Electronic Supporting Information

Linkage induced enhancement of fluorescence in metal-carbene bond directed metallacycles and cages

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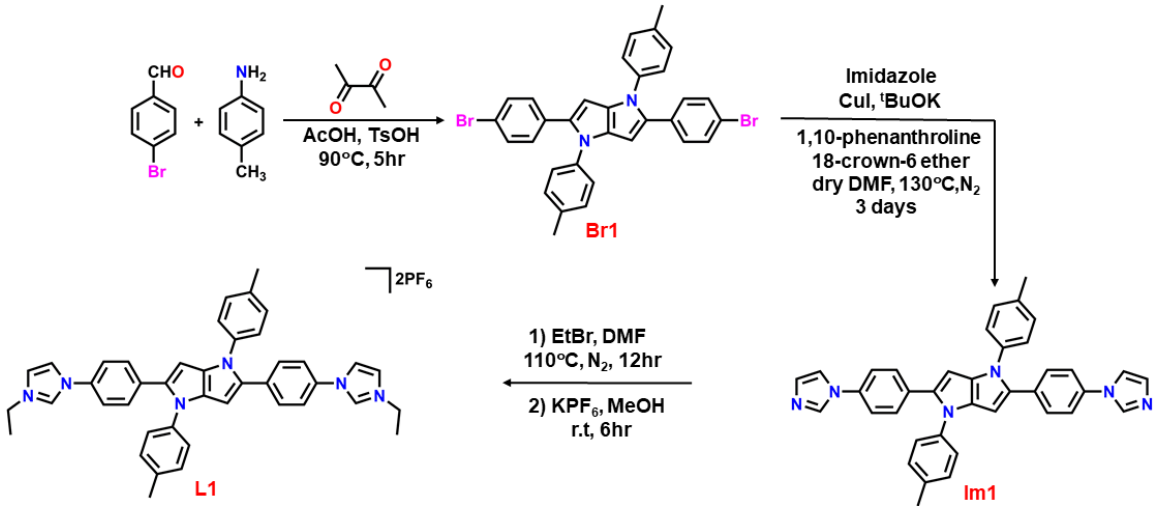
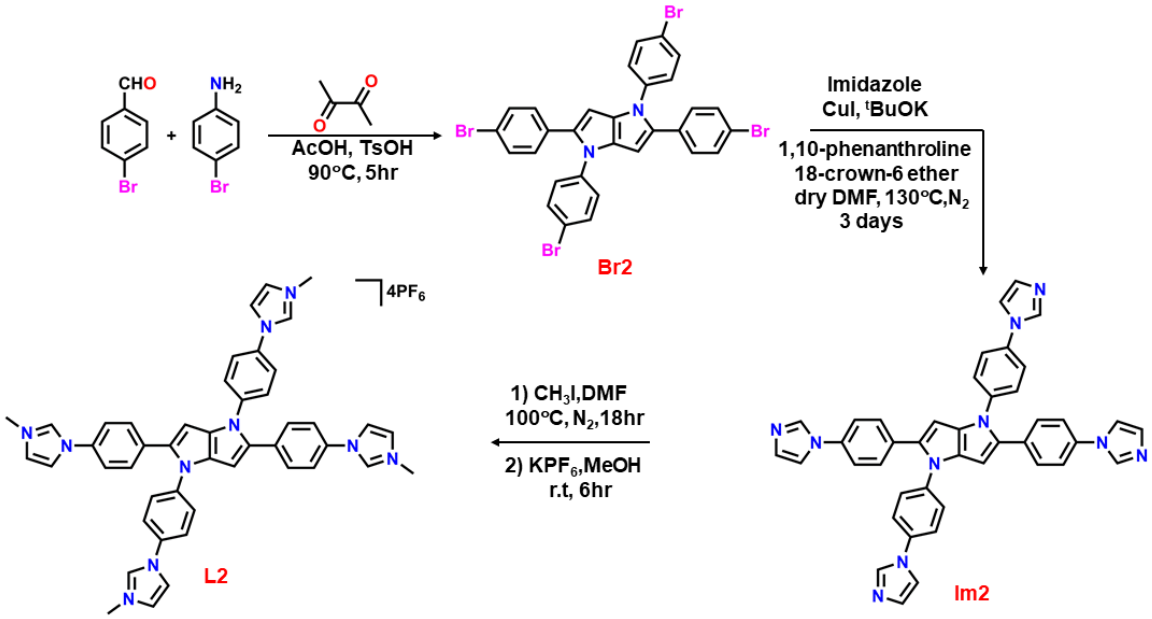
1. Synthesis and characterization of the compounds:



Scheme S1: Synthetic routes for the preparation of the ligand **L1**.



Scheme S2: Synthetic routes for the preparation of the ligand **L2**.

1.1 Materials and Methods:

General chemicals and the solvents were purchased from commercially available suppliers and were used without further purification. All the reactions were carried out under nitrogen atmosphere. The NMR spectra of the newly prepared materials were recorded on BRUKER 400 MHz and 500 MHz spectrometers. The chemical shifts (δ) in the ^{1}H NMR spectra were reported in ppm relative to the tetramethylsilane, which was used as an internal standard (δ = 0.00 ppm) or the resonance of the proton resulting from partial deutoriation of the NMR solvents: $CDCl_3$ (δ = 7.26 ppm), CD_3CN (δ = 1.94 ppm) and DMSO-*d*$_6$ (δ = 2.50 ppm). ^{13}C NMR spectra were recorded using the same instruments at 100 MHz, 125 MHz and all the chemical shifts (δ) were reported in ppm relative to external $CDCl_3$ at 77.8-77.2 ppm, CD_3CN at 1.32, 118.26 ppm and DMSO-*d*$_6$ at 39.52 ppm. Electrospray ionization mass spectra were recorded using Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer along with the use of standard spectroscopic grade solvents. Electronic absorption spectra and emission spectra were recorded on a LAMBDA 750 UV/Vis spectrophotometer and HORIBA JOBIN YVON made Fluoromax-4 spectrometer.

1.2 Synthesis

Synthesis of (Br1): Br1 was synthesized according to the previous literature report.[1] A two-neck round-bottom flask was charged with glacial acetic acid (20 mL) followed by addition of bromobenzaldehyde (12 mmol), *p*-toluidine (12 mmol) and TsOH(1.2 mmol). The mixture was stirred at 90°C for 45 min. Then butane-2, 3-dione (6 mmol) was slowly added to it and the resulting mixture was stirred at 100°C for 4h. The reaction mixture was then cooled to room temperature. The precipitate was filtered off and washed with cold acetic acid. The solid was recrystallized from AcOEt and dried under vacuum to give a yellowish compound. Yield: 1.8 g (3.03 mmol, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (d, 4H), 7.19-7.13 (m, 8H), 7.07 (d, 4H), 6.35 (s, 2H), 2.38 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.64, 136.24, 135.29, 133.05, 132.42, 131.73, 130.33, 129.94, 125.59, 120.50, 95.01, 21.49 ppm.

Synthesis of (Im1): Im1 was prepared by following previous literature procedure.[2] An oven-dried 100 mL two-neck round bottom flask was charged with CuI (16.0 mg, 0.08 mmol), 1,10-phenanthroline (30.3 mg, 0.16 mmol) and dry DMF (5 mL) and degassed. The brown solution was heated at 120°C for 5 min. Compounds **Br1** (500.0 mg, 0.84 mmol), imidazole (458.4 mg, 6.73 mmol), potassium tert-butoxide (755.6 mg, 6.73 mmol) and a pinch of 18-crown-6 were added to the above solution and the final mixture was heated at 130°C for 72 h. The final brown residue was stirred with 100 mL of water for 10 min and then filtered. The residue was extracted with 300 mL $CHCl_3$ followed by treatment with sodium sulphate. Evaporation of the solvent yielded solid yellow product. Yield: 350 mg (0.61 mmol, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (s, 2H, N-CH-N), 7.32 (d, 4H, imidazole- H), 7.30 (d, 8H), 7.22 (d, 8H), 6.42 (s, 2H), 2.40 ppm (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.64 (N-C-N), 136.45, 135.22, 133.47, 132.64, 131.73, 130.43, 130.33, 129.94, 129.70, 125.68,

125.58, 121.68, 95.21, 21.52 ppm. HRMS (ESI): $C_{38}H_{30}N_6$, $[M+H]^+$ = 571.2565 (calcd) found: 571.3889.

Synthesis of L1: A 50 mL round bottom flask was charged with **Im1** (150.0 mg, 0.26 mmol) and an excess amount of ethyl bromide (114.6 mg, 1.05 mmol). 3.5 mL DMF was added to the mixture and heated to 110°C for 12 h. A yellow compound was precipitated which was filtered off, washed with diethyl ether and dried in vacuum to give a yellow solid. This solid was dissolved in 15 mL methanol and a solution of KPF_6 (482.24 mg, 2.62 mmol) in water was added to it. The mixture was stirred for 6 h at room temperature. Again, a yellow precipitate formed and that was filtered, washed with diethyl ether, dried in vacuum. Yield: 165.0 mg (0.18 mmol; 68.3%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 9.75 (s, 2H, N-CH-N), 8.28 (s, 2H), 8.01 (s, 2H), 7.68 (d, 4H), 7.44 (d, 4H), 7.30 (d, 4H), 7.23 (d,4H), 6.60 (s, 2H), 4.25 (q, 4H), 2.36 (s, 6H), 1.49 ppm (t, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 136.75 (N-C-N), 135.92, 134.87, 134.23, 134.18, 132.47, 132.44, 130.16, 128.55, 125.24, 122.98, 121.53, 120.82, 95.61, 44.79, 20.57, 14.79 ppm. ESI-MS (m/z) = 773.4681 $[M-PF_6]^+$ (calcd 773.2956), 314.2518 $[M-2PF_6]^{2+}$ (calcd 314.1657).

Synthesis of 1: L1 (30 mg, 0.032 mmol) was dissolved in acetonitrile (2.5 mL). Ag_2O (8.32 mg, 0.035 mmol) was added to this solution. The resulting solution was stirred at 70°C for 24 h under exclusion of light. After cooling to room temperature, the suspension was filtered through celite to obtain a clear solution. The filtrate was concentrated to 2 mL. Excess diethyl ether was added to this solution which gave a yellow solid. The solid was collected by filtration, washed with diethyl ether and dried under vacuum. Yield: 20 mg (0.011 mmol, 35%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.87 (s, 2H), 7.79 (s, 2H), 7.69 (br s, 4H), 7.21 (d, 4H), 7.11 (d, 4H), 6.80 (d, 4H), 6.32 (s, 2H), 4.34 (q, 4H), 2.27 (s, 6H), 1.51 ppm (t, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 178.65 (N-C-N), 137.45, 136.66, 135.11, 133.88, 133.15, 131.86, 129.80, 128.68, 124.57, 122.88, 122.07, 95.70, 47.06, 20.52, 17.10 ppm. ESI-MS (m/z) = 1613.376 $[M-PF_6]^+$ (calcd 1613.405), 734.1931 $[M-2PF_6]^{2+}$ (calcd 734.2208).

Synthesis of (Br2): It was synthesized following the procedure used for the synthesis of **Br1.** Here, bromobenzaldehyde (12 mmol), 4-bromoaniline (12 mmol), TsOH (1.2 mmol) and butane-2, 3-dione (6 mmol) were used as starting materials. Yield: 2.1 g (2.89 mmol, 24%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, 4H), 7.37 (d, 4H), 7.12 (d, 4H), 7.06 (d, 4H), 6.36 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.37, 135.73, 132.92, 132.49, 131.99, 130.01, 127.09, 121.18, 120.04, 116.85, 95.79 ppm.

Synthesis of (Im2): Im2 was prepared following the same method of **Im1**. CuI (35.5 mg, 0.18 mmol), 1,10-phenanthroline (67.3 mg, 0.37 mmol), **Br2** (1110 mg, 1.86 mmol), imidazole (1272 mg, 18.68 mmol), potassium tert-butoxide (1886.47 mg, 16.81 mmol) and a pinch of 18-crown-6 were used as starting materials. Yield: 1.0 g (1.48 mmol, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (s, 2H, N-CH-N), 7.87 (s, 2H, N-CH-N), 7.48-7.42 (m, 8H), 7.38-7.31 (m, 8H), 7.28-7.21 (m, 8H), 6.51 ppm (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 138.88, 135.86, 135.67, 135.53, 135.36, 135.20, 132.40, 132.12, 130.92, 130.71, 129.56, 126.62, 122.47, 121.47, 118.26, 118.09, 95.88 ppm. HRMS (ESI): $C_{42}H_{30}N_{10}$, [*M*+H] $^{+}$ = 675.2688 (calcd) found: 675.424.

Synthesis of L2: A 100 mL round bottom flask was charged with **Im2** (300 mg, 0.44 mmol) and excess iodomethane (1262.11 mg, 8.89 mmol). 10 mL 1-propanol was added to this mixture and reaction mixture was heated to 100°C for 18 hr. A yellow compound was precipitated which was filtered off, washed with diethyl ether and dried in vacuum. This solid was dissolved in 30 mL methanol and a solution of KPF_6 (809.86 mg, 1.126 mmol) in water was added to it. The mixture was stirred for 6 h at room temperature. Again, a yellow precipitate formed and that was filtered, washed off with diethyl ether, dried in vacuum. Yield: 450 mg (0.342 mmol, 78%). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ = 9.77 (s, 2H), 9.72 (s, 2H), 8.30 (s, 2H), 8.25 (s, 2H), 7.98-7.94 (m, 4H), 7.88 (d, 4H), 7.73 (d, 4H), 7.63 (d, 4H), 7.52 (d, 4H), 6.80 (s, 2H), 3.97 (s, 3H), 3.94 ppm (s, 3H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ = 139.94 (N-C-N), 135.98, 135.70, 134.56, 133.77, 132.88, 132.54, 132.21, 129.08, 126.61, 124.66, 124.58, 123.03, 121.67, 120.90, 120.63, 97.38, 36.26, 36.21 ppm. ESI-MS (m/z) = 512.1716 $[M\text{-}2PF_6]^{2+}$ (calcd 512.1438), 293.1182 $[M\text{-}3PF_6]^{3+}$ (calcd 293.1078), 183.5878 $[M\text{-}4PF_6]^{4+}$ (calcd 183.5898).

Synthesis of 2: Ag^{I}-C_{NHC} complex **2** was synthesized by following the same synthetic path used for complex **1**. Free ligand **L2** (22 mg, 0.016 mmol) and Ag_2O (8.4 mg, 0.036 mmol) were used as starting material. Yield: 18 mg (0.007mmol, 43%). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ = 7.87 (d, 3H, 2:1, *syn*:*anti*), 7.79 (d, 3H, 2:1, *syn*:*anti*), 7.75 (d, 3H, 2:1, *syn*:*anti*), 7.73 (br s, 3H, 2:1, *syn*:*anti*), 7.69 (d, 4H, *syn*), 7.67 (d, 4H, *syn*), 7.58 (d, 2H, *anti*), 7.52 (d, 2H, *anti*), 7.45 (d, 4H, *syn*), 7.40 (d, 2H, *anti*), 7.33 (d, 2H, *anti*), 7.20 (d, 4H, anti), 6.47 (s, 2H, *syn*), 6.33 (s, 1H, *anti*), 4.08 (s, 6H, *syn*), 4.02 (s, 6H *syn*), 3.95 (s, 3H, *anti*), 3.92 ppm (s, 3H, *anti*). ^{13}C NMR (125 MHz, CD_3CN): δ = 181.00, 140.46, 140.31, 140.08, 139.33, 138.99, 138.69, 138.14, 136.52, 135.37, 134.57, 134.28, 134.00, 132.76, 130.19, 129.28, 129.15, 126.99, 126.50, 126.12, 125.44, 125.19, 124.99, 124.83, 123.38, 122.97, 122.85, 98.78, 98.52, 98.07, 39.97, 39.69 ppm. ESI-MS (m/z) = 1091.1528 $[M\text{-}2PF_6]^{2+}$ (calcd 1091.1024), 679.1064 $[M\text{-}3PF_6]^{3+}$ (calcd 679.0802), 473.0744 $[M\text{-}4PF_6]^{4+}$ (calcd 473.069).

Transmetalation of 1 to 3: A clear solution of complex **1** (12 mg, 0.006 mmol) in DMSO was treated with solid [Au(THT)Cl] (4.8 mg, 0.015 mmol). The reaction mixture was stirred at room temperature for 12 h and the resulting suspension was passed through a celite bed. The filtrate was treated with excess ethyl acetate which gave light yellow precipitate. The solid was collected by filtration, washed with diethyl ether and dried in vacuum. Yield: 9 mg (0.004 mmol, 68%). ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ = 7.77 (s, 2H), 7.74 (s, 2H), 7.62 (d, 4H), 7.36 (d, 4H), 7.28 (d, 4H), 7.22 (d, 4H), 6.56 (s, 2H), 4.25 (q, 4H), 2.35 (s, 6H), 1.45 ppm (t, 6H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ = 167.53, 136.84, 136.79, 135.68, 134.33, 133.54, 132.13, 130.17, 128.13, 125.04, 124.76, 122.48, 121.96, 95.53, 47.23, 20.63, 16.33

ppm. ESI-MS (m/z) = 1791.5382 $[M\text{-}PF_6]^+$ (calcd 1791.5288), 823.2855 $[M\text{-}2PF_6]^{2+}$ (calcd 823.2823).

Transmetalation of 2 to 4: Transmetalation reaction of $Ag^I\text{-}C_{NHC}$ complex **2** (20.0 mg, 0.011 mmol) followed the same synthetic path like complex **3** using four equivalents of [Au(THT)Cl] (8.0 mg, 0.025 mmol). Yield: 11 mg (0.003 mmol, 34%). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.89 (s, 4H, *syn*), 7.83 (s, 2H, *anti*), 7.81 (s, 4H, *syn*), 7.79 (s, 2H, *anti*), 7.75 (d, 4H, *syn*), 7.68 (d, 4H, *syn*), 7.63 (d, 2H, *anti*), 7.51 (d, 2H, *anti*), 7.48 (d, 4H, *syn*), 7.42 (d, 2H, *anti*), 7.33 (d, 2H, *anti*), 7.20 (d, 4H, *syn*), 6.50 (s, 2H, *syn*), 6.38 (s, 1H, *anti*), 4.12 (s, 3H, *anti*), 4.11 (s, 6H, *syn*), 4.07 (s, 3H, *anti*), 4.06 (s, 6H, *syn*) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 179.65, 138.82, 138.74, 137.65, 137.45, 137.03, 136.81, 134.02, 133.93, 133.12, 132.84, 132.63, 132.48, 131.55, 128.68, 128.07, 125.87, 125.52, 125.10, 124.61, 124.50, 124.13, 123.59, 123.46, 122.74, 122.27, 122.07, 121.78, 97.52, 97.48 ppm. ESI-MS (m/z) = 1269.6527 $[M\text{-}2PF_6]^{2+}$ (calcd 1269.7253), 798.1018 $[M\text{-}3PF_6]^{3+}$ (calcd 798.1621), 562.2297 $[M\text{-}4PF_6]^{4+}$ (calcd 562.3805).

Preparation of solution for AIE study: Initially, stock solutions (10^{-4} M) of **Im1**, **Im2** were prepared using spectroscopy grade DCM. The required amounts of the aliquots from the stock solutions were transferred to 4 mL glass vials. After addition of the appropriate amount of DCM for dilution, spectroscopy grade hexane was added to the solutions under vigorous stirring to afford (10^{-5} M) solutions with varying hexane-DCM ratios (10%-90%). The photophysical studies were carried out immediately.

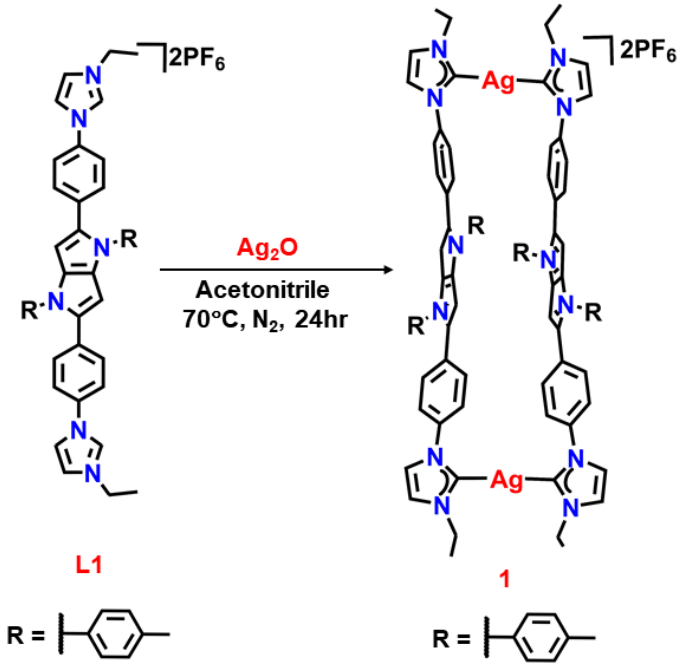
Fluorescence quantum yield measurement: For fluorescence quantum yield measurement, quinine sulphate was chosen as reference. The quantum yields were measured using the following equation

$$\phi_c = [\phi_r \{(1 - 10^{-Ac}) \times N_c^2 \times D_c\}] / \{(1 - 10^{-Ac}) \times N_r^2 \times D_r\}$$

Where ϕ_m and ϕ_r is the radiative quantum yields of the compounds and reference respectively; A_c is the absorbance of the compound and A_r is the absorbance of the reference; D_c is the area of emission of the compound and D_r is the area of emission of the reference, N_c and N_r are the refractive indices of the compound and reference solutions, respectively.

Optimisation methods: All the theoretical calculations were performed using Gaussian 09 package.[3] **1**, **2**, **3** and **4** were optimized using hybrid B3LYP functional with a mixed basis set 6-31G (for C, H and N) and LANL2DZ (for Ag/Au).[4] No symmetry constraints were used during the optimization procedure. All the TD-DFT calculations were carried out using hybrid B3LYP functional with mixed basis set 6-31G (for C, H and N) and SDD (for Ag/Au).

1.3 Synthesis and characterization of 1



Scheme S3: Schematic presentation of the synthesis of **1**.

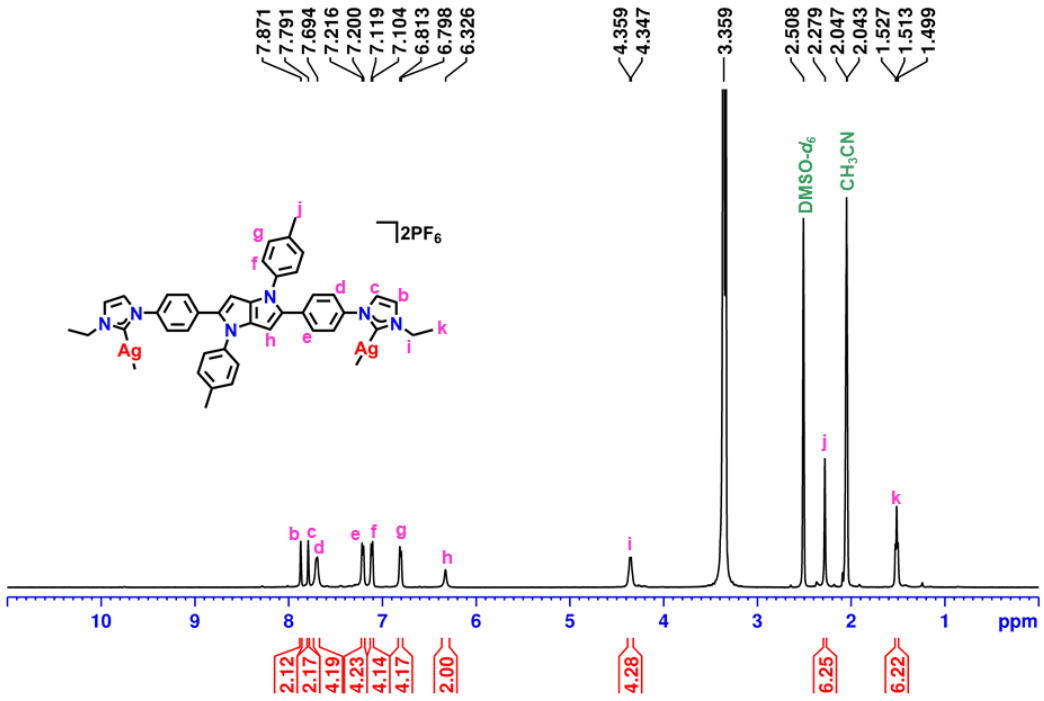


Fig. S1: ^{1}H NMR spectrum of **1** (DMSO-d_6, 298 K).

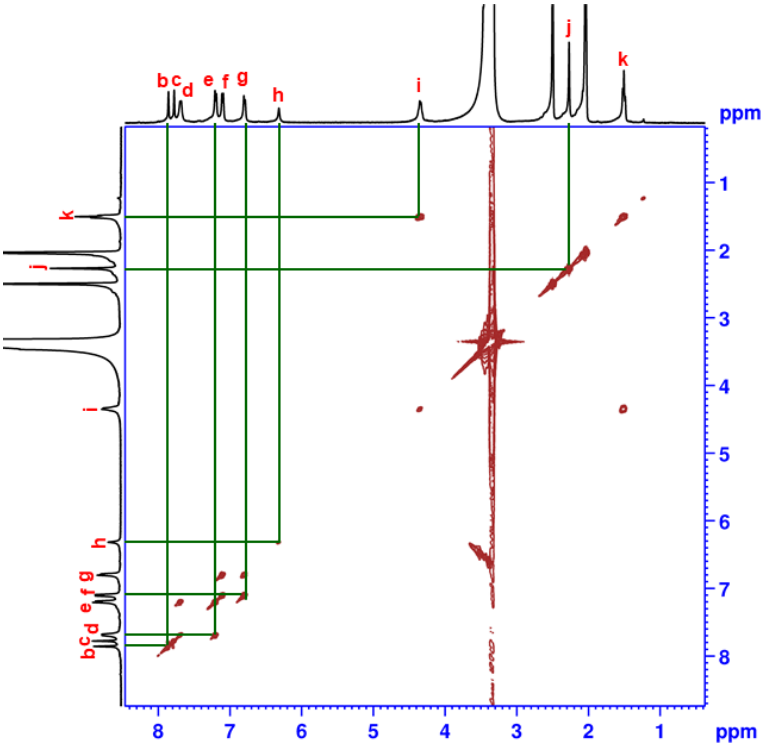


Fig. S2: ^{1}H - ^{1}H COSY spectrum of **1** (DMSO-d_6, 298 K). The rectangular positions show the interaction between neighbouring protons.

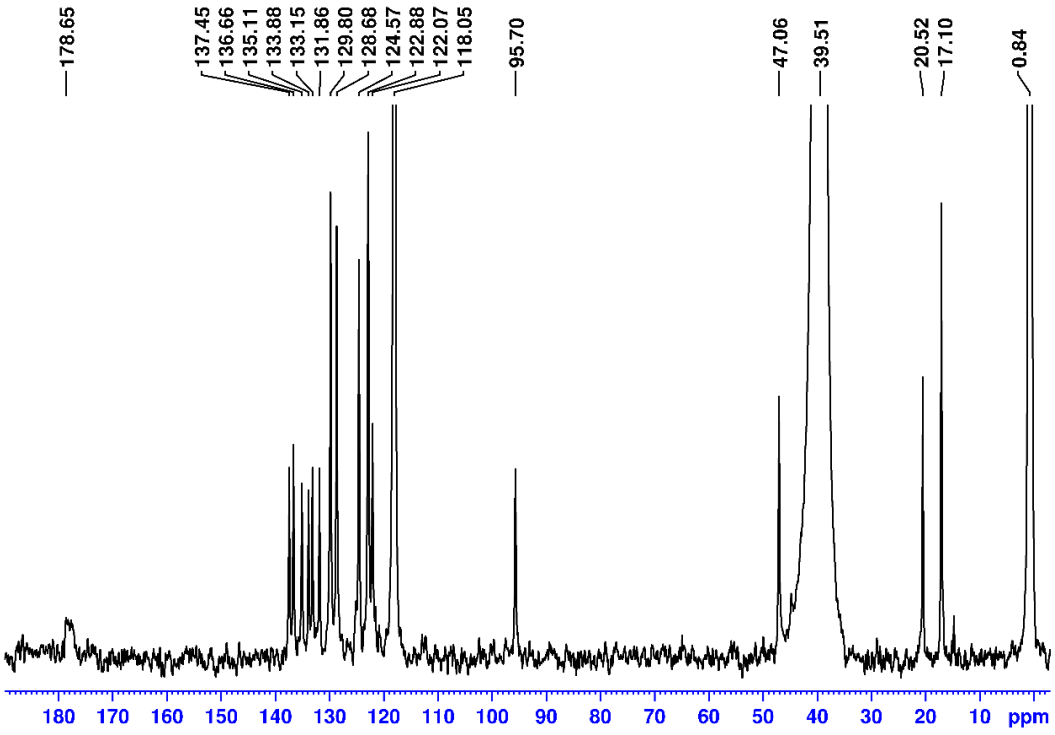


Fig. S3: ^{13}C NMR spectrum of **1** (DMSO-d_6, 298 K).

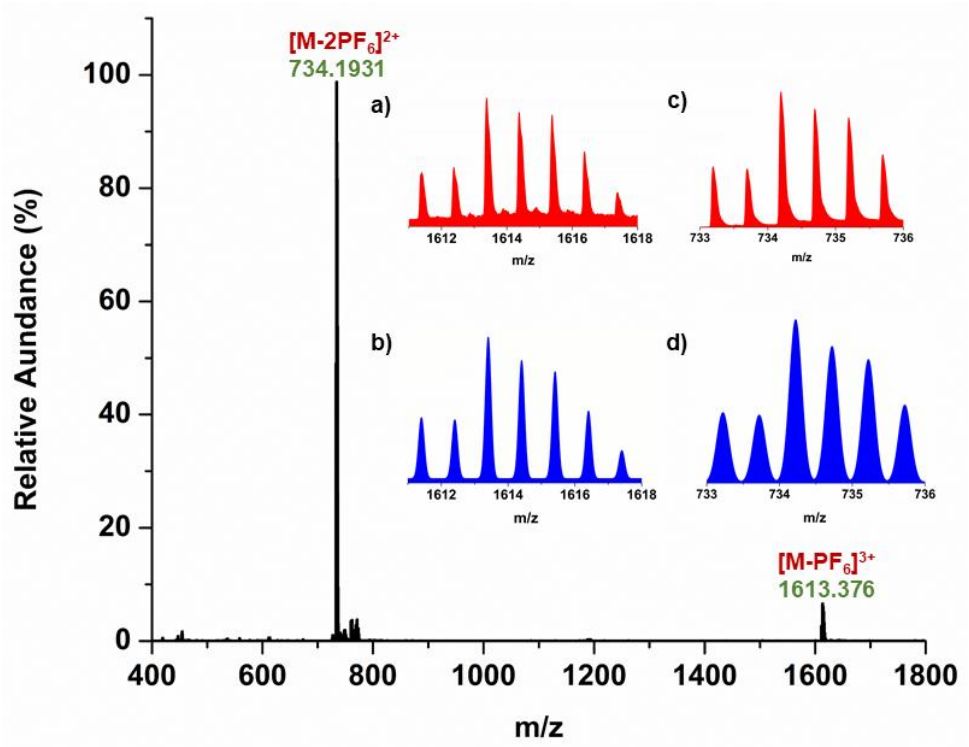
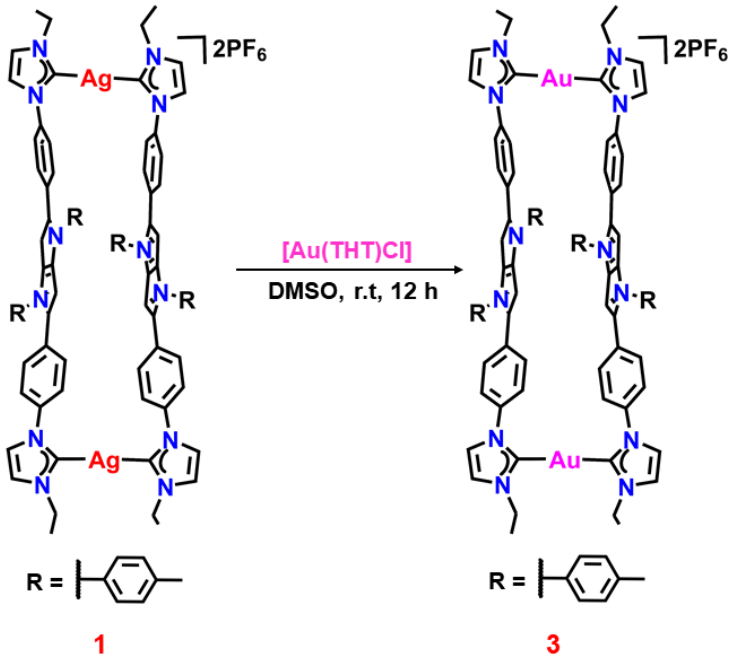


Fig. S4: Electrospray ionization mass spectrum of **1**. Isotopic distribution patterns: a) experimental (red) b) theoretical (blue) of the **[M-PF$_6$]$^{1+}$** fragment and c) experimental (red) c) theoretical (blue) of the **[M-2PF$_6$]$^{2+}$** fragment.

1.4 Synthesis and characterization of 3



Scheme S4: Synthetic scheme for **3**.

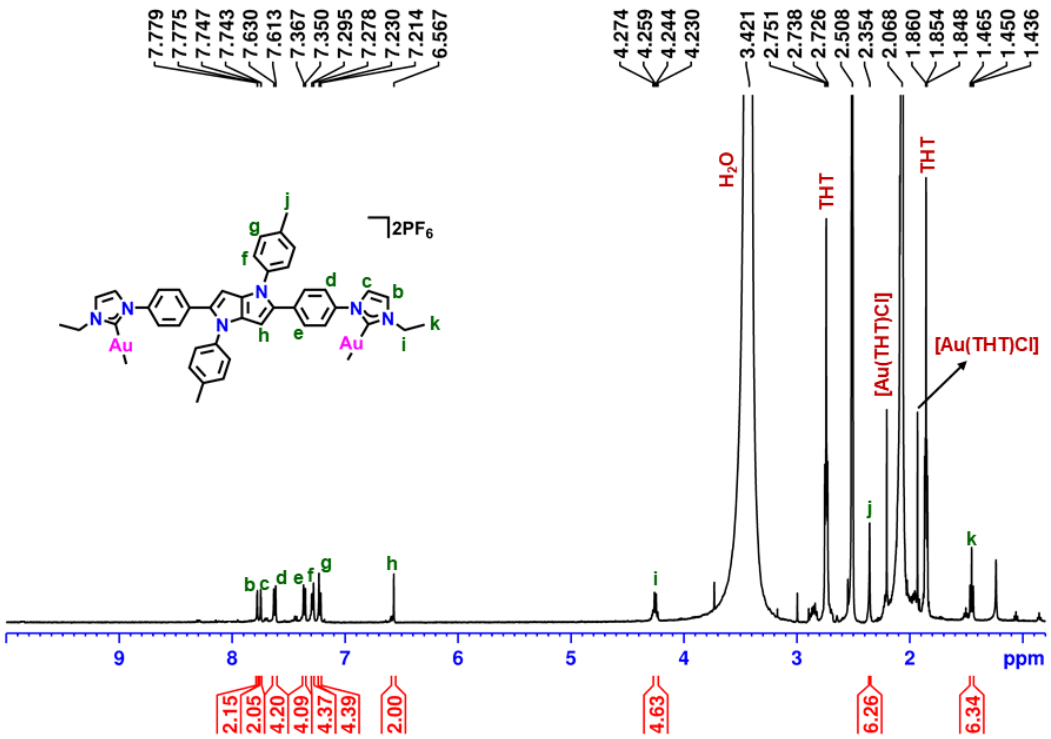


Fig. S5: ^{1}H NMR spectrum of **3** (DMSO-d_6, 298 K).

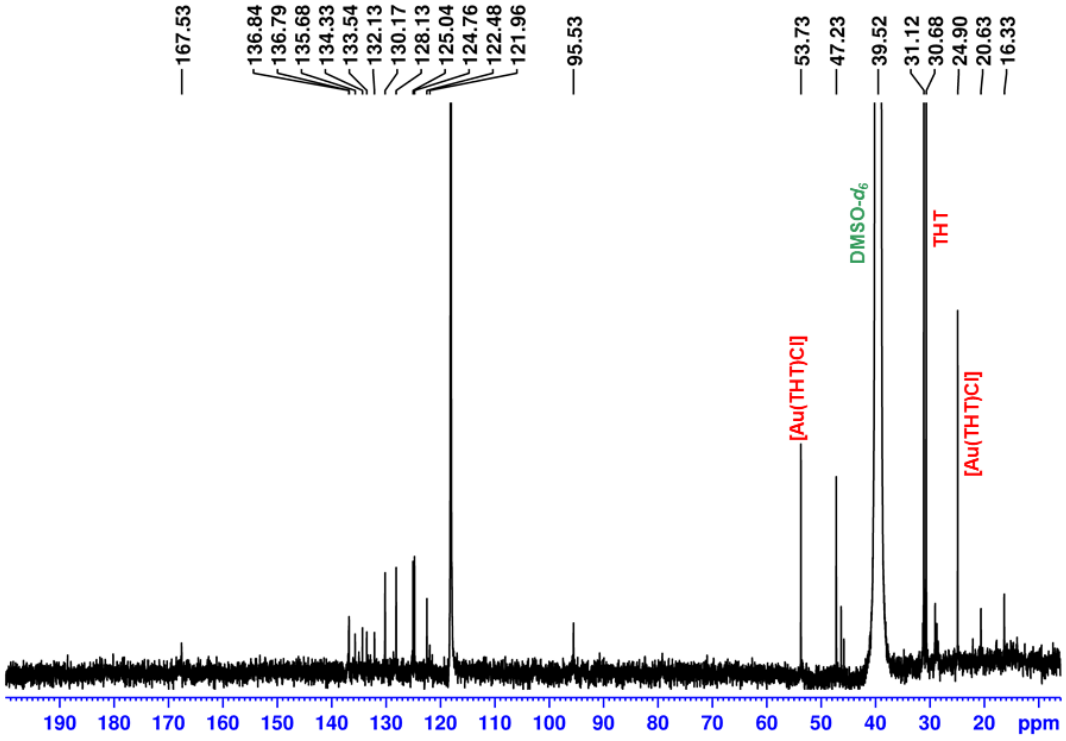


Fig. S6: ^{13}C NMR spectrum of **3** (DMSO-d_6, 298 K).

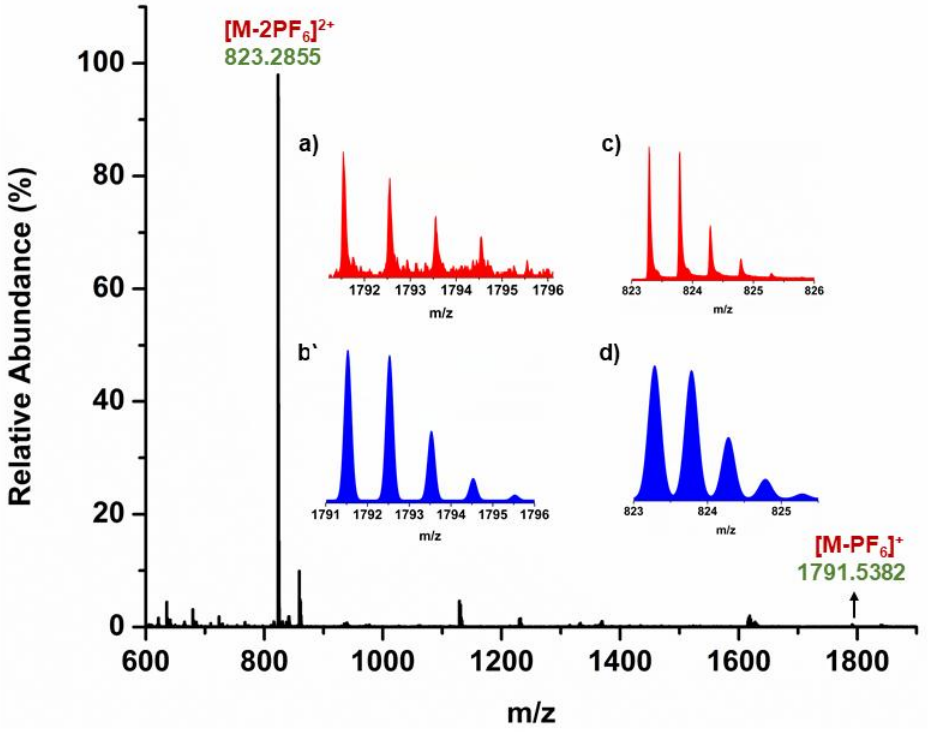
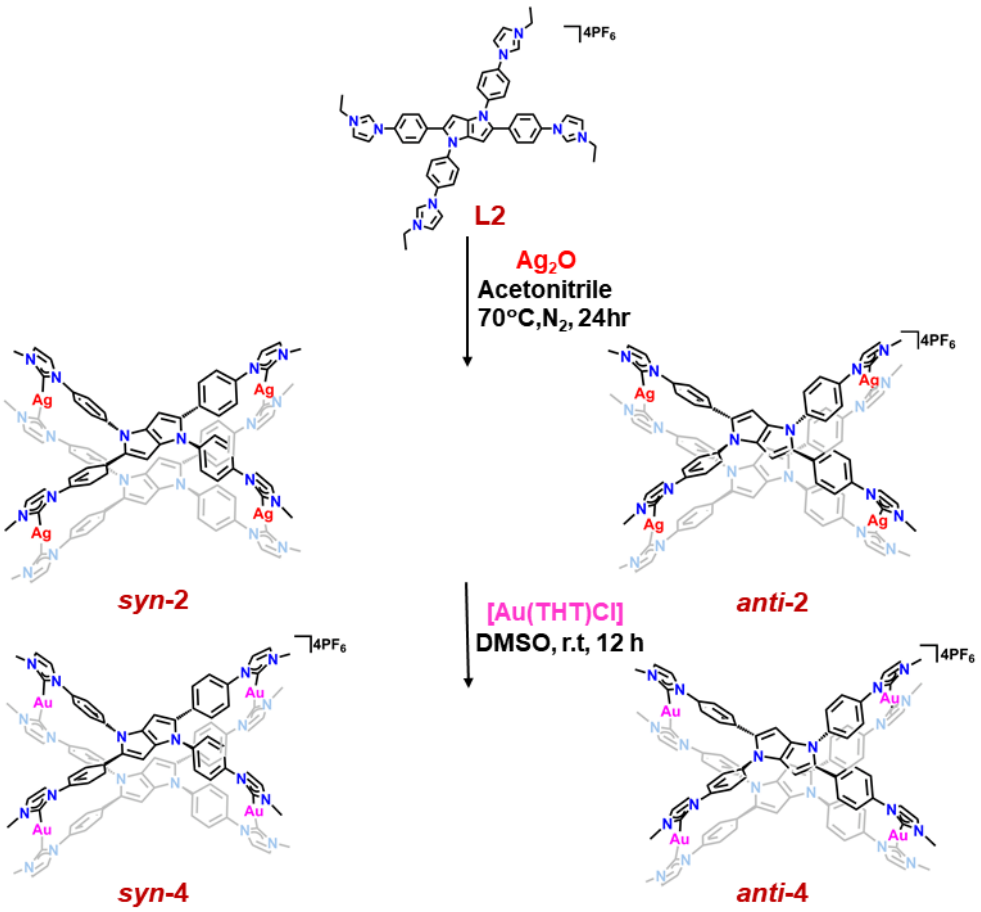


Fig. S7: Electrospray ionization mass spectrum of **3**. Isotopic distribution patterns: a) experimental (red) b) theoretical (blue) of the **[M-PF$_6$]$^{1+}$** fragment and c) experimental (red) c) theoretical (blue) of the **[M-2PF$_6$]$^{2+}$** fragment.

1.5 Synthesis and characterization of 2 and 4



Scheme S5: Synthetic scheme for **2** and **4**.

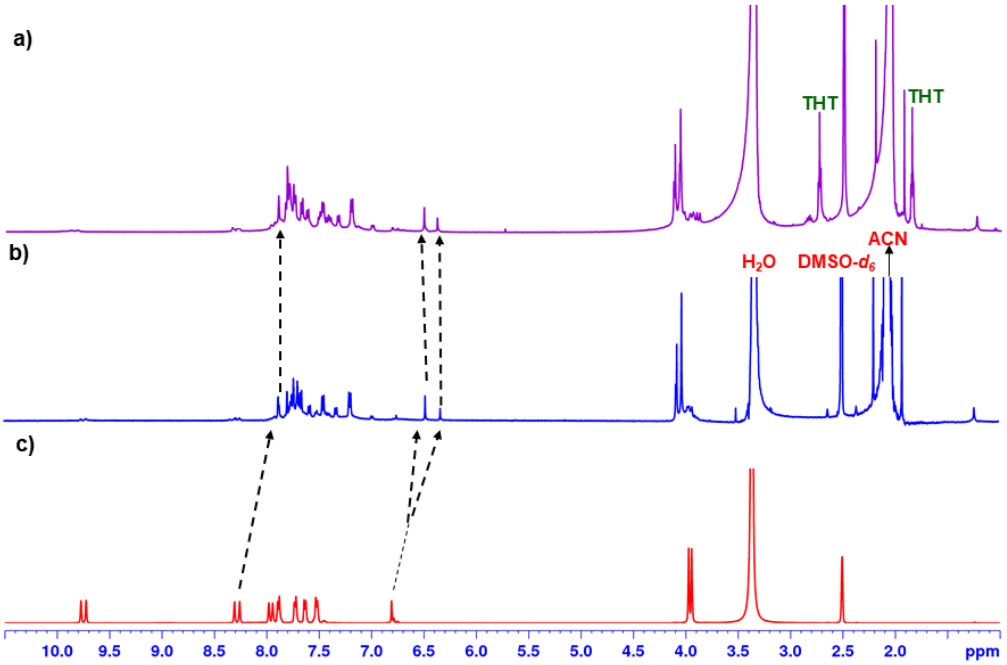


Fig. S8. [1]H NMR spectra of a) complex **4** (in situ); b) complex **2** and c) ligand **L2** in DMSO-d_6.

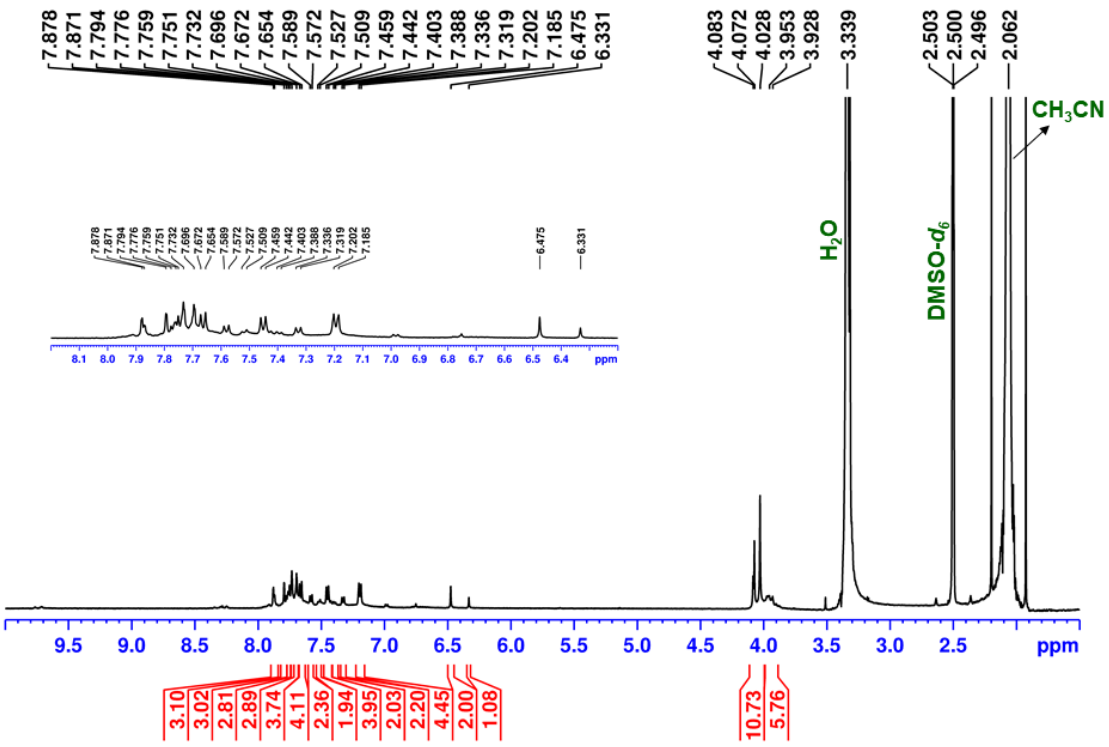


Fig. S9:[1]H NMR spectrum of **2** (DMSO-d_6, 298 K).

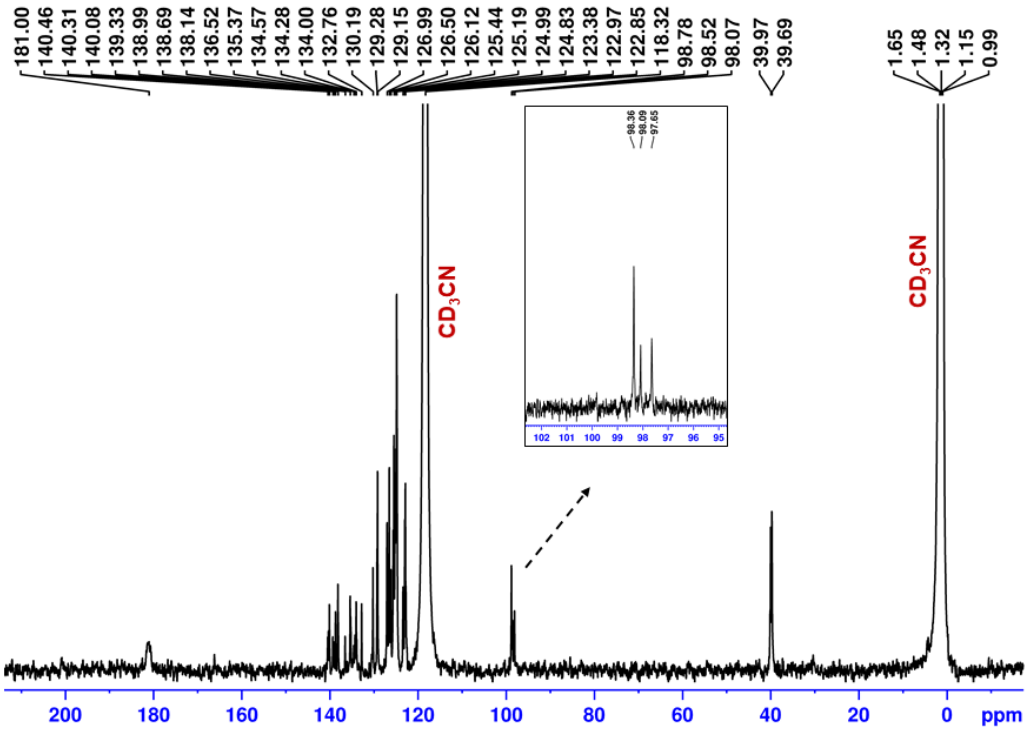


Fig. S10: ^{13}C NMR spectrum of **2** (CD_3CN, 298 K).

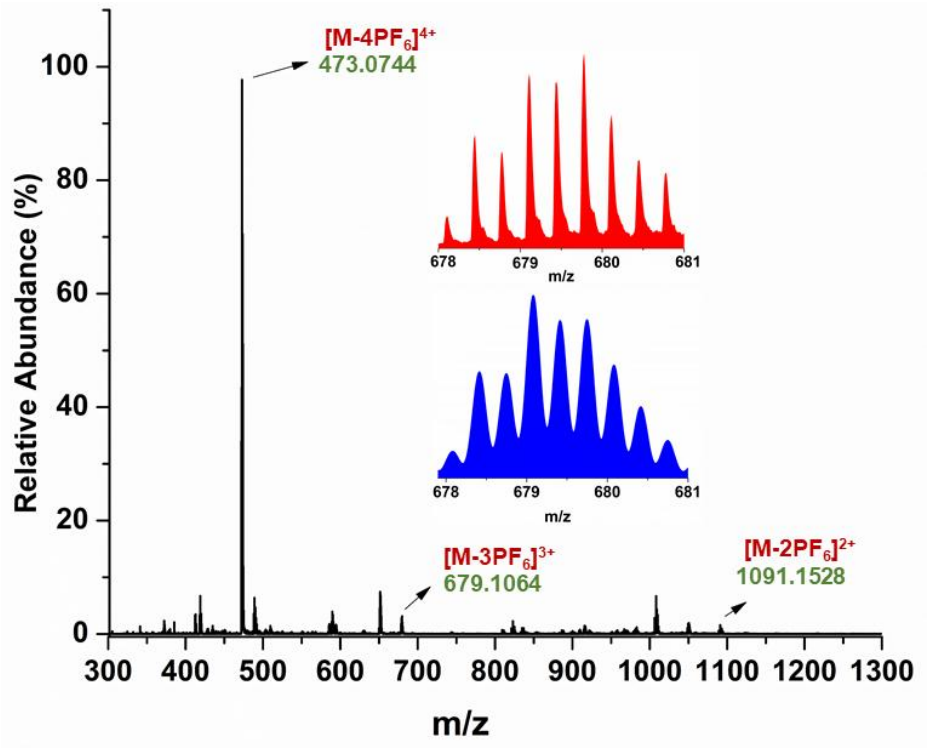


Fig. S11: Electrospray ionization mass spectrum of **2**. Isotopic distribution patterns: experimental (red) and theoretical (blue) of the **[M-3PF$_6$]$^{3+}$** fragment.

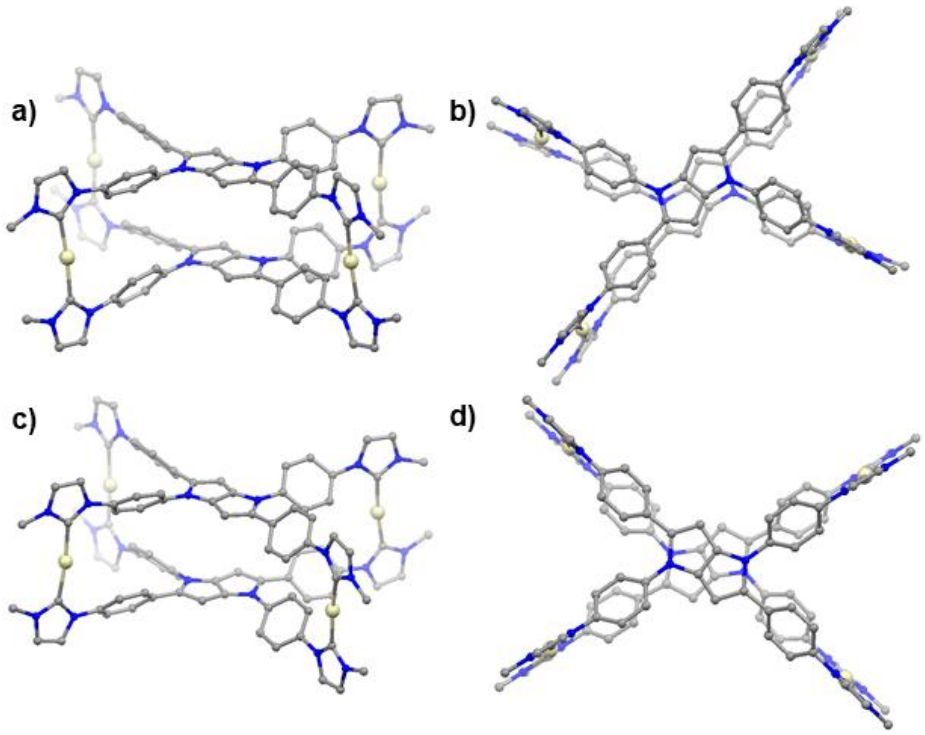


Fig. S12. Optimised structures of the complex **2:** a) side view of *syn*-**2** b) top view of *syn*-**2** c) side view of *anti*-**2** d) top view of *anti*-**2**. Color codes: Carbon (grey), Nitrogen (blue), Silver (light yellow). H-atoms are omitted for clarity.

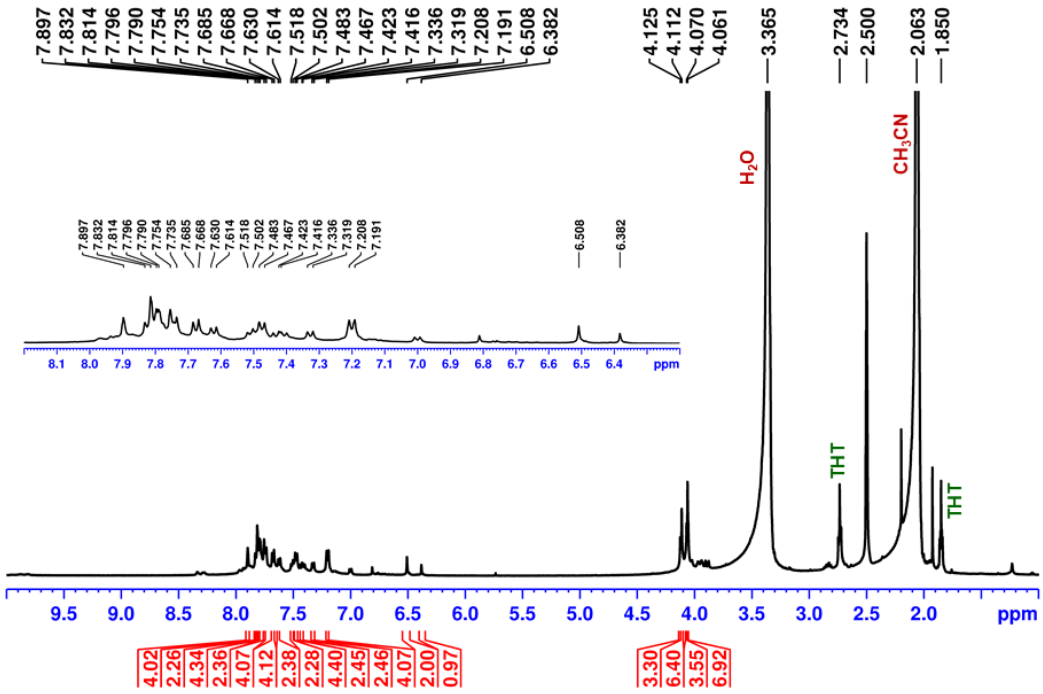


Fig. S13: ^{1}H NMR spectrum of **4** (DMSO-d_6, 298 K).

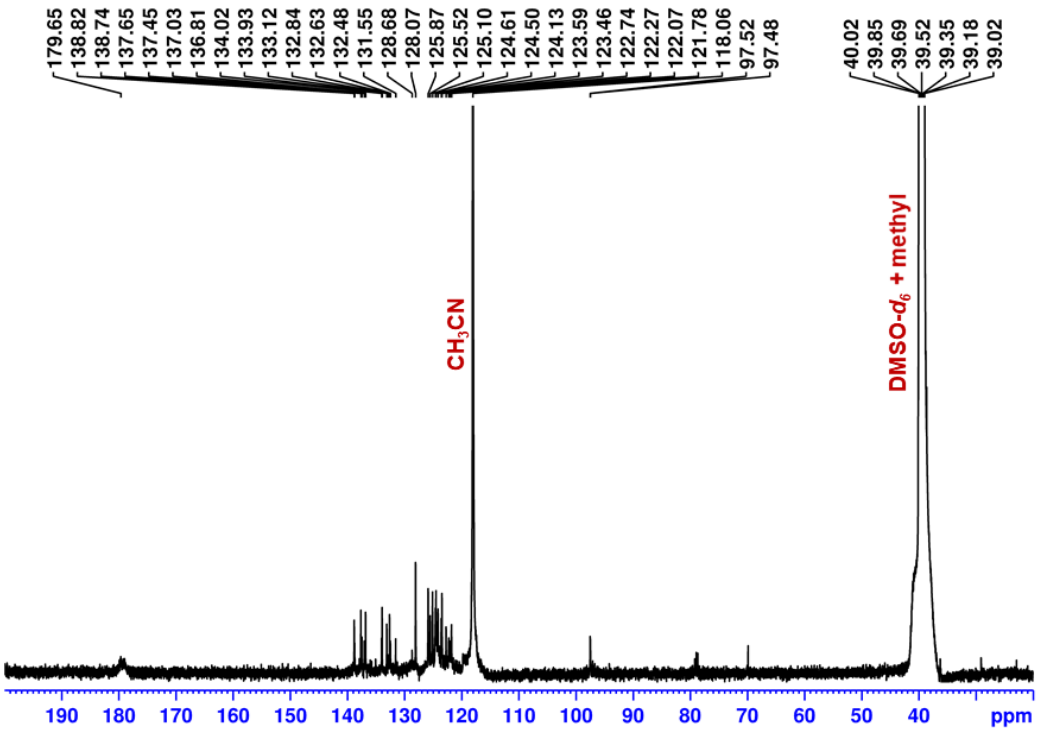


Fig. S14: ^{13}C NMR spectrum of **4** (DMSO-d_6, 298 K).

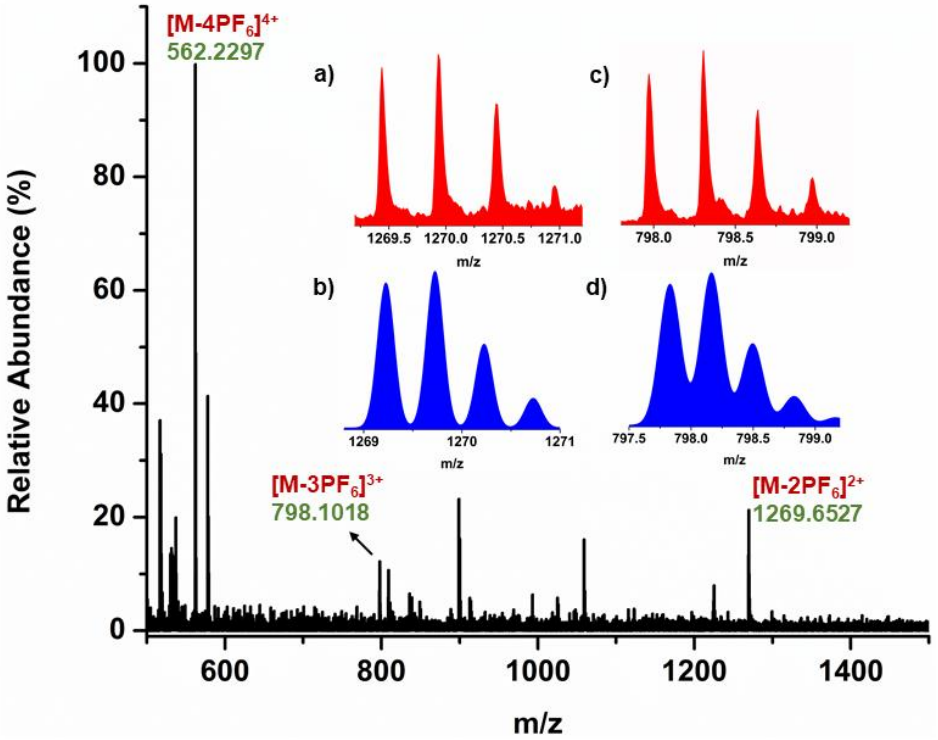


Fig. S15: Electrospray ionization mass spectrum of **4**. Isotopic distribution patterns: a) experimental (red) b) theoretical (blue) of the **[M-2PF$_6$]$^{2+}$** fragment and c) experimental (red) d) theoretical (blue) of the **[M-3PF$_6$]$^{3+}$** fragment.

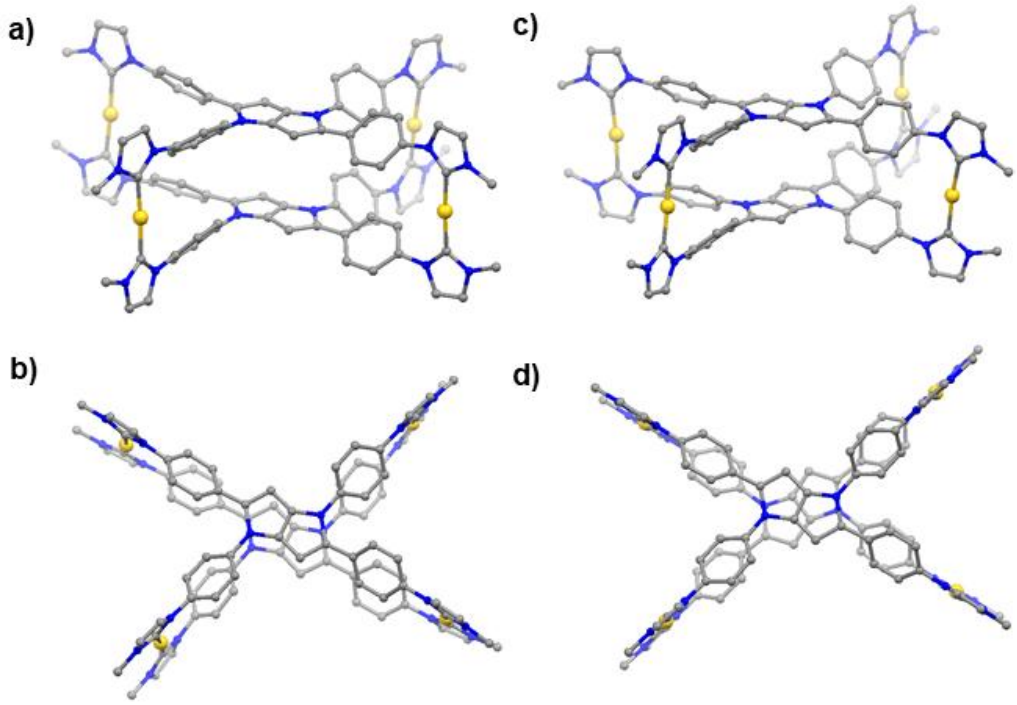


Fig. S16. Optimised structures of the complex **4:** a) side view of *syn*-**4** b) top view of *syn*-**4** c) side view of *anti*-**4** d) top view of *anti*-**4**. Color codes: Carbon (grey), Nitrogen (blue), Gold (golden yellow). H-atoms are omitted for clarity.

2. Normalized absorption and emission spectra of the metal complexes and free ligands in acetonitrile:

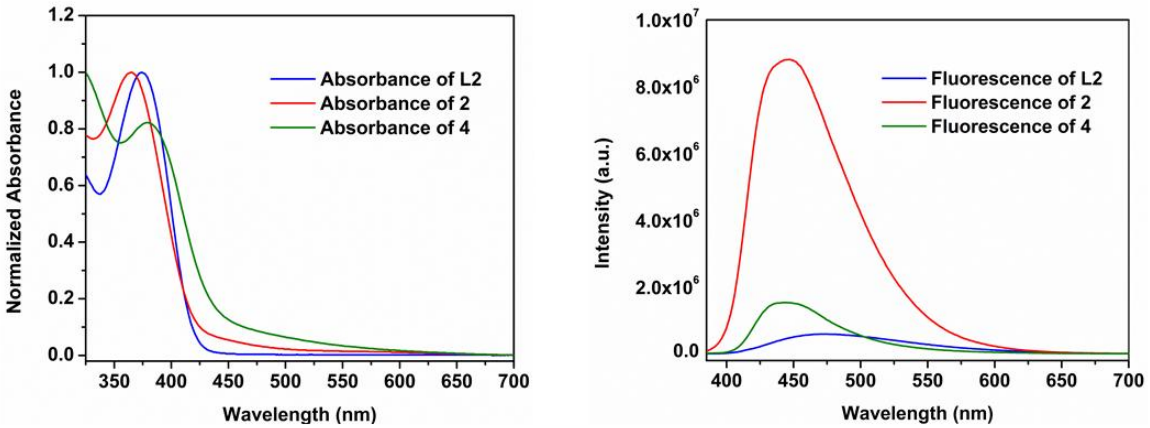


Fig. S17: (Left) Normalized absorbance spectra of **L2, 2** and **4** at room temperature in CH_3CN (10^{-5}M solution); (Right) Emission spectra of compounds **L2, 2** and **4** at room temperature in CH_3CN (10^{-5}M solution).

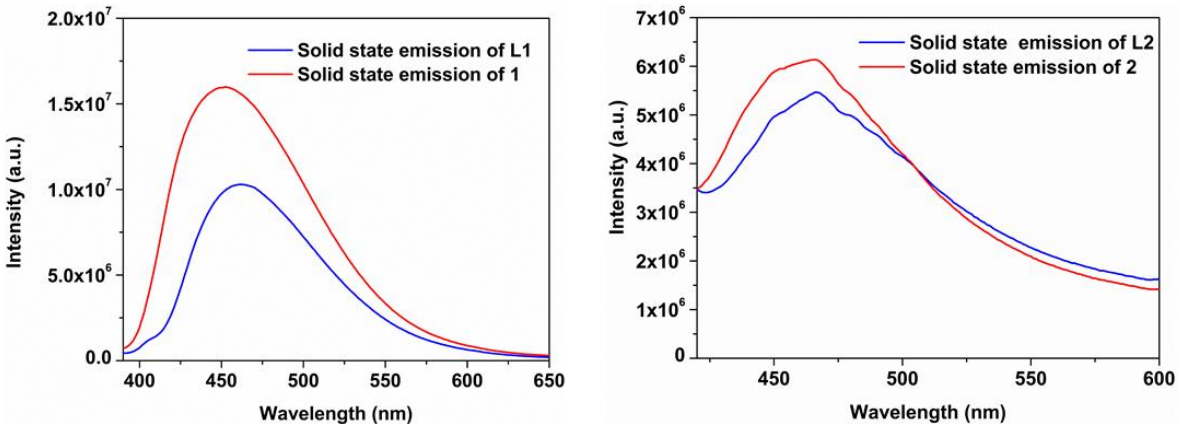


Fig. S18: (Left): Solid state emission spectra of **L1, 1.** (Right): Solid state emission spectra of compounds **L2, 2**.

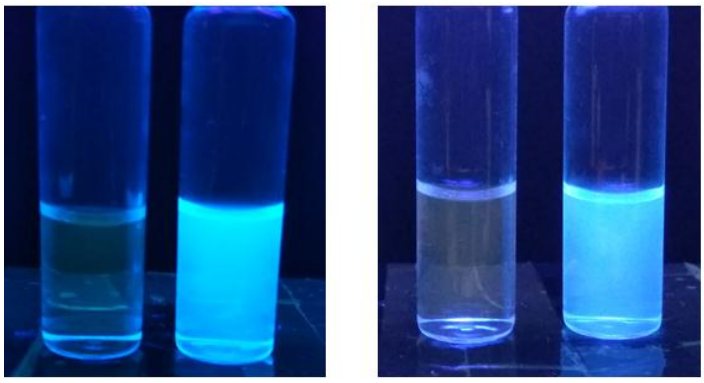


Fig. S19: Images of **L1**, Ag-complex **1** (Left) and **L2,** Ag-complex **2** (Right) in CH_3CN under UV radiation of 365nm.

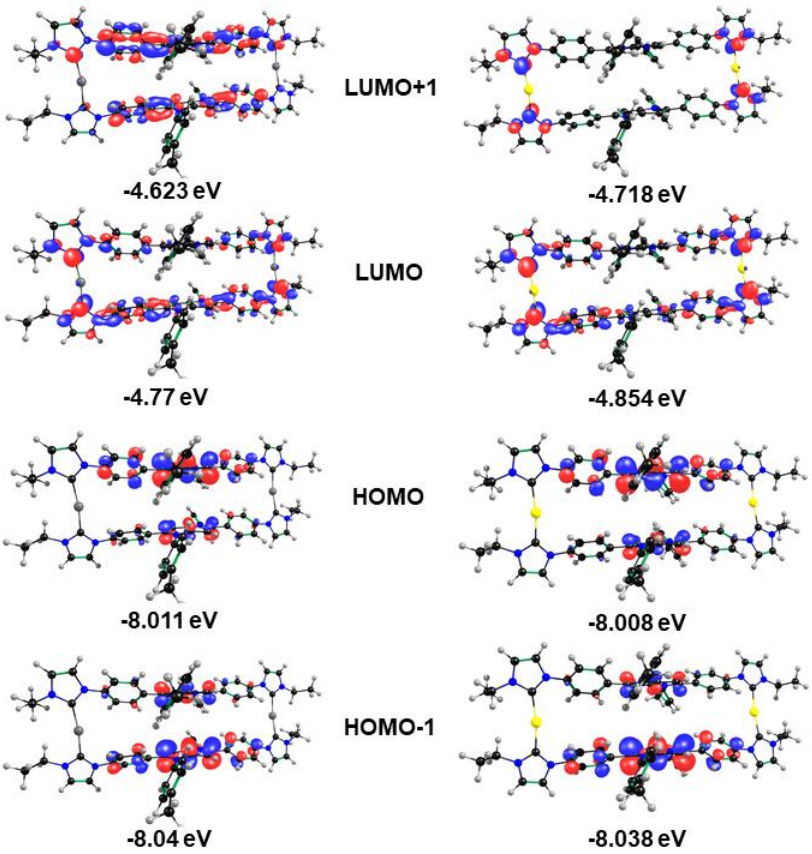


Fig. S20. Frontier molecular orbitals in ground state: (left) Ag-complex **1** and (right) Au-complex **3**.

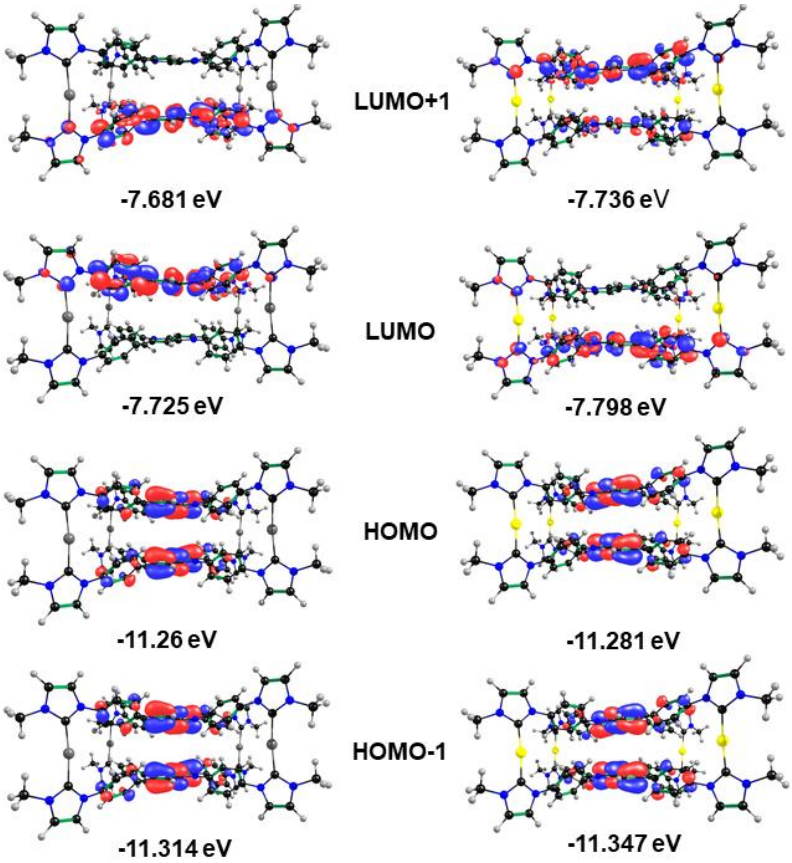


Fig. S21: Frontier molecular orbital in ground state: (left): Ag-complex **2** and (Right): Au-complex **4**.

Table 1. Absorption and emission maxima of the free ligands, Ag^{I}-C_{NHC} and Au^{I}-C_{NHC} complexes, and their corresponding quantum yields.

Compound	Absorption Maxima (nm)	Emission Maxima (nm)	Quantum Yield
L1	380	498	3.2
1	366	453	32
3	377	457	17.5
L2	374	472	3.4
2	365	451	28
4	381	443	9.5

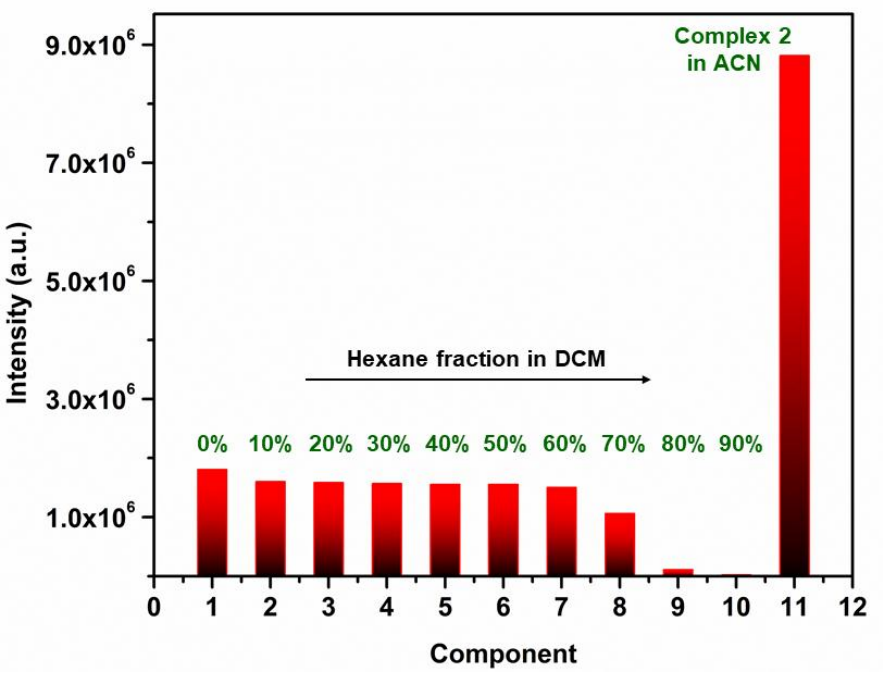


Fig. S22: Bar diagram showing the comparison in emission intensities between **Im2** in different hexane fractions in dichloromethane (DCM) (10^{-5}M solution) and **2** in acetonitrile (10^{-5}M solution).

3. NMR spectra of the intermediate compounds:

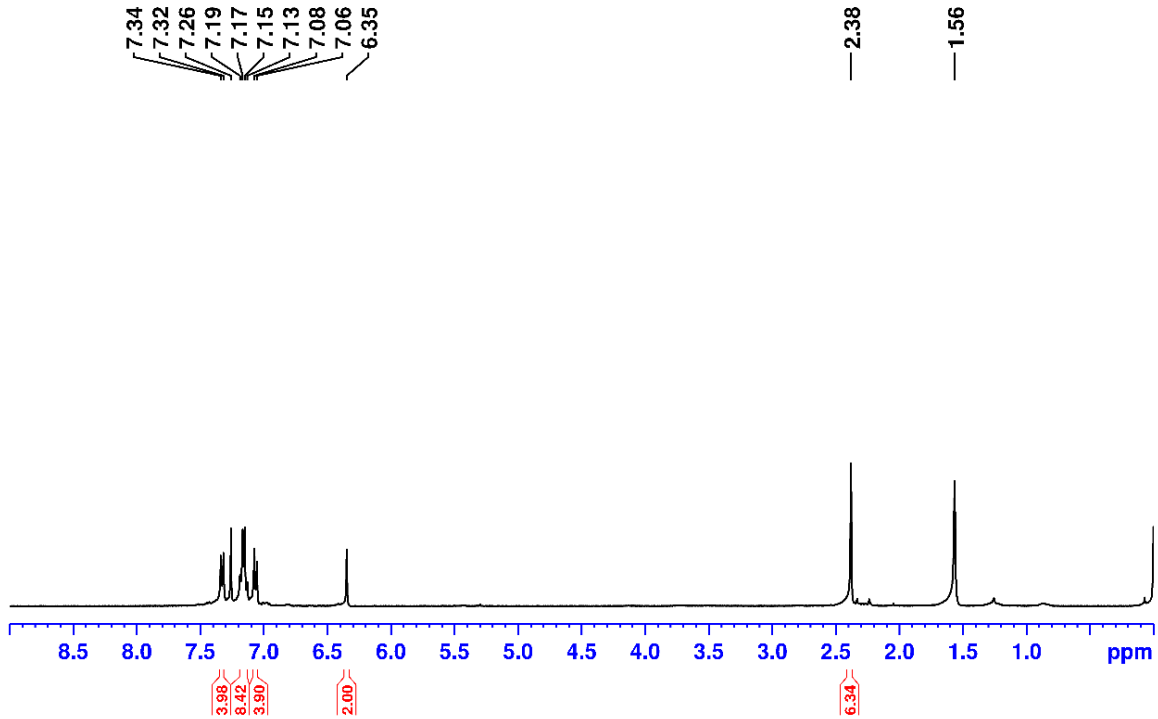


Fig. S23: ^{1}H NMR spectrum of compound **Br1** ($CDCl_3$, 298 K).

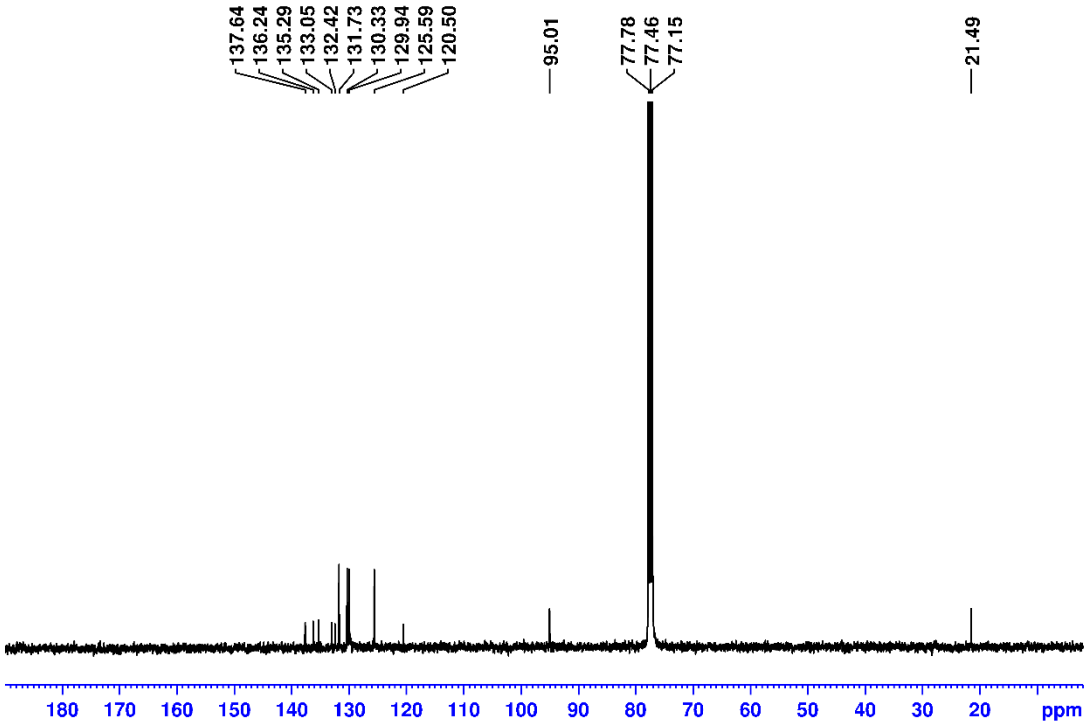


Fig. S24: ^{13}C NMR spectrum of compound **Br1** ($CDCl_3$, 298 K).

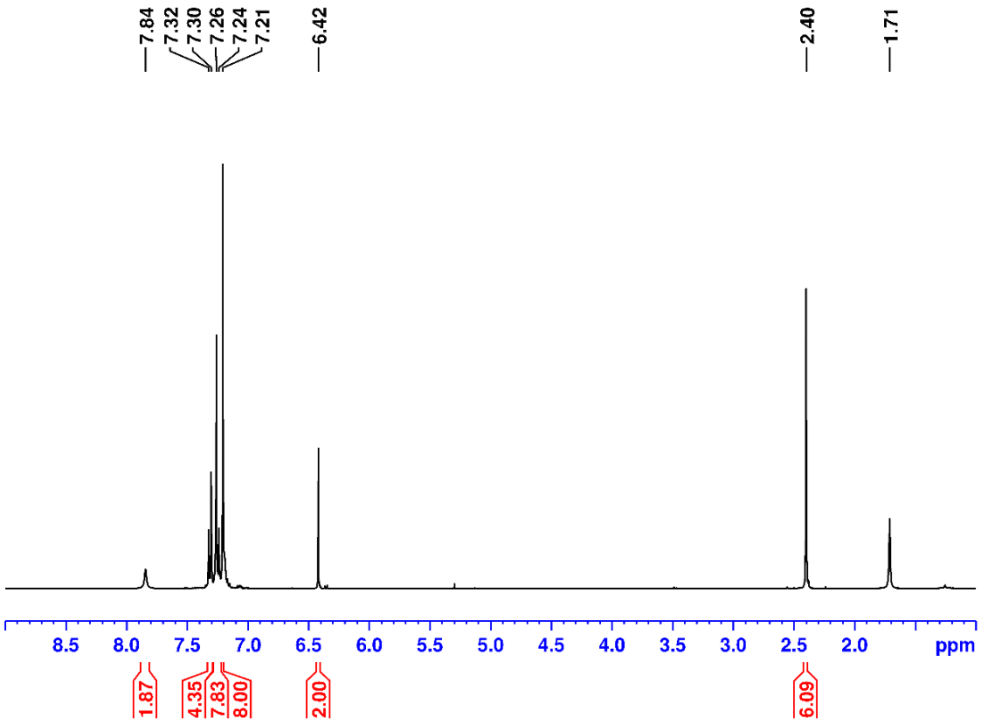


Fig. S25: ^{1}H NMR spectrum of compound **Im1** ($CDCl_3$, 298 K).

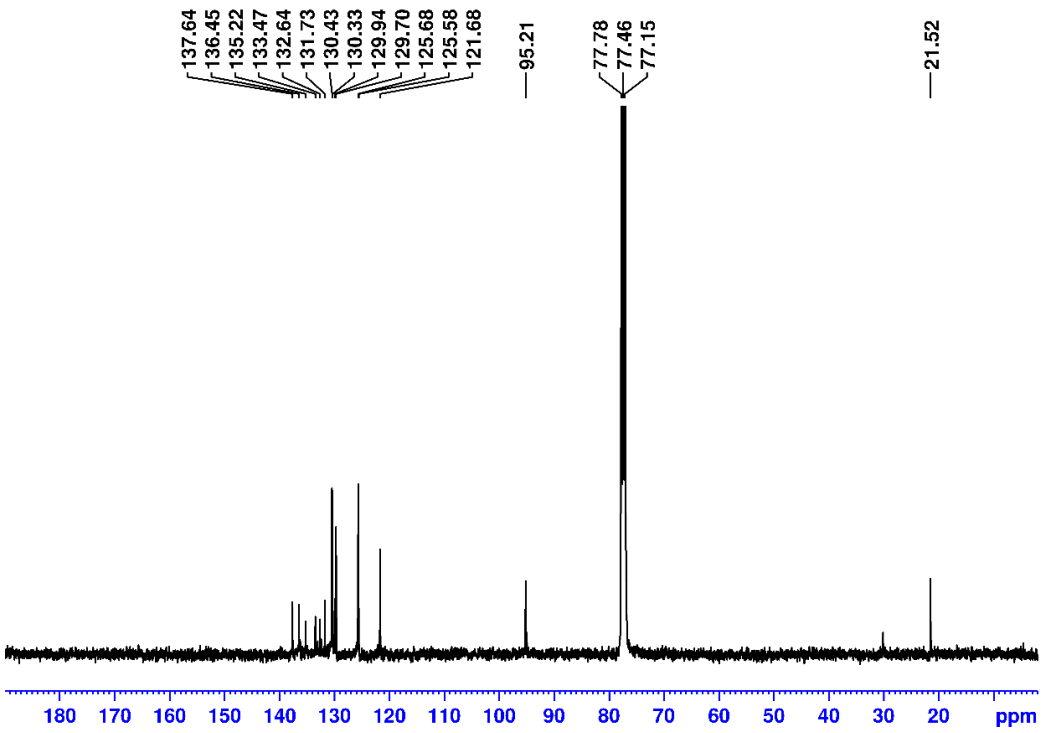


Fig. S26: ^{13}C NMR spectrum of compound **Im1** ($CDCl_3$, 298 K).

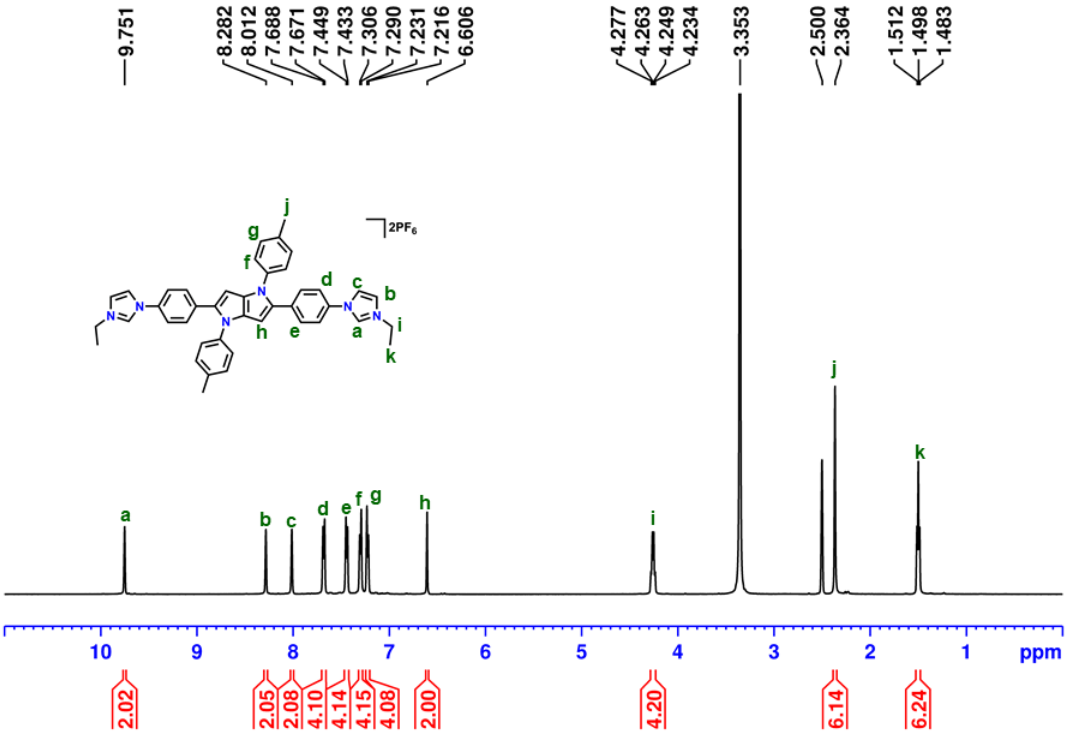


Fig. S27: ^{1}H NMR spectrum of compound **L1** (DMSO-d_6, 298 K).

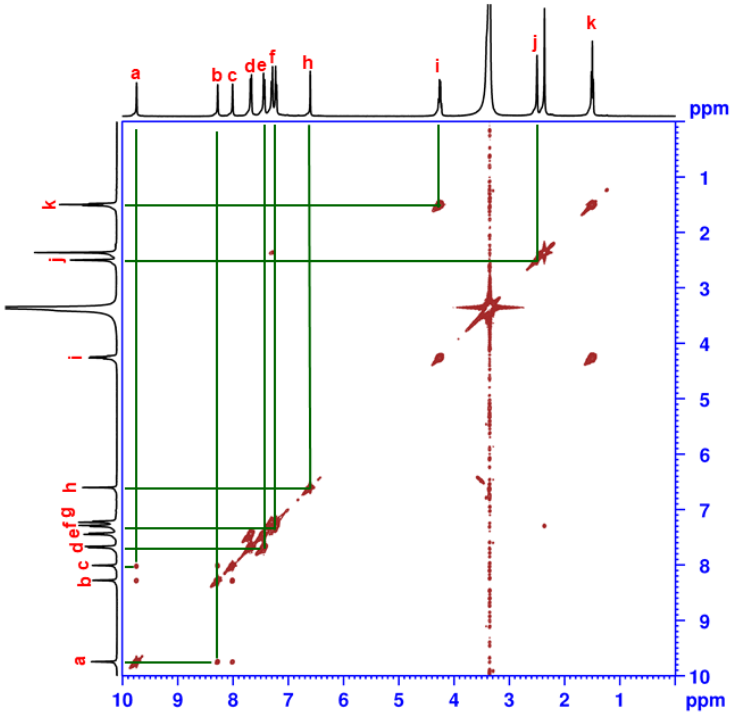


Fig. S28: ^{1}H - ^{1}H COSY spectrum of **L1** (DMSO-d_6, 298 K). The rectangular position shows the interaction between neighbouring protons.

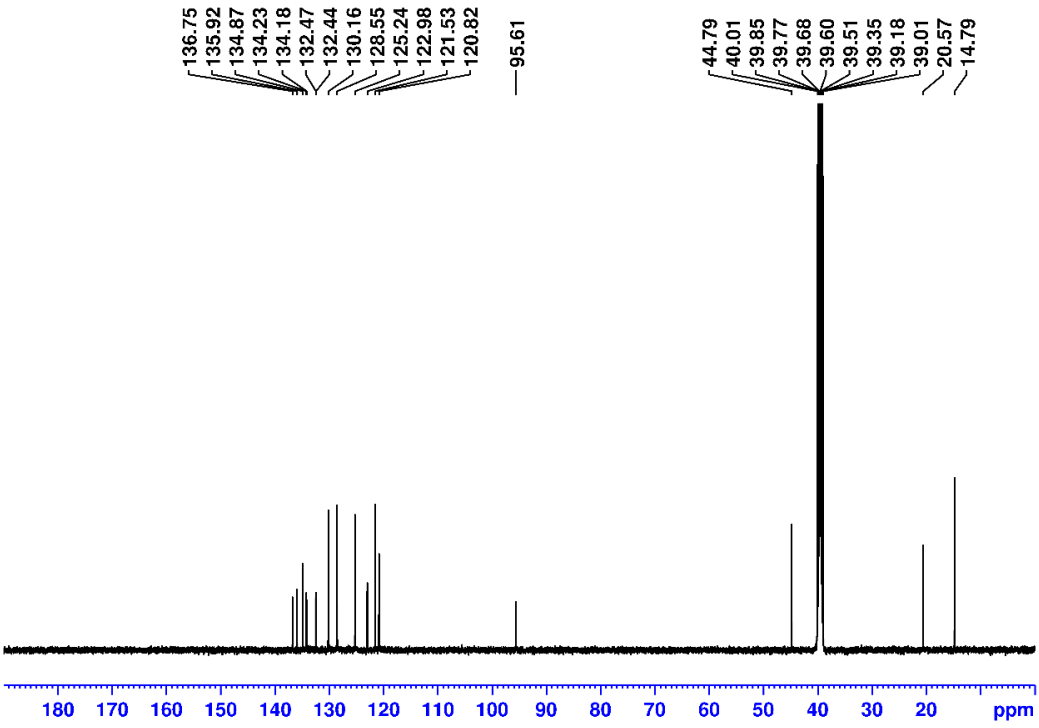


Fig. S29: ^{13}C NMR spectrum of compound **L1** (DMSO-d_6, 298 K).

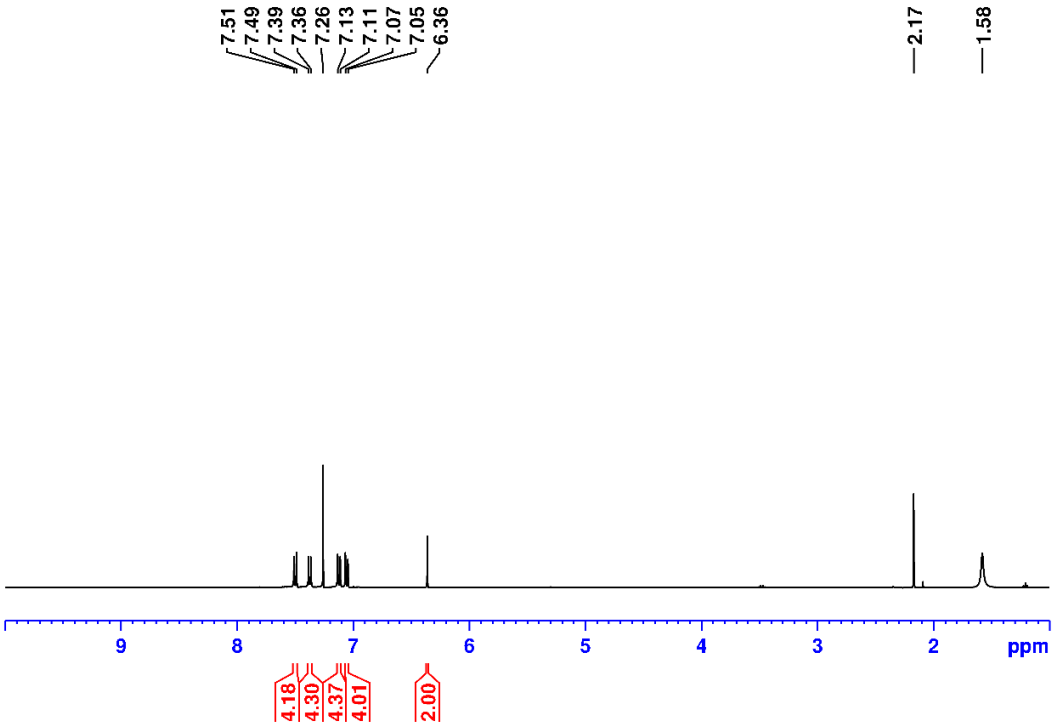


Fig. S30: ^{1}H NMR spectrum of compound **Br2** ($CDCl_3$, 298 K).

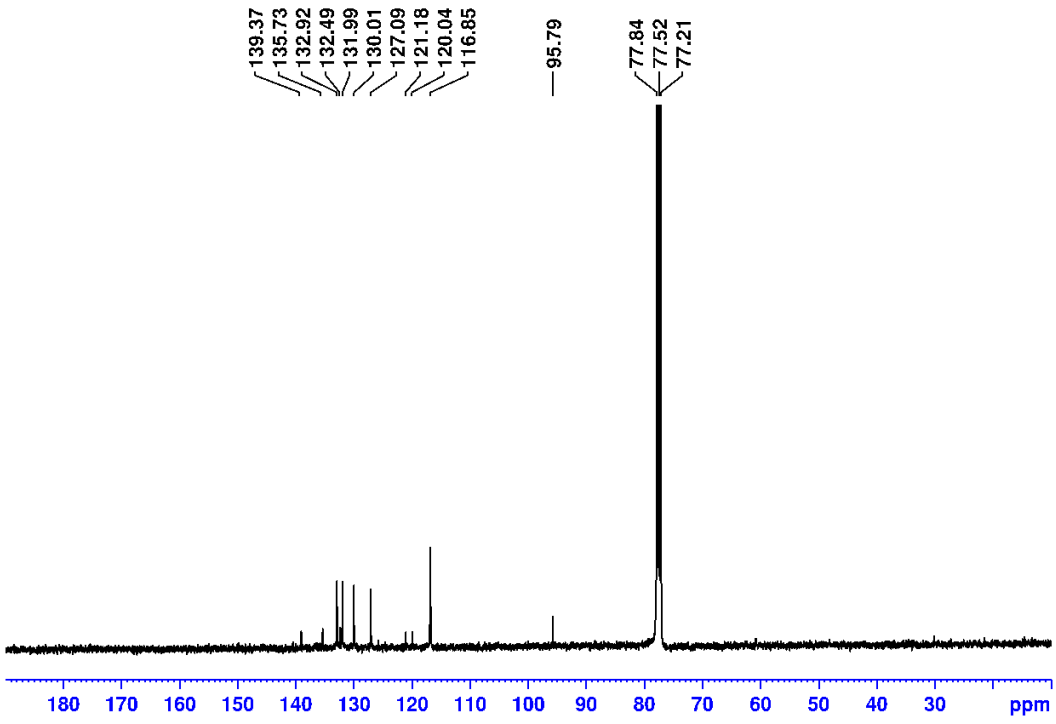


Fig. S31: ^{13}C NMR spectrum of compound **Br2** ($CDCl_3$, 298 K).

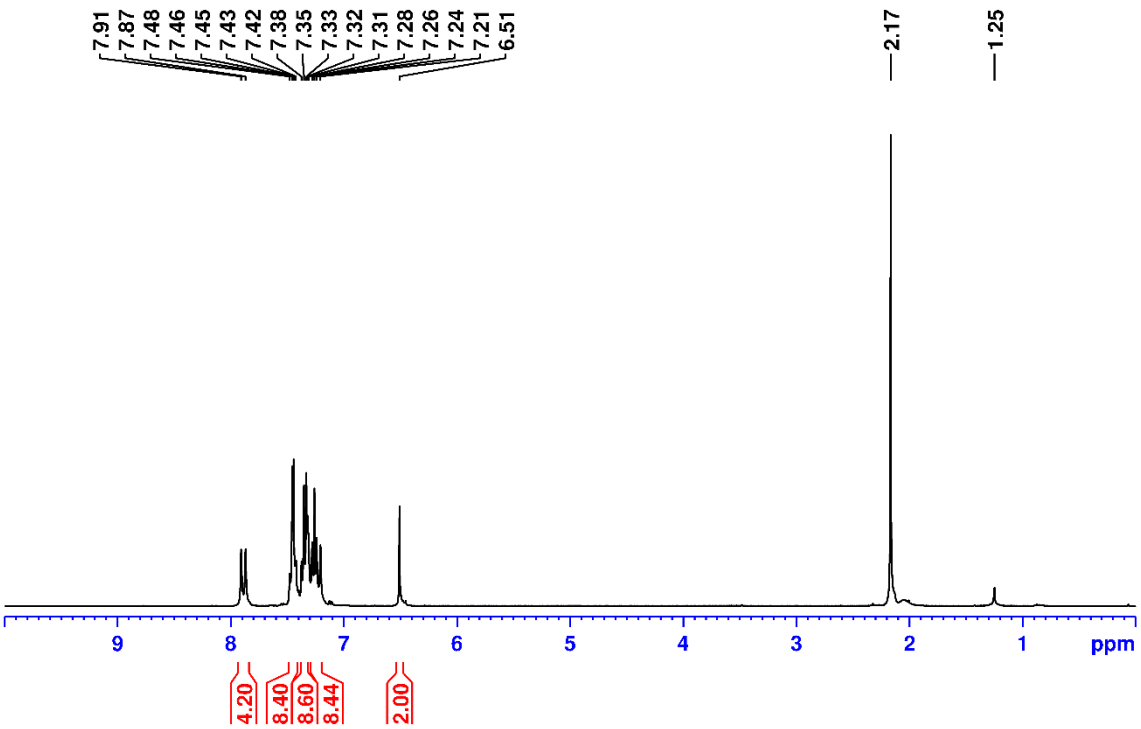


Fig. S32: ^{1}H NMR spectrum of compound **Im2** ($CDCl_3$, 298 K).

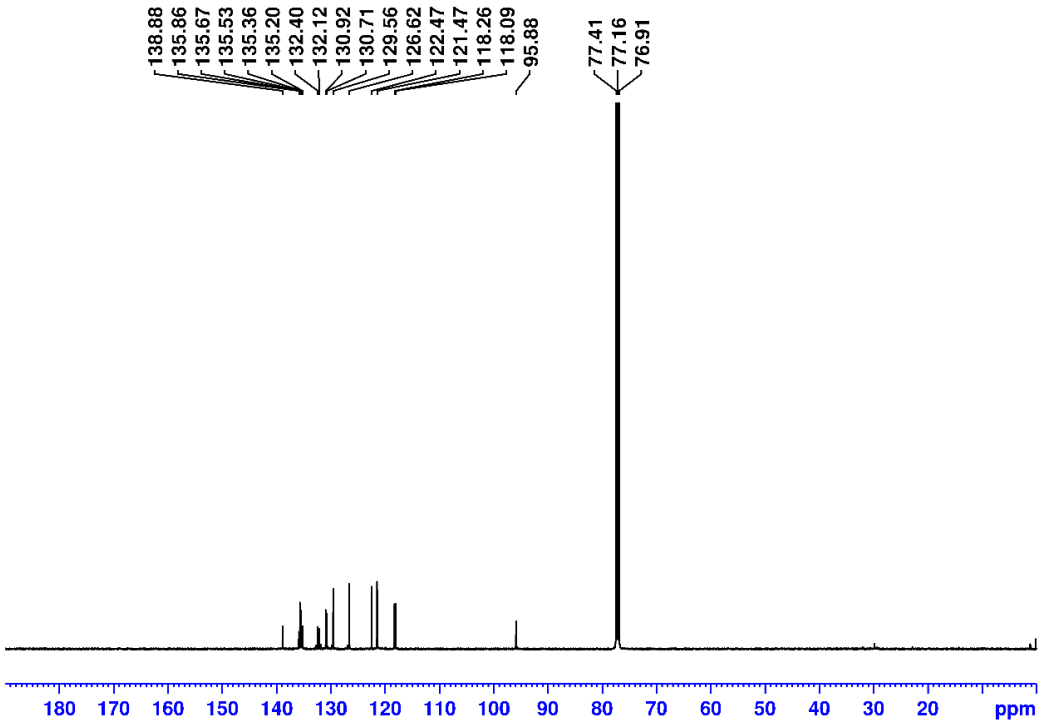


Fig. S33: ^{13}C NMR spectrum of compound **Im2** ($CDCl_3$, 298).

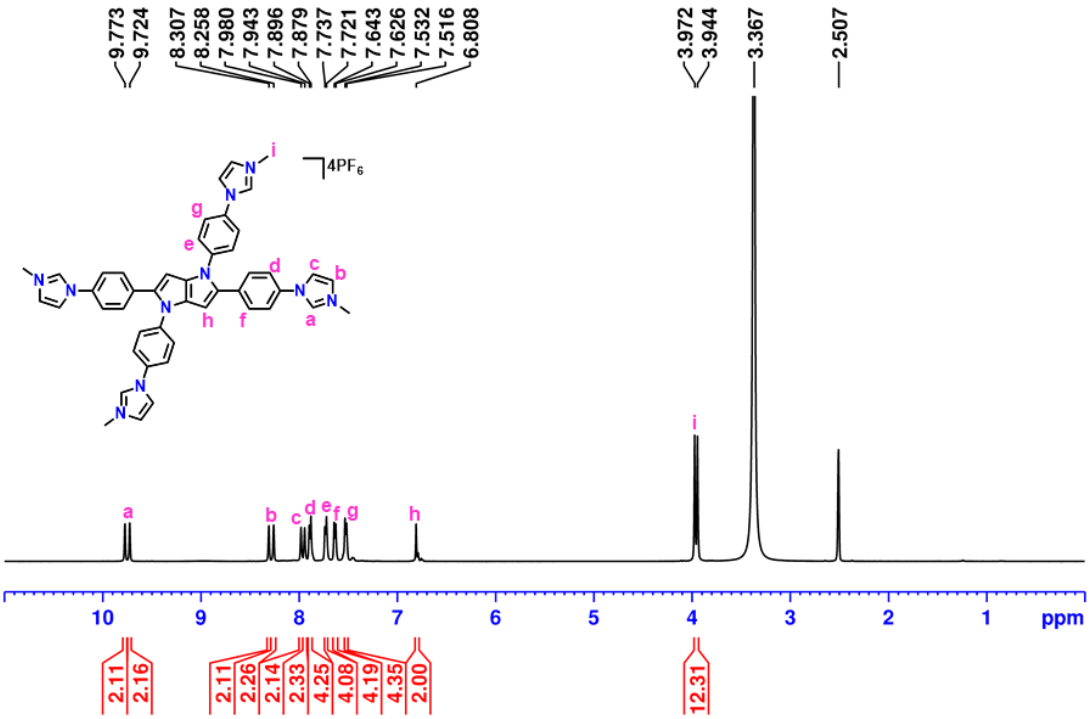


Fig. S34: ^{1}H NMR spectrum of compound **L2** (DMSO-d_6, 298 K).

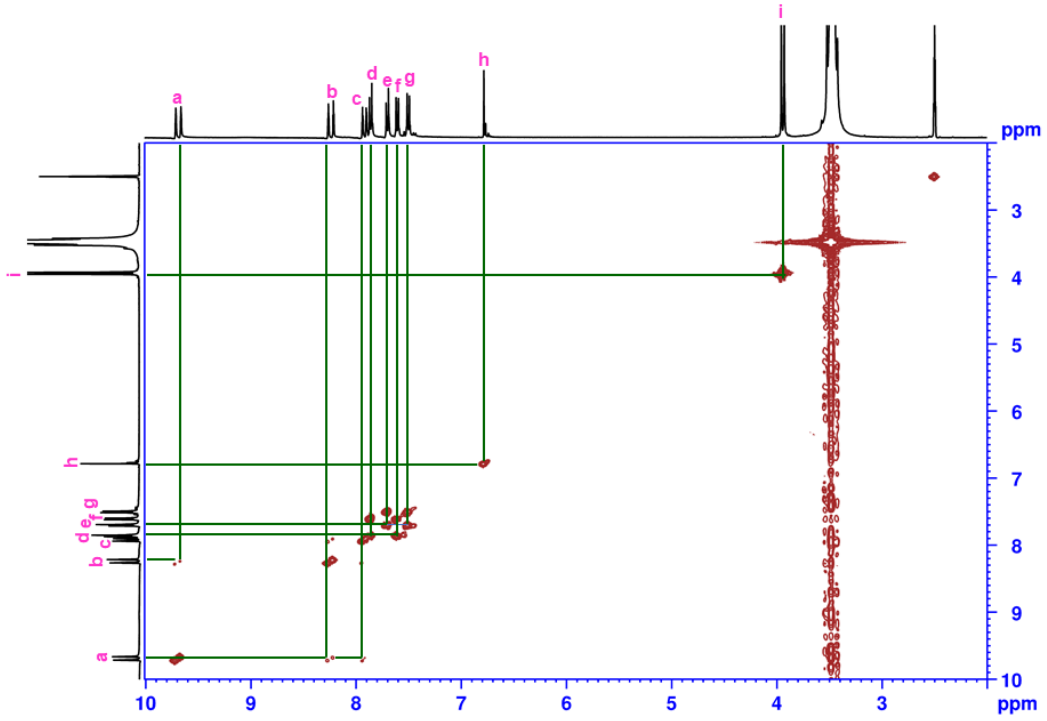


Fig. 35:^{1}H - ^{1}H COSY spectrum of **L2** (DMSO-d_6, 298 K). The rectangular position shows the interaction between neighbouring protons.

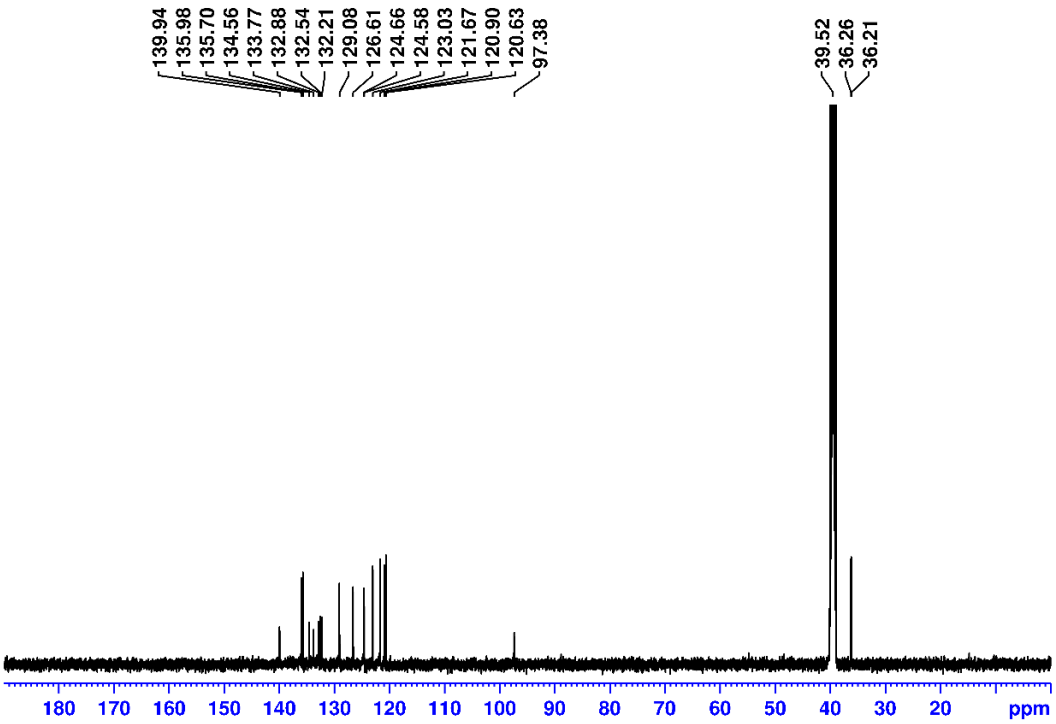


Fig. S36: ^{13}C NMR spectrum of compound **L2** (DMSO-d_6, 298 K).

4. Mass spectra of the building blocks:

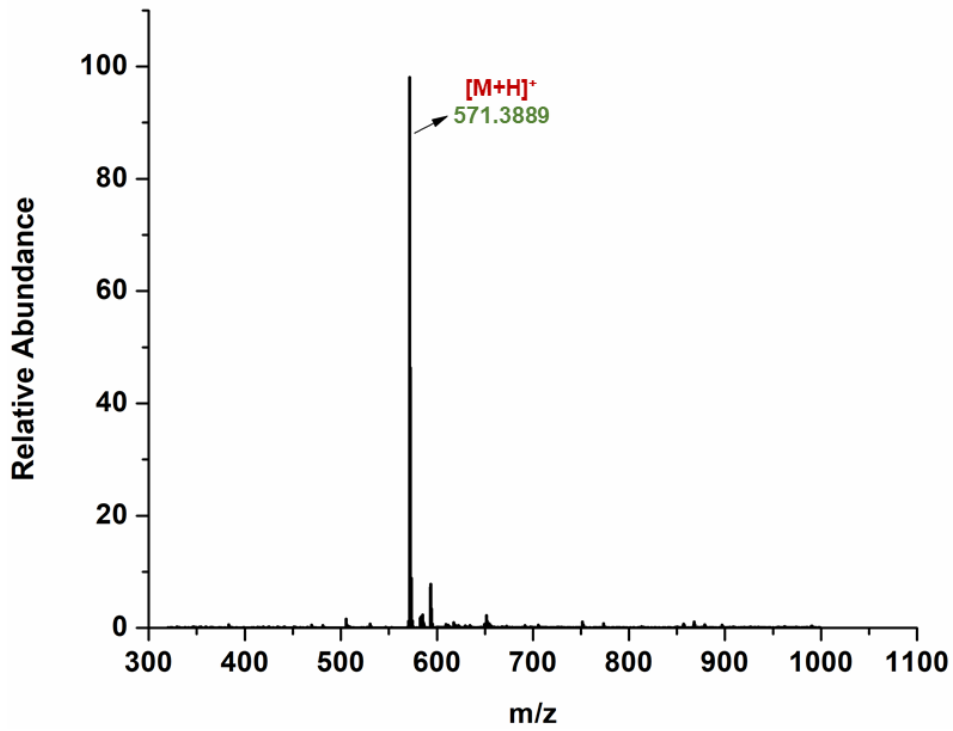


Fig. S37: Mass spectrum of compound **Im1**.

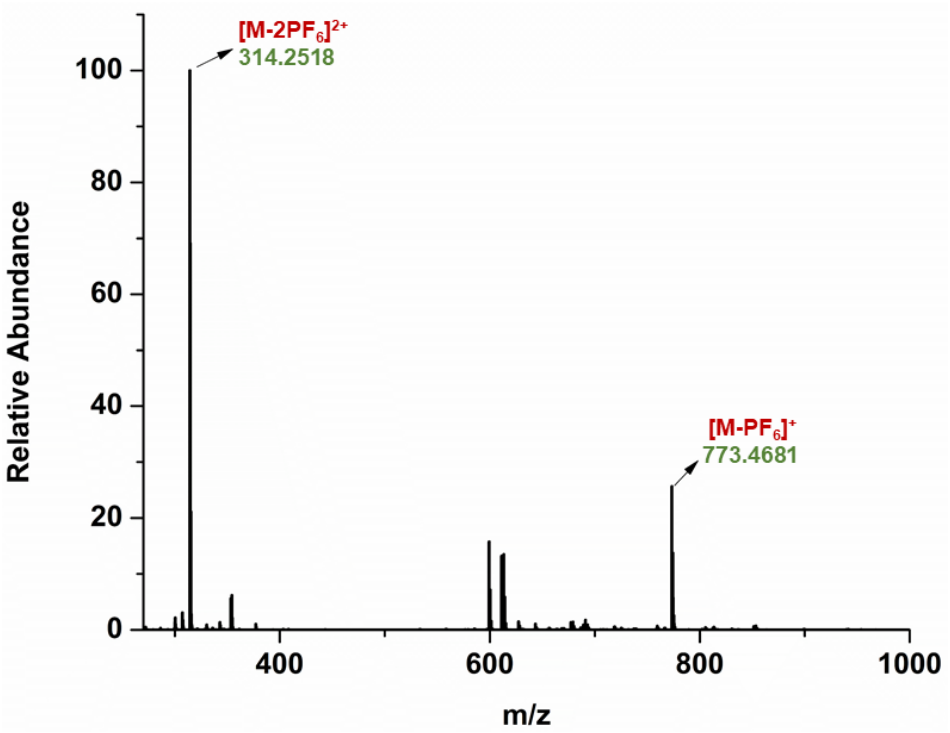


Fig. S38: Mass spectrum of compound **L1**.

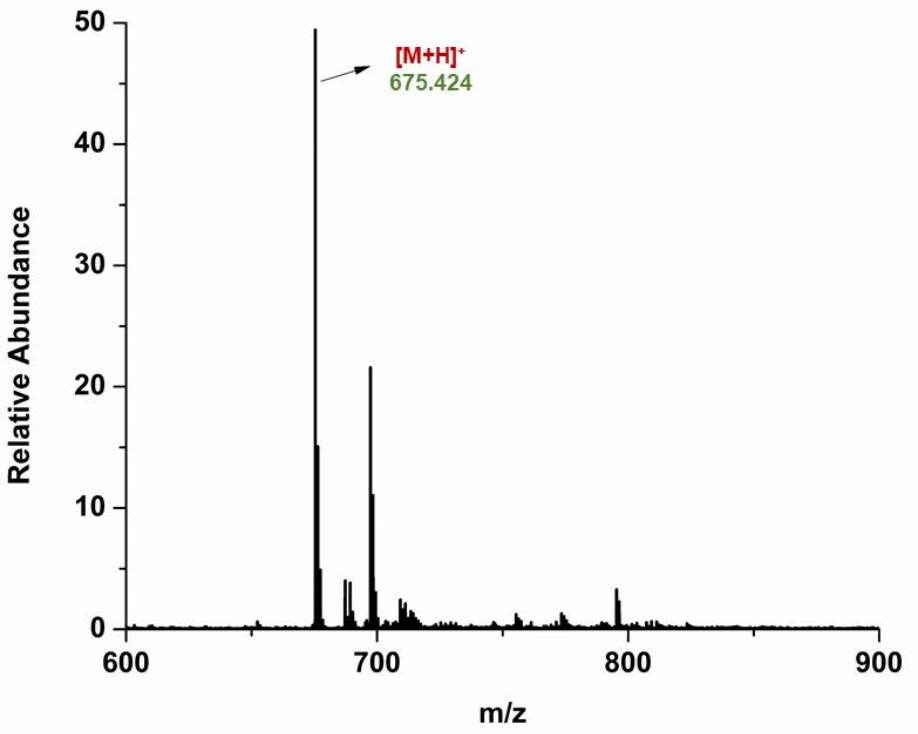


Fig. S39: Mass spectrum of compound **Im2**.

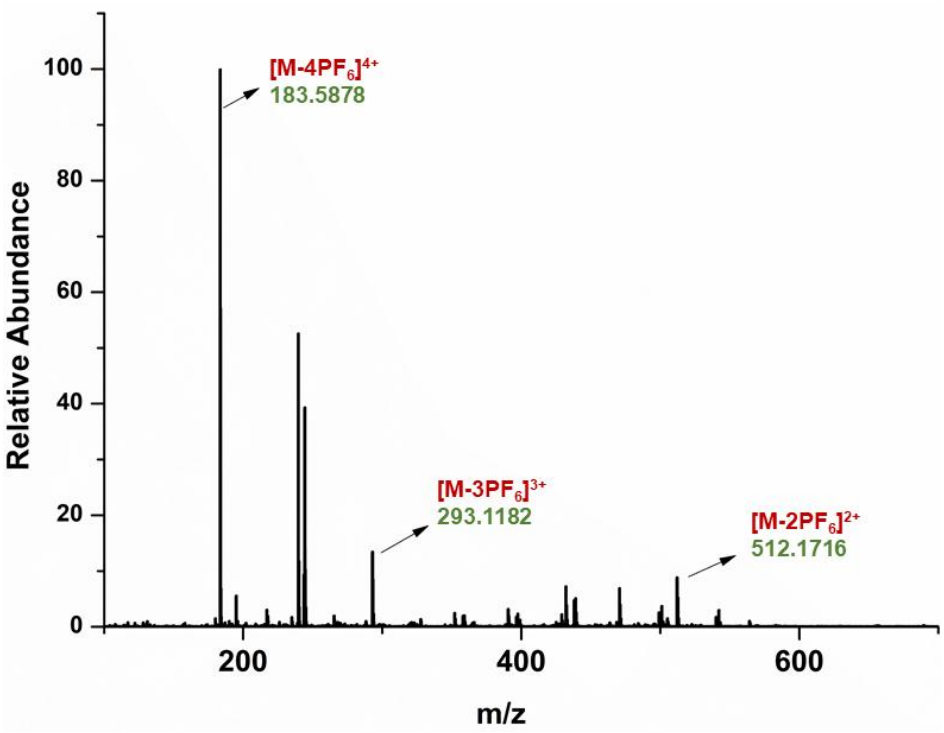


Fig. S40: Mass spectrum of compound L**2**.

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4. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.