

One pot conversion of fluorophores to phosphorophores.

Matan Soll^{a‡}, Kolanu Sudhakar^{a‡}, Natalia Fridman^a, Alexander Müller^b, Beate Röder^b and Zeev Gross^{a‡*}

^a *Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32,000, Israel*

^b *AG Photobiophysik, Humboldt-Universität zu Berlin MNF, Newtonstrass 1512489 Berlin, Germany*

1.0	Table of Contents	Page No. S1-S2
2.0	Experimental Section	S2
2.1	Methods and Materials	S2-S3
2.2	Synthesis	S3-S5
2.3	References	S5-S6
2.4	Spectra	S6-S18
Fig. S1	¹ H NMR spectrum of non-aromatic product from the reaction between (H₃)tpfc and NIS in Methanol as solvent and recorded spectrum in CDCl ₃ solvent.	S6
Fig. S2	¹ H NMR of (H₃)(I₄-tpfc)	S7
Fig. S3	¹⁹ F NMR of (H₃)(I₄-tpfc)	S7
Fig. S4	High resolution APCI mass spectrum of (H₃)(I₄-tpfc)	S8
Fig. S5	¹ H NMR of (I₄-tpfc)Cu	S8
Fig. S6	¹⁹ F NMR of (I₄-tpfc)Cu	S9
Fig. S7	High resolution APCI mass spectrum of (I₄-tpfc)Cu	S9
Fig. S8	¹ H NMR of (I₄-tpfc)Ag	S10
Fig. S9	¹⁹ F NMR of (I₄-tpfc)Ag	S10
Fig. S10	High-resolution APCI Mass spectrum of (I₄-tpfc)Ag .	S11
Fig. S11	¹ H NMR of (tpfc)Au	S12
Fig. S12	¹⁹ F NMR of (tpfc)Au	S12
Fig. S13	High-resolution APCI mass spectrum of (tpfc)Au .	S13
Fig. S14	¹ H NMR of (I₄-tpfc)Au	S14
Fig. S15	¹⁹ F NMR of (I₄-tpfc)Au	S14
Fig. S16	High-resolution APCI mass spectrum of (I₄-tpfc)Au .	S15
Fig. S17	¹ H NMR of (I₃-tpfc)Ag (contaminated by unreacted (tpfc)Ag)	S16
Fig. S18	¹⁹ F NMR of (I₃-tpfc)Ag (contaminated with unreacted (tpfc)Ag)	S16
Fig. S19	APCI mass spectrum of (I₃-tpfc)Ag (contaminated with unreacted	S17

(tpfc)Ag)

Fig. S20	¹ H NMR spectrum of (I₃-tpfc)Au (contaminated with unreacted (tpfc)Au).	S18
Fig. S21	¹⁹ F NMR spectrum of (I₃-tpfc)Au (contaminated with unreacted (tpfc)Au).	S18
Fig. S22	Absorption spectra, in toluene at RT, of (H ₃)tpfc, (tpfc)Cu, (tpfc)Ag, (tpfc)Au, (H ₃)(I ₄ -tpfc), (I ₄ -tpfc)Cu, (I ₄ -tpfc)Ag, and (I ₄ -tpfc)Au	S19
Fig. S23	Emission spectra, in toluene at RT and with λ _{ex} = 405 nm, of (H ₃)tpfc, (tpfc)Cu, (tpfc)Ag, (H ₃)(I ₄ -tpfc), (I ₄ -tpfc)Cu, (I ₄ -tpfc)Ag, (I ₄ -tpfc)Au.	S19
Fig. S24	(a) Full emission spectra of (H ₂)tpp, (H ₃)tpfc, upon excitation at 405 nm of toluene solutions with identical optical density. (b) Emission spectra of the (tpfc)M and (I ₄ -tpfc)M complexes, with M = Cu, Ag, and Au.	S20
Fig. S25	Crystal structures of (tpfc)Au.	S21
Table S1	X-ray crystallography data of (tpfc)Au, (I ₄ -tpfc)Cu, (I ₄ -tpfc)Ag, (I ₄ -tpfc)Au.	S21
Table S2	Absorption data of all the compounds.	S22

2. Experimental

2.1 Methods and Materials.

Commercially available reagents and chemicals were procured from sigma-Aldrich. Analytical reagent (AR) grade solvents were used for the reactions while spectroscopic grade solvents were used for photophysical properties and ASTM silica gel (230-400 mesh) and Sigma-Aldrich (Fluka) Aluminum oxide neutral were used for column chromatography. Thin-layer chromatography was performed on Merck-precoated silica gel 60-F₂₅₄ plates. Either gravity or flash chromatography was performed for purification of all compounds. All the reactions were carried out under aerobic conditions while the spectroscopic sample prepared under nitrogen atmosphere.

2.1.1 Physical Methods. ¹H and ¹⁹F NMR spectra were recorded Bruker Avance III 400 spectrometer equipped with a 5 mm, automated tuning, and matching broad band probe (BBFO) with z-gradients, operating at 400.4 MHz for ¹H and 376.7 MHz for F, respectively. Chemical shifts are reported in ppm relative to the residual hydrogen atoms in the deuterated solvent CDCl₃ (δ = 7.26). High-resolution mass spectra for the non-iodinated compounds were performed on a Bruker Maxis Impact mass spectrometer, using APCI (atmospheric pressure chemical ionization) direct probe in either positive or negative mode. High-resolution mass spectra for the iodinated compound was performed on a Waters LCT Premier mass spectrometer, using TOF electron spray positive mode in CH₃CN/water 70:30, flow 0.25.

2.1.2 Crystal Structure Determination. The single-crystal material was immersed in Paratone–N oil and was quickly fished with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen. Data collection was performed using monochromated Mo K α radiation, $\lambda = 0.71073$ Å, using ϕ and ω scans to cover the Ewald sphere.¹ Accurate cell parameters were obtained with the amount of indicated reflections.² The structure was solved by direct methods (SHELXS-97)³ and refined by full-matrix least-squares methods against F^2 (SHELXL-97).⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotopically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Software used for molecular graphics: Mercury 3.5.⁵

2.1.3 Spectroscopy. Absorption spectra of the samples were measured on an HP 8453 diode array spectrophotometer in toluene. Steady-state fluorescence spectra of the investigated compounds were measured in 1 cm \times 1 cm quartz optical cells using a combination of a CW xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as a detector system (Lot-Oriel, Instaspec IV).⁶ Fluorescence lifetimes were measured by the time-correlated single photon counting (TCSPC) technique, using the frequency-doubled pulses of a Ti:sapphire laser (Coherent Mira 900, 405 nm, fwhm 200 fs) for excitation. The instrument response function was 33 ps, as measured at excitation wavelength with Ludox.⁷ A self-made routine was applied to minimize the least-squares error between the model function convoluted with instrument response function and the measured data set. Triplet lifetimes were determined for each corrole in air-saturated and nitrogen-flushed Toluene solution. The optical densities of the samples were adjusted to OD = 0.200 at 405 nm for the steady state measurements and to OD = 0.200 at the excitation wavelength for flash photolysis measurements. The singlet oxygen measurements in toluene were performed using samples with an OD = 0.200 at 405 nm.

2.2 Synthesis 5,10,15-tris(pentafluorophenyl)corrole (H₃)tpfc,⁸⁻¹⁰ Cu(III)-5,10,15-tris(pentafluorophenyl)corrole (tpfc)Cu,^{11,12} Ag(III)-5,10,15-tris(pentafluorophenyl)corrole¹³ were synthesized according to the literature procedures.

2.2.2 Gold(III)-5,10,15-tris(pentafluorophenyl)corrole (tpfc)Au: 5,10,15-tris(pentafluorophenyl)corrole (0.1 g, 0.12 mmol) was added to a solution of gold acetate (0.9 g, 0.24 mmol) in pyridine (10 mL) stirred at room temperature under N₂ atmosphere. TLC analysis show complete consumption of starting material after 1 h and the solvent was evaporated under reduced pressure without heating. The product was purified on Alumina column chromatography with CH₂Cl₂-hexane 4:1 v/v furnished the desired product (0.014 g) as a purple solid in 12% yield. ¹H NMR (601 MHz, CDCl₃) δ , ppm 9.26 (d, $J = 4.5$ Hz, 2H), 8.96 (d, $J = 4.8$ Hz, 2H), 8.80 (d, $J = 4.3$ Hz, 4H). ¹⁹F NMR (377 MHz, CDCl₃) δ , ppm -136.95 (dt, $J = 22.3$ Hz), -150, -151.97-161.29. HRMS (APCI-

TOF) m/z : $[M]^+$ Calcd. for $C_{37}H_8AuF_{15}N_4$: 990.0170; Found 990.0151. UV/Vis (Toluene) λ_{max} nm ($\epsilon \times 10^4$): 400 (4.32), 421 (16.72), 493 (0.59), 530 (0.95), 564 (3.98),

2.2.3 2,3,17,18-tetraiodo-5,10,15-tris(pentafluorophenyl)corrole (H_3)(I_4 -tpfc): 5,10,15-tris(pentafluorophenyl)corrole (0.1 g, 0.12 mmol) and N-iodosuccinamide (0.14 g, 0.63 mmol) in dry Pyridine (10 ml) was added to a stirred mixture in the aerobic condition at room temperature for 1 h. TLC analysis show complete consumption of starting material and remove the solvent by vacuum. Reaction mixture was washed with sodium thiosulfate solution to quench the excess of iodine, collected in CH_2Cl_2 and dried with anhydrous Na_2SO_4 . Purification of the residue by column chromatography on silica gel (CH_2Cl_2 –hexane, 1:4, v/v) furnished the product (0.62 g) as a purple solid in 40% yield. 1H NMR (200 MHz, $CDCl_3$) δ , ppm 8.47 (d, $J = 4.8$ Hz, 2H), 8.22 (d, $J = 4.9$ Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -137.15 – -137.27 (m, 2F), -137.53 (d, $J = 16.4$ Hz, 4F), -151.32 (t, 2F), -151.50 (t, $J = 21.0$ Hz, 1F), -160.96 (dd, $J = 21.5, 15.4$ Hz, 2F), -161.57 (t, $J = 18.3$ Hz, 4F). HRMS (APCI-TOF) m/z : $[M]^+$ Calcd for $C_{37}H_7F_{15}I_4N_4$: 1299.6609; Found 1298.6747. UV/Vis (Toluene) λ_{max} nm ($\epsilon \times 10^4$): 421 (11.84), 443 (12.40), 594 (4.40), 618 (4.06), 665 (1.70).

2.2.4 General procedure for one-pot synthesis of the tetraiodinated metallocorroles, (I_4 -tpfc)M: 5,10,15-tris(pentafluorophenyl)corrole (100 mg, 1 eq.) and N-iodosuccinamide (280 mg, 10 eq.) and metal acetate (2 to 10 eq.) in dry pyridine (10 mL) were stirred under aerobic condition at room temperature until full consumption of the starting material was indicated by TLC (1 to 6 h), after which the pyridine was evaporated. The solids were dissolved in CH_2Cl_2 , washed with aqueous sodium thiosulfate, and the organic phase was dried by anhydrous Na_2SO_4 and evaporated. **(a) Copper(III)-2,3,17,18-tetraiodo-5,10,15-tris(pentafluorophenyl)corrole (I_4 -tpfc)Cu:** Purification by column chromatography on neutral alumina (CH_2Cl_2 –hexane, 1:6, v/v) furnished the product (0.129 g, 76% yield.) as a purple colored solid. 1H NMR (300 MHz, $CDCl_3$) δ , ppm 6.96 (dd, $J = 11.5, 4.5$ Hz, 2H). 1H NMR (600 MHz, $CDCl_3$) δ , ppm 6.97 (d, $J = 3.7$ Hz, 2H), 6.93 (d, $J = 3.9$ Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -137.06 – -137.40 (m, 6F), -150.53 (t, $J = 20.9$ Hz, 1F), -150.72 (t, $J = 21.0$ Hz, 2F), -159.60 – -159.78 (m, 2F), -160.61 (td, $J = 21.8, 6.6$ Hz, 4F). HRMS (APCI-TOF) m/z : $[M]^+$ Calcd for $C_{37}H_4N_4F_{15}I_4Cu$ 1359.5671; Found 1358.5325. UV/Vis (toluene) λ_{max} nm ($\epsilon \times 10^4$): 418 (15.61), 573 (2.61), 714 (0.21). **(b) Silver(III)-2,3,17,18-tetraiodo-5,10,15-tris(pentafluorophenyl)-corrole (I_4 -tpfc)Ag:** Purification by column chromatography on neutral aluminium oxide (CH_2Cl_2 –hexane, 1:4, v/v) furnished the product (0.079 g, 45% yield) as a dark red colored solid. 1H NMR (400 MHz, $CDCl_3$) δ , ppm 8.70 (d, $J = 4.9$ Hz, 2H), 8.62 (d, $J = 4.8$ Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -136.81 – -137.02 (m, 6F), -150.90 (t, $J = 20.9$ Hz, 1F), -151.20 (t, $J = 21.0$ Hz, 2F), -160.65 (dt, $J = 22.2, 7.0$ Hz, 2F), -161.70 (dt, $J = 22.9, 7.4$ Hz, 4F). HRMS (APCI-TOF) m/z : $[M]^+$ Calcd for $C_{37}H_4N_4F_{15}I_4Ag$ 1403.5421; Found 1403.5099. UV/Vis (Toluene) λ_{max} nm ($\epsilon \times 10^4$): 434 (21.32), 542 (1.90), 585 (11.56), 648 (0.18). **(c) Gold(III)-**

2,3,17,18-tetraiodo-5,10,15-tris(pentafluorophenyl)corrole (I_4 -tpfc)Au: Purification by column chromatography on neutral alumina (CH_2Cl_2 –hexane, 2:9, v/v) furnished the product (0.099 g, 53% yield) as a red colored solid. 1H NMR (200 MHz, $CDCl_3$) δ , ppm 8.81 (d, J = 5.0 Hz, 2H), 8.72 (d, J = 5.0 Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -136.69 (dd, J = 24.2, 7.8 Hz, 4F), -136.87 (dd, J = 22.9, 7.1 Hz, 2F), -150.95 (t, J = 20.9 Hz, 1F), -151.37 (t, J = 21.0 Hz, 2F), -160.71 (dt, J = 22.4, 11.3 Hz, 2F), -161.84 (td, J = 22.9, 7.4 Hz, 4F). HRMS (APCI-TOF) m/z : $[M]^+$ Calcd for $C_{37}H_4N_4F_{15}I_4Au$ 1493.6041; Found 1493.6041. UV/Vis (Toluene) λ_{max} nm ($\epsilon \times 10^4$): 427 (17.20), 505 (0.61), 542 (1.59), 583 (10.04).

2.2.5 Silver(III)- 2,17,18-triiodo-5,10,15-tris(pentafluorophenyl)corrole (I_3 -tpfc)Ag: Silver(III)-5,10,15-tris(pentafluorophenyl)corrole (tpfc)Ag (0.05 g, 0.055 mmol) and N-iodosuccinamide (0.123 g, 0.55 mmol) in dry pyridine (10 ml) was refluxed for 12 h under nitrogen. TLC analysis and absorption spectra were show inseparable mixture of product and reactant. Purification by flash column chromatography on neutral aluminum oxide (CH_2Cl_2 –hexane, 2:9, v/v) furnished the product (0.039 g) as a red colored solid in 55% yield. 1H NMR (400 MHz, $CDCl_3$) δ , ppm 8.74 (d, 2H), 8.80 (d, 2H), 9.54 (1H, s). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -136.50 (m), -151.45 (m), -161.37 (m), -162.03 (m). APCI-MS m/z : 1279.601 $[M]^+$. UV/Vis (Toluene) λ_{max} nm: 427 (17.20), 533 (1.59), 576 (10.04).

2.2.6 Gold(III)- 2,17,18-triiodo-5,10,15-tris(pentafluorophenyl)corrole (I_3 -tpfc)Au: Gold(III)-5,10,15-tris(pentafluorophenyl)corrole (tpfc)Au (0.02 g, 0.02 mmol) and N-iodosuccinamide (0.045 g, 0.2 mmol) in dry pyridine (8 ml) was refluxed for 24 h under nitrogen. TLC analysis show inseparable mixture of product and reactant. Purification by flash column chromatography on neutral aluminum oxide (CH_2Cl_2 –hexane, 2:8, v/v) furnished the mixture of (I_3 -tpfc)Au (52%) and unreacted starting material (30%) collected. Analyzed mixture product by 1H NMR (400 MHz, $CDCl_3$) δ , ppm 8.73 to 8.79 (m, 2H), 8.84 (d, 2H), 9.54 (1H, s). ^{19}F NMR (377 MHz, $CDCl_3$) δ , ppm -137.04 (m), -151.45 to -153.45 (m), -161.67 (m), -162.98 (m).

2.3 References:

1. Nonius, B. V. Kappa CCD Software. Nonius BV, Delft, The Netherlands, 1999.
2. Otwinowski, Z.; Minor, W. Otwinowski, W., Eds.; Academic Press: New York, 1996; p 276.
3. Sheldrick, G. M. *Acta Cryst., Sect. A: Fund. Cryst.* **1990**, *46*, 467-473.
4. ORTEP, TEXSAN *Structure Analysis Package*, Molecular Structure Corp., The Woodlands, TX, 1999.
5. Mercury Software CCDC: <http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury>.
6. Korth, O.; Hanke, T.; Rückmann, I.; Röder, B. *Exp. Tech. Phys.* **1995**, *41*, 25–36.

- Makarov, S.; Litwinski, C.; Ermilov, E. A.; Suvorova, O.; Röder, B.; Wöhrle, D. *Chem. Eur. J.* **2006**, *12*, 1468–1474.
- Gross, Z.; Galili, N.; Botoshansky, M.; Simkhovich, L.; Blalser, D.; Boese, R.; Saltsman, I.; Goldberg, I. *Organic Lett.*, **1999**, *1*, 599-602.
- Gryko, D.T.; Koszarna, B. *Org. Biomol. Chem.*, **2003**, *1*, 350–357.
- Blumenfeld, C.; Fisher, K.J.; Henling, L.M.; Grubbs, R.H.; Gray, H.B.; Virgil, S.C. *Eur. J. Org. Chem.* **2015**, 3022–3025.
- Wasbotten, I. H.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8104-8116.
- Luobeznova, I.; Simkhovich, L.; Goldberg, I.; Gross, Z. *Eur. J. Inorg. Chem.* **2004**, 1724-1732
- Stefanelli, M.; Shen, J.; Zhu, W.; Mastroianni, M.; Mandoj, F.; Nardis, S.; Ou, Z.; Kadish, K. M.; Fronczek, F. R.; Smith, K. M.; Paolesse, R. *Inorg. Chem.* **2009**, *48*, 6879-6887.

2.4. Spectra

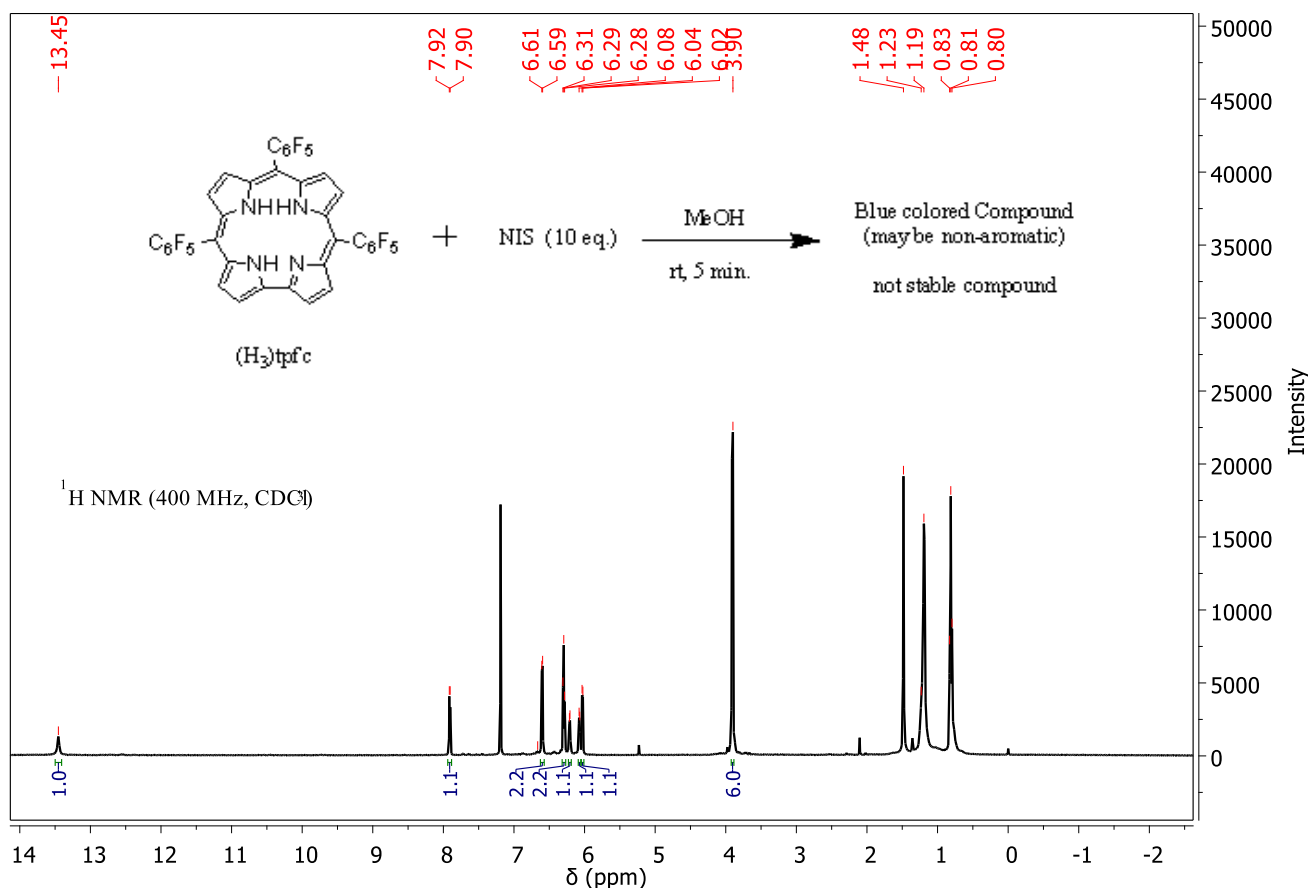


Fig. S1: 1H NMR spectrum of non-aromatic product from the reaction between $(H_3)tpfc$ and NIS in Methanol as solvent and recorded spectrum in $CDCl_3$ solvent.

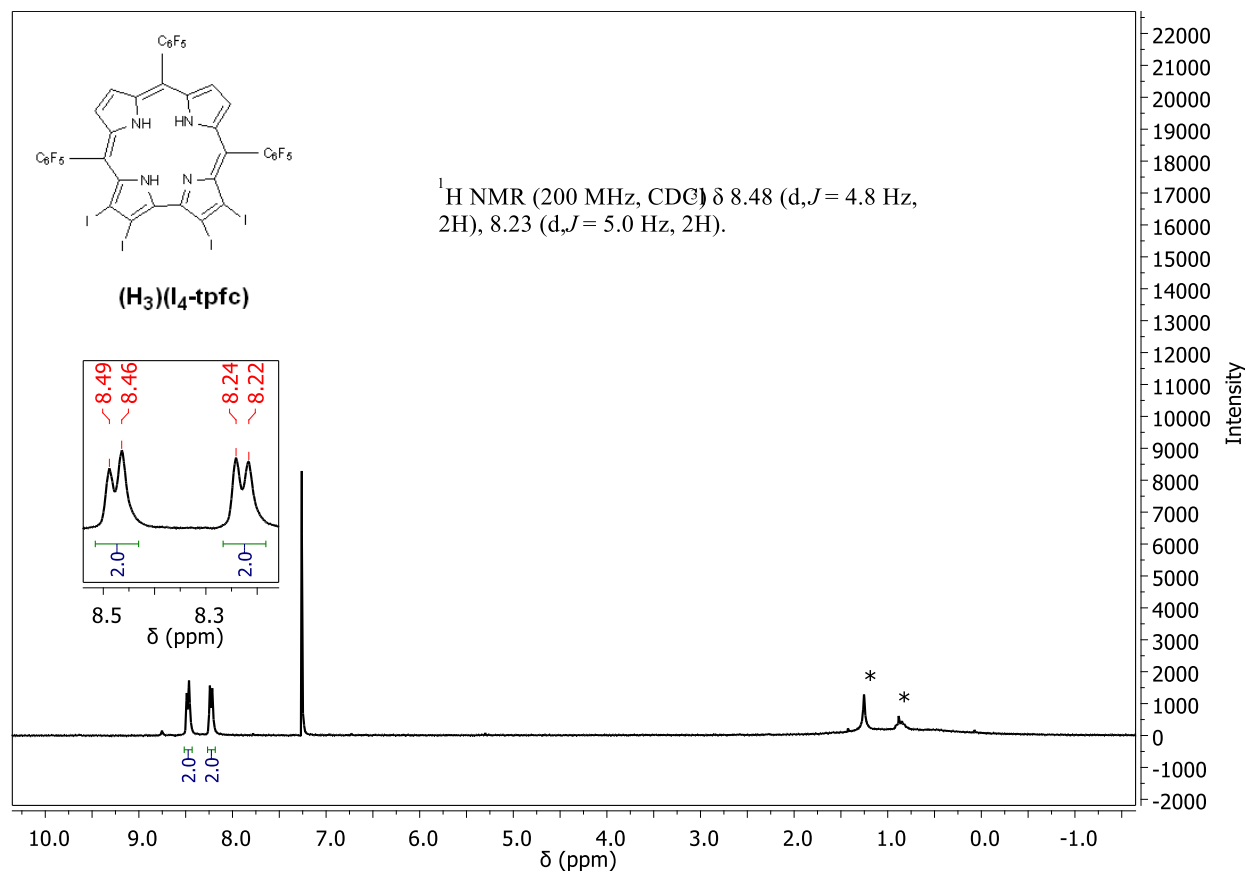


Fig. S2: ¹H NMR spectrum of **(H₃)(I₄-tpfc)** were recorded at 400 MHz in CDCl₃ solvent. ‘*’ indicates solvents impurities.

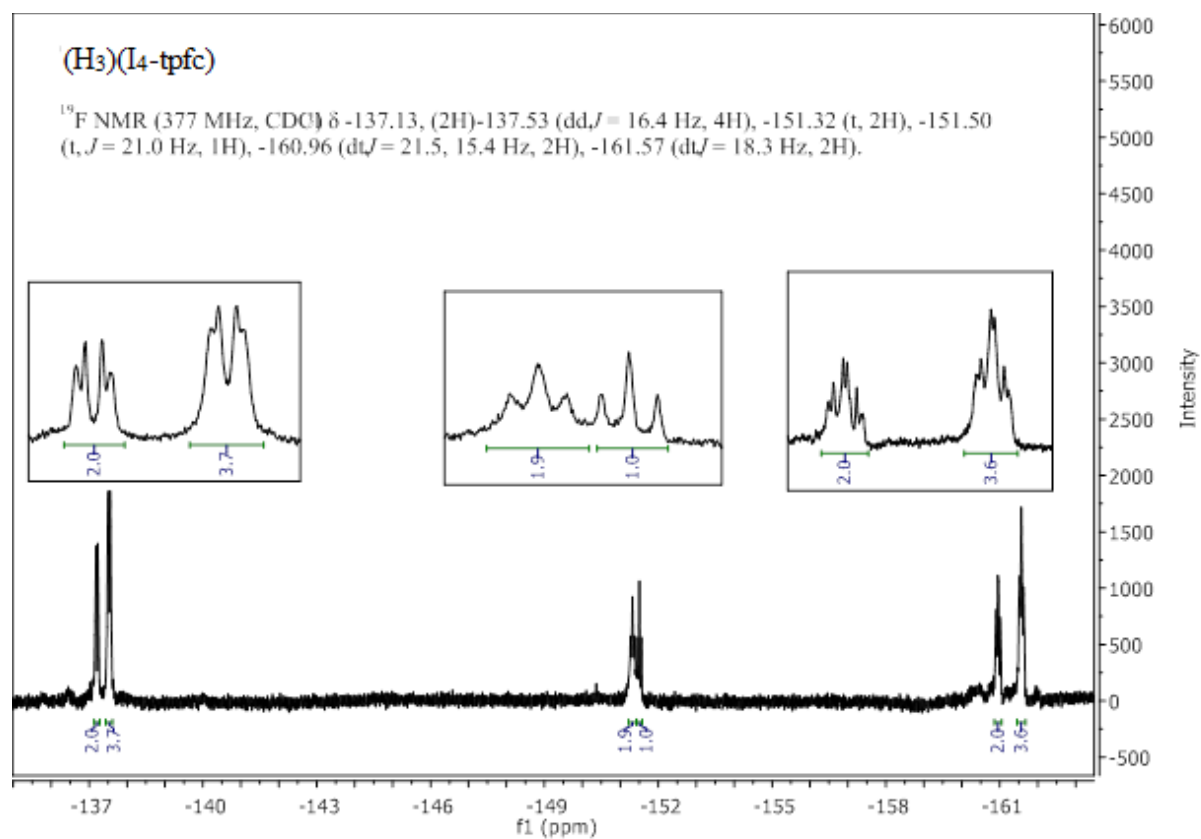


Fig. S3: ¹⁹F NMR spectrum of **(H₃)(I₄-tpfc)** were recorded at 377 MHz in CDCl₃ solvent.

Single Mass Analysis

Tolerance = 20.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: On (Carbon range ± 5) (Set 0 < Cl < 9, 0 < Br < 9 and 0 < S < 7 for enhanced filtering)

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

855 formula(e) evaluated with 19 results within limits (up to 2 closest results for each mass)

Elements Used:

C: 30-40 H: 0-10 N: 0-5 F: 10-20 I: 0-4 Ir: 0-2

22-Feb-2016

Gr_2879n 66 (0.524) Cm (57.72)

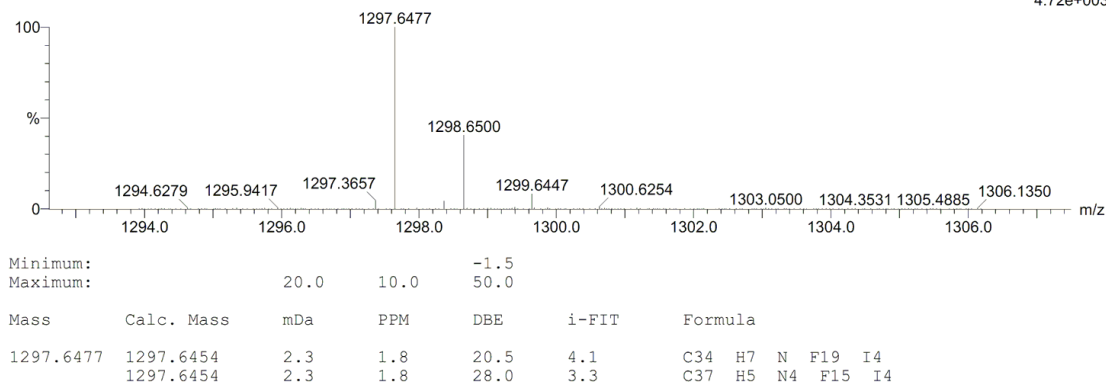
(H₃)(I₄-tpfc)TOF MS ES-
4.72e+003

Fig. S4: High resolution APCI mass spectrum of (H₃)(I₄-tpfc) with calculated mass 1297.6454

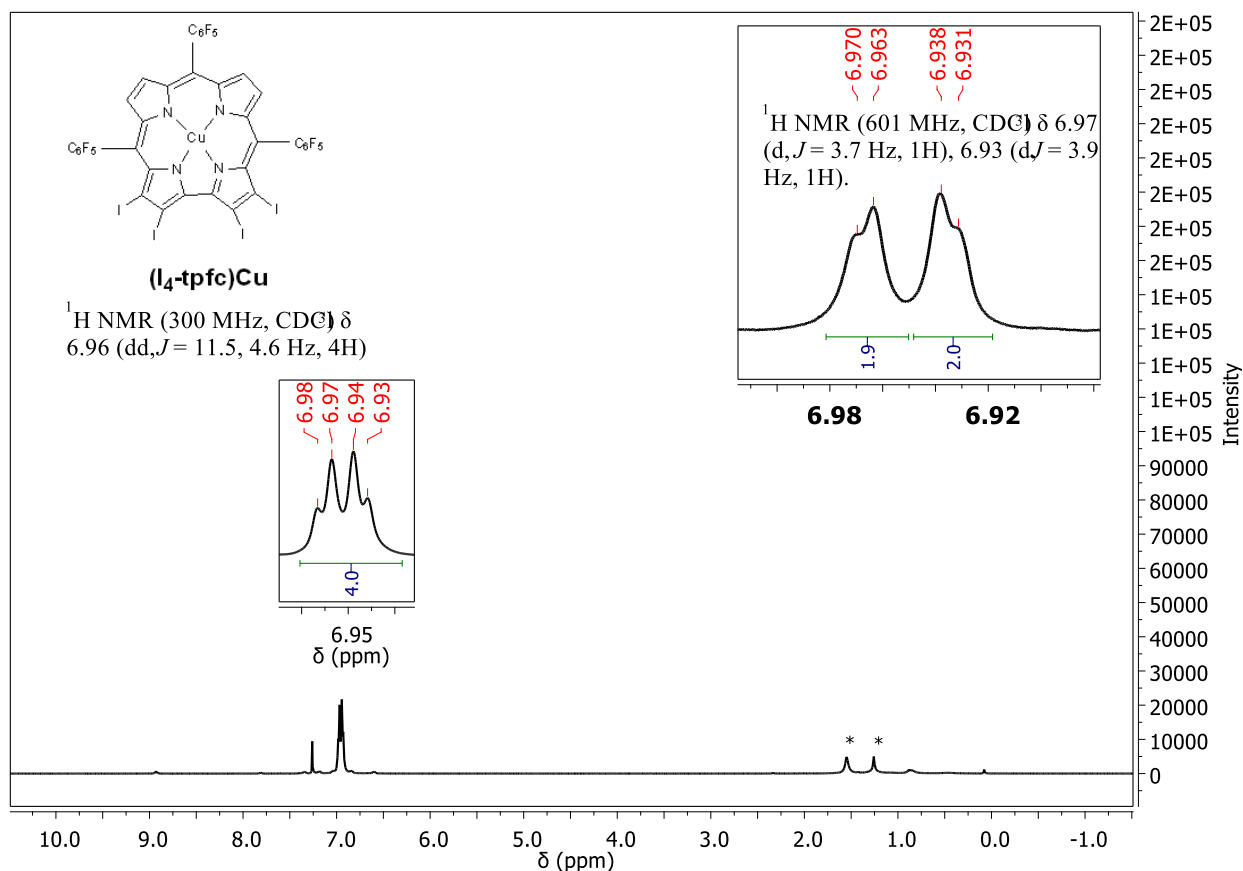


Fig. S5: ¹H NMR spectrum of (I₄-tpfc)Cu were recorded at 400 MHz in CDCl₃ solvent and “*” Indicates solvent impurities. Inset spectrum clarify two different doublets recorded at 601 MHz.

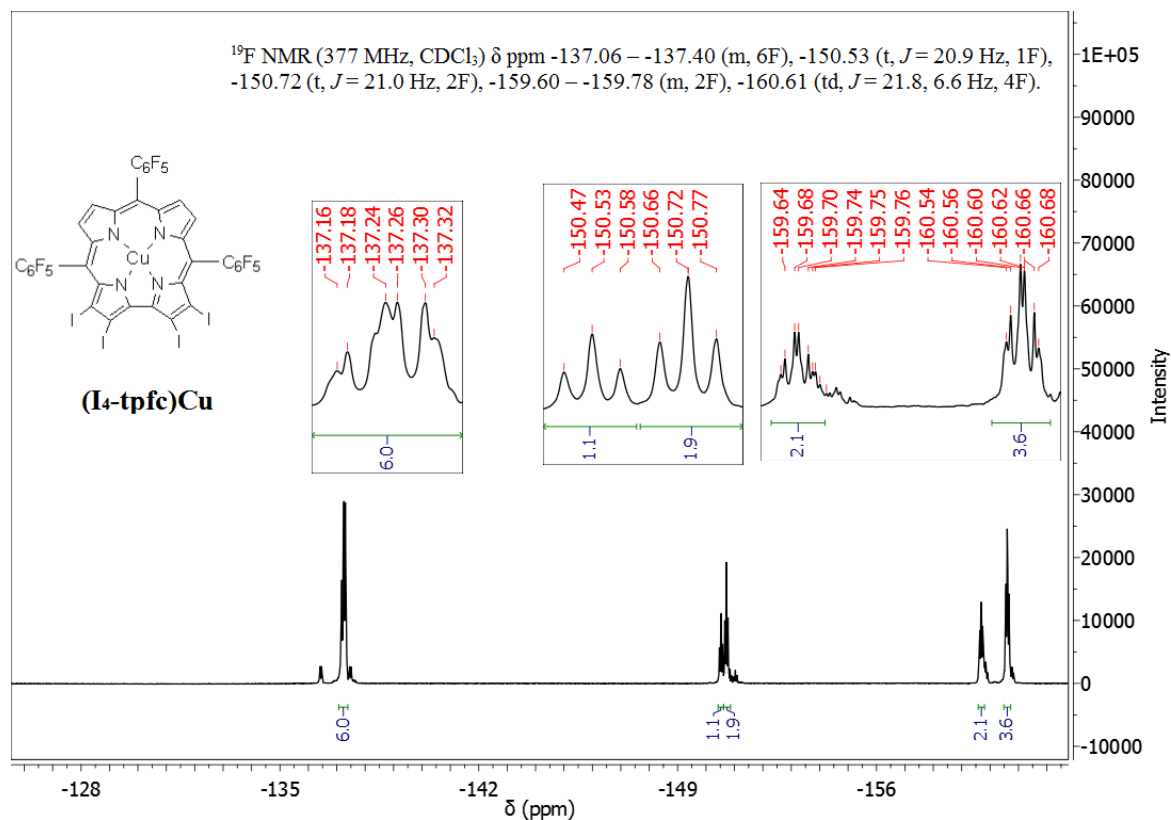


Fig. S6: ¹⁹F NMR spectrum of **(I₄-tpfc)Cu** were recorded at 377 MHz in CDCl₃ solvent.

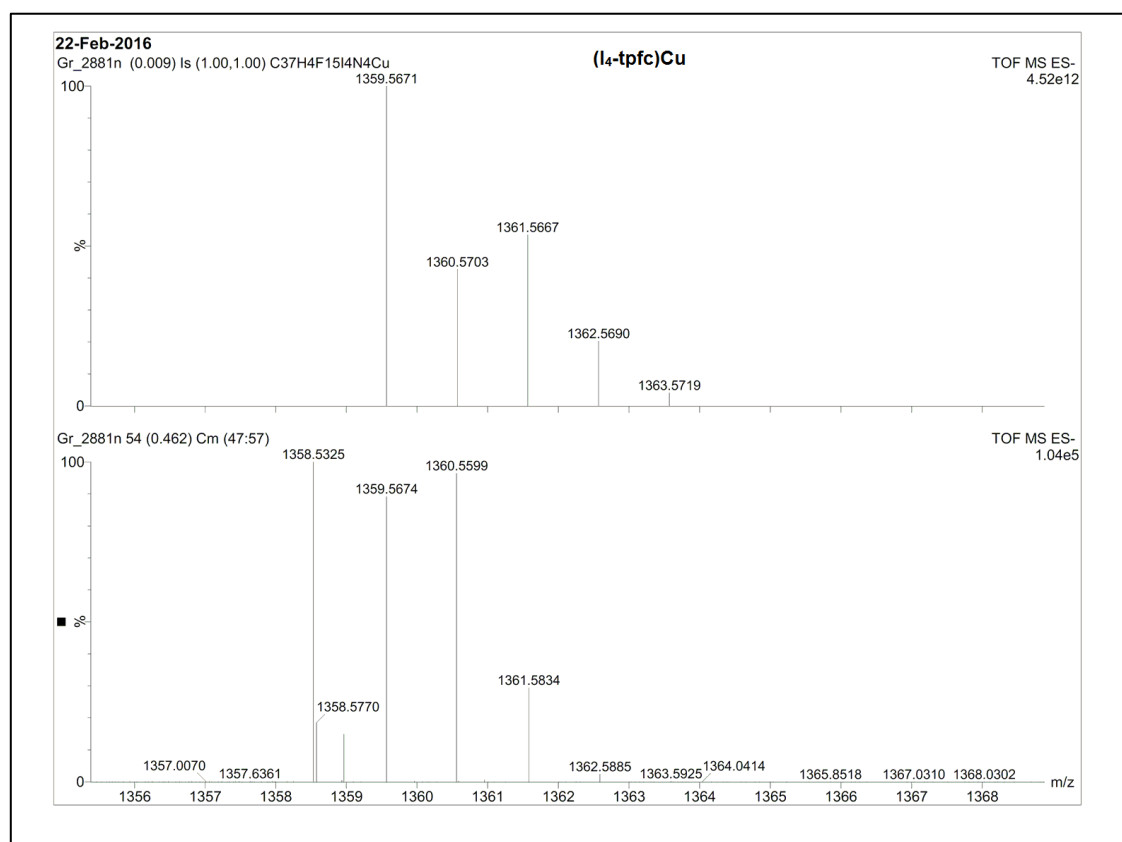


Fig. S7: High resolution APCI mass spectrum of **(I₄-tpfc)Cu** with calculated mass 1359.5671.

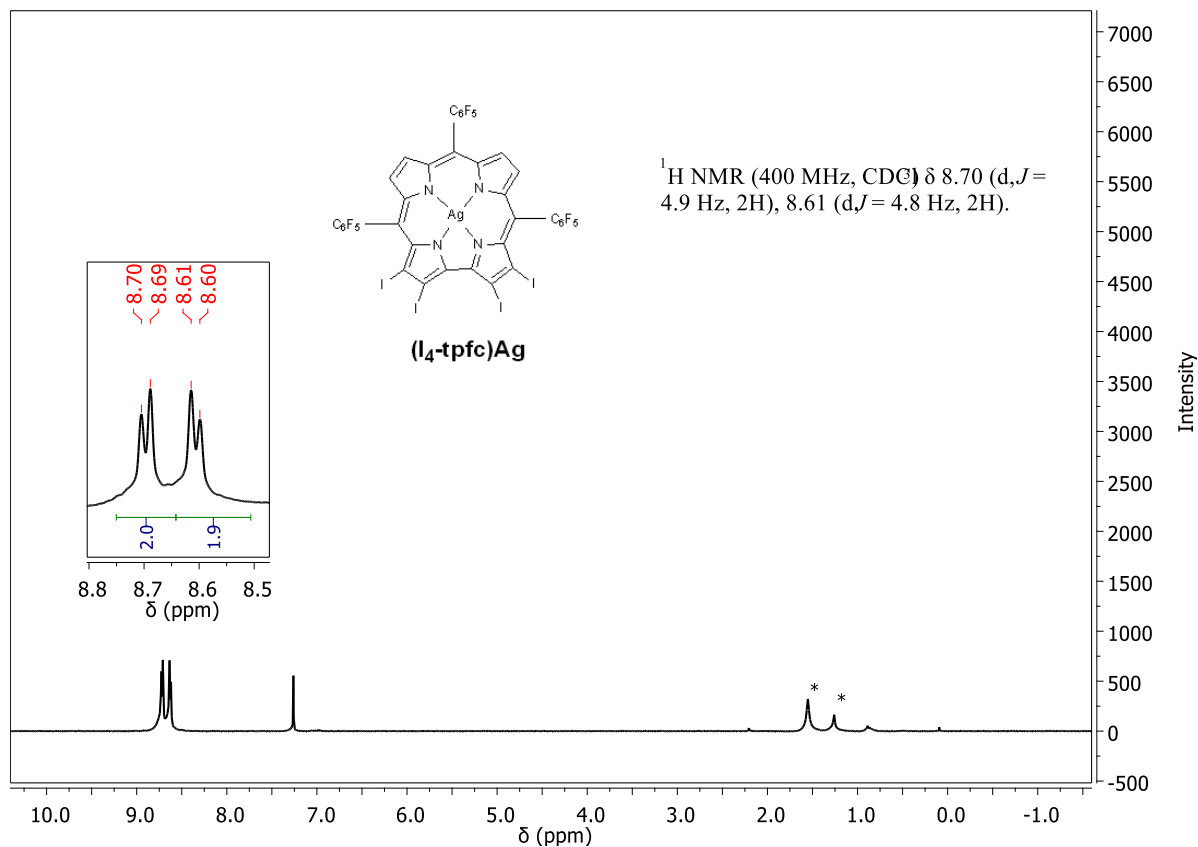


Fig. S8: ¹H NMR spectrum of **(I₄-tpfc)Ag** were recorded at 400 MHz in CDCl₃ solvent and ‘*’ indicates solvents impurities.

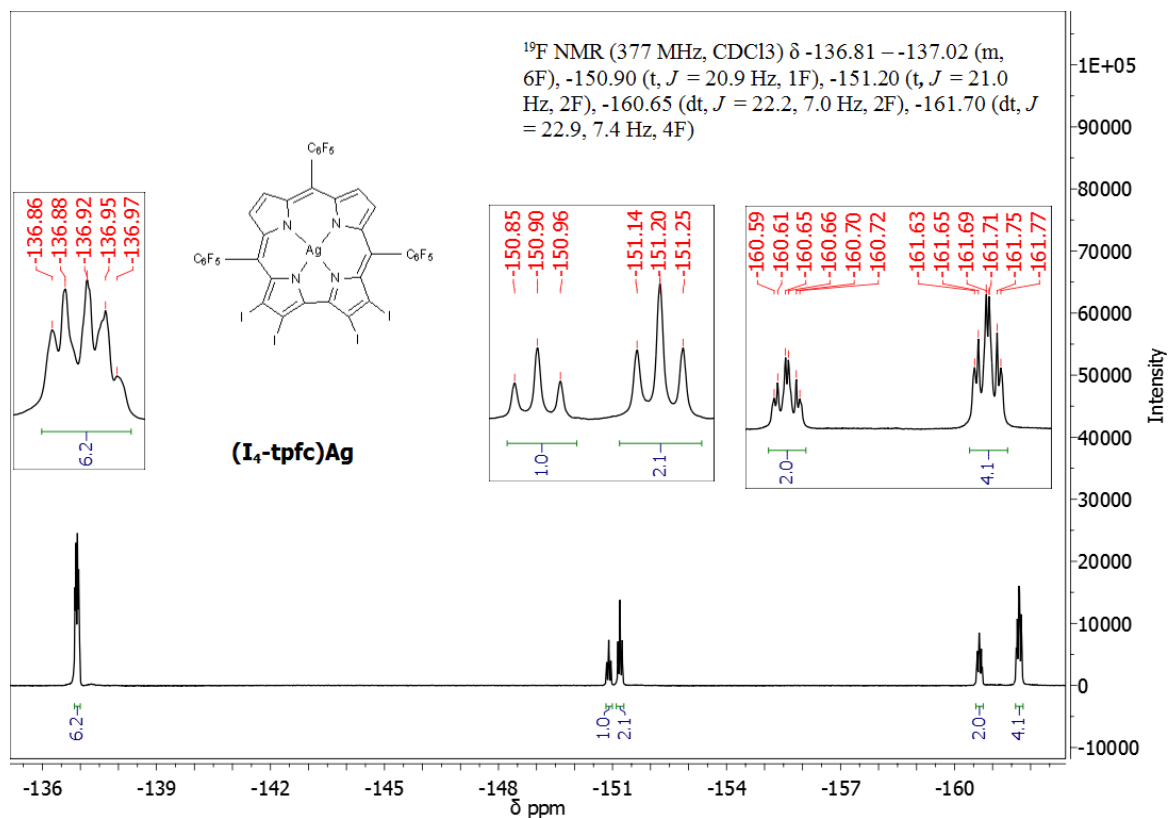


Fig. S9: ¹⁹F NMR spectrum of **(I₄-tpfc)Ag** were recorded at 377 MHz in CDCl₃ solvent.

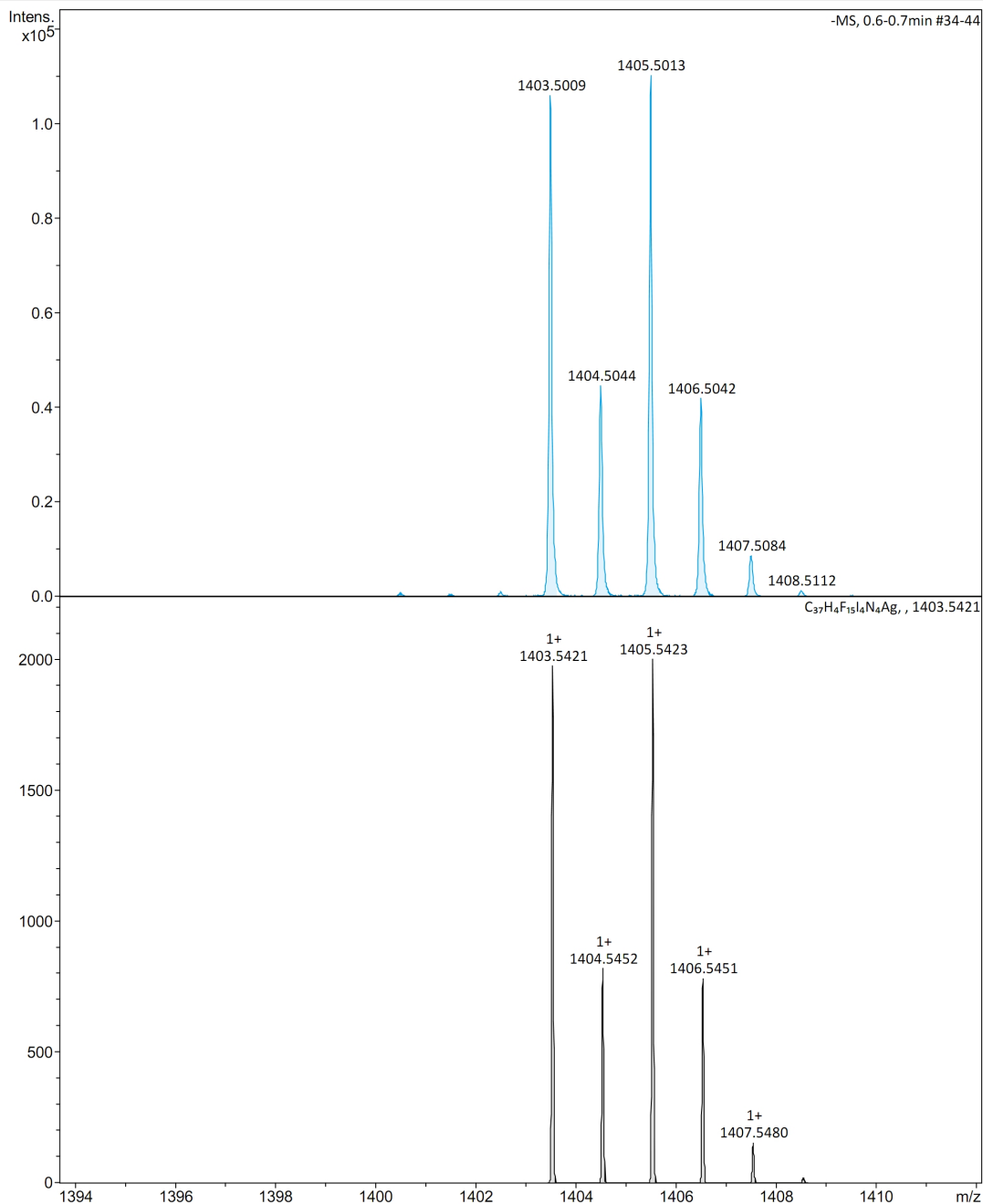
Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_3043n000001.d
Method APCI_neg_SolidProbe.m
Sample Name Ag-TPFC-4i
Comment

Acquisition Date 3/29/2016 2:20:42 PM

Operator Larisa Panz
Instrument maXis impact



Bruker Compass DataAnalysis 4.2

printed: 9/13/2016 9:45:53 AM

by: Larisa Panz

Page 1 of 1

Fig. S10: High-resolution APCI Mass spectrum of (**I₄-tpfc**)Ag with calculated mass 1403.5421.

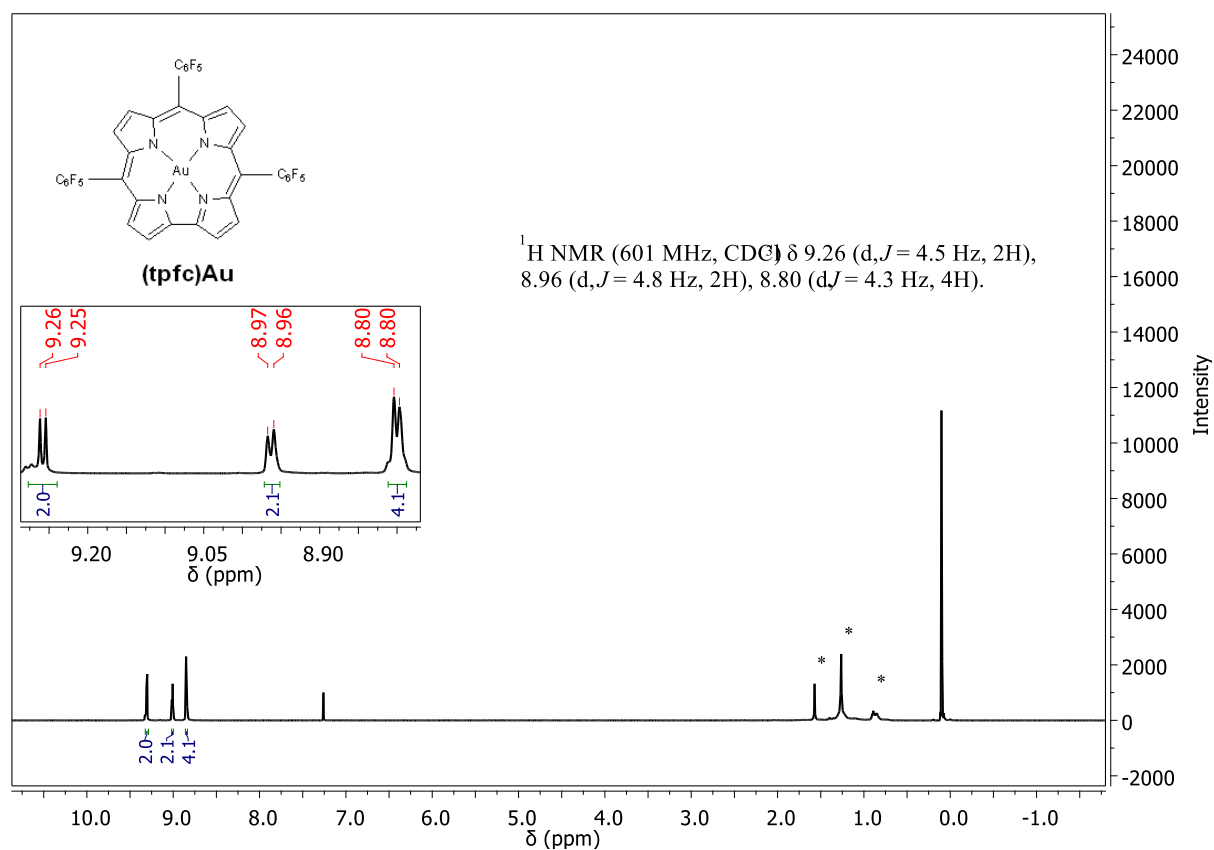


Fig. S11: ^1H NMR spectrum of **(tpfc)Au** were recorded at 400 MHz in CDCl_3 solvent and ‘*’ indicates solvents impurities.

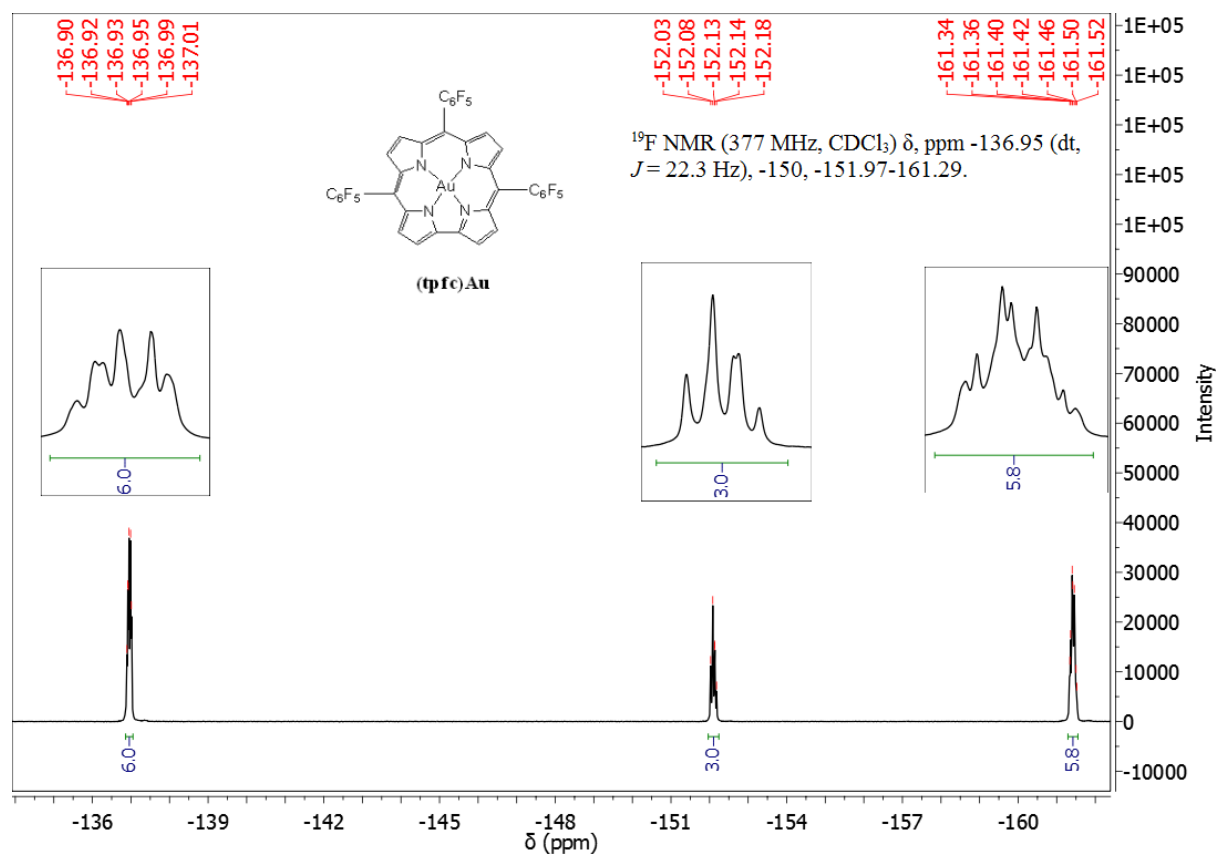


Fig. S12: ^{19}F NMR spectrum of **(tpfc)Au** were recorded at 377 MHz in CDCl_3 solvent.

Generic Display Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_3830n000001.d
Method APCI_pos_SolidProbe.m
Sample Name TPFC)Au
Comment

Acquisition Date 9/12/2016 2:11:57 PM

Operator Larisa Panz
Instrument maXis impact

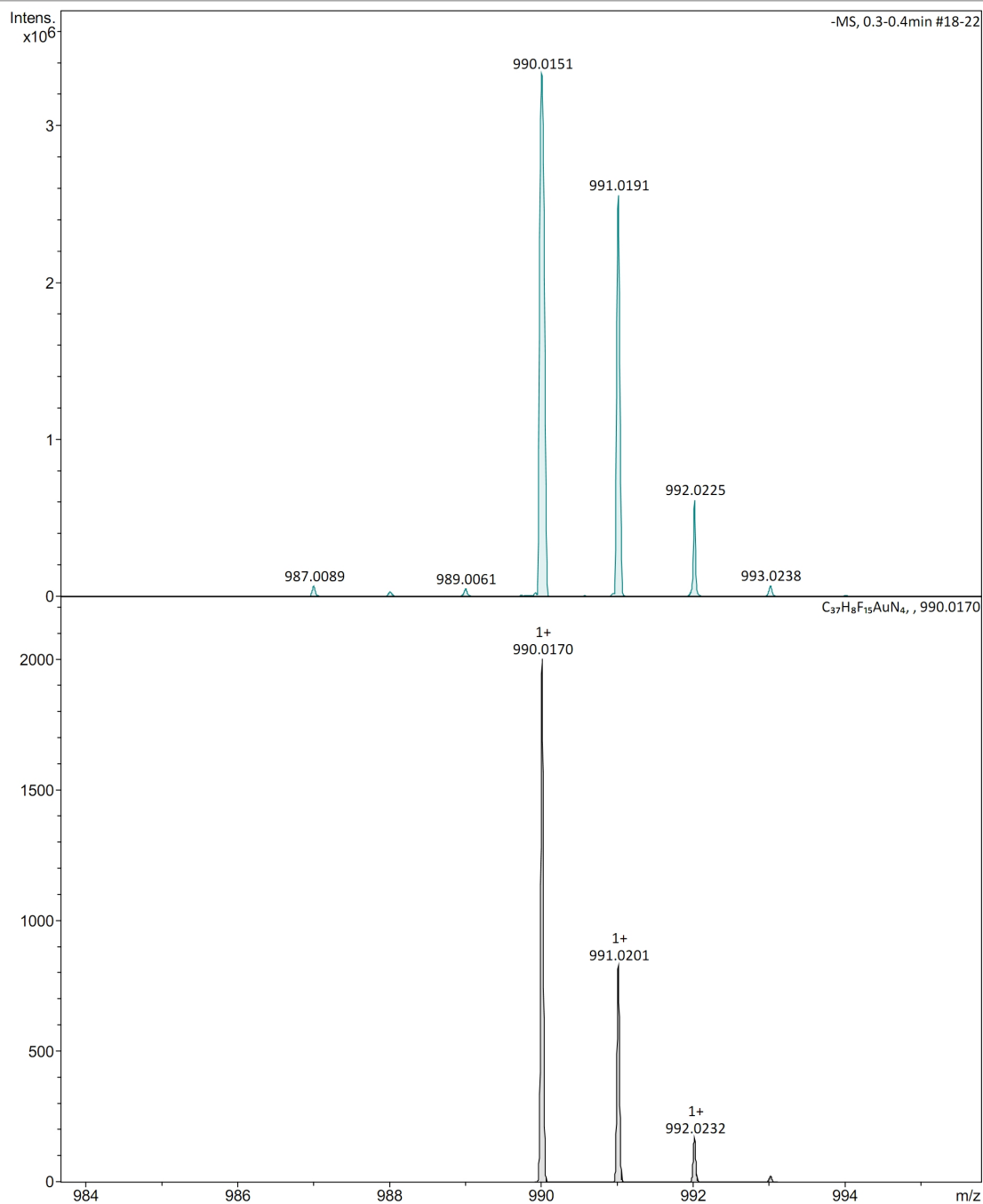


Fig. S13: High-resolution APCI mass spectrum of (tpfc)Au with molecular weight 990.0170

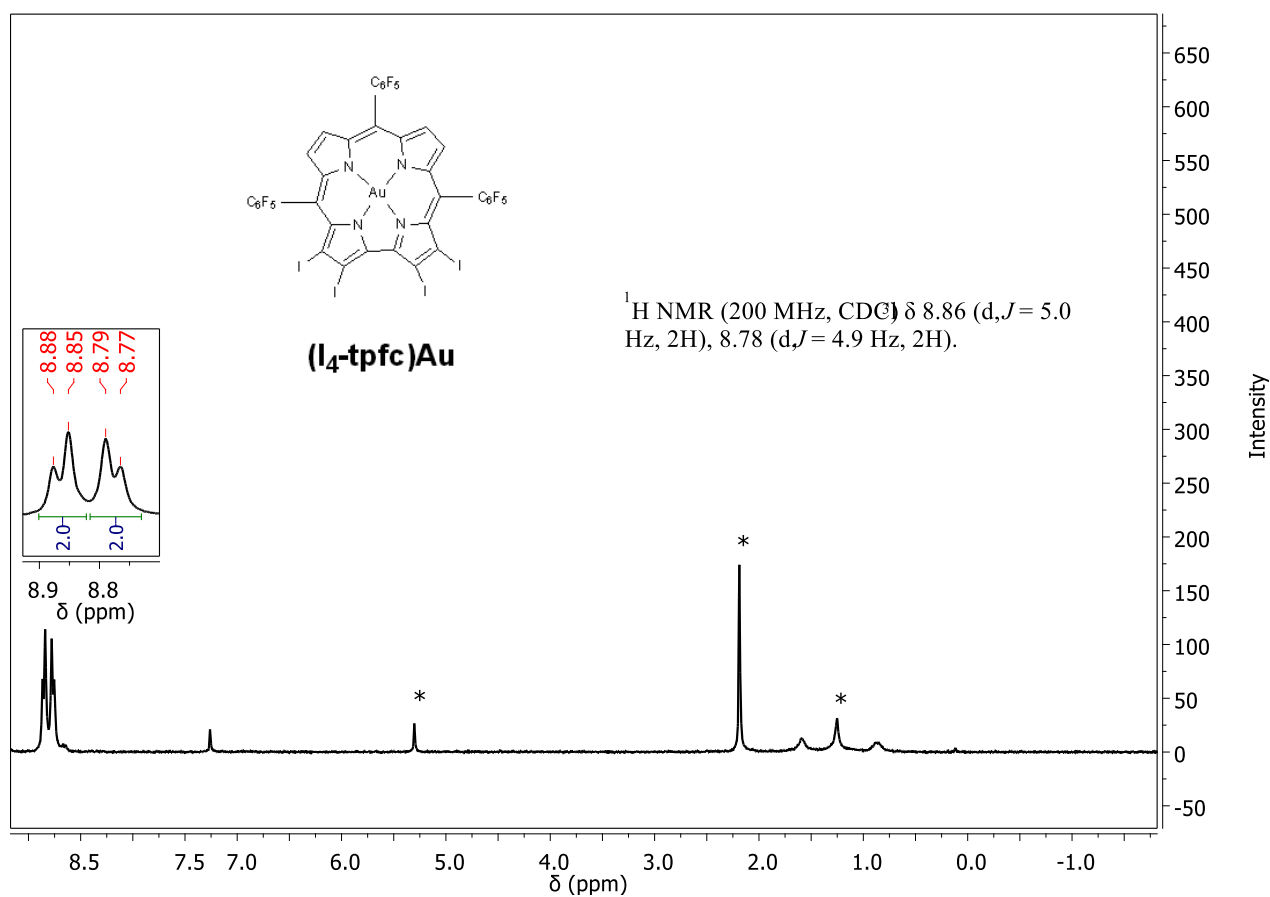


Fig. S14: ^1H NMR spectrum of $(\text{I}_4\text{-tpfc})\text{Au}$ were recorded at 400 MHz in CDCl_3 solvent.

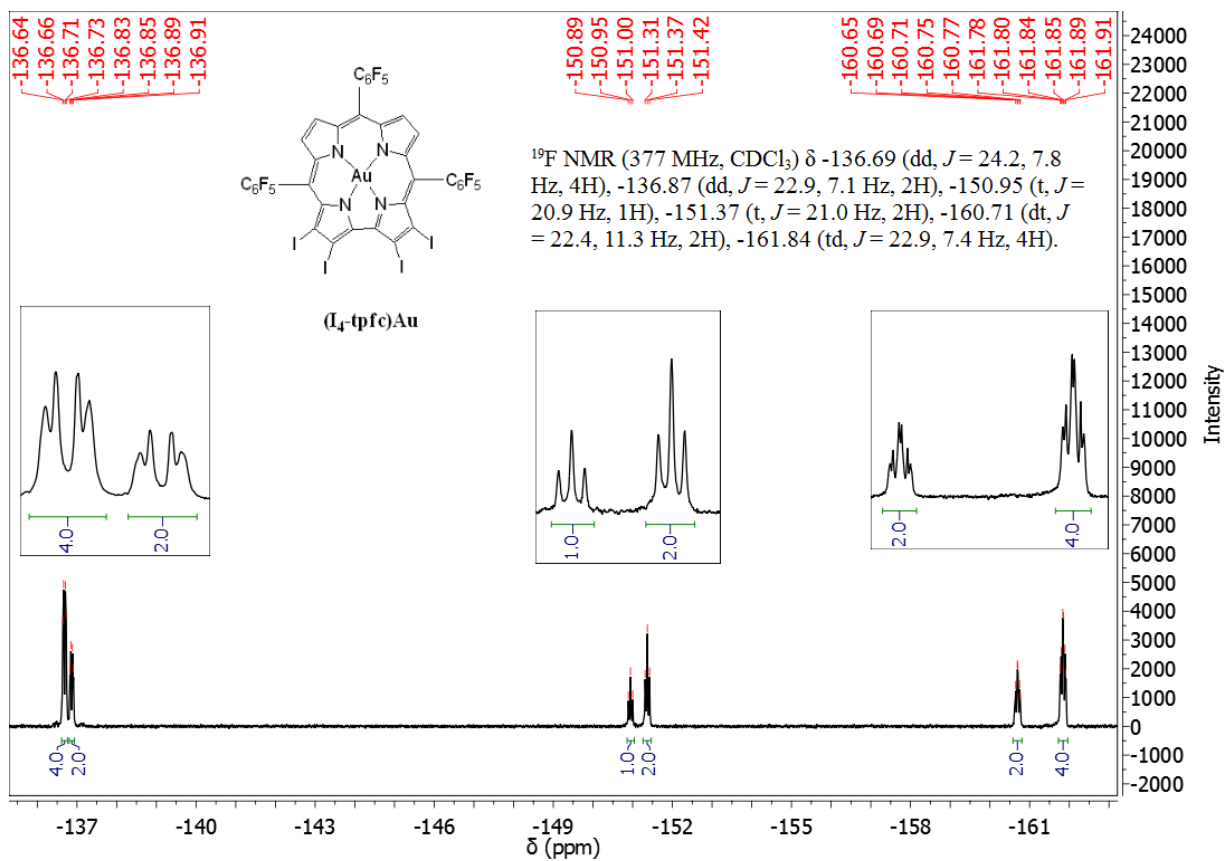


Fig. S15: ^{19}F NMR spectrum of $(\text{I}_4\text{-tpfc})\text{Au}$ were recorded at 377 MHz in CDCl_3 solvent.

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\Gross\Gr_3831n000004.d
Method APCI_pos_SolidProbe.m
Sample Name (I4-TPFC)Au
Comment

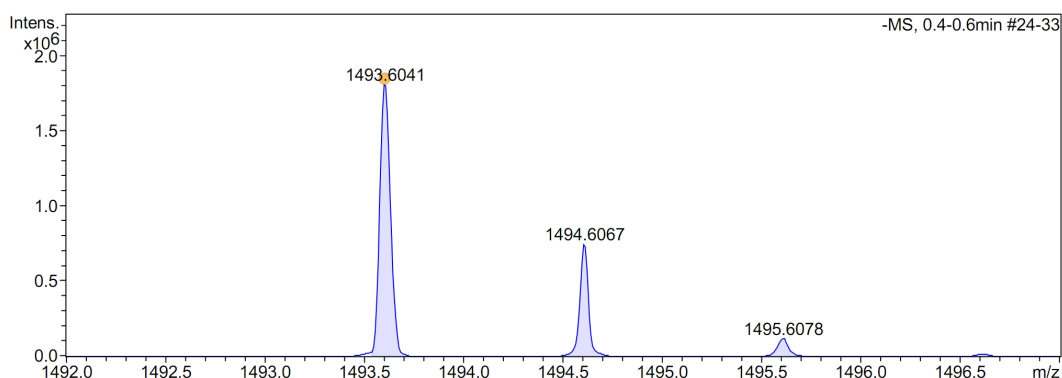
Acquisition Date 9/12/2016 2:00:51 PM

Operator Larisa Panz
Instrument maXis impact 282001.00128

Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	120 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	2500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	2000 nA	Set APCI Heater	300 °C

-MS, 0.4-0.6min #24-33



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	#	mSigma	Score	rdb	e ⁻	Conf	N-Rule	err [mDa]
1493.6041	1	C37H3AuF15I4N4	1492.5963	-3.2	601.8	1	100.00	28.5	even		ok		4.7
	2	C37H5AuF15I4N4	1494.6119	1345.5	888.6	2	0.00	27.5	even		ok		2010.9
	3	C36H5AuF15I4N4O	1498.6068	4007.6	890.9	3	0.00	26.5	even		ok		6005.9
	4	C36H3AuF15I4N4O	1496.5912	2666.2	891.0	4	0.00	27.5	even		ok		3990.2
	5	C35H3AuF15I4N4O2	1500.5861	5321.3	893.3	5	0.00	26.5	even		ok		7985.1
	6	C35H5AuF15I4N4O	1486.6068	-4032.1	894.1	6	0.00	25.5	even		ok		5994.2
	1	C37H3AuF15I4N4	1492.5963	-3.2	601.8	1	100.00	28.5	even		ok		4.7
	2	C37H5AuF15I4N4	1494.6119	1345.5	888.6	2	0.00	27.5	even		ok		2010.9
	3	C36H5AuF15I4N4O	1498.6068	4007.6	890.9	3	0.00	26.5	even		ok		6005.9
	4	C36H3AuF15I4N4O	1496.5912	2666.2	891.0	4	0.00	27.5	even		ok		3990.2
	5	C35H3AuF15I4N4O2	1500.5861	5321.3	893.3	5	0.00	26.5	even		ok		7985.1
	6	C35H5AuF15I4N4O	1486.6068	-4032.1	894.1	6	0.00	25.5	even		ok		5994.2

Gr_3831n000004.d

Bruker Compass DataAnalysis 4.2

printed: 9/12/2016 2:09:14 PM

by: Larisa Panz

Page 1 of 1

Fig. S16: High-resolution APCI mass spectrum of (I4-tpfc)Au with calculated mass 1493.6041

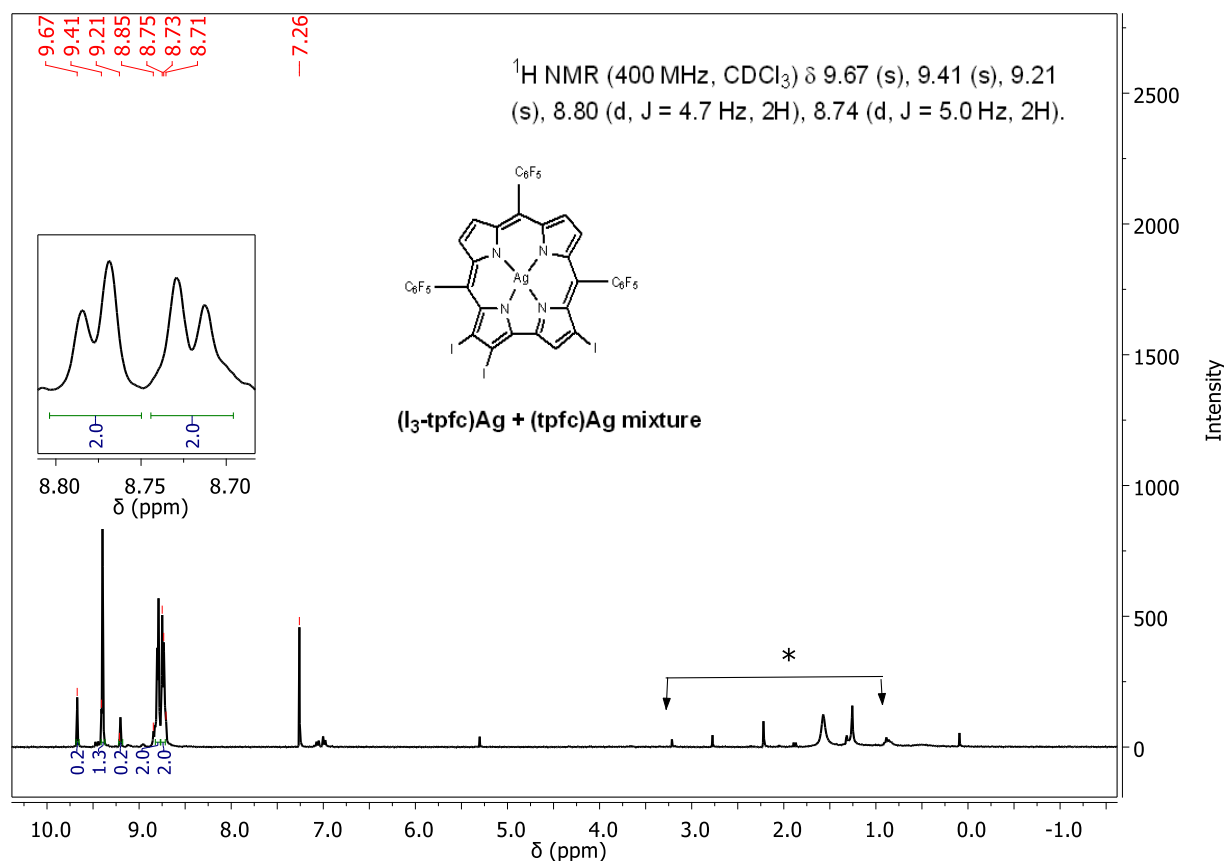


Fig. S17: ^1H NMR spectrum of **(I₃-tpfc)Ag** (contaminated by unreacted **(tpfc)Ag**) were recorded at 400 MHz in CDCl_3 solvent.

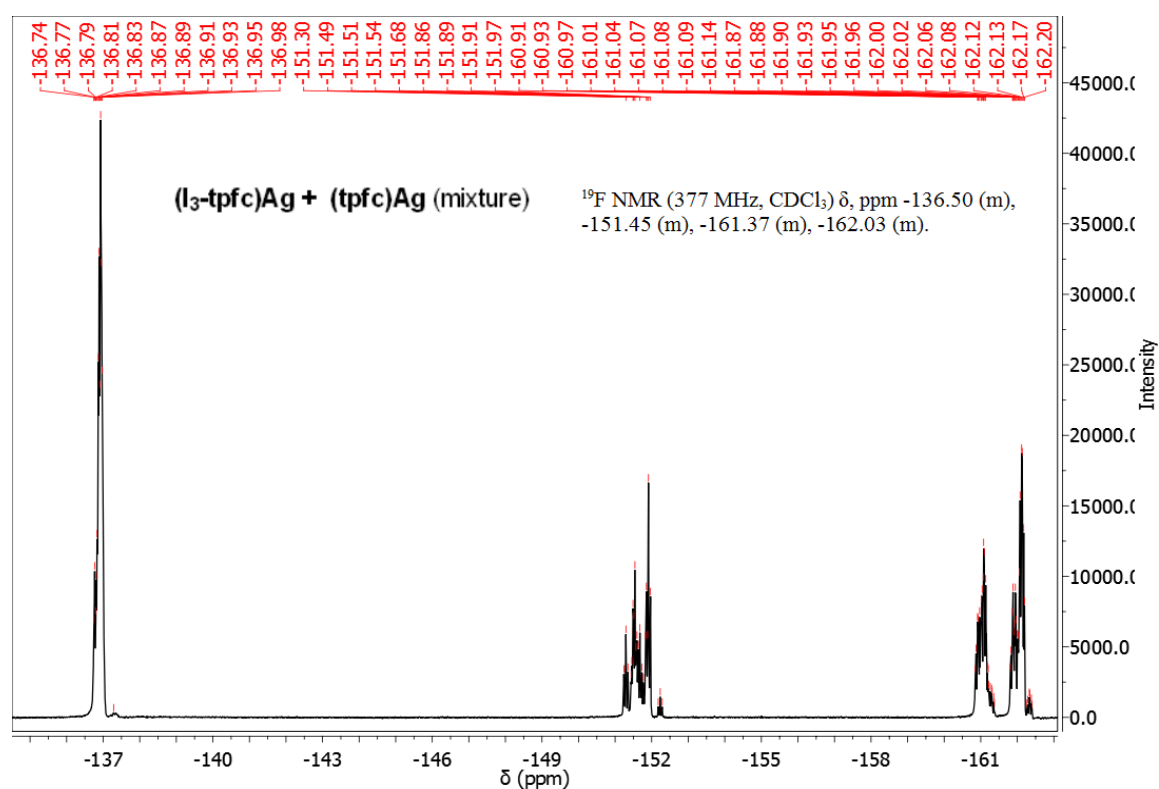


Fig. S18: ^{19}F NMR spectrum of **(I₃-tpfc)Ag** (contaminated with unreacted **(tpfc)Ag**) were recorded at 377 MHz in CDCl_3 solvent.

Display Report

Analysis Info

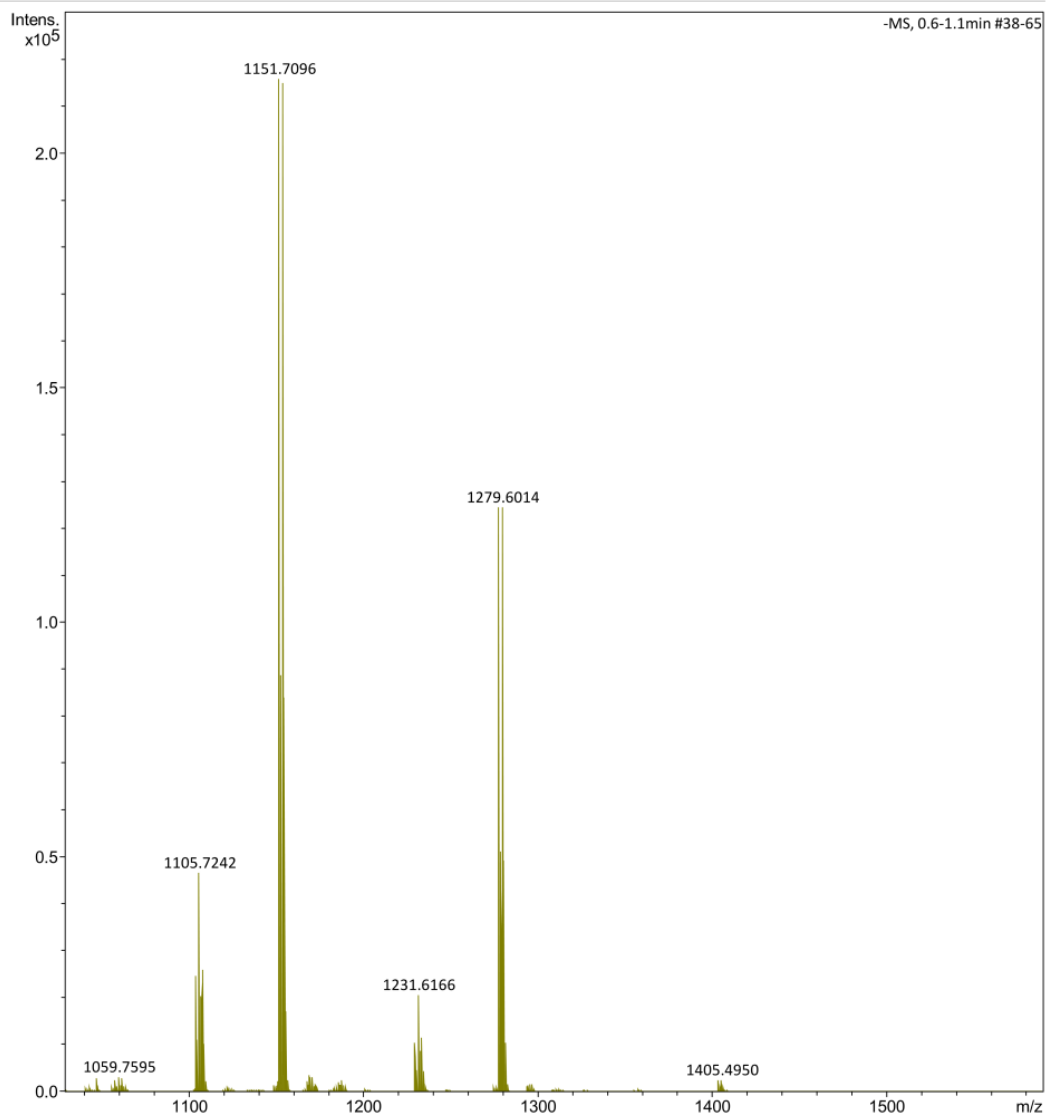
Analysis Name D:\Data\Gross\Gr_3052n000003.d
Method APCI_neg_SolidProbe.m
Sample Name Ag-TPFCI-m
Comment

Acquisition Date 3/31/2016 6:50:38 AM

Operator Larisa Panz
Instrument maXis impact 282001.00128

Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	120 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.5 l/min
Scan End	2500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	2000 nA	Set APCI Heater	200 °C



Gr_3052n000003.d

Bruker Compass DataAnalysis 4.2

printed: 3/31/2016 6:52:27 AM

by: Larisa Panz

Page 1 of 1

Fig. S19: APCI mass spectrum of **(I₃-tpfc)Ag** (contaminated with unreacted **(tpfc)Ag**) molecular weight 1277.6459

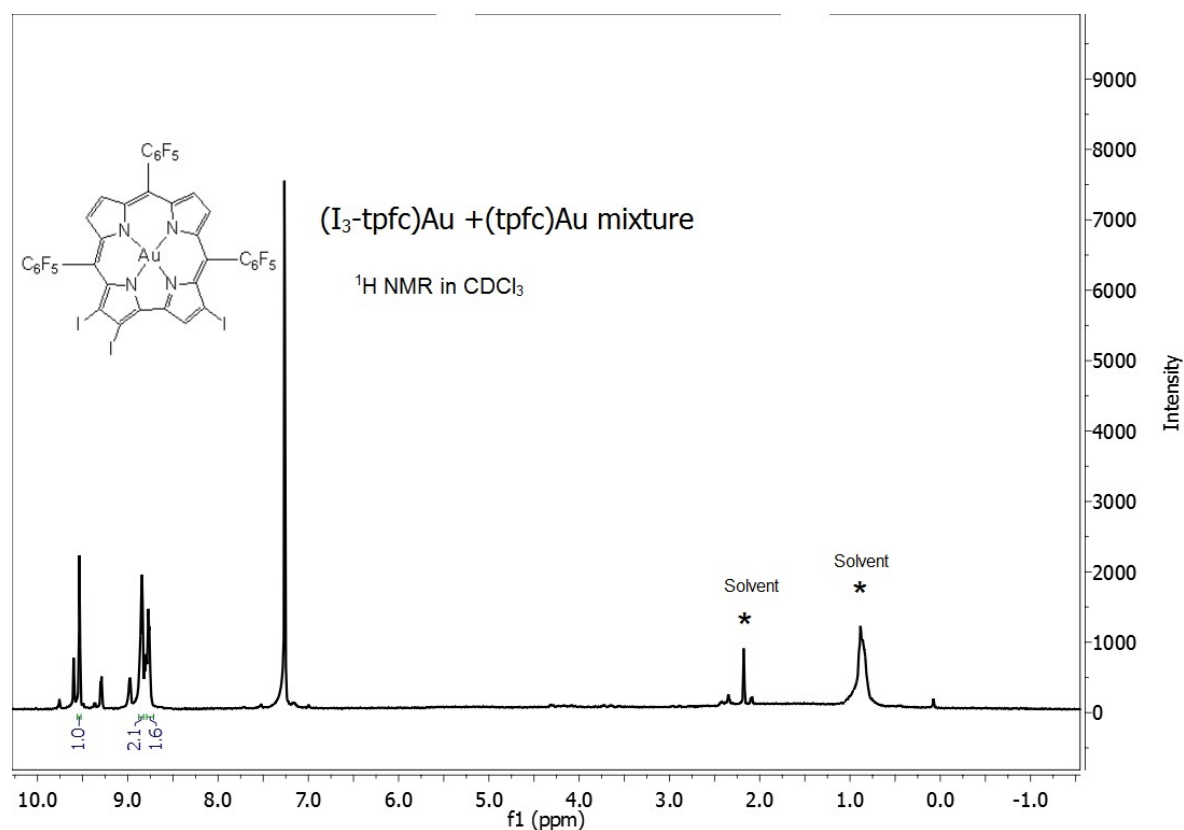


Fig. S20: ¹H NMR spectrum of (I₃-tpfc)Au (contaminated with unreacted (tpfc)Au) were recorded at 400 MHz in CDCl₃ solvent.

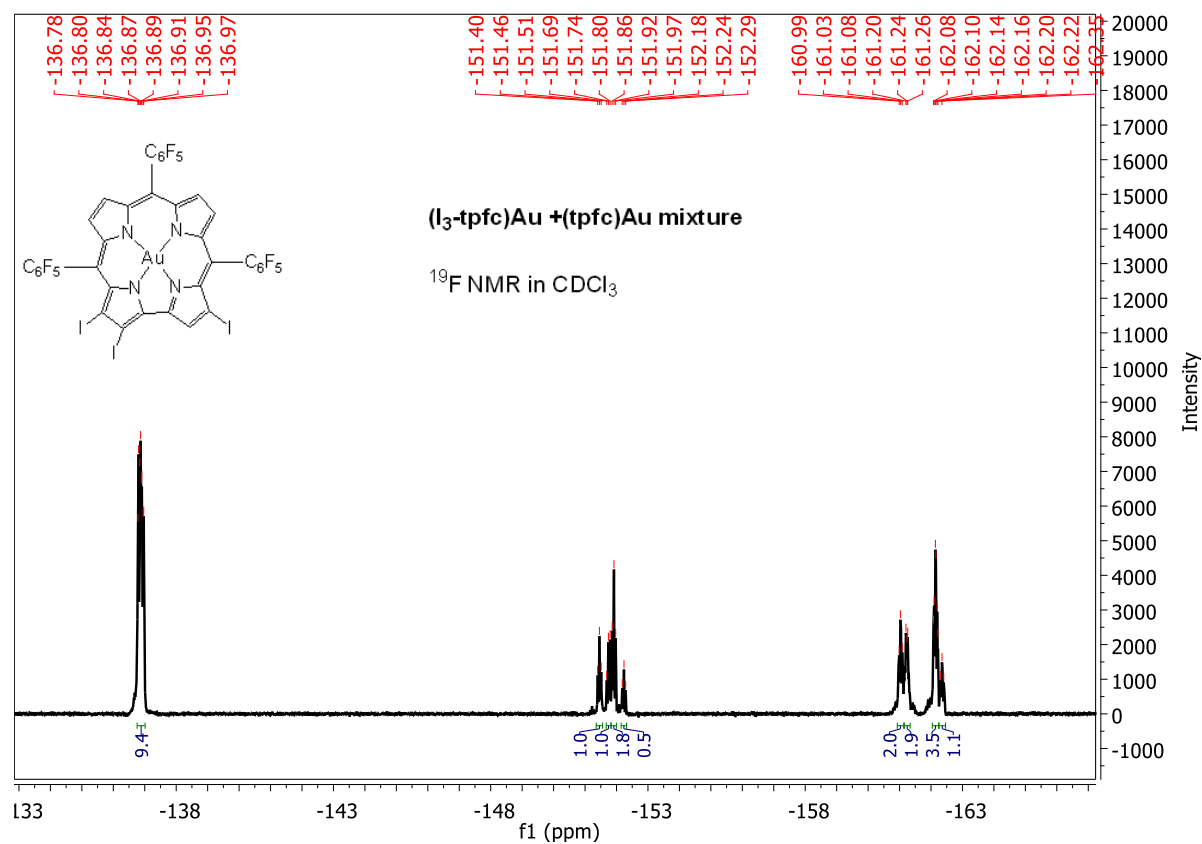


Fig. S21: ¹⁹F NMR spectrum of (I₃-tpfc)Au (contaminated with unreacted (tpfc)Au) were recorded at 377 MHz in CDCl₃ solvent.

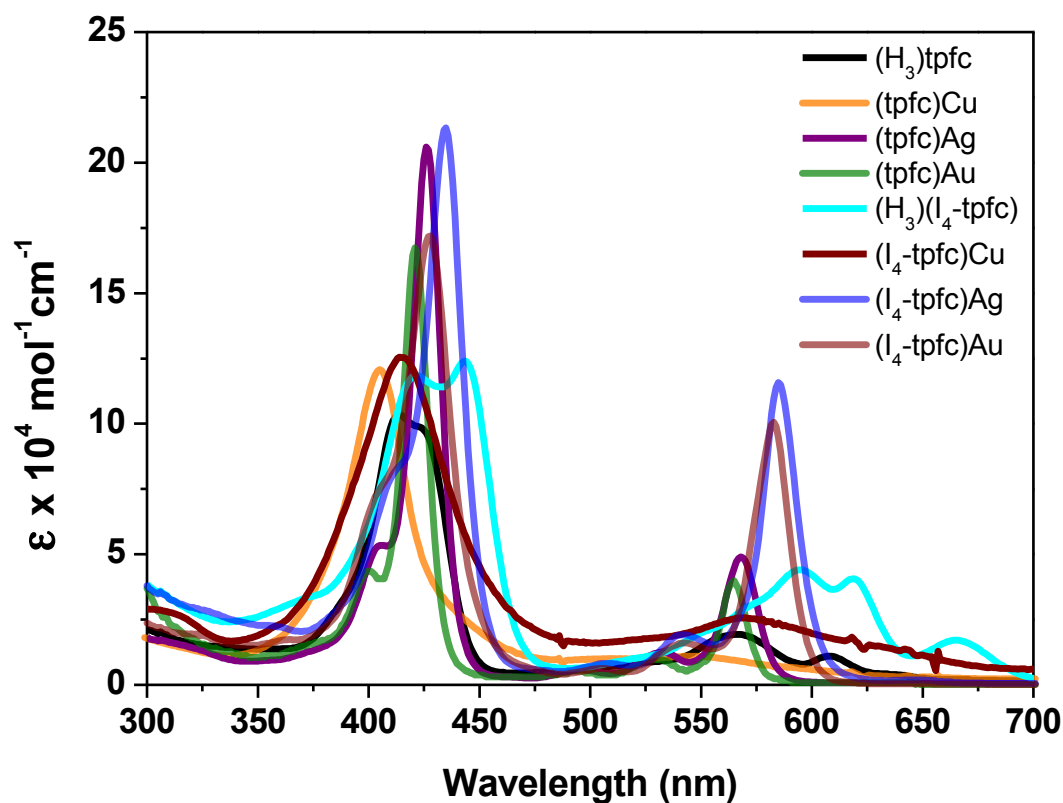


Fig. S22: Absorption spectra, in toluene at RT, of $(H_3)tpfc$, $(tpfc)Cu$, $(tpfc)Ag$, $(tpfc)Au$, $(H_3)(I_4-tpfc)$, $(I_4-tpfc)Cu$, $(I_4-tpfc)Ag$, and $(I_4-tpfc)Au$

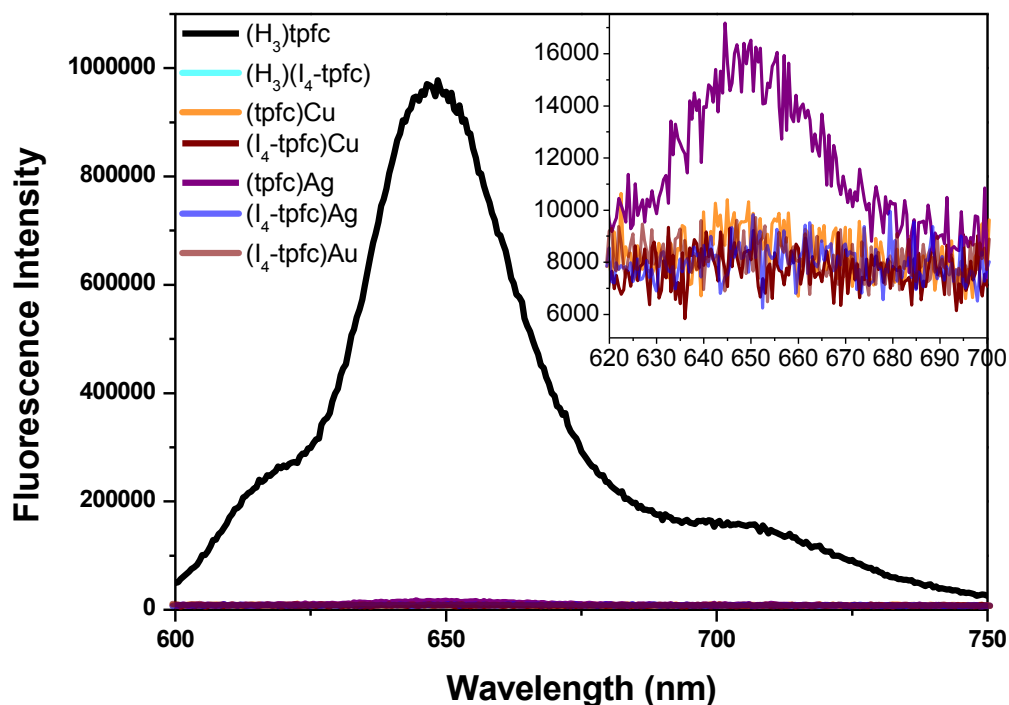


Fig. S23: Emission spectra, in toluene at RT and with $\lambda_{ex} = 405$ nm, of $(H_3)tpfc$, $(tpfc)Cu$, $(tpfc)Ag$, $(H_3)(I_4-tpfc)$, $(I_4-tpfc)Cu$, $(I_4-tpfc)Ag$, $(I_4-tpfc)Au$. Inset graph in between range of 620 to 700 nm for clarity.

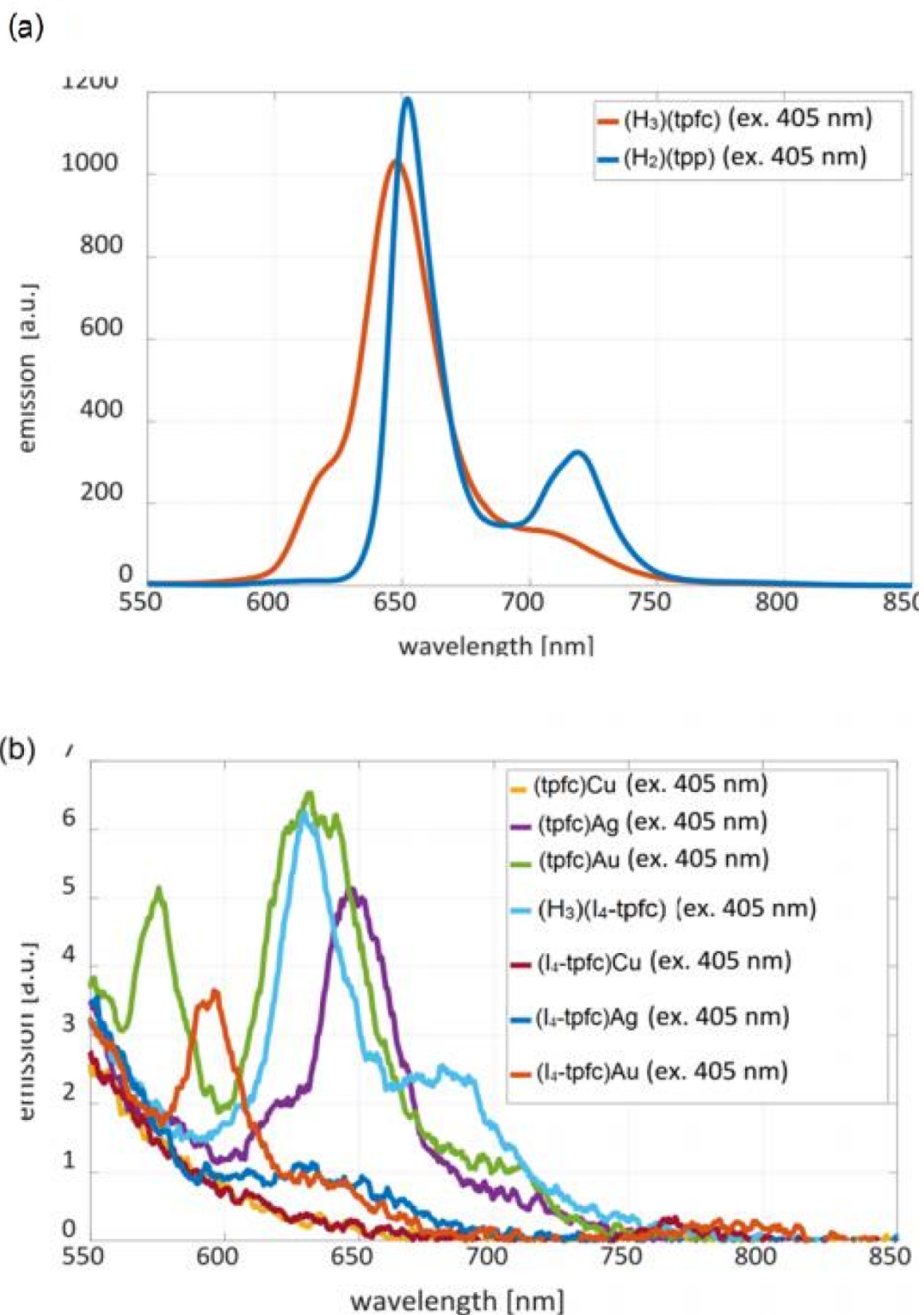


Fig. S24: (a) Full emission spectra of $(H_2)tpc$, $(H_3)tpfc$, upon excitation at 405 nm of toluene solutions with identical optical density. (b) Emission spectra of the $(tpfc)M$ and $(l_4-tpfc)M$ complexes, with $M = Cu, Ag$, and Au .

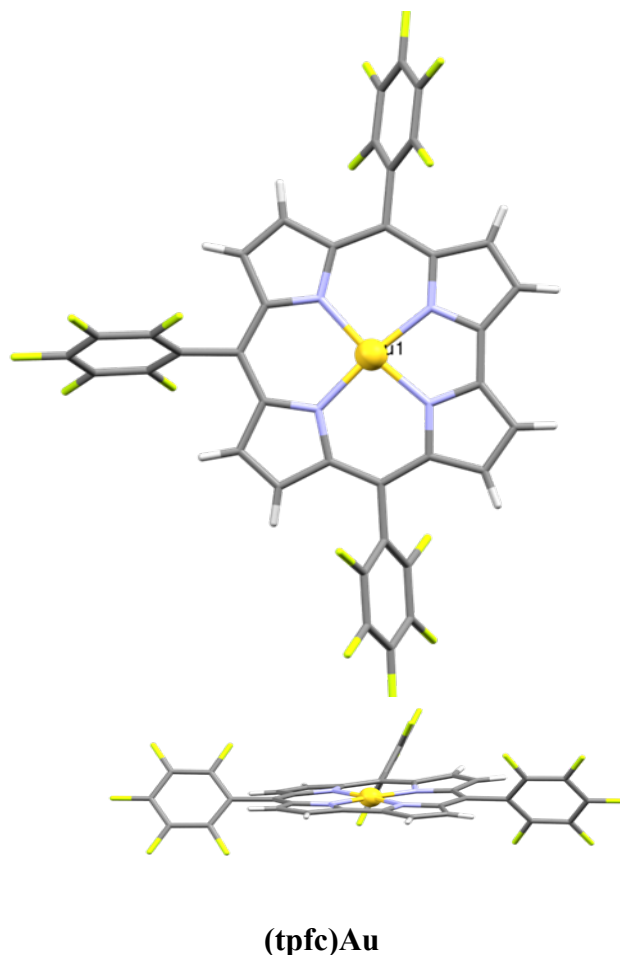


Fig. S25: Crystal structures of (tpfc)Au.

Table S1: X-ray crystallography data of (tpfc)Au, (I₄-tpfc)Cu, (I₄-tpfc)Ag, (I₄-tpfc)Au.

entry	(tpfc)Au	(I ₄ -tpfc)Cu	(I ₄ -tpfc)Ag	(I ₄ -tpfc)Au
Empirical formula	3(C ₃₇ H ₈ Au F ₁₅ N ₄), 2(CHCl ₃)	C ₃₇ H ₄ CuF ₁₅ I ₄ N ₄ , CH ₂ Cl ₂	C ₃₇ H ₄ AgF ₁₅ I ₄ N ₄ , CH ₂ Cl ₂	C ₃₇ H ₄ AuF ₁₅ I ₄ N ₄ , C ₆ H ₆ , C ₆
Formula mass	3210.07	1445.51	1489.84	1644.18
Dimensions [mm]	0.30 x 0.24 x 0.12	0.33 x 0.21 x 0.15	0.15 x 0.12 x 0.03	0.12 x 0.09 x 0.06
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
a [Å]	21.092 (2)	20.0190 (4)	19.9970 (4)	7.33 (2)
b [Å]	21.092 (2)	13.8650 (3)	13.8870 (4)	22.65 (5)
c [Å]	45.876 (3)	15.7270 (6)	15.3230 (6)	28.20 (11)
V [Å ³]	20409(3)	4061.5 (2)	4038.4 (2)	4581 (24)
Space group	I 41/a	P 21/c	P 21/c	P 21/c
Z	8	4	4	4
M(Mo-K _α) [mm ⁻¹]	0.6081	0.5983	0.8946	0.7143
R ₁	0.0296	0.0485	0.0789	0.0752
Reflections measured	7584	5954	5994	6946
2θ _{max} [°]	48	48	48	48
Temperature (K)	200 (2)	200 (2)	200 (2)	200 (2)

Table S2: Absorption data of all the compounds.

Compound	Absorption,				
	λ_{max} , nm (log ϵ , x $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) ^a				
(H₃)tpfc		413 (10.3)	566 (1.93)	607 (1.09)	
(tpfc)Cu		404 (12.11)	545 (1.09)		
(tpfc)Ag	406 (5.34)	426 (20.58)	532 (1.25)	568 (4.89)	
(tpfc)Au	400 (4.34)	421 (16.72)	530 (0.95)	564 (3.98)	
(H₃)(I₄-tpfc)	421 (11.84)	443 (12.40)	594 (4.41)	618 (4.06)	665 (1.70)
(I₄-tpfc)Cu		414(14.11)	569 (2.57)		
(I₄-tpfc)Ag		434 (21.32)	542 (1.90)	585 (11.56)	
(I₄-tpfc)Au		427 (17.20)	542 (1.59)	583 (10.04)	

^aSolvent: Toluene, Error limits: λ_{max} , ± 1 nm, log ϵ , $\pm 10\%$.