Supplementary Material (ESI) for Chemical Communications

Supporting Information for: Effect of Dendrimer Generation on Electron Self-Exchange Kinetics between Metal (tris-bipyridine) Core Dendrimers

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Syntheses

General Considerations.

Nuclear magnetic resonance spectra were acquired on Varian 300 or 400MHz spectrometer or Bruker Avance 500MHz spectrometer. MALDI-MS investigations were carried out using a Bruker Proflex + (Bruker Daltonics, Billerica, MA) linear MALDI-TOF instrument with a 1.2 m flight tube. Dithranol was used as matrix. Elemental analysis was performed by Atlantic Microlaboratories.

Materials

All chemicals were purchased from Aldrich or Acros and were used as received unless otherwise indicated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried, distilled by vacuum transfer, and stored in a dry box under nitrogen atmosphere. $CDCl_2$ was dried over P_2O_5 for overnight and distilled by vacuum transfer. CD_3CN was dried over CaH_2 and distilled by vacuum transfer. The synthesis of dendrons up to the second generation,[1, 2] dendrimers up to the first generation,[1] $Fe(G2Bpy)_3(PF_6)_2$,[2] d_8-bpy,[3] $M(G_0bpy)_3(PF_6)_2$, and $M(bpy)_3(PF_6)_3$ (M=Ru and Fe) have been reported previously.[4]

G_3Bpy. This compound was prepared in a manner analogous to that previously reported for G_2Bpy.[2] Yield: 84% (1.38g); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.2 (br, 28H), 1.5-1.8 (m 80H), 2.2 (br, 28H), 2.6 (t, 4H), 3.9 (br, 24H), 5.0 (s, 32H), 6.7 (d, 24H), 6.9 (d, 32H), 7.0-7.2 (m, 56H), 7.3-7.6 (m, 82H), 8.2 (s, 2H), 8.5 (br, 2H). Anal. Calcd. for $C_{362}H_{360}N_2O_{28}$: C, 83.83; H, 7.00; N, 0.54; found: C, 83.60; H, 7.00; N, 0.54.

Ru(G_2Bpy)$_3$(PF_6)$_2$. This complex was prepared in a manner analogous to that previously reported for Ru(G_1bpy)$_3$(PF_6)$_2$ [1] alternatively using chloroform/ethanol solvent mixture (2:1 v/v) and adding a molar equivalent of $AgNO_3$ to reaction mixture. Yield: 98% (0.28g); ^{1}H NMR (CD_2Cl_2:CD_3CN=5:1, v/v) δ (ppm) 1.2 (m, 4H), 1.4-1.6 (br, 30H), 2.0-2.4 (m, 12H), 2.6 (t, 4H), 3.7 (t, 8H), 4.9 (s,16H), 6.7 (d, 8H), 6.8 (d, 16H), 6.9-7.1 (m, 26H), 7.2-7.4 (m, 42H), 8.0 (s, 2H). MALDI-TOF MS (matrix: dithranol); m/z Calcd 7534.7 (M-PF_6); found 7535.1. Anal. Calcd for $C_{510}H_{504}F_{12}RuN_6O_{36}P_2$: C, 79.71; H, 6.61; N, 1.09; found: C, 79.43; H, 7.63; N, 1.08.

Fe(G_3Bpy)$_3$(PF_6)$_2$. To a solution of G_3Bpy (0.16 g, 0.03 mmol) in 30 mL of acetonitrile/1,2-dichloroethane (1/1, v/v) was added Fe(CH_3CN)$_6$(PF_6)$_2$[5] (0.006 g, 0.01 mmol) in 5 mL of acetonitrile. The reaction mixture was refluxed for 12h. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and added dropwise while stirring to 150 mL of petroleum ether. The resulting purple precipitate was filtered, washed with ethanol, and dried: yield 94% (0.15 g); 1H NMR (CD_2Cl_2:CD_3CN=5:1, v/v) δ (ppm) 1.2 (br, 28H), 1.5-1.8 (m 80H), 2.2 (br, 28H), 2.6 (br, 4H), 3.9 (br, 24H), 5.0 (s, 32H), 6.7 (br, 24H), 6.9 (br, 32H), 7.0-7.2 (m, 56H), 7.3-7.6 (m, 84H), 8.1 (s, 2H). Anal. Calcd. for $C_{1086}H_{1080}F_{12}FeN_6O_{84}P_2$: C, 82.00; H, 6.84; N, 0.53; found: C, 80.74; H, 6.80; N, 0.64. The difficulties faced in the characterization of hyperbranched molecules have been noted. Many authors have noted that dendrimers show discrepancies between the calculated and observed analyses due to trace impurities and the tendency toward solvent inclusion. The presence of water or other solvents perhaps contained within the dendritic cavities leads to significant errors in the analyses.[6]

$Fe(d_8\text{-bpy})_3(PF_6)_3$.[4] d_8-bpy and $FeSO_4.7H_2O$ were added to 25mL of H_2O and warmed gently until all solid had dissolved. The solution was then filtered into a flask immersed in an ice bath and 2-3mL of 1M H_2SO_4 added. After further cooling, an excess of PbO_2 was added and the solution was mixed thoroughly until all traces of red color had disappeared leaving a blue solution. This solution was filtered into a cold aqueous solution of KPF_6

whereupon the blue solid of the desired complex precipitated immediately. The product was filtered, washed first with a small amount of cold water, then chloroform, and dried over P_2O_5 under vacuum.

$Ru(d_8\text{-bpy})_3(PF_6)_3$.[4] d_8-bpy and $RuCl_3$ were added to 25mL of 2-methoxyethanol. The mixture was heated by microwave reactor and kept at 120°C for 1 h. The solution was then filtered into a flask immersed in an ice bath and 2-3mL of 1M H_2SO_4 added. After further cooling, an excess of PbO_2 was added and the solution was mixed thoroughly until all traces of orange color had disappeared leaving a emerald green solution. This solution was filtered into a cold aqueous solution of KPF_6 whereupon the emerald green solid of the desired complex precipitated immediately. The product was filtered, washed first with a small amount of cold water, then chloroform, and dried over P_2O_5 under vacuum.

$M(d_8\text{-bpy})^{3+}$ oxidants were characterized by comparing its kinetic data with $M(bpy)^{3+}$ oxidants. All kinetic data that could be acquired using $M(bpy)_3{}^{3+}$ and $M(d_8\text{-bpy})_3{}^{3+}$ as oxidants were the same within experimental error. As these compounds were not stable for long periods of time at room temperature, they were stored below 5 °C and used rapidly after warming above this temperature

NMR Kinetic measurements

Bruker 500MHz with VT temperature unit was used for variable temperature NMR studies. Sample solutions for NMR measurement were prepared freshly in the dry box prior to use. Solutions of Metal(II) core dendrimers (M = Ru and Fe) in CD_2Cl_2:CD_3CN (5:1 v/v) were prepared and transferred to 5 mm Kontes brand threaded NMR tubes in the dry box. Total concentration was empirically chosen as a minimum concentration to show measurable NMR line broadenings. Aliquots (typically 10uL) of the oxidants ($NOPF_6$ or $M(d_8\text{-bpy})_3^{3+}$) in $CDCN_3$ were added to the NMR tube between each NMR measurements. Line widths were determined by fitting the experimental signals to a Lorenzian function using commercially available NUTs (Acorn software) and are reported in Hertz.

For various temperature kinetic studies the similar temperature range that was studied by Wahl *et al* on some similar compounds was used.[7-9] Sample tubes were equilibrated in the NMR probe at a given temperature for 10-15 min before acquisitions. Oxidized form of G0 complexes were stable enough for several weeks if it is stored below 5°C. However, oxidized form of higher generation dendrimers were very unstable at room temperature and could not be isolated from reaction mixture. It was reduced back to original oxidation state during purification steps. Instead, more stable oxidants, $M(d_8\text{-bpy})_3^{3+}$ were prepared and oxidized form of higher generation dendrimers were generated *in situ* during kinetic experiments using this oxidant.

The unbranched (e.g. zeroth generation) complexes, $Ru(G_0Bpy)_3^{2+}$ and $Fe(G_0Bpy)_3^{2+}$ could be oxidized chemically by lead(IV) oxide in acidic aqueous solution, isolated and added directly to the reduced form. The same spectral characteristics were obtained when $M(bpy)_3^{3+}$ was used as a sacrificial oxidant. ^{1}H-NMR spectra showed large contact shift for both cases (Figure 2A). The singlet corresponding to the methyl protons at 2.5 ppm on the dimethyl-bipyridine ligand was used to calculate the rate constant as it showed useful chemical shift movements and line broadening as the relative degree of oxidation of the complex was changed. The rate of the electron self-exchange for G0 complexes was found to be in the fast exchange limit, indicated by the linear relationship between the mole fraction, f_p and the chemical shift. The electron self-exchange rate constant was calculated using approximate equation in the fast exchange limit eq (1). The rates are provided in Table 2.

$$k_{ex} = \frac{4\pi f_p f_d (\delta\nu)^2}{(W_{DP} - f_d W_D - f_p W_P) C_{tot}} \qquad (1)$$

For the first through third generation dendrimers, ^{1}H-NMR line broadening experiment data were fit to the slow exchange equation (2) and average k_{ex} values were determined from slopes of plots $\pi(W_{DP}-W_D)$ vs the concentration of added oxidant ($Fe(d_8\text{-}Bpy)_3(PF_6)_3$, Figure S1). It was confirmed that (1) there was complete reduction of the sacrificial oxidant by NMR, that (2) $M(G_nBpy)_3^{3+}$ could be generated as the sole species using stoichiometric sacrificial oxidant (3) and that the line width and spectral appearance did not change any further upon addition of excess $Fe(d_8\text{-}Bpy)_3(PF_6)_3$. The resonance of the proton in the ortho position to the dendron on the bipyridine ligand near 8.2ppm in ^{1}H-NMR spectra was monitored. This signal was chosen instead of the methylene signal analogous to the methyl signal in $M(G_0Bpy)_3^{2+}$ to avoid the necessity to deconvolute spin-spin coupling of the methylene group from line broadening due to exchange. In the slow, exchange limit:

$$k_{ex} = \frac{\pi(W_{DP} - W_D)}{[P]} \qquad (2)$$

where $\delta\nu$ is the contact shift in Hz (chemical shift movements caused by paramagnetic electrons, that is the chemical shift difference between pure diamagnetic and pure paramagnetic species which are measured separately), f_p and f_d are the mole fractions of paramagnetic and diamagnetic species respectively, W_P, W_D, and W_{DP} are the peak width (full line width at half-maximum) for paramagnetic species only, diamagnetic species only, and the mixture of two species respectively, C_{tot} is total molar concentration and [P] is molar concentration of paramagnetic species. Values for f_p for the fast exchange system were more precisely determined using eq. (5) to reduce uncertainties in the measurement of concentration .

$$f_p = \frac{|v_{dp} - v_d|}{\delta v} \tag{3}$$

assuming that the chemical shifts vary linearly with mole fraction. v_d and v_{dp} are the resonance frequency of the diamagnetic species and the mixture respectively.

In several attempts, ^{1}H-NMR line broadening for $Ru(G_nbpy)_3^{3+}$(n=1, 2) occurred after a considerable amount of oxidant (c.a. 0.3 mole fraction) was added. The y-intercept in a line broadening vs $[Ru(Gn)_3^{3+}]$ plot was significantly different from its expected value of zero although the data followed a linear behavior in the plot. It was thought that ruthenium complexes are more sensitive for reductive impurities in dendrimer solution comparing with iron complexes due to their relatively higher thermodynamic redox potentials. Indeed, $Ru(bpy)_3^{3+}$ is more unstable at room temperature compared with $Fe(bpy)_3^{3+}$. Thus, slightly modified methods were employed to determine the electron self exchange rate for ruthenium core dendrimers. Small volumes of concentrated oxidant, $Ru(bpy)_3^{3+}$ solution were added to dendrimer solution to oxidize spurious reductive impurities until line broadening occurred. The oxidized dendrimers produced were unstable toward re-reduction at room temperature and were observed to become reduced back to their original oxidation states within around 1 hour as evidenced by a disappearance of line-broadening indicative of the self-exchange with oxidized dendrimer. After this treatment, another line broadening experiment was performed within 20 min. During this time, no considerable line narrowing by adventitious reduction was observed and successive broadened signals were observed giving linearity in a plot of line broadening vs $Ru(G_n\text{-}bpy)_3^{3+}$ plot and near zero intercept (Figure S3).

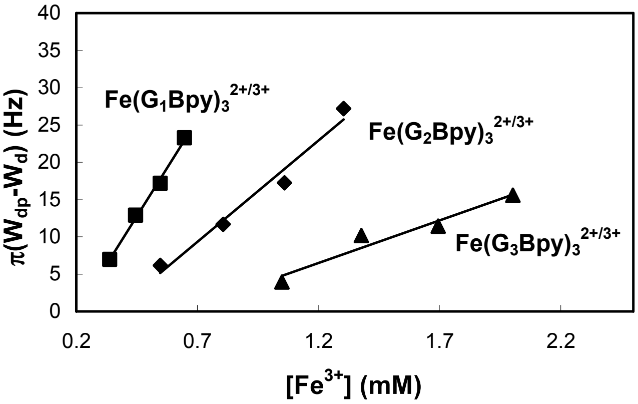


Figure S1. A plot of line broadening versus the concentration of $Fe(G_nBpy)_3^{3+}$ (n = 1, 2, 3).

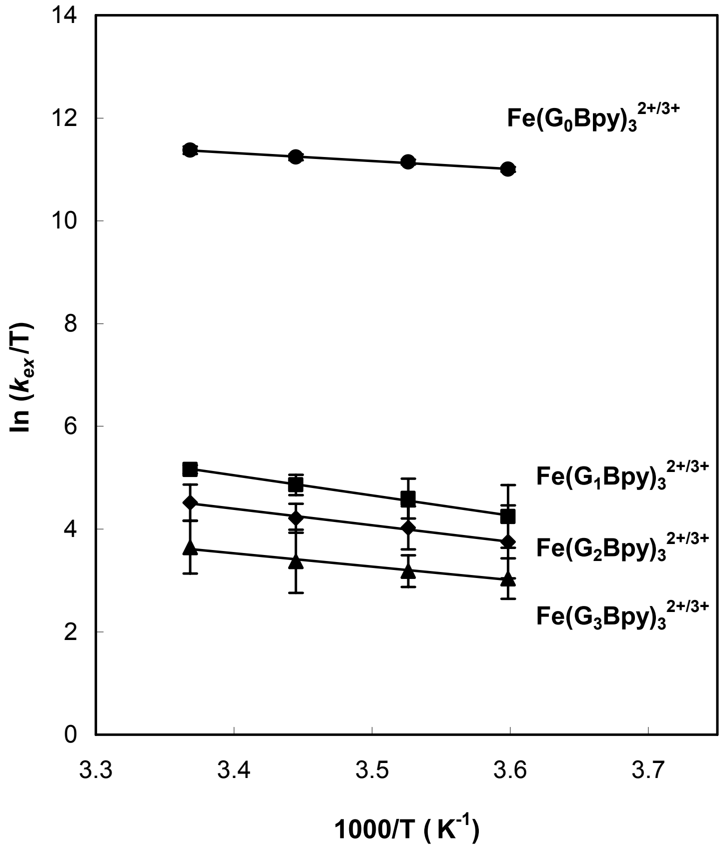


Figure S2. Eyring plot of electron self-exchange rate constants for Fe(G$_n$Bpy)$_3^{2+/3+}$.

Table S1. NMR kinetic data for M(G0Bpy), M=Fe or Ru

Comp.	Temp(K)	Wd(Hz)	Wp(Hz)	vd(Hz)	vp(Hz)	Ctot(mM)	fp	Wdp(Hz)	vdp(Hz)
Fe(G0Bpy)	297	1.64	48.06	1270	7706.64	11.2	0.017	31.30	1383.35
						11.3	0.034	61.11	1494.30
						11.3	0.050	94.36	1604.96
						11.4	0.065	125.58	1703.94
	290	1.09	46.10	1268	7841.84	11.2	0.017	37.20	1380.94
						11.3	0.035	72.80	1495.97
						11.3	0.052	111.01	1611.05
						11.4	0.066	146.96	1700.37
	284	1.59	44.33	1265	7976.34	11.2	0.017	44.32	1381.20
						11.3	0.035	86.67	1499.58
						11.3	0.052	130.54	1613.39
						11.4	0.067	172.45	1713.10
	278	2.29	42.21	1262.14	8120.62	11.2	0.017	52.50	1376.48
						11.3	0.034	103.73	1493.55
						11.3	0.050	153.15	1603.43
						11.4	0.065	203.64	1705.72
Ru(G0Bpy)	297	1.84	384.57	1267.95	11606.95	10.7	0.012	52.40	1393.58
						10.7	0.029	119.28	1570.48
						10.8	0.053	203.83	1819.48
						10.8	0.075	259.78	2048.07

Table S2. NMR kinetic data for M(G_nBpy) (M=Fe or Ru, n=1,2 or 3)

Comp.	Temp. (K)	W_d (Hz)	$[Fe^{3+}]$ (mM)	W_{dp} (Hz)	Comp.	Temp. (K)	W_d (Hz)	$[Fe^{3+}]$ (mM)	W_{dp} (Hz)
Fe(G_1Bpy)	297	4.34	0.34	6.55	Fe(G_2Bpy)	297	5.99	0.55	7.94
			0.44	8.44				0.81	9.70
			0.55	9.80				1.06	11.48
			0.65	11.75				1.30	14.64
	290	4.58	0.34	6.66		290	6.19	0.55	8.57
			0.44	7.61				0.81	9.57
			0.55	9.15				1.06	11.47
			0.65	10.23				1.30	13.20
	284	4.85	0.34	6.69		284	6.57	0.55	8.78
			0.44	7.16				0.81	9.36
			0.55	8.54				1.06	11.31
			0.65	9.29				1.30	12.38
	278	5.18	0.34	6.91		278	6.98	0.55	9.34
			0.44	7.02				0.81	9.57
			0.55	8.11				1.06	11.50
			0.65	8.67				1.30	11.87

Table S3. NMR kinetic data for M(G_nBpy) (M=Fe or Ru, n=1,2 or 3)

Comp.	Temp. (K)	W_d (Hz)	[Fe^{3+}] (mM)	W_{dp} (Hz)	Comp.	Temp. (K)	W_d (Hz)	[Fe^{3+}] (mM)	W_{dp} (Hz)
Fe(G_3Bpy)	297	17.31	1.05	18.56	Ru(G_1Bpy)	297	4.02	3.81	13.41
			1.38	20.55				3.75	18.44
			1.69	20.94				3.69	24.44
			2.00	22.26				3.64	29.41
	290	17.27	1.05	19.94				3.58	36.02
			1.38	21.43				3.53	37.85
			1.69	22.22				3.48	42.45
			2.00	22.52	Ru(G_2Bpy)	297	6.08	0.45	11.68
	284	17.33	1.05	21.77				0.67	16.12
			1.38	22.55				0.88	20.30
			1.69	23.42				1.08	24.35
			2.00	23.78				1.28	26.78
	278	18.79	1.05	23.30				1.47	30.26
			1.38	23.59					
			1.69	24.31					
			2.00	25.02					

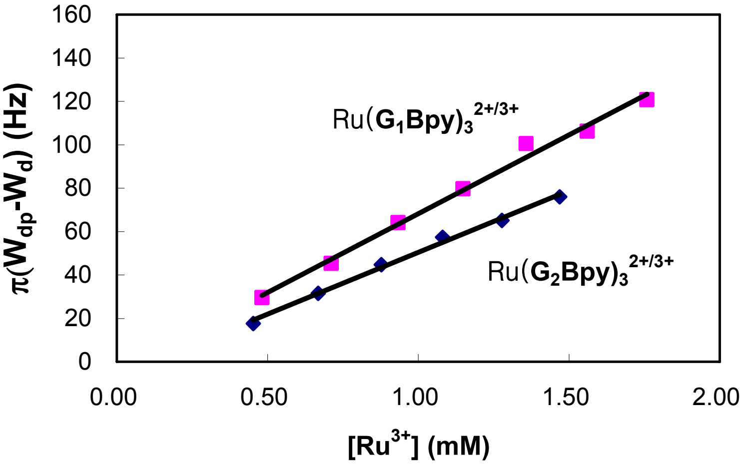


Figure S3. A plot of line broadening versus the concentration of $Ru(GnBpy)_3^{3+}$ (n = 1, 2).

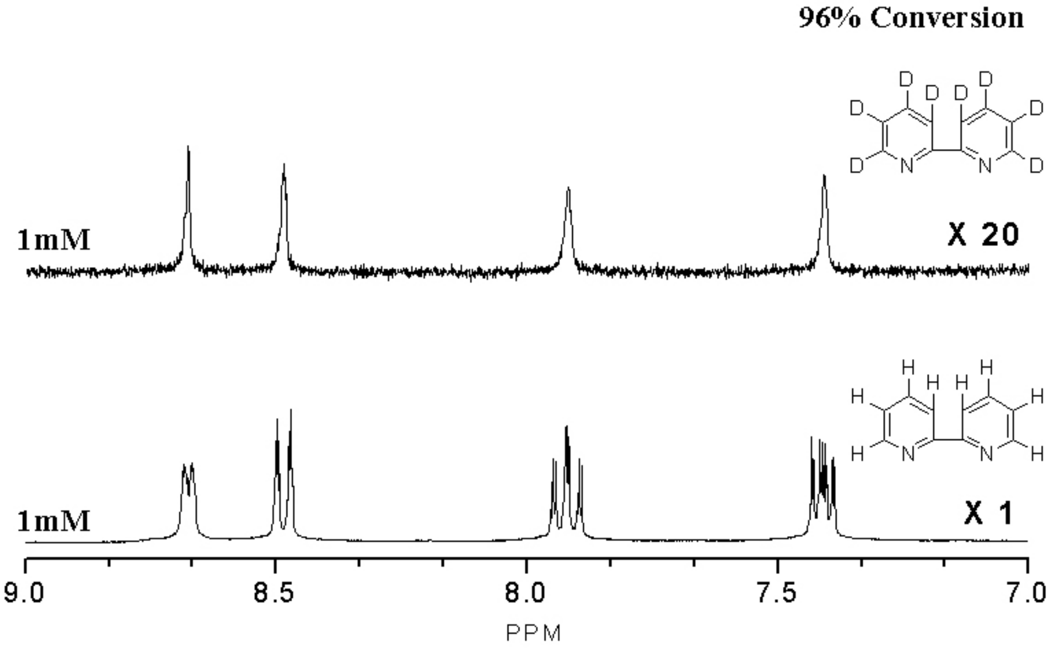


Figure S4. ^1H-NMR spectra for ^1H-bipyridine and ^2H-bipyridine.

Figure S5. ^{1}H NMR of G$_1$Bpy Dendron.

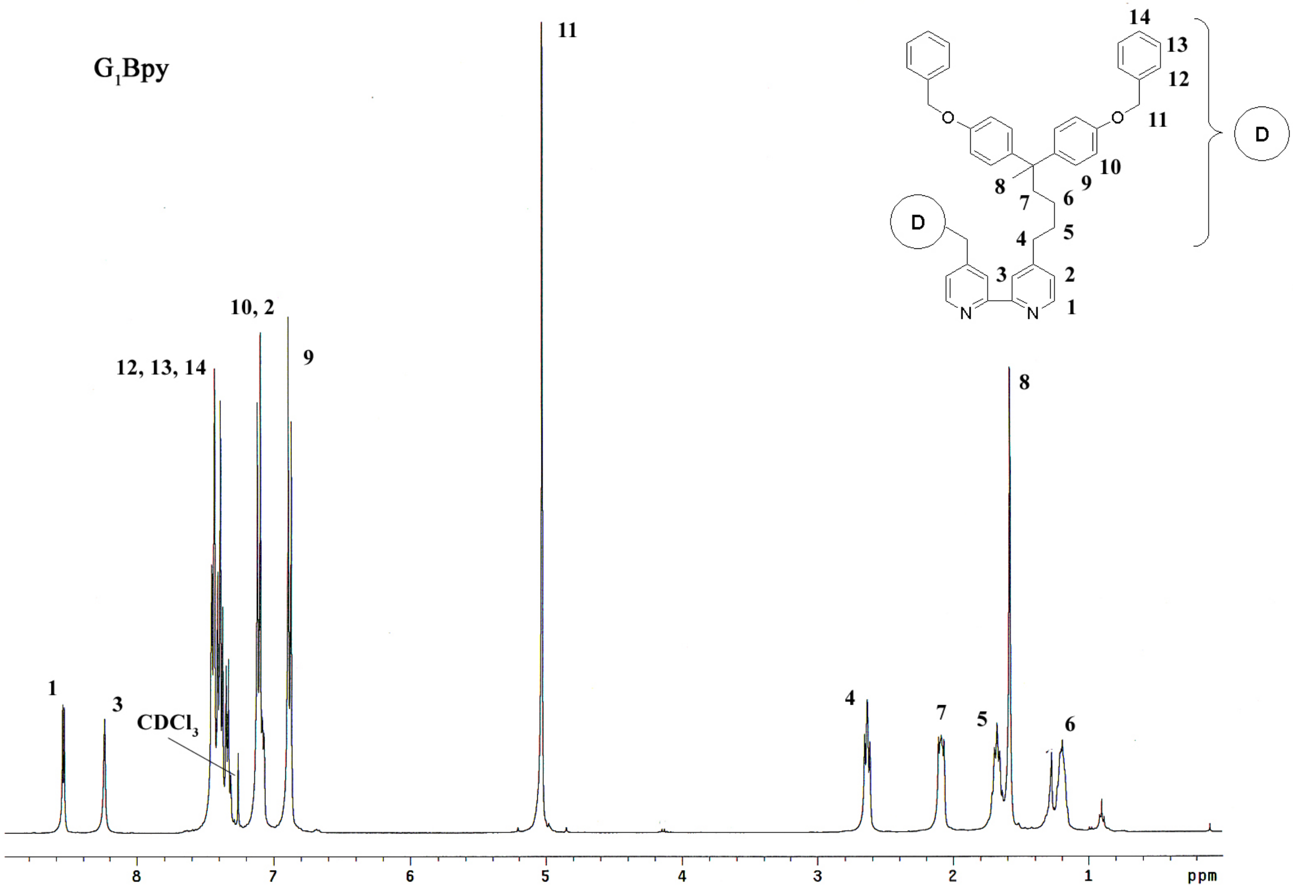


Figure S6. ^{1}H NMR of G_2Bpy Dendron.

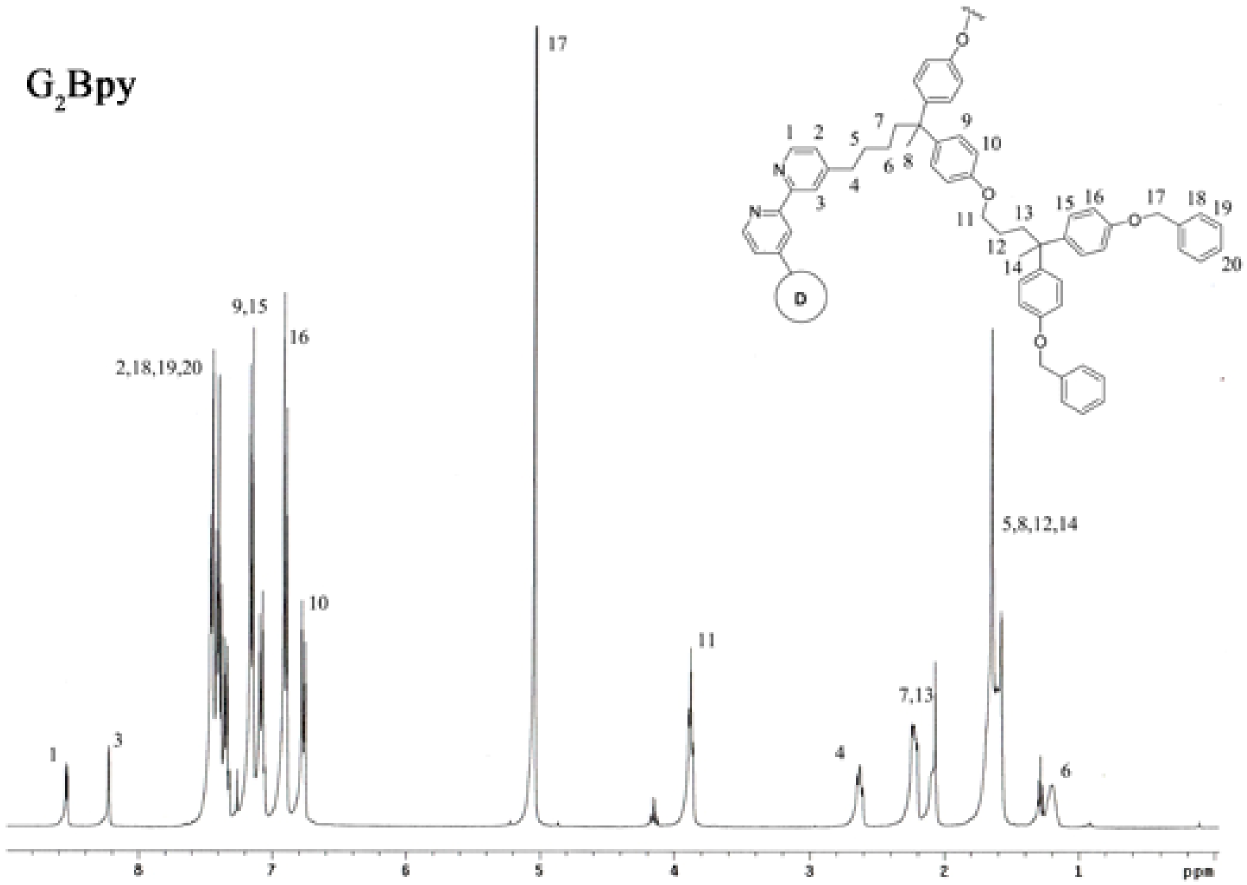


Figure S7. ^{1}H NMR of G_3Bpy Dendron.

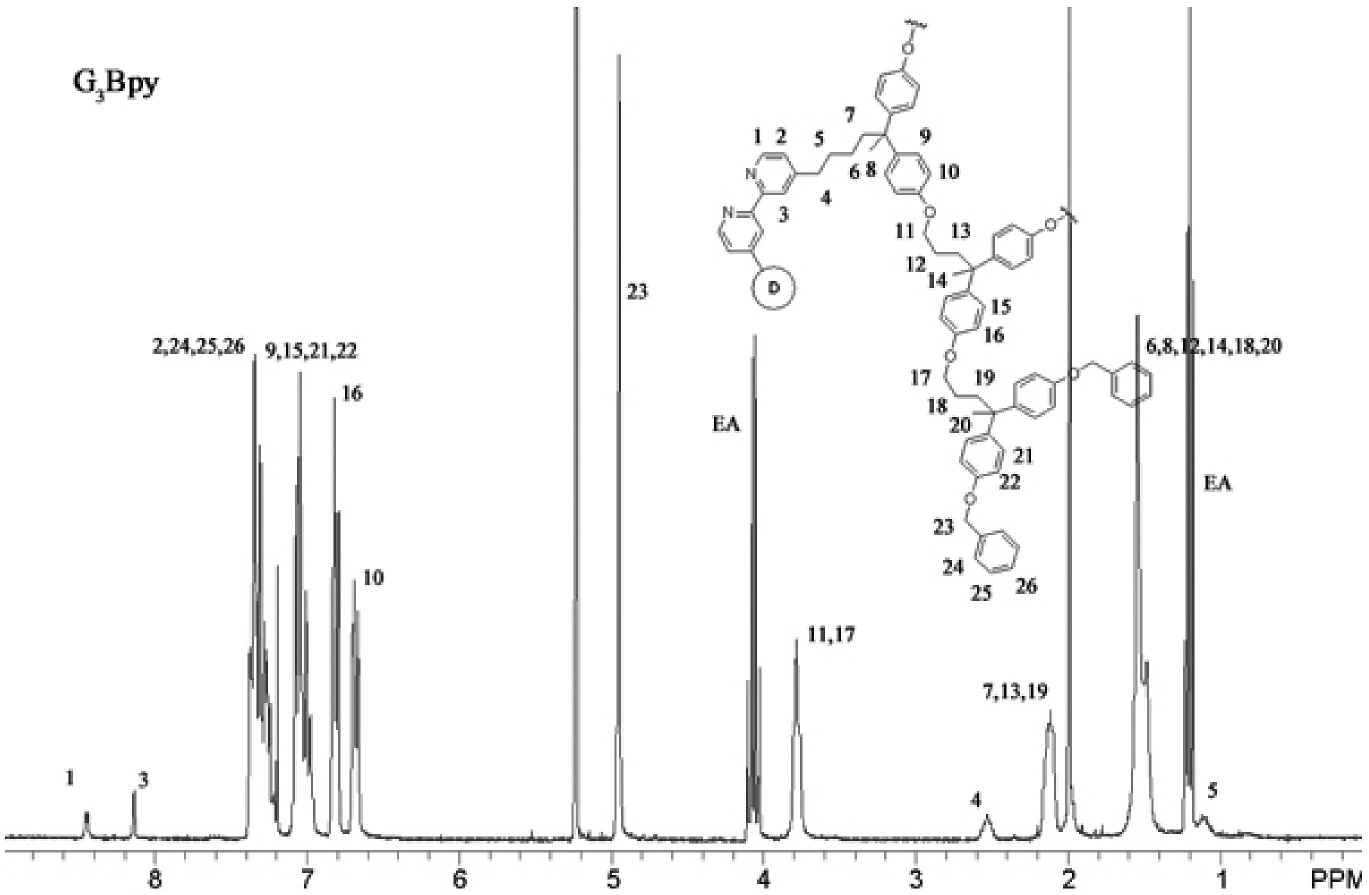


Figure S8. ^{1}H NMR of $Fe(G_1Bpy)_3(PF_6)_2$.

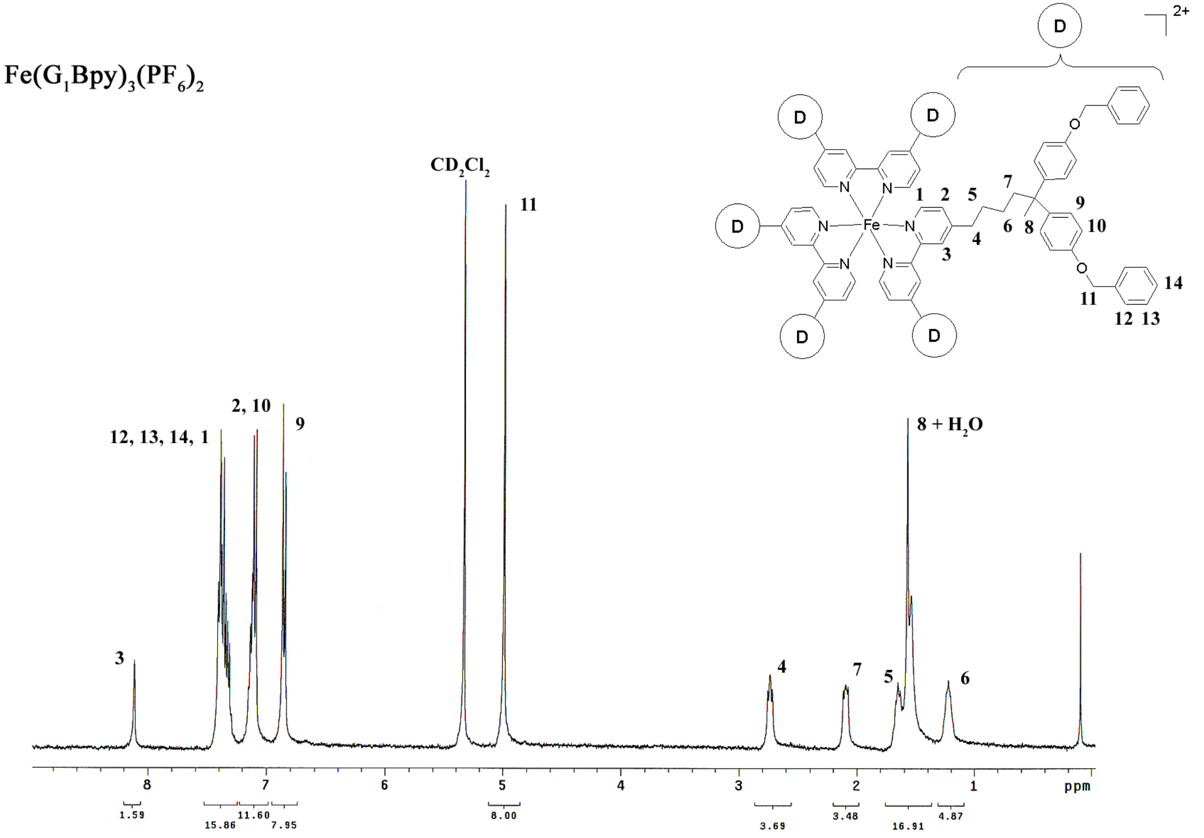


Figure S9. ^{1}H NMR of $Fe(G_2Bpy)_3(PF_6)_2$.

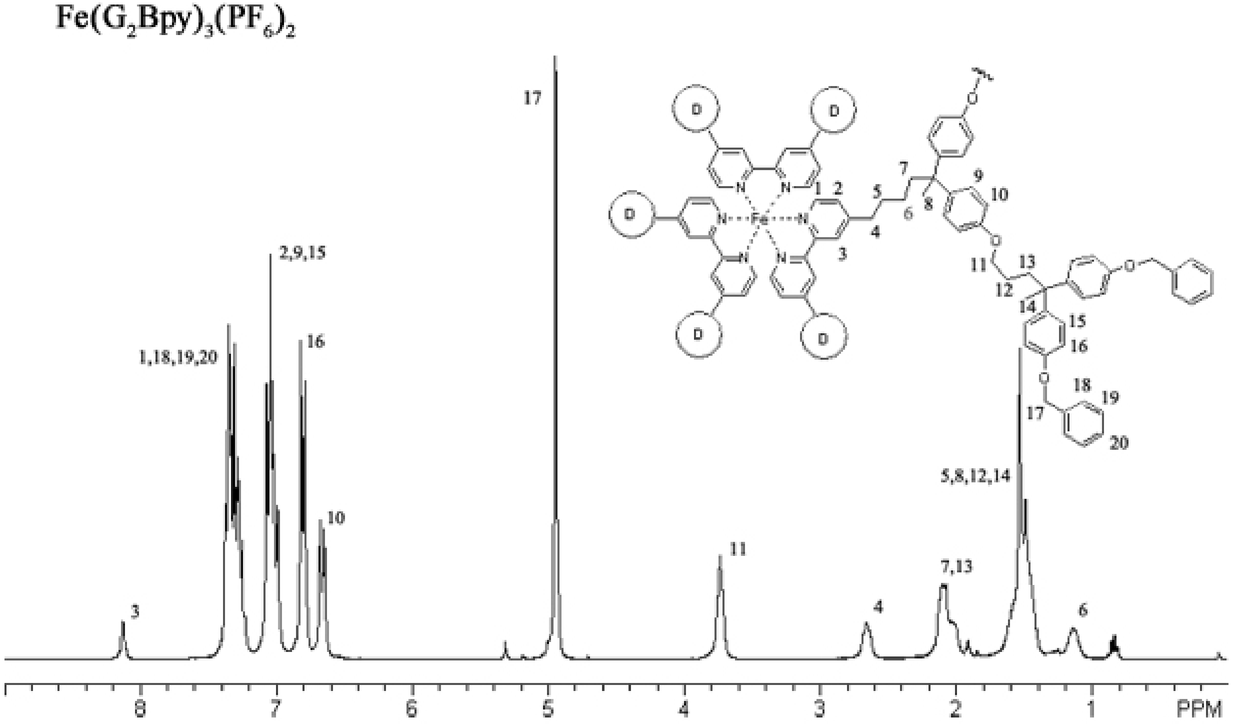


Figure S10. ^{1}H NMR of $Fe(G_3Bpy)_3(PF_6)_2$.

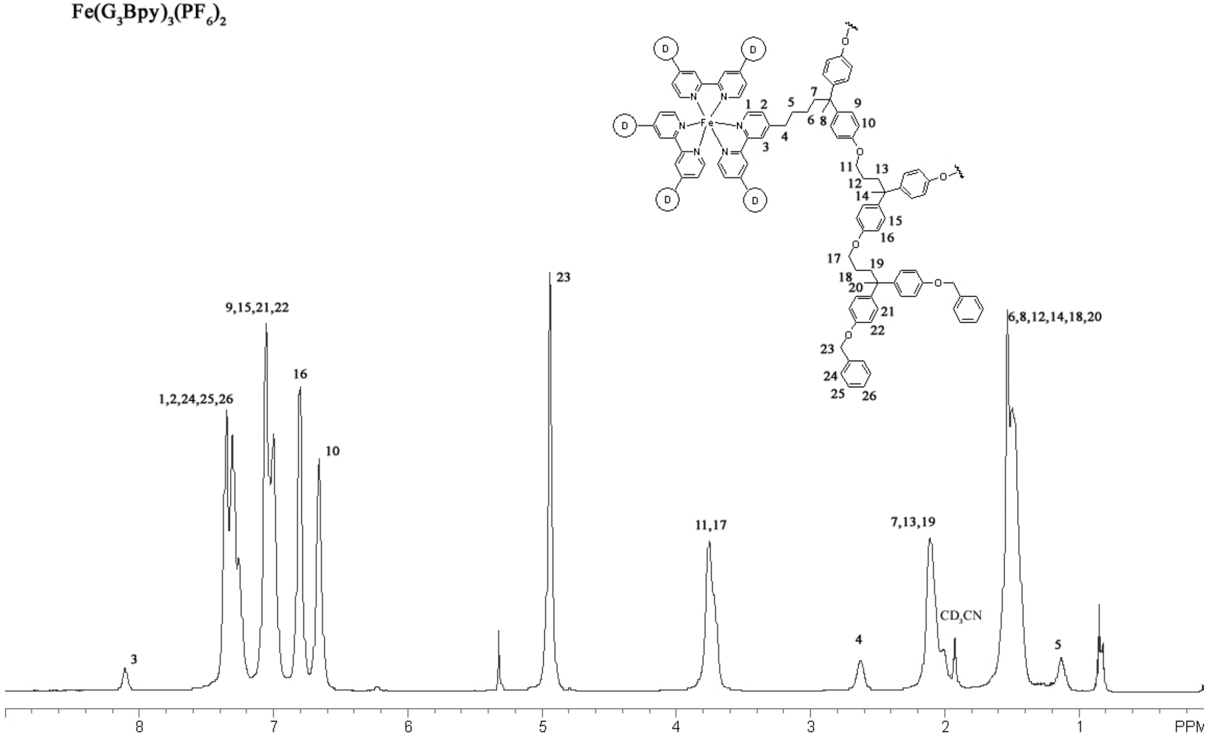


Figure S11. ^{1}H NMR of Ru(G$_1$Bpy)$_3$(PF$_6$)$_2$.

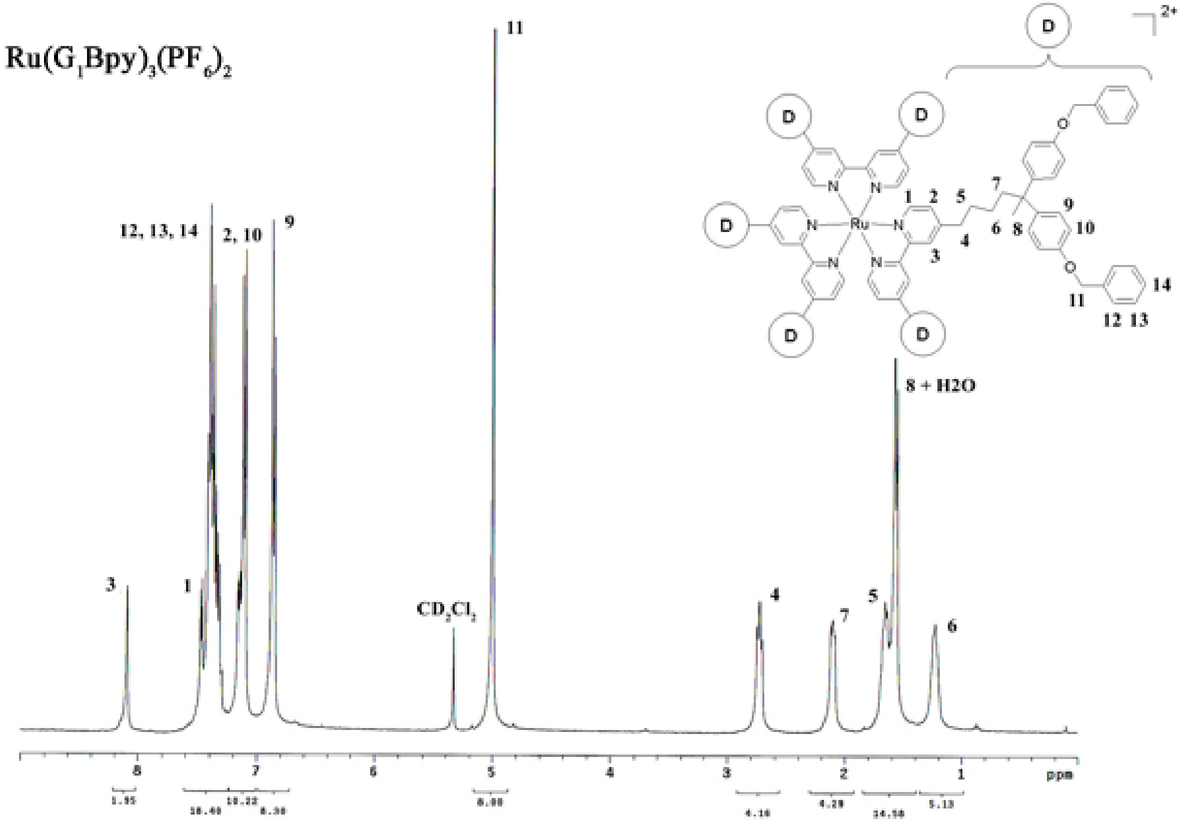
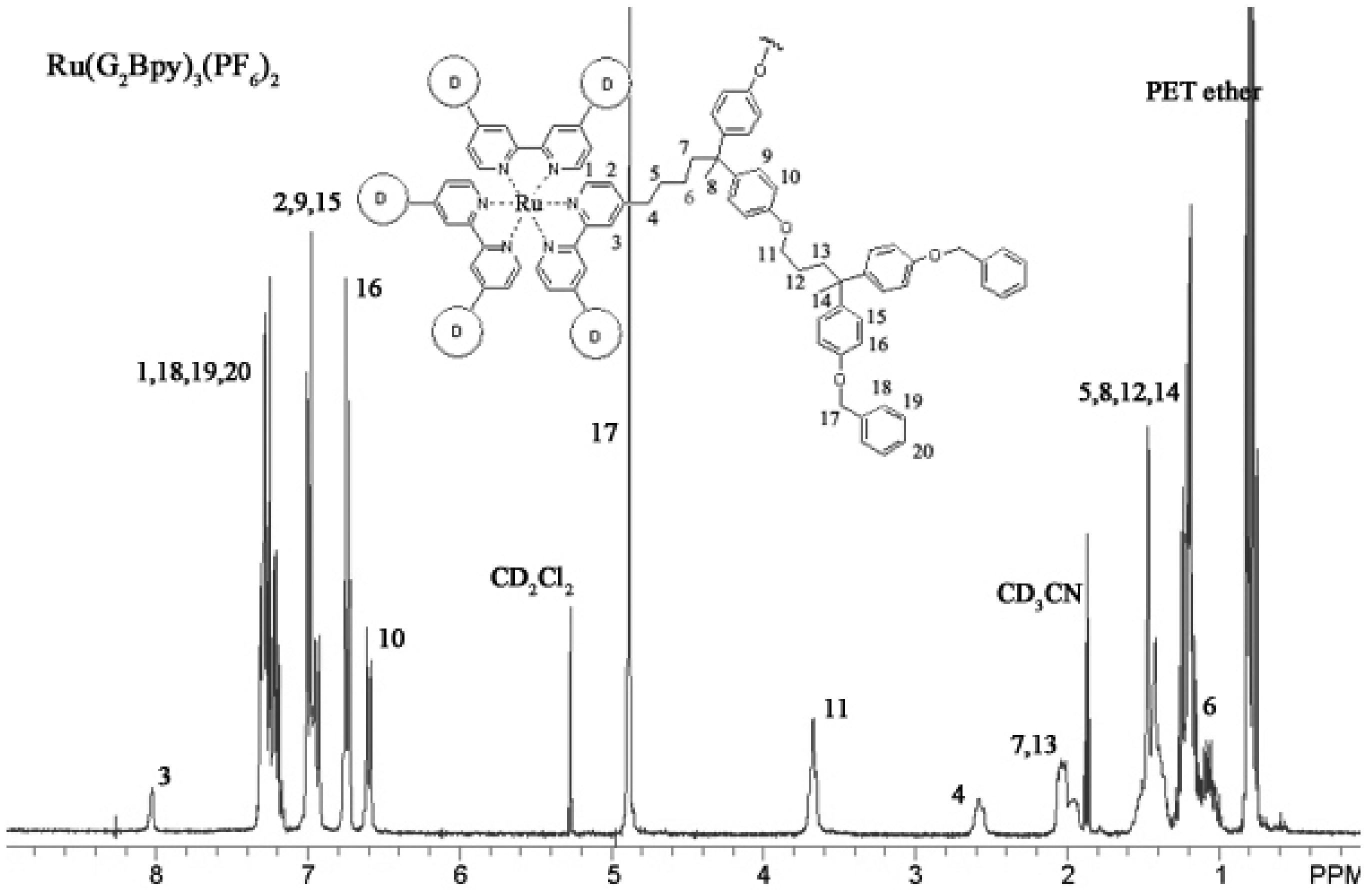


Figure S12. ^{1}H NMR of $Ru(G_2Bpy)_3(PF_6)_2$.



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