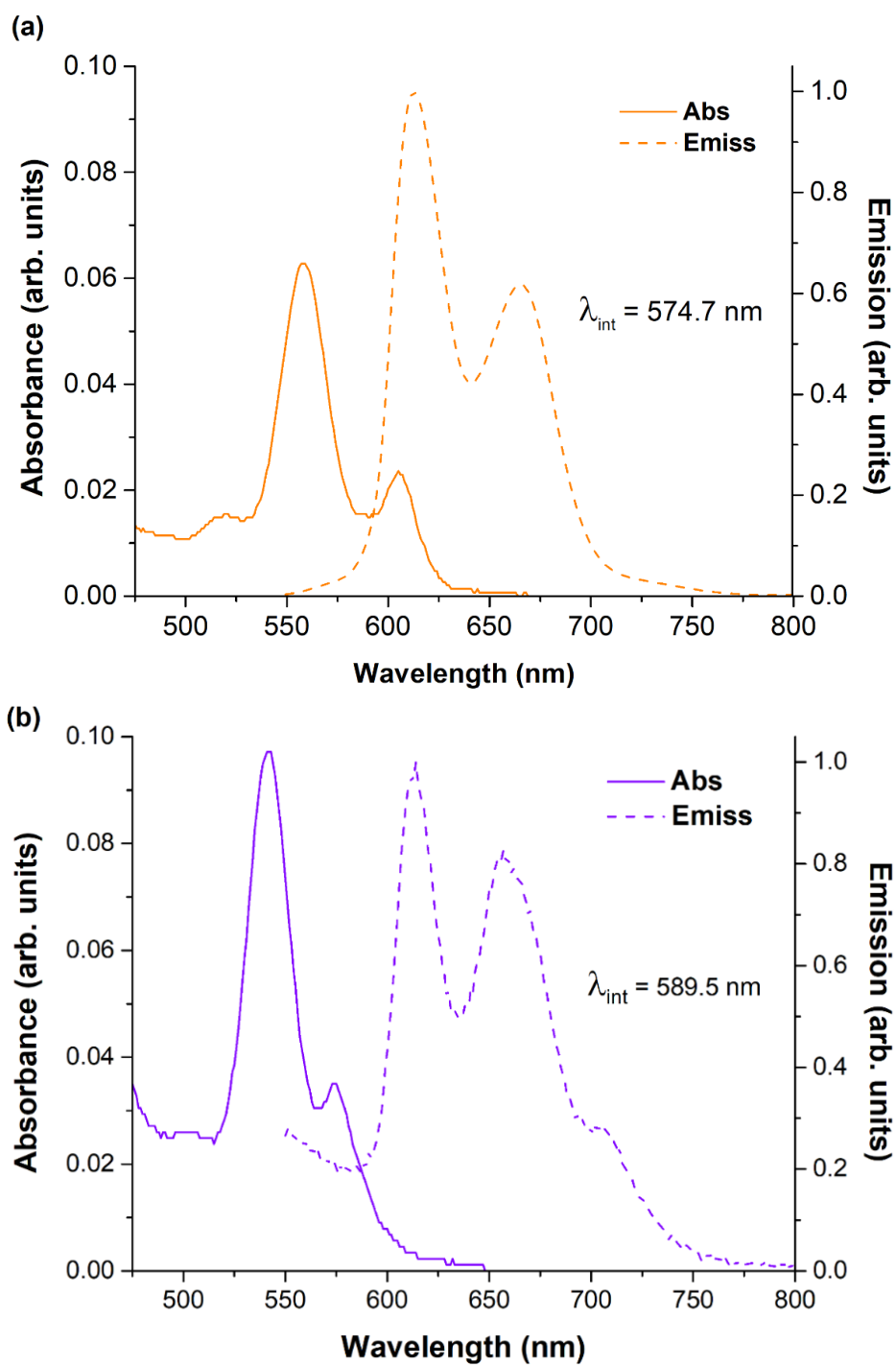
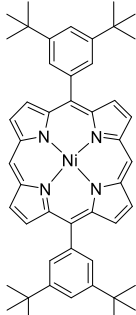
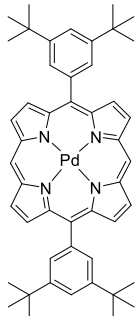


Figure S25. Spectral overlap of the normalised absorption spectrum with the normalised fluorescence spectrum of (a) porphyrin **5a** and (b) porphyrin **5b** in a 3:1 volume ratio chlorobenzene:acetonitrile mixture. ($[5a] = [5b] = 2.5 \times 10^{-6}$ M; $\lambda_{exc5a} = 420$ nm; $\lambda_{exc5b} = 418$ nm).

Table S2. Photovoltaic characteristics obtained for PSC devices employing porphyrin Zn(II) complex **3a** and the corresponding Ni(II) and Pd(II) complexes as HTMs.^a

HTM	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
3a	11.35	0.80	0.69	6.39
	7.67	0.70	0.57	3.06
	6.85	0.73	0.54	2.70

^a the HTM precursor solution was prepared considering 0.5 equiv. of LiTFSI, 0.03 equiv. of FK209 and 3.3 equiv. of TBP per mol of HTM.

Table S3. Individual photovoltaic characteristics of a batch of twelve PSC devices using spiro-OMeTAD as HTM, and the corresponding mean values with standard deviations.^a

Device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
1	19.58	1.01	0.71	14.31
2	19.97	0.98	0.70	13.91
3	20.08	1.00	0.72	14.74
4	19.16	1.00	0.73	14.16
5	20.85	1.03	0.70	15.32
6	20.86	1.03	0.69	15.14
7	20.87	1.00	0.69	14.70
8	20.34	1.01	0.69	14.47
9	20.17	1.03	0.73	15.37
10	20.05	1.02	0.73	15.15
11	19.75	1.03	0.74	15.24
12	19.68	1.03	0.73	15.08
Mean	20.11	1.01	0.71	14.80
σ	0.52	0.02	0.02	0.47

^a the HTM precursor solution was prepared considering 0.5 equiv. of LiTFSI, 0.03 equiv. of FK209 and 3.3 equiv. of TBP per mol of HTM.

Table S4. Individual photovoltaic characteristics of a batch of twelve PSC devices using *meso*-free Zn(II) porphyrin complex **3a** as HTM, and the corresponding mean values with standard deviations.^a

Device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
1	11.50	0.79	0.64	5.89
2	11.05	0.79	0.64	5.70
3	10.74	0.82	0.62	5.57
4	11.35	0.80	0.69	6.39
5	11.32	0.80	0.65	6.04
6	11.39	0.81	0.64	6.02
7	12.34	0.81	0.65	6.68
8	11.71	0.79	0.65	6.12
9	12.68	0.79	0.71	7.30
10	11.57	0.79	0.75	6.95
11	10.58	0.80	0.74	6.41
12	9.12	0.83	0.76	5.84
Mean	11.28	0.80	0.68	6.24
σ	0.86	0.01	0.05	0.50

^a the HTM precursor solution was prepared considering 0.5 equiv. of LiTFSI, 0.03 equiv. of FK209 and 3.3 equiv. of TBP per mol of HTM.

Table S5. Individual photovoltaic characteristics of a batch of twelve PSC devices using Zn(II)-dibrominated porphyrin **4a** as HTM, and the corresponding mean values with standard deviations.^a

Device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
1	8.15	0.79	0.71	4.68
2	7.48	0.77	0.73	4.27
3	9.52	0.74	0.67	4.85
4	8.37	0.78	0.69	4.62
5	7.95	0.76	0.70	4.31
6	9.67	0.83	0.71	5.80
7	9.66	0.81	0.72	5.71
8	8.88	0.80	0.72	5.23
9	9.85	0.74	0.75	5.55
10	8.28	0.75	0.71	4.50
11	8.03	0.77	0.73	4.58
12	7.38	0.77	0.76	4.39
Mean	8.60	0.78	0.72	4.87
σ	0.85	0.03	0.02	0.53

^a the HTM precursor solution was prepared considering 0.5 equiv. of LiTFSI, 0.03 equiv. of FK209 and 3.3 equiv. of TBP per mol of HTM.

Table S6. Individual photovoltaic characteristics of a batch of twelve PSC devices using Zn(II)-based porphyrin doubly functionalised with carbazole **5a** as HTM, and the corresponding mean values with standard deviations.^a

Device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
1	14.07	0.97	0.71	9.93
2	13.53	0.95	0.75	9.78
3	12.45	0.93	0.79	9.32
4	14.48	0.96	0.70	9.89
5	13.79	0.96	0.73	9.87
6	13.02	0.94	0.68	8.54
7	12.25	0.93	0.76	8.88
8	14.08	0.96	0.72	9.97
9	13.03	0.96	0.78	10.01
10	14.27	0.93	0.71	9.63
11	12.16	0.94	0.77	8.94
12	12.44	0.92	0.75	8.80
Mean	13.30	0.95	0.74	9.46
σ	0.81	0.02	0.03	0.51

^a the HTM precursor solution was prepared considering 0.5 equiv. of LiTFSI, 0.03 equiv. of FK209 and 3.3 equiv. of TBP per mol of HTM.

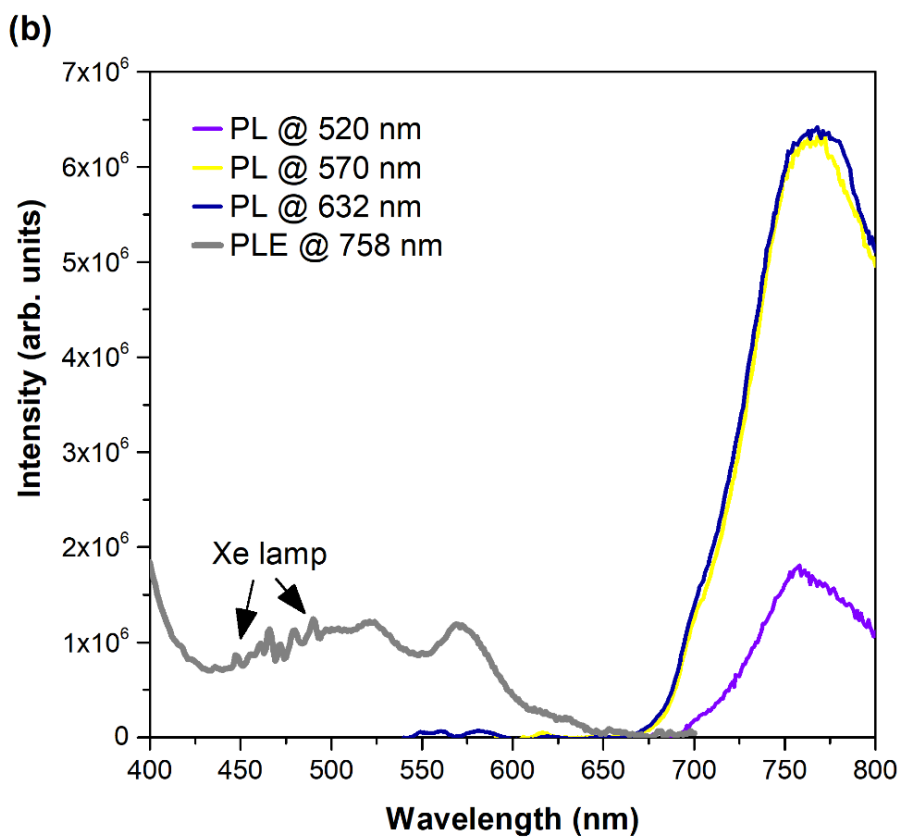
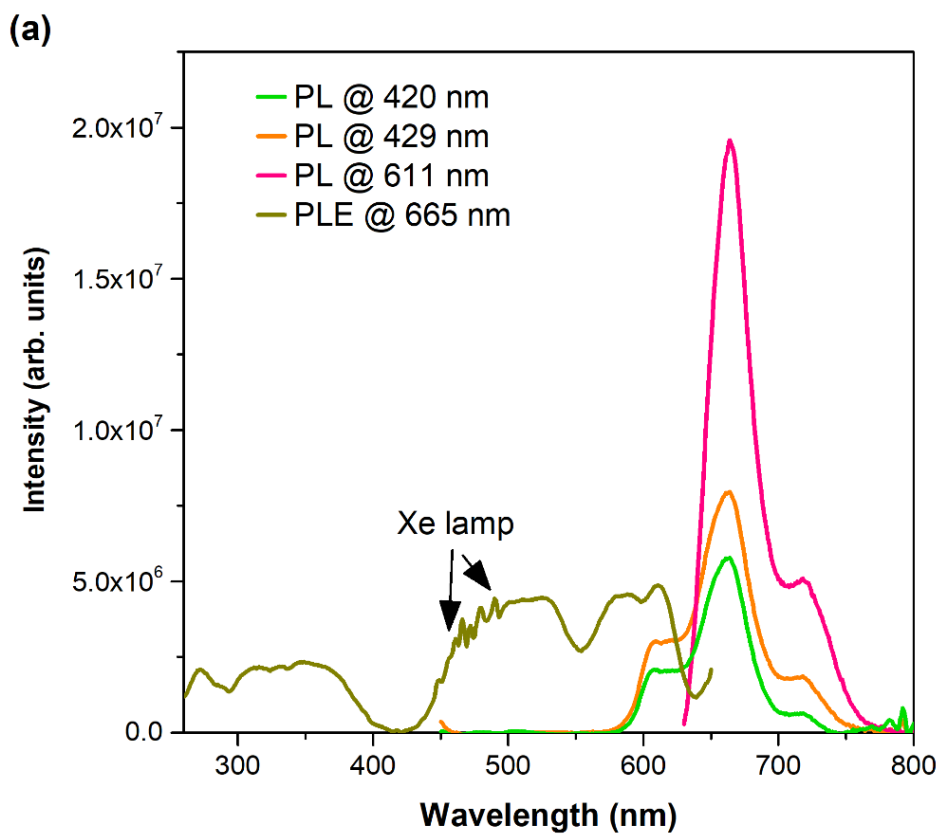


Figure S26. Photoluminescence at different excitation wavelengths and photoluminescence excitation of the powder (a) **5a** ($\lambda_{em} = 665$ nm) and (b) **5b** ($\lambda_{em} = 758$ nm).

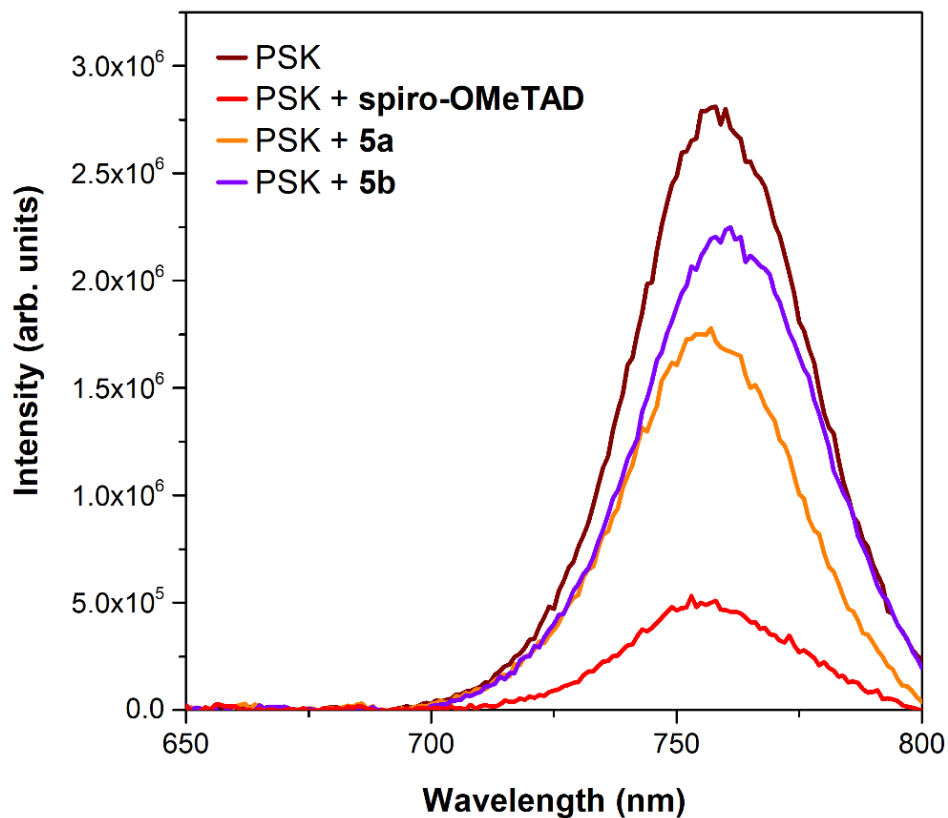


Figure S27. Photoluminescence under the excitation wavelength of 632 nm of perovskite-HTM films based on spiro-OMeTAD and porphyrin **5a** and **5b**, with the photo incidence placed on the glass substrate.

References

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- 2 J. W. Buchler, in *Porphyrins and Metalloporphyrins*, Smith KM. (Ed.). Elsevier: Amsterdam, 1975; Chapter 5, pp 157.
- 3 S. DiMugno, V. S. Y. Lin and J. M. Therien, *J. Org. Chem.*, 1993, **58**, 5983.