Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A stable *iso*-bacteriochlorin mimics from porpholactone: design, synthesis and optical property

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1. General information

Commercially available reagents were used without further purification. Deuterium solvents were stored with 4 Å molecular sieves.

UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrometer equipped with an Agilent 89090A thermostat (±0.1^{o}C).Fluorescence spectra were recorded on Edinburgh Instruments Ltd. FLS920 lifetime and steady state spectrometer at 293 K. IR spectra were recorded on a Bruker VECTOR22 FT-IR spectrometer as KBr pellets. ESI-MS were recorded on BrukerAPEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometerusing electrospray ionization. ^{1}H spectra were recorded on Bruker-400 MHz NMR. ^{19}F and ^{13}C NMR spectra were recorded on Bruker-500 MHz NMR. All ^{1}H NMR experiments were reported in δ units, parts per million (ppm), all coupling constants were in Hz and measured relative to the signal for residual chloroform (7.26 ppm) in the deuterated solvent $CDCl_3$. For ^{19}F NMR spectra, CF_3COOH was used as external reference at 0 ppm. Cyclic voltammetry experiments were recorded on Shanghai Chenhua CHI660C electrochemical workstation work, glassy carbon electrode was selected as working electrode, auxiliary electrode was platinum wire electrode and SCE (saturated calomel electrode) was reference electrode. All samples were recorded in dichloromethane with 0.1M $^{t}Bu_4NPF_6$ as electrolyte, the scan rate was 0.1 V s^{-1} and $E_{1/2}$were calculated basedon peak position for the internal standard $FeCp_2$ ($E_{1/2}$ = 0.45 V vs. SCE).

Computational studies were carried out by DFT method, which were implemented using Gaussian 09 Package. The geometry optimization and molecular orbitals of complexes **1a** and **2a** were calculated by B3LYP hybrid functional [1], and the double zeta polarized 6-31G* basis set[2] was employed for C, H, O, N and F atoms in the calculations. Unit of energies of molecular orbitals were converted from Hatree to eV.

Computational studies of Zn1a and Zn 2a were performed by Pro. Kobayashi, which were also implemented using Gaussian 09 Package with B3LYP functional and 6-31G* basis set.

Meso-tetrakispentafluorophenylporpholactone(H_2F_{20}TPPL,**1**) was synthesized according to the literature. [3]

Meso-tetrakispentafluorophenylporphyrin(H_2F_{20}TPP, **2**) was synthesized according to the literature.[4]

[1].Becke A. D., *J. Chem. Phys*. **1993**, *98*, 5648; Lee C, Yang W, Parr R. G., *Phys. Rev. B*, **1998**, *37*, 785;

[2]. Rassolov V. A., Ratner M. A., Pople J. A., Redfern P. C., Curtiss L. A.,*J.Comput.Chem.*,**2001**, *22*, 976.

[3]. Yi Yu,HongbinLvand Jun-Long Zhang, *Adv. Synth.Catal.*,**2012**, *354*, 3509 – 3516;

[4]. J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, **1989**, *54*, 828-836;

2. Synthetic section

2.1 Synthesis of *adjacent*-dihydroporpholactone **(1a)**

To a mixture of meso-tetrakispentafluorophenylporpholactone (0.1mmol, 100mg) and Woollins' Reagent (0.1mmol, 53mg) in Schlenk tube, 7 mL toluene and Me_2PhSiH (0.25mmol, 38 μL) were added in golovebox. The solution was heated to reflux for 3 days under nitrogen. The solvent was removed by rotary evaporation and the residue was purified through silica column to give product **1a** with isolated yield of 40%. Eluent: CH_2Cl_2: petroleum ether, 1:8.

2.2 Synthesis of tetrahydroporphyrin (**2a**)

To a mixture of meso-tetrakispentafluorophenylporphyrin (0.1 mmol, 97 mg) and Woollins' Reagent (0.1mmol, 53mg) in Schlenk tube, 7 mL toluene and Me_2PhSiH (10 mmol, 1.5 mL) were added in golovebox. The solution was heated to reflux for 3 days under nitrogen. The solvent was removed by rotary evaporation and the residue was purified through silica column to give product **2a** with isolated yield of 70%. Eluent: CH_2Cl_2: petroleum ether, 1:5.

2.3 Synthesis of **Zn 1a** and **Zn 2a**

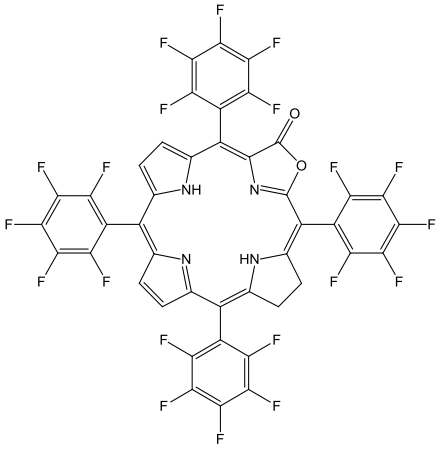
General method: ligands (0.1 mmol) was refluxed with 10 equivalents of $Zn(OAc)_2$ (1 mmol, 180 mg) in a mixed solvent ($MeOH:CHCl_3$=1:1) under nitrogen for 5 hours. The solvent was removed by rotary evaporation and the residue was purified through silica column avoiding strong light. Isolated yields of **Zn 1a**and **Zn 2a** were all over 90%. Eluent: ethyl acetate: petroleum ether, 1:4.

2.4 Synthesis of **1a NPs**

PLGA-NP loaded with **1a** were prepared by modified literature method: adding 5μmol **1a**and 10 mgPLGA（PLGA, Daigang Biomaterial Co., Ltd., Jinan, China) into1 mL dichloromethane, the primary solution was added to 10 mL aqueous poly(vinyl alcohol) (PVA,2.5wt% in deionized water; MW 30,000-70,000 Da from Sigmae Aldrich) dropwise, then sonicated for 40 s at 4^{o}C, the mixturewas stirred overnight to evaporate the organic solvent, forming **1a**-loaded PLGA-NP. After removing large particles by centrifugation at 5000 rpm for 30 min, the particles were collected by ultracentrifugation at 19,000 rpm for 30min,washed three times to remove non-entrapped PVA, and then filtered to get **1aNPs**.

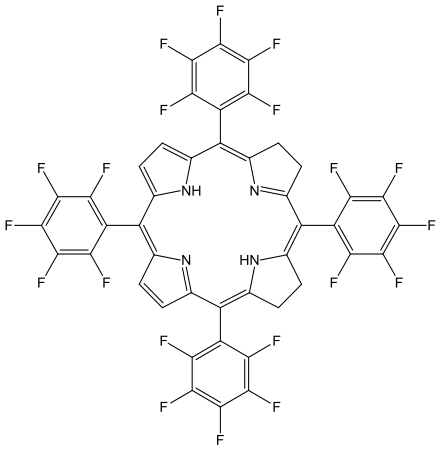
2.5 Characterization information

■ *adjacent*-Dihydroporpholactone **(1a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ=7.74 (d, *J* = 4.8 Hz , 1H), 7.54 (s, 2H), 7.28 (d, *J* = 4.8 Hz, 1H), 4.86 (s, 1H), 3.97 (s, 1H), 3.83 (m, 2H), 3.74 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ = -57.93 (dd, *J*=22.3, 7.1, 2F), -58.15 (dd, *J*=23.4, 8.2, 2F), -58.34 (dd, *J*=23.3, 7.5, 2F), -59.35 (dd, *J*=22.9, 7.2, 2F), -71.47 (t, *J*=20.8, 1F), -71.81 (dt, *J*=34.1, 20.8, 2F), -72.10 (t, *J*=20.8, 1F), -80.44 (td, *J*=22.9, 8.1, 2F), -80.80 (dt, *J*=22.5, 7.3, 2F), -81.02 (dt, *J*=21.7, 6.8, 2F), -81.73 (dt, *J*=22.1, 7.1, 2F).^{13}C NMR (125MHz, $CDCl_3$):δ = 164.62, 161.76, 158.63, 157.55, 153.83, 150.63, 146.47, 144.46, 135.93, 135.41, 134.69, 130.85, 128.68, 123.08, 121.74, 113.78, 112.14, 109.29, 95.52, 83.37, 68.18, 31.93, 31.35, 30.29, 29.70, 29.35, 28.94, 23.78, 22.98, 22.68, 14.06, 1.01, -0.03. UV−vis(CH_2Cl_2) λ_{max}, nm(logε) 361(4.96), 380(5.02), 414(4.38), 496(3.73), 533(4.12), 573(4.39); fluorescence (CH_2Cl_2) λ_{max}, nm 582, 628, ϕ = 0.47, τ= 3.88 ns; IR (cm^{-1}) : 989, 1265,1325, 1501, 1527, 1603, 1780 (C=O); ESI-MS m/z $[M + H]^+$: Calcd. for C43H11F20N4O2+ 995.05572, found 995.05433.

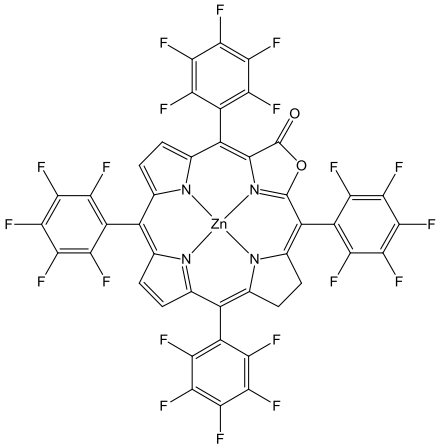
■ Tetrahydroporphyrin (**2a**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 4.4 Hz, 2H), 7.01 (d, *J* = 4.4 Hz, 2H), 4.85 (s, 2H), 3.44 (d, *J* = 3.8 Hz, 8H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.45 (dd, *J* = 23.2, 7.7 Hz), -60.83 (dd, *J* = 23.6, 8.1 Hz), -61.22 (dd, *J* = 24.1, 8.3 Hz), -74.64 (t, *J* = 20.8 Hz), -75.06 (t, *J* = 20.8 Hz), -75.54 (t, *J* = 20.8 Hz), -82.23 (td, *J* = 23.7, 8.4 Hz), -83.38 (td, *J* = 23.4, 8.2 Hz), -83.98 (dt, *J* = 22.8, 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.11, 156.53, 154.55, 152.13, 152.13, 146.18, 144.22, 138.99, 137.05, 131.44, 128.36, 120.51, 114.91, 113.04, 111.34, 102.79, 97.04, 92.49, 91.66, 36.23, 34.31, 31.94, 30.13, 29.98 – 29.54, 29.36, 28.87, 22.69, 14.07, 1.02, -0.06. UV−vis(CH_2Cl_2) λ_{max}, nm (logε) 345(4.51), 361(4.70),

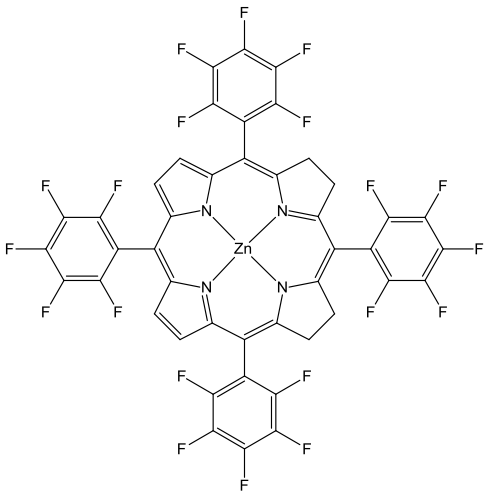
378(4.81), 402(4.50), 510(3.85), 548(4.05), 591(4.24); fluorescence (CH_2Cl_2) λ_{max}, nm 603, 640, ϕ = 0.55, τ=5.63 ns; IR (cm^{-1}): 987, 1038, 1207, 1328, 1497, 1520, 1587; ESI-MS m/z $[M + H]^+$: Calcd. For C44H15F20N4+ 979.09719, found 979.09839.

- Zinc(II) *adjacent*-dihydroporpholactone **(Zn 1a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 4.6 Hz, 1H), 7.86 (dd, *J* = 18.3, 4.4 Hz, 2H), 7.61 (d, *J* = 4.6 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.88 – 3.81 (m, 2H).^{19}F NMR (377 MHz, $CDCl_3$) δ -138.06 (dd, *J* = 23.3, 7.7 Hz), -138.44 (ddd, *J* = 32.3, 23.8, 8.0 Hz), -139.37 (dd, *J* = 23.5, 7.6 Hz), -152.43 (dt, *J* = 35.4, 20.9 Hz), -152.77 (t, *J* = 20.9 Hz), -152.97 (t, *J* = 20.9 Hz), -160.91 (td, *J* = 23.8, 8.4 Hz), -161.14 (td, *J* = 23.6, 8.0 Hz), -161.61 (dt, *J* = 23.2, 7.8 Hz), -162.31 (dt, *J* = 23.3, 7.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.12, 191.46, 171.33, 165.33, 164.94 , 164.94, 164.94, 161.86, 155.91 , 154.76, 147.48, 146.78, 145.36, 145.06, 144.85, 142.90, 140.91, 139.30, 138.55, 137.15, 132.79, 127.75 , 125.81, 125.59, 122.72, 116.53 – 114.86, 112.56, 112.01, 107.80, 100.54, 96.18, 81.27, 70.03, 52.94, 36.68, 34.05, 32.94, 31.18, 29.85, 28.35, 24.77, 22.84, 14.25, 0.13. UV−vis(CH_2Cl_2) λ_{max}, nm (logε) 392 (4.89), 408(5.03), 499 (3.62), 529 (3.46), 570(3.91),618(4.58); fluorescence (CH_2Cl_2) λ_{max}, nm 628, 676, ϕ = 0.13,τ=0.70 ns; ESI-MS m/z $[M + DMSO + H]^+$: Calcd. forC45H15F20N4O3SZn+ 1134.98315, found 1134.98718.

- Zinc(II) tetrahydroporphyrin (**Zn 2a**)



^{1}H NMR (300 MHz, cdcl$_3$) δ 7.68 (d, *J* = 4.4 Hz, 2H), 7.19 (d, *J* = 4.3 Hz, 2H), 3.55 (s, 8H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.60 (d, *J* = 17.9 Hz), -138.74 – -139.04 (m), -139.21 (dd, *J* = 24.2, 7.6 Hz), -152.98 (t, *J* = 20.9 Hz), -153.62 (t, *J* = 20.9 Hz), -153.97 (t, *J* = 20.8 Hz), -160.18 – -160.47 (m), -161.38 – -161.65 (m), -162.18 (t, *J* = 18.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.54, 159.18, 152.08, 141.83,

132.79, 132.13, 129.24, 129.08, 120.94, 97.61, 90.77, 60.56, 36.48, 34.60, 33.33, 30.94, 29.72, 22.71, 14.11, 13.86, 1.04, -0.00.UV−vis(CH_2Cl_2) λ_{max}, nm (logε) 369(4.70), 387(4.85), 403(5.00), 520(3.70), 558(4.00), 603(4.67); fluorescence (CH_2Cl_2) λ_{max}, nm 608, 663, ϕ = 0.08,τ=1.08 ns; ESI-MS m/z [M + H]$^+$: Calcd. ForC44H13F20N4Zn+ 1041.94834, found 1042.01799.

3. DFT calculation

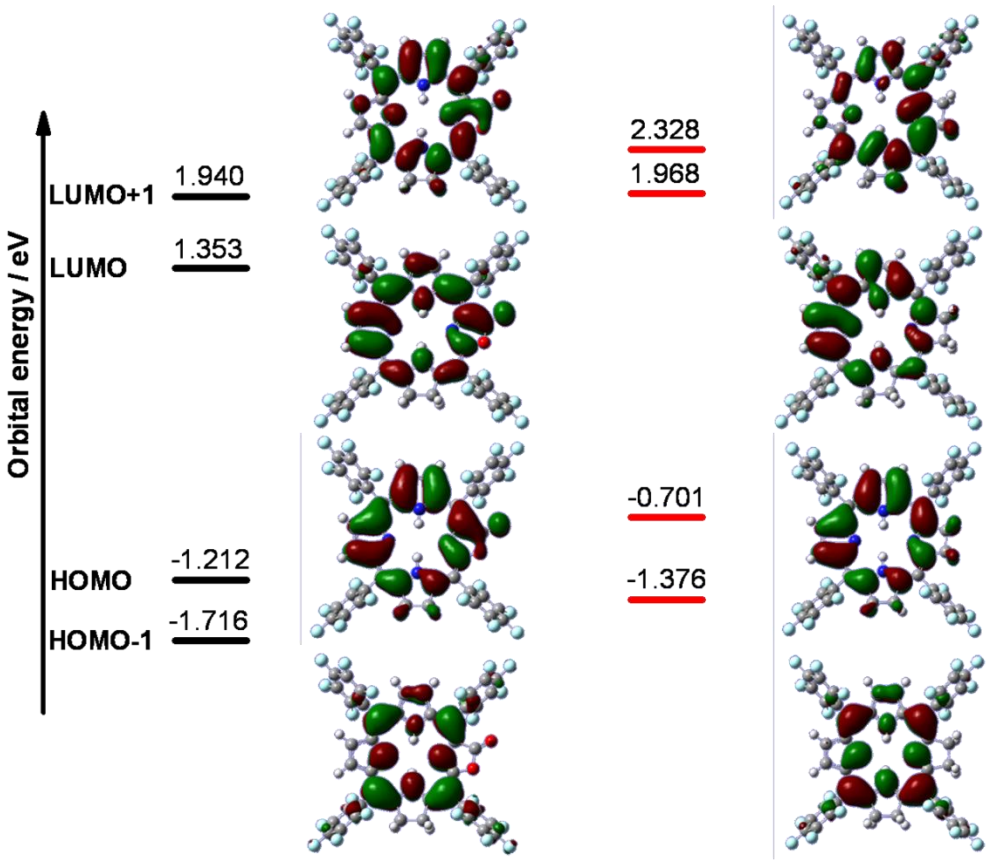


Figure S1. Molecular orbital and orbital energy diagram of **1a** (left) and **2a** (right).

4. UV-*vis* spectra

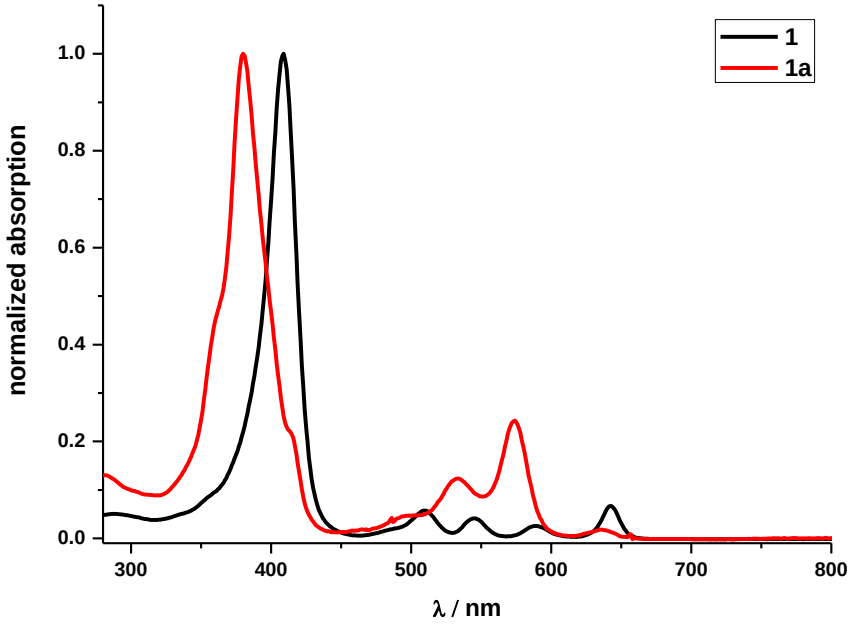


Figure S2. Normalized absorption of **1** and **1a** DCM.

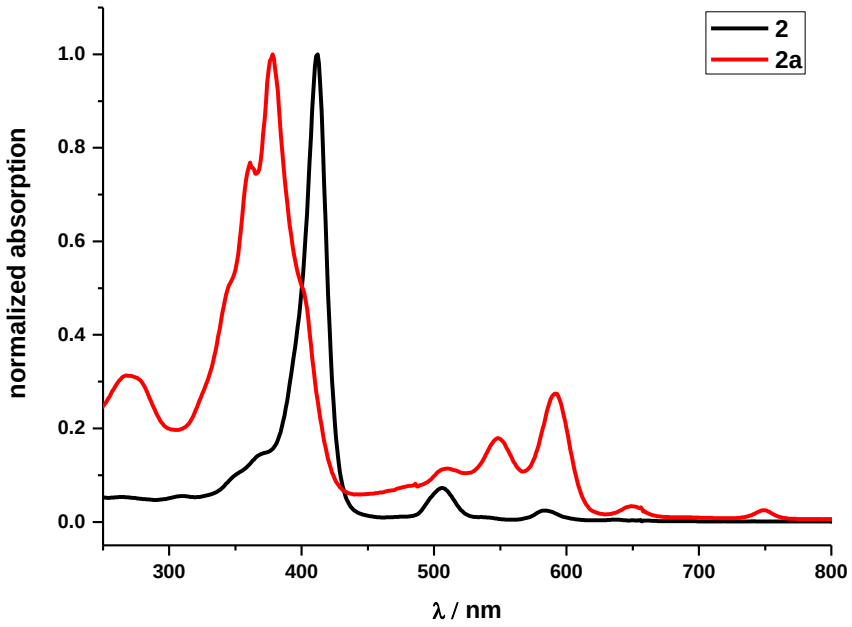


Figure S3. Normalized absorption of **2** and **2a** in DCM.

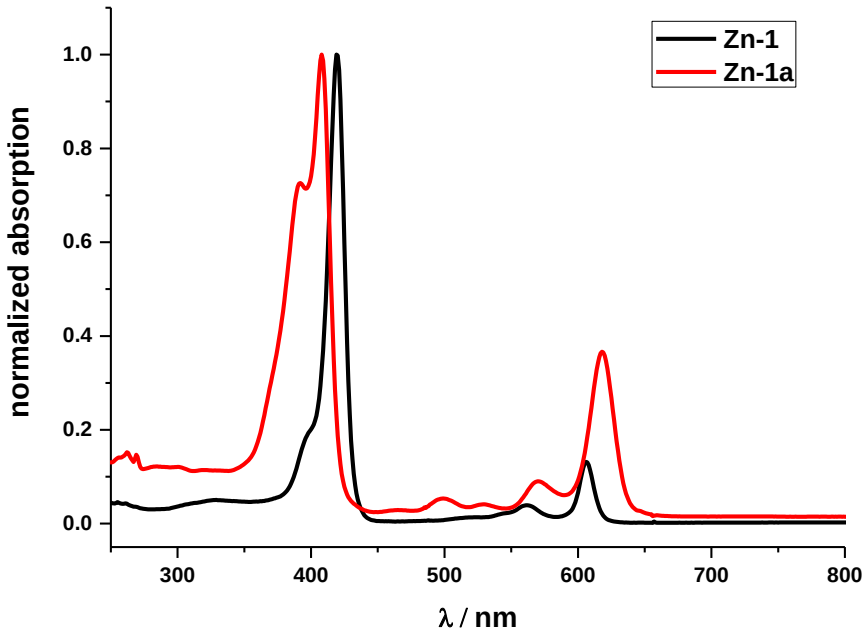


Figure S4. Normalized absorption of **Zn-1** and **Zn-1a** in DCM.

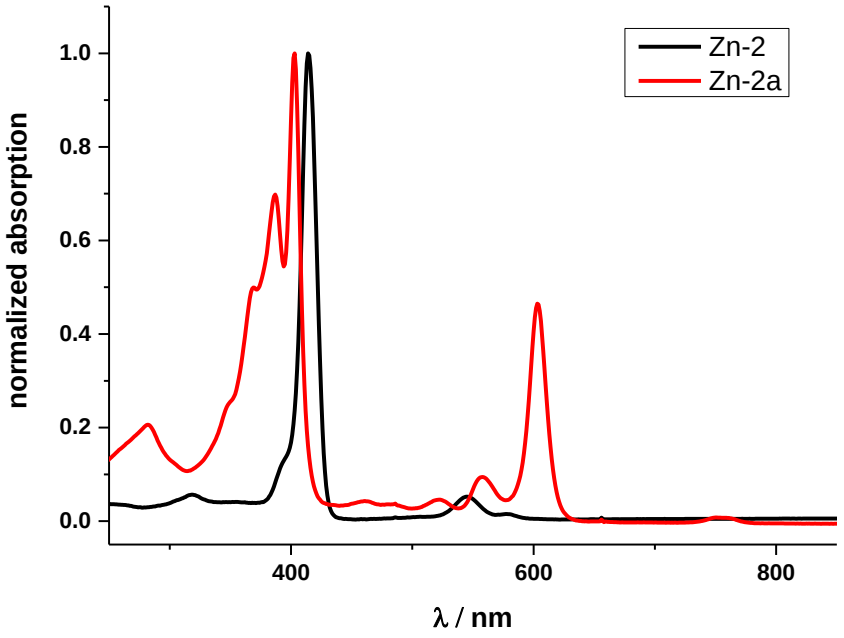


Figure S5. Normalized absorption of **Zn-2** and **Zn-2a** in DCM.

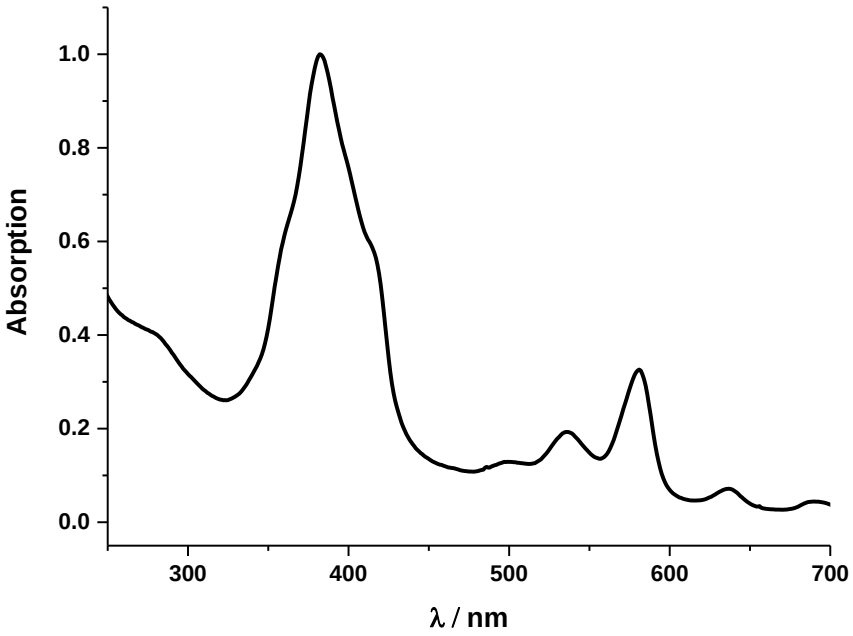


Figure S6. Normalized absorption of **1a-NPs** in H_2O.

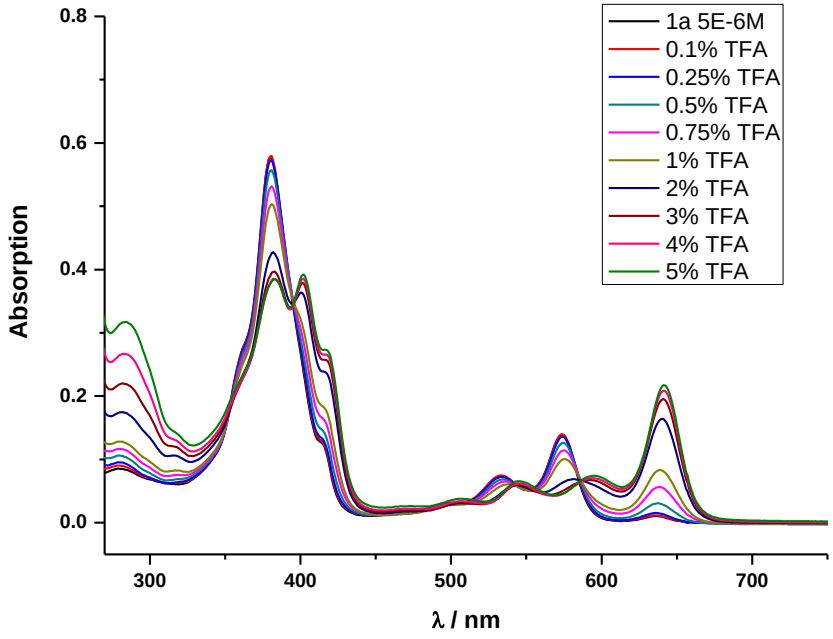


Figure S7. Titration of TFA into DCM solution of **1a** (5×10^{-6}M).

5. Fluorescence spectra

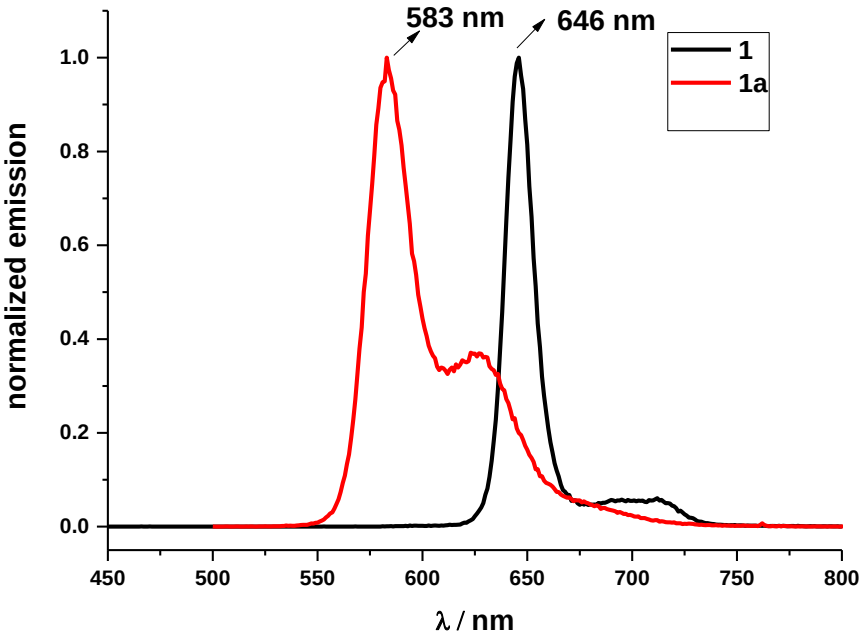


Figure S8. Normalized emission of **1** and **1a** in DCM.

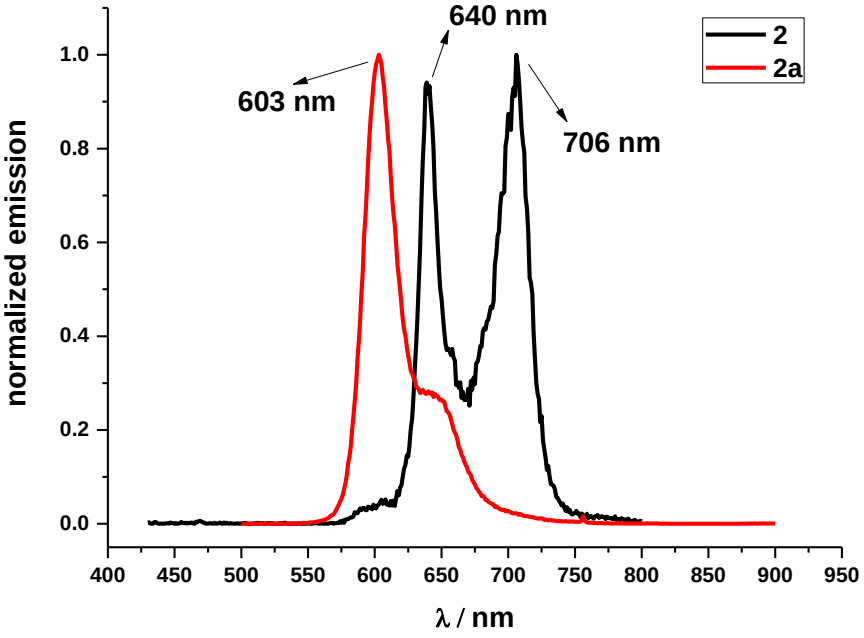


Figure S9. Normalized emission of **2** and **2a** in DCM.

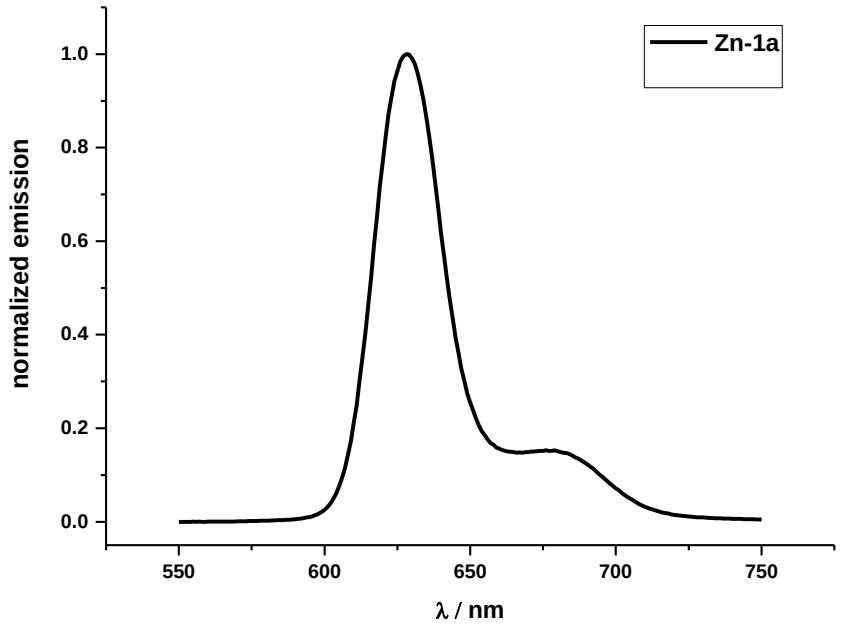


Figure S10. Normalized emission of **Zn-1a** in DCM.

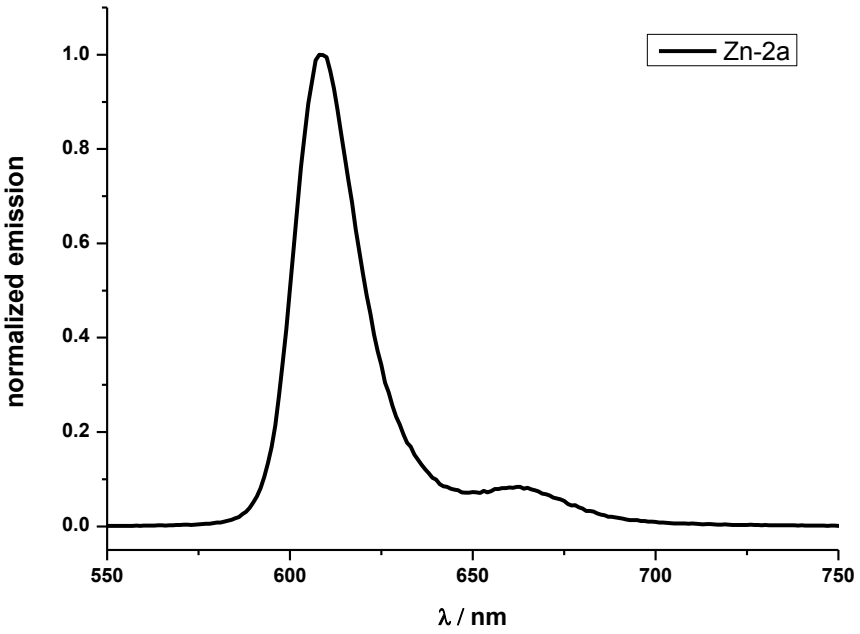


Figure S11. Normalized emission of **Zn-2a** in DCM.

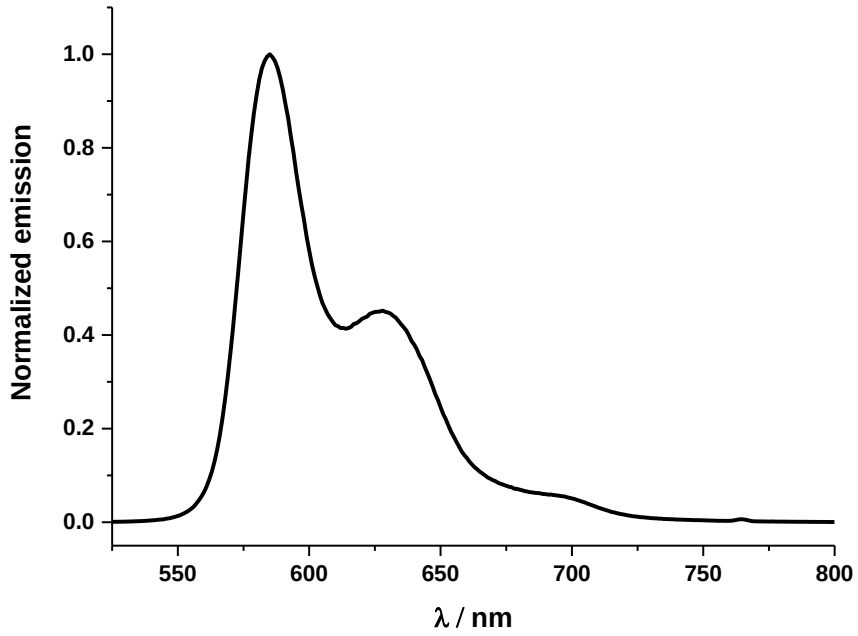


Figure S12. Normalized emission of **1a-NPs** in H_2O.

6. Cyclic voltammetry

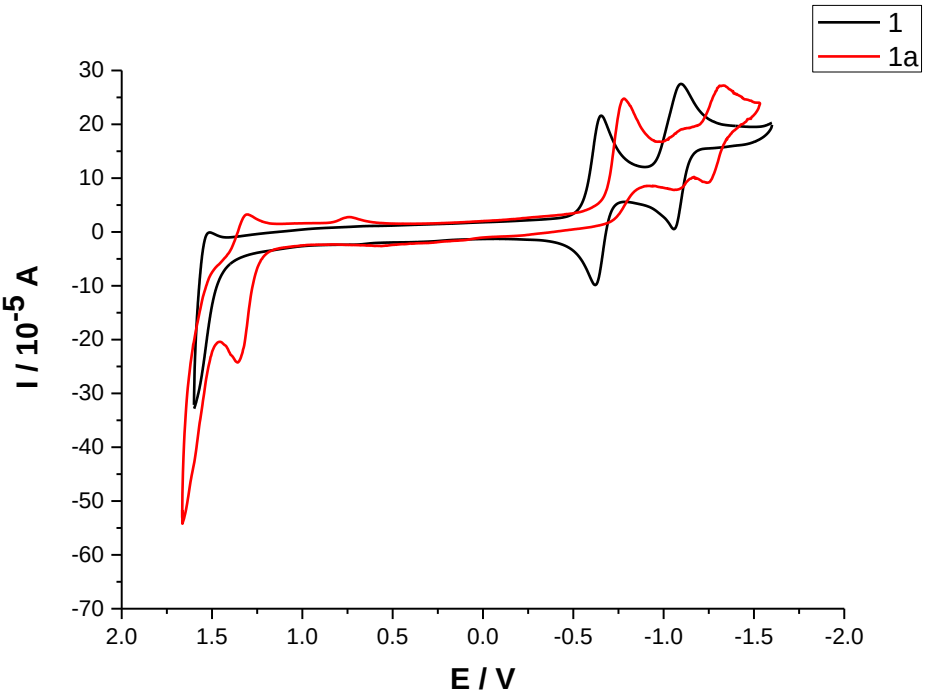


Figure S13. Cyclic voltammograms of **1** and **1a**.

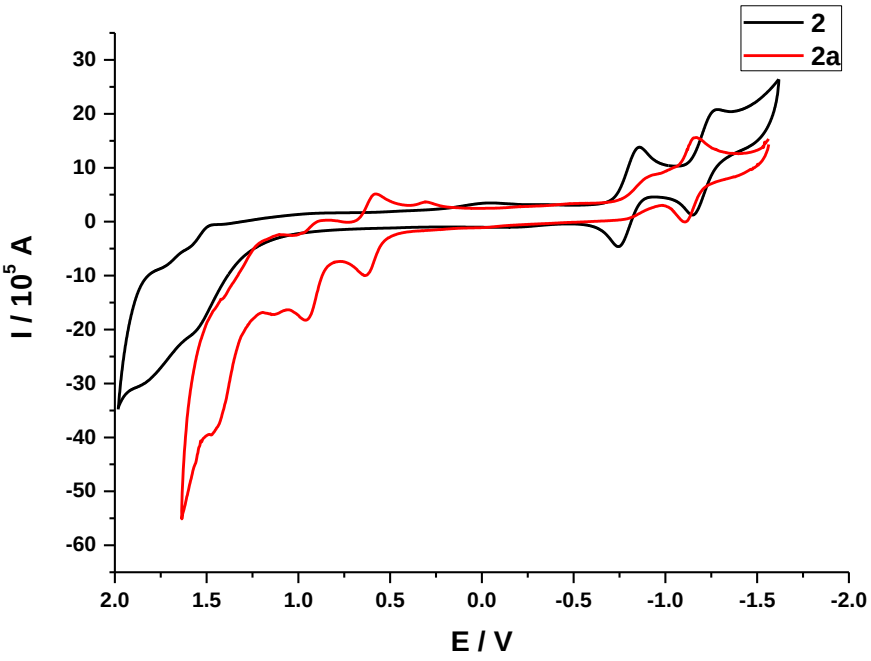


Figure S14. Cyclic voltammograms of **2** and **2a**.

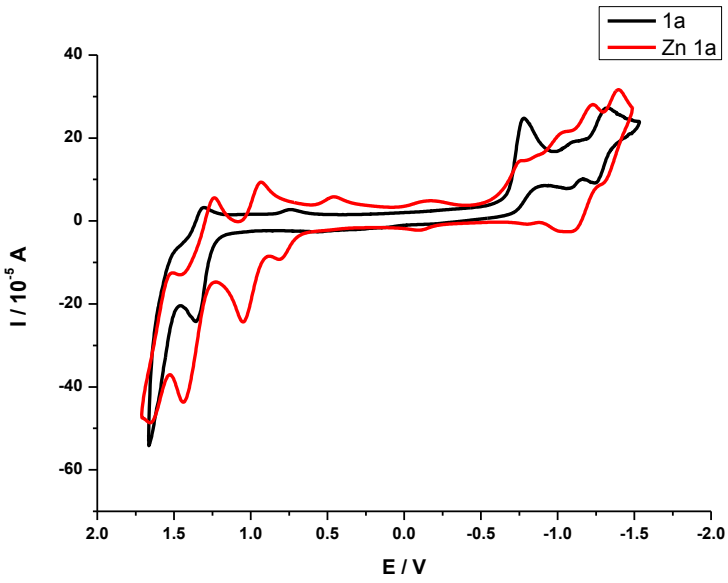


Figure S15. Cyclic voltammograms of **1a** and **Zn-1a**.

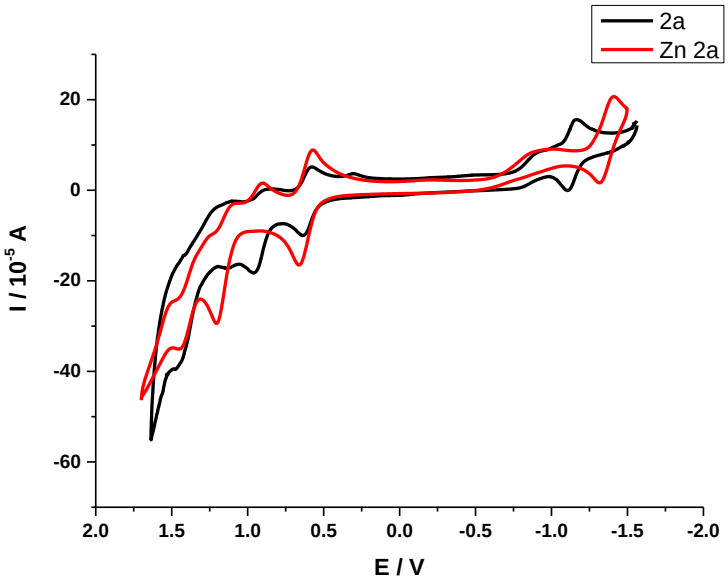


Figure S16. Cyclic voltammograms of **2a** and **Zn-2a**.

Table S1. Photophysical, parameters, electrochemical parameters and calculation results of **1**, **1a**, **Zn1a**, **2**, **2a** and **Zn2a**.

Parameters	**1**	**1a**	**Zn-1a**	**2**	**2a**	**Zn-2a**
Soret bands/nm ($\log\varepsilon/cm^{-1}M^{-1}$)	409(5.18)	361(4.69), 380(5.02), 414(4.38)	392(4.89), 408(5.03)	411(5.14)	345(4.51), 361(4.70), 378(4.81), 402(4.50)	369(4.70), 387(4.85), 403(5.00)
Q bands/nm ($\log\varepsilon/cm^{-1}M^{-1}$)	510(3.95), 545(3.81), 589(3.60), 642(4.03)	496(3.73), 533(4.12), 573(4.39)	499(3.62), 529(3.46), 570(3.91), 618(4.58)	506(3.98) 540(2.96) 582(3.46) 636(2.38)	510(3.85), 548(4.05), 591(4.24)	520(3.70), 558(4.00), 603(4.67)
Emissions/nm	646	582	628	641 707	603	608
Φ_F	0.13	0.47	0.13	0.04	0.55	0.08
τ_{Fl}/ns	6.37	3.88	0.70	6.53	5.63	1.08
k_r/s^{-1}	2.0×10^7	1.2×10^8	1.9×10^8	6.1×10^6	9.8×10^7	7.4×10^7
k_{nr}/s^{-1}	1.3×10^8	1.4×10^8	1.2×10^9	1.5×10^8	8.0×10^7	8.5×10^8
$E^{1/2}_{ox}$/V	1.70	1.33	0.99	1.53	0.92	0.62
$E^{1/2}_{re}$/V	-0.59	-0.78	-1.16	-0.80	-1.13	-1.36
$E^{1/2}_{ox}$-$E^{1/2}_{re}$/V	2.29	2.11	2.15	2.33	2.05	1.98
LUMO+1/eV	1.415	1.940		1.534	2.328	
LUMO/eV	1.118	1.353		1.486	1.968	
HOMO/eV	-1.522	-1.212		-1.307	-0.701	
HOMO-1/eV	-1.637	-1.716		-1.422	-1.376	
Δ(LUMO-HOMO)/eV	2.640	2.565		2.793	2.667	

7. ESI-MS spectra

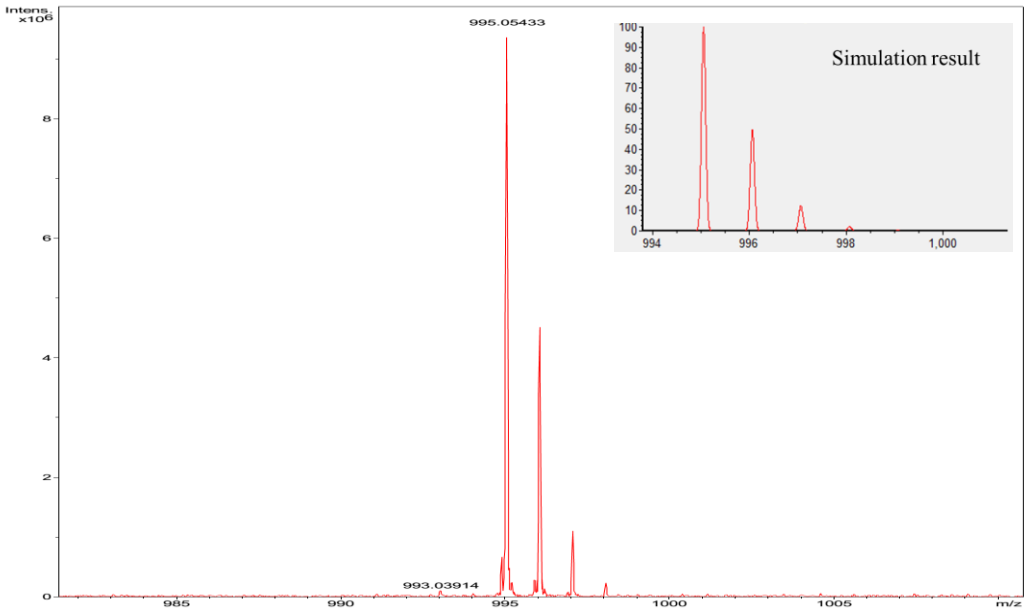


Figure S17. HR-MS(ESI) of **1a**.

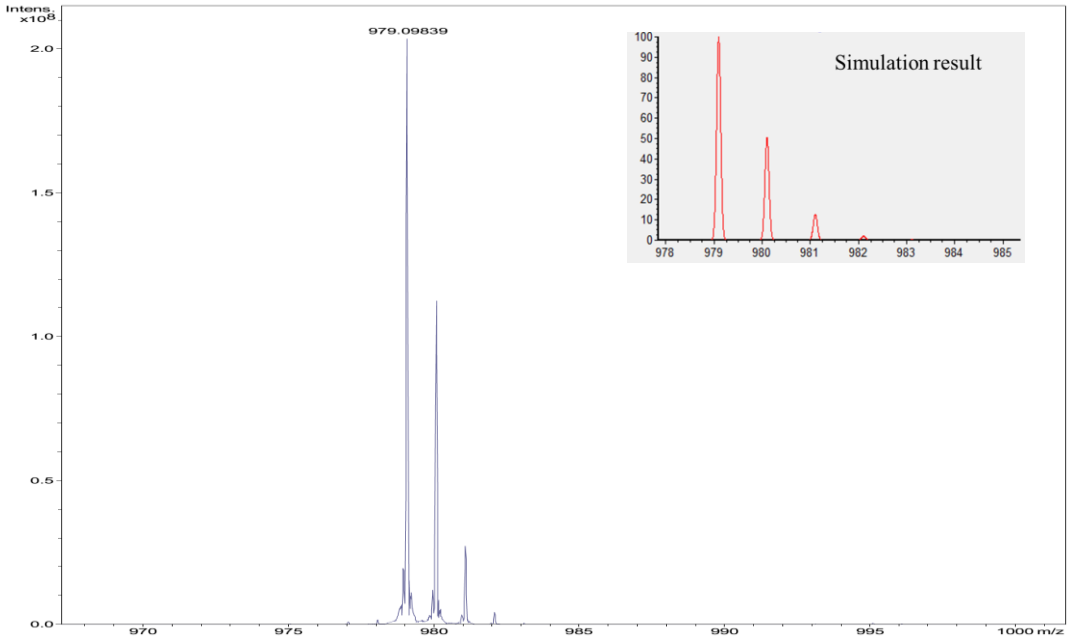
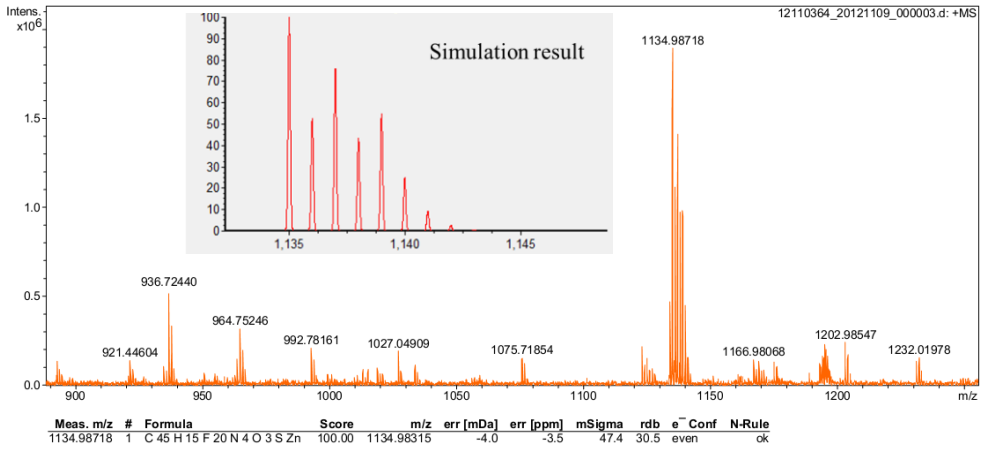
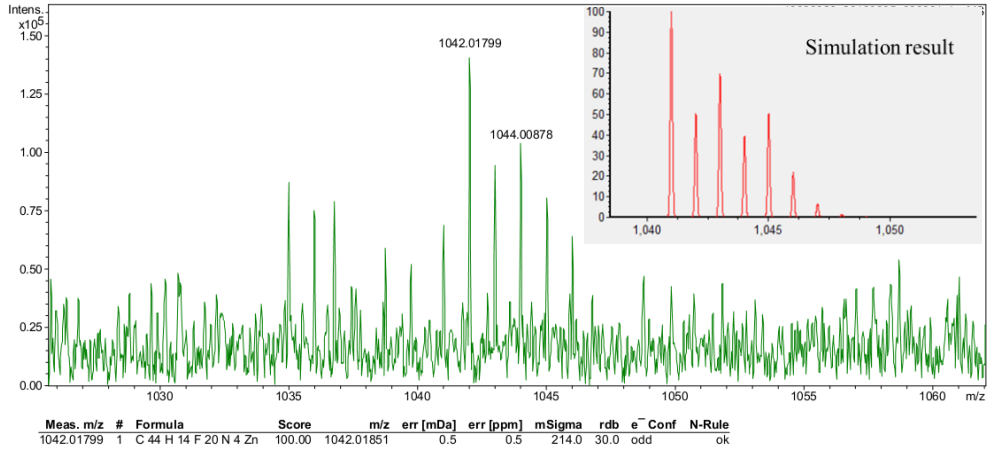


Figure S18. HR-MS(ESI) of **2a**.



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1134.98718	1	C 45 H 15 F 20 N 4 O 3 S Zn	100.00	1134.98315	-4.0	-3.5	47.4	30.5	even	ok

Figure S19. HR-MS(ESI) of **Zn-1a**.



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1042.01799	1	C 44 H 14 F 20 N 4 Zn	100.00	1042.01851	0.5	0.5	214.0	30.0	odd	ok

Figure S20. HR-MS(ESI) of **Zn-2a**.

8. FT-IR spectra

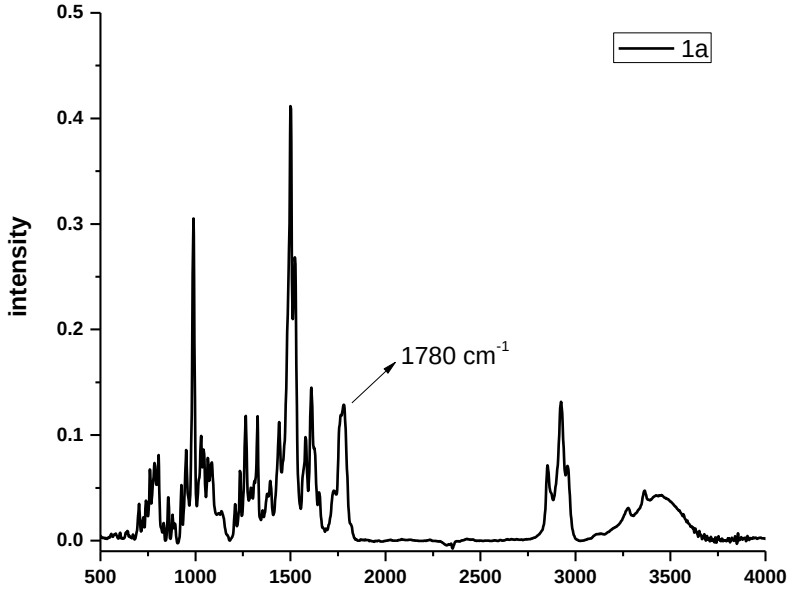


Figure S21. FT-IR spectra of **1a**.

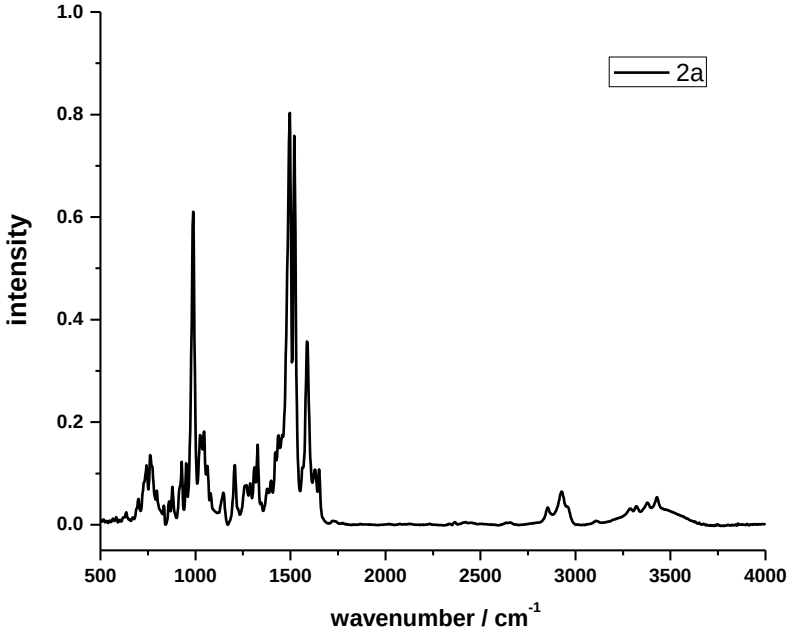


Figure S22. FT-IR spectra of **2a**.

9. ^{1}H, ^{19}F, ^{13}C and 2D NMR spectra

9.1 ^{1}H NMR

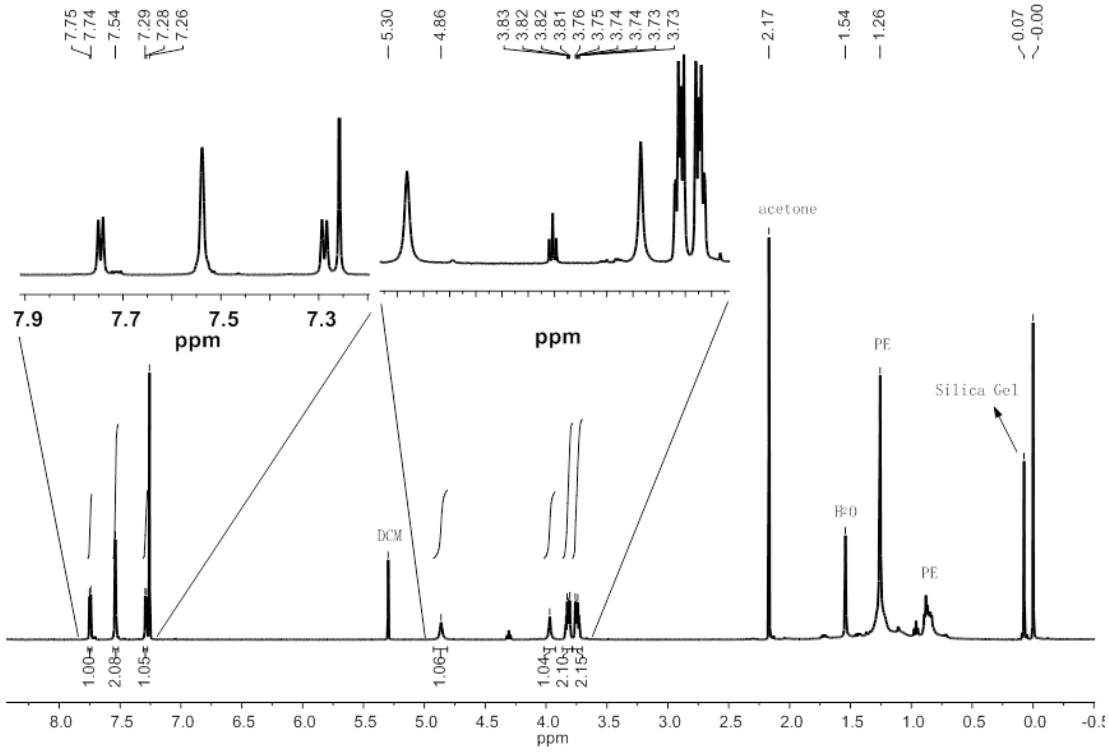


Figure S23. ^{1}H NMR spectra of **1a** in $CDCl_3$.

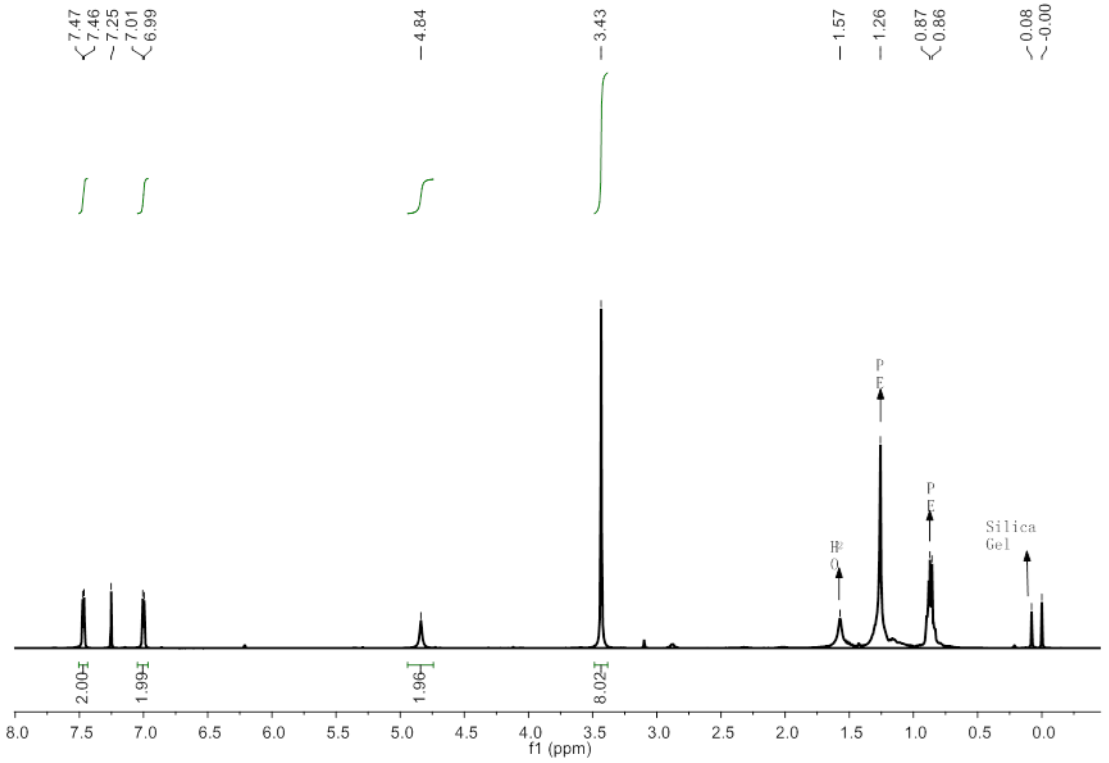


Figure S24. ^{1}H NMR spectra of **2a** in $CDCl_3$.

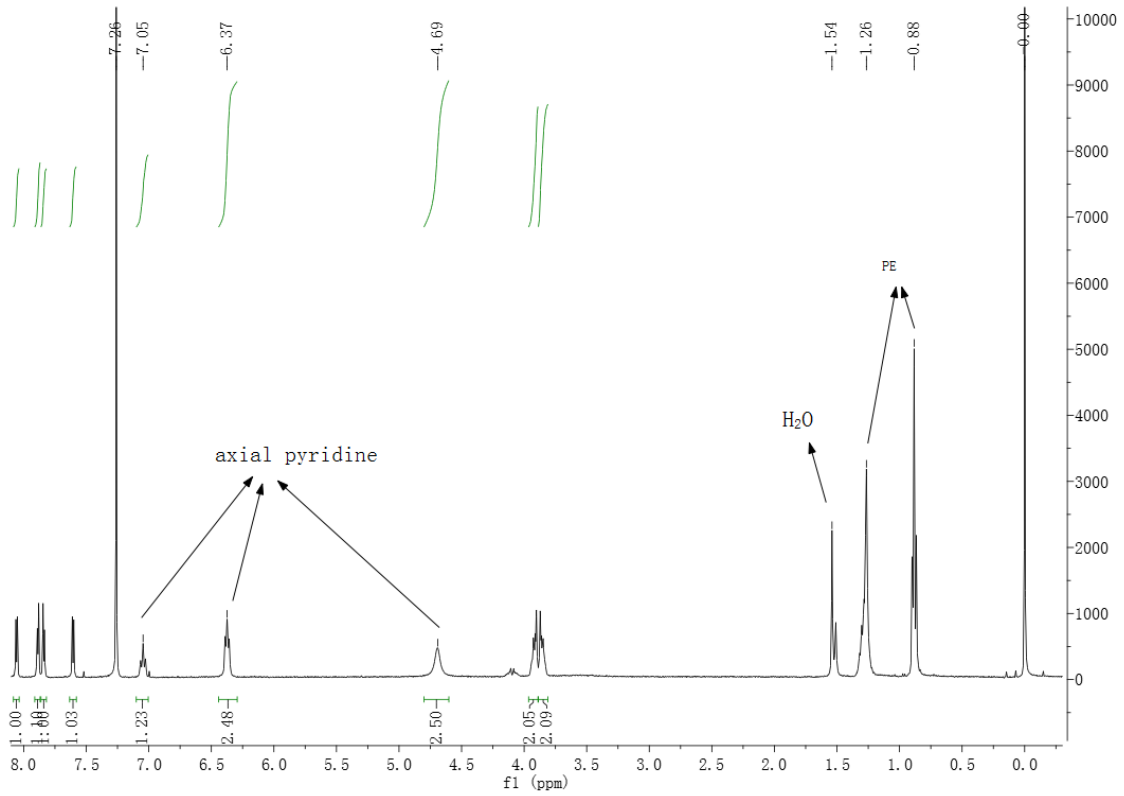


Figure S25. ^{1}H NMR spectra of **Zn-1a** in $CDCl_3$.

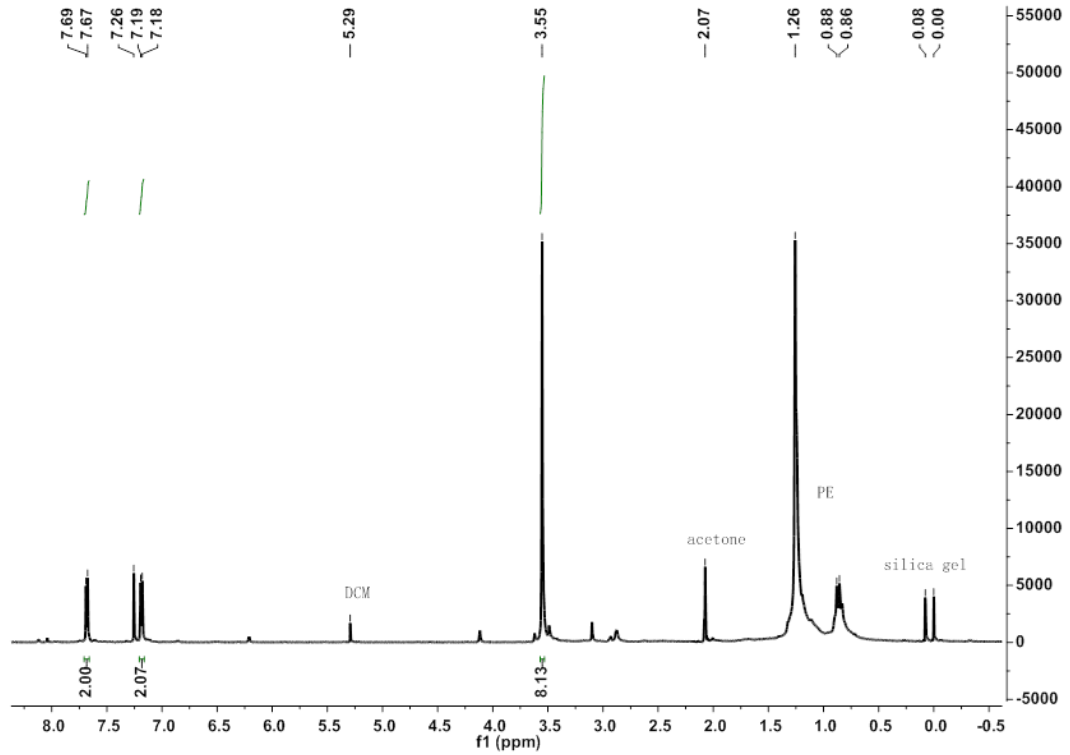


Figure S26. ^{1}H NMR spectra of **Zn-2a** in $CDCl_3$.

9.2 ^{19}F NMR

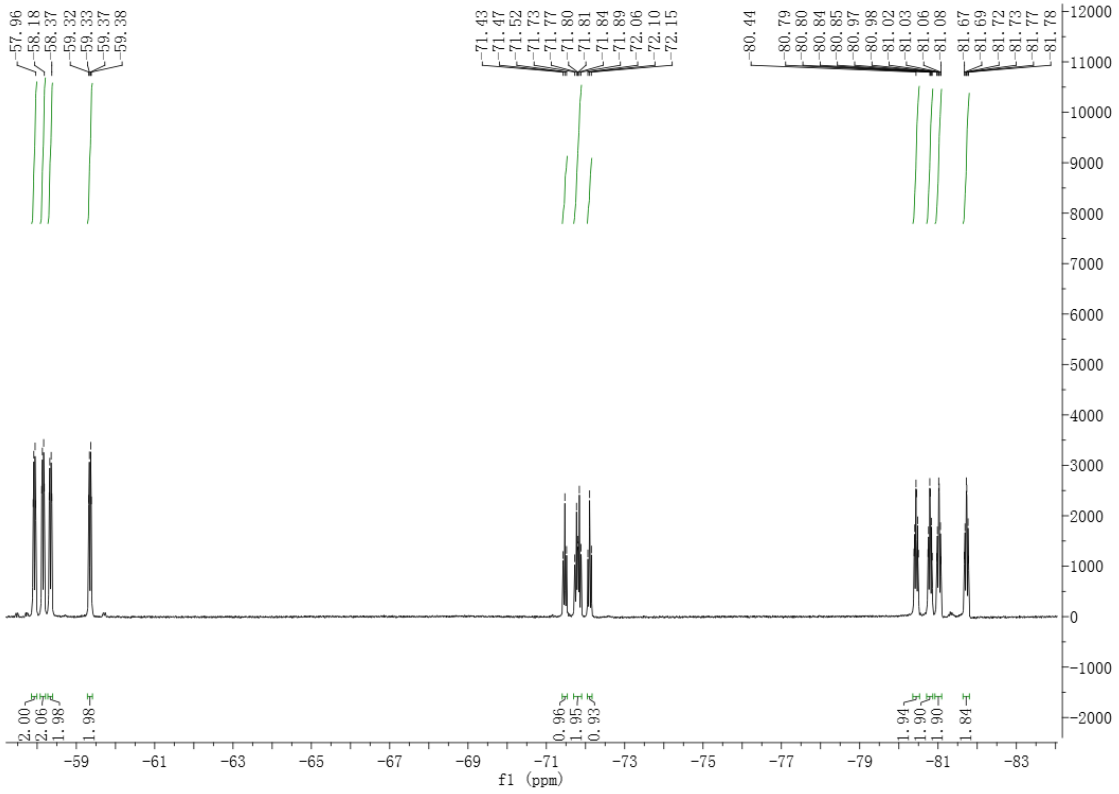


Figure S27. ^{19}F NMR spectra of **1a** in $CDCl_3$, CF_3COOH as external reference.

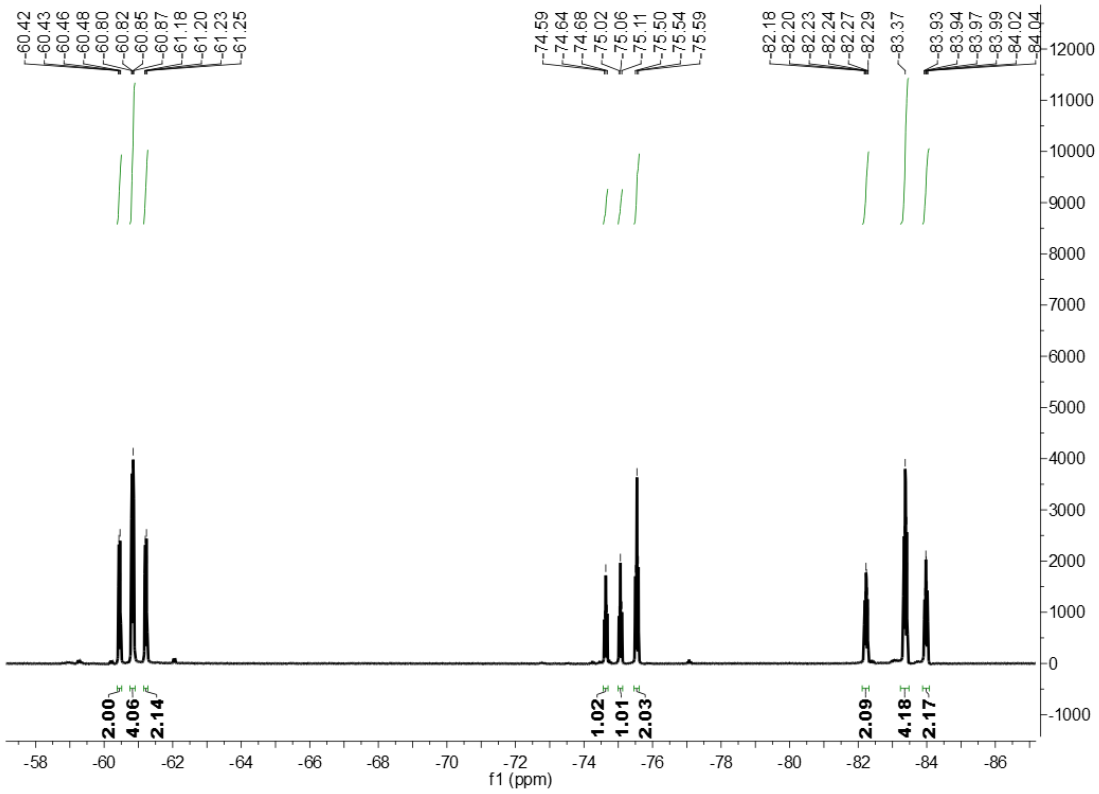


Figure S28. ^{19}F NMR spectra of **2a** in $CDCl_3$, CF_3COOH as external reference.

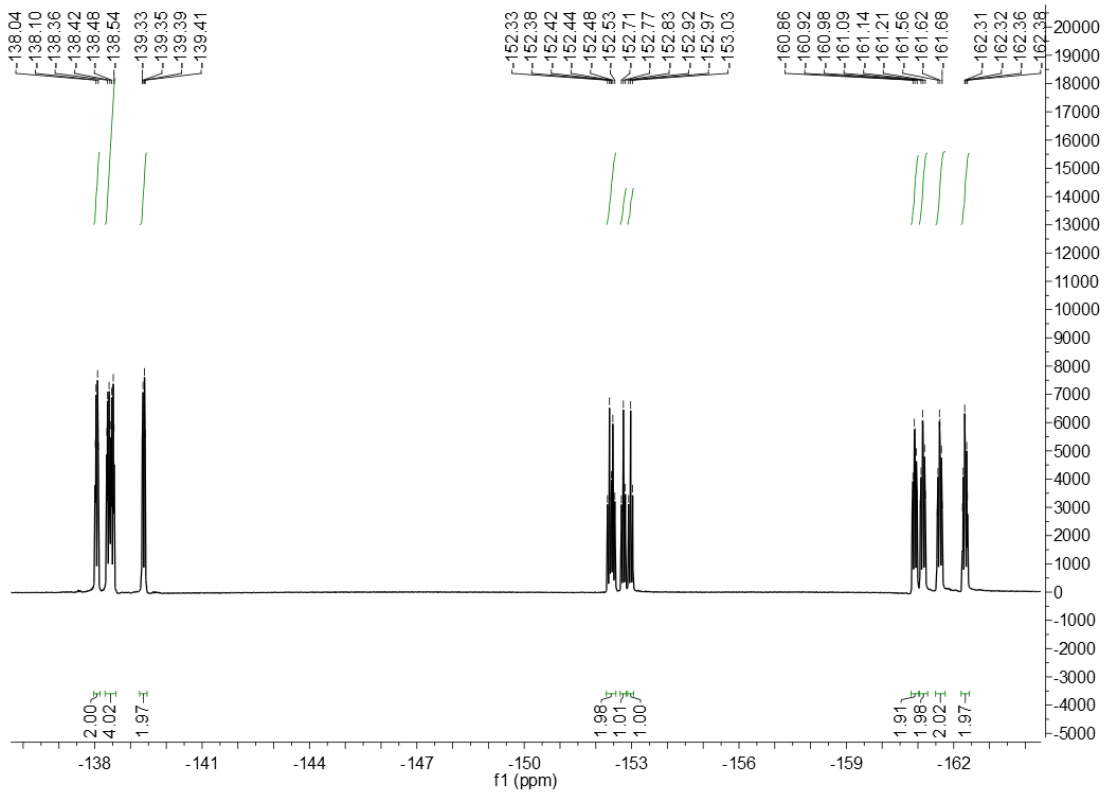


Figure S29. ^{19}F NMR spectra of **Zn-1a** in $CDCl_3$, CF_3COOH as external reference.

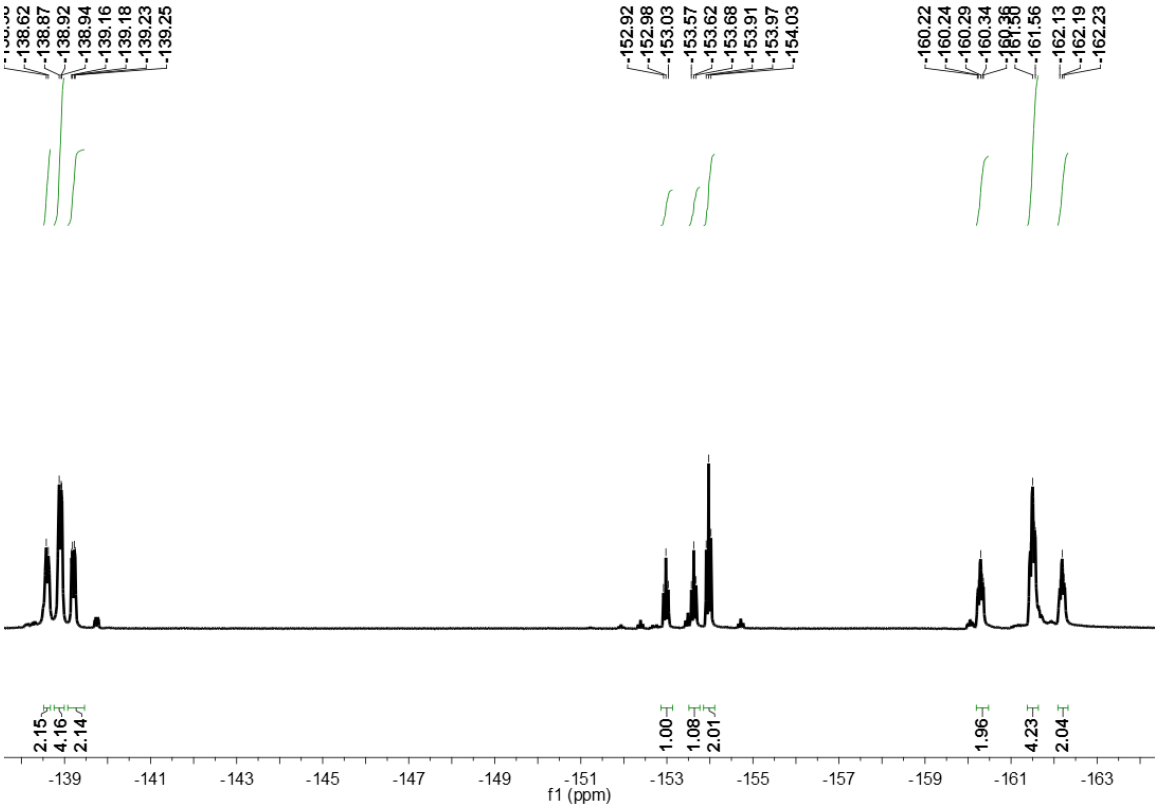


Figure S30. ^{19}F NMR spectra of **Zn-2a** in $CDCl_3$, CF_3COOH as external reference.

9.3 ^{13}C NMR

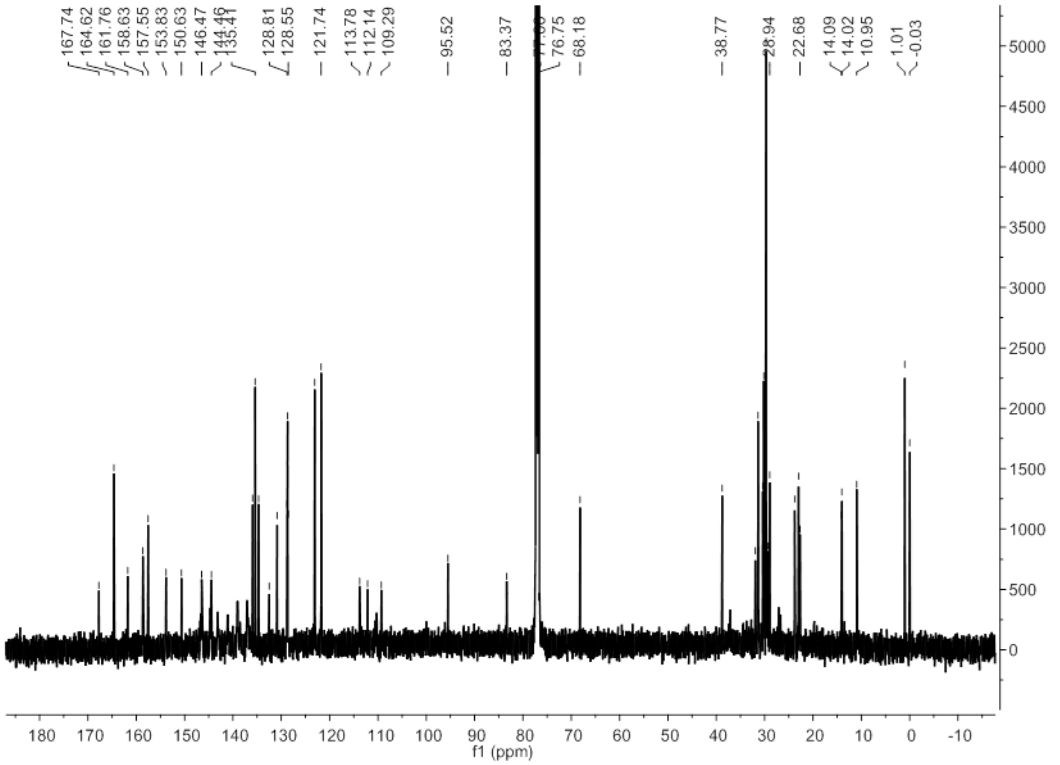


Figure S31. ^{13}C NMR spectra of **1a** in $CDCl_3$.

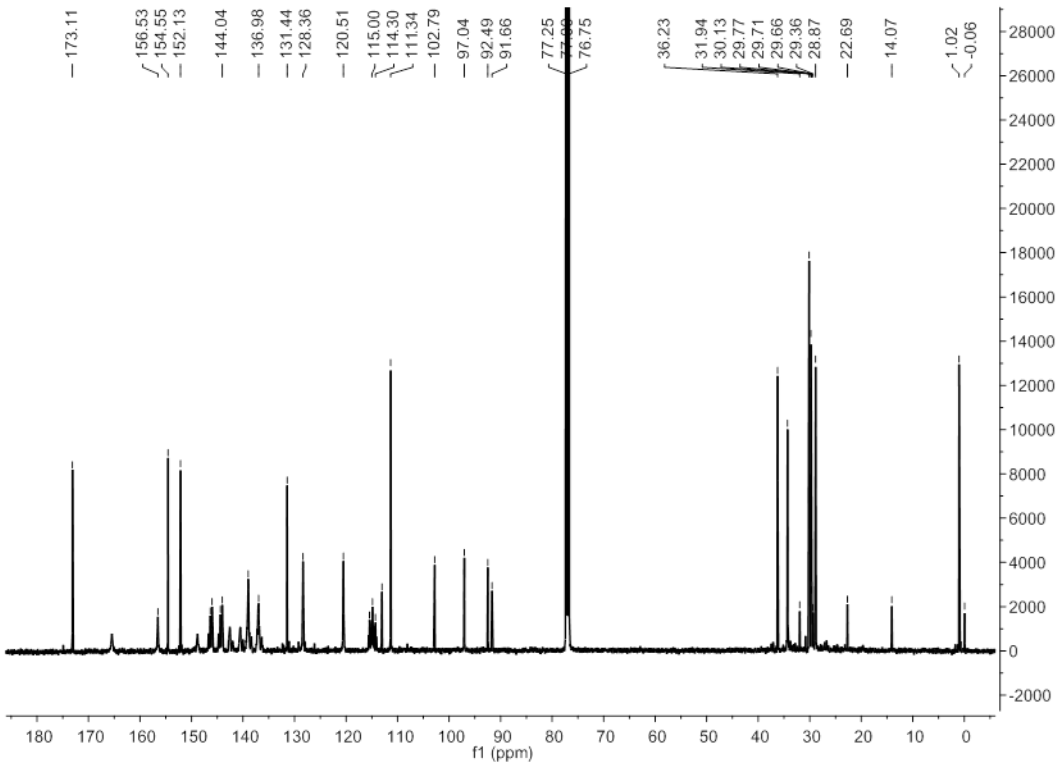


Figure S32. ^{13}C NMR spectra of **2a** in $CDCl_3$.

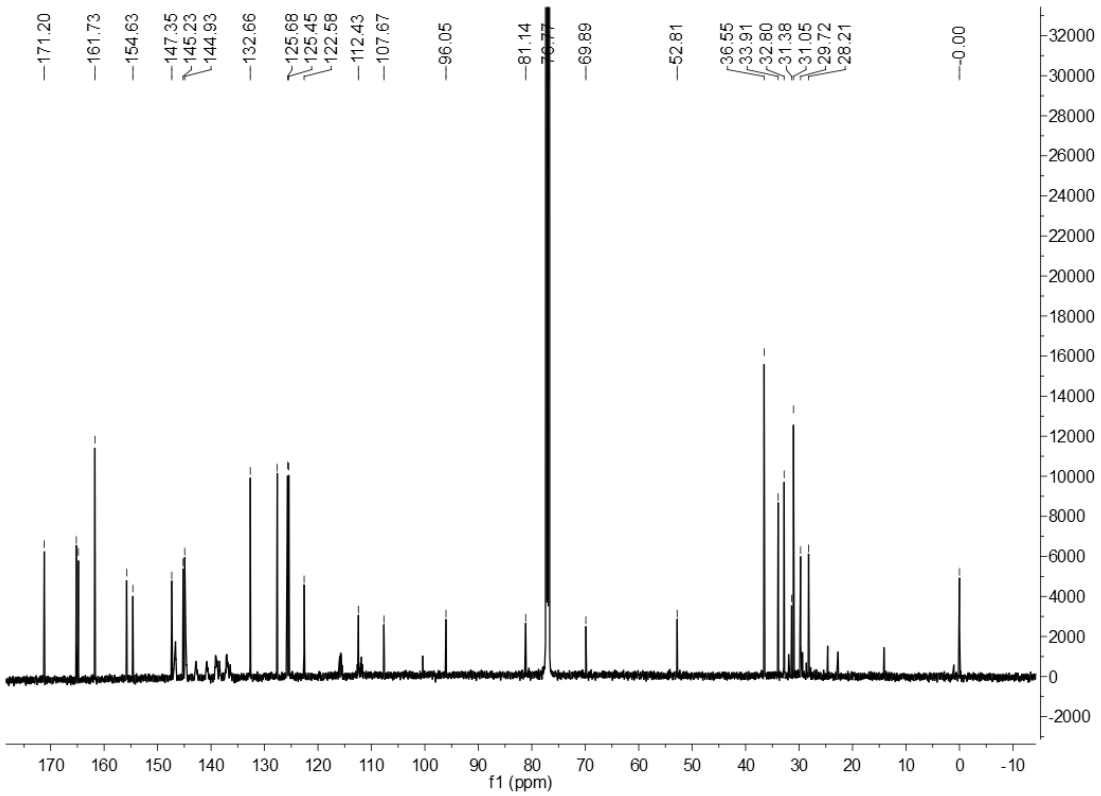


Figure S33. ^{13}C NMR spectra of **Zn-1a** in $CDCl_3$.

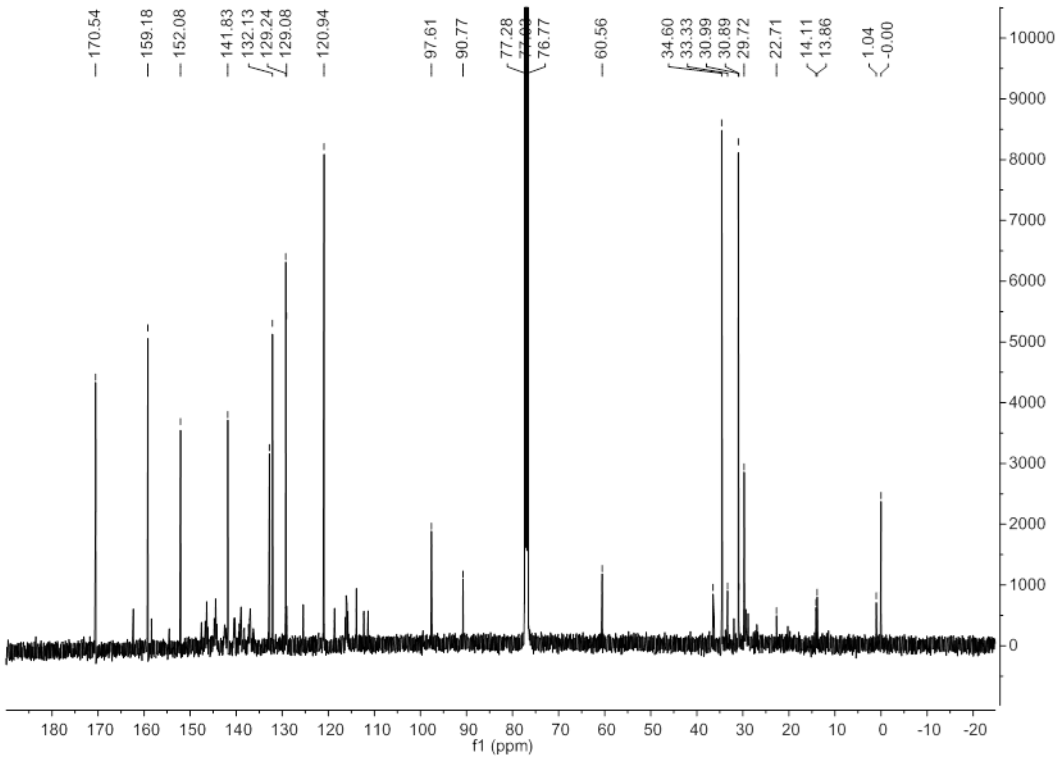


Figure S34. ^{13}C NMR spectra of **Zn-2a** in $CDCl_3$.

10. 2D NMR

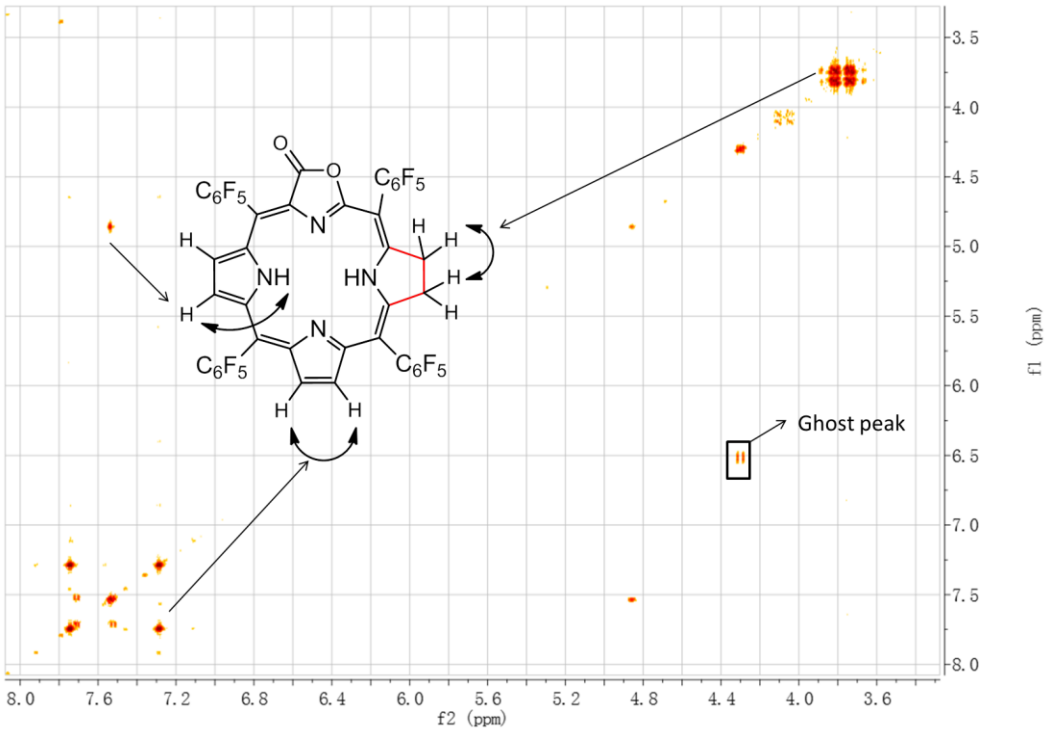


Figure S35.H-H 2D COESY NMR spectra of **1a** in $CDCl_3$.

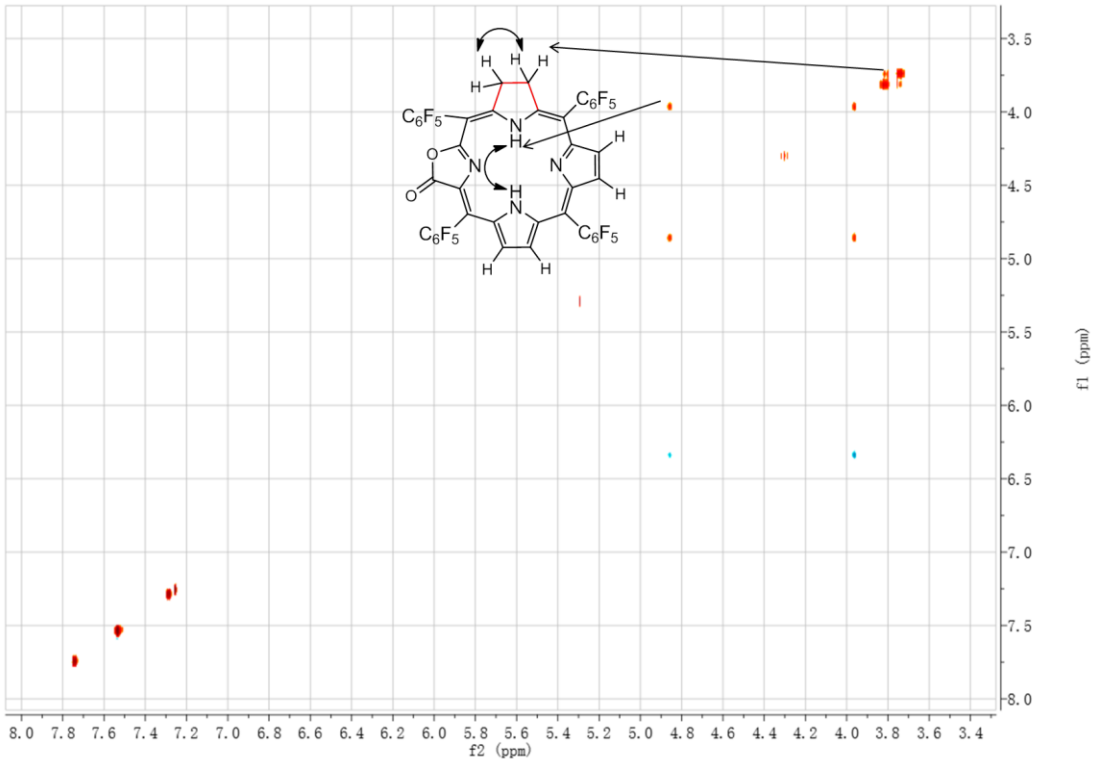


Figure S36.H-H 2D NOESY NMR spectra of **1a** in $CDCl_3$.

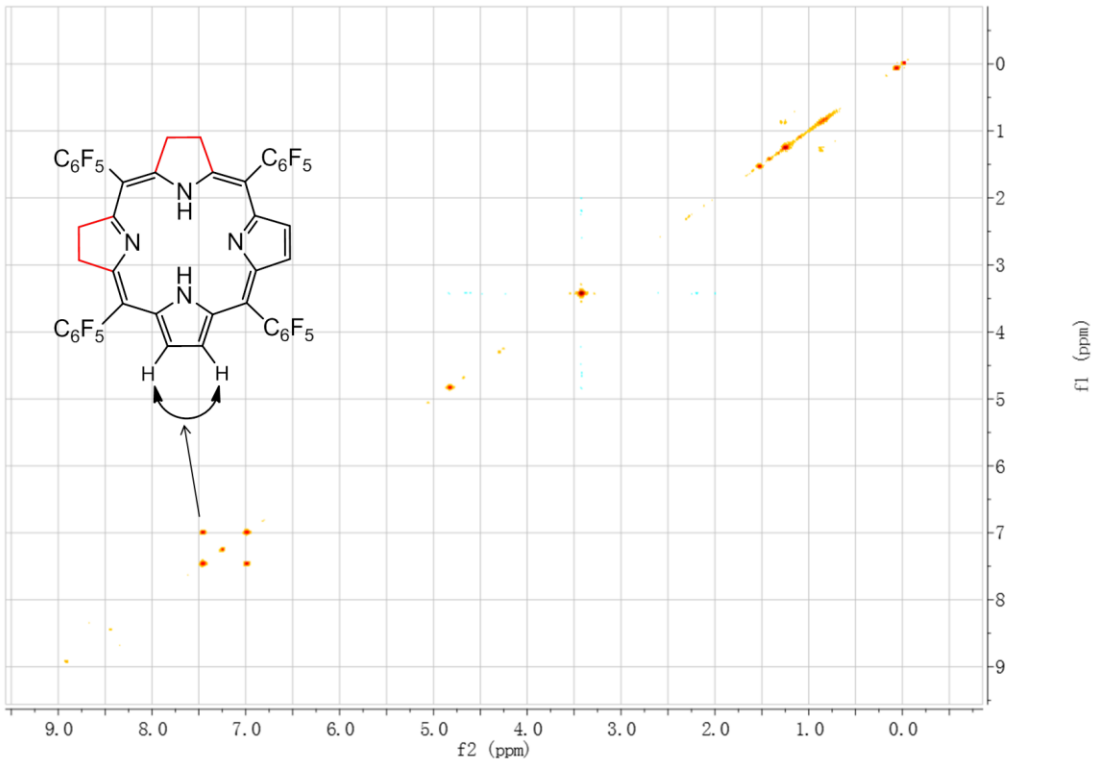


Figure S37.H-H 2D COESY NMR spectra of **2a** in $CDCl_3$.

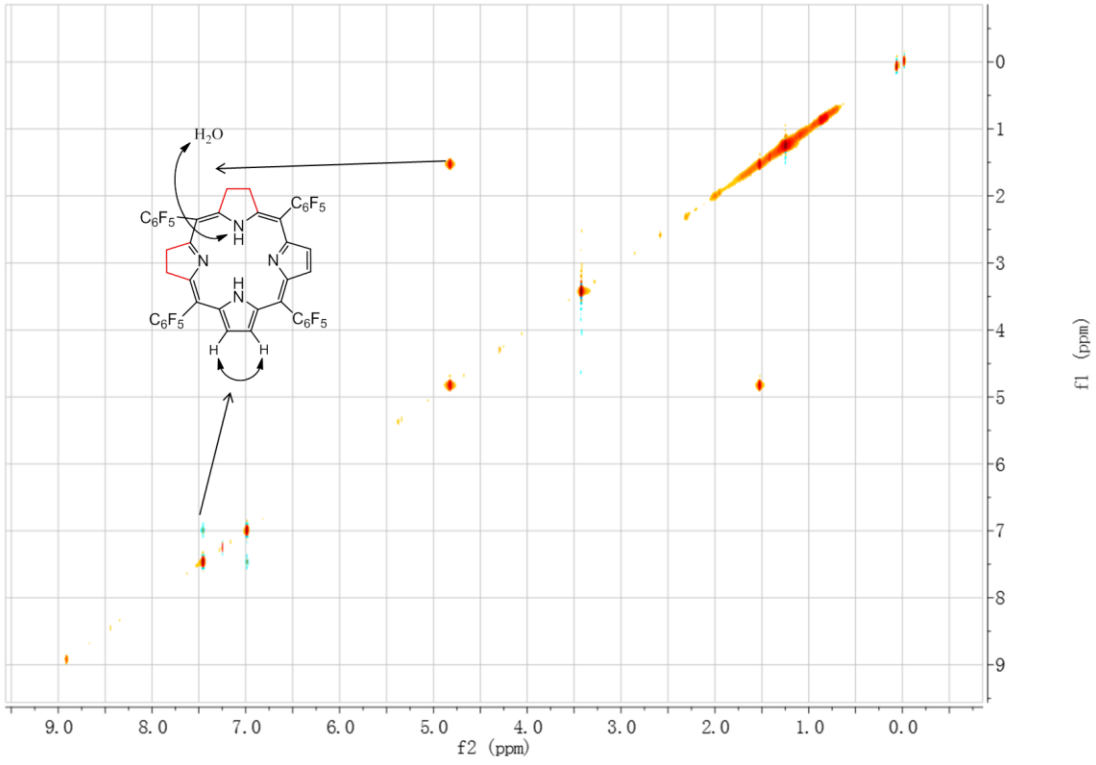


Figure S38.H-H 2D NOESY NMR spectra of **2a** in $CDCl_3$.

11. Stability of 1a, 2a and their Zn complexes

11.1 Stability of free ligands toward mCPBA

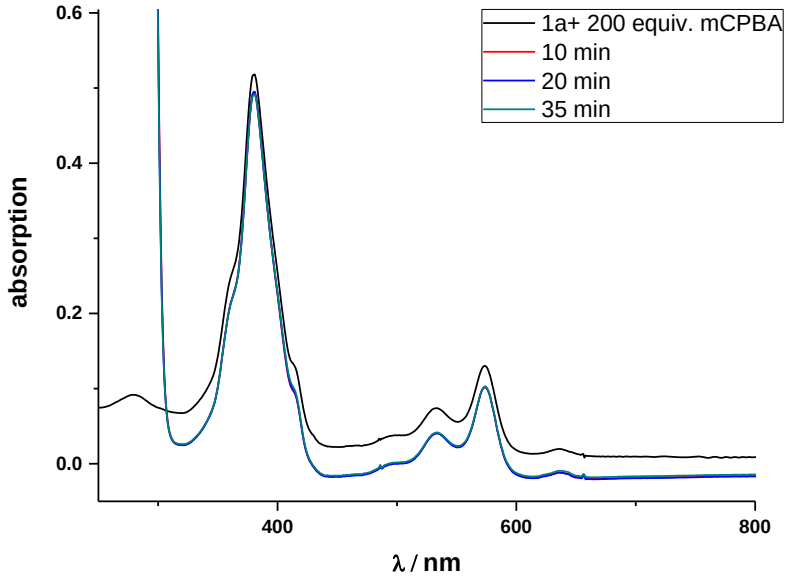


Figure S39. Stability of **1a** (6×10^{-6}M) towards *m*CPBA in DCM.

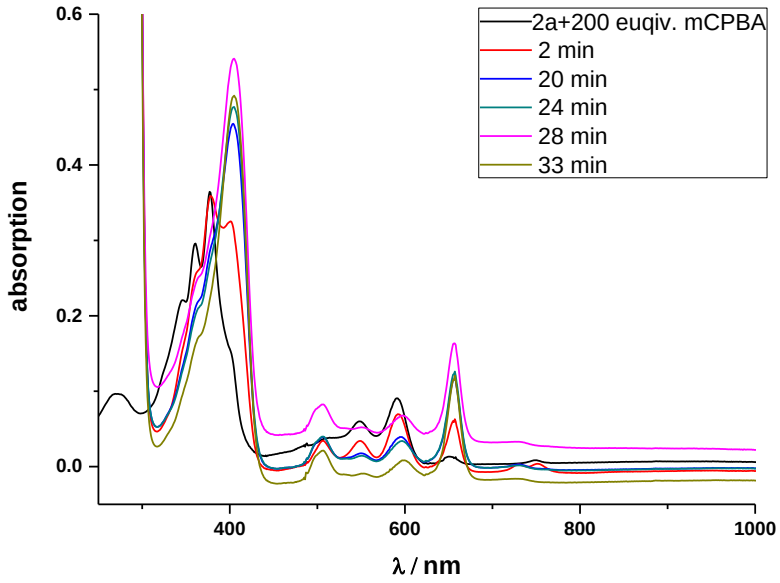


Figure S40. Stability of **2a** (6×10^{-6}M) towards *m*CPBA in DCM.

11.2 Stability of free ligands toward DDQ

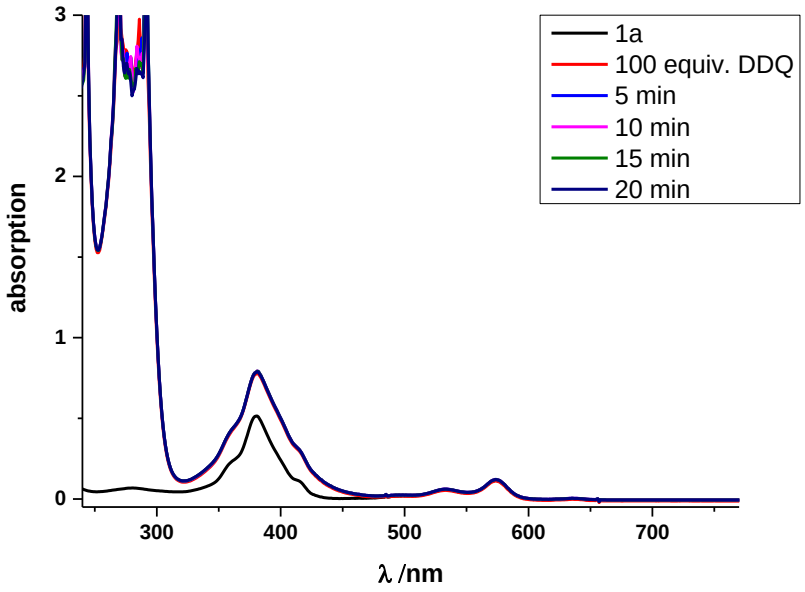


Figure S41. Stability of **1a** (6×10^{-6}M) towards DDQ in DCM.

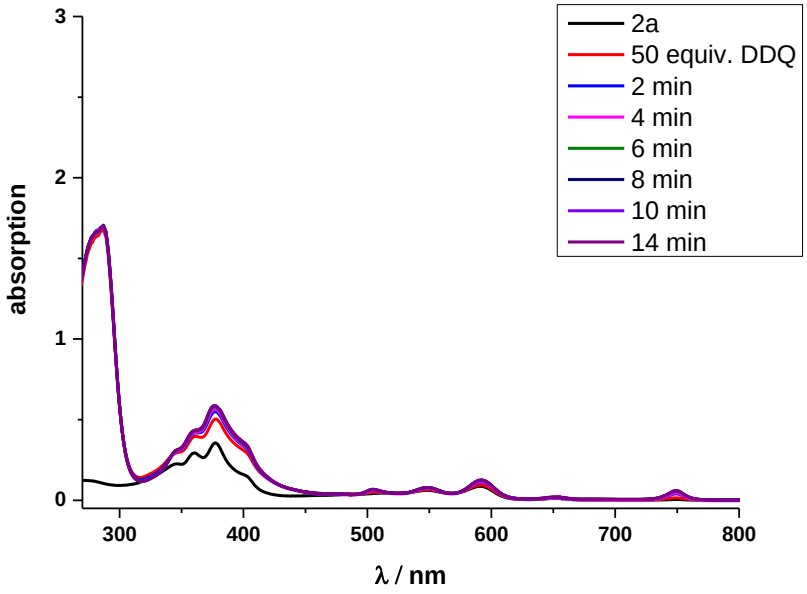


Figure S42. Stability of **2a** (6×10^{-6}M) towards DDQ in DCM.

11.3 Stability of free ligands toward 365 nm irridiation

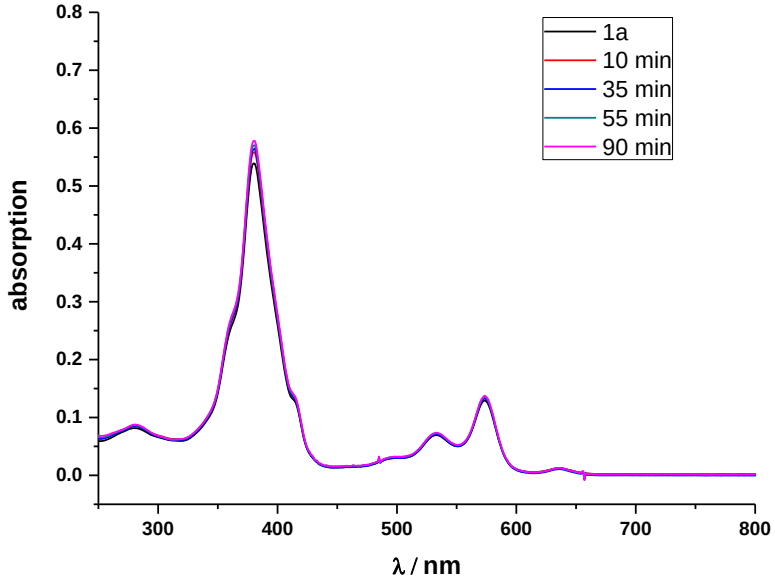


Figure S43. Stability of **1a** (6×10^{-6}M) towards 365 nm UV light in DCM.

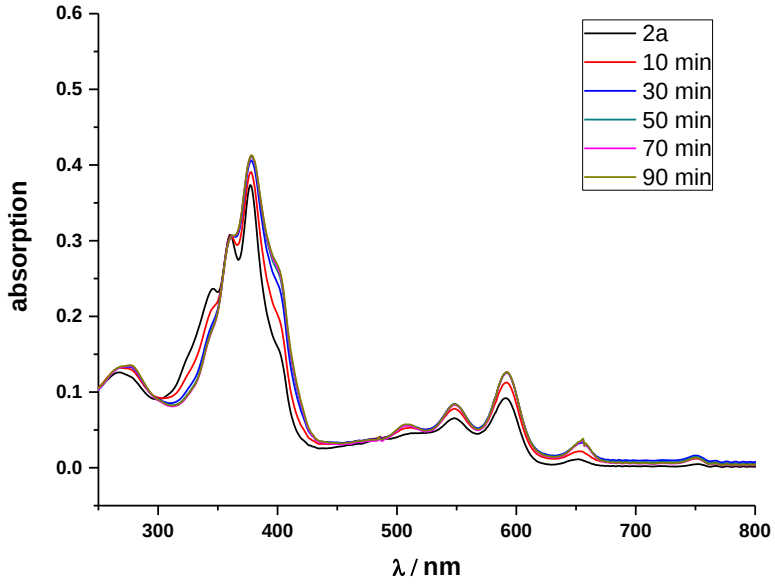


Figure S44. Stability of **2a** (6×10^{-6}M) towards 365 nm UV light in DCM.

11.4 Decay of free ligands with 10 equiv. mCPBA

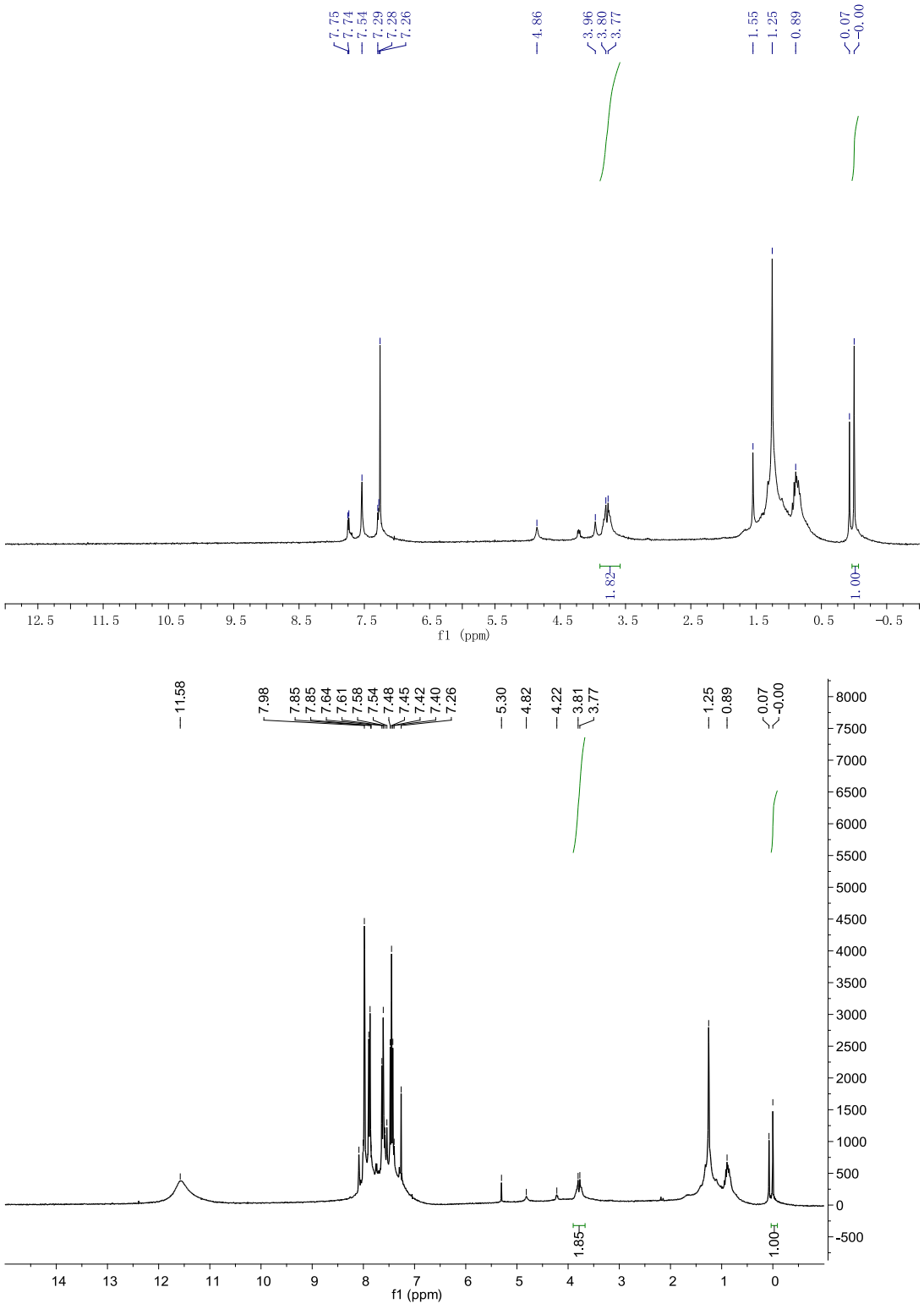


Figure S45. ^{1}H NMR change of the reaction of **1a** and 10 equivalents of mCPBA in $CDCl_3$.Upper: before the reaction; lower: after adding mCPBA for 1 day. Integration based on TMS. (Recorded on Varian 300MHz NMR)

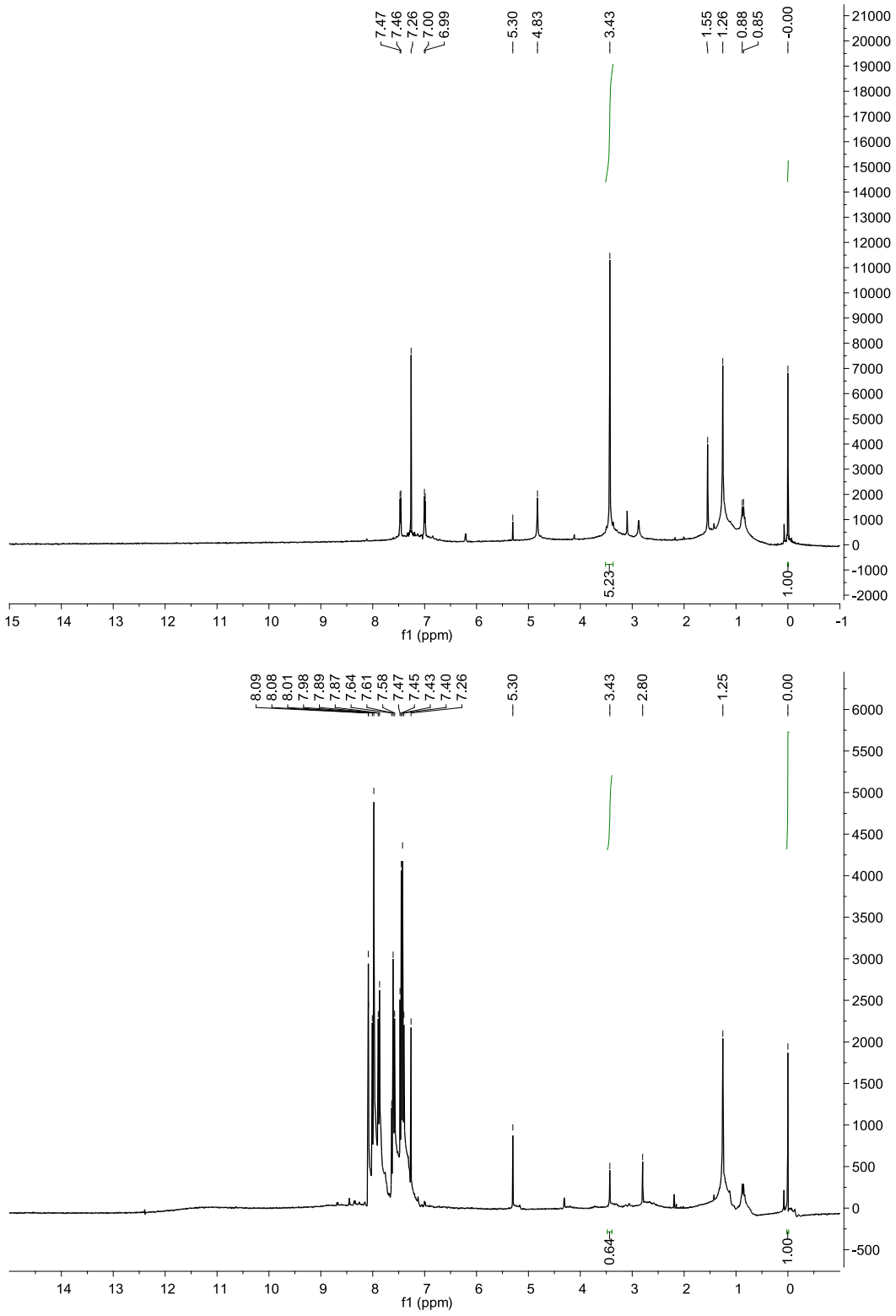


Figure S46.[1]H NMR change of the reaction of **2a** and 10 equivalents of mCPBAin $CDCl_3$.Upper: before the reaction; lower: after adding mCPBA for 1 day.Integration based on TMS. (Recorded on Varian 300MHz NMR)

11.5 Stability of Zn complexes toward mCPBA

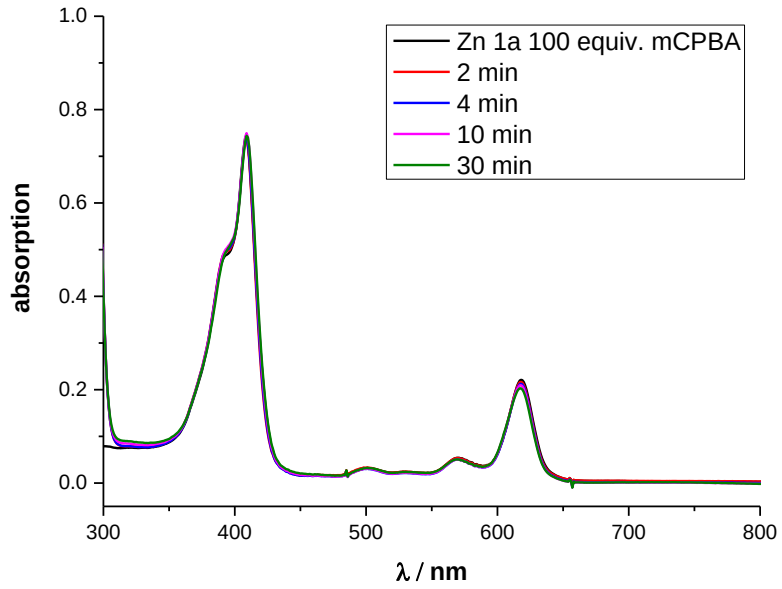


Figure S47. Stability of **Zn1a** (5×10^{-6}M) towards mCPBA in DCM.

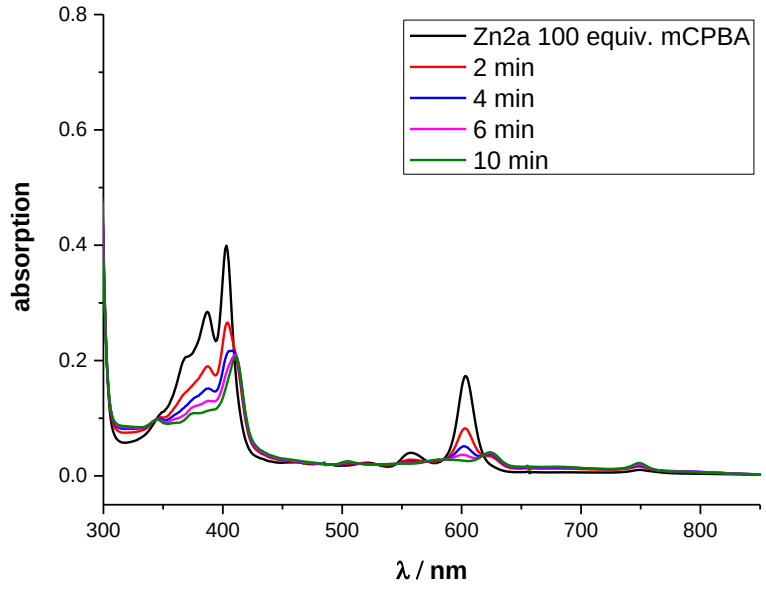


Figure S48. Stability of **Zn2a** (5×10^{-6}M) towards mCPBA in DCM.

11.6 Stability of free ligands toward 365 nm irridiation

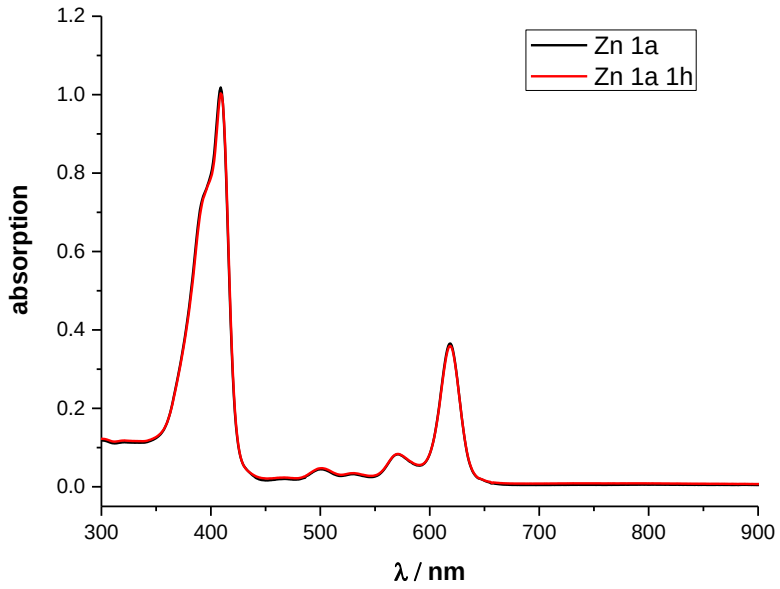


Figure S49. Stability of **Zn1a** (6×10^{-6}M) towards 365 UV light in DCM.

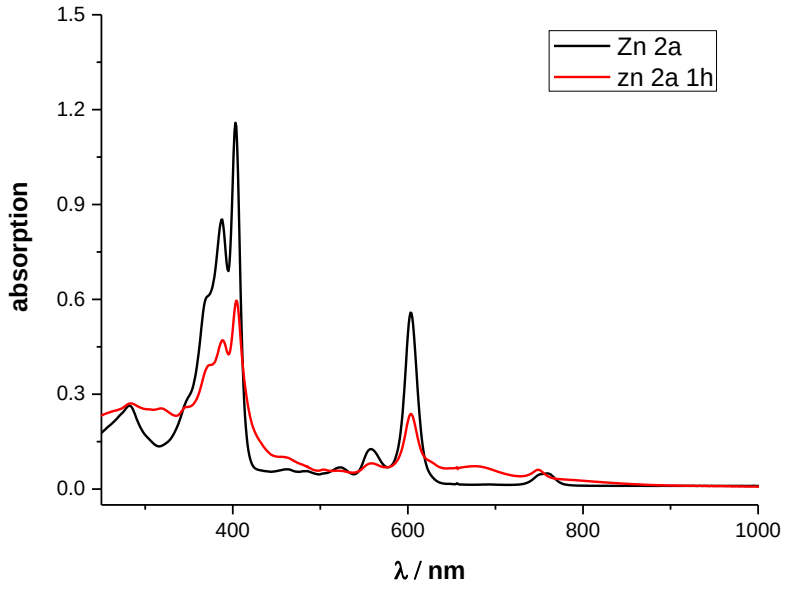


Figure S50. Stability of **Zn2a** (1×10^{-5}M) towards 365 UV light in DCM.

12. Cell imaging details

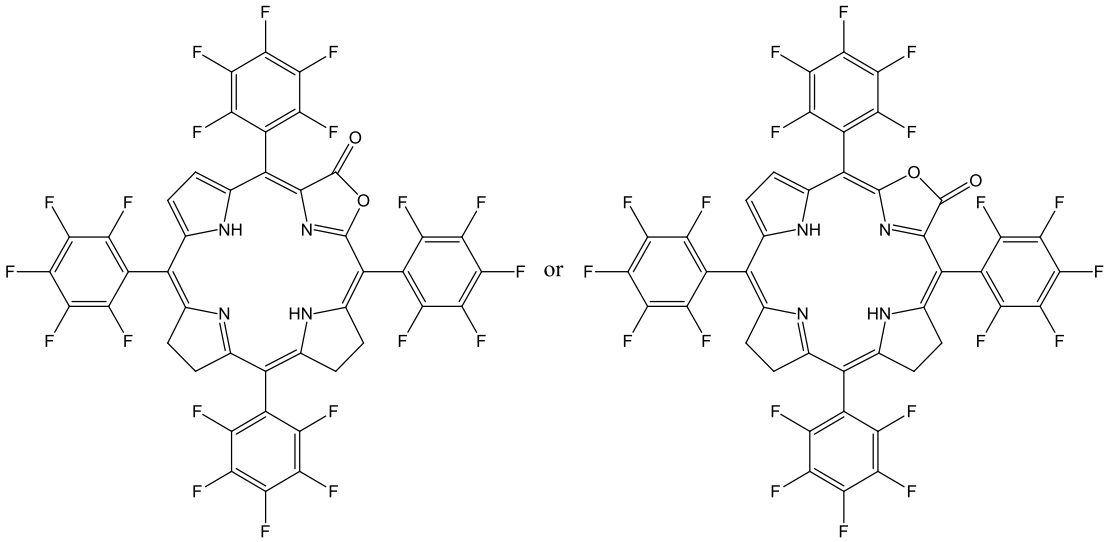
12.1 Cellular Uptake and imaging

HeLa cells were seeded on sterile glass coverslips in cell culture dishes containing complete media and allowed to grow to about 80% confluence. **1a NPs**(1mM) was added to complete media to a final concentration of 10μM. After 4hours, cells were washed with PBS buffer for three times. Images of living cells were performed using Nikon A1R-si Laser Scanning Confocal Microscope (Japan), equipped with lasers of 405/488/543/638 nm. The settings for confocal microscopy were as follow: 60×immersion oil objective with resolution 1024 × 1024, 405 nm excitation wavelength and 700/75 detector. Differential interference contrast (DIC) and fluorescent images were processed and analyzed using Image J.

12.2 Co-localization

HeLa cells were placed on sterile glass coverslips in cell culture dishes containing complete media and allowed to grow to about 80% confluence. Complexes (1mM dissolved in DMSO) were added to complete media to a final concentration of 10μM. After incubated for 24 h, cells were treated with 1μMLysoTracker® Green DND-26 for 30 min and washed with PBS buffer for three times. Images of living cells were performed using Nikon A1R-si Laser Scanning Confocal Microscope (Japan), equipped with lasers of 405/488/543/638 nm. The settings for confocal microscopy were as follow: 60×immersion oil objective with resolution 1024 ×1024, 405 nm excitation wavelength and 700/75 detector for**1a NPs** and 488 nm excitation wavelength and 515/30 detector for LysoTracker® Green DND-26. Differential interference contrast (DIC) and fluorescent images were processed and analyzed using Image J and Pearson's correlation coefficient was calculated via Colocalization analysis in Image J plugins.

13. Side-product of 1: tetrahydroporpholactone (1b)



1b was side-product of 1a with a isolated yield of about 20%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.94 (s, 1H), 6.54 (s, 1H), 6.24 (s, 1H), 3.36 (ddd, *J* = 14.4, 10.8, 6.0 Hz, 4H), 3.06 (dd, *J* = 17.1, 8.6 Hz, 4H).^{19}F NMR (471 MHz, $CDCl_3$) δ -58.38 (dd, *J* = 23.2, 7.6 Hz), -59.07 (dd, *J* = 23.7, 8.1 Hz), -59.53 (dd, *J* = 23.4, 8.0 Hz), -60.05 (dd, *J* = 23.0, 7.4 Hz), -71.55 (t, *J* = 20.8 Hz), -72.03 (t, *J* = 20.9 Hz), -73.06 (t, *J* = 20.8 Hz), -73.33 (t, *J* = 20.8 Hz), -79.57 (td, *J* = 23.0, 8.0 Hz), -80.93 (tt, *J* = 22.4, 7.3 Hz), -82.17 (dt, *J* = 22.5, 7.3 Hz).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.78, 164.43, 160.97, 156.12, 155.09, 154.05, 146.08, 144.13, 142.90, 140.85, 139.75 – 138.53, 137.40 – 136.19, 130.70, 123.37, 121.65, 114.65, 114.51, 114.35, 114.01, 113.83, 113.67, 113.49, 110.73, 110.55, 110.40, 109.88, 109.76, 109.61, 101.60, 93.22, 84.34, 36.63, 30.27, 29.85, 29.69, 29.28.UV−vis (CH_2Cl_2) $_{max}$, nm (log) 358(4.91) , 375(5.10), 485 (4.00), 518 (4.23), 554 (4.30); fluorescence (CH_2Cl_2) $_{max}$, nm 570, 608, = 0.75, τ= 6.46 ns; IR (cm^{-1}) : 989, 1274, 1329, 1499, 1520, 1776 (C=O), 2924, 3308, 3404; ESI-MS m/z $[M + H]^+$: Calcd. For C43H13F20N4O2+ 997.07137, found 997.07328.

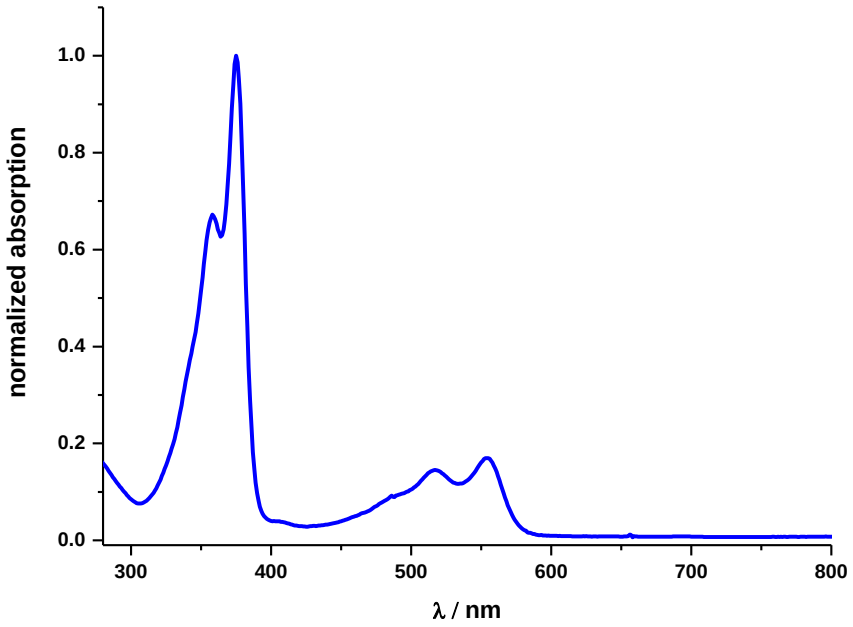


Figure S51. Normalized absorption of **1b** in DCM.

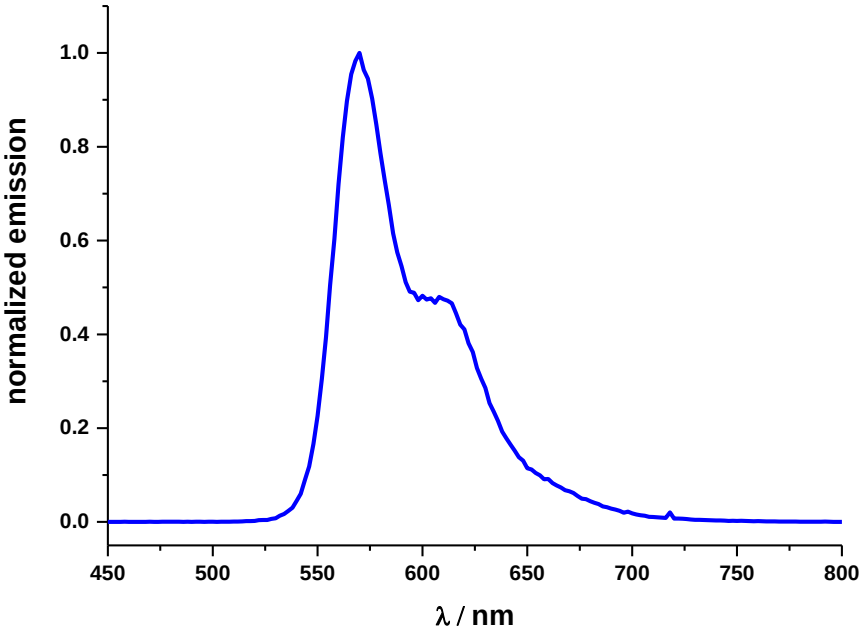


Figure S52. Normalized emission of **1b** in DCM.

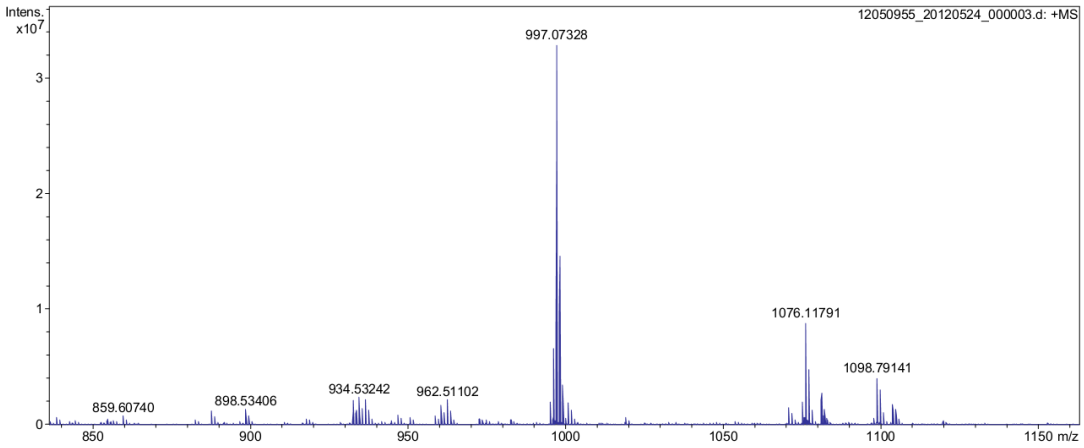


Figure S53. HR-MS(ESI) of **1b**.

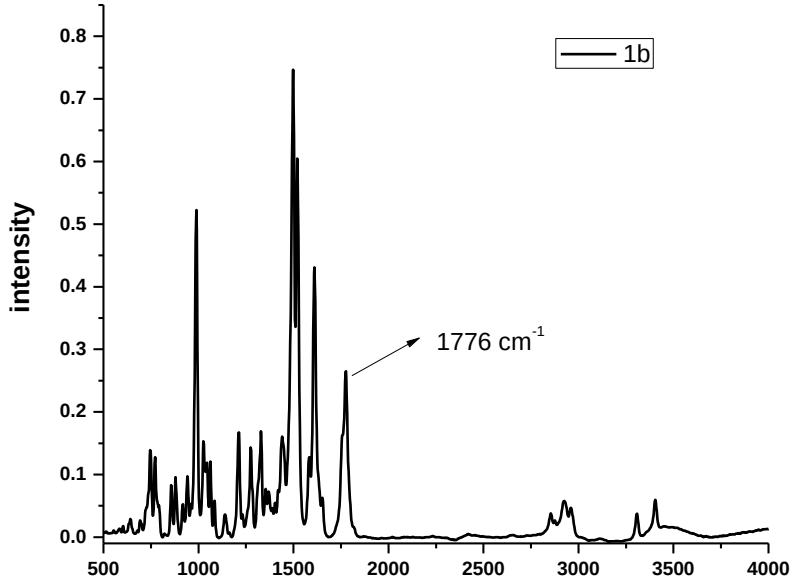


Figure S54. FT-IR spectra of **1b**.

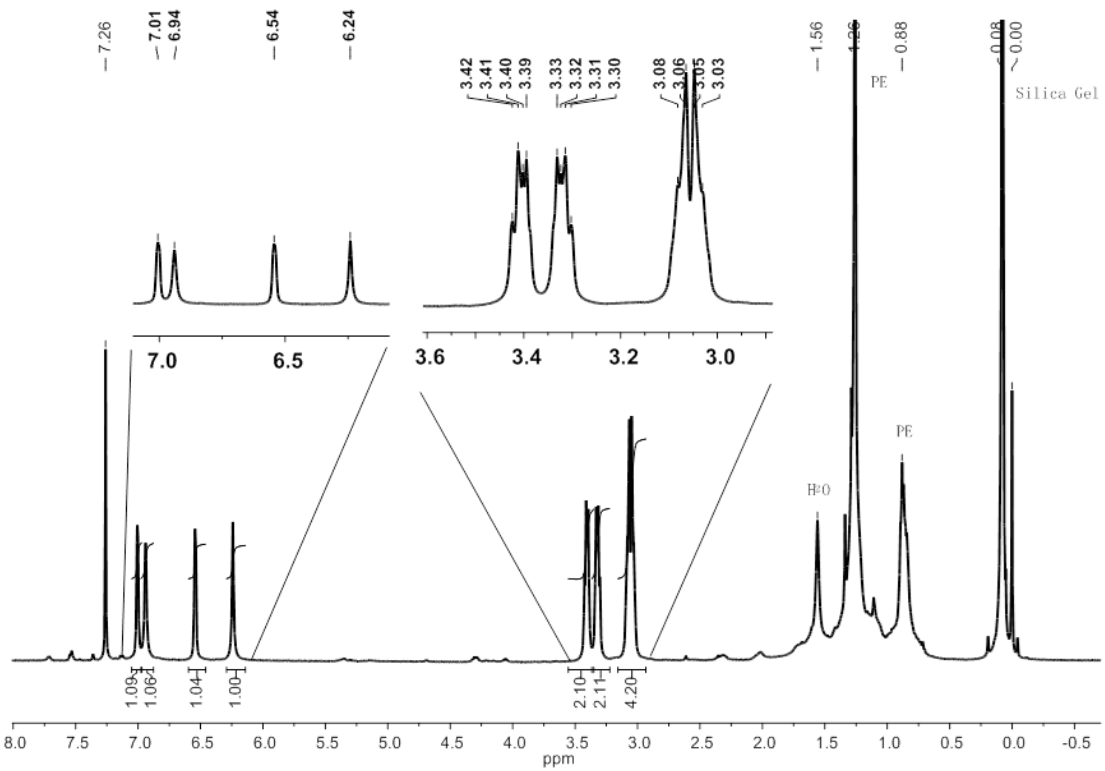


Figure S55. ^{1}H NMR spectra of **1b** in $CDCl_3$.

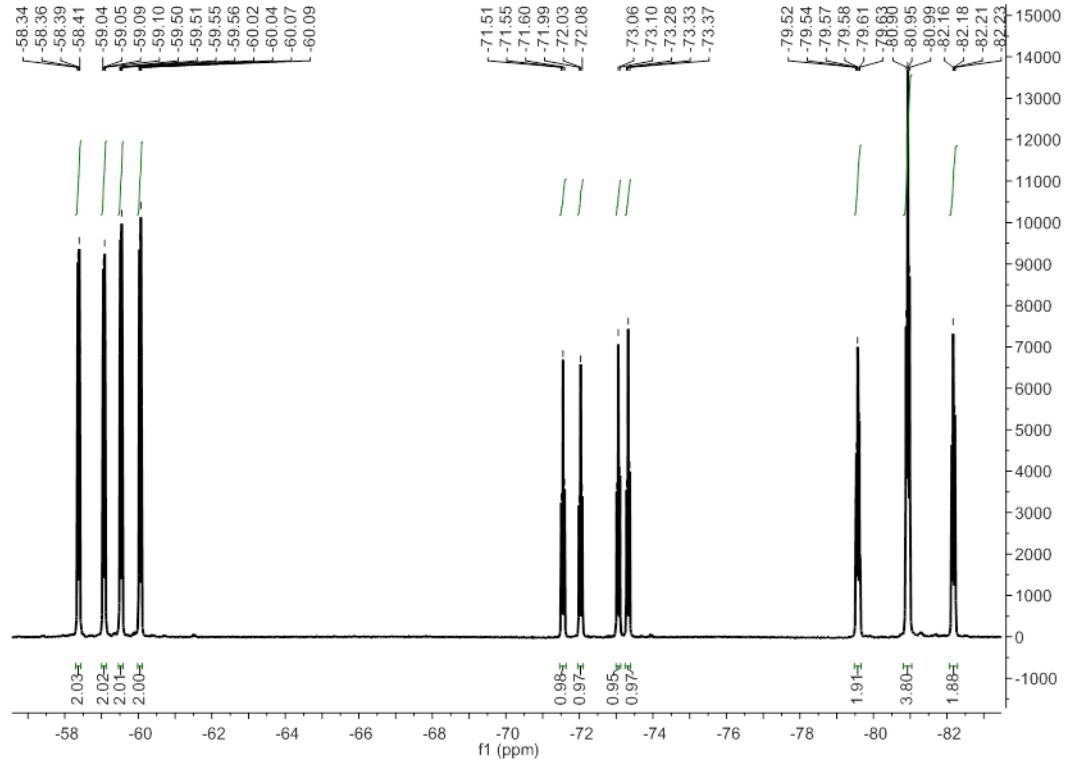


Figure S56. ^{19}F NMR spectra of **1b** in $CDCl_3$.

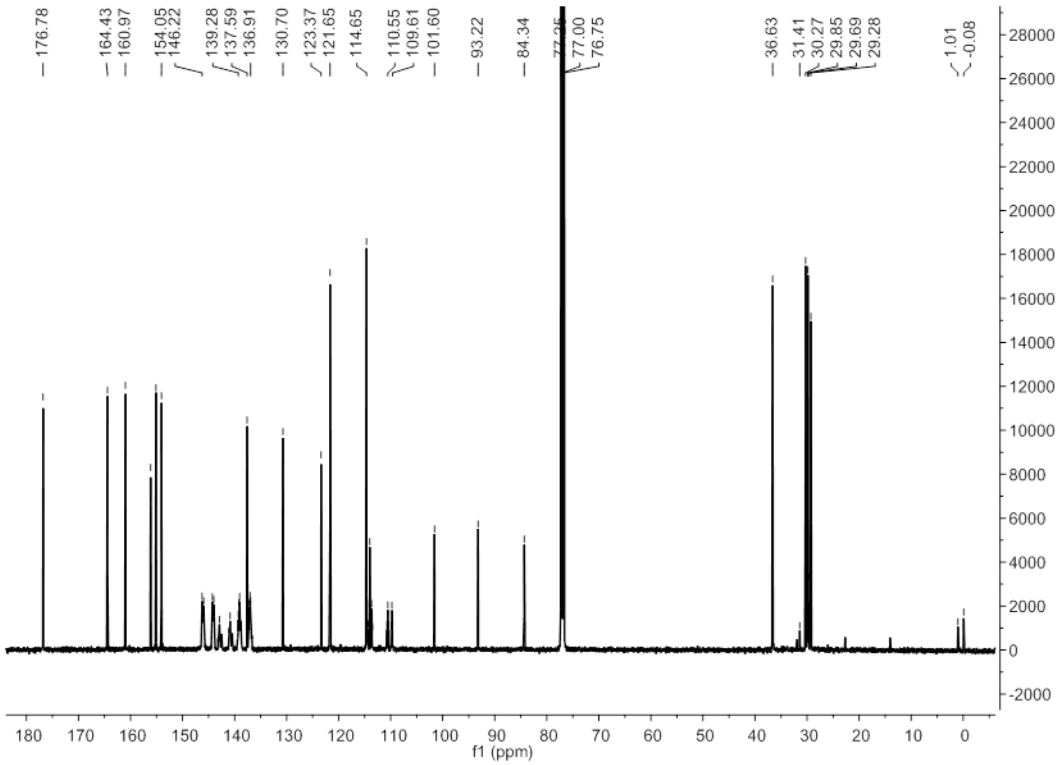


Figure S57. ^{13}C NMR spectra of **1b** in $CDCl_3$.