Supporting Information for

"Co^{III}(cyclam) Oligoynyls: Monomeric Oligoynyl Complexes and Dimeric Complexes with an Oligoyn-diyl Bridge"

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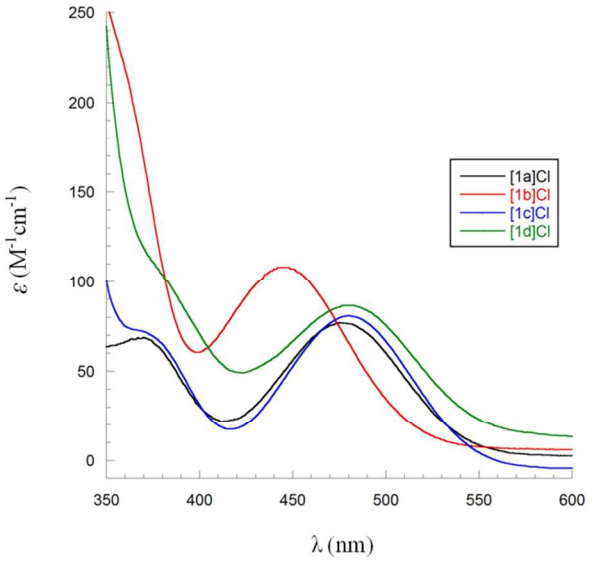

Figure S1. UV-vis plot of **[1a-d]Cl** in MeOH.

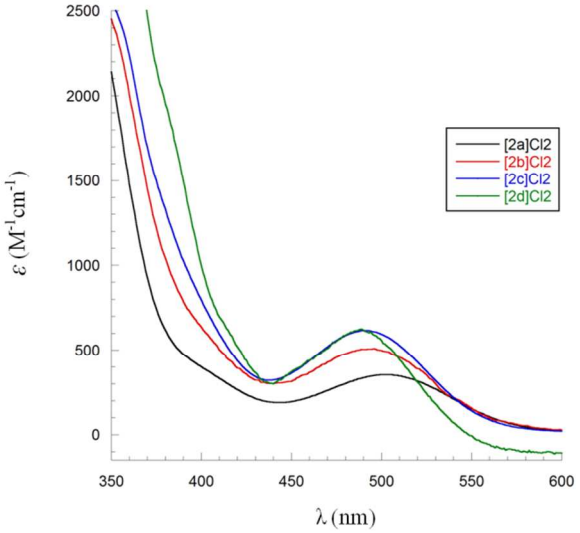

Figure S2. UV-vis plot of **[2a-d]Cl_2** in MeOH.

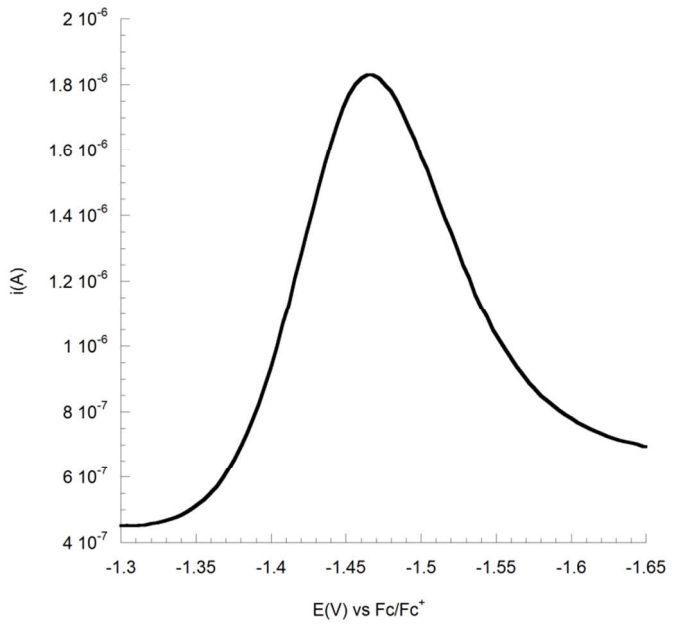

Figure S3. Differential pulse voltammagram showing the 1st reduction (Co^{III}/Co^{II}) of [**2a**]$(PF_6)_2$ in MeCN with 0.1 M NBu_4BF_4 under Taube-Richardson conditions (pulse amplitude = 10 mV).

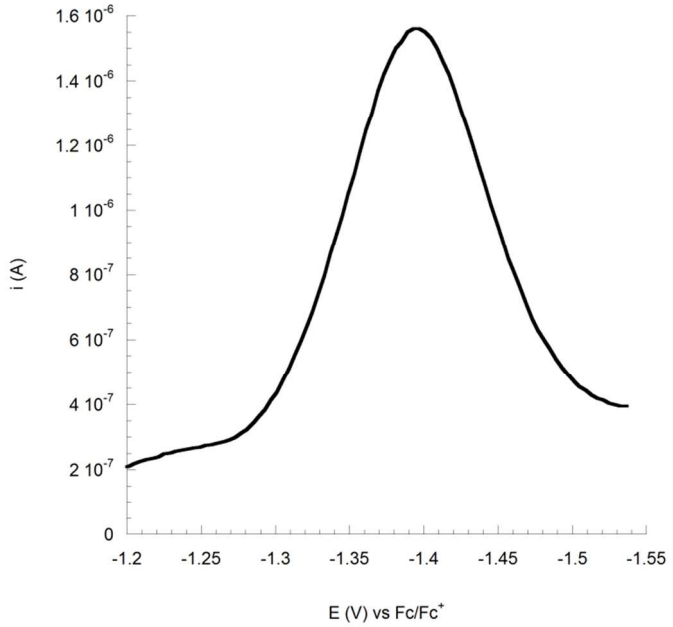

Figure S4. Differential pulse voltammagram showing the 1st reduction (Co^{III}/Co^{II}) of [**2b**]$(PF_6)_2$ in MeCN with 0.1 M NBu_4BF_4 under Taube-Richardson conditions (pulse amplitude = 10 mV).

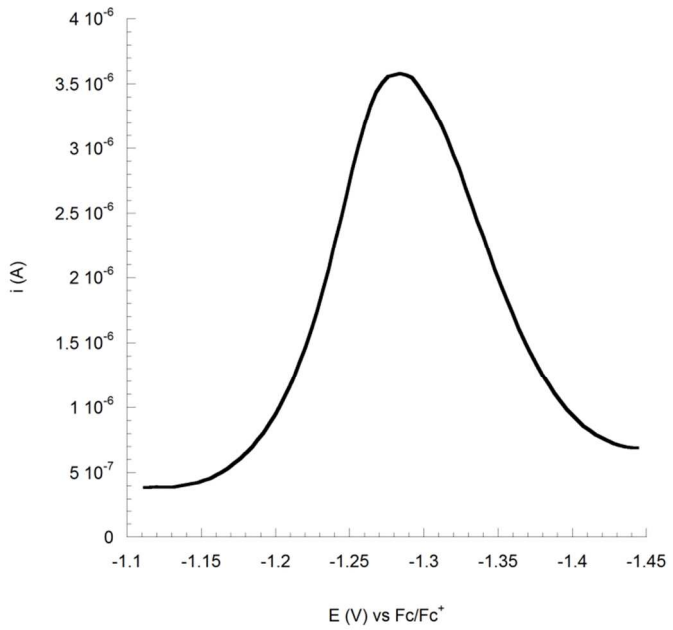

Figure S5. Differential pulse voltammagram showing the 1st reduction (Co^{III}/Co^{II}) of **[2c](PF$_6$)$_2$** in MeCN with 0.1 M NBu_4BF_4 under Taube-Richardson conditions (pulse amplitude = 10 mV).

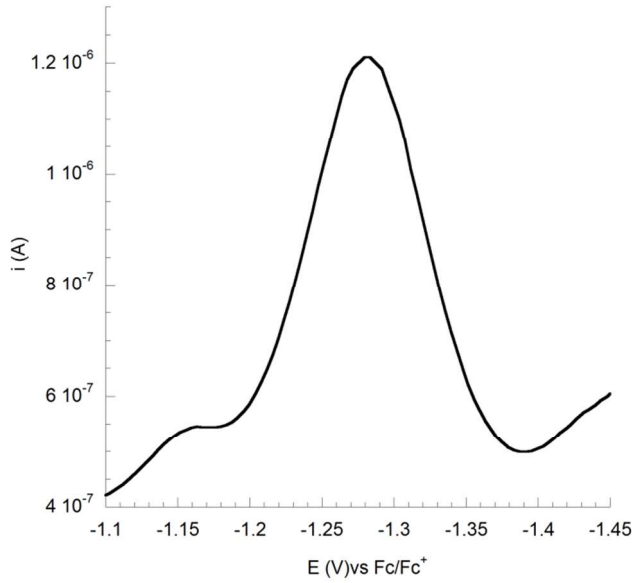

Figure S6. Differential pulse voltammagram showing the 1st reduction (Co^{III}/Co^{II}) of **[2d](PF$_6$)$_2$** in MeCN with 0.1 M NBu_4BF_4 under Taube-Richardson conditions (pulse amplitude = 10 mV).

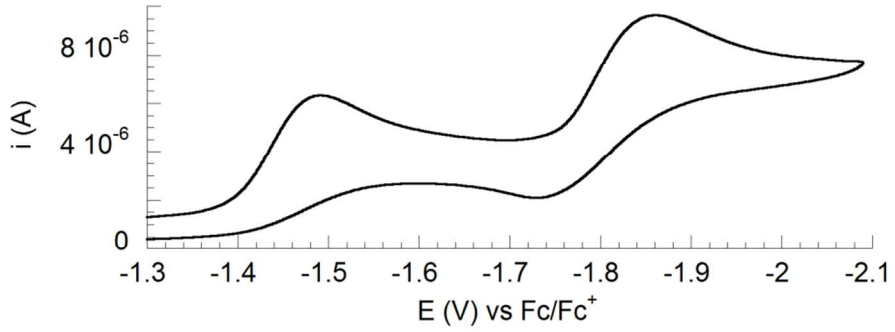

Figure S7. Cyclic Voltammagram showing the 1st and 2nd reductions of **[2a]Cl$_2$** in MeCN with 0.1 M NBu_4PF_6 at 0.010 V/s.

Computational Details

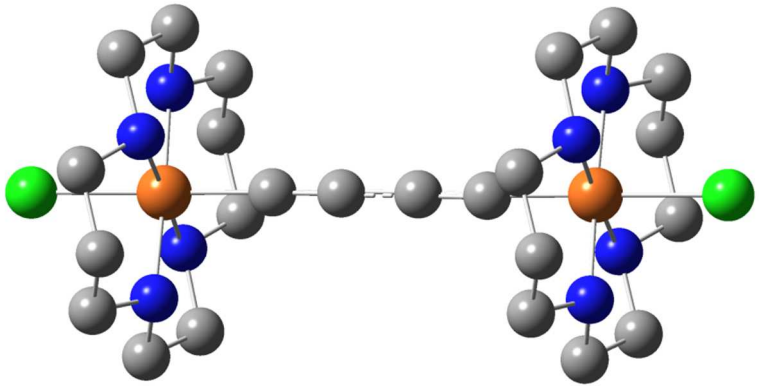

Figure S8. Fully optimized structure of **[2a]**$^{2+}$ using DFT method at the LanL2DZ level.

Table S1. Relevant bond lenghts (Å) and angles (deg) computed for **[2a]**$^{2+}$.

Co1-N1	2.0174
Co1-N2	2.0084
Co1-N3	2.0084
Co1-N4	2.0174

Co1-Cl1	2.3689
Co1-C1	1.9200
C1-C2	1.2457
C2-C3	1.3848
C3-C4	1.2457
Cl1-Co1-C1	179.025

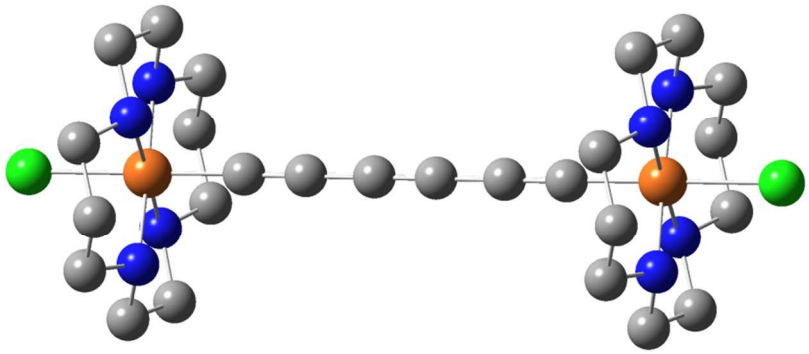

Figure S9. Fully optimized structure of **[2b]**$^{2+}$ using DFT method at the LanL2DZ level.

Table S2. Relevant bond lenghts (Ǻ) and angles (deg) computed for **[2b]**$^{2+}$.

Co11-N11	2.0082
Co11-N12	2.0184
Co11-N13	2.0184
Co11-N14	2.0082

Co11-Cl11	2.3677
Co11-C11	1.9111
C11-C12	1.2461
C12-C13	1.3707
C13-C13’	1.2386
Cl11-Co11-C11	178.802

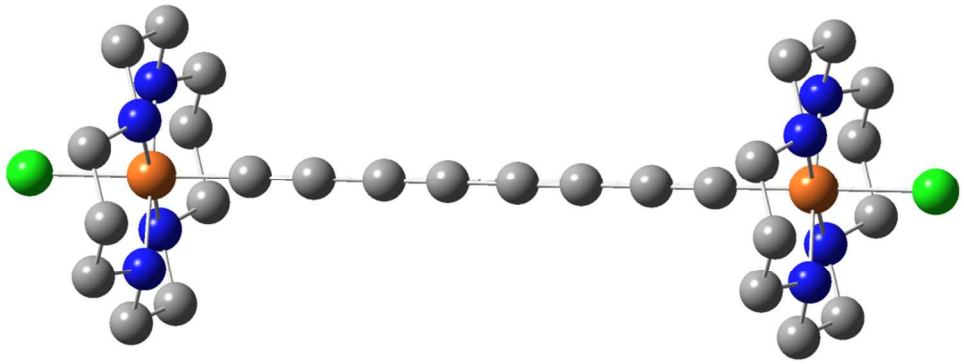

Figure S10. Fully optimized structure of **[2c]**$^{2+}$ using DFT method at the LanL2DZ level.

Table S3. Relevant bond lenghts (Ǻ) and angles (deg) computed for **[2c]**$^{2+}$.

Co1-N11	2.0082
Co1-N12	2.0082
Co1-N13	2.0188
Co1-N14	2.0188

Co1-Cl1	2.3680
Co1-C1	1.9069
C1-C2	1.2466
C2-C3	1.3669
C3-C4	1.2400
C4-C5	1.3569
C5-C6	1.2400
C6-C7	1.3669
C7-C8	1.2466
Cl1-Co1-C1	178.701

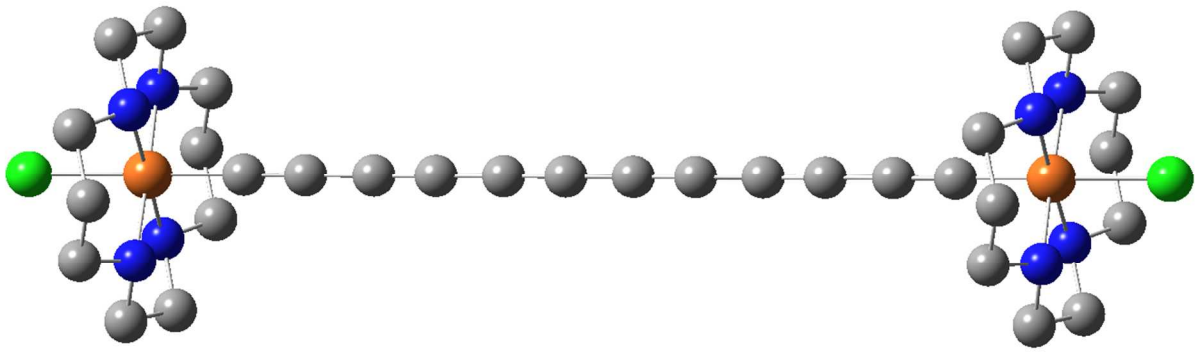

Figure S11. Fully optimized structure of **[2d]**$^{2+}$ using DFT method at the LanL2DZ level.

Table S4. Relevant bond lenghts (Ǻ) and angles (deg) computed for **[2d]**$^{2+}$.

Co11-N11	2.0082
Co11-N12	2.0082

Co11-N13	2.0188
Co11-N14	2.0188
Co11-Cl1	2.3694
Co11-C1	1.9038
C11-C12	1.2468
C12-C13	1.3644
C13-C14	1.2416
C14-C15	1.3509
C15-C16	1.2434
C16-C16’	1.3487
Cl11-Co11-C11	178.635

Table S5. Crystal data for **[1a-d]**Cl.

	[1a]Cl · MeOH	**[1b]**Cl · MeOH	**[1c]**Cl · MeOH	**[1d]**Cl · 2 MeOH
molecular formula	$C_{23}H_{53}Cl_2CoN_4OSi$	$C_{19}H_{30}ClCoN_4O$	$C_{15}H_{29}Cl_2CoN_4O$	$C_{18}H_{33}Cl_2CoN_4O_2$
fw, g mol^{-1}	575.61	424.85	411.25	467.31
space group	$C2/c$	$P2_1/n$	$C2/c$	$P2_1/n$
a, Å	38.735	12.196	24.824	10.746
b, Å	8.678	12.107	7.639	17.410
c, Å	18.452	14.984	19.786	12.714
α, °	90.00	90.00	90.00	90.00
β, °	90.87	107.90	96.77	100.50
γ, °	90.00	90.00	90.00	90.00
V, Å^3	6201.5	2105.40	3725.87	2338.90
Z	8	4	8	4
ρ_{calcd}, g cm^{-3}	1.233	1.340	1.466	1.327
T, K	150	200	150	150
final R indicies	$R1$ = 0.0411	$R1$ = 0.0547	$R1$ = 0.0373	$R1$ = 0.0362
($I > 2\sigma(I)$)	$wR2$ = 0.0977	$wR2$ = 0.153	$wR2$ = 0.0860	$wR2$ = 0.0827
GOF on F^2	1.057	1.055	1.066	1.030

Table S6. Crystal data for **[2a-d]**Cl_2.

	[**2a**]Cl_2	[**2b**]Cl_2 · 4 MeOH	[**2c**]Cl_2· 5 MeOH	[**2d**]Cl_2 · EtOAc · 2 MeOH
molecular formula	$C_{26}H_{56}Cl_4Co_2N_8O_2$	$C_{30}H_{64}Cl_4Co_2N_8O_4$	$C_{33}H_{68}Cl_4Co_2N_8O_5$	$C_{38}H_{64}Cl_4Co_2N_8O_4$
fw, g mol^{-1}	772.44	860.567	916.61	956.63
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.020	10.789	9.844	7.939
b, Å	9.862	14.391	15.481	14.889
c, Å	11.87	15.047	15.963	19.981
α, °	105.88	63.56	96.647	100.89
β, °	106.44	73.33	91.394	90.70
γ, °	93.77	75.37	108.290	92.01
V, Å^3	855.47	1982.64	2289.7	2317.6
Z	1	2	2	2
ρ_{calcd}, g cm^{-3}	1.499	1.442	1.330	1.371
T, K	150	150	200	150
final R indicies	$R1$ = 0.0442	$R1$ = 0.0531	$R1$ = 0.1084	$R1$ = 0.0587
($I > 2\sigma(I)$)	$wR2$ = 0.0891	$wR2$ = 0.1562	$wR2$ = 0.2906	$wR2$ = 0.1618
GOF on F^2	1.078	0.958	1.041	1.040