Supporting Information for

Mono- and dinuclear metal complexes containing the 1,5,9-triazacyclododecane ([12]aneN$_3$) unit and their interaction with DNA

Alfredo Medina-Molner[a], Melanie Rohner[a], Devaraj Pandiarajan[a] and Bernhard Spingler*[a]

University of Zürich, Winterthurerstr. 190, CH 8057 Zürich, Switzerland.

Fax: +41 44 635 68 03; Tel: +41 44 635 46 56;

E-mail: spingler@chem.uzh.ch

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Synthesis of 1,4-butylenebistriflate (slightly modified from reference[1]):

Trifluoromethanesulfonic acid anhydride (11.9 ml, 72.1 mmol) dissolved in dry DCM (60 ml) was slowly added to a solution of 1,4-butanediol (3 ml, 33.6 mmol) and triethylamine (9.8 ml, 70.4 mmol) in dry DCM (60 ml) in an ice bath. While the anhydride was being added, the reaction solution became brown-orange. After overnight stirring in the absence of light, the reaction solution was extracted several times with water. The DCM phase was dried over Na_2SO_4, 1,4-butylenebistriflate[1] was obtained as a brown oil which crystallised after a few minutes (11.6 g, 98%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.02 (*t*, J = 5.4 Hz, 4H, $OCH_2C\mathbf{H}_2$) and 4.68 ppm (*t*, J = 5.7 Hz, 4H, $OC\mathbf{H}_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 25.51 ($OCH_2\mathbf{C}H_2$), 75.97 ($O\mathbf{C}H_2$) and 118.70 (*q*, J = 319.4 Hz, $\mathbf{C}F_3$).

Reference:

1. R. W. Alder, D. D. Ellis, R. Gleiter, C. J. Harris, H. Lange, A. G. Orpen, D. Read and P. N. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1657-1668.

Table S1. Crystal data and structure refinement for **L4·4TfOH**, **$L3Cu_2(NO_3)_2(TfO)_2 \cdot (CH_3OH)_{0.7}(H_2O)_{0.3}$**, **$6 \cdot 2H_2O$** and **$[L4Ni_2(AcO)_2(BPh_4)_2(NCCH_3)_2] \cdot THP$**.

	L4·4TfOH	**$L3Cu_2(NO_3)_2(TfO)_2 \cdot (CH_3OH)_{0.7}(H_2O)_{0.3}$**	**$6 \cdot 2H_2O$**	**$[L4Ni_2(AcO)_2(BPh_4)_2(NCCH_3)_2] \cdot THP$**
CCDC number	1021590	1021588	1021589	1021591
Empirical formula	$C_{26}H_{52}F_{12}N_6O_{12}S_4$	$C_{23.7}H_{49.4}Cu_2F_6N_8O_{13}S_2$	$C_{28}H_{60}N_6Ni_2O_{10}$	$C_{83}H_{110}B_2N_8Ni_2O_5$
Diffractometer	Stoe IPDS	Stoe IPDS	Stoe IPDS	Stoe IPDS
Temperature [K]	183	183	183	183
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Formula weight	996.98	959.71	758.24	1438.83
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P21/n	P-1	P-1	P-1
a [Å]	10.3354(8)	9.3134(8)	8.6958(13)	11.2739(8)
b [Å]	17.2802(9)	12.3928(9)	8.7403(13)	12.8908(9)
c [Å]	11.9040(10)	16.8732(13)	12.3998(19)	14.9803(10)
α [°]	90	93.869(9)	102.060(18)	104.807(8)
β [°]	94.109(10)	97.990(10)	105.113(18)	97.878(9)
γ [°]	90	90.512(10)	94.828(18)	107.244(8)
Volume [$Å^3$]	2120.6(3)	1923.9(3)	880.1(2)	1956.0(2)
Z	2	2	1	1
Density (calculated) [Mg/m^3]	1.561	1.657	1.431	1.221
Absorption coefficient [mm^{-1}]	0.338	1.311	1.130	0.537
F(000)	1036	991	406	770
Crystal size [mm^3]	0.60 x 0.24 x 0.24	0.18 x 0.14 x 0.03	0.33 x 0.21 x 0.17	0.38 x 0.29 x 0.20
Crystal description	colourless needle	blue plate	blue cube	blue block
Theta range for data collection [°]	2.92 to 30.00	2.67 to 27.48	3.40 to 30.42	2.87 to 30.03
Index ranges	-14<=h<=14, -24<=k<=24, -16<=l<=16	-12<=h<=12, -16<=k<=16, -21<=l<=21	-12<=h<=12, -12<=k<=12, -17<=l<=17	-15<=h<=15, -17<=k<=16, 0<=l<=21
Reflections collected	33989	22273	15881	10463
Independent reflections	6158 [R(int) = 0.0512]	8190 [R(int) = 0.0660]	4836 [R(int) = 0.0554]	10463
Reflections observed	4590	5256	4373	7107

Criterion for observation	>2sigma(I)	>2sigma(I)	>2sigma(I)	>2sigma(I)
Completeness to theta	99.3 %	92.9 % to 27.48°	90.5 % to 30.42°	91.5 % to 30.03°
Absorption correction	Numerical	Numerical	Numerical	Numerical
Max. and min. transmission	0.9408 and 0.8718	0.9617 and 0.7981	0.8433 and 0.7265	0.9003 and 0.8221
Data / restraints / parameters	6158 / 0 / 279	8190 / 0 / 506	4836 / 0 / 218	10463 / 0 / 453
Goodness-of-fit on F^2	1.108	0.902	1.088	0.805
Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1748	R1 = 0.0612, wR2 = 0.1446	R1 = 0.0403, wR2 = 0.1117	R1 = 0.0464, wR2 = 0.1232
R indices (all data)	R1 = 0.0808, wR2 = 0.1944	R1 = 0.0891, wR2 = 0.1561	R1 = 0.0437, wR2 = 0.1150	R1 = 0.0620, wR2 = 0.1290
Largest diff. peak and hole [e.$Å^{-3}$]	0.359 and -0.428	0.586 and -0.826	0.441 and -0.840	0.505 and -0.360

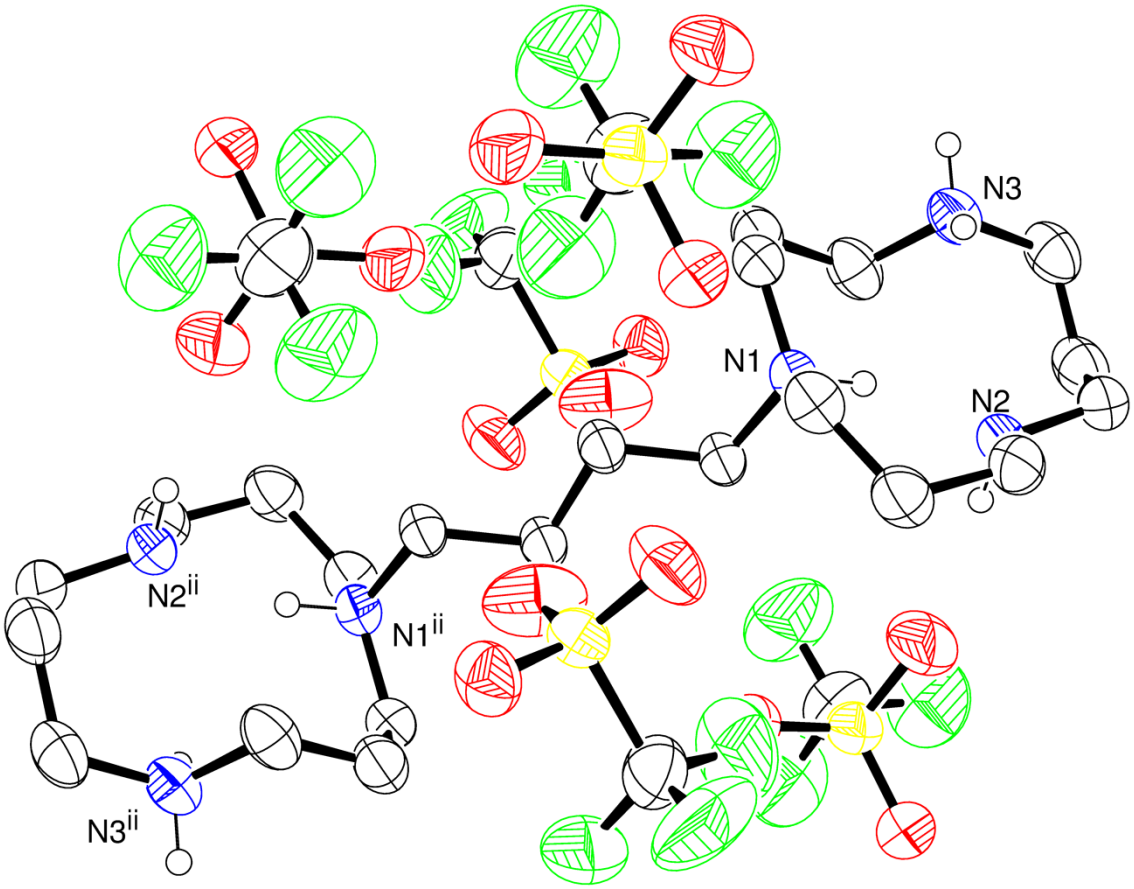

Figure S1. ORTEP representation of **L4·4TfOH** at 50 % probability. Non-acidic hydrogen atoms were omitted for clarity.

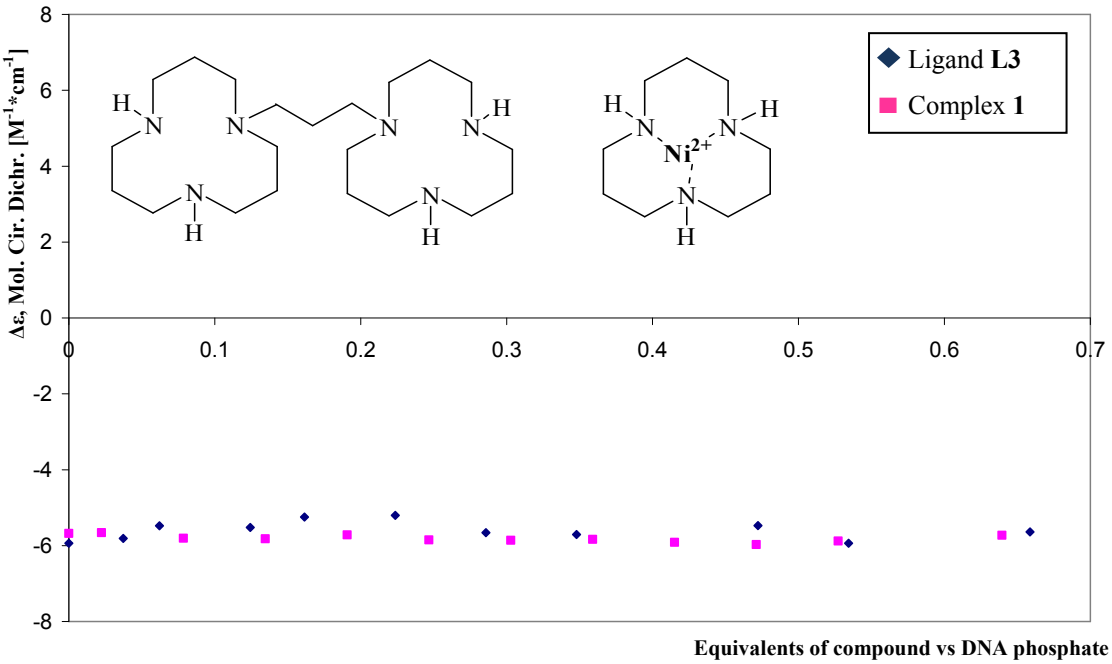

Figure S2. Circular dichroic response at 255nm of poly d(GC) versus equivalents of ligand **L3·6TfOH** (blue) and complex **1** (pink).

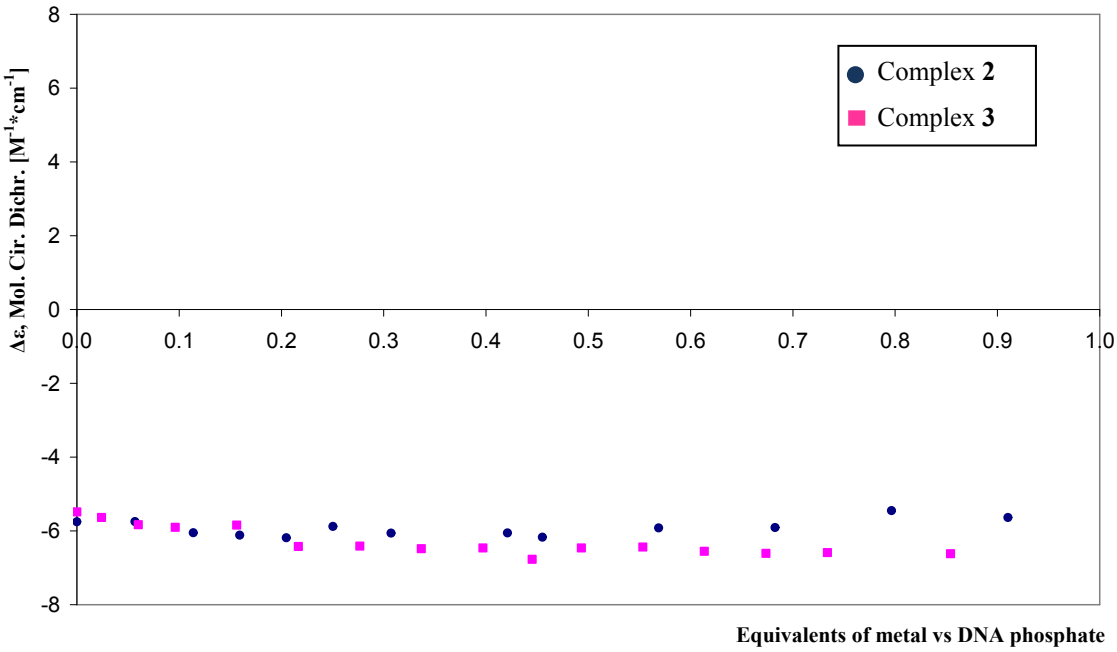

Figure S3. Circular dichroic response at 255nm of poly d(GC) versus metal equivalents of complexes **2** (blue) and **3** (pink).

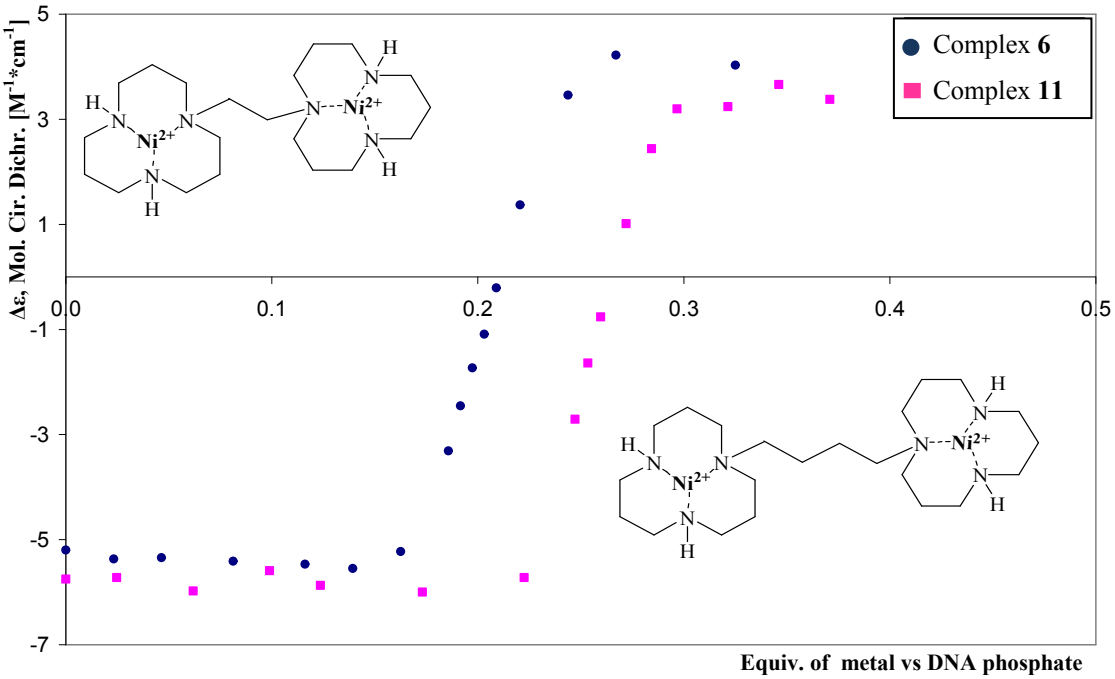

Figure S4. Circular dichroic response at 255nm of poly d(GC) versus metal equivalents of complexes **6** (blue) and **11** (pink).

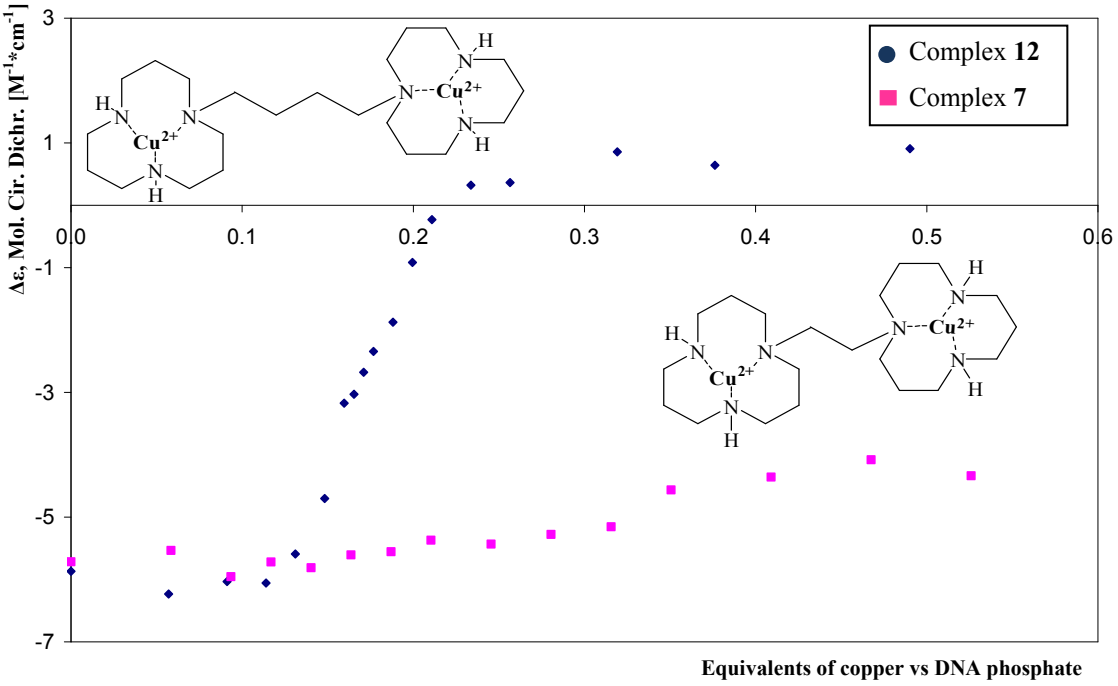

Figure S5. Circular dichroic response at 255nm of poly d(GC) versus metal equivalents of complexes **7** (pink) and **12** (blue).

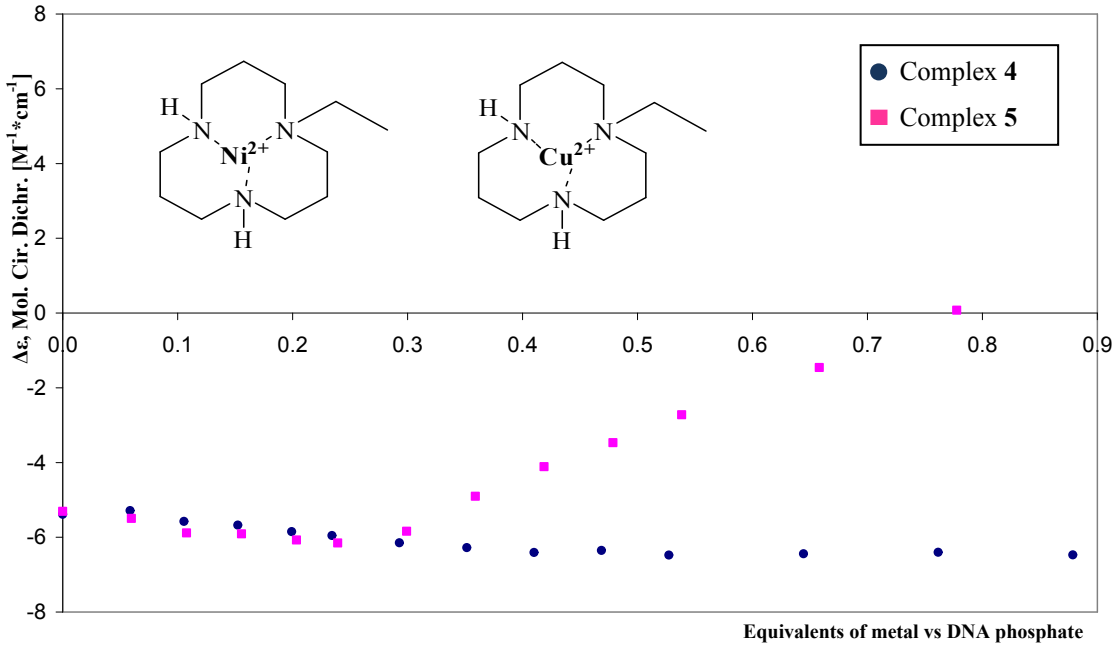

Figure S6. Circular dichroic response at 255nm of poly d(GC) versus metal equivalents of complexes **4** (blue) and **5** (pink).

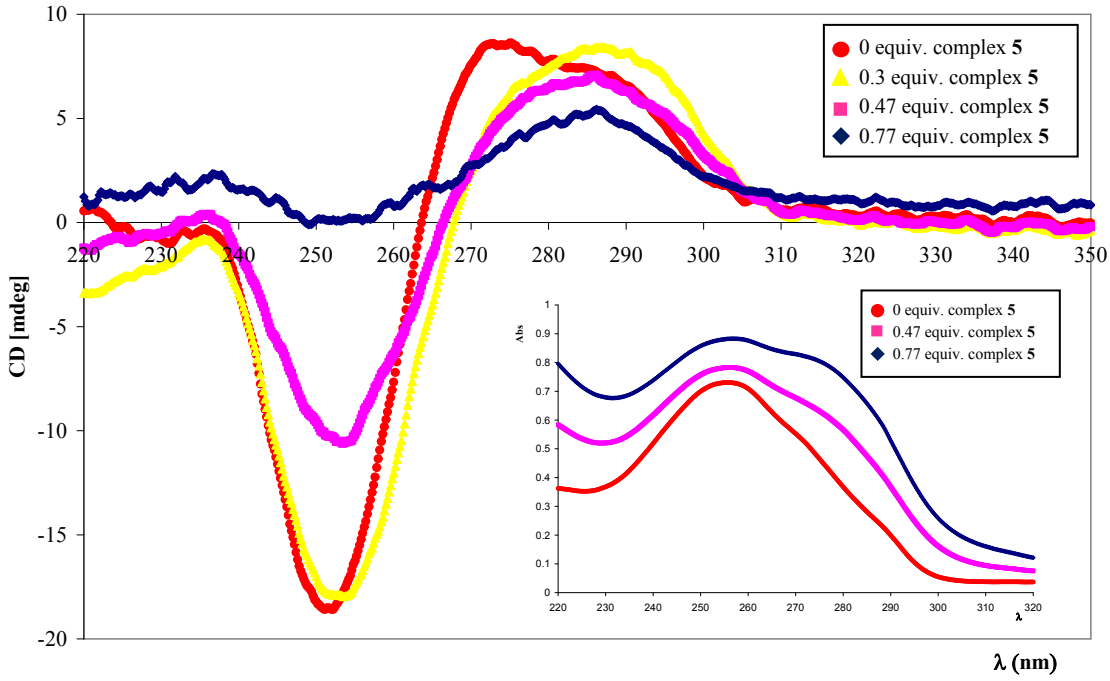

Figure S7. Circular dichroism response versus wavelength of complex **5** versus phosphates; on the bottom right, UV plot at different equivalents of complex **5**.

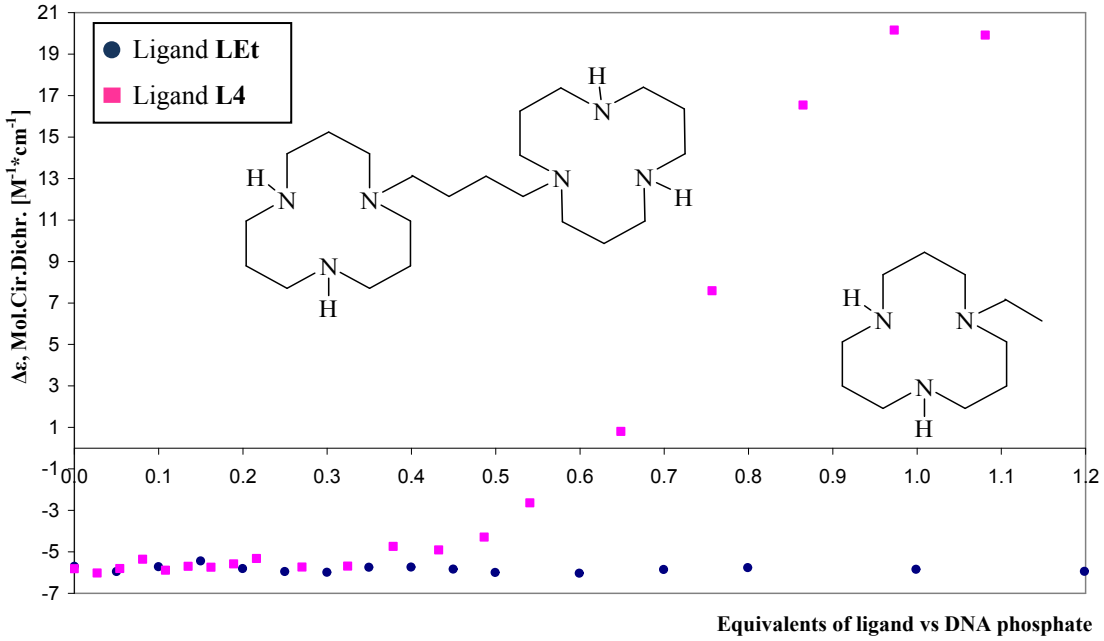

Figure S8. Circular dichroic response at 255nm of poly d(GC) versus ligand equivalents of **LEt·3TfOH** (blue) and **L4·6TfOH** (pink).

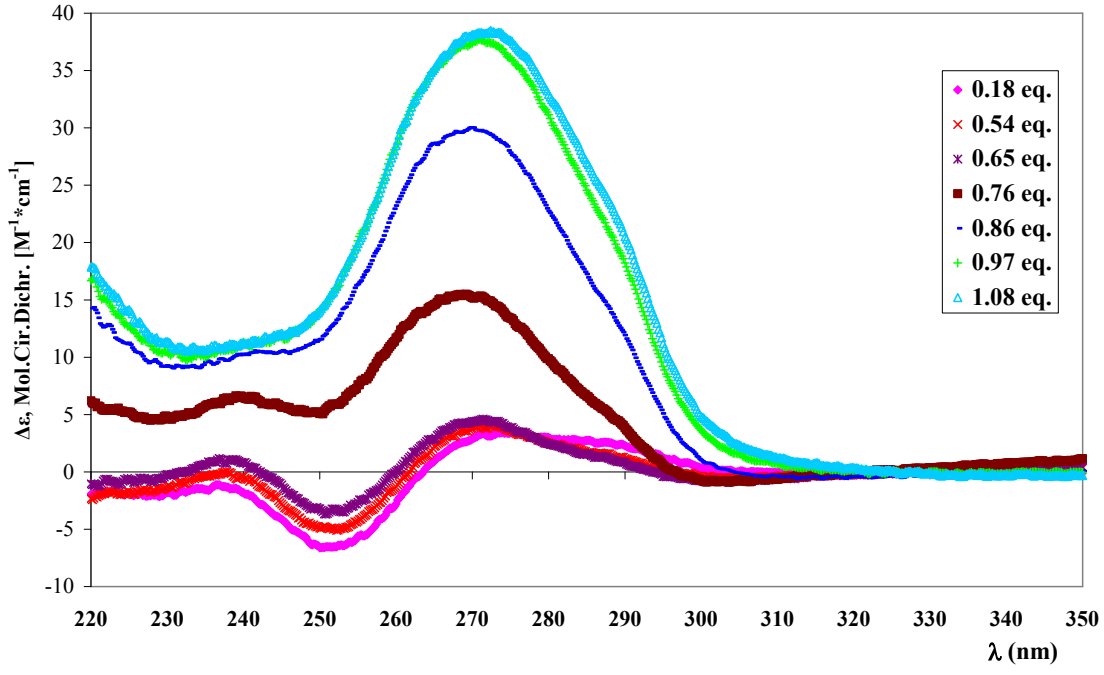

Figure S9. Circular dichroism response of different equivalents of ligand **L4** versus DNA phosphates.

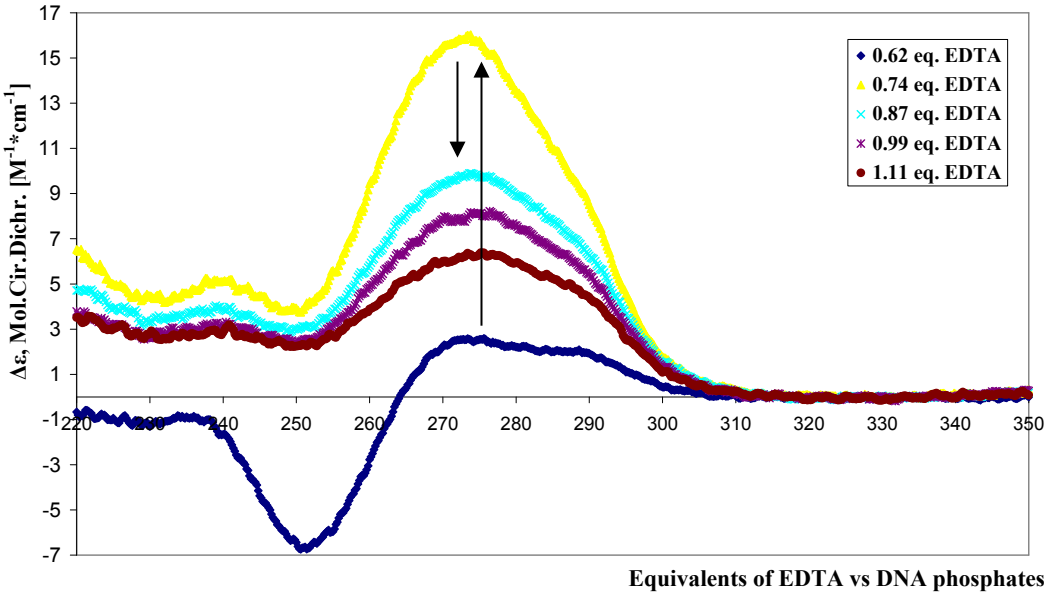

Figure S10. Circular dichroism response of different equivalents of EDTA versus DNA phosphates of poly d(GC).

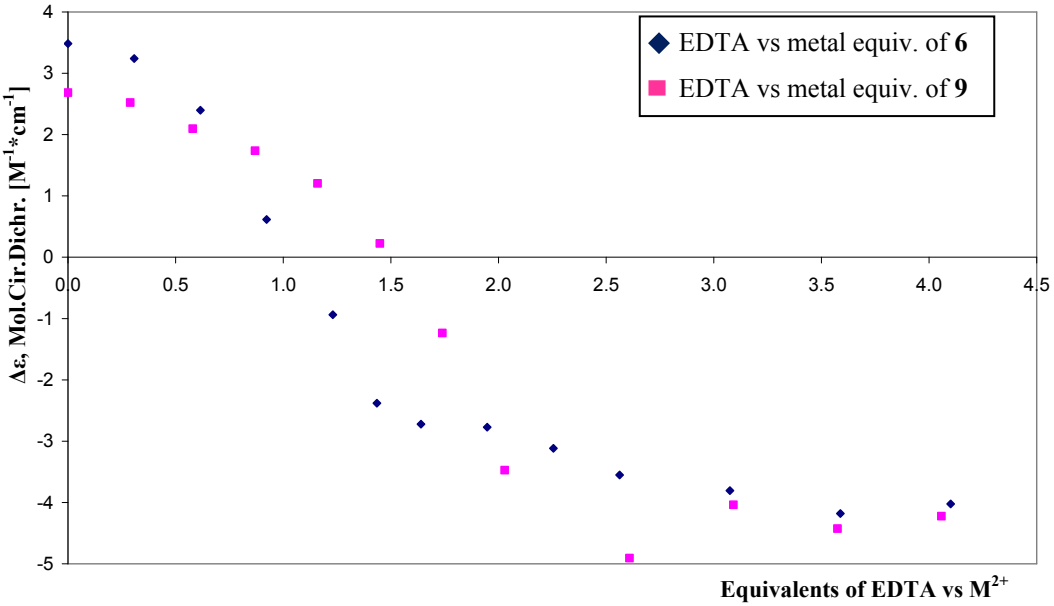

Figure S11. Circular dichroism response at 255nm plotted against equivalents of EDTA versus metal equivalents of **6** (blue) and **9** (pink).