Metal Corroles as Electrocatalysts for Oxygen Reduction

James P. Collman,* Marina Kaplun, Richard A. Decréau

Supplementary information.

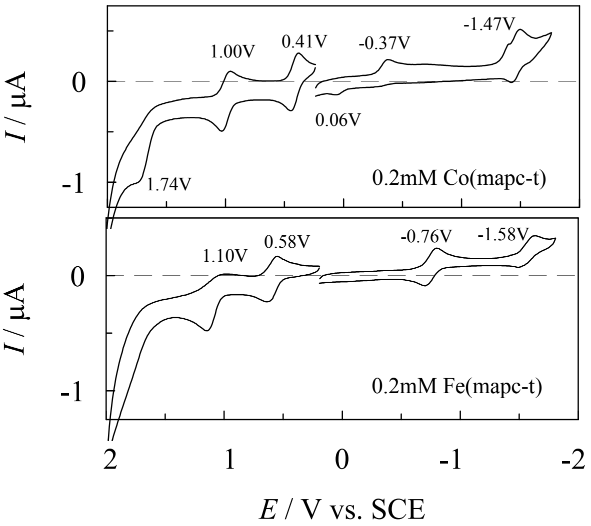


Figure S1. Cyclic voltammograms of 0.2 mM Co(mapc-t) and Fe(mapc-t) in MeCN, 0.1 M $TBAPF_6$, $v = 0.1\ V\ s^{-1}$, N_2.

The first reduction (–0.37 V for Co and –0.76 V for Fe) is M(III/II) transition.

1ml cell, Pt working (0.785 mm^2) and auxiliary electrodes, reference electrode Ag/0.1M $AgNO_3$, MeCN, 0.1 M $TBAPF_6$. Recalculated to SCE using ferrocene as an internal standard: $E^{0/}(Fc/Fc^+)$ = 0.039 V vs. Ag/0.1M $AgNO_3$; 0.382 V vs. SCE.

Results on Co(mapc-t).

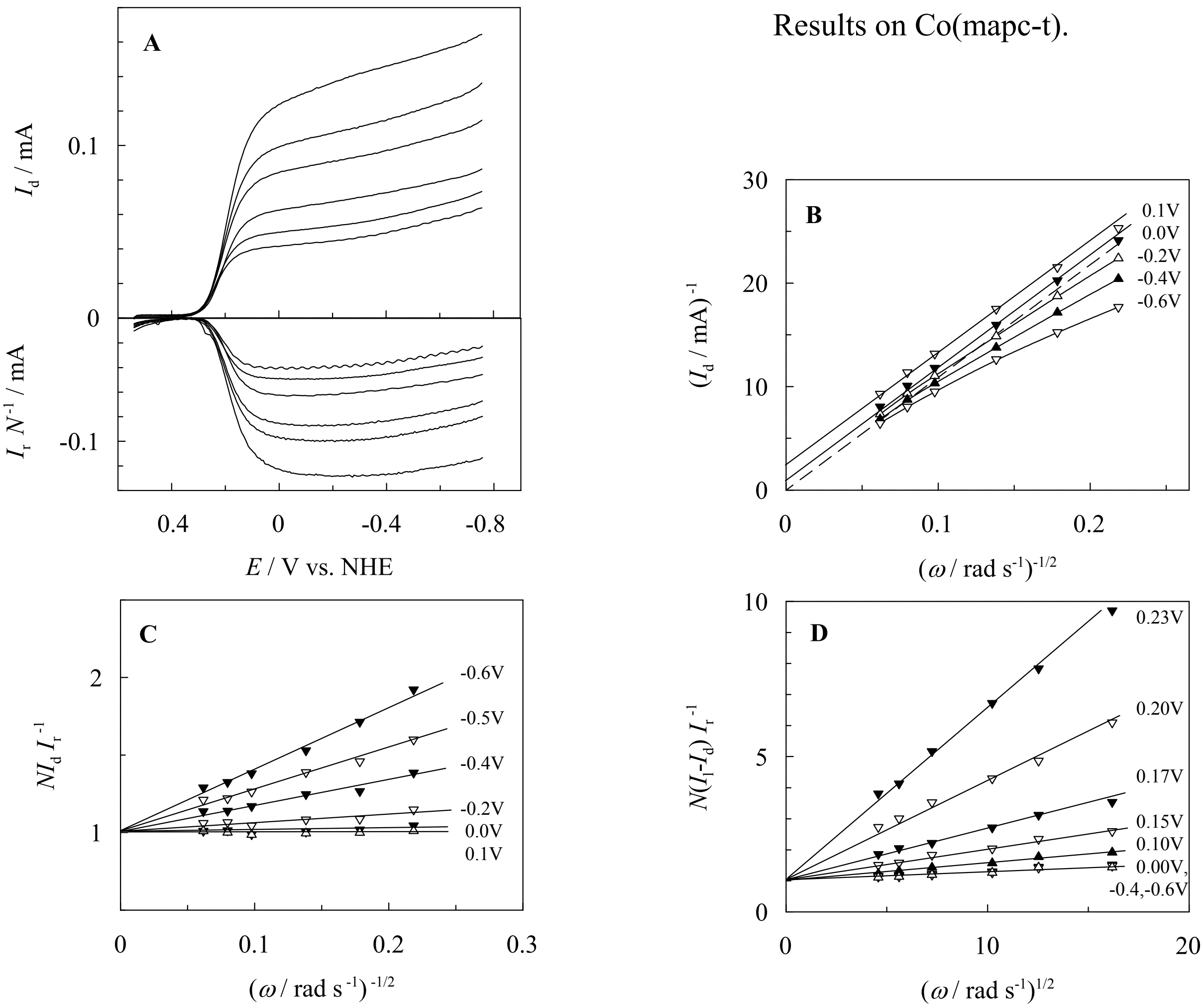


Figure S2. (A) Rotating ring disk electrode data for the reduction of 0.24 mM O_2 at Co(mapc-t) adsorbed on EPG. 0.1M KNO_3, pH 7, E_{ring} = 0.5V *vs.* SCE, $v = 0.02\ V\ s^{-1}$, rotation speeds are 200, 300, 500, 1000, 1500, 2500 rpm, $\Gamma = 1.5\ nmol\ cm^{-2}$. **(B)** Koutecky-Levich plots of the data from (A) at different potentials. The dashed line represents the response calculated for the diffusion limited two-electron reduction. **(C)** The ratio of the disk to ring current as a function of $\omega^{-1/2}$ obtained from data of (A). **(D)** The plot of $N(I_l–I_d)/I_r$ *vs*. $\omega^{1/2}$ obtained from data of (A).

Results on Fe(tpfc)Cl.

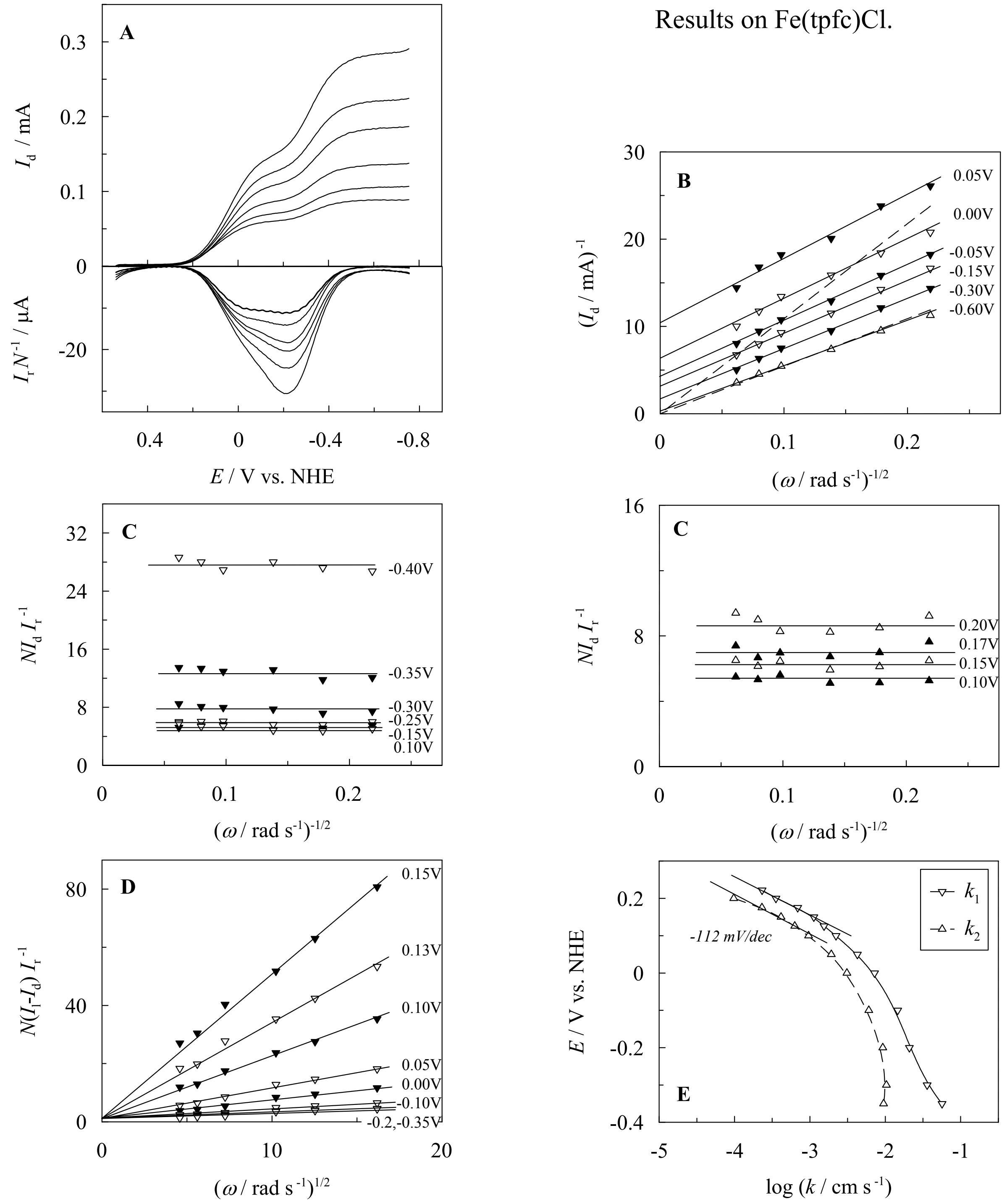


Figure S3. (A) Rotating ring disk electrode data for the reduction of O_2 at Fe(tpfc)Cl adsorbed on EPG. 0.1M KNO_3, pH 7, E_{ring} = 0.5V *vs.* SCE, v = 0.02 V s^{-1}, rotation speeds are 200, 300, 500, 1000, 1500, 2500 rpm, Γ = 1.5 nmol cm^{-2}. **(B)** Koutecky-Levich plots of the data from (A) at different potentials. The dashed line represents the response calculated for the diffusion limited two- and four-electron reduction. **(C)** The ratio of the disk to ring current as a function of $\omega^{-1/2}$ obtained from data of (A). **(D)** The plot of $N(I_l-I_d)/I_r$ *vs.* $\omega^{1/2}$ obtained from data of (A). **(E)** Potential dependence of the heterogeneous rate constants for the $2e^-$ (k_2) and $4e^-$ (k_1) reduction of O_2.

Results on Fe(mapc-t).

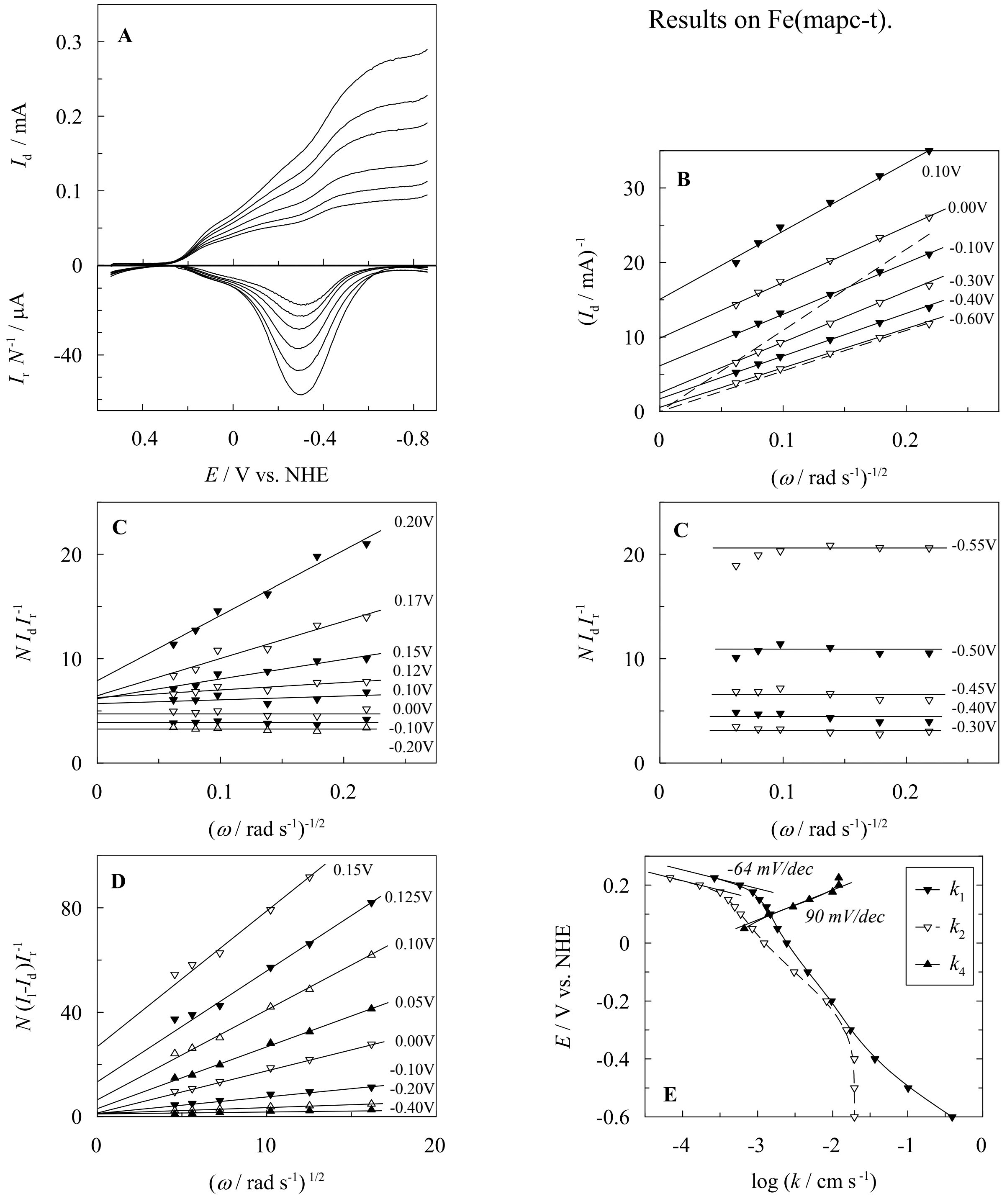
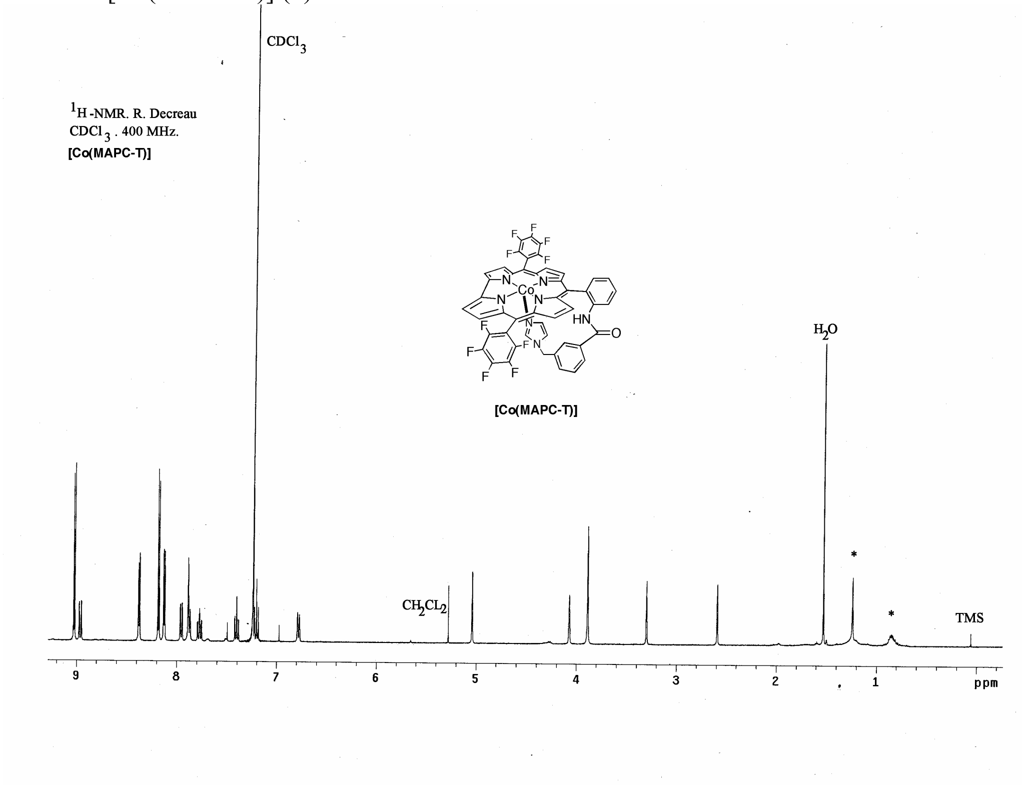
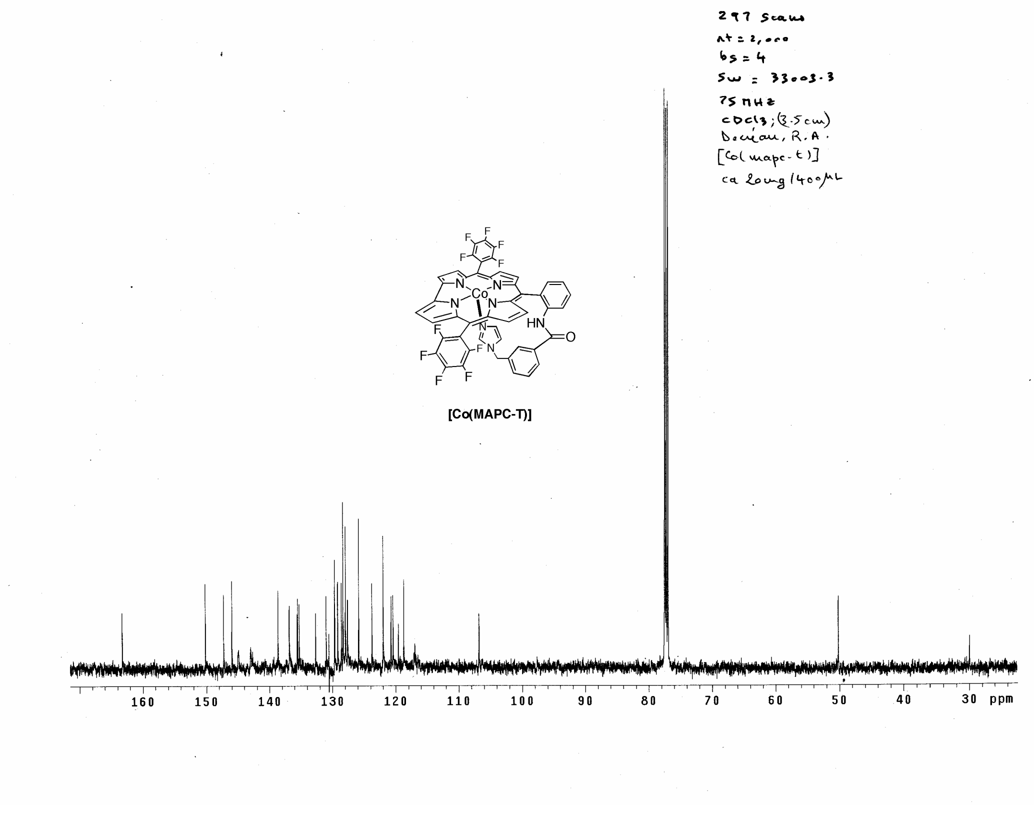


Figure S4. **(A)** Rotating ring disk electrode data for the reduction of O_2 at Fe(mapc-t) adsorbed on EPG. 0.1M KNO_3, pH 7, E_{ring} = 0.5V *vs.* SCE, v = 0.04 V s^{-1}, rotation speeds are 200, 300, 500, 1000, 1500, 2500 rpm, Γ = 3.0 nmol cm^{-2}. **(B)** Koutecky-Levich plots of the data from (A) at different potentials. The dashed line represents the response calculated for the diffusion limited two- and four-electron reduction. **(C)** The ratio of the disk to ring current as a function of $\omega^{-1/2}$ obtained from data of (A). **(D)** The plot of $N(I_l–I_d)/I_r$ *vs.* $\omega^{1/2}$ obtained from data of (A). **(E)** Potential dependence of the heterogeneous rate constants for the 2e$^-$ (k_2) and 4e$^-$ (k_1) reduction of O_2 and for catalytic dismutation of H_2O_2 (k_4).

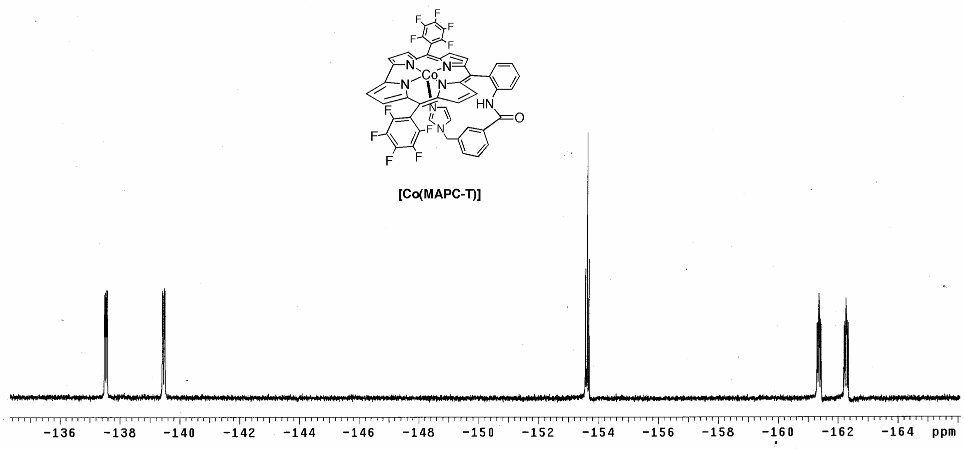
[1]H-NMR [Co(MAPC-T)] (**6**)



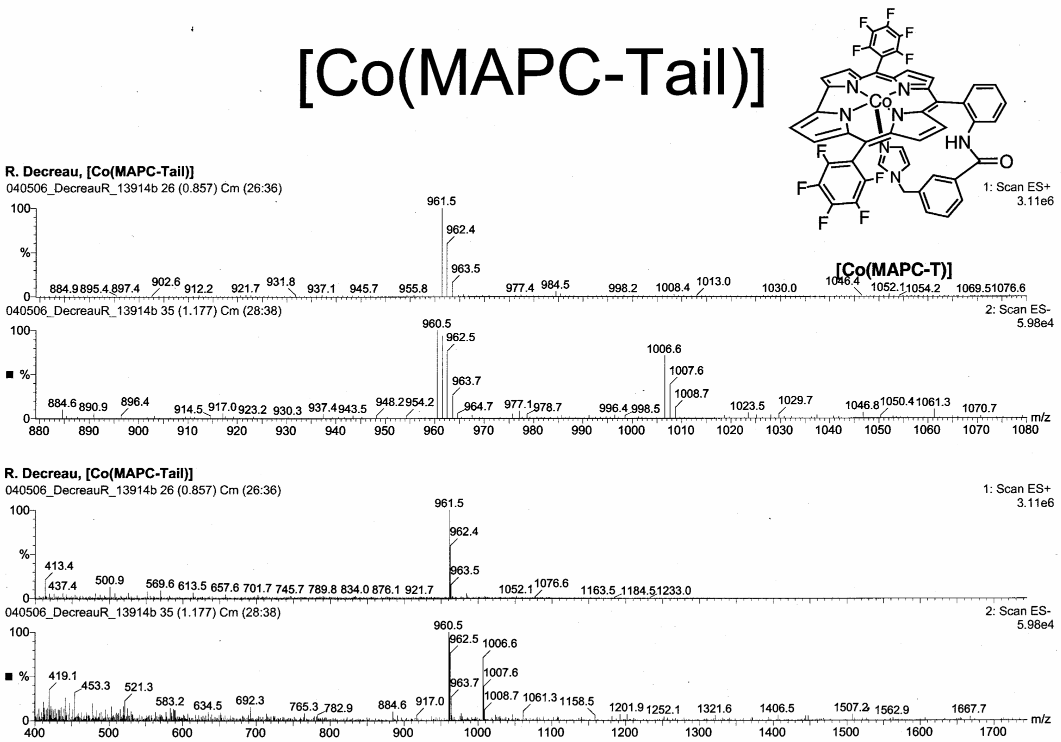
[13]C-NMR [Co(MAPC-T)] (**6**)



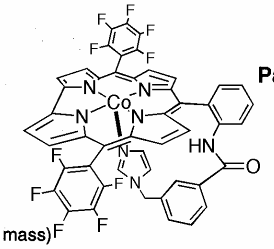
[19]F-NMR [Co(MAPC-T)] (**6**)



MS [Co(MAPC-T)] (**6**)



HRMS [Co(MAPC-T)] (**6**)

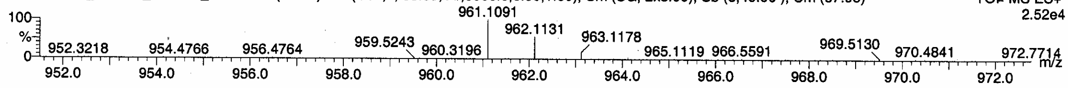


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

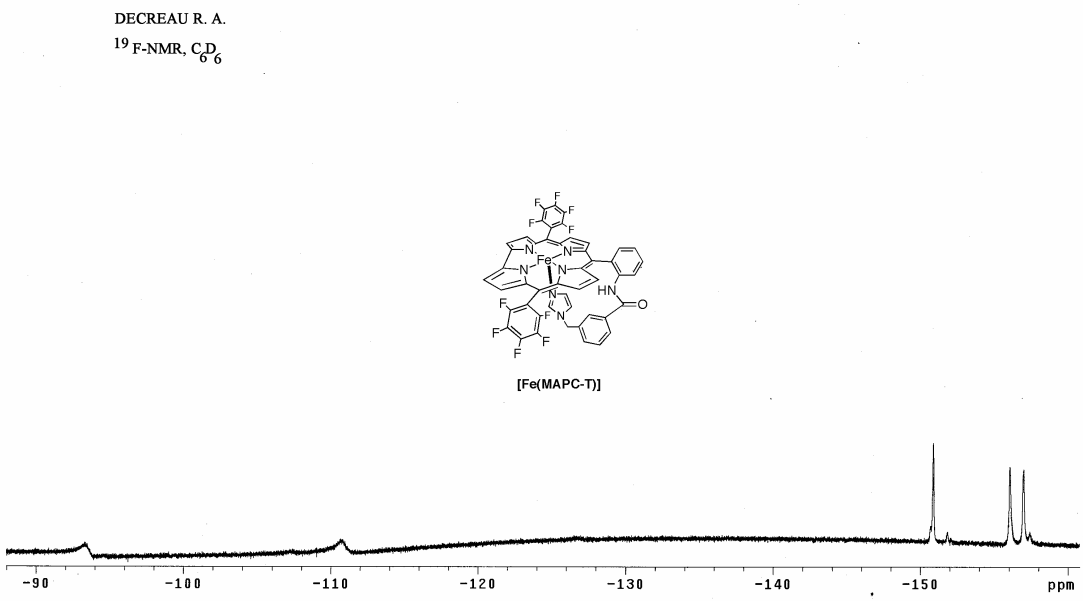
Monoisotopic Mass, Odd and Even Electron Ions
28109 formula(e) evaluated with 236 results within limits (up to 200 closest results for each mass)

Richard Decreau, [Co(TIAPC-T)] Cone V = 38 Coll V = 10.0 **[Co(MAPC-T)]** 05-May-2005 13:30:34
DECREAUR_050505_15596B_HRMS 91 (1.570) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (3,40.00); Cm (67:95) TOF MS ES+ 2.52e4

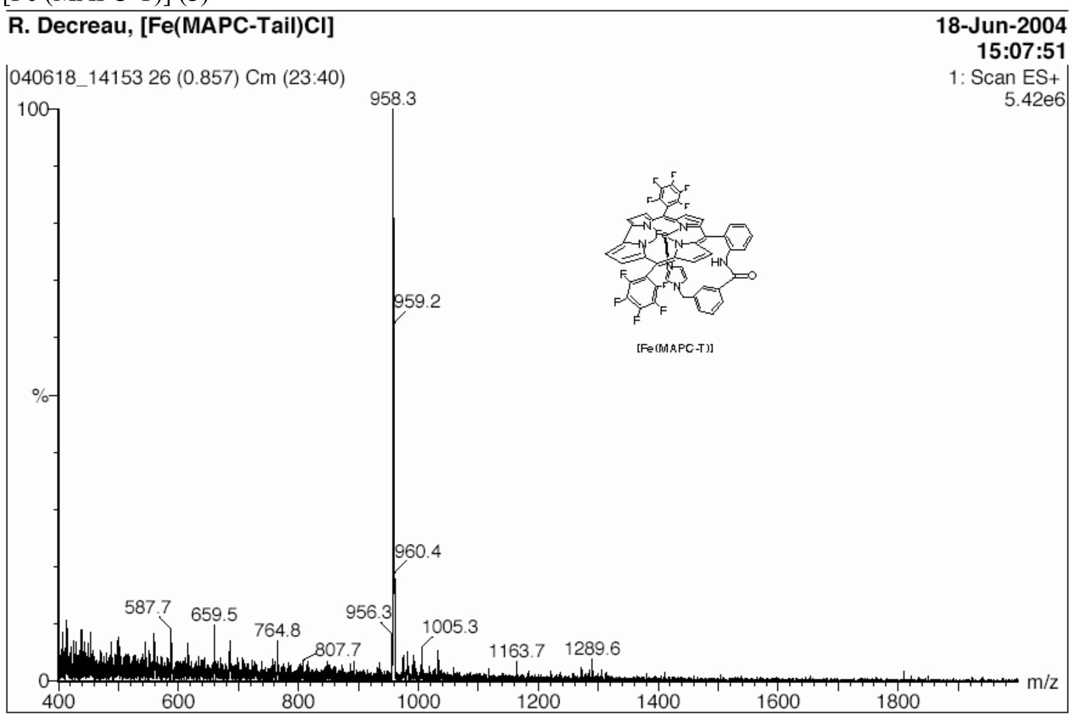


Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
961.1091	961.1051	4.0	4.2	47.5	188	C61 H23 N F7 Co
	961.1053	3.8	3.9	34.5	97	C43 H18 N8 O9 F9
	961.1054	3.7	3.9	31.5	121	C42 H24 N9 O6 F8 Co
	961.1054	3.7	3.8	24.0	180	C39 H26 N6 O6 F12 Co
	961.1055	3.6	3.8	45.5	81	C51 H17 N8 O9 F4
	961.1055	3.6	3.7	38.0	5	C48 H19 N5 O9 F8
	961.1055	3.6	3.7	42.5	62	C50 H23 N9 O6 F3 Co
	961.1055	3.6	3.7	36.0	78	C44 H15 N9 O4 F12
	961.1055	3.6	3.7	30.5	96	C45 H21 N2 O9 F12
	961.1056	3.5	3.7	35.0	18	C47 H25 N6 O6 F7 Co
	961.1056	3.5	3.6	33.0	105	C43 H21 N10 O F11 Co
	961.1056	3.5	3.6	27.5	118	C44 H27 N3 O6 F11 Co
	961.1057	3.4	3.6	49.0	159	C56 H18 N5 O9 F3
	961.1057	3.4	3.5	47.0	98	C52 H14 N9 O4 F7
	961.1057	3.4	3.5	41.5	83	C53 H20 N2 O9 F7
	961.1057	3.4	3.5	46.0	144	C55 H24 N6 O6 F2 Co
	961.1057	3.4	3.5	39.5	12	C49 H16 N6 O4 F11
	961.1058	3.3	3.5	44.0	79	C51 H20 N10 O F6 Co
	961.1058	3.3	3.5	38.5	65	C52 H26 N3 O6 F6 Co
	961.1058	3.3	3.4	36.5	30	C48 H22 N7 O F10 Co
	~~961.1058~~	~~3.3~~	~~3.4~~	~~31.0~~	~~16~~	~~C49 H28 O6 F10 Co~~
	961.1059	3.2	3.3	49.5	191	C60 H25 N3 O6 F Co
	961.1059	3.2	3.3	43.0	99	C54 H17 N3 O4 F10
	961.1060	3.1	3.3	47.5	156	C56 H21 N7 O F5 Co
	961.1060	3.1	3.2	42.0	145	C57 H27 O6 F5 Co
	961.1060	3.1	3.2	40.0	80	C53 H23 N4 O F9 Co
	961.1061	3.0	3.1	46.5	168	C59 H18 O4 F9
	961.1062	2.9	3.0	43.5	157	C58 H24 N O F8 Co
	961.1064	2.7	2.8	30.5	152	C40 H19 N8 O10 F10
	961.1065	2.6	2.7	27.5	167	C39 H25 N9 O7 F9 Co
	961.1066	2.5	2.6	41.5	14	C48 H18 N8 O10 F5
	961.1066	2.5	2.6	34.0	70	C45 H20 N5 O10 F9
	961.1067	2.4	2.5	38.5	4	C47 H24 N9 O7 F4 Co
	961.1067	2.4	2.5	31.0	90	C44 H26 N6 O7 F8 Co
	961.1068	2.3	2.4	29.0	158	C40 H22 N10 O2 F12 Co
	961.1068	2.3	2.4	23.5	165	C41 H28 N3 O7 F12 Co
	961.1068	2.3	2.4	45.0	111	C53 H19 N5 O10 F4
	961.1068	2.3	2.4	43.0	36	C49 H15 N9 O5 F8
	961.1068	2.3	2.3	37.5	17	C50 H21 N2 O10 F8
	961.1069	2.2	2.3	42.0	89	C52 H25 N6 O7 F3 Co
	961.1069	2.2	2.3	35.5	54	C46 H17 N6 O5 F12
	961.1069	2.2	2.3	40.0	23	C48 H21 N10 O2 F7 Co
	961.1069	2.2	2.3	34.5	3	C49 H27 N3 O7 F7 Co
	961.1070	2.1	2.2	32.5	75	C45 H23 N7 O2 F11 Co
	961.1070	2.1	2.2	27.0	87	C46 H29 O7 F11 Co
	961.1070	2.1	2.2	48.5	175	C58 H20 N2 O10 F3
	961.1070	2.1	2.1	46.5	122	C54 H16 N6 O5 F7
	961.1071	2.0	2.1	44.5	56	C50 H12 N10 F11
	961.1071	2.0	2.1	45.5	163	C57 H26 N3 O7 F2 Co
	961.1071	2.0	2.1	39.0	38	C51 H18 N3 O5 F11
	961.1071	2.0	2.1	43.5	106	C53 H22 N7 O2 F6 Co
	961.1071	2.0	2.1	38.0	91	C54 H28 O7 F6 Co
	961.1072	1.9	2.0	36.0	25	C50 H24 N4 O2 F10 Co
	961.1072	1.9	1.9	50.0	181	C59 H17 N3 O5 F6
	961.1073	1.8	1.9	48.0	139	C55 H13 N7 F10

^{19}F-NMR [Fe(MAPC-T)] (**5**)

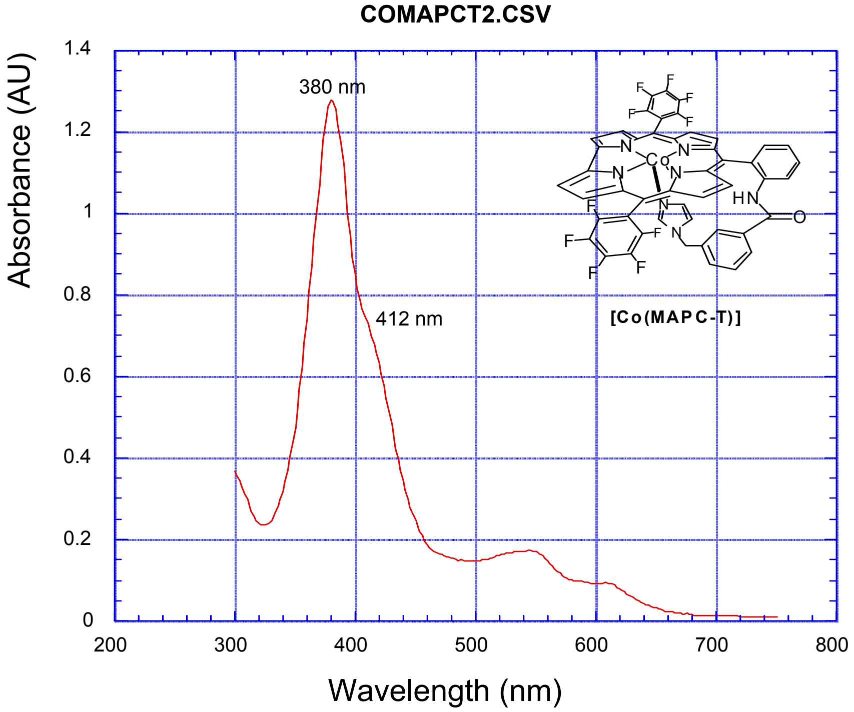


MS [Fe (MAPC-T)] (**5**)



UV/VIS [Co(mapc-t)] (**6**)

DECREAU RA



UV/VIS [Fe(mapc-t)] (**5**)

DECREAU RA