Supporting Information for

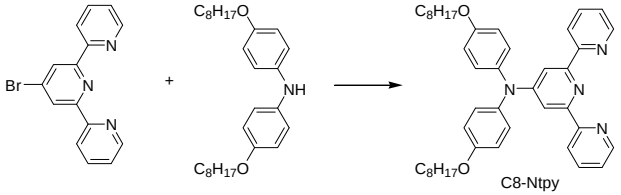
Tunable Self-assembly and Morphology-Dependent Photo-conductivity of a Donor-Acceptor-Structured Diruthenium Complex

Meng-Jia Sun, Xinliang Zhang, Yu-Wu Zhong,* Chuanlang Zhan,* and Jiannian Yao*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190; University of Chinese Academy of Sciences, Beijing 100049, China

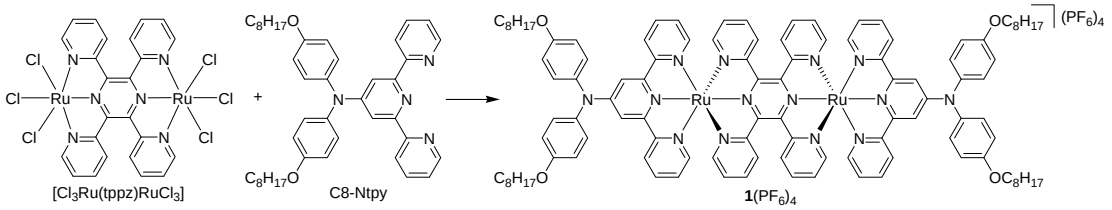
*zhongyuwu@iccas.ac.cn; clzhan@iccas.ac.cn; jnyao@iccas.ac.cn

Synthesis



Synthesis of Ligand C8-Ntpy. To a 100 mL oven-dried pressure vessel were added 4-bromo-2,2;6,2"-terpyridine (0.77 mmol, 240 mg), 4,4'-di-*n*-octoxydiphenylamine[1] (0.15 mmol, 488 mg), and 10 mL dry toluene. The mixture was bubbled with nitrogen for 15 min, followed by the addition of $Pd_2(dba)_3$ (0.038 mmol, 34.8 mg), dppf (0.038 mmol, 21.6 mg) and $NaOBu^t$ (0.92 mmol, 88.8 mg). The vessel was sealed and the system was stirred at 120 ℃ for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was subjected to flash column chromatography on silica gel (eluent: dichloromethane/ethyl acetate/NH_4OH, 30/3/1), to afford 277 mg of ligand **C8-Ntpy** as a pale yellow liquid in 55% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 - 8.58 (m, 4H), 7.85 (s, 2H), 7.79 (t, *J* = 16.8 Hz, 2H), 7.24 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 4H), 6.90 (d, *J* = 9.2 Hz, 4H), 3.96 (t, *J* = 13.2 Hz, 4H), 1.83 – 1.76 (m, 4H), 1.47 - 1.45 (m, 4H), 1.30 - 1.36 (m, 16H), 0.88 - 0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.03, 156.64, 156.39, 149.13, 138.76, 136.74, 128.30, 123.58, 121.51, 115.81, 109.07, 68.38, 53.73, 32.11, 29.67, 29.61, 29.54, 26.37, 22.95, 14.41. Calcd HRMS-EI for $C_{43}H_{52}N_4N_2$ [M^+]: 656.4090. Found: 656.4099.

[1] Hostettler, N.; Fürer, S. O.; Bozic-Weber, B.; Constable, E. C.; Housecroft, C. E. *Dyes and Pigments* **2015**, *116*, 124.



Synthesis of Complex **1**$(PF_6)_4$. To a 100 mL flask were added Ligand **C8-Ntpy** (0.42 mmol, 277 mg), $[Cl_3Ru(tppz)RuCl_3]$ (0.15 mmol, 120.5 mg), and 5 mL dry ethylene glycol. The mixture was stirred at 160 ℃ for 2 h. After cooling to room temperature, 2 mL saturated KPF_6 aqueous solution was added for anion exchange. After filtration and washing successively with water and ether, the obtained solid was subjected to column chromatography on silica gel (eluent: acetonitrile/water/saturated aqueous KNO_3, 30/1/0.05) followed by anion exchange using KPF_6, to afford 208 mg of **1**$(PF_6)_4$ in 56% yield as a purple solid. ^{1}H NMR (400MHz, CD_3CN): δ 8.93 (d, *J* = 8.0 Hz, 4H), 8.22 (d, *J* = 8.0 Hz, 4H), 7.98 (s, 4H), 7.91 - 7.94 (m, 8H), 7.87 (t, *J* = 15.6 Hz, 4H), 7.54 - 7.58 (m, 12H), 7.51 (t, *J* = 13.2 Hz, 4H), 7.17 - 7.19 (m, 12H), 4.10 (t, *J* = 13.2 Hz, 8H), 1.77 – 1.93 (m, 8H), 1.48-1.52 (m, 8H), 1.33 - 1.28 (m, 32H), 0.89 - 0.91 (m, 12H). ^{13}C NMR (100 MHz, CD_3CN): δ 158.72, 158.17, 157.04, 155.66, 154.19, 153.85, 153.14, 150.40, 138.83, 137.64, 137.00, 129.56, 129.19, 128.85, 127.47, 124.57, 116.57, 110.26, 68.57, 31.81, 30.11, 29.30, 29.23, 25.99, 22.61, 13.63. MALDI-TOF MS (m/z): 1146.4 for $[M - Ru(C8\text{-}Ntpy)]^+$, 1899.7 for $[M - 4PF_6]^+$, 2048.8 for $[M - 3PF_6]^+$, 2193.8 for $[M - 2PF_6]^+$. Anal. Calcd for $C_{110}H_{120}F_{24}N_{14}O_4P_4Ru_2 \cdot 2H_2O$: C, 52.42; H, 4.96; N, 7.78. Found: C, 52.03; H, 4.98, N, 7.74.

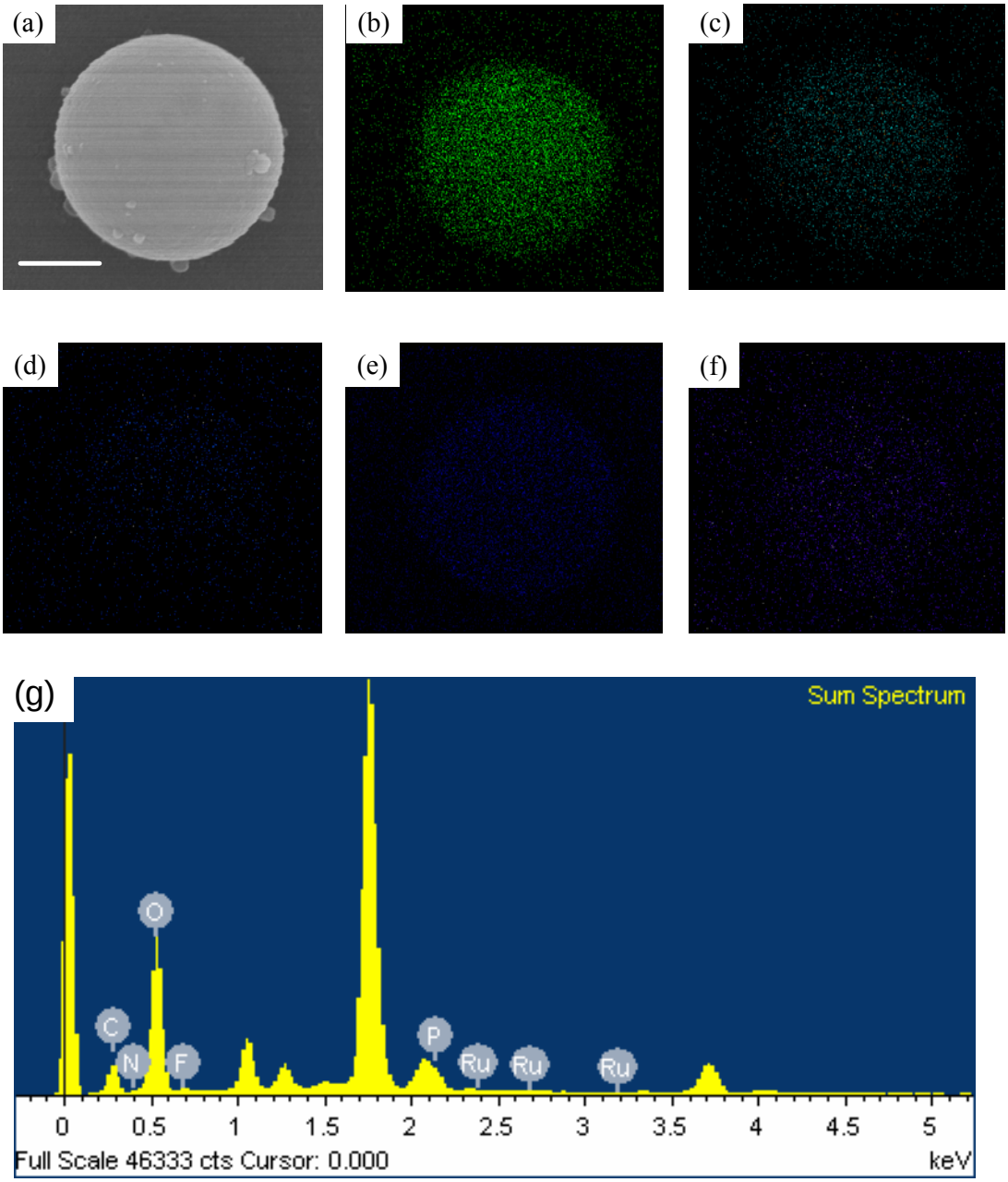


Figure S1. EDS data of a single nanosphere. (a) SEM image of the nanosphere. The scale bar is 50 nm. (b-f) Distributions of elements carbon (b), fluorine (c), nitrogen (d), phosphine (e) and ruthenium (f). (g) The sum spectrum.

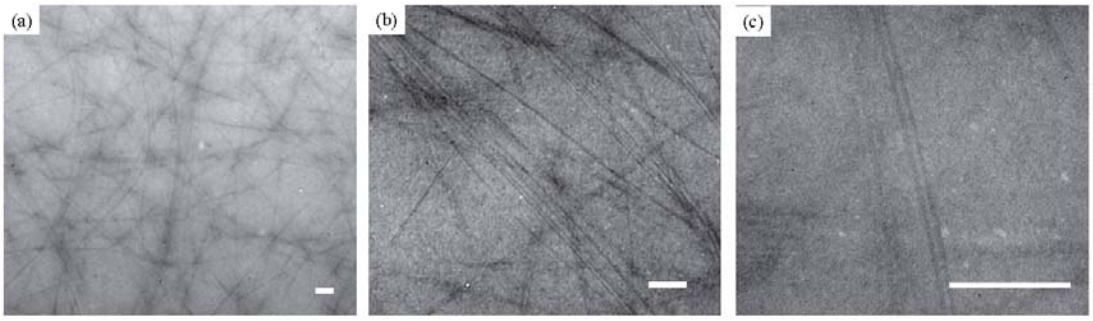
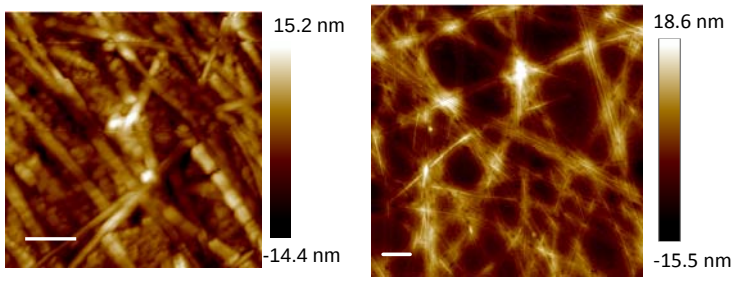


Figure S2. TEM images of thin films prepared by spin-coating of **1**$(PF_6)_4$ in $CHCl_3$. The scale bar is 250 nm.



(a) (b)

Figure S3. (a) AFM image of a drop-coating film of **1**$(PF_6)_4$ in $CHCl_3$. (b) AFM image of the nanowire film on a Au-coated Si substrate prepared by spin-coating of **1**$(PF_6)_4$ in $CHCl_3$. The scale bar is 500 nm.

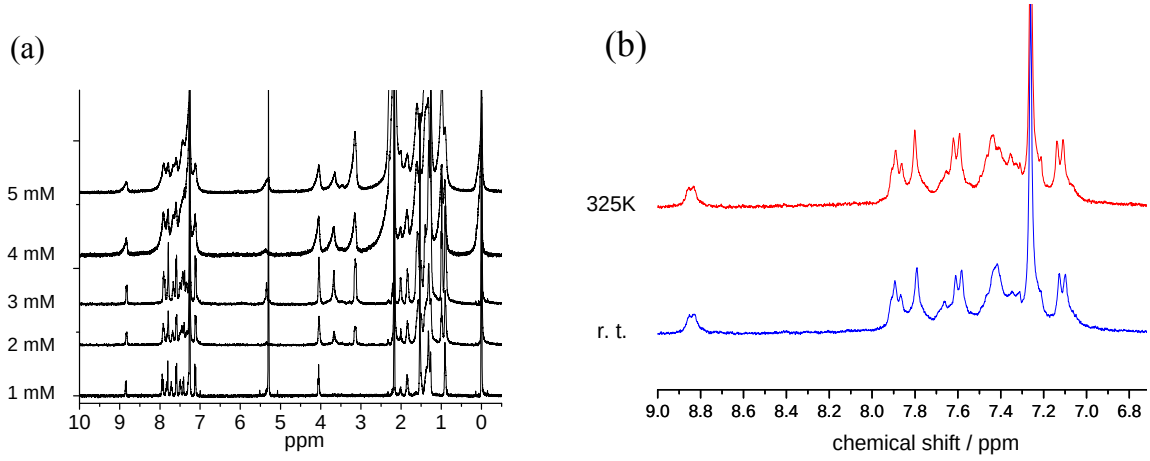


Figure S4. (a) Concentration-dependent ^1H NMR spectra of **1**$(PF_6)_4$ in $CDCl_3$ at room temperature. (b) ^1H NMR spectra of **1**$(PF_6)_4$ (4 mM) in $CDCl_3$ at room temperature and 325 K.

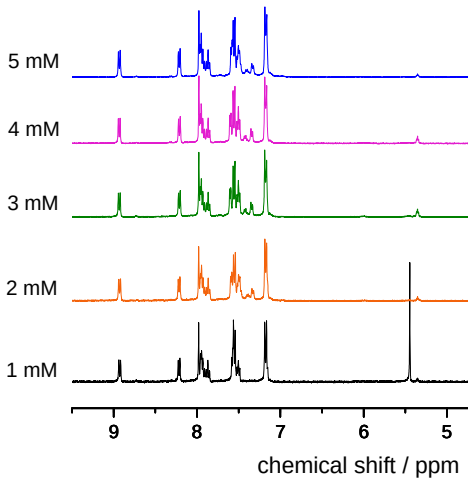


Figure S5. Concentration-dependent ^{1}H NMR spectra of **1**$(PF_6)_4$ in CD_3CN at room temperature.

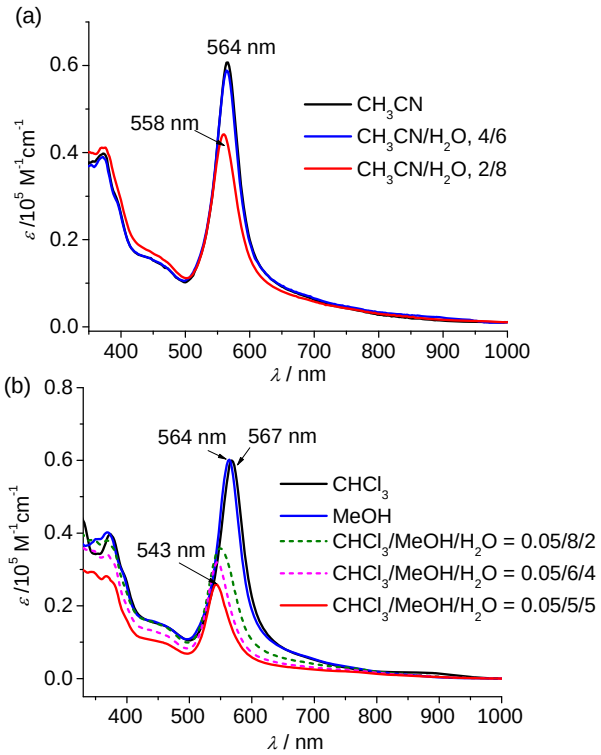


Figure S6. UV-vis absorption spectra of **1**$(PF_6)_4$ in mixed CH_3CN and H_2O at 0.04 mM (a) and mixed $CHCl_3$, MeOH, and H_2O at 0.2 mM.

Computational Methods.

DFT calculations were carried out in the *Gaussian* 09 package using the B3LYP hybrid functional.[2] The electronic structures were optimized using a general basis set with the Los Alamos effective core potential LANL2DZ basis set for Ru and 6-31G* for other atoms.[3] The solvation effects in acetonitrile solutions are taken into account for all calculations with the conductor-like polarizable continuum model (CPCM).[4] No symmetry constraints were used in the optimization (nosymm keyword was used). Frequency calculations have been performed with the same level of theory to ensure the optimized geometries to be local minima. All orbitals have been computed at an isovalue of 0.02 e/bohr^3.

[2] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
[3] Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.
[4] Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.

Cartesian coordinates of DFT-optimized structure of (Me-**1**)$^{4+}$:

Charge = 4; multiplicity=1

Ru	-3.34622196	0.00150682	-0.00188445
C	-5.14006738	-2.29523334	-0.53304933
C	-2.92391683	-3.02885420	-0.68468256
C	-6.03789087	-1.14607525	-0.27174034
C	-5.60030817	-3.57631307	-0.84000778
C	-3.32496398	-4.32555396	-0.99264630
C	-4.68769543	-4.60297024	-1.07168317
C	-6.03820383	1.14821128	0.26869924
N	-3.79720550	-2.03261994	-0.45866988
N	-5.37378031	0.00118047	-0.00161212
C	-5.14069118	2.29768274	0.52971430
C	-5.60128329	3.57863208	0.83669857
C	-2.92474866	3.03205038	0.68074349
C	-4.68895409	4.60560934	1.06806387
C	-3.32614988	4.32863949	0.98871006
N	-3.79776397	2.03551501	0.45500655
H	-1.87384481	-2.77099572	-0.61625386
H	-6.66405372	-3.77152999	-0.89891521
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C	-3.42332391	-1.37576128	4.18493871
H	-1.71811698	-1.93703957	5.38760480
C	-1.59089189	-0.53643369	2.29329634
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C	-3.81401309	-0.86765953	2.94854045
H	-4.17687035	-1.67944806	4.90256485
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C	5.60063939	3.58383208	-0.82660445

N	3.79762402	2.03861399	-0.45110294
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C	2.92531176	-3.03088265	0.66670094
C	4.68797482	4.61151859	-1.05345918
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C	3.32674305	-4.32878254	0.96906697
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H	5.03951896	5.61073011	-1.28781835
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H	2.57910983	-5.09535225	1.13803466
H	2.57736931	5.10020688	-1.14372024
Ru	3.34671919	0.00252361	-0.00300210
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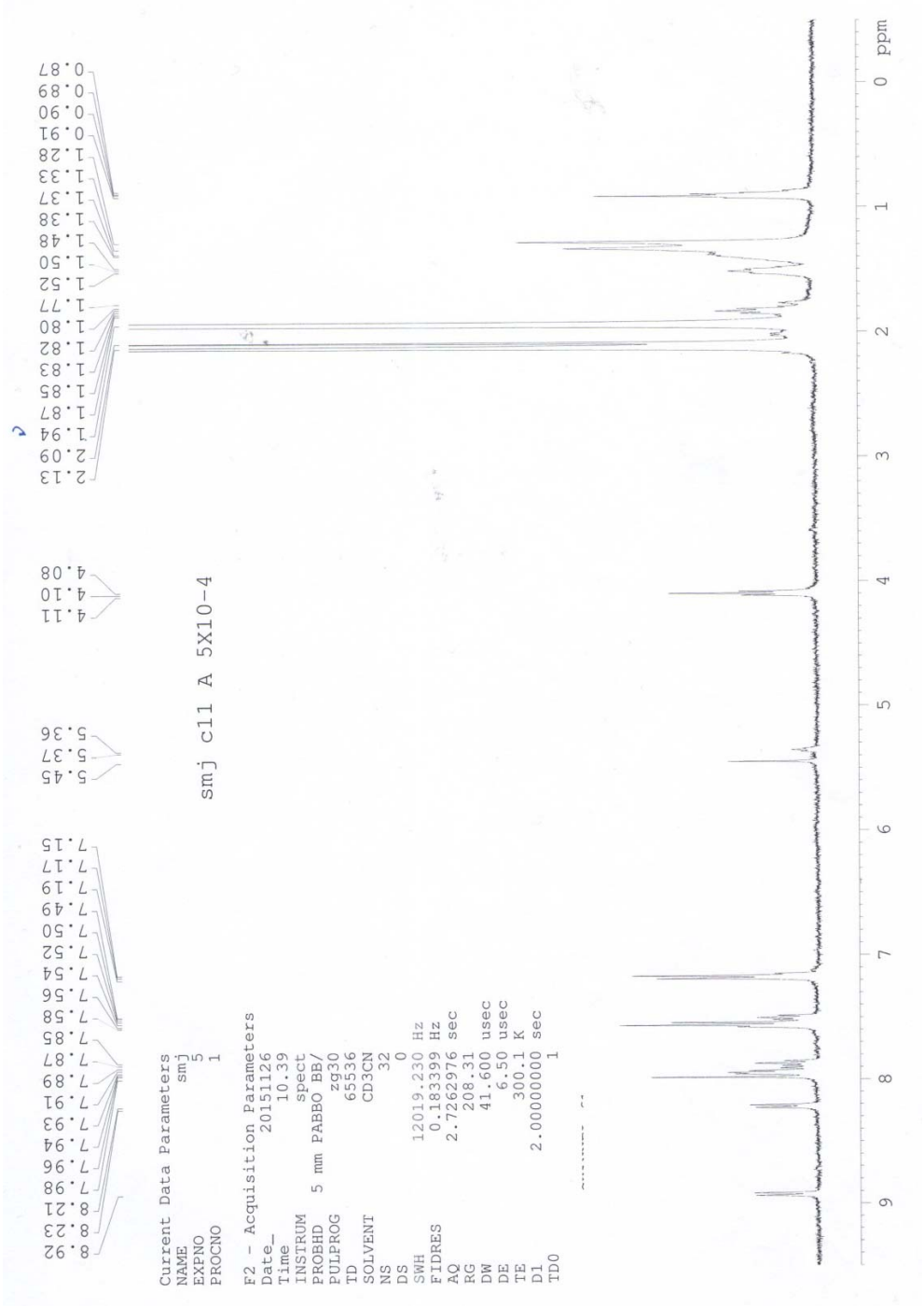
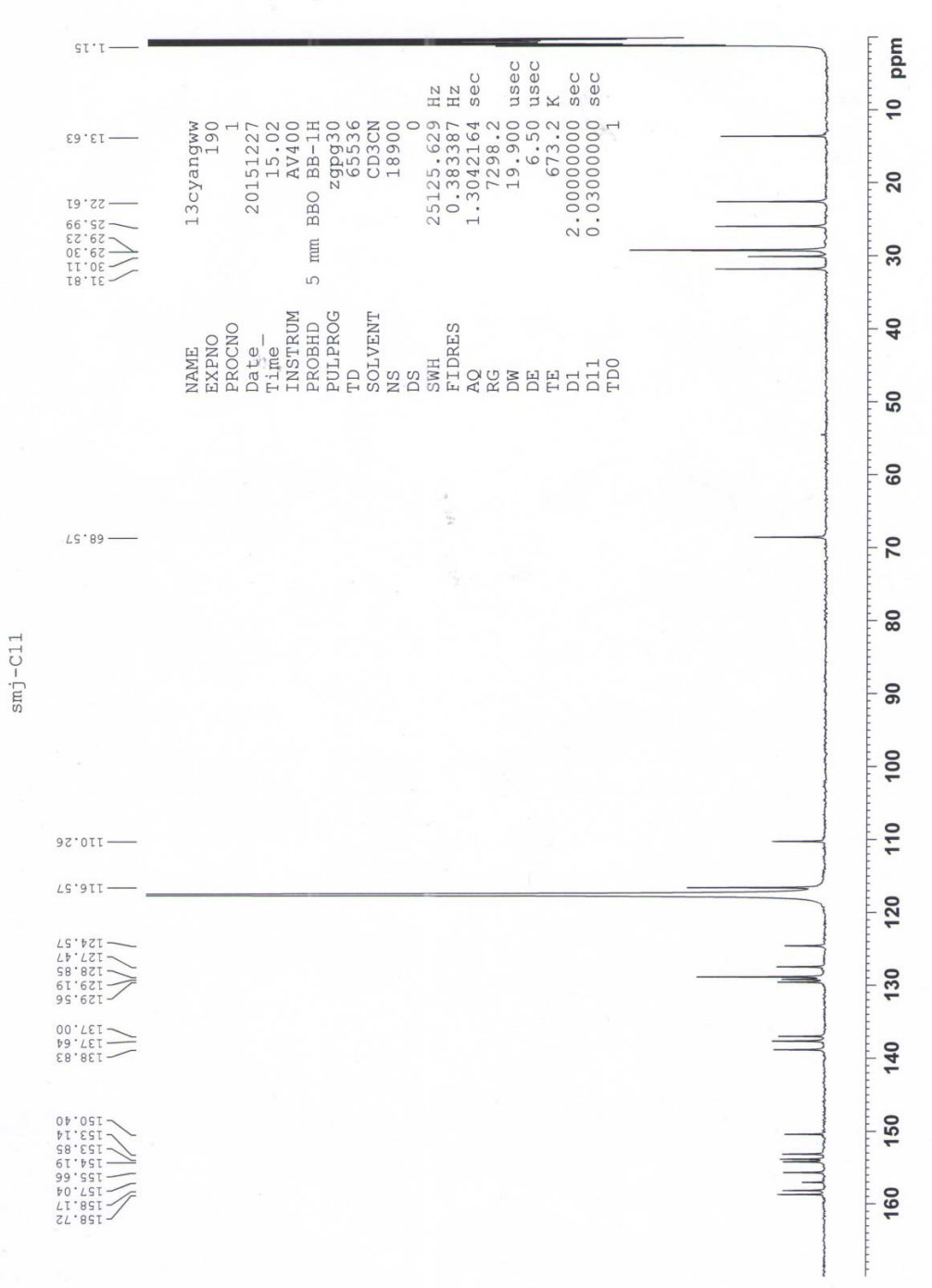
H	7.95236208	-2.10111357	0.46837907
H	7.95164320	2.10730378	-0.47631968

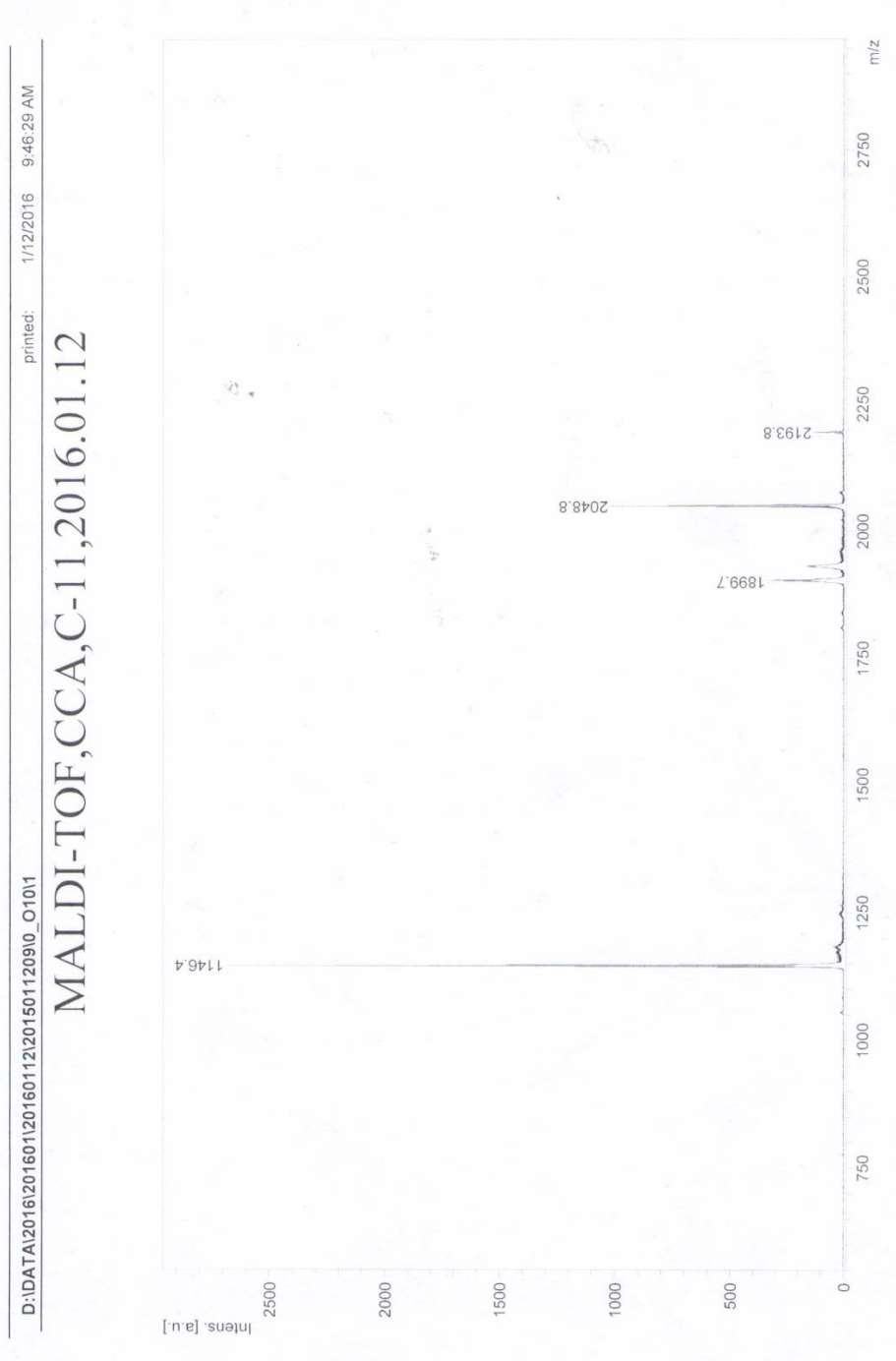
^{1}H NMR spectrum of **1**$(PF_6)_4$ in CD_3CN:



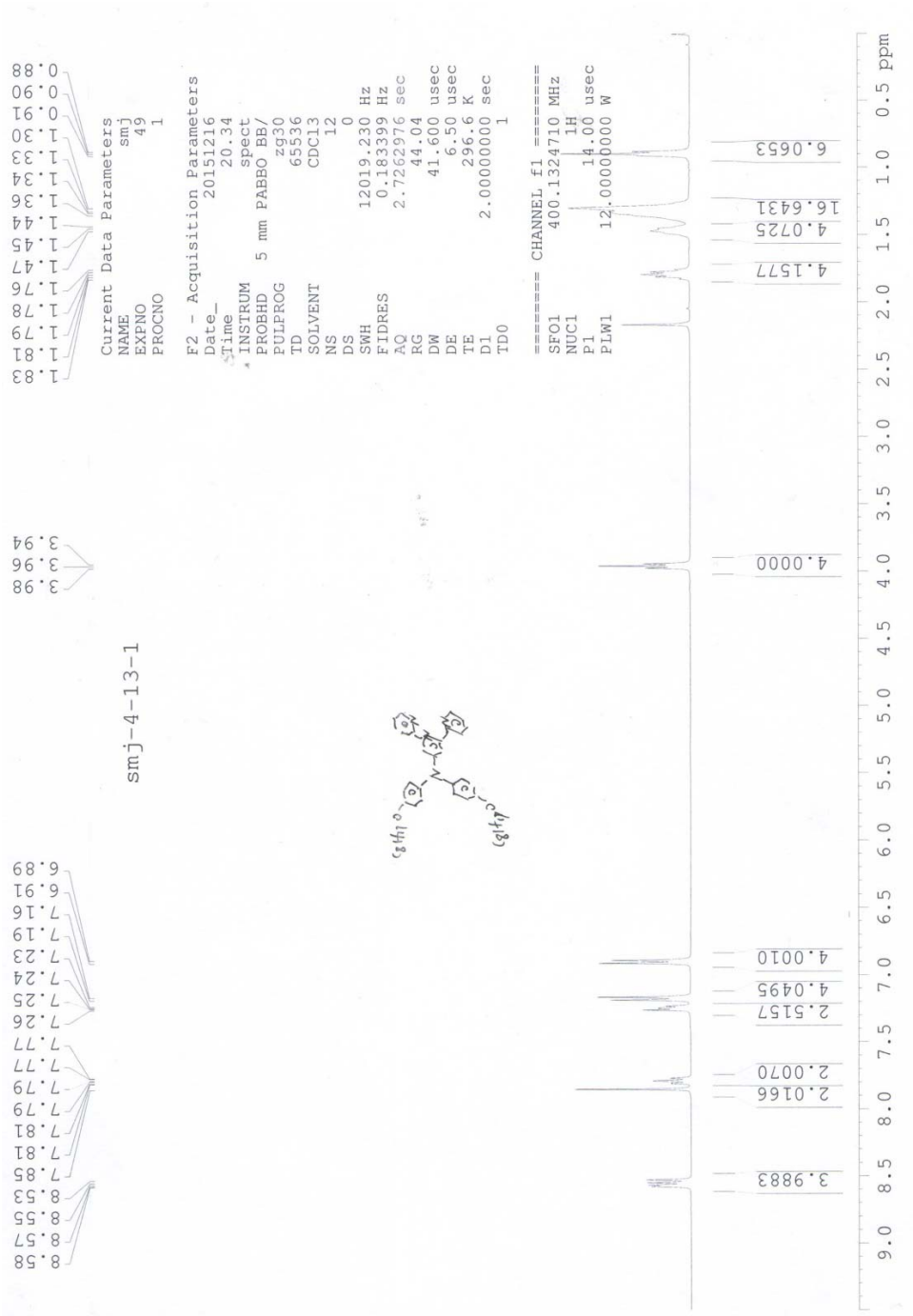
^{13}C NMR spectrum of **1**$(PF_6)_4$ in CD_3CN:



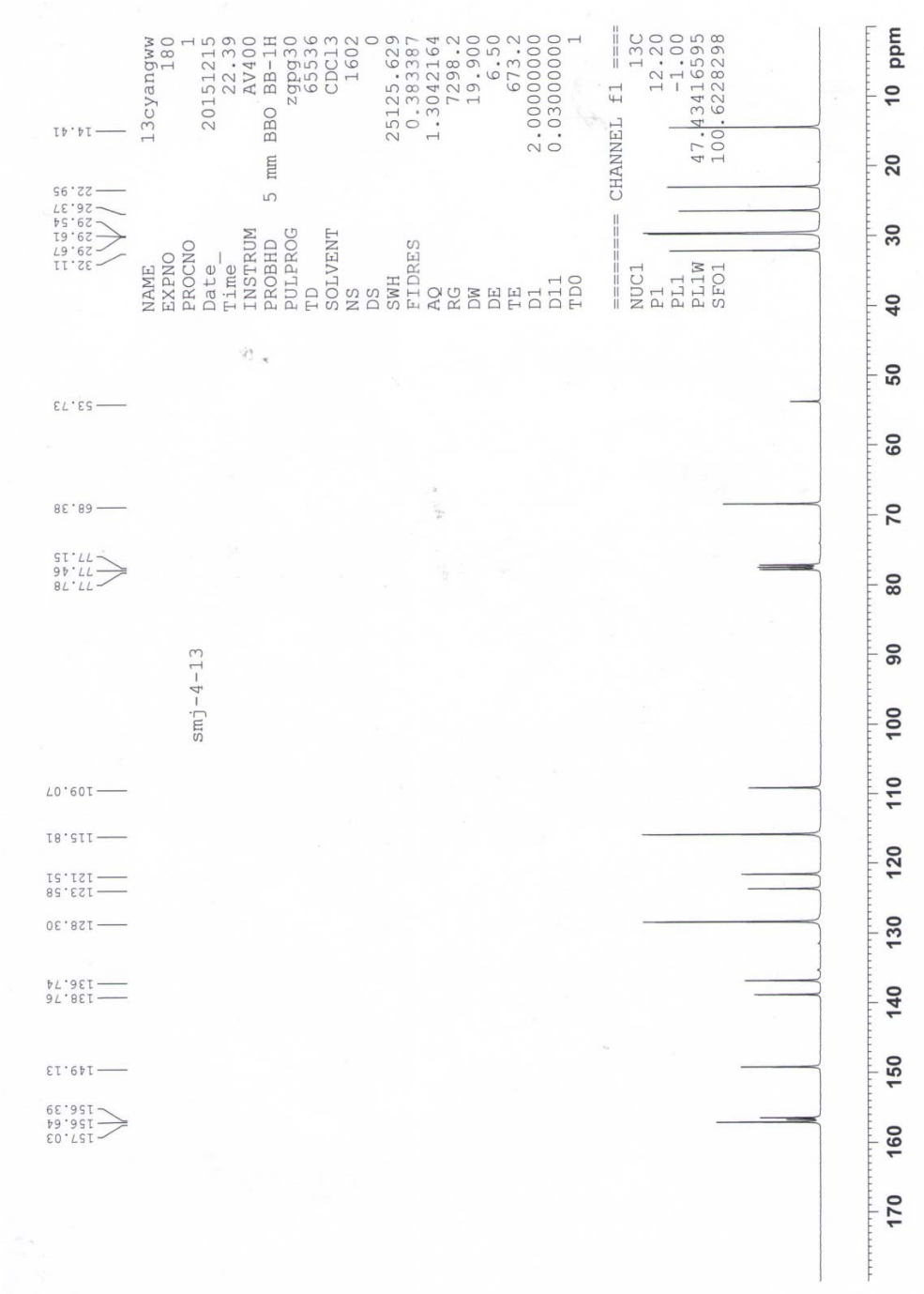
MALDI-TOF mass spectrum of **1**$(PF_6)_4$:



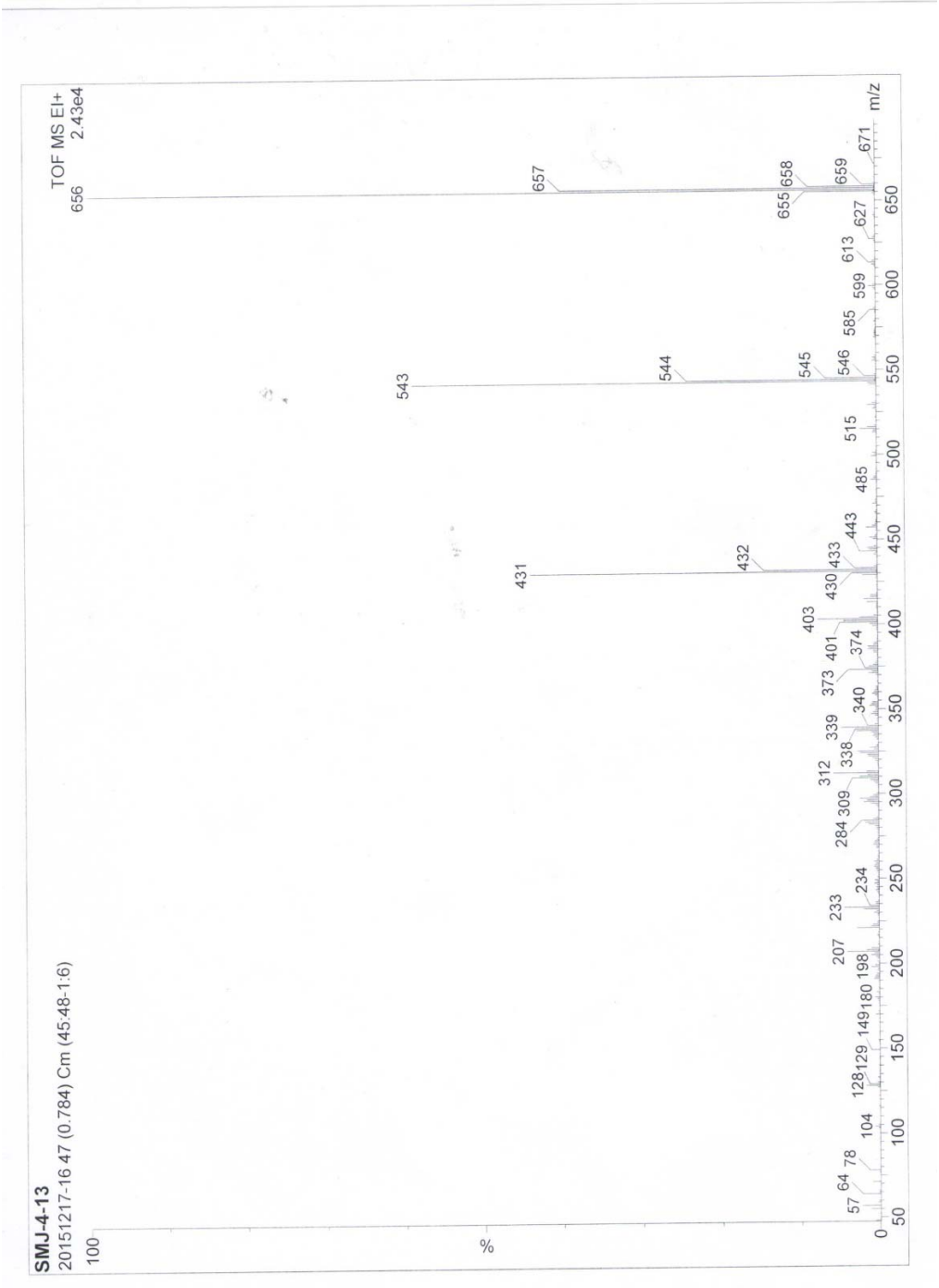
^{1}H NMR spectrum of Ligand **C8-Ntpy**:

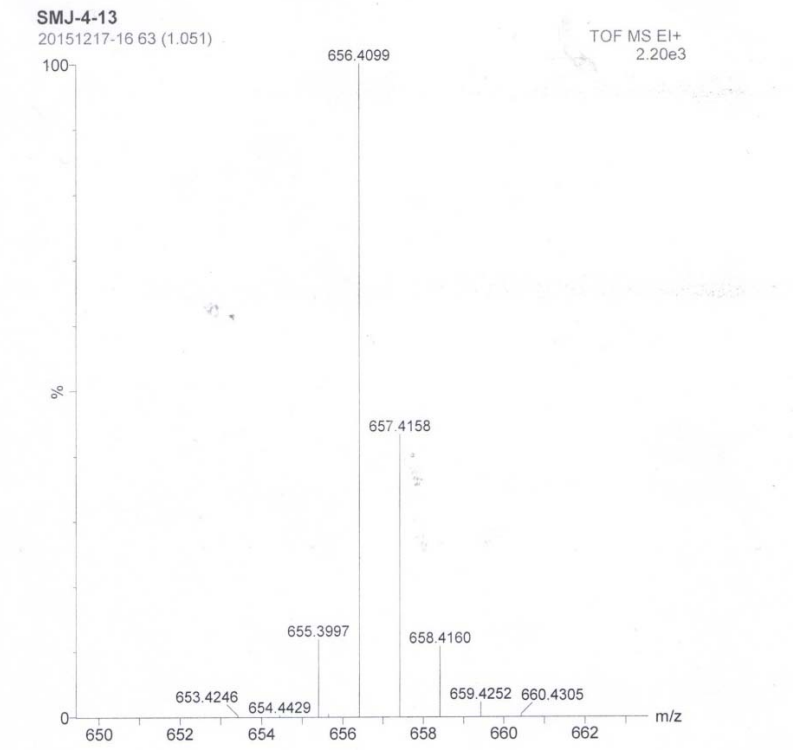


^{13}C NMR spectrum of Ligand **C8-Ntpy**:



EI-MS spectrum of Ligand **C8-Ntpy**:





Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
60 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
656.4099	100.00	656.4090	0.9	1.3	20.0	1	C43 H52 N4 O2