Electronic Supplementary Material (ESI) for Dalton Transactions.

Control of Clustering Behavior in Anionic Cerium(III) Corrole Complexes: From Oligomers to Monomers

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Outline

UV/Vis Spectra

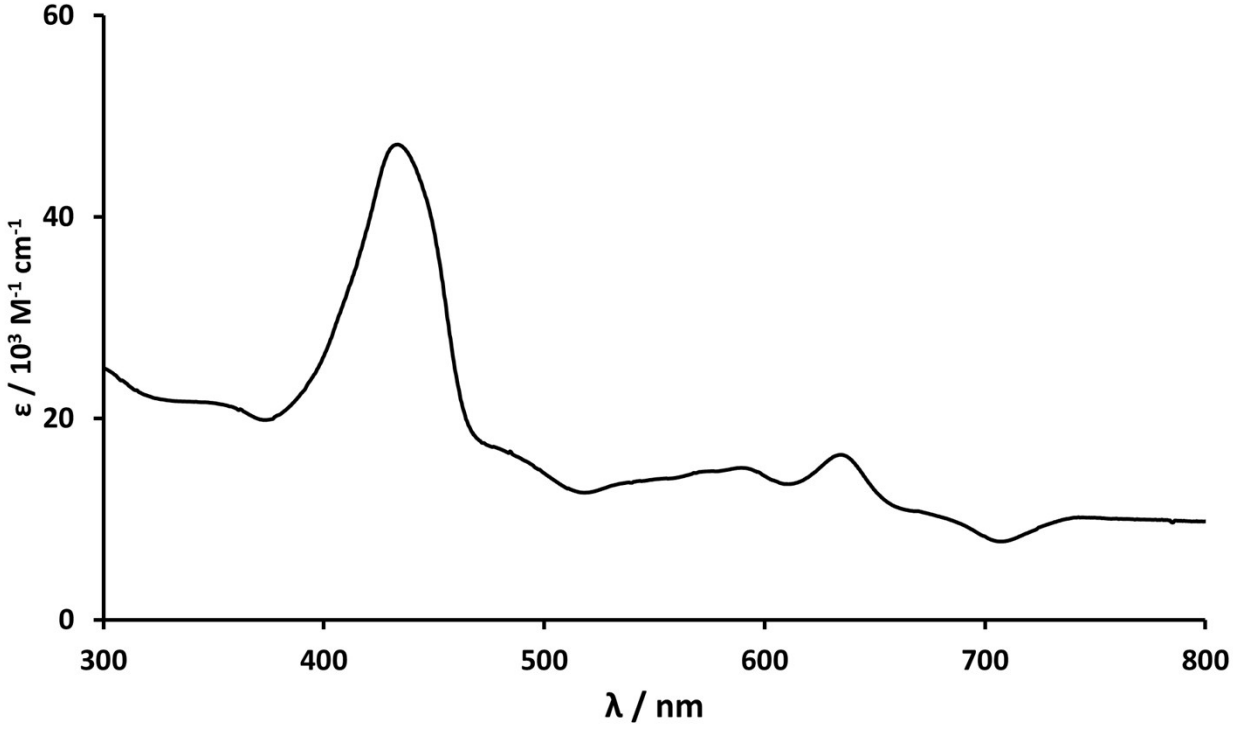

Figure S1 UV/Vis spectrum of **1a** in THF

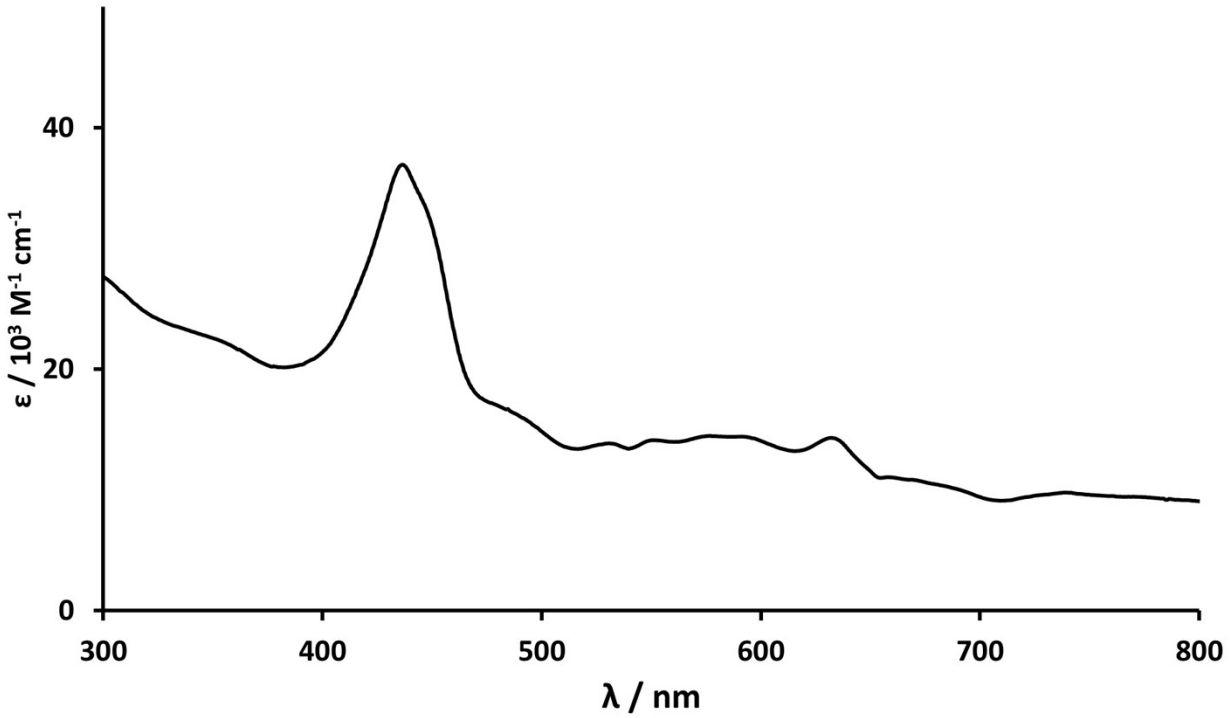

Figure S2 UV/Vis spectrum of **1b** in THF

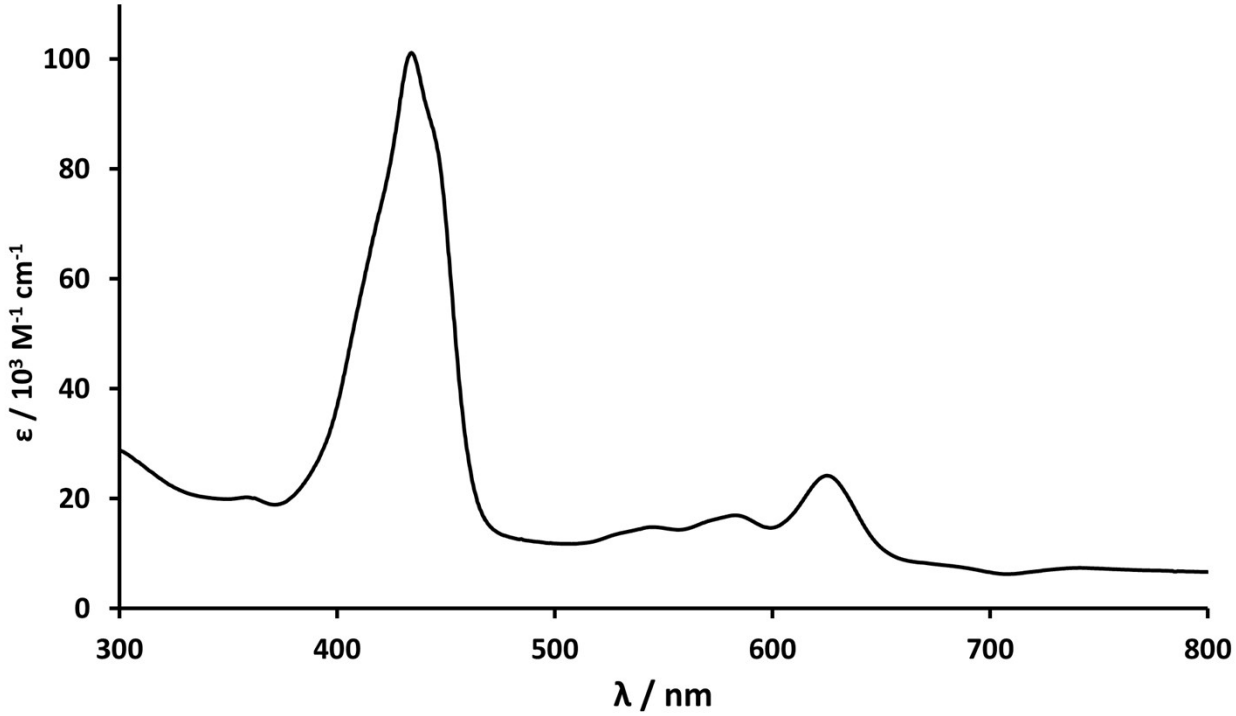

Figure S3 UV/Vis spectrum of **2a** in THF

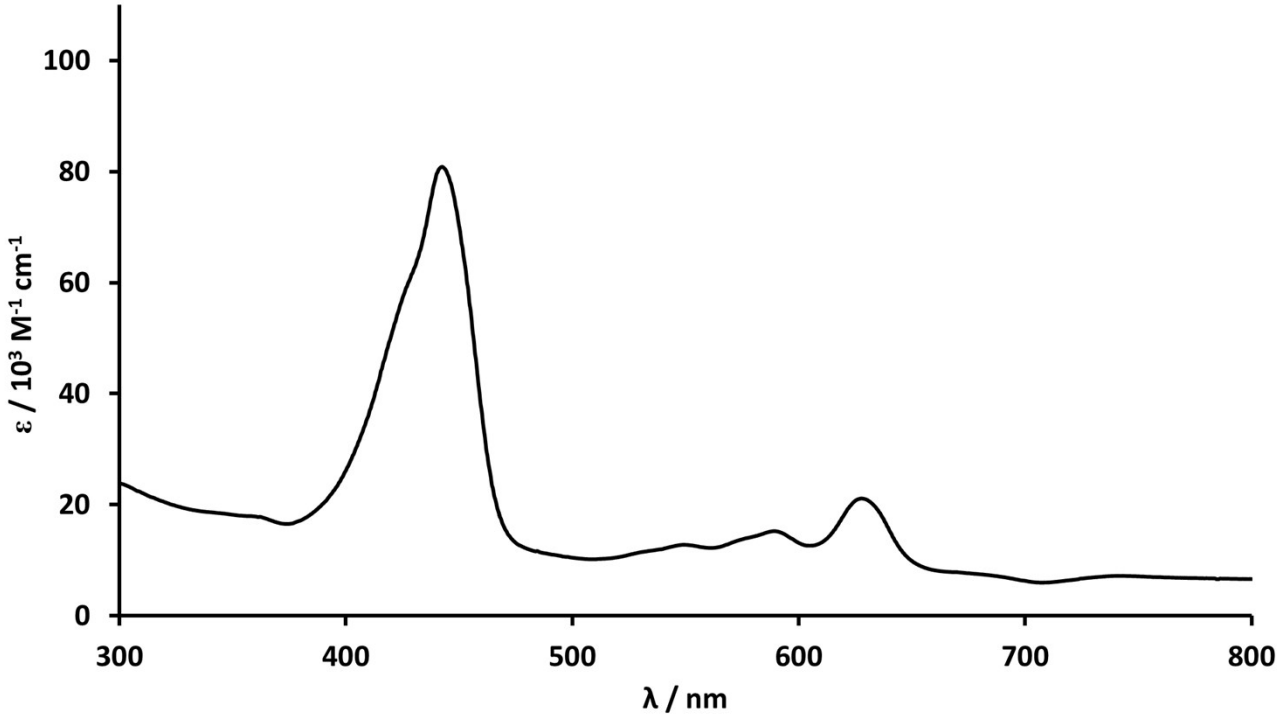

Figure S4 UV/Vis spectrum of **2b** in THF

Crystallographic details

Table S1 Crystallographic information

	1a	**1b**[#]	**2a**[#]	**2b**	**3b**$^{+}$
Chemical formula	$C_{60}H_{58}N_4O_2Ce_1\ Na_1$	$C_{71}H_{88}N_6O_9Ce_1\ Na_1$	$C_{106}H_{94}N_{20}O_2B_1Ce_2\ K_2$	$C_{71}H_{83}N_{12}O_7B_1Ce_1\ K_1$	$C_{81}H_{91}N_6O_7Lu_1Na_1$
M_r	1030.21	1332.58	2060.07	1406.52	1458.55
Crystal system	Tetragonal	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$I4_1/a$	P-1	P-1	*Pbca*	P-1
a (Å)	28.2049(3)	14.408(1)	11.1309(5)	12.505(1)	12.9649(3)
b (Å)	28.2049(3)	14.500(1)	13.3627(6)	26.201(2)	13.6515(3)
c (Å)	26.1852(5)	20.559(1)	19.9803(8)	41.444(3)	21.1015(3)
α (°)	90	86.245(4)	107.040(2)	90	85.729(1)
β (°)	90	69.911(3)	103.868(2)	90	73.465(2)
γ (°)	90	66.398(4)	97.317(2)	90	77.853(2)
V (Å^3)	20830.8(6)	3688.5(4)	2685.3(2)	13578(1)	3499.7(1)
Z	16	2	1	8	2
Densitiy (g cm^{-3})	1.314	1.200	1.269	1.376	1.384
F(000)	8496	1394	1050	5848	1514
Radiation Type	MoK_α	Synchrotron	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	0.928	0.818	0.966	0.795	1.477
Crystal size	0.34	0.05	0.12	0.1	0.22
	0.22	0.05	0.02	0.03	0.11
	0.16	0.04	0.02	0.03	0.05
Meas. Refl.	154079	53951	33820	115529	124720
Indep. Refl.	12429	13397	9860	12431	18098
Obsvd. [$I > 2\sigma(I)$] refl.	9085	9802	7809	7263	16012
R_{int}	0.0713	0.0939	0.0665	0.1683	0.0478
R [$F^2 > 2\sigma(F^2)$]	0.0453	0.0890	0.0479	0.0628	0.0332
wR(F^2)	0.1462	0.2183	0.1106	0.1738	0.0783
S	1.085	1.035	0.995	1.004	1.080
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.337, -0.498	3.866, -1.945	1.551, -1.278	1.281, -0.581	1.150, -0.755
CCDC	1482209	1498990	1482208	1482207	1498989

Due to strong disorder, one equivalent of Toluene has been squeezed from the crystal structure.

* Due to strong disorder, it was not possible to refine the methyl hydrogens on one of the toluene moleules.

Table S2 Important bond lengths and angles

Atoms	1a	1b	2a	2b	3b
O200 – Ce1	2.558(3)	2.713(5)	-	-	-
O201 – Ce1	-	2.820(5)	-	-	-
N1 – Ce1/Lu1	2.430(3)	2.463(7)	2.429(3)	2.402(5)	2.225(2)
N2 – Ce1/Lu1	2.455(5)	2.464(5)	2.472(3)	2.419(5)	2.224(2)
N3 – Ce1/Lu1	2.445(3)	2.463(6)	2.489(3)	2.453(5)	2.225(2)
N4 – Ce1/Lu1	2.433(3)	2.419(6)	2.442(3)	2.424(5)	2.210(1)
N1 – Na1/K1	2.623(3)	-	2.884(3)	-	-
N2 – Na1/K1	2.501(3)	-	2.790(3)	-	-
N3 – Na1/K1	2.469(3)	-	2.833(3)	-	-
N4 – Na1/K1	2.511(3)	-	2.965(3)	-	-
$N_{4\ plane}$ – Na1/K1	1.660(1)	-	2.116(1)	-	-
$N_{4\ plane}$ – Ce1/Lu1	1.524(1)	1.497(1)	1.506(1)	1.439(1)	1.091(1)
C100 – Na1	2.650(5)	-	-	-	-
C101 – Na1	2.592(5)	-	-	-	-
C102 – Na1	2.621(5)	-	-	-	-
C103 – Na1	2.700(5)	-	-	-	-
C104 – Na1	2.716(5)	-	-	-	-
Cp_{cent} – Ce1/Lu1	2.599(1)	2.666(1)	-	-	2.335(1)
N10 – Ce1	-	-	2.630(3)	2.668(5)	-
N20 – Ce1	-	-	2.600(3)	2.676(5)	-
N30 – Ce1	-	-	2.621(3)	2.651(5)	-
Tp_{cent} – Ce1	-	-	1.914(1)	1.986(1)	-
K1 – O1	-	-	2.643(3)	-	-
Ce1 – Ce1	7.983(1)	-	12.065(1)	-	-
$N_{4\ plane}$ – Ce1 – Cp_{cent}	151.1(1)	146.6(1)	-	-	177.4
$N_{4\ plane}$ – Ce1 – Tp_{cent}	-	-	176.7(1)	175.1(1)	-

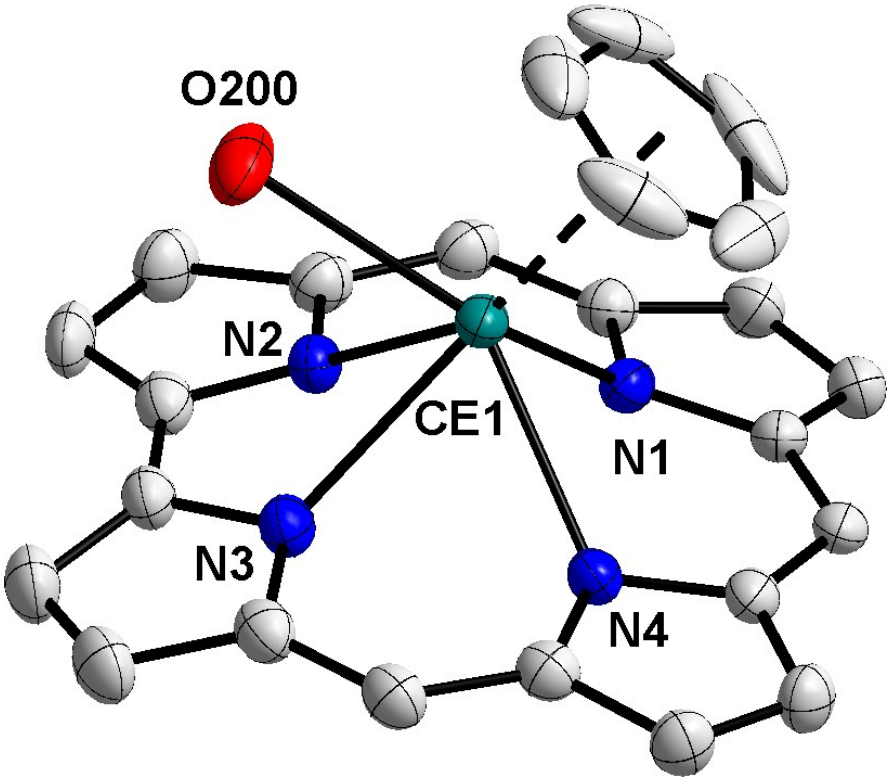

Figure S5 ORTEP view of monomeric view of **1a**. Thermal ellipsoids are shown at a probability level of 50%. Hydrogen and sodium atoms, as well as the carbon atoms of the THF ligand and the mesityl and anisole residues on the corrole ligand have been omitted for clarity.

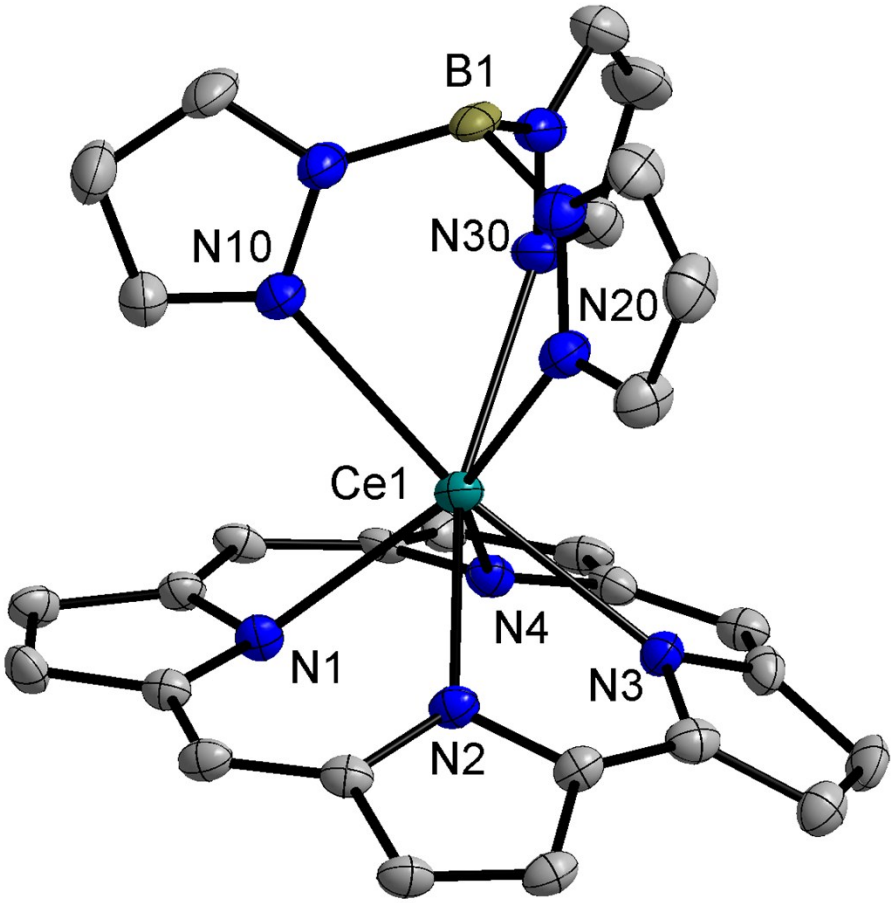

Figure S6 ORTEP view of monomeric view of **2a.** Thermal ellipsoids are shown at a probability level of 50%. Hydrogen and sodium atoms, as well as the mesityl and anisole residues on the corrole ligand have been omitted for clarity.

Comparison Tables for other macrocyclic f-element complexes

Table S3 Selected bond lengths in comparable early lanthanide and cerium porphyrin complexes

Atoms	Ce_2TPP_2Pc[1]	Ce_2OEP_3[2]	(TPP)Ce(Pc)Gd(OEP)[3]	NdTp(TPP)[4]	NdTp(TPP)[5]	Nd(TPP)I[5]
N1 – Ce/Nd	2.459	2.496	2.468	2.465	2.476	2.444
N2 – Ce/Nd	2.453	2.524	2.467	2.439	2.428	2.413
N3 – Ce/Nd	2.485	2.503	2.462	2.429	2.448	2.438
N4 – Ce/Nd	2.477	2.482	2.458	2.458	2.451	2.452
$N_{4\ plane}$ – Ce/Nd	1.352	1.395	1.337	1.305	1.298	1.286
$N5_{Tp}$ – Ce/Nd	-	-	-	2.585	2.629	.
$N7_{Tp}$ – Ce/Nd	-	-	-	2.612	2.592	.
$N9_{Tp}$ – Ce/Nd	-	-	-	2.642	2.617	.
Tp_{cent} – M	-	-	-	1.906	1.895	-
$N_{4\ plane}$ – Ce1 – Tp_{cent}	-					

TPP = Tetraphenylporphyrine, OEP = octaethylporphyrine, Pc = Phtalocyanine, Tp = Trispyrazolylborate

Table S4 selected bond lengths in comparable Lu porphyrin complexes

Atoms	$LuPc^{Fc}Por$[6]	LuPcTPP [7]	$Lu_2{}^{Xanth}Por$[8]	$Lu_2{}^{Xanth}Por$[8]	$OEPLuCH(TMS)_2$[9]
N1 – Lu	2.393	2.415	2.321	2.304	2.236
N2 – Lu	2.395	2.404	2.299	2.317	2.254
N3 – Lu	2.383	2.394	2.312	2.323	2.297
N4 – Lu	2.390	2.412	2.335	2.321	2.255
$N_{4\ plane}$ – Lu	1.222	1.261	1.091	1.072	0.919

TPP = Tetraphenylporphyrine, OEP = octaethylporphyrine, Pc = Phtalocyanine, ^{Xanth}Por = Xanthene linked porphyrin, ^{Fc}Por = Ferrocene decorated prophyrine

Table S5 Selected bond lengths in comparable Ln/An(corrole) complexes

Atoms	CorLaDME[10]	CorGdTACN [10]	CorTbDME [10]	Eu_2Pc_2Cor[11]	ThClCor[12]	UClCor [12]
N1 – M	2.442	2.343	2.327	2.571	2.413	2.357
N2 – M	2.429	2.294	2.317	2.582	2.394	2.313
N3 – M	2.445	2.299	2.308	2.578	2.368	2.293
N4 – M	2.432	2.352	2.323	2.629	2.356	2.338
$N_{4\ plane}$ – M	1.467	1.262	1.274	1.793	1.403	1.330

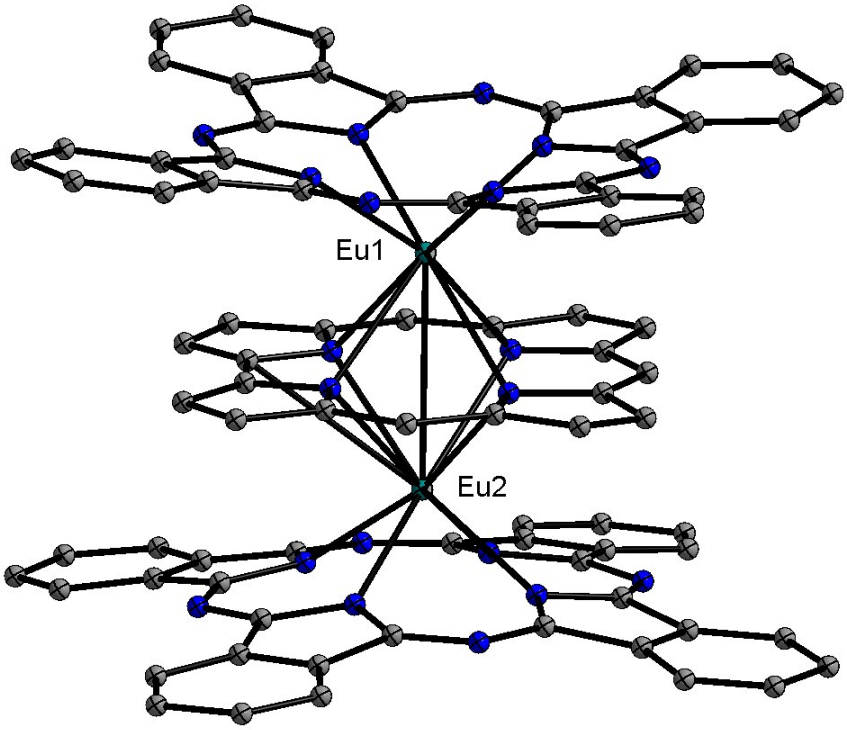

Figure S7: Ball and stick model of Eu_2Pc_2Cor reported by Kadish *et al.*; 4-chlorophenyl substituents on the corrole as well as octoxy residues in the phthalocyanine ligand have been omitted for clarity.

Literature

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