Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information (ESI)

Preparation and ion recognition features of porphyrin-chalcone type compounds as efficient red-fluorescent materials

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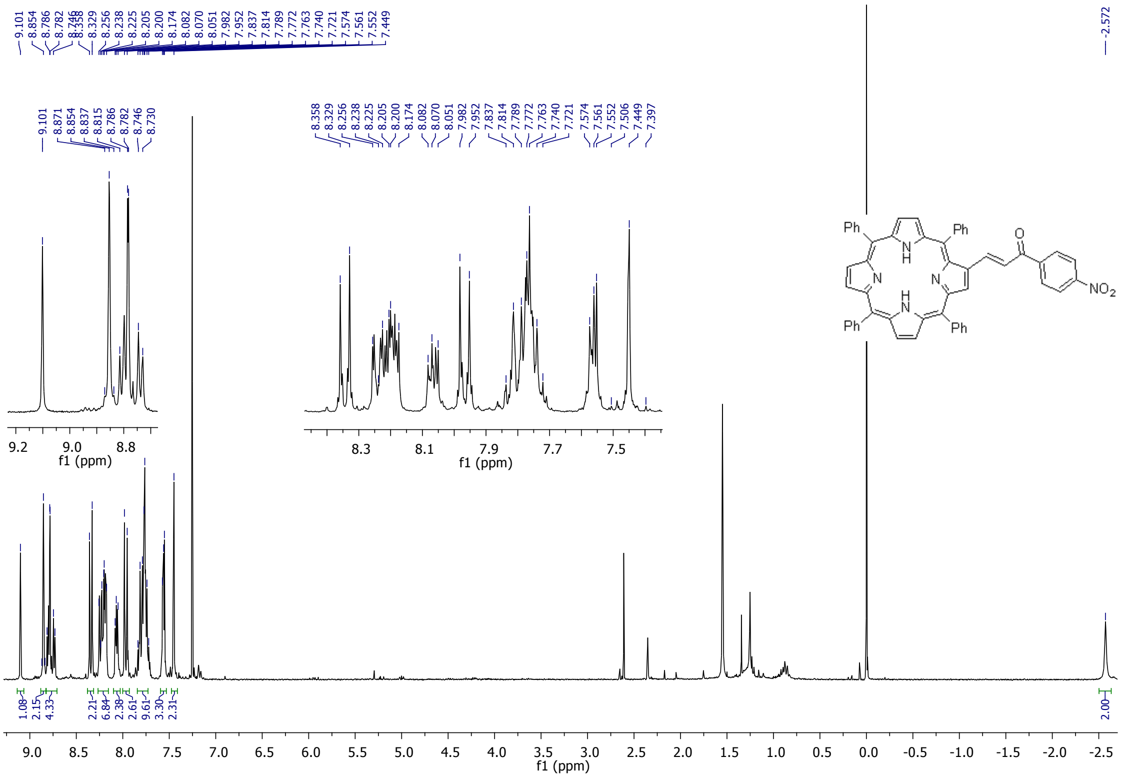


Figure 1_SM - ^{1}H NMR spectrum of compound **4a.**

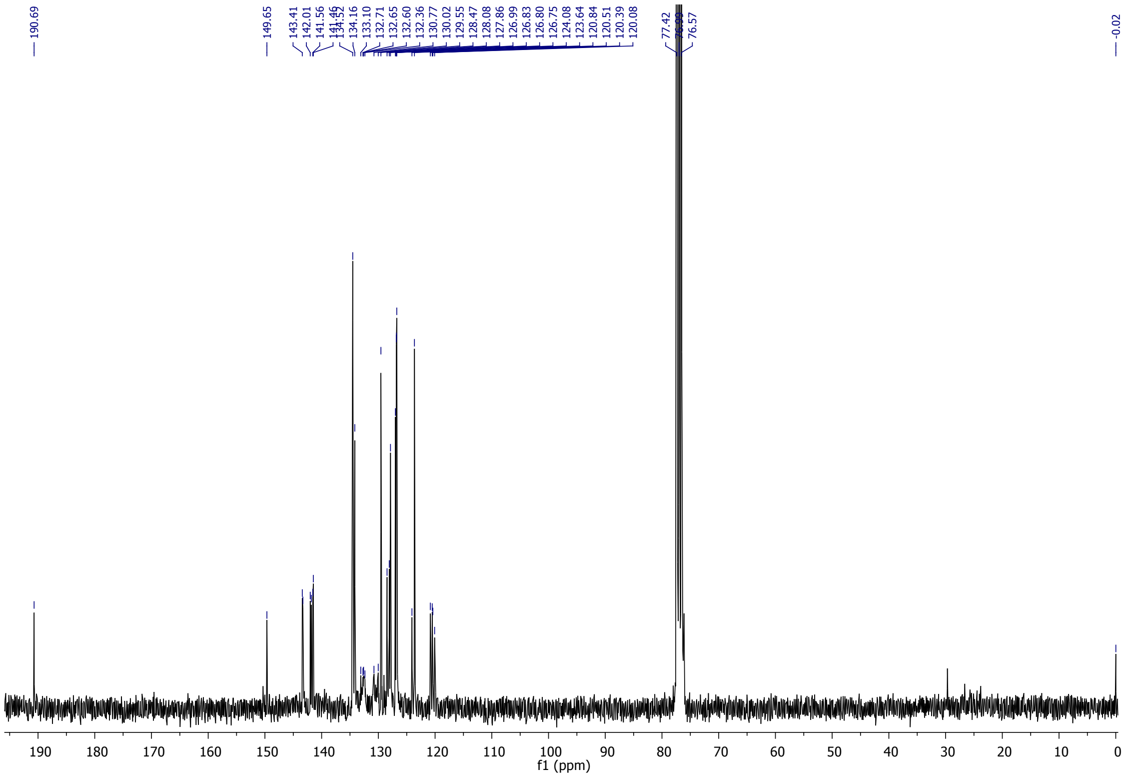


Figure 2_SM - ^{13}C NMR spectrum of compound **4a.**

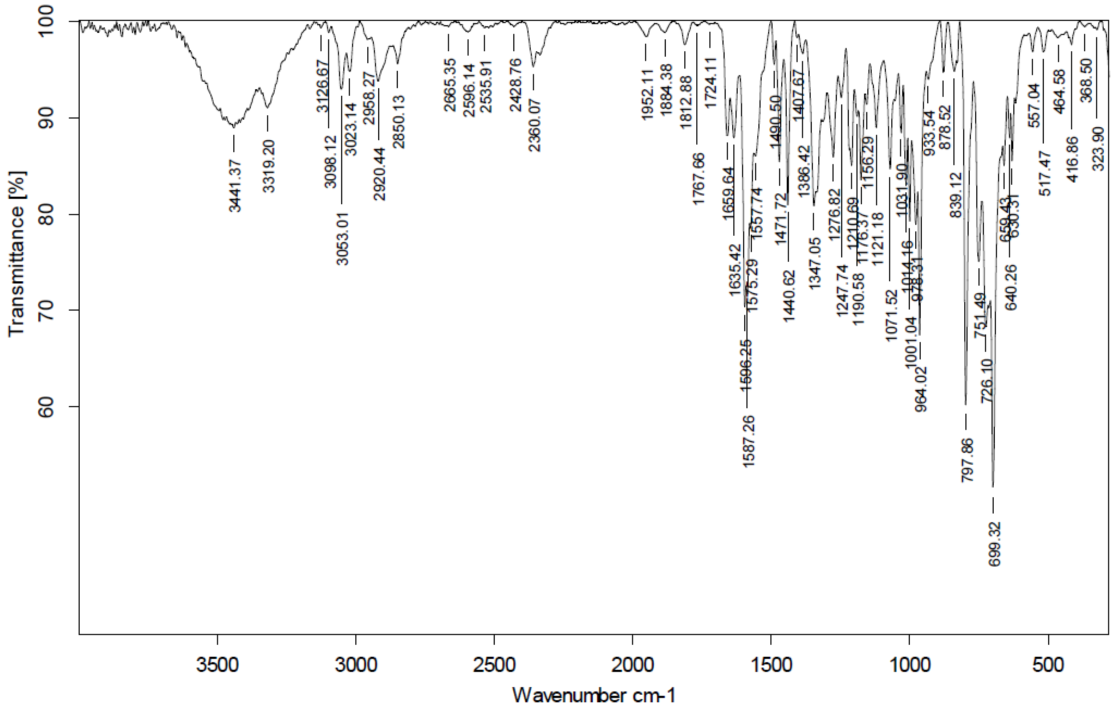


Figure 3_SM - Infra-red spectrum of compound **4a.**

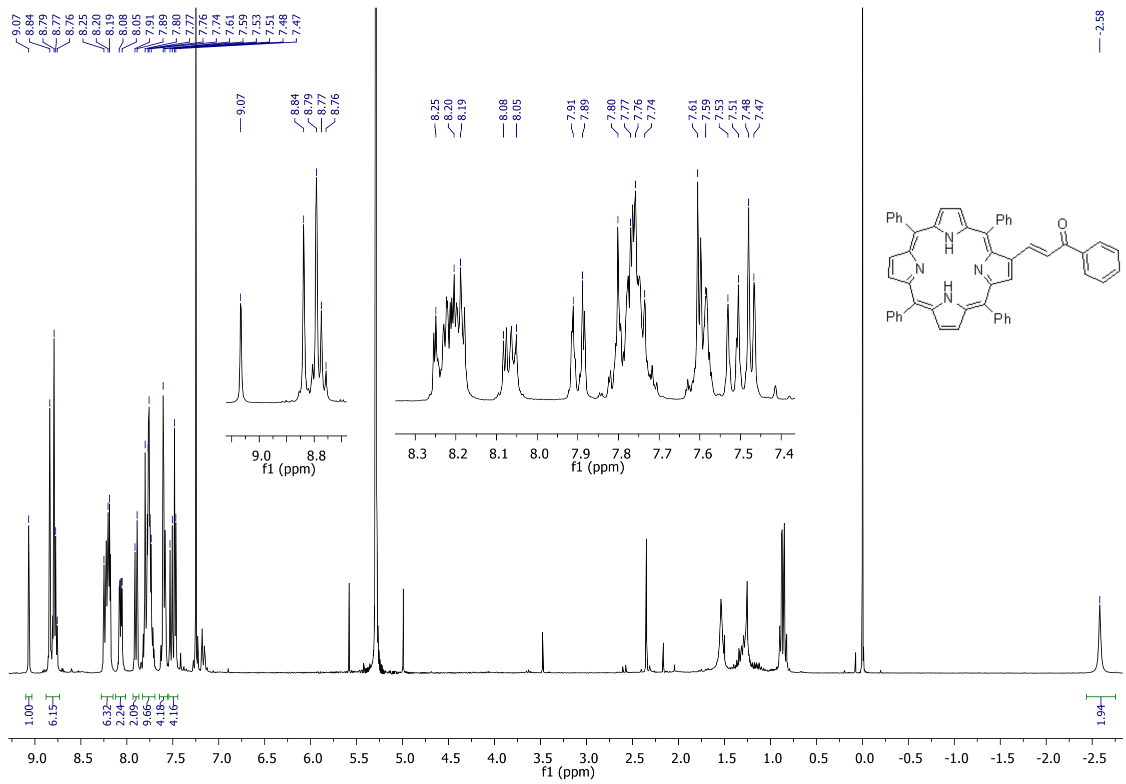


Figure 4_SM - ^{1}H NMR spectrum of compound **4b.**

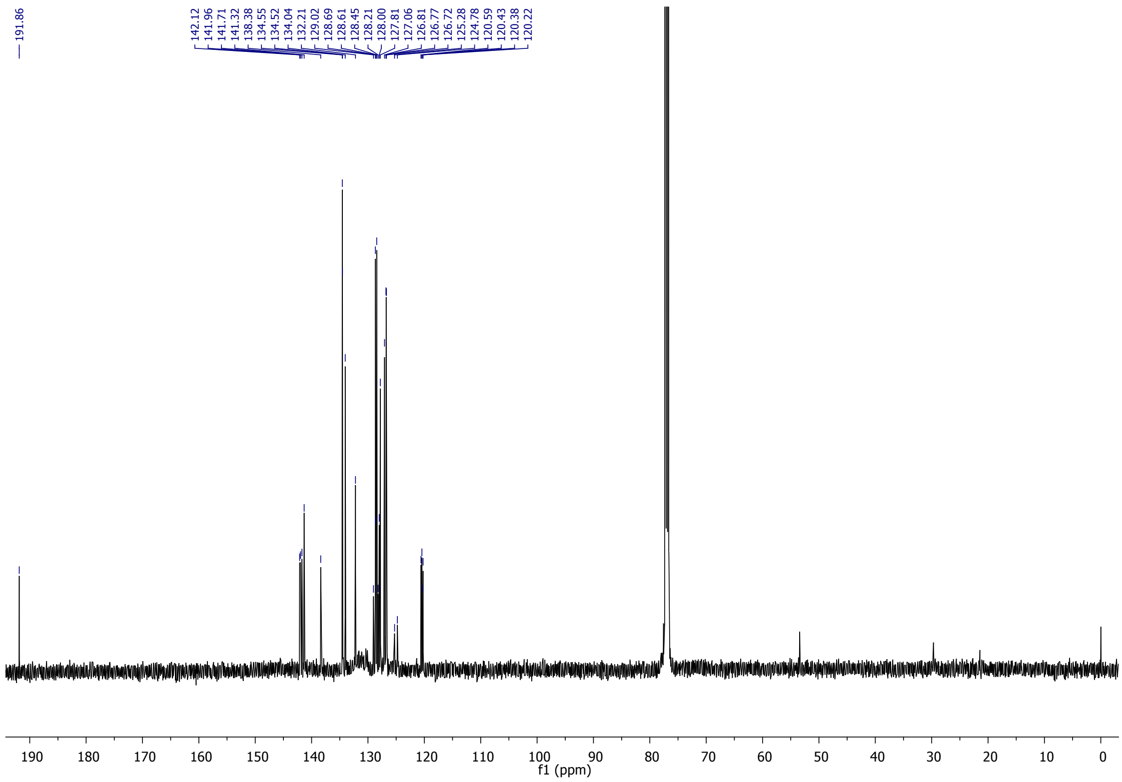


Figure 5_SM - ^{13}C NMR spectrum of compound **4b.**

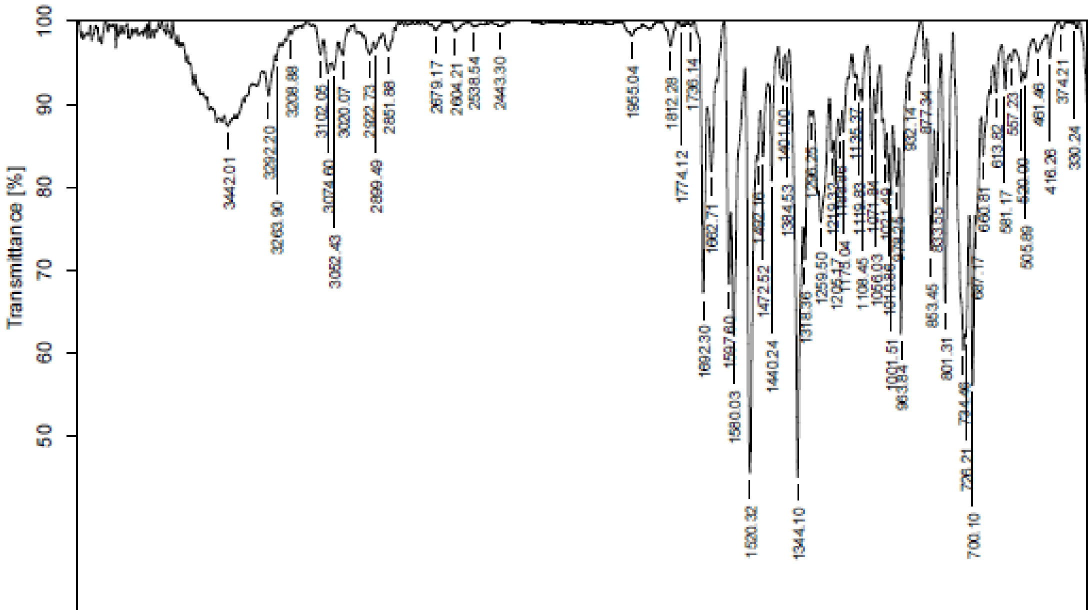


Figure 6_SM - Infra-red spectrum of compound **4b.**

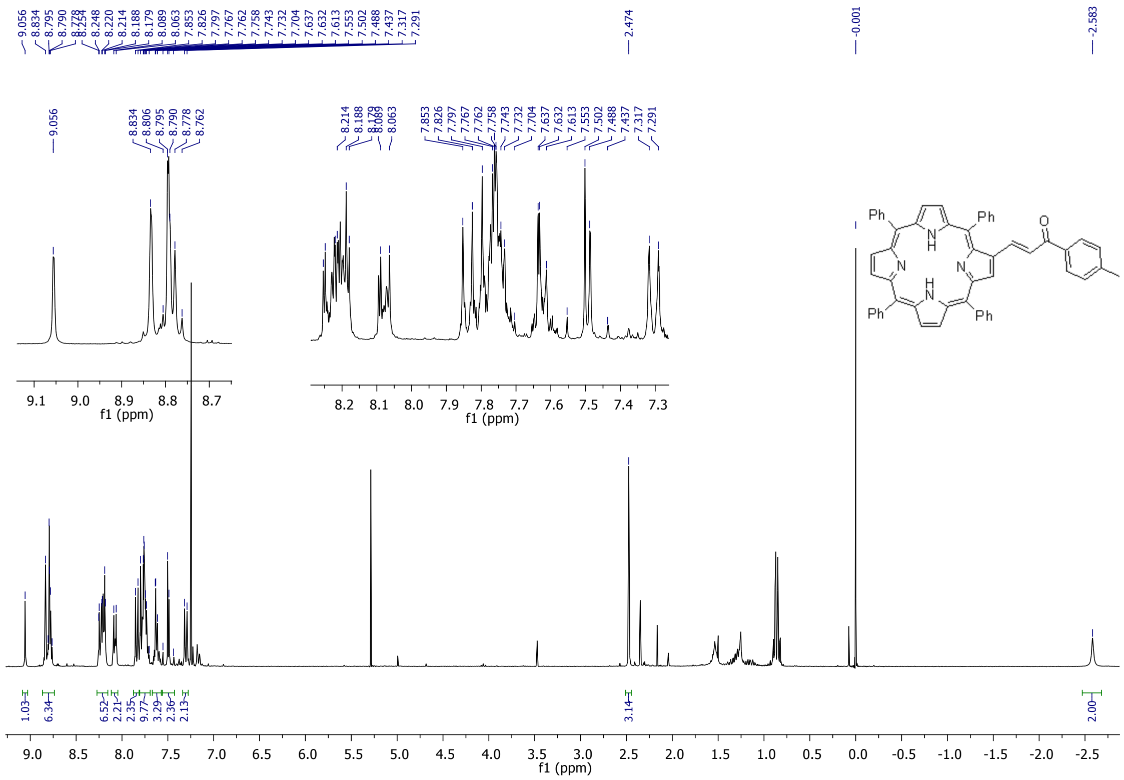


Figure 7_SM - ^{1}H NMR spectrum of compound **4c.**

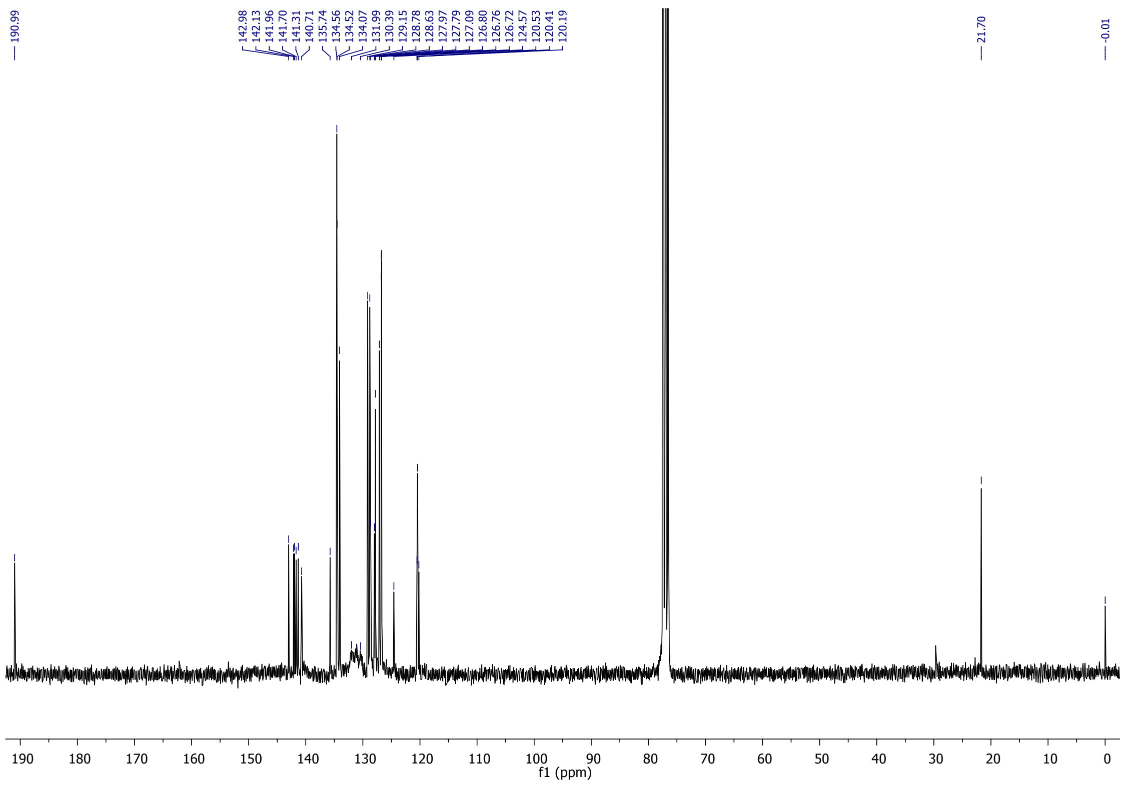


Figure 8_SM - ^{13}C NMR spectrum of compound **4c.**

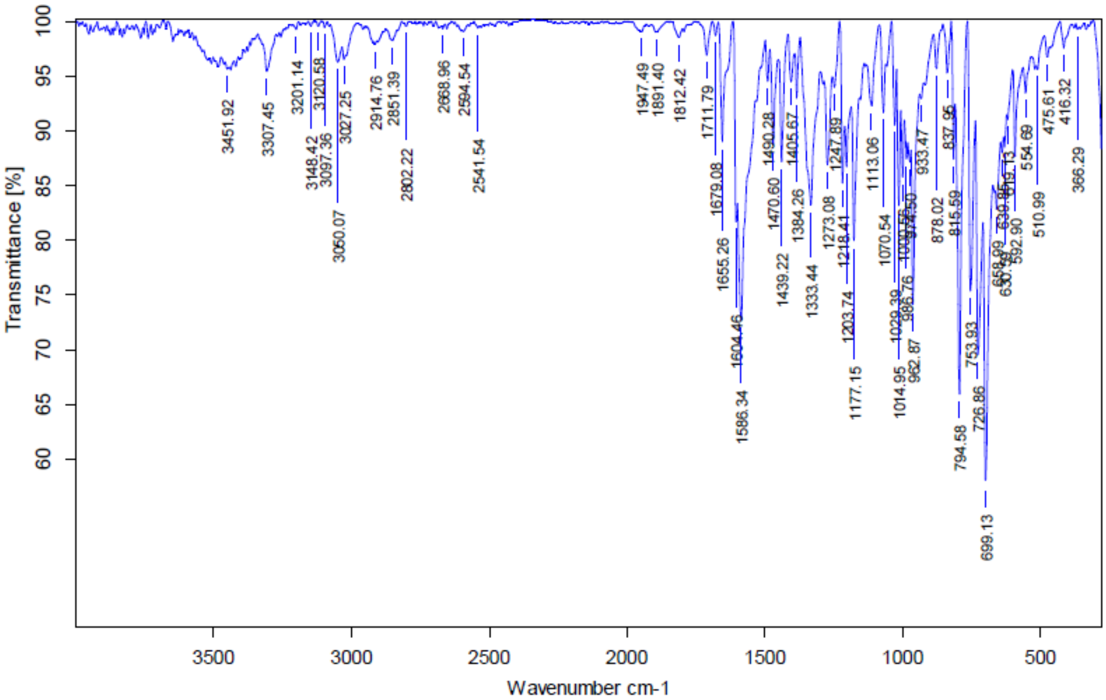


Figure 9_SM - Infra-red spectrum of compound **4c.**

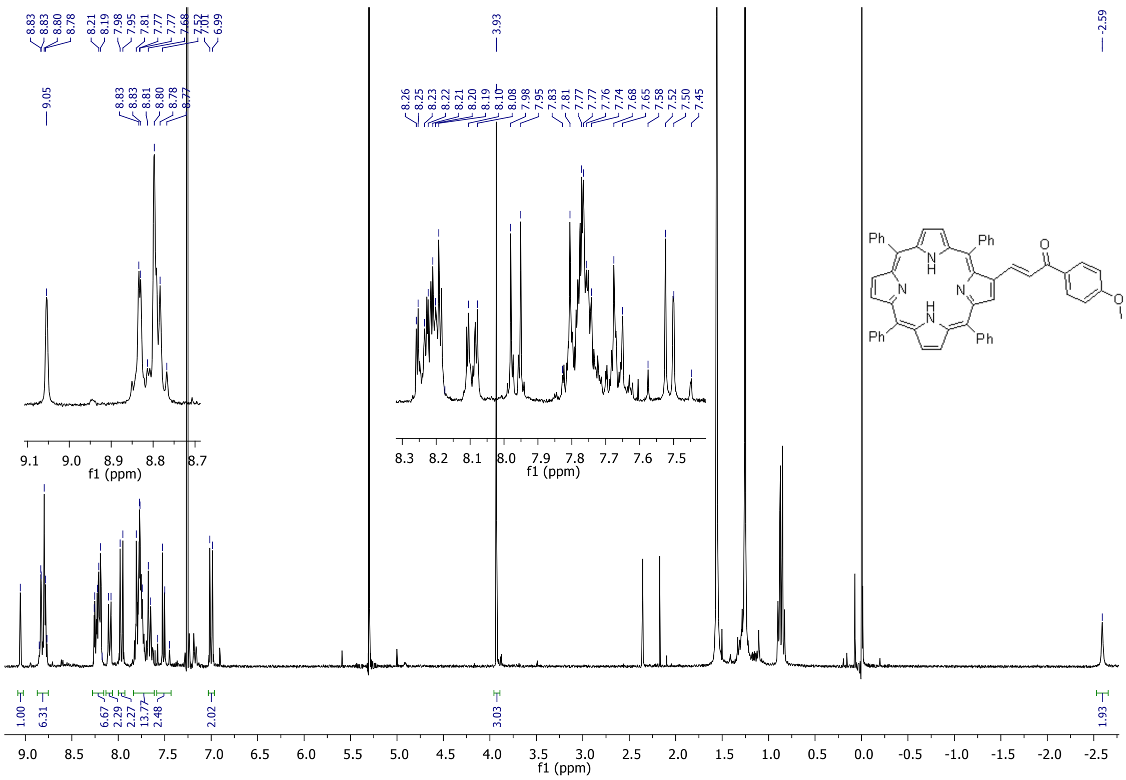


Figure 10_SM – [1]H NMR spectrum of compound **4d.**

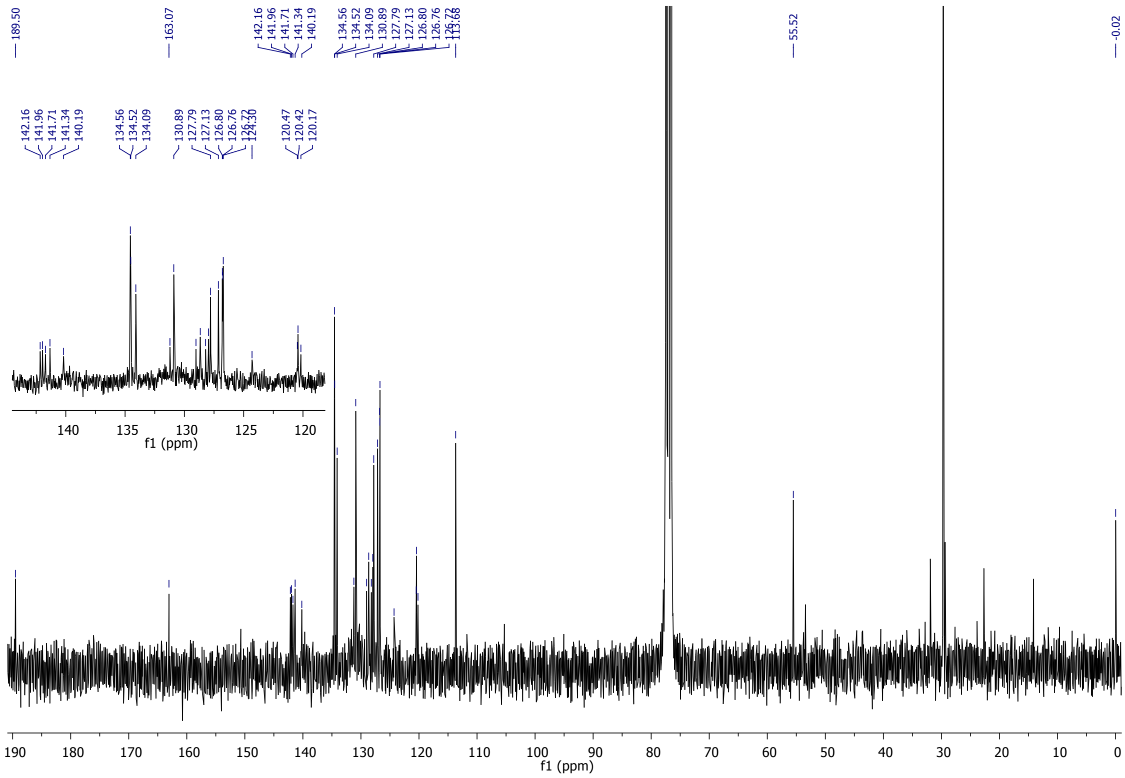


Figure 11_SM - ^{13}C NMR spectrum of compound **4d.**

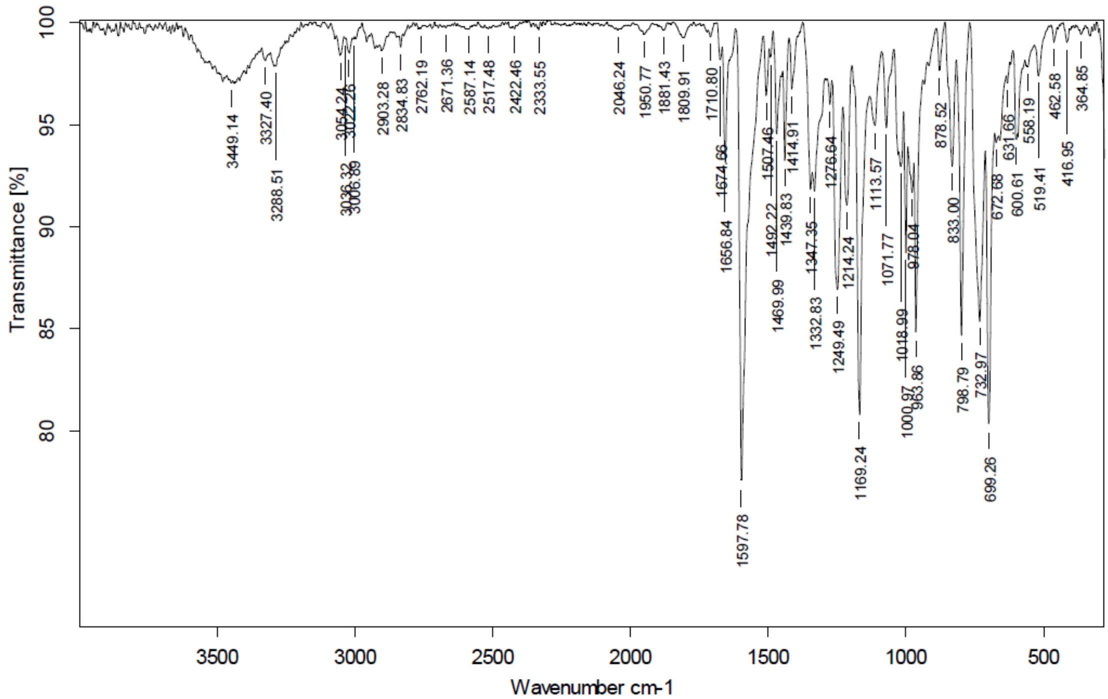


Figure 12_SM - Infra-red spectrum of compound **4d.**

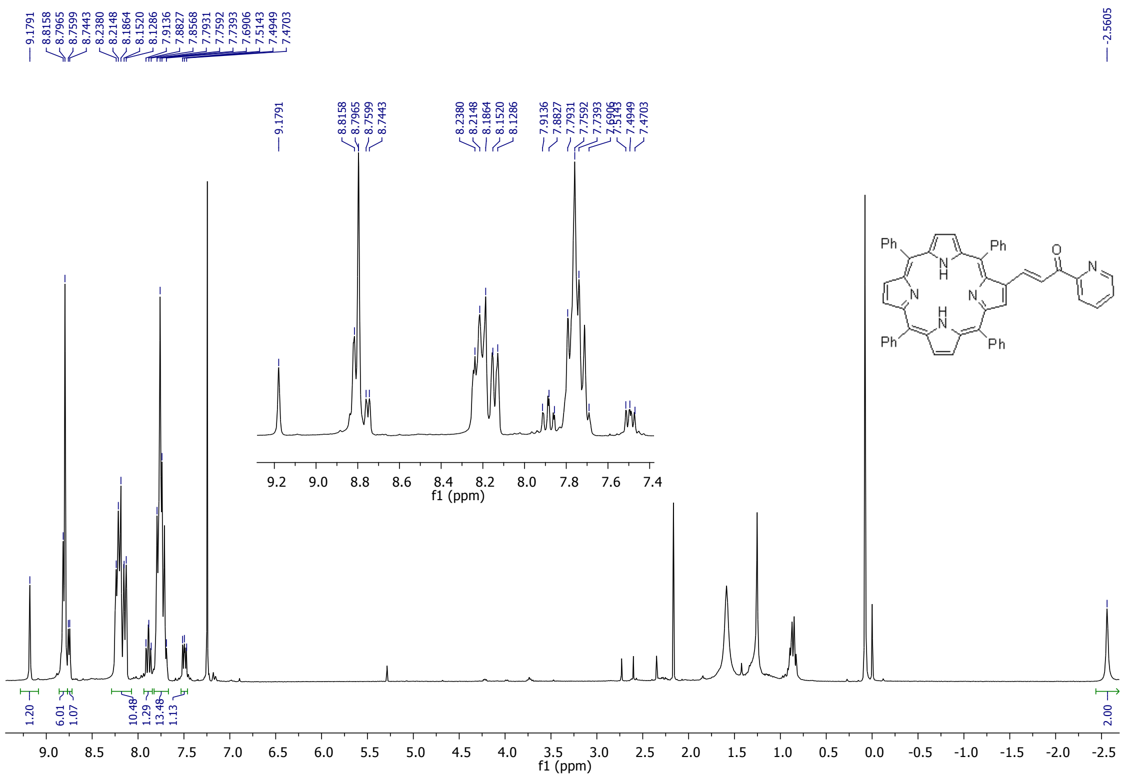


Figure 13_SM - ^{1}H NMR spectrum of compound **4e.**

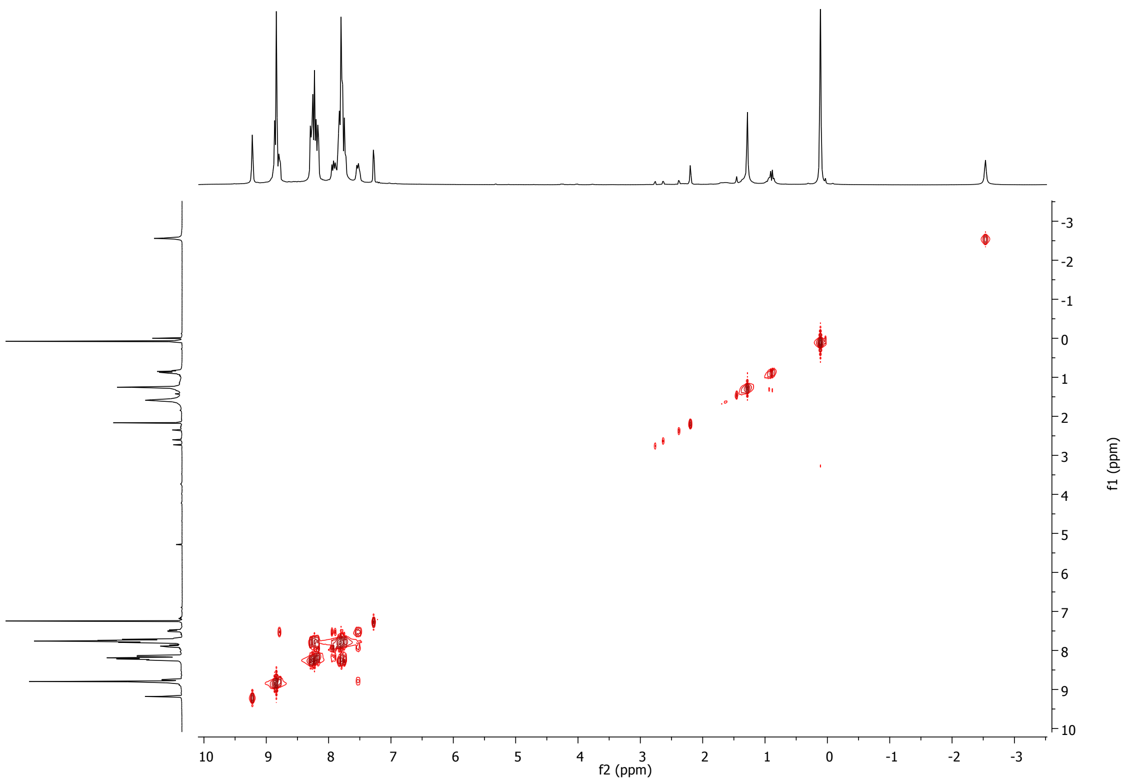


Figure 14_SM – COSY spectrum of compound **4e.**

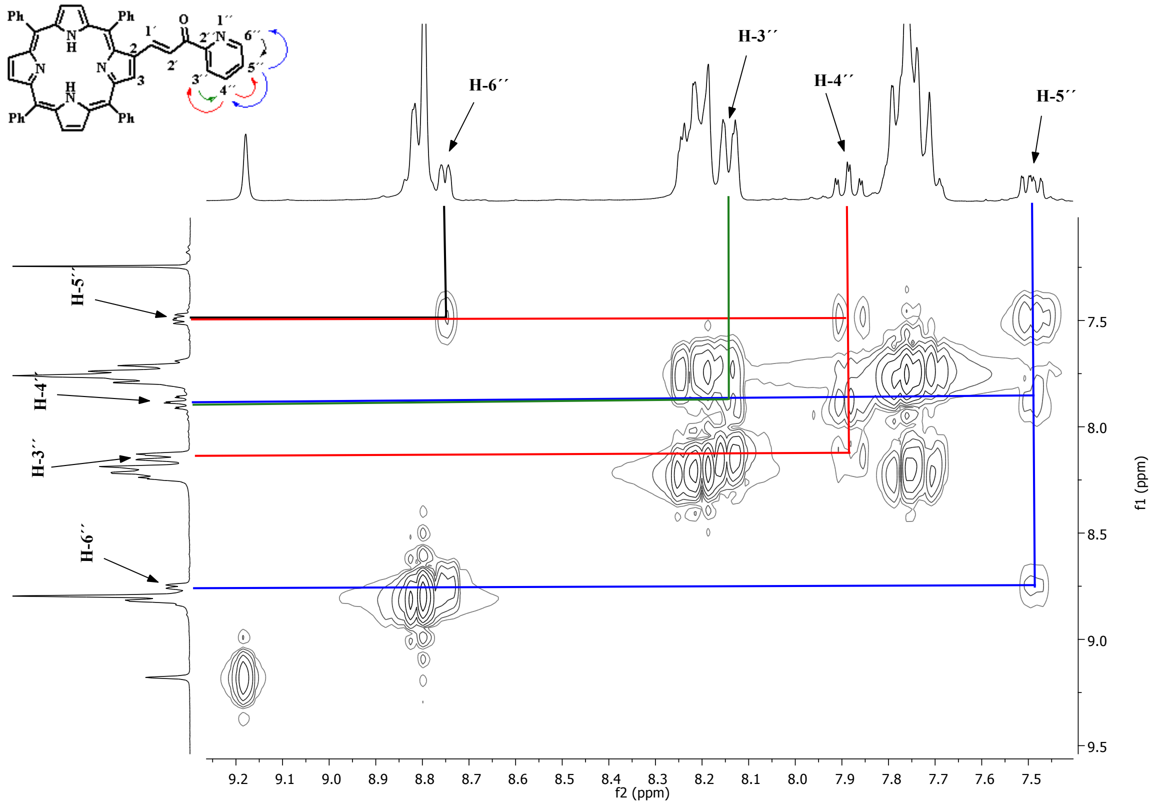


Figure 15_SM – Partial COSY spectrum of compound **4e.**

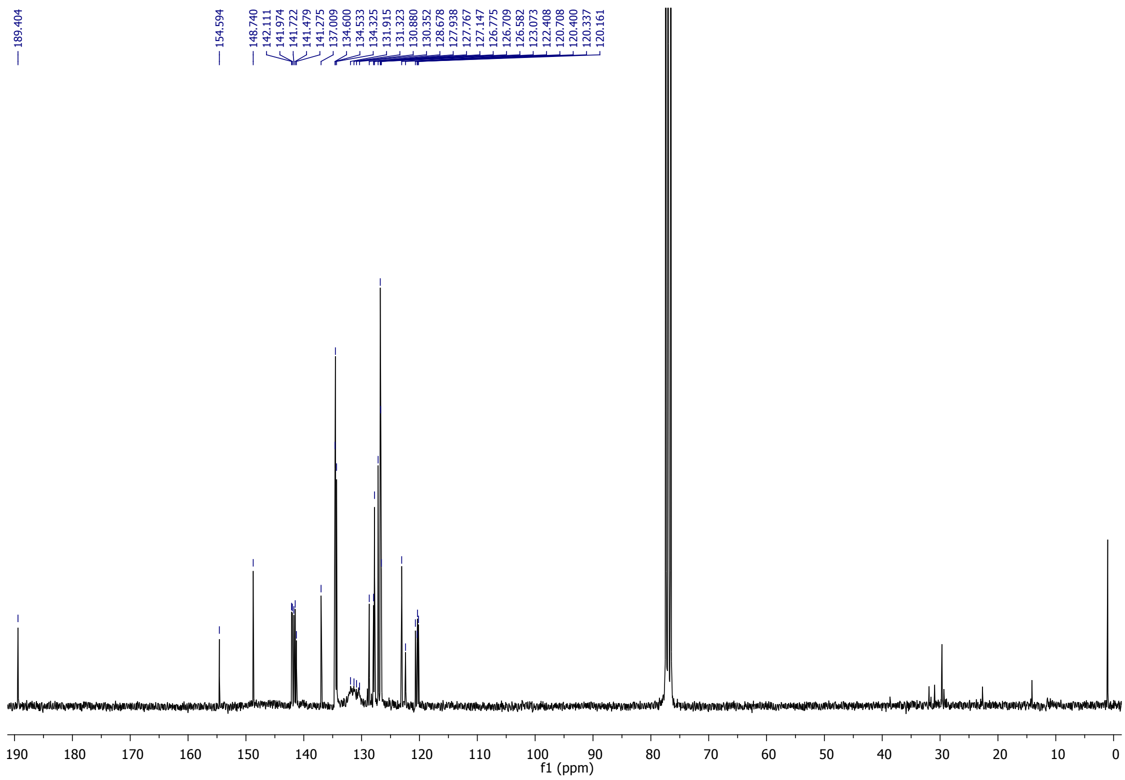


Figure 16_SM – ^{13}C NMR spectrum of compound **4e.**

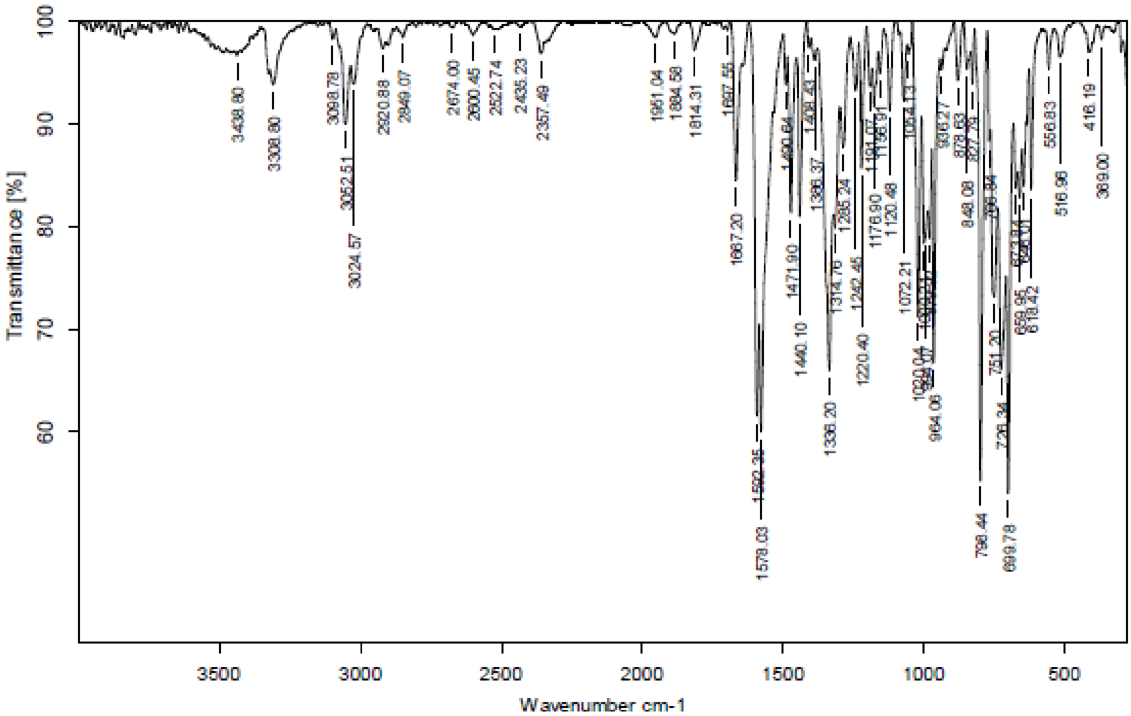


Figure 17_SM - Infra-red spectrum of compound **4e.**

II - Photophysical characterization data

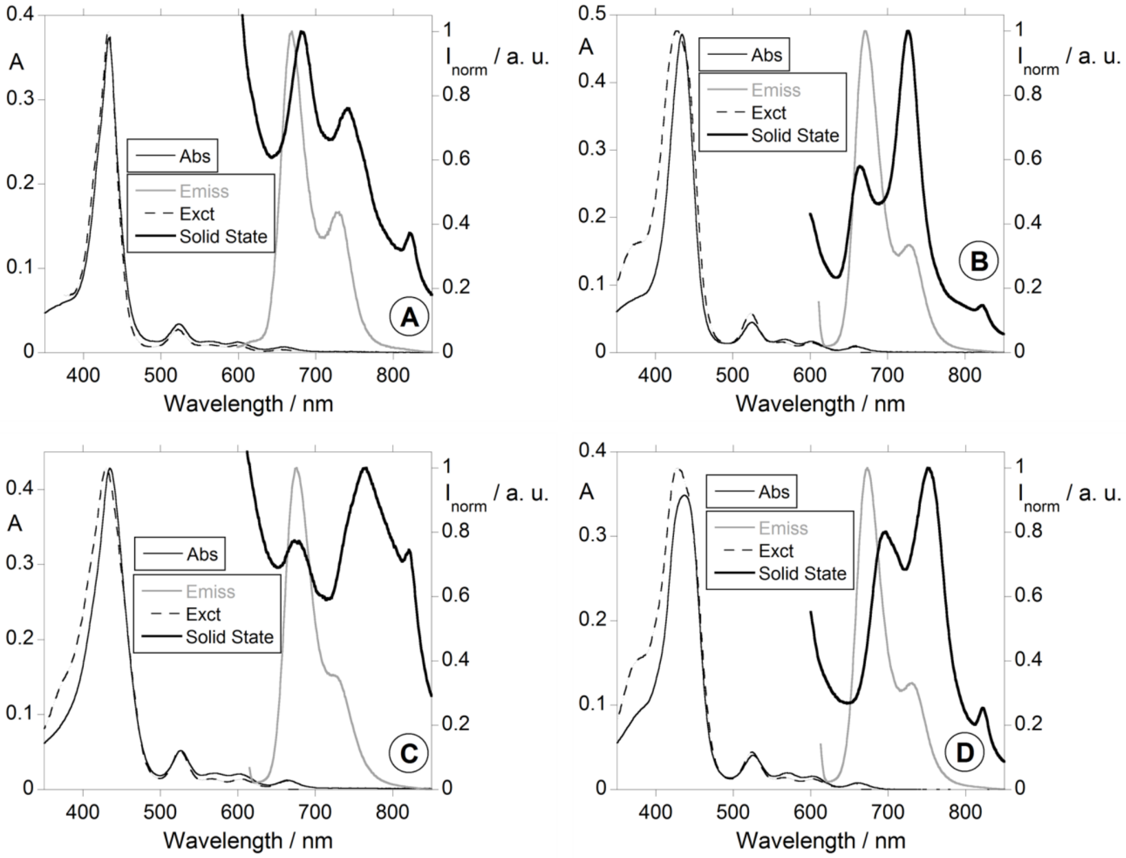


Figure 18_SM - Absorption and normalized emission and excitation of compounds **4a** (**A**), **4b** (**B**), **4d** (**C**) and **4e** (**D**) in $CHCl_3$ ([**4a**] = [**4b**] = [**4d**] = [**4e**] = 2.50 x 10^{-6} M, $\lambda_{exc\mathbf{4a}}$ = 602 nm and $\lambda_{emiss\mathbf{4a}}$ = 728 nm; $\lambda_{exc\mathbf{4b}}$ = 599 nm and $\lambda_{emiss\mathbf{4b}}$ = 728 nm; $\lambda_{exc\mathbf{4d}}$ = 601 nm and $\lambda_{emiss\mathbf{4c}}$ = 727 nm; $\lambda_{exc\mathbf{4e}}$ = 603 nm and $\lambda_{emiss\mathbf{4e}}$ = 731 nm) and emission of spectra in solid state at room temperature.

III - Metal ion titrations data

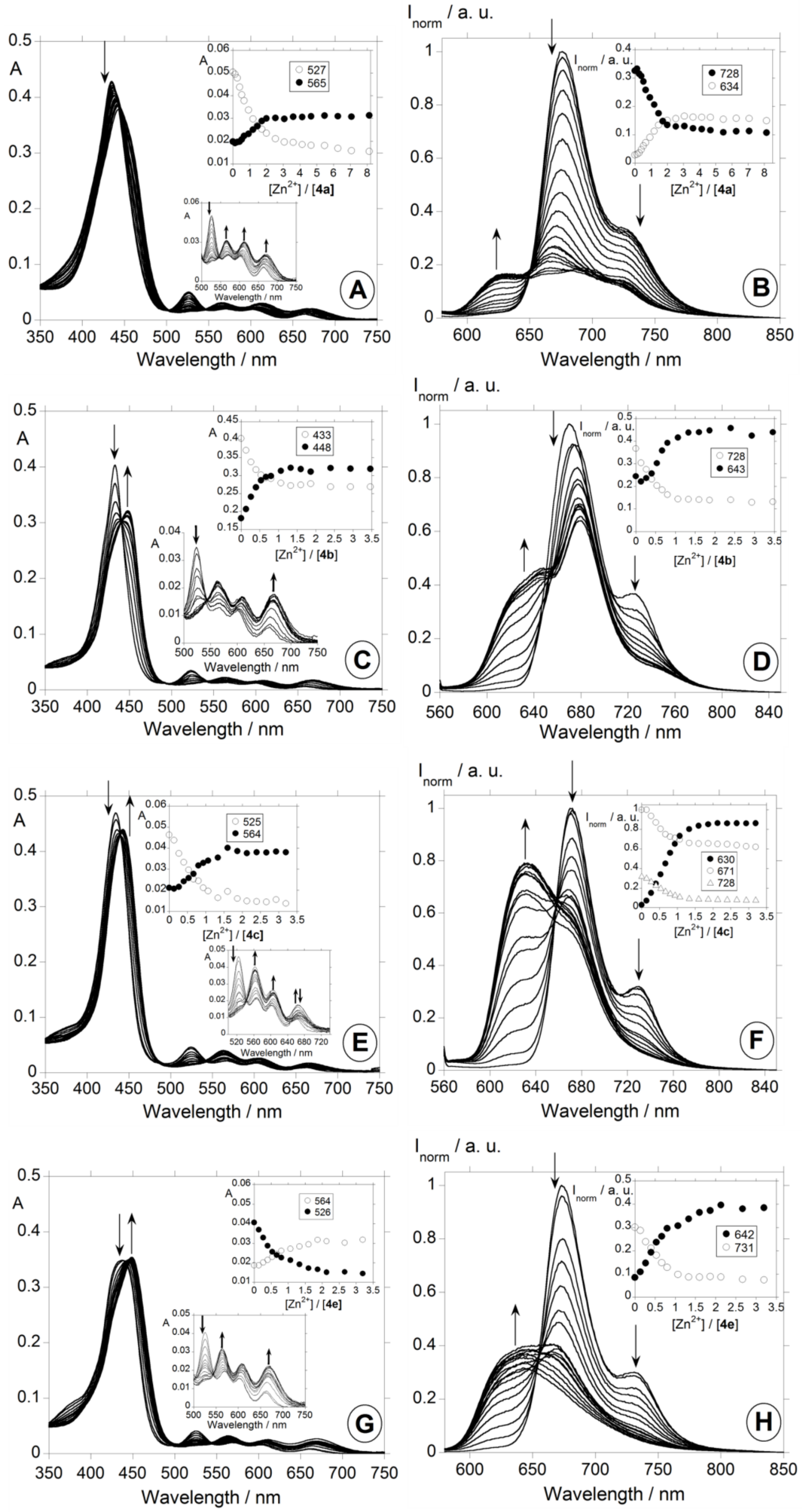


Figure 19_SM – Spectrophotometric (**A**, **C**, **E** and **G**) and spectrofluorimetric (**B**, **D**, **F** and **H**) titrations of compounds **4a**, **4b**, **4c** and **4e** in chloroform as a function of added Zn^{2+} in acetonitrile. The insets show the absorption at 527 and 565 nm (**A**), 433 and 448 nm (**C**), 525 and 564 nm (**E**) and 526 and 564 nm (**G**); and the normalized fluorescence intensity at 634 and 728 nm (**B**), 643 and 728 nm (**D**), 630, 671 and 728 nm (**F**) and 642 and 731 nm (**H**) ([**4a**] = [**4b**] = [**4c**] = [**4e**] = 2.50 x 10^{-6} M; $\lambda_{exc\mathbf{4a}}$ = 548 nm, $\lambda_{exc\mathbf{4b}}$ = 542 nm, $\lambda_{exc\mathbf{4c}}$ = 545 nm, $\lambda_{exc\mathbf{4e}}$ = 545 nm).

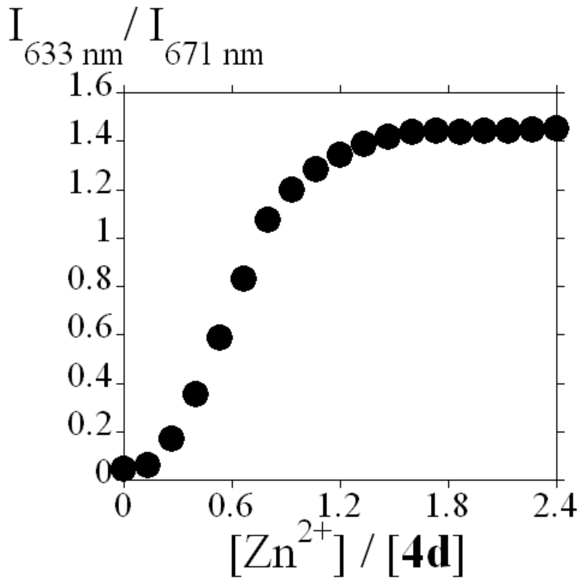


Figure 20_SM - Ratio ($I_{norm(633nm)}/I_{norm(671\ nm)}$ changes as a function of the Zn^{2+} concentration.

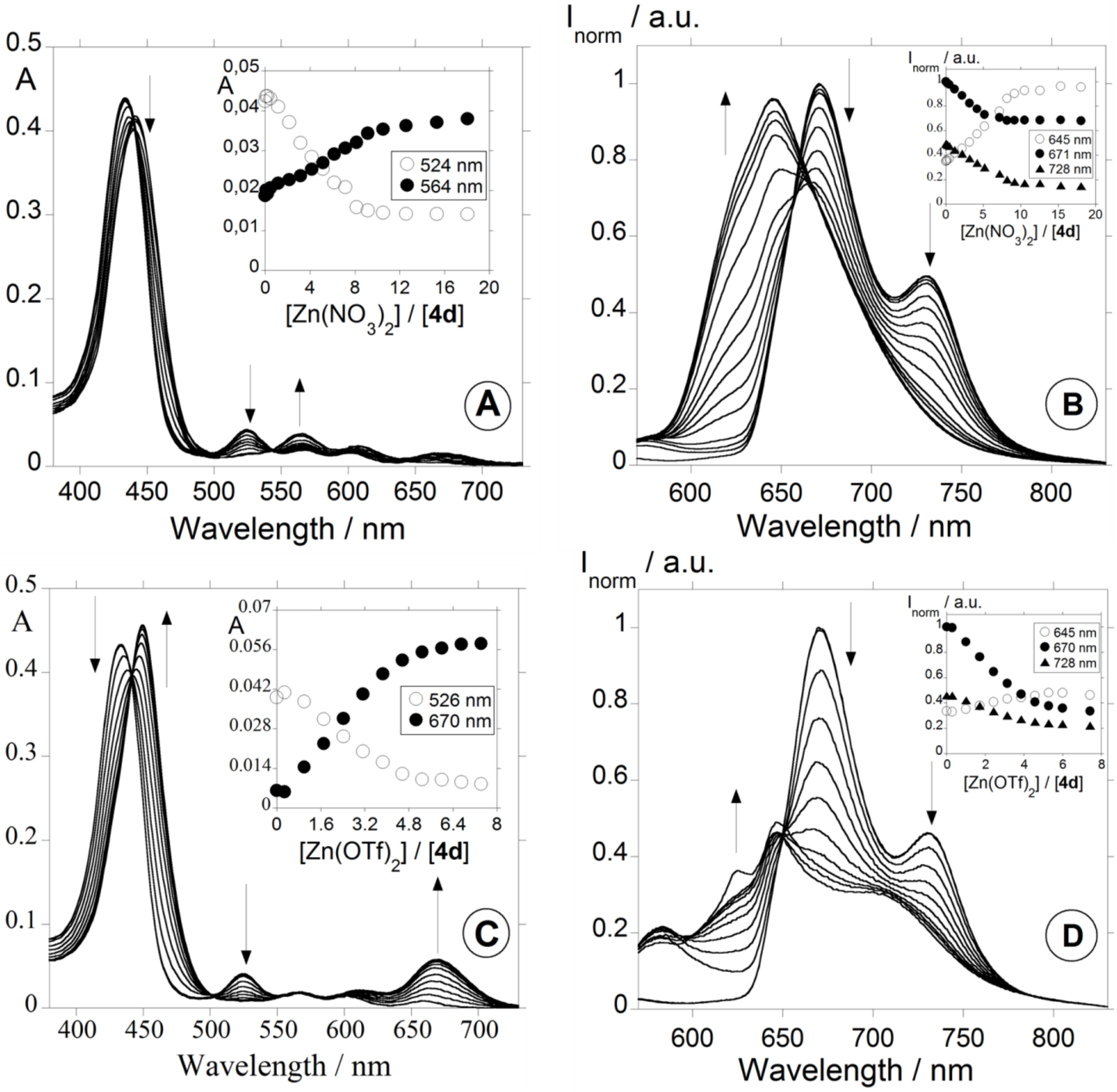


Figure 21_SM – Spectrophotometric (**A** and **C**) and spectrofluorimetric (**B** and **D**) titrations of compound **4d** in chloroform as a function of added $Zn(NO_3)_3$ and $Zn(OTf)_2$ in acetonitrile. The insets show the absorption at 524 and 564 nm (**A**) and 526 and 670 nm (**C**); and the normalized fluorescence intensity at 645, 671 and 728 nm (**B** and **C**) ([**4d**] = 2.50×10^{-6} M, $\lambda_{exc\mathbf{4d}}$ = 549 nm).

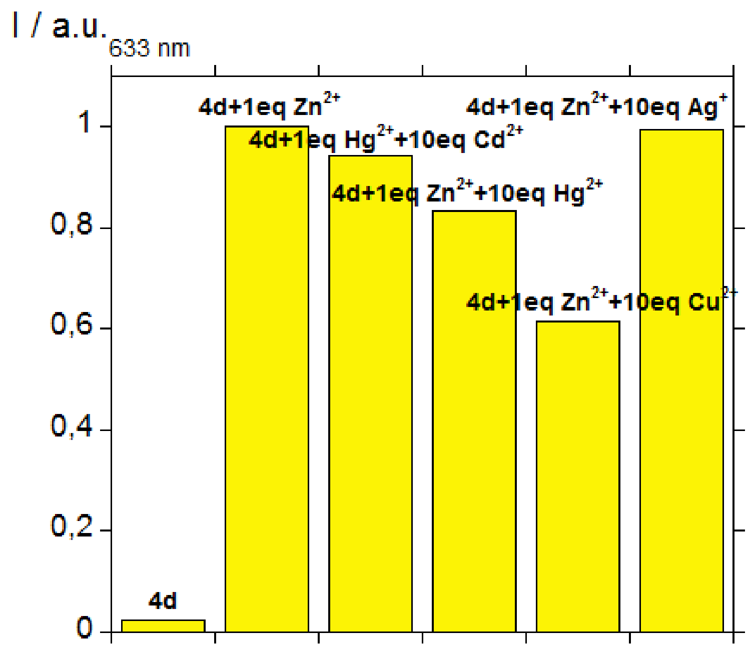


Figure 22_SM - Comparative fluorescence response of chemosensor **4d** (2.50×10^{-6} M, $\lambda_{exc\mathbf{4d}}$ = 549 nm) to Cu^{2+}, Hg^{2+}, Cd^{2+} and Ag^{+} (10 equiv.) in chloroform after the addition of $Zn(BF_4)_2.xH_2O$ (1 equiv.).

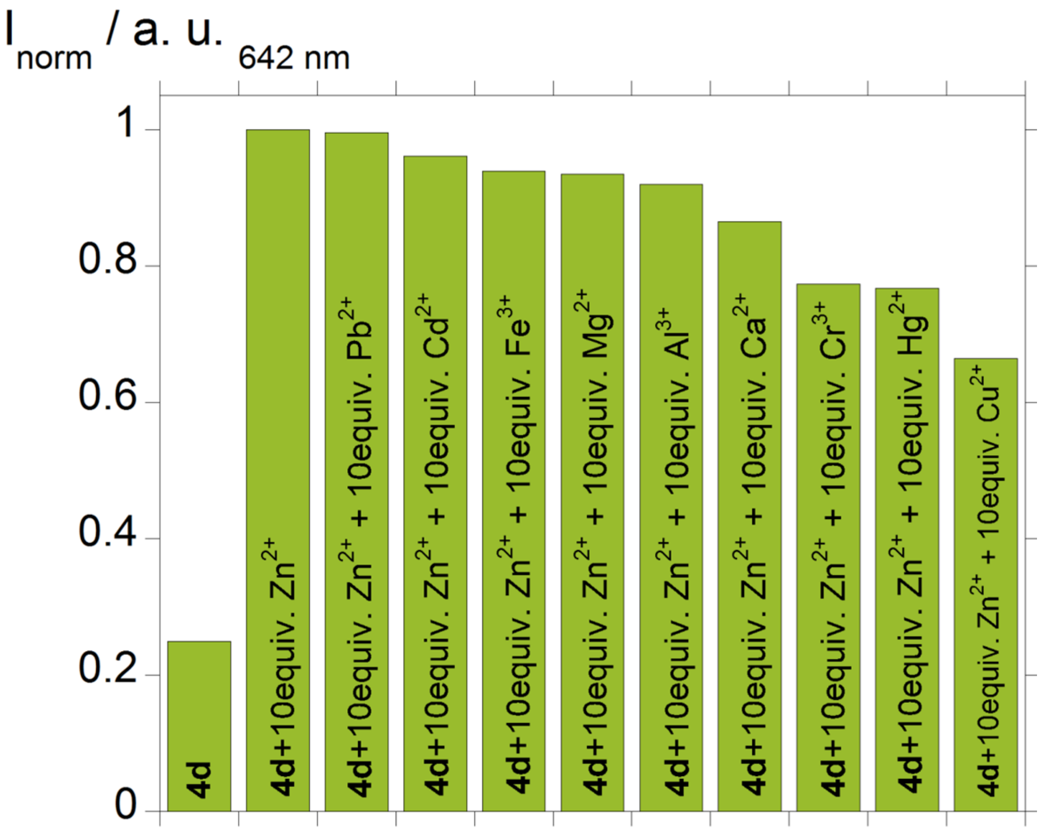


Figure 23_SM - Comparative fluorescence response of chemosensor **4d** (2.50×10^{-6} M, $\lambda_{exc\mathbf{4d}}$ = 549 nm) to Pb^{2+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Hg^{2+}, and Cu^{2+} (10 equiv.) after the addition of $Zn(NO_3)_2.xH_2O$ (10 equiv.).

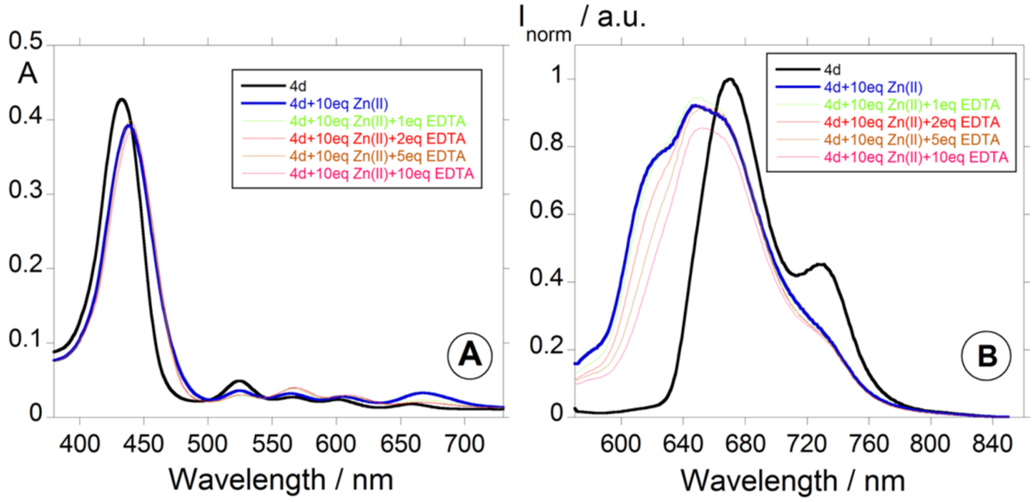


Figure 24_SM - Comparative absorption and fluorescence response of chemosensor **4d** in chloroform (2.50 x 10^{-6} M, $\lambda_{exc\mathbf{4d}}$ = 549 nm) to 1, 2, 5 and 10 equiv. of ethylenediaminetetraacetic acid (EDTA) in acetonitrile after the addition of Zn^{2+} (10 equiv.) in acetonitrile.

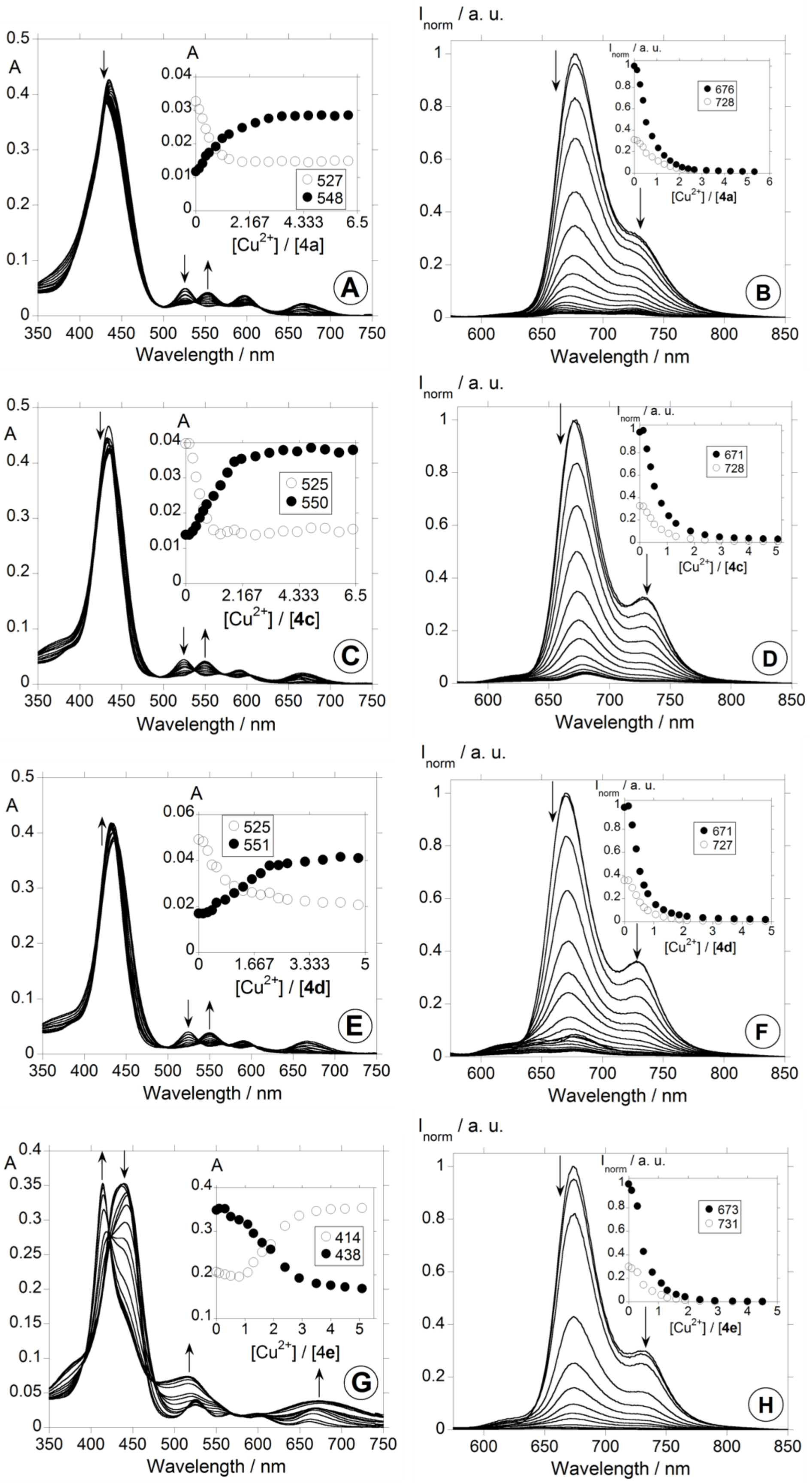


Figure 25_SM - Spectrophotometric (**A**, **C**, **E** and **G**) and spectrofluorimetric (**B**, **D**, **F** and **H**) titrations of compounds **4a**, **4c**, **4d** and **4e** in chloroform as a function of added Cu^{2+} in acetonitrile. The insets show the absorption at 527 and 548 nm (**A**), 525 and 550 nm (**C**), 525 and 551 nm (**E**) and 414 and 438 nm (**G**); and the normalized fluorescence intensity at 676 and 728 nm (**B**), 676 and 728 nm (**D**), 671 and 728 nm (**F**) and 673 and 731 nm (**H**) ([**4a**] = [**4c**] = [**4d**] = [**4e**] = 2.50 x 10^{-6} M; $\lambda_{\mathbf{exc4a}}$ = 548 nm, $\lambda_{\mathbf{exc4c}}$ = 545 nm, $\lambda_{\mathbf{exc4d}}$ = 549 nm, $\lambda_{\mathbf{exc4e}}$ = 545 nm).

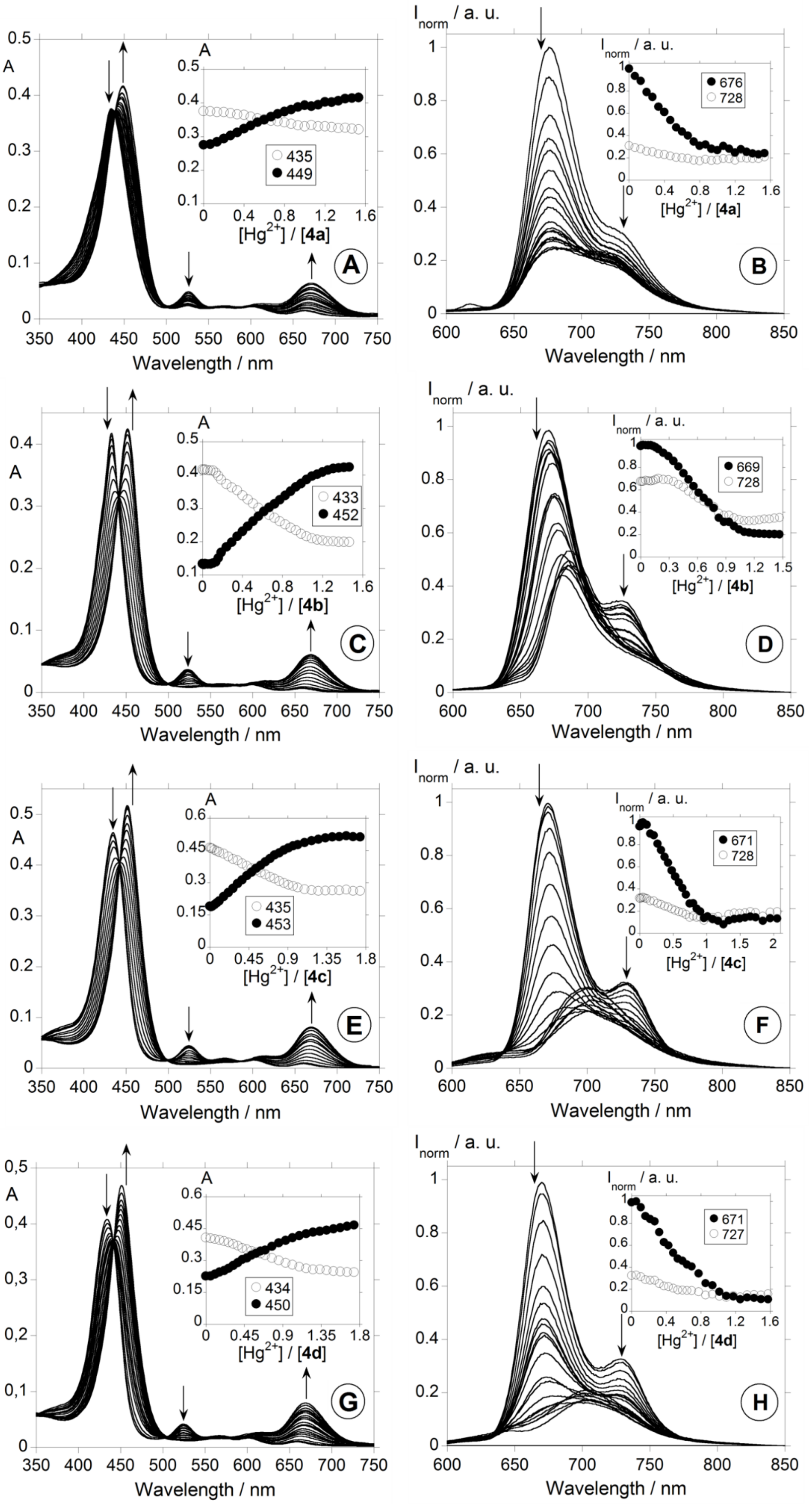


Figure 26_SM – Spectrophotometric (**A**, **C**, **E** and **G**) and spectrofluorimetric (**B**, **D**, **F** and **H**) titrations of compounds **4a**, **4b**, **4c** and **4d** in chloroform as a function of added Hg^{2+} in acetonitrile. The insets show the absorption at 435 and 449 nm (**A**), 433 and 452 nm (**C**), 435 and 453 nm (**E**) and 434 and 450 nm (**G**); and the normalized fluorescence intensity at 676 and 728 nm (**B**), 669 and 728 nm (**D**), 671 and 728 nm (**F**) and 671 and 727 nm (**H**) ([**4a**] = [**4b**] = [**4c**] = [**4e**] = 2.50 x 10^{-6} M; $\lambda_{exc\mathbf{4a}}$ = 548 nm, $\lambda_{exc\mathbf{4b}}$ = 542 nm, $\lambda_{exc\mathbf{4c}}$ = 545 nm, $\lambda_{exc\mathbf{4d}}$ = 549 nm).

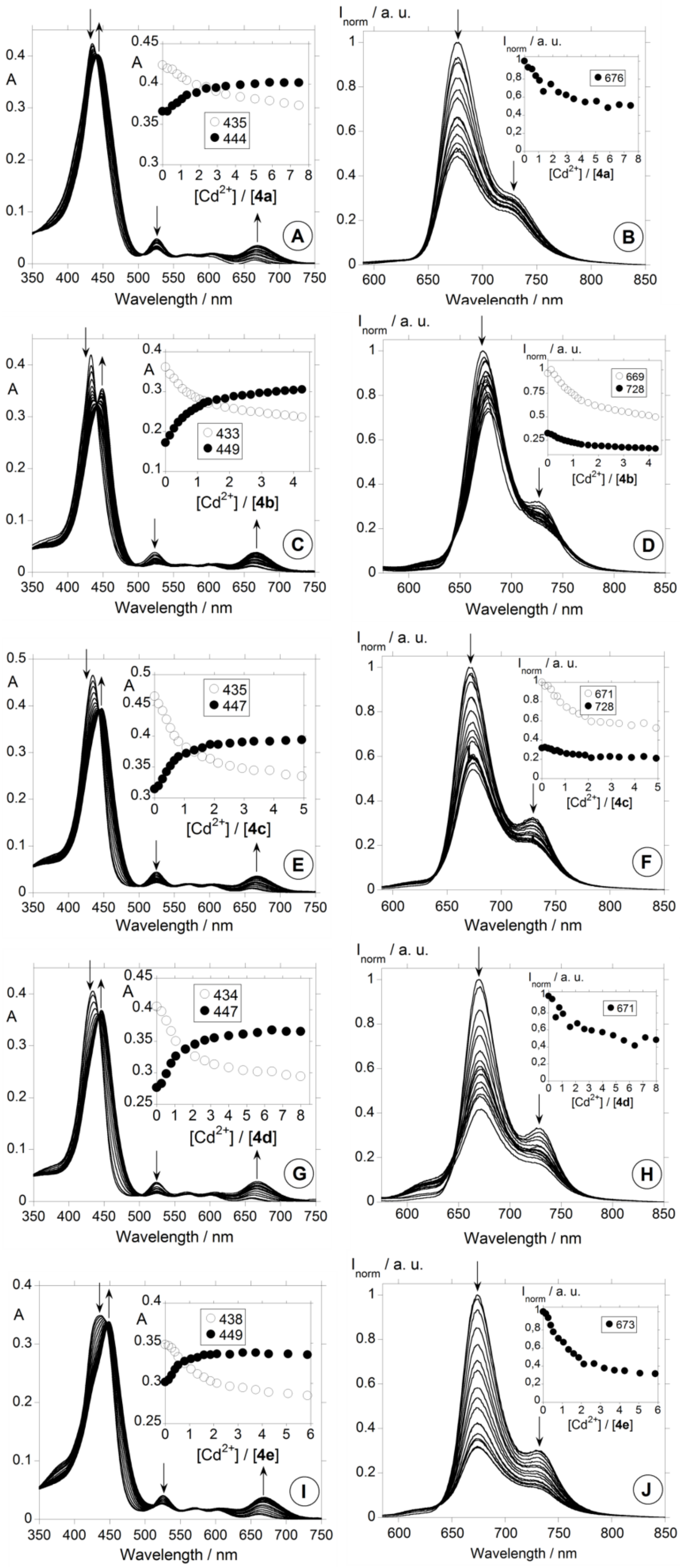


Figure 27_SM - Spectrophotometric (**A**, **C**, **E**, **G** and **I**) and spectrofluorimetric (**B**, **D**, **F**, **H** and **J**) titrations of compounds **4a**, **4b**, **4c**, **4d** and **4e** in chloroform as a function of added Cd^{2+} in acetonitrile. The insets show the absorption at 435 and 444 nm (**A**), 433 and 449 nm (**C**), 435 and 447 nm (**E**) 434 and 447 nm (**G**) and 438 and 479 nm (**I**); and the normalized fluorescence intensity at 676 nm (**B**), 669 and 728 nm (**D**), 671 and 728 nm (**F**), 671 (**H**) and 673 nm (**J**) (**[4a]** = **[4b]** = **[4c]** = **[4e]** = 2.50 x 10^{-6} M; $\lambda_{exc\mathbf{4a}}$ = 548 nm, $\lambda_{exc\mathbf{4b}}$ = 542 nm, $\lambda_{exc\mathbf{4c}}$ = 545 nm, $\lambda_{exc\mathbf{4d}}$ = 549 nm, $\lambda_{exc\mathbf{4e}}$ = 545 nm).

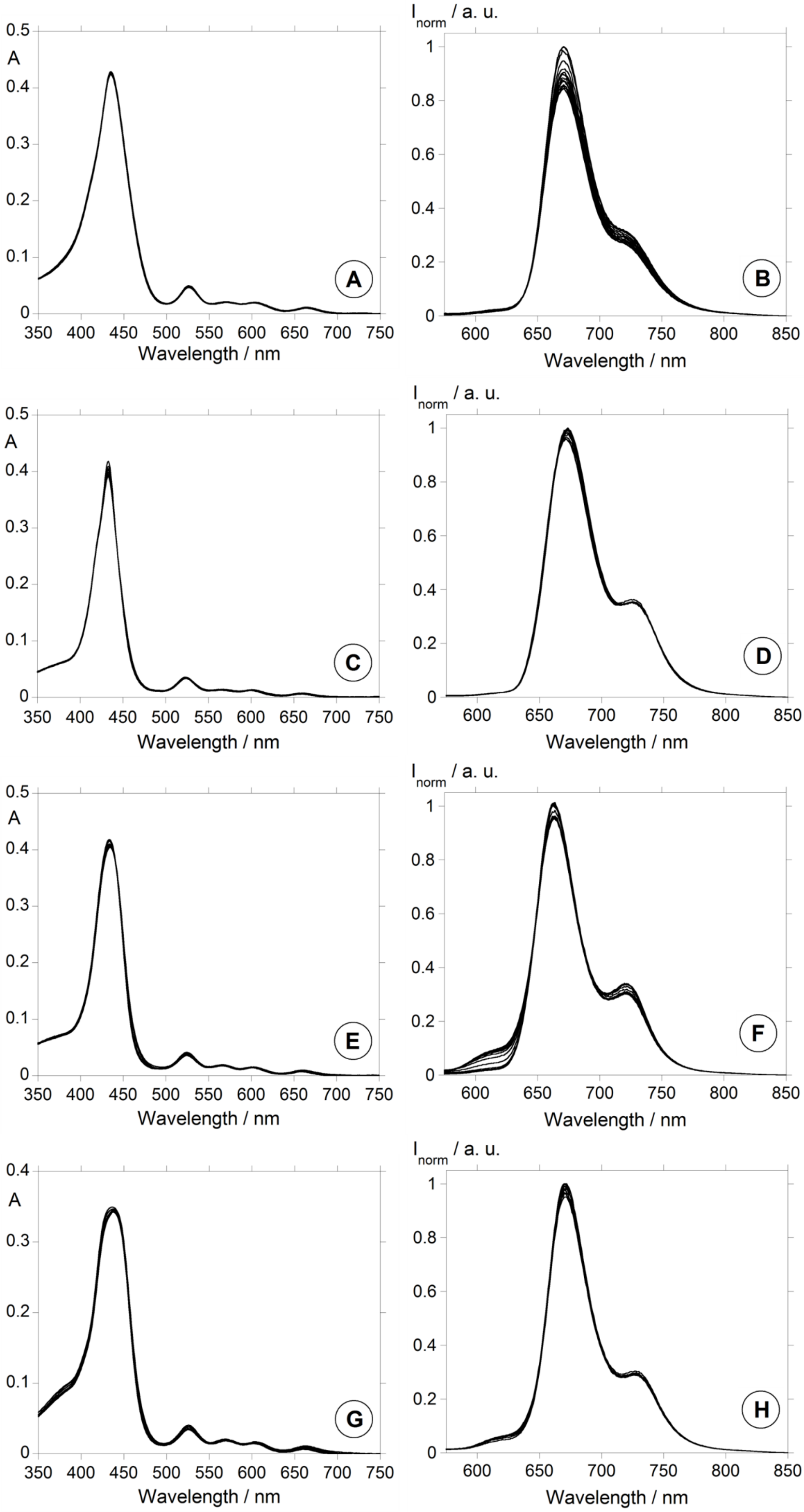


Figure 28_SM – Spectrophotometric (**A**, **C**, **E** and **G**) and spectrofluorimetric (**B**, **D**, **F** and **H**) titrations of compounds **4a**, **4b**, **4d** and **4e** in chloroform as a function of added Ag^+ in acetonitrile ([**4a**] = [**4b**] = [**4d**] = [**4e**] = 2.50 x 10^{-6} M; $\lambda_{exc\mathbf{4a}}$ = 548 nm, $\lambda_{exc\mathbf{4b}}$ = 542 nm, $\lambda_{exc\mathbf{4d}}$ = 549 nm, $\lambda_{exc\mathbf{4e}}$ = 545 nm).

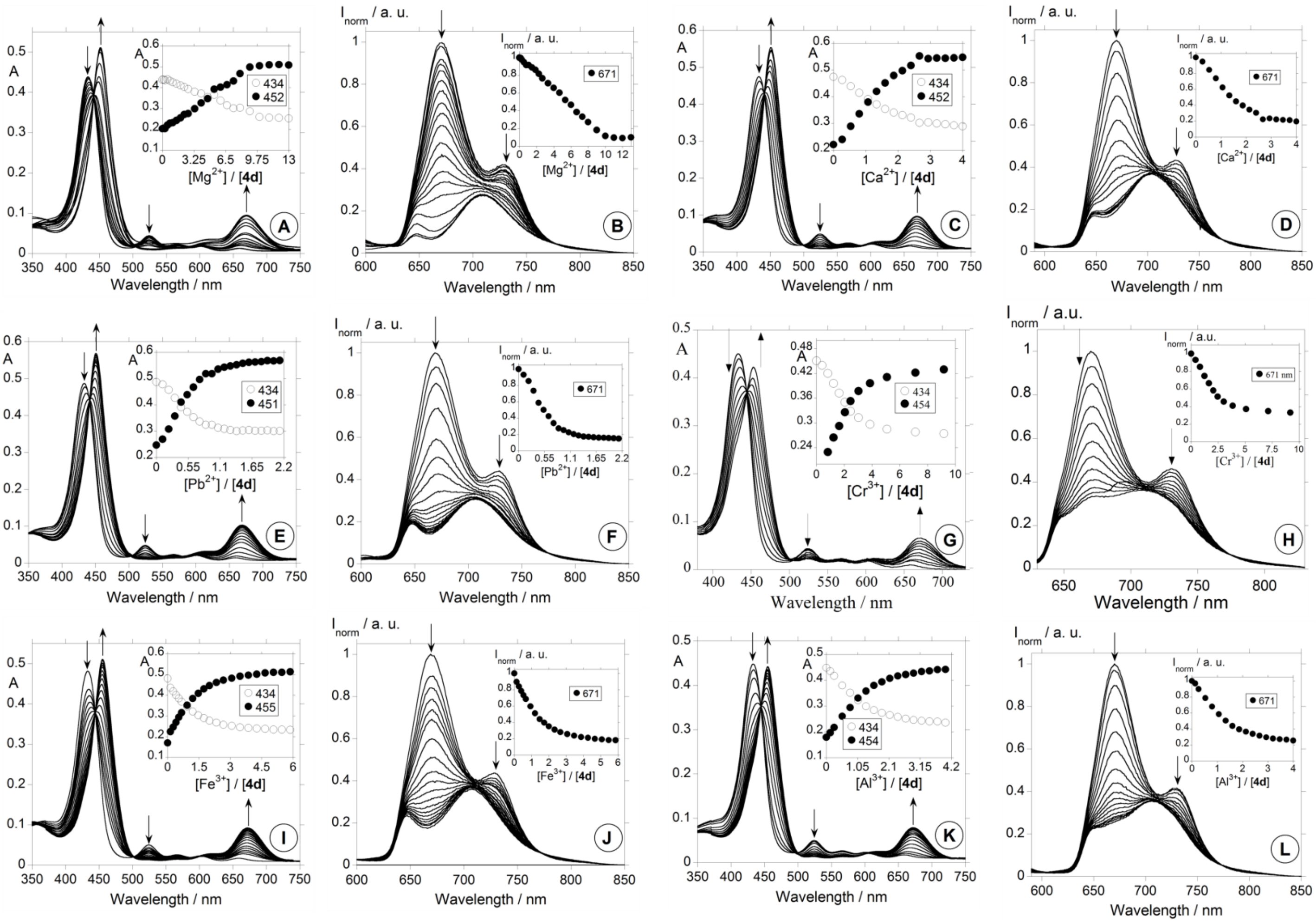


Figure 29_SM - Spectrophotometric (**A**, **C**, **E**, **G**, **I** and **K**) and spectrofluorimetric (**B**, **D**, **F**, **H**, **J** and **L**) titrations of compound **4d** in chloroform as a function of added Mg^{2+} (**A** and **B**), Ca^{2+} (**C** and **D**), Pb^{2+} (**E** and **F**), Cr^{3+} (**G** and **H**), Fe^{3+} (**I** and **J**) and Al^{3+} (**K** and **L**) in acetonitrile. The insets show the absorption at 434 and 452 nm (**A** and **C**), 434 and 451 nm (**E**), 434 and 454 nm (**G** and **K**) and 434 and 455 nm (**I**); and the normalized fluorescence intensity at 671 nm (**B**, **D**, **F**, **H**, **J** and **L**) ([**4d**] = 2.50 x 10^{-6} M, $\lambda_{exc\mathbf{4d}}$ = 549 nm; [Mg^{2+}] = [Ca^{2+}] = [Cr^{3+}] = [Fe^{3+}] = [Al^{3+}] = 1.00 x 10^{-3} M; [Pb^{2+}] = 4.70 x 10^{-3} M). (**G** and **H**)

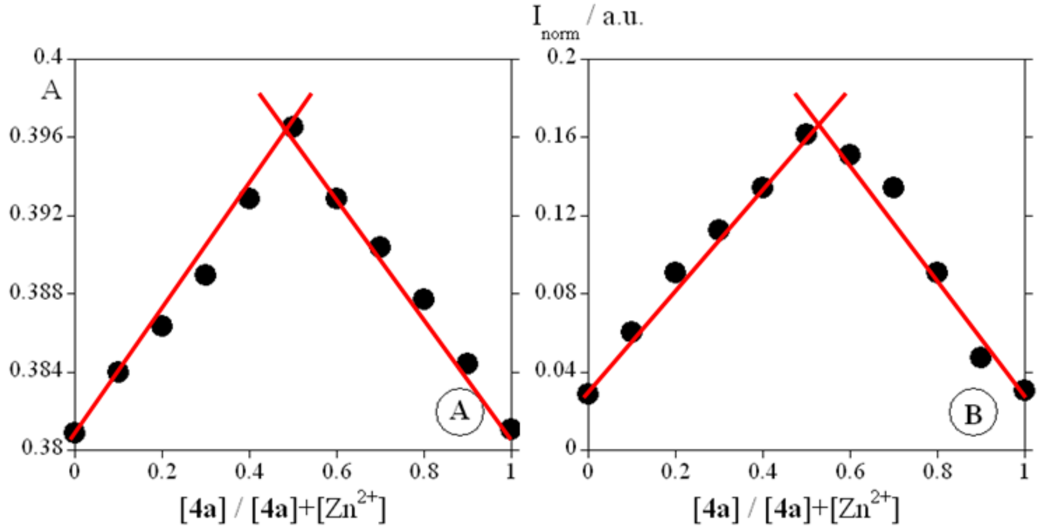


Figure 30_SM - Job's plot for the UV-Vis (**A**) and fluorescence emission (**B**) titration profiles of compound **4a** (2.50×10^{-6} M) with Zn^{2+} shows 1:1 (**4a**:Zn^{2+}) complex stoichiometry: (**A**) with respect to 433 nm and (**B**) with respect to 634 nm.

Table 1_SM - Stability constants for chemosensor **4d** in the presence of $Zn(NO_3)_2.xH_2O$, $Zn(OTf)_2.xH_2O$ $Mg(OTf)_2.xH_2O$, $Pb(OTf)_2.xH_2O$, $Ca(BF_4)_2$, $Cr(NO_3)_3.xH_2O$, $Fe(NO_3)_3$ and $Al(NO_3)_3$ in $CHCl_3$ for an interaction 1:1 (metal:ligand).

Compound	**Interaction (M:L)**	**Σ log β (Abs)**	**Σ log β (Emiss)**
4d	$Zn(NO_3)_2.xH_2O$	$6.58 \pm 1.07 \times 10^{-3}$	$6.54 \pm 9.77 \times 10^{-2}$
	$Zn(OTf)_2.xH_2O$	$6.85 \pm 2.07 \times 10^{-3}$	$6.81 \pm 1.92 \times 10^{-2}$
	$Mg(OTf)_2.xH_2O$	$4.33 \pm 3.45 \times 10^{-3}$	$2.78 \pm 1.47 \times 10^{-2}$
	$Ca(BF_4)_2$	$5.75 \pm 2.21 \times 10^{-3}$	$5.74 \pm 8.70 \times 10^{-3}$
	$Pb(OTf)_2.xH_2O$	$7.45 \pm 3.11 \times 10^{-3}$	$7.54 \pm 1.30 \times 10^{-2}$
	$Cr(NO_3)_3.xH_2O$	$5.33 \pm 1.31 \times 10^{-3}$	$5.39 \pm 5.39 \times 10^{-2}$
	$Fe(NO_3)_3$	$5.83 \pm 2.35 \times 10^{-3}$	$5.80 \pm 8.35 \times 10^{-3}$
	$Al(NO_3)_3$	$5.94 \pm 1.84 \times 10^{-3}$	$5.86 \pm 2.19 \times 10^{-2}$

Table 2_SM - Limits of detection (LOD) and quantification (LOQ) in ppb for Zn^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+} and Ag^{+} with compounds **4a-e**.

Compound	Metal ion	LOD	LOQ
4a	Zn^{2+}	160 ± 10	240 ± 10
	Cu^{2+}	150 ± 10	950 ± 10
	Hg^{2+}	60 ± 10	260 ± 10
	Cd^{2+}	270 ± 10	1090 ± 10
4b	Zn^{2+}	80 ± 10	240 ± 10
	Cu^{2+}	70 ± 10	270 ± 10
	Hg^{2+}	230 ± 10	430 ± 10
	Cd^{2+}	270 ± 10	550 ± 10
4c	Zn^{2+}	160 ± 10	240 ± 10
	Cu^{2+}	70 ± 10	150 ± 10
	Hg^{2+}	190 ± 10	330 ± 10
	Cd^{2+}	180 ± 10	410 ± 10
	Ag^{+}	380 ± 10	780 ± 10
4d	Zn^{2+}	240 ± 10	560 ± 10
	Cu^{2+}	70 ± 10	320 ± 10
	Hg^{2+}	130 ± 10	190 ± 10
	Cd^{2+}	550 ± 10	1090 ± 10
4e	Zn^{2+}	160 ± 10	320 ± 10
	Cu^{2+}	70 ± 10	150 ± 10
	Hg^{2+}	330 ± 10	410 ± 10
	Cd^{2+}	140 ± 10	270 ± 10

IV - NMR titrations

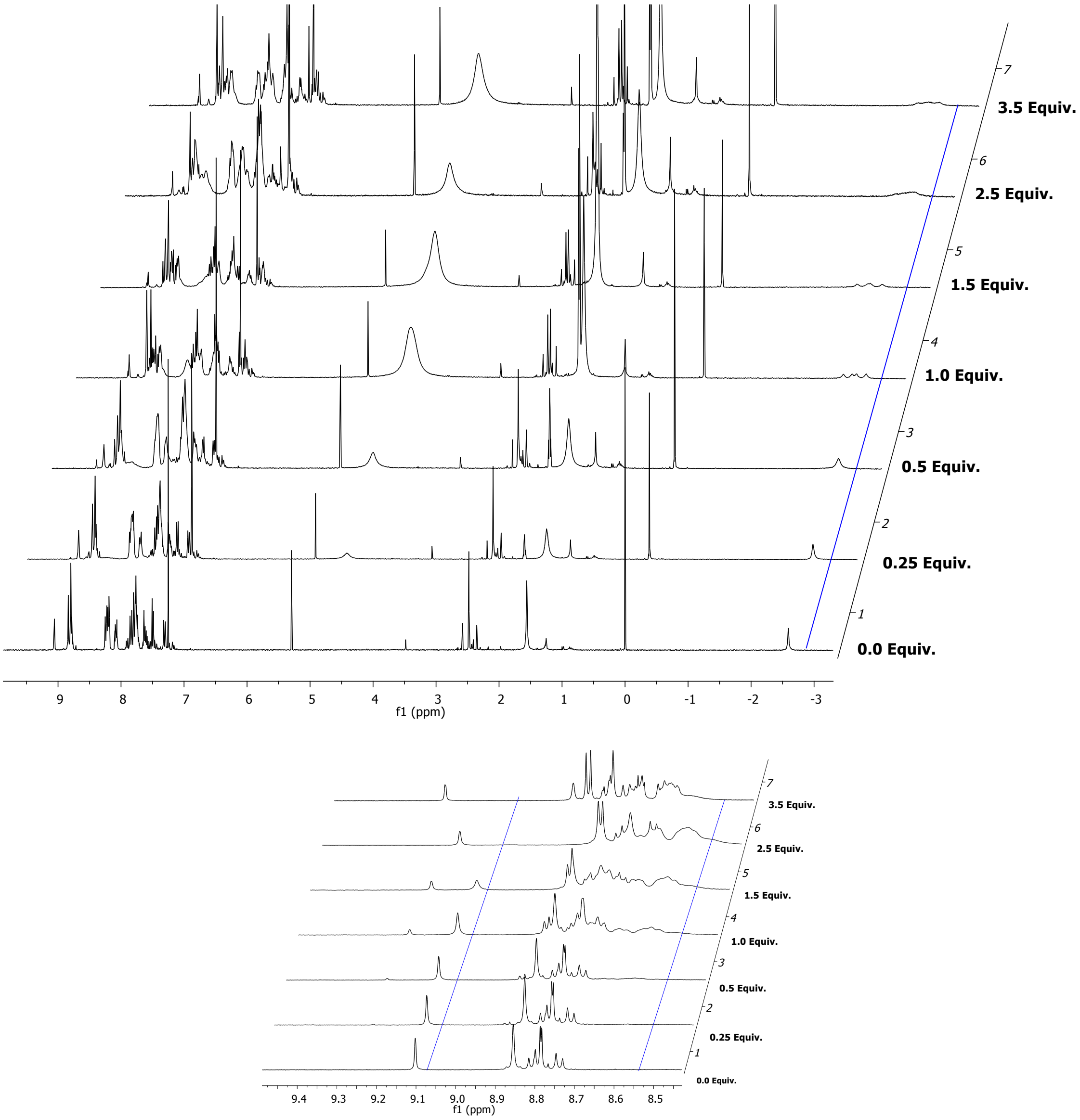


Figure 30_SM - [1]H NMR spectra of **4c** (2.5×10^{-3} mM) in $CDCl_3$ upon addition of increasing amounts of Zn^{2+} (from 0 to 3.5 equiv) in CD_3CN.

V - MALDI-TOF-MS titrations data

Table 3_SM - Major peaks observed in the metal titration of chemosensor **4b** followed by MALDI-TOF-MS.

Metal	Stoichiometry (ligand:metal)	Dried-droplet		Layer-by-Layer	
		m/z	**Relative intensity (%)**	***m/z***	**Relative intensity (%)**
Zn^{2+}	1:1	745.13 806.01	100.00 [**4b**+H]$^+$ 38.00 [(**4b**-2H)+Zn]$^{+\bullet}$	745.15 806.05	100.00 [**4b**+H]$^+$ 16.00 [(**4b**-2H)+Zn]$^{+\bullet}$
	1:2	745.20 806.10	100.00 [**4b**+H]$^+$ 91.00 [(**4b**-2H)+Zn]$^{+\bullet}$		
Hg^{2+}	1:1	745.36	100.00 [**4b**+H]$^+$	744.16 944.10	100.00 [**4b**]$^{+\bullet}$ 17.00 [(**4b**-2H)+Hg]$^{+\bullet}$
	1:2	745.17	100.00 [**4b**+H]$^+$		
Cu^{2+}	1:1	805.05	100.00 [(**4b**-2H)+Cu]$^{+\bullet}$	745.13 805.07	100.00 [**4b**+H]$^+$ 79.00 [(**4b**-2H)+Cu]$^{+\bullet}$
	1:2	805.05	100.00 [(**4b**-2H)+Cu]$^{+\bullet}$		
Cd^{2+}	1:1	745.18	100.00 [**4b**+H]$^+$	745.17 854.06	100.00 [**4b**+H]$^+$ 5.00 [(**4b**-4H)+Cd]$^{+\bullet}$
	1:2	745.18	100.00 [**4b**+H]$^+$		
Ag^+	1:1	745.13 851.01	100.00 [**4b**+H]$^+$ 86.00 [(**4b**-H)+Ag]$^{+\bullet}$	745.15 850.96	41.00 [**4b**+H]$^+$ 100.00 [(**4b**-H)+Ag]$^{+\bullet}$
	1:2	745.13 851.01	56.00 [**4b**+H]$^+$ 100.00 [(**4b**-H)+Ag]$^{+\bullet}$		

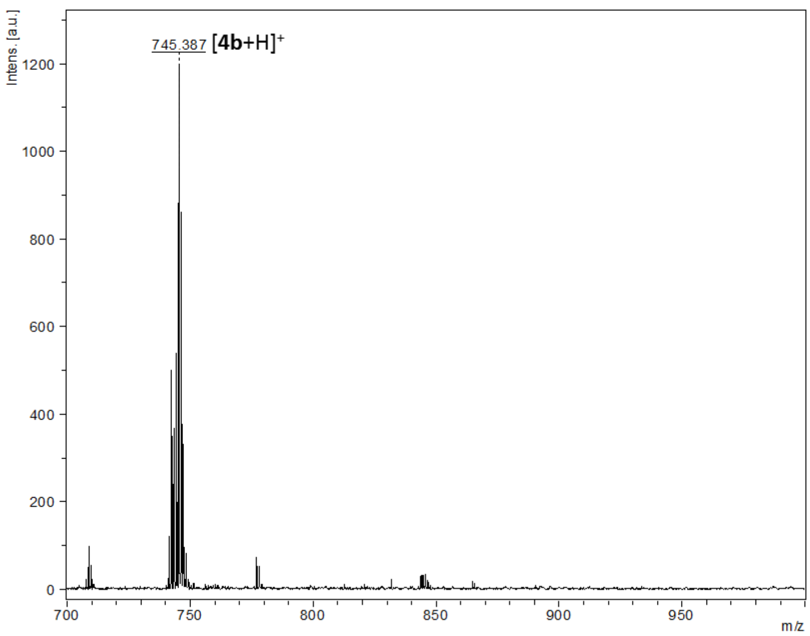
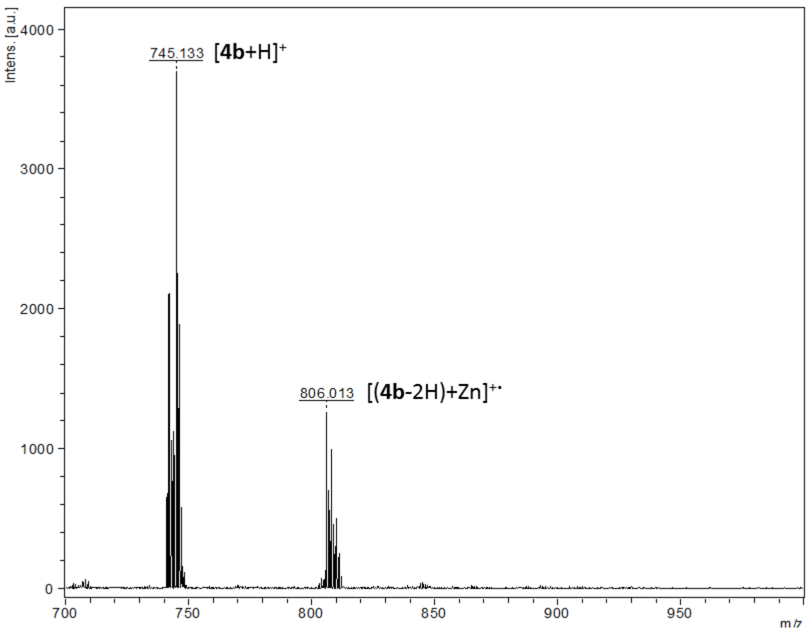


Figure 31_SM - MALDI-TOF mass spectra of compound **4b.**



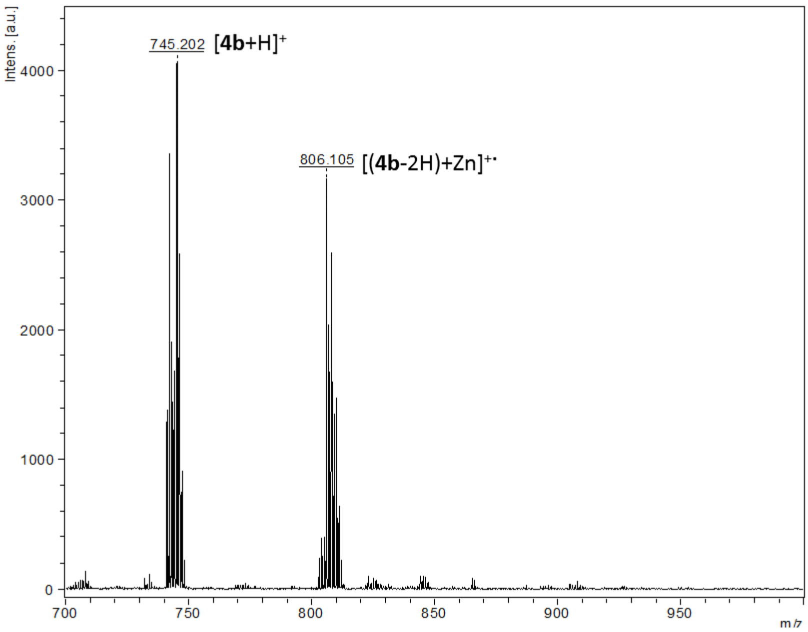


Figure 32_SM - MALDI-TOF mass spectra of compound **4b** after titration with 1 equiv. (above) and 2 equiv. of $Zn(BF_4)_2.xH_2O$) (below) (*dried-droplet method*).

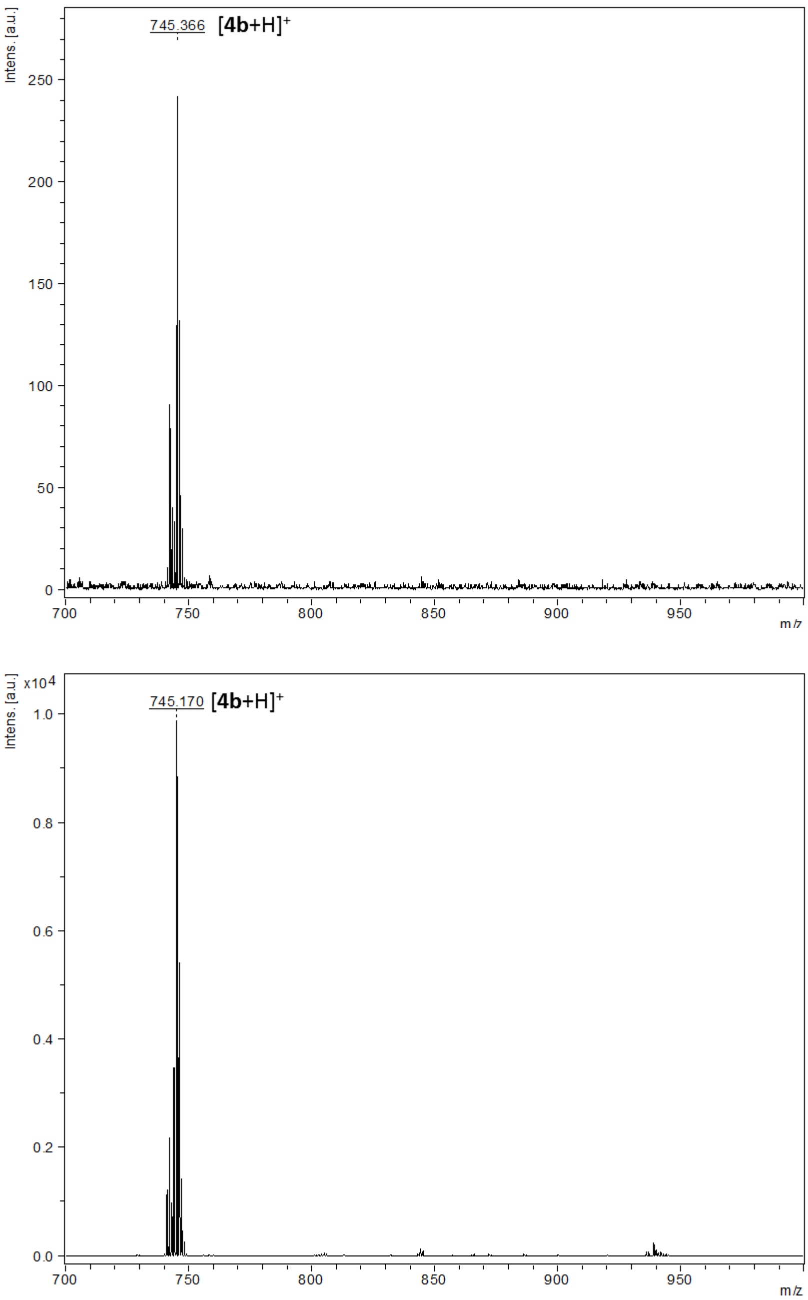
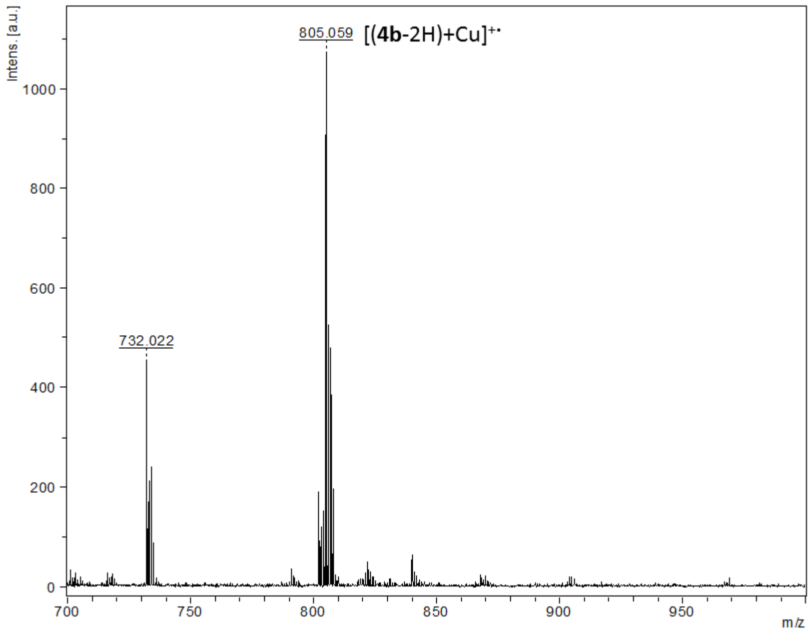


Figure 33_SM - MALDI-TOF mass spectra of compound **4b** after titration with 1 equiv. (above) and 2 equiv. of $Hg(BF_4)_2.xH_2O$) (below) (*dried-droplet method*).



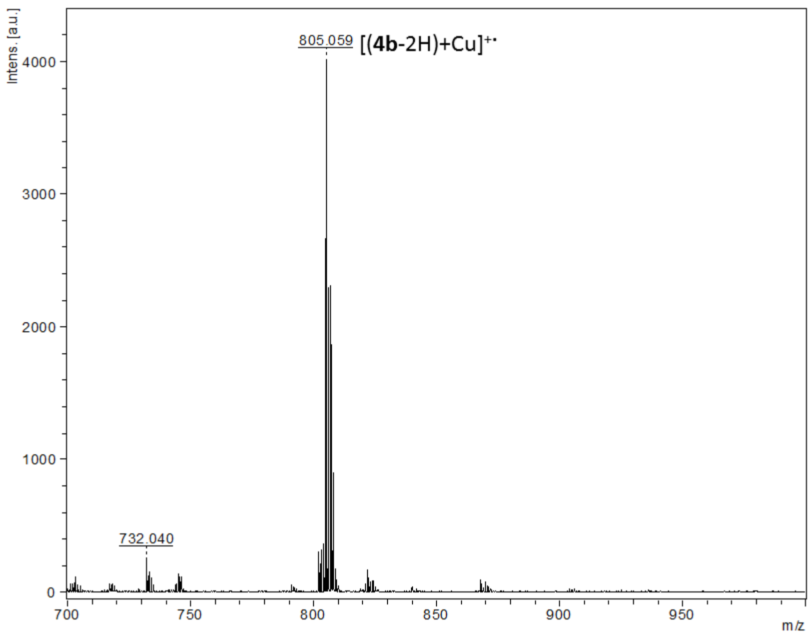
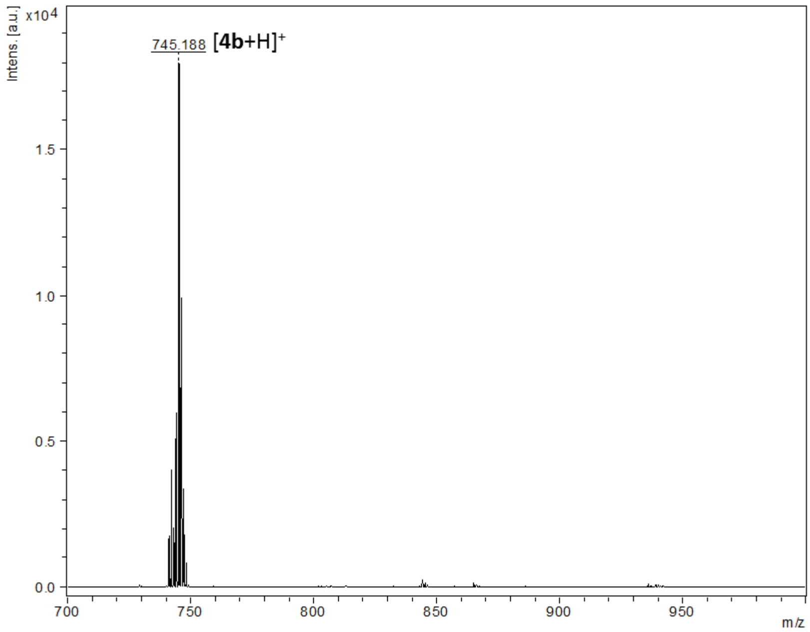


Figure 34_SM - MALDI-TOF mass spectra of compound **4b** after titration with 1 equiv. (above) and 2 equiv. of $Cu(BF_4)_2.xH_2O$) (below) (*dried-droplet method*).



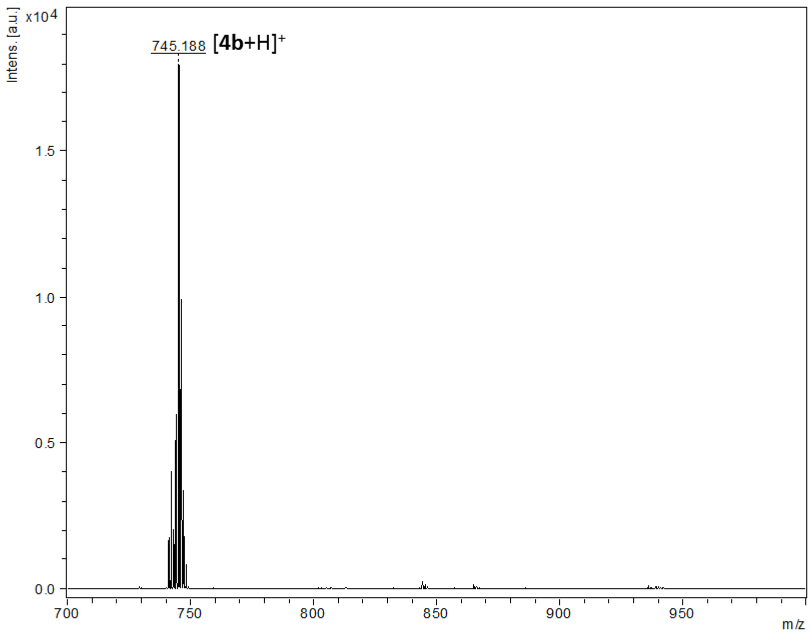


Figure 35_SM - MALDI-TOF mass spectra of compound **4b** after titration with 1 equiv. (above) and 2 equiv. of $Cd(BF_4)_2.xH_2O$) (below) (*dried-droplet method*).

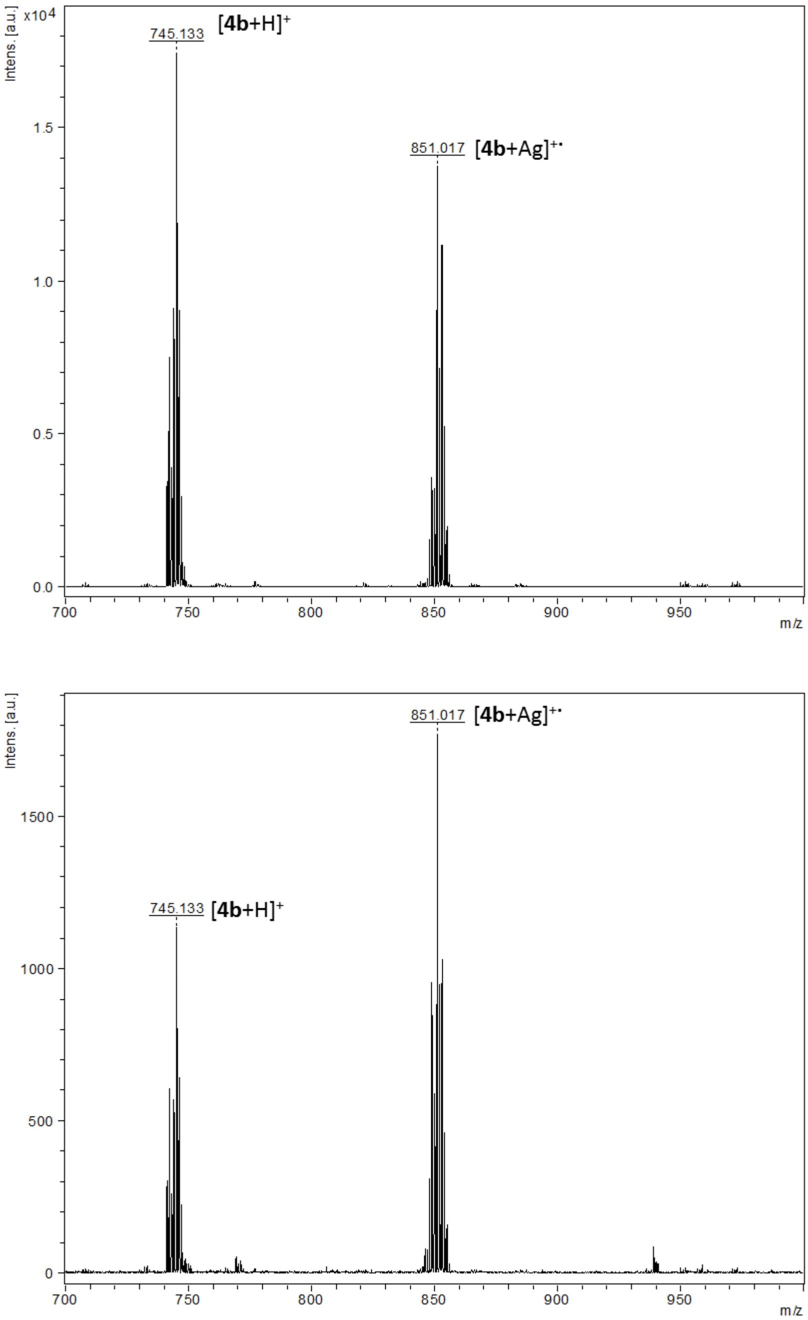


Figure 36_SM - MALDI-TOF mass spectra of compound **4b** after titration with 1 equiv. (above) and 2 equiv. of $Ag(BF_4).xH_2O$) (below) (*dried-droplet method*).

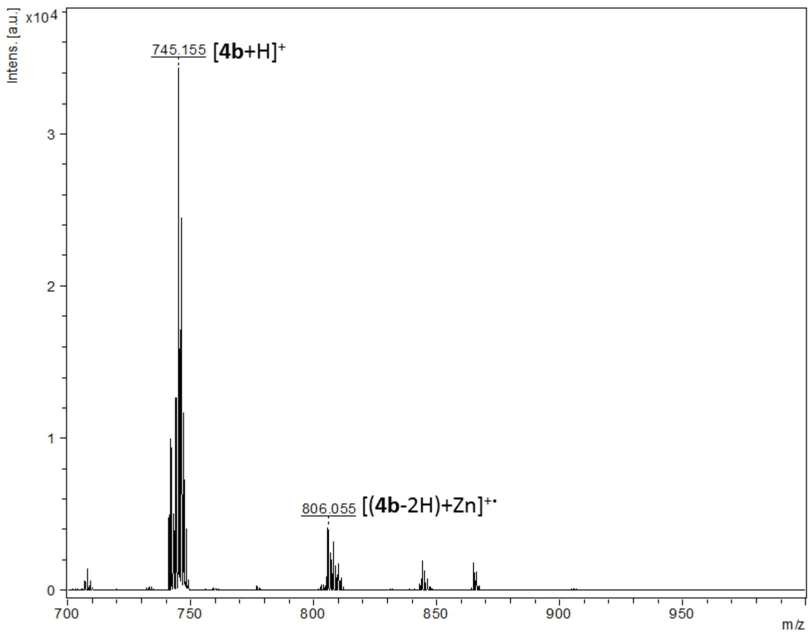


Figure 37_SM - MALDI-TOF mass spectra of compound **4b** after titration with of $Zn(BF_4)_2.xH_2O$ (*layer-by-layer method*).

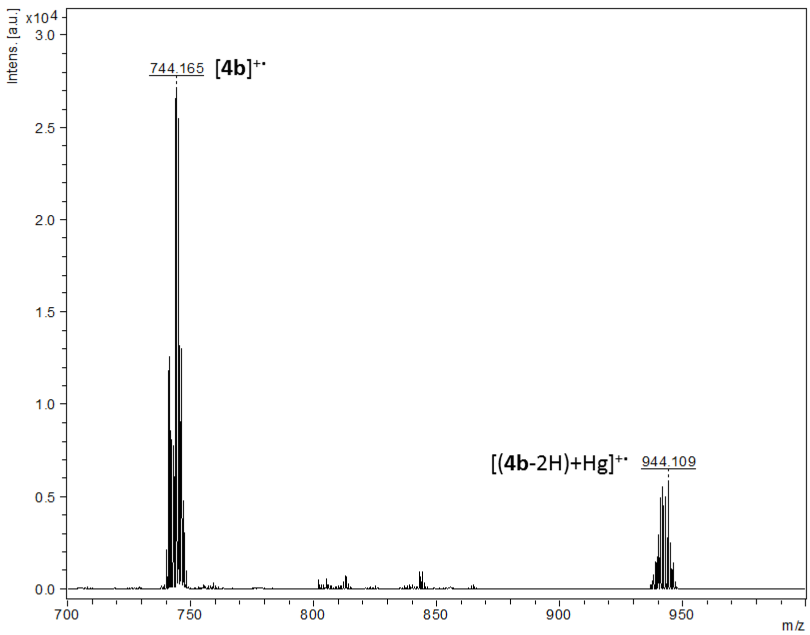


Figure 38_SM. MALDI-TOF mass spectra of compound **4b** after titration with of $Hg(BF_4)_2.xH_2O$ (*layer-by-layer method*).

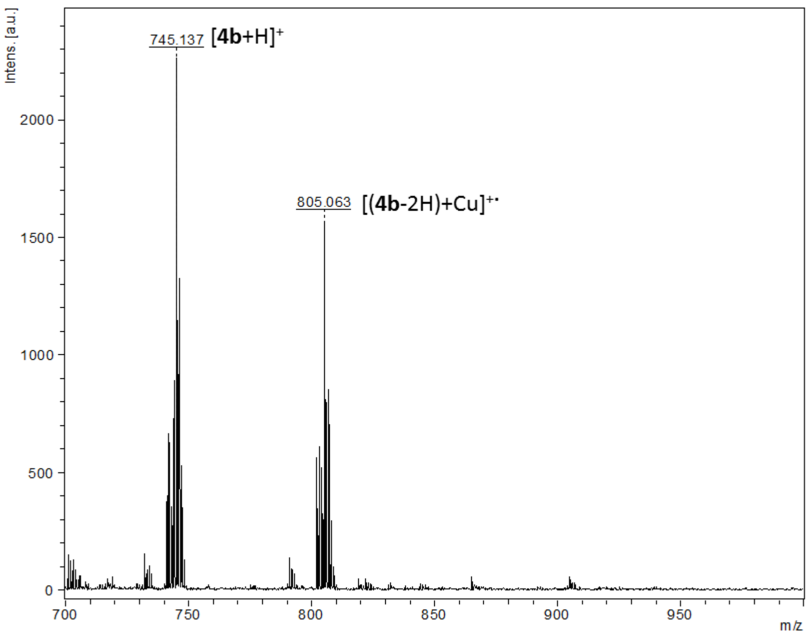


Figure 39_SM - MALDI-TOF mass spectra of compound **4b** after titration with of $Cu(BF_4)_2.xH_2O$ (*layer-by-layer method*).

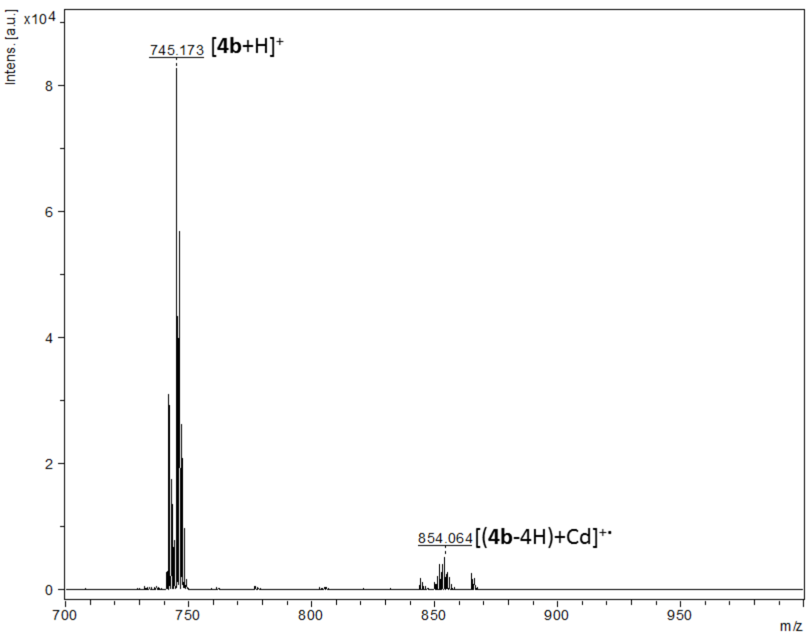


Figure 40_SM - MALDI-TOF mass spectra of compound **4b** after titration with of $Cd(BF_4)_2.xH_2O$ (*layer-by-layer method*).

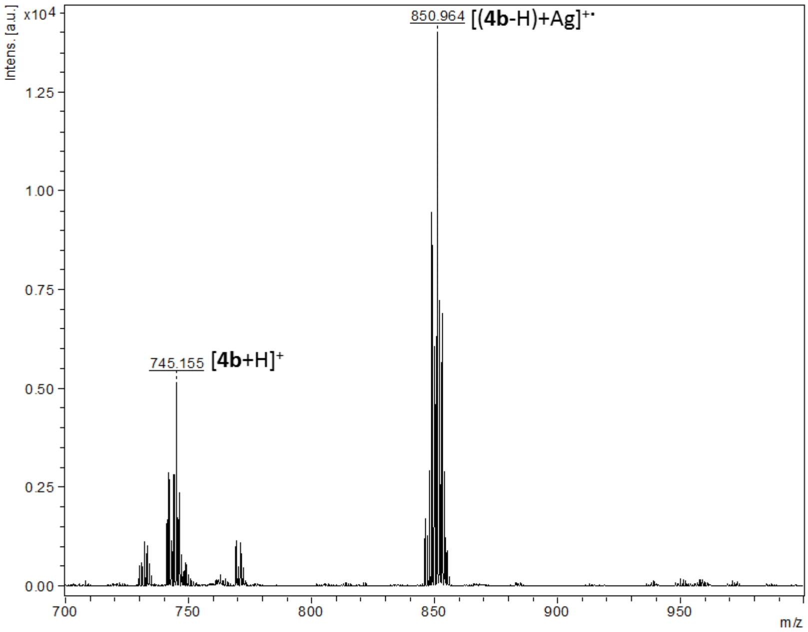


Figure 41_SM - MALDI-TOF mass spectra of compound **4b** after titration with of $Ag(BF_4).xH_2O$ (*layer-by-layer method*).

Table 4_SM - Major peaks observed in the metal titration of chemosensor **4d** followed by MALDI-TOF-MS.

Metal	Stoichiometry (ligand:metal)	Dried-droplet		Layer-by-Layer	
		m/z	**Relative intensity (%)**	***m/z***	**Relative intensity (%)**
Zn^{2+}	1:1	775.17 836.08	100.00 [**4d**+H]$^{+}$ 41.00 [(**4d**-2H)+Zn]$^{+\bullet}$	775.09 835.99	100.00 [**4d**+H]$^{+}$ 18.00 [(**4d**-3H)+Zn]$^{+\bullet}$
	1:2	775.10 835.96	100.00 [**4d**+H]$^{+}$ 96.00 [(**4d**-3H)+Zn]$^{+\bullet}$		
Hg^{2+}	1:1	775.26	100.00 [**4d**+H]$^{+}$	775.11 974.03	100.00 [**4d**+H]$^{+}$ 17.00 [(**4d**-2H)+Hg]$^{+\bullet}$
	1:2	775.26	100.00 [**4d**+H]$^{+}$		
Cu^{2+}	1:1	775.24 835.17	100.00 [**4d**+H]$^{+}$ 21.00 [(**4d**-2H)+Cu]$^{+\bullet}$	775.09 835.02	100.00 [**4d**+H]$^{+}$ 54.00 [(**4d**-2H)+Cu]$^{+\bullet}$
	1:2	835.09 852.13	100.00 [(**4d**-2H)+Cu]$^{+\bullet}$ 35.00 [(**4d**-3H)+Cu+H_2O]$^{+\bullet}$		
Cd^{2+}	1:1	775.28 884.20	100.00 [**4d**+H]$^{+}$ 38.00 [(**4d**-4H)+Cd]$^{+\bullet}$	775.09 883.95	100.00 [**4d**+H]$^{+}$ 17.00 [(**4d**-5H)+Cd]$^{+\bullet}$
	1:2	775.28 884.20	100.00 [**4d**+H]$^{+}$ 41.00 [(**4d**-4H)+Cd]$^{+\bullet}$		
Ag^{+}	1:1	775.19 881.07	100.00 [**4d**+H]$^{+}$ 68.00 [**4d**+Ag]$^{+\bullet}$	775.09 880.92	30.00 [**4d**+H]$^{+}$ 100.00 [(**4d**-H)+Ag]$^{+\bullet}$
	1:2	775.17 881.05	82.00 [**4d**+H]$^{+}$ 100.00 [**4d**+Ag]$^{+\bullet}$		

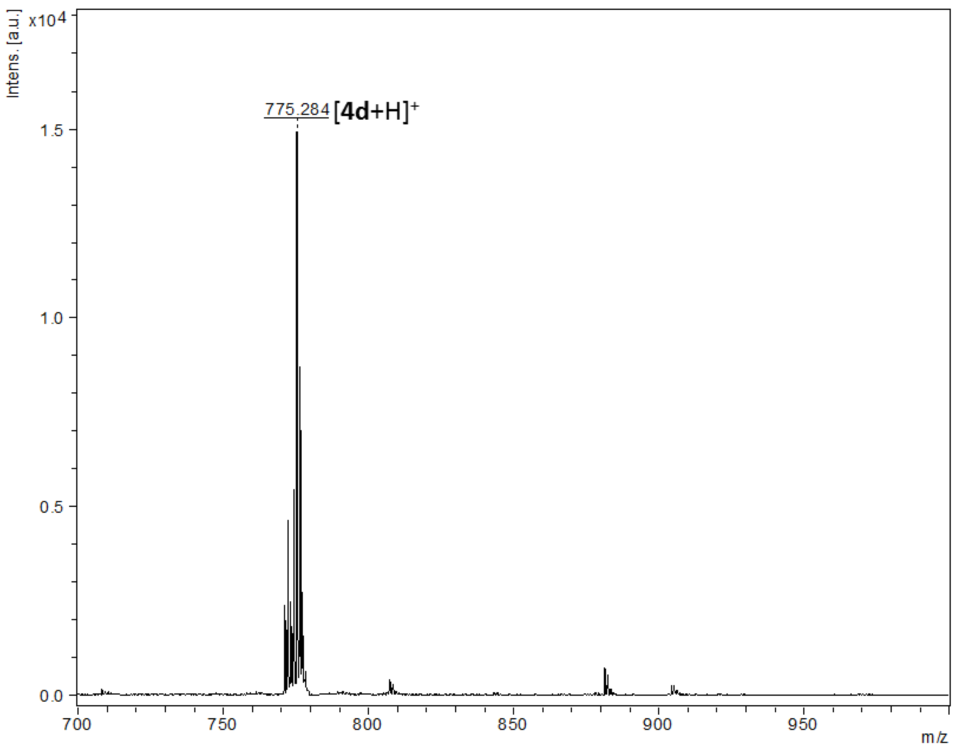


Figure 42_SM - MALDI-TOF mass spectra of compound **4d.**

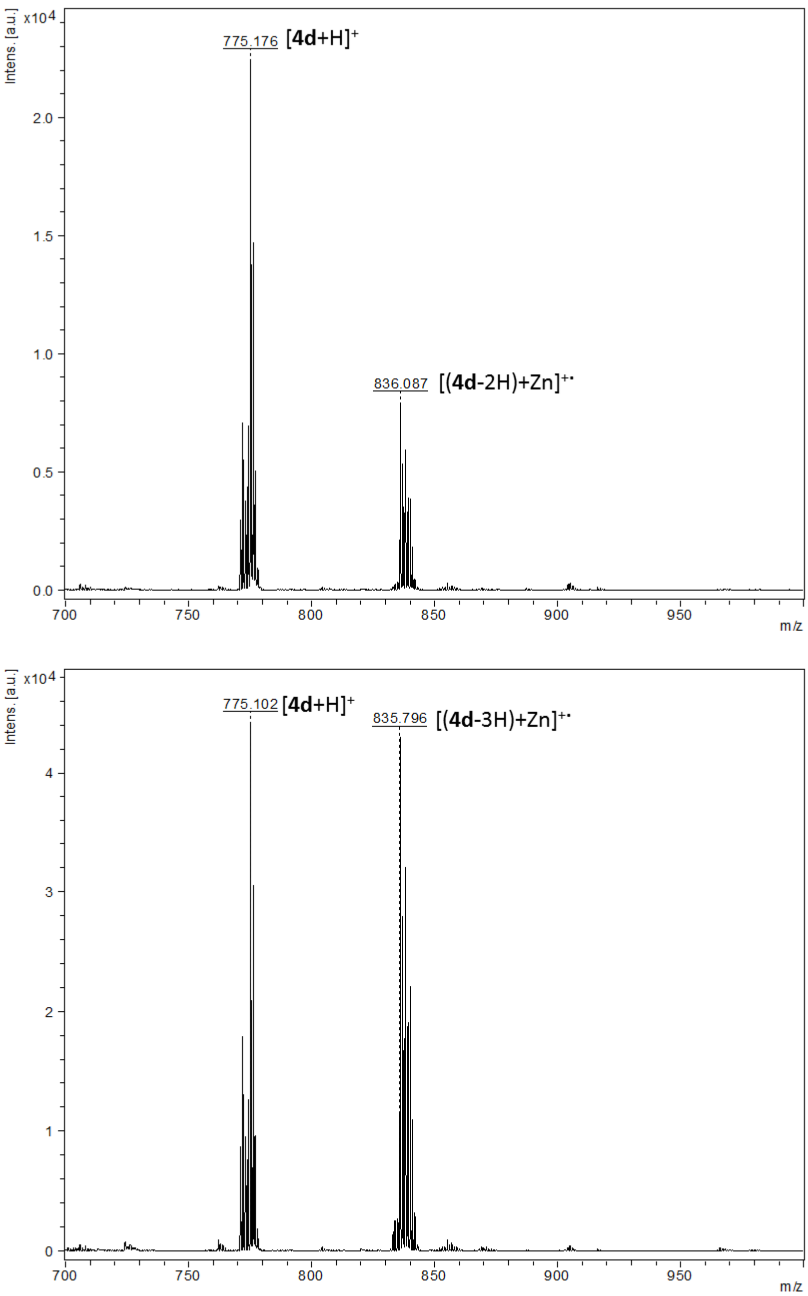


Figure 43_SM - MALDI-TOF mass spectra of compound **4d** after titration with 1 equiv. (above) and 2 equiv. of $Zn(BF_4)_2.xH_2O$ (below) (*dried-droplet method*).

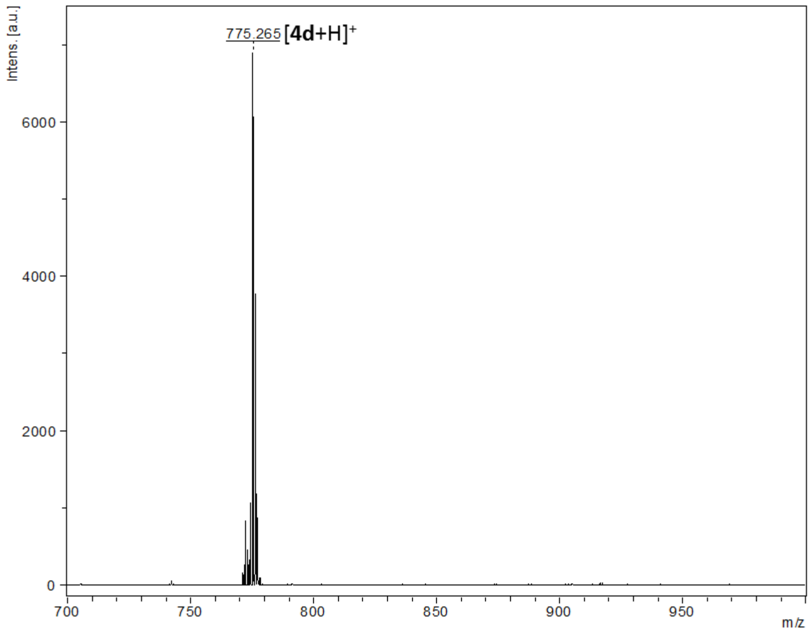


Figure 44_SM - MALDI-TOF mass spectra of compound **4d** after titration with 1 equiv. and 2 equiv. of $Hg(BF_4)_2.xH_2O$ (*dried-droplet method*).

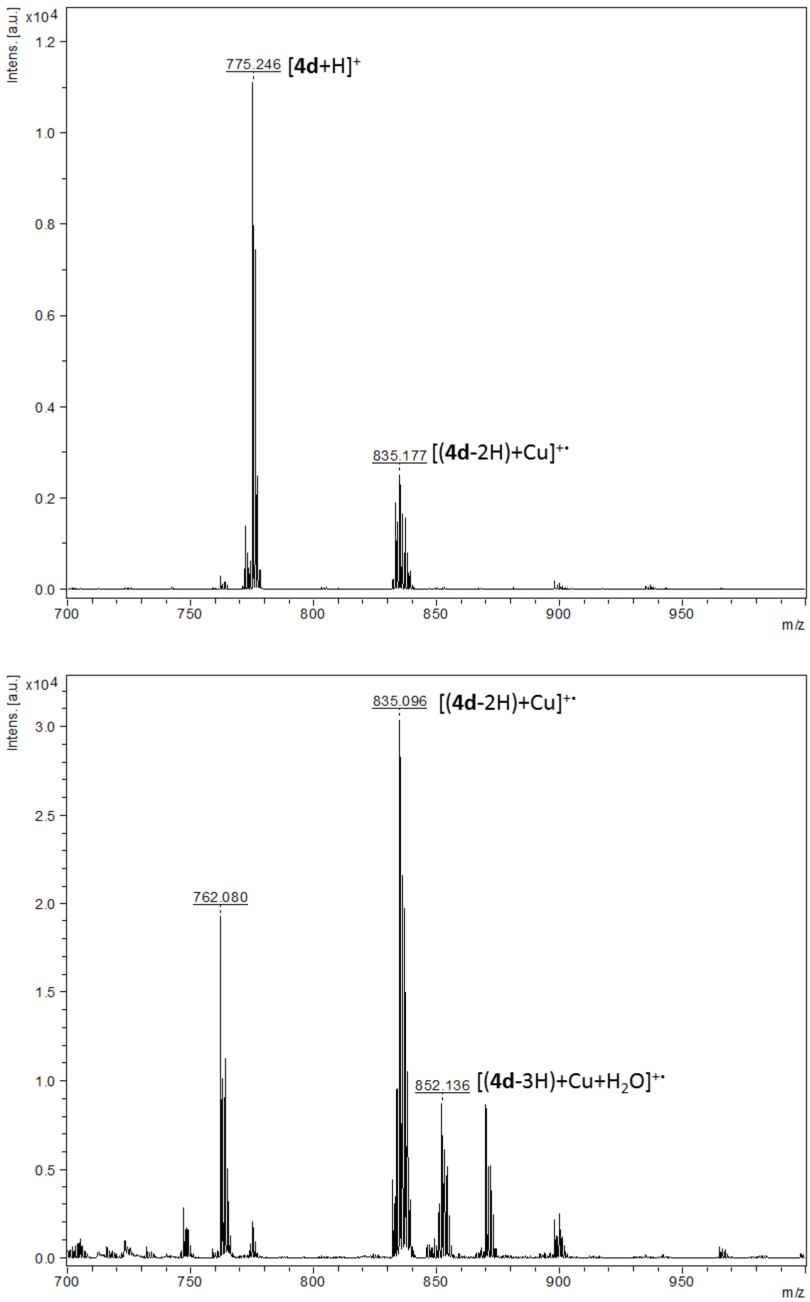


Figure 45_SM - MALDI-TOF mass spectra of compound **4d** after titration with 1 equiv. (above) and 2 equiv. of $Cu(BF_4)_2.xH_2O$ (below) (*dried-droplet method*).

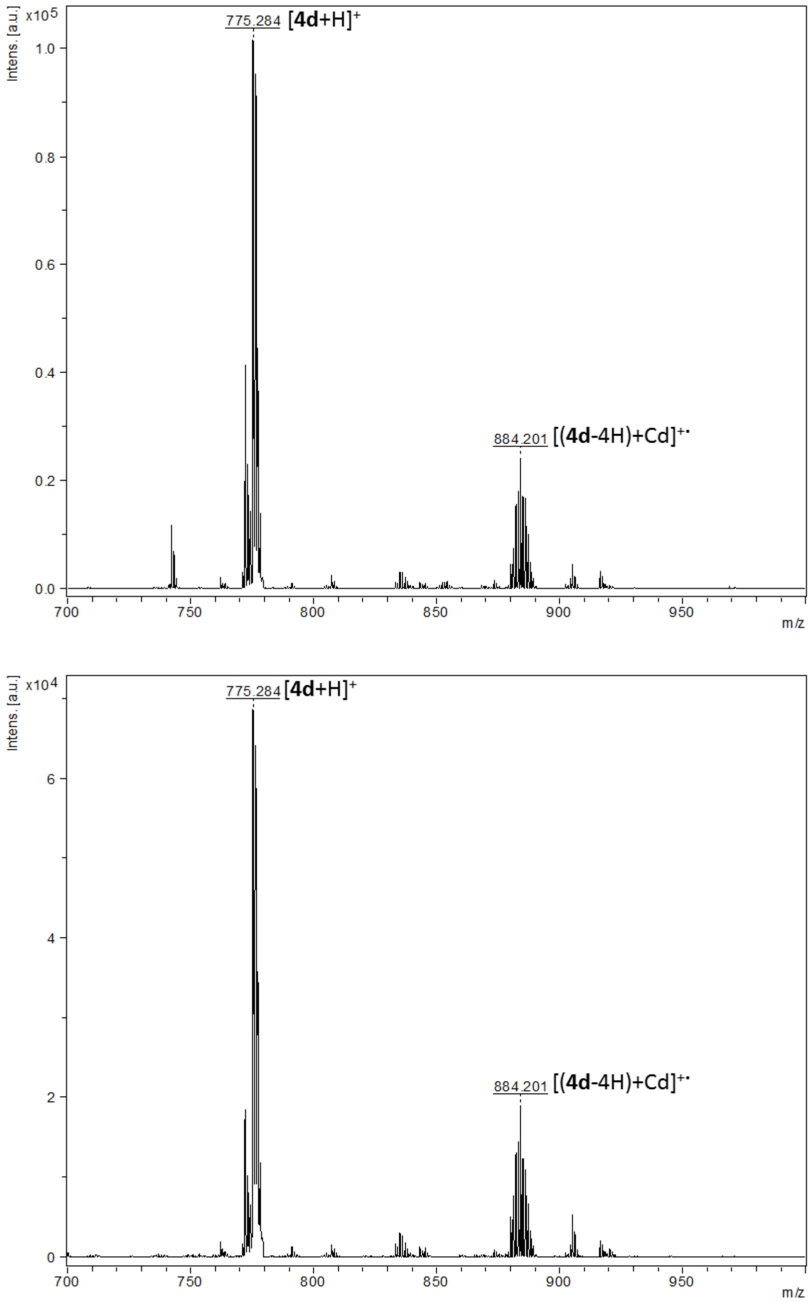
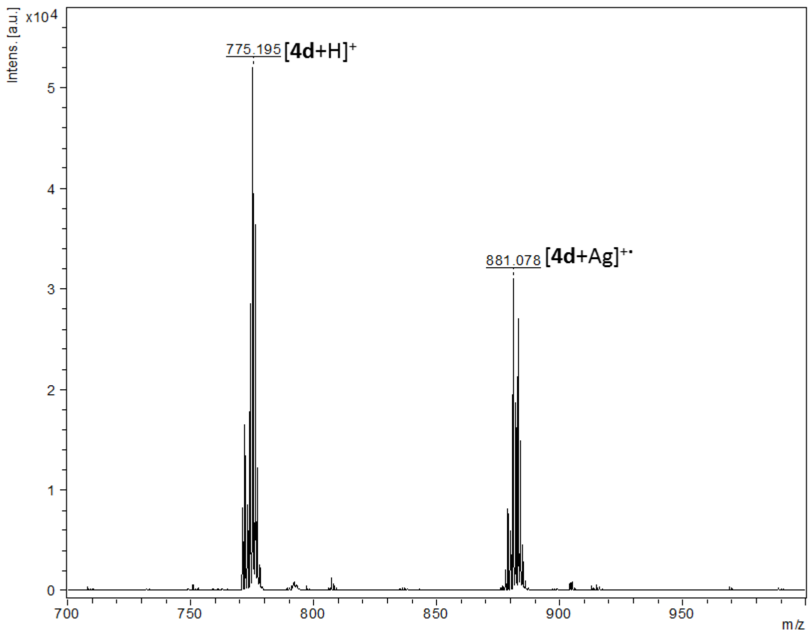


Figure 46_SM - MALDI-TOF mass spectra of compound **4d** after titration with 1 equiv. (above) and 2 equiv. of $Cd(BF_4)_2.xH_2O$ (below) (*dried-droplet method*).



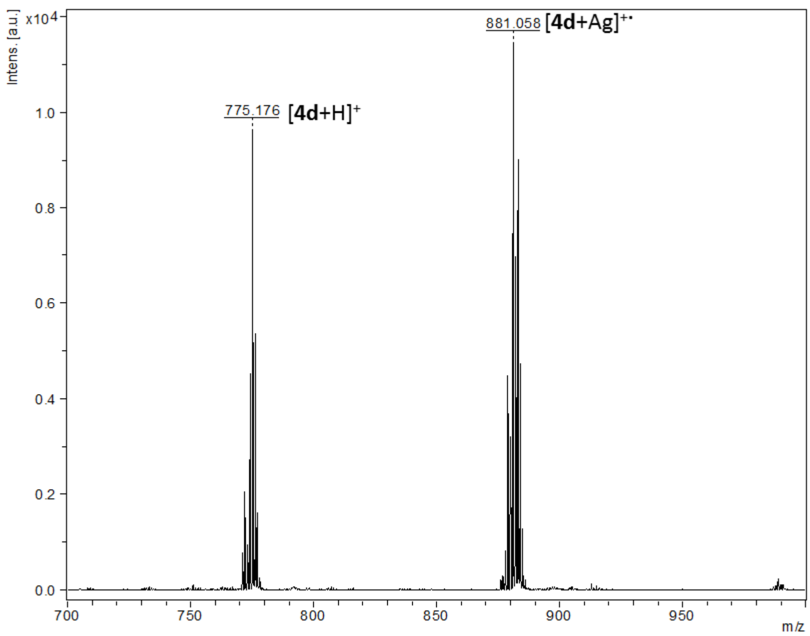


Figure 47_SM - MALDI-TOF mass spectra of compound **4d** after titration with 1 equiv. (above) and 2 equiv. of $Ag(BF_4).xH_2O$ (below) (*dried-droplet method*).

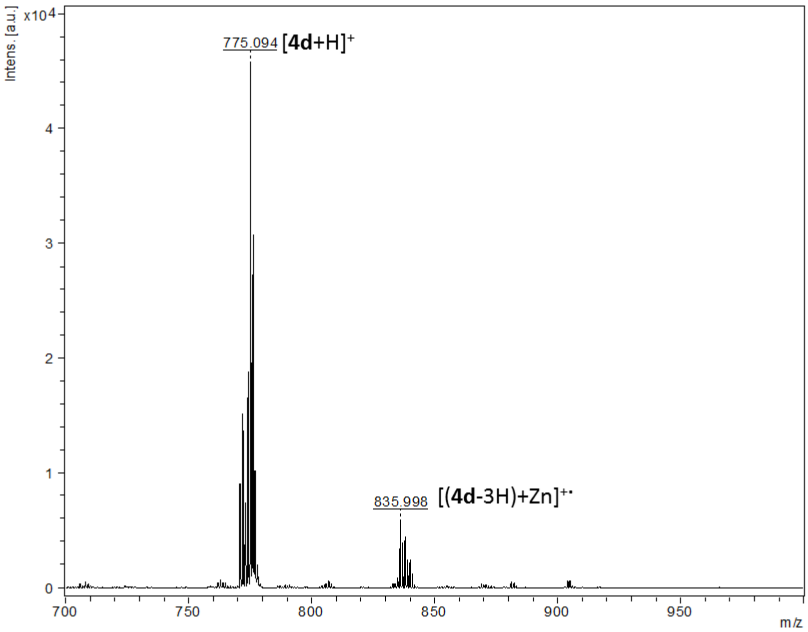


Figure 48_SM - MALDI-TOF mass spectra of compound **4d** after titration with of $Zn(BF_4)_2.xH_2O$ (*layer-by-layer method*).

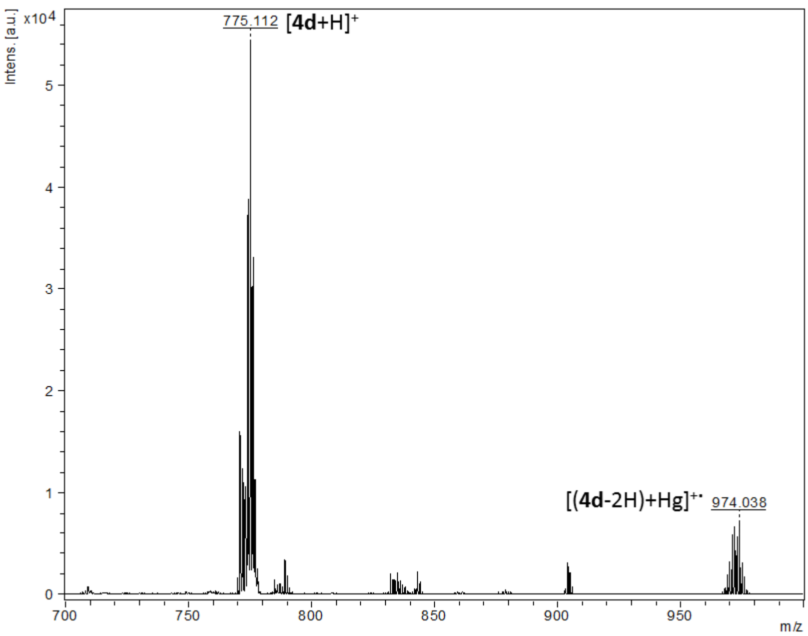


Figure 49_SM - MALDI-TOF mass spectra of compound **4d** after titration with of $Hg(BF_4)_2.xH_2O$ (*layer-by-layer method*).

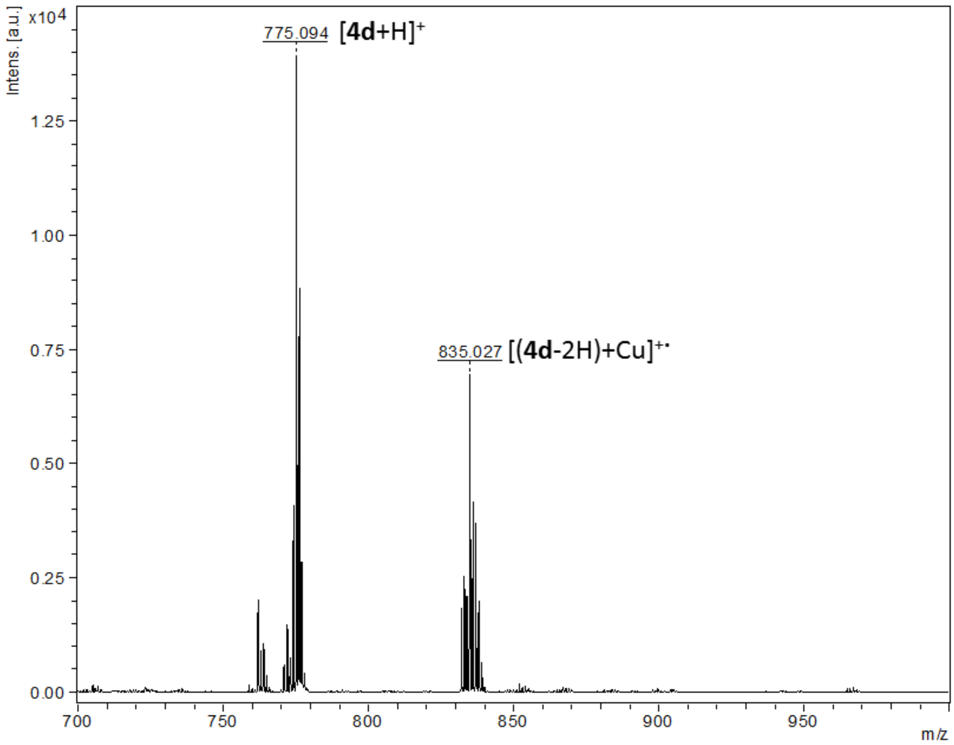


Figure 50_SM - MALDI-TOF mass spectra of compound **4d** after titration with of $Cu(BF_4)_2.xH_2O$ (*layer-by-layer method*).

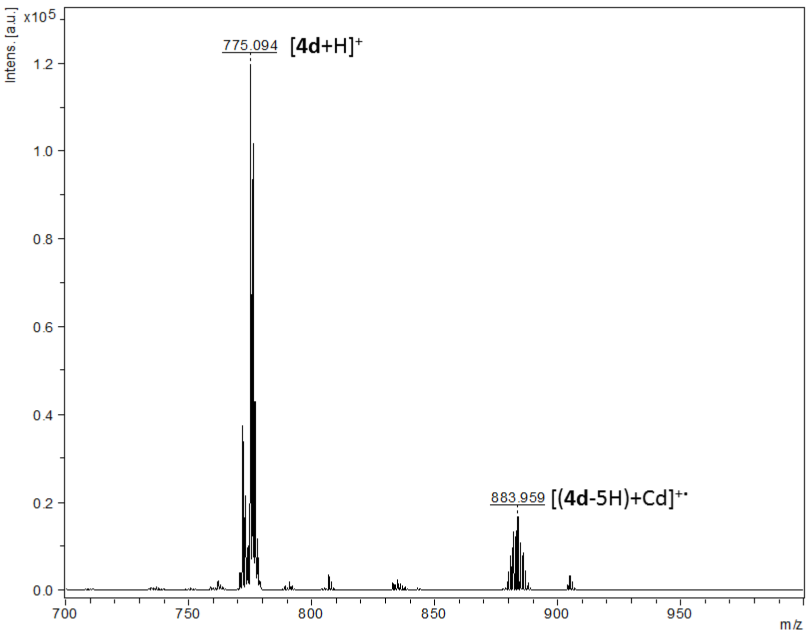


Figure 51_SM - MALDI-TOF mass spectra of compound **4d** after titration with of $Cd(BF_4)_2.xH_2O$ (*layer-by-layer method*).

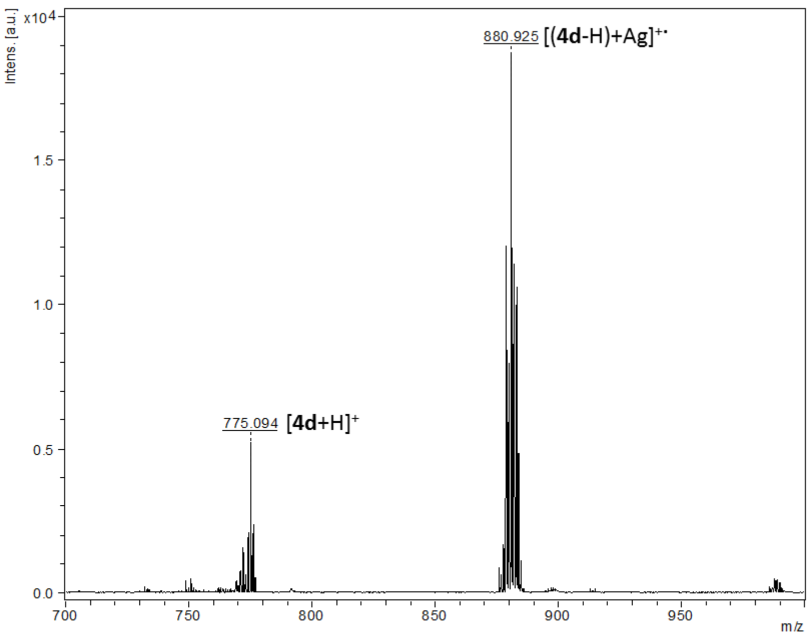


Figure 52_SM - MALDI-TOF mass spectra of compound **4d** after titration with of $Ag(BF_4).xH_2O$ (*layer-by-layer method*).

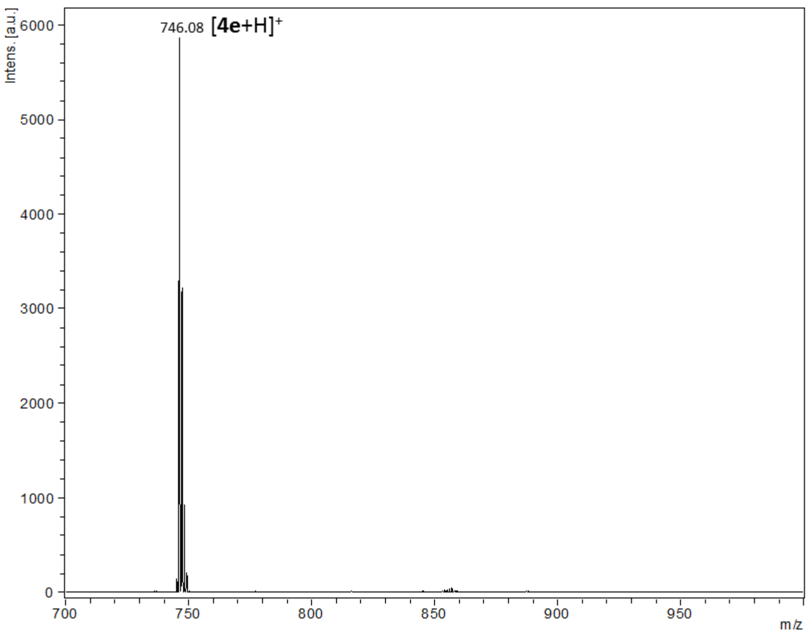


Figure 53_SM - MALDI-TOF mass spectra of compound **4e.**

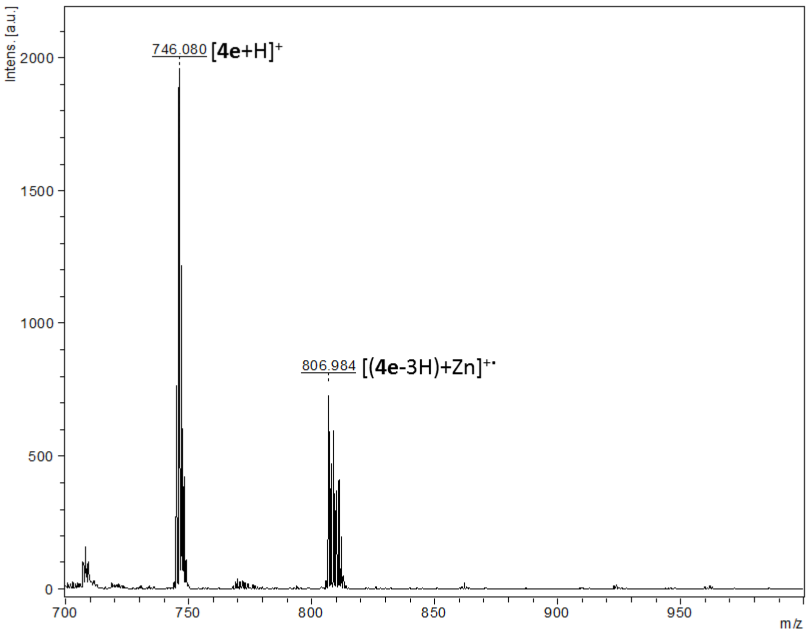


Figure 54_SM - MALDI-TOF mass spectra of compound **4e** after titration with 2 equiv. of $Zn(BF_4)_2.xH_2O$ (*dried-droplet method*).

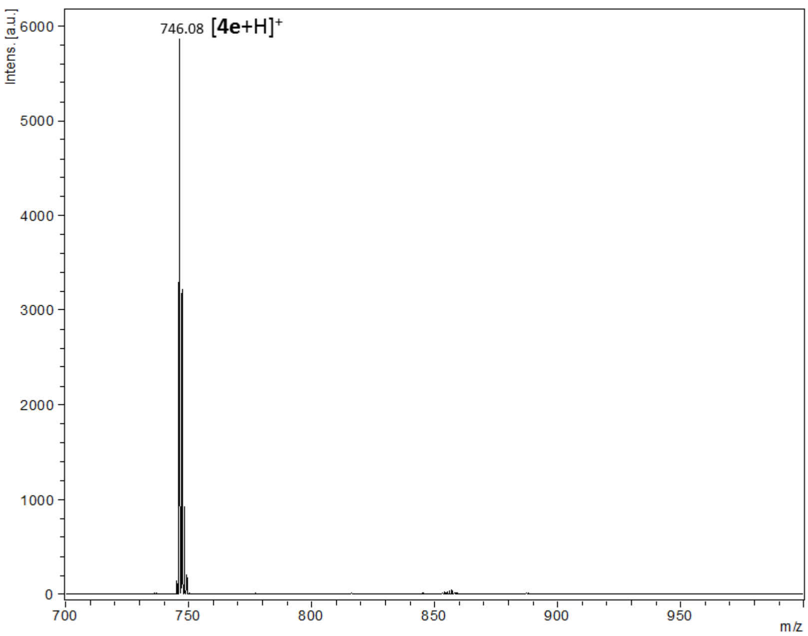


Figure 55_SM - MALDI-TOF mass spectra of compound **4e** after titration with 1 equiv. and 2 equiv. of $Hg(BF_4)_2.xH_2O$ (*dried-droplet method*).

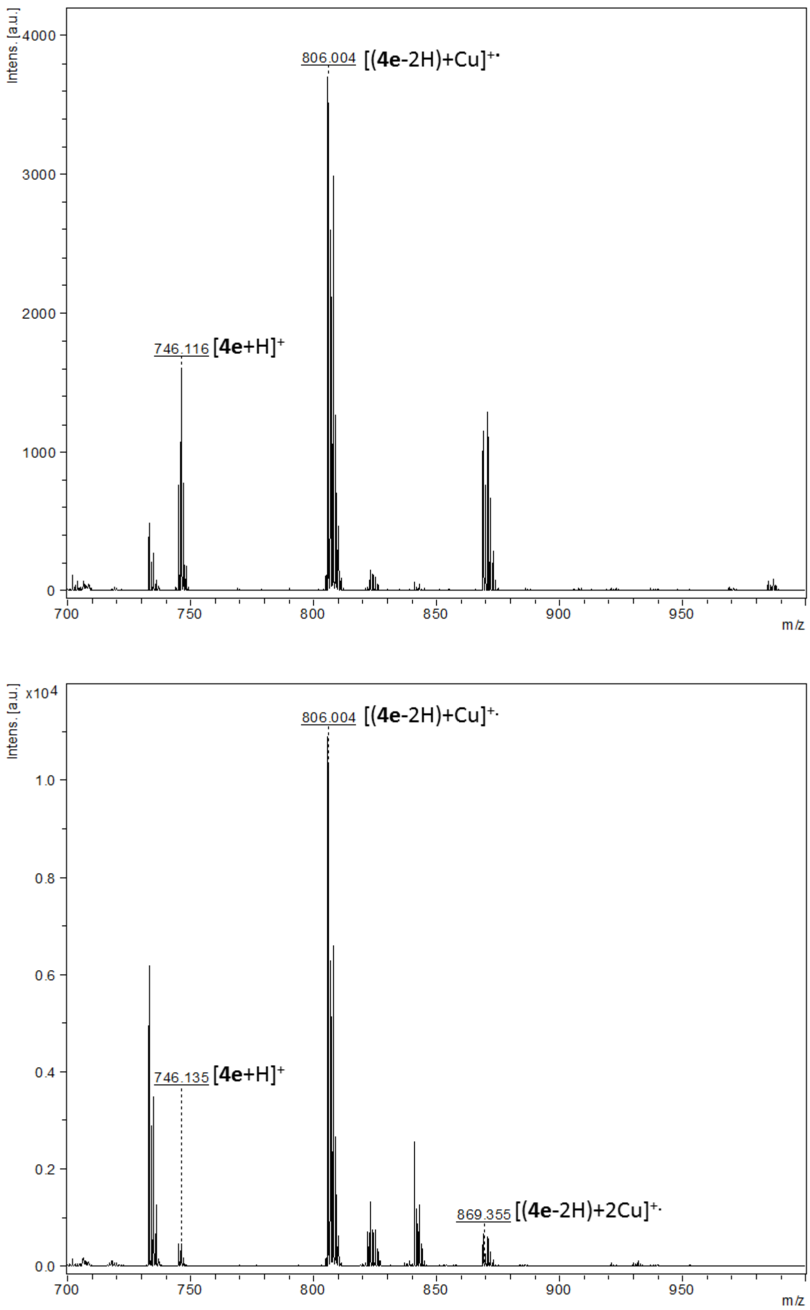


Figure 56_SM - MALDI-TOF mass spectra of compound **4e** after titration with 1 equiv. (above) and 2 equiv. of $Cu(BF_4)_2.xH_2O$ (below) (*dried-droplet method*).

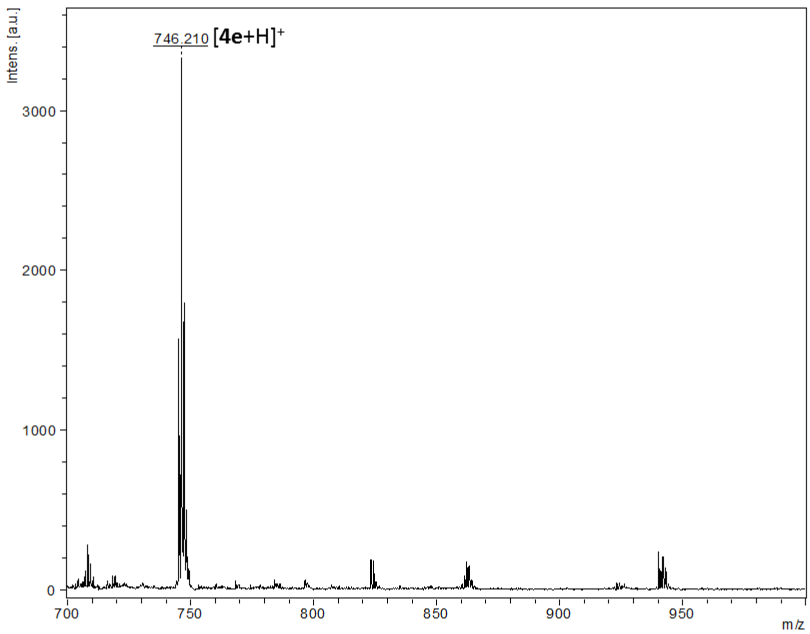
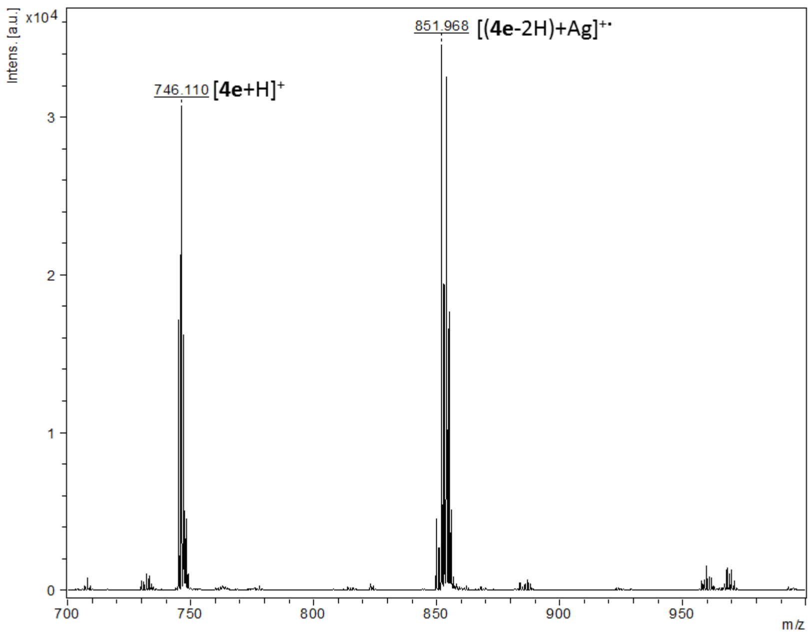


Figure 57_SM - MALDI-TOF mass spectra of compound **4e** after titration with 1 equiv. and 2 equiv. of $Cd(BF_4)_2.xH_2O$ (*dried-droplet method*).



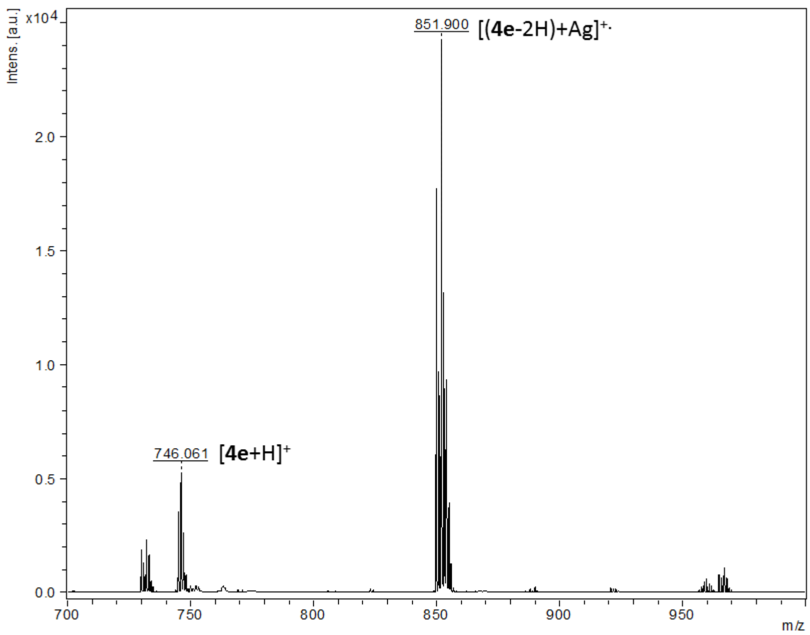


Figure 58_SM - MALDI-TOF mass spectra of compound **4e** after titration with 1 equiv. (above) and 2 equiv. of $Ag(BF_4).xH_2O$ (below) (*dried-droplet method*).

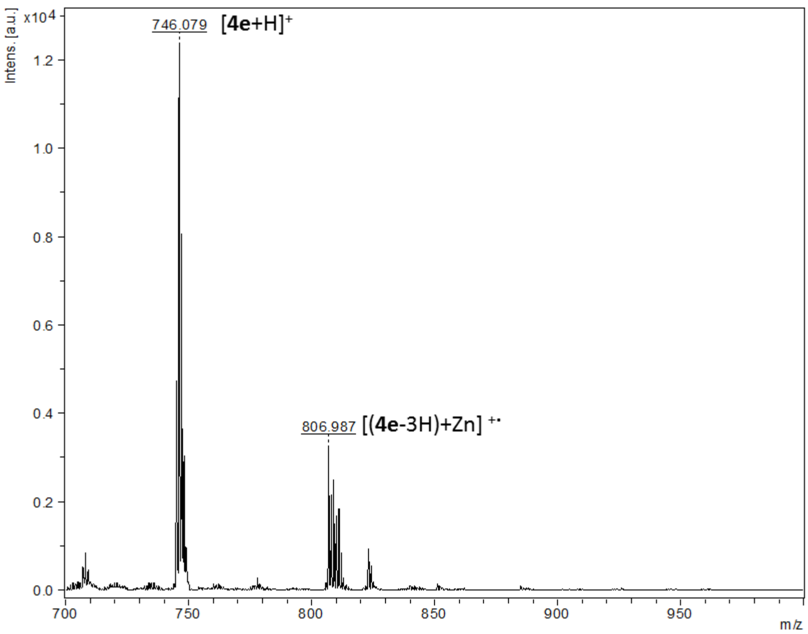


Figure 59_SM - MALDI-TOF mass spectra of compound **4e** after titration with of $Zn(BF_4)_2.xH_2O$ (*layer-by-layer method*).

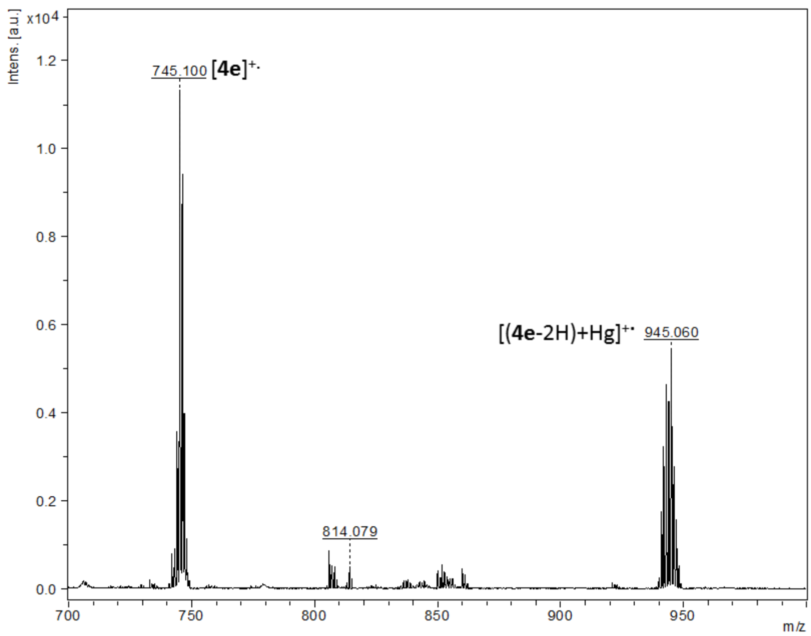


Figure 60_SM - MALDI-TOF mass spectra of compound **4e** after titration with of $Hg(BF_4)_2.xH_2O$ (*layer-by-layer method*).

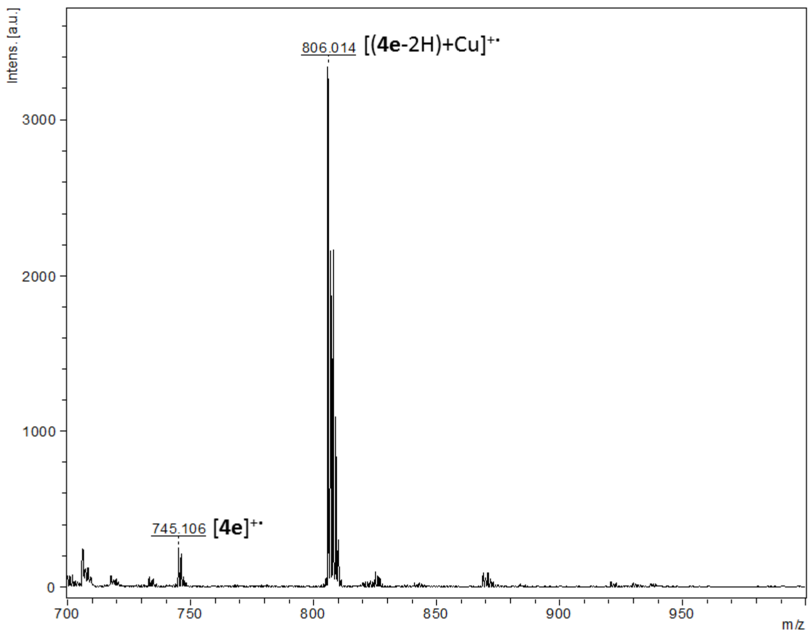


Figure 61_SM - MALDI-TOF mass spectra of compound **4e** after titration with of $Cu(BF_4)_2.xH_2O$ (*layer-by-layer method*).

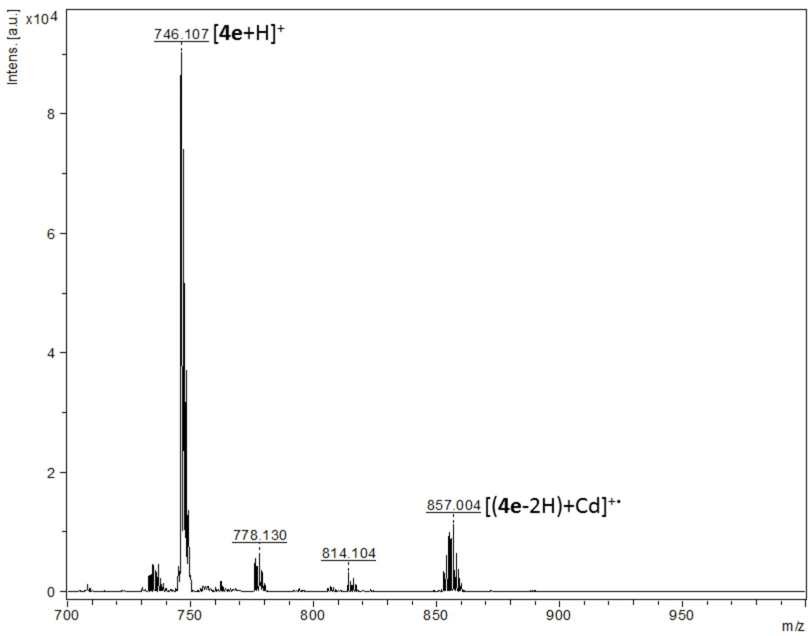


Figure 62_SM - MALDI-TOF mass spectra of compound **4e** after titration with of $Cd(BF_4)_2.xH_2O$ (*layer-by-layer method*).

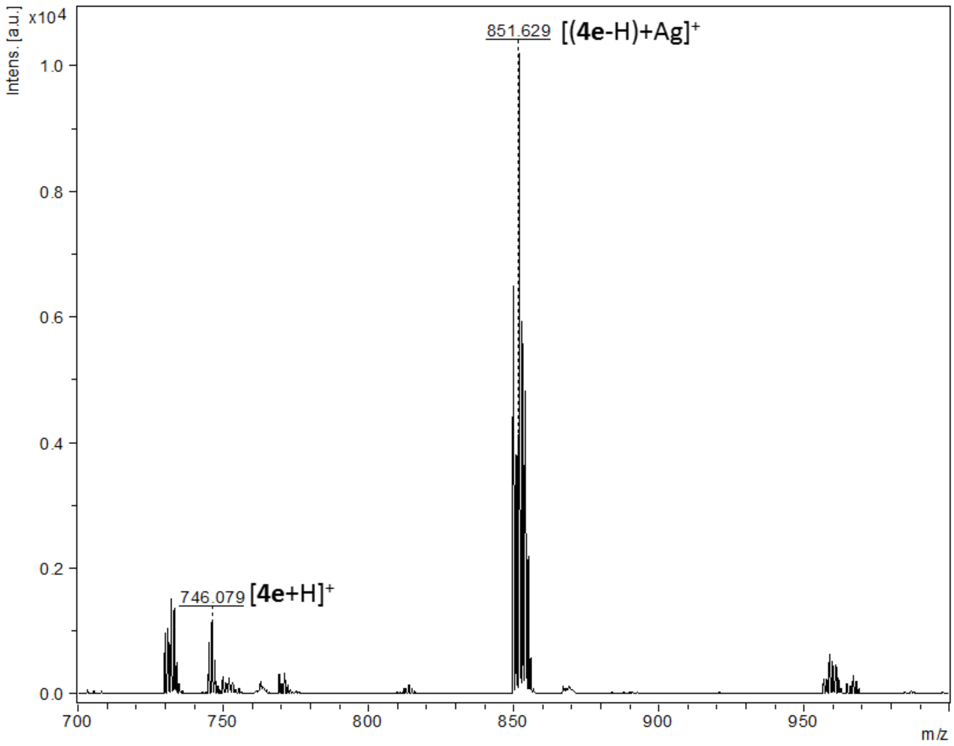


Figure 63_SM - MALDI-TOF mass spectra of compound **4e** after titration with of $Ag(BF_4).xH_2O$ (*layer-by-layer method*).