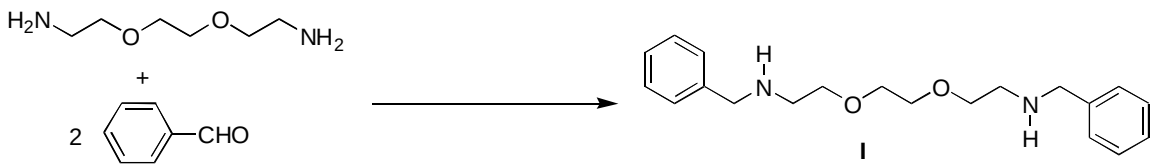
Electronic Supplementary Information (ESI)

Cryptand 2a

Step 1



Method 1: Melt

Benzaldehyde (3g, 28mmol) was heated in an oil bath with stirring. 2,2'-(ethylenedioxy)bis(ethylamine) (2.1g, 14.2mmol) was added drop-wise, and the mixture cooled to room temperature after emission of H_2O vapour had ceased. The resulting imine was suspended in 30mL of MeOH, and $NaBH_4$ (6.48g, 0.171 mol) was added portion-wise under $N_{2(g)}$, before stirring for two and a half hours. The mixture was evaporated to dryness, and dissolved in H_2O. The product was extracted into $CHCl_3$, and dried over $MgSO_4$. Filtration followed by solvent removal and drying *in vacuo* yielded a brown oil (3.72g, 80% yield).

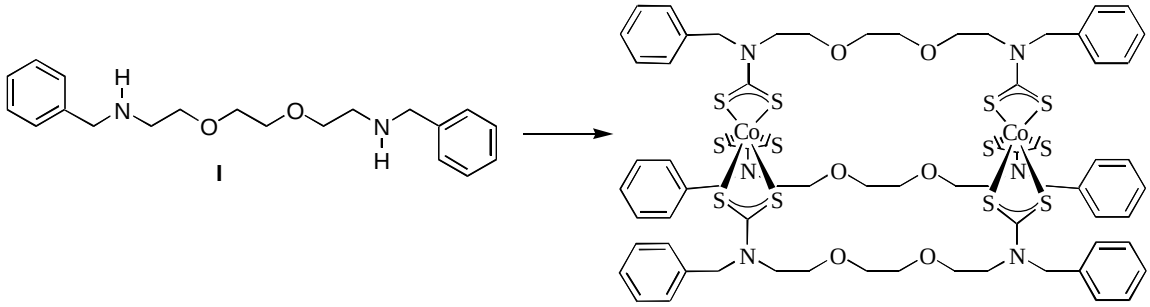
Method 2: Dean-Stark

The benzaldehyde and 2,2'-(ethylenedioxy)bis(ethylamine) were dissolved in 120mL toluene and refluxed for 4 hours using Dean-Stark apparatus to remove H_2O, encouraging imine formation. The mixture was cooled and the toluene removed under vacuum. The resulting imine was then suspended in 30mL MeOH, and reduced to the amine (3.72g, 80% yield), as above.

d **^{1}H NMR ($CDCl_3$, 300 MHz, 288K):** 1.90 (2H, s, $ArCH_2N$**H**, exchange broadened), 2.78 (4H, t, ^{3}J=5.3Hz, $ArCH_2NHC$**H_2**), 3.57 (8H, m [two indistinguishable triplets of similar chemical shift], $ArCH_2NHCH_2C$**H_2**OC**H_2**-), 3.77 (4H, s, ArC**H_2**), 7.30 (10H, m, **ArH**)

ESMS m/z: 329.2 $[M+H^+]^+$

Step 2



0.5g (1.5mmol) of **I** was dissolved in 30mL of acetonitrile or THF. Et_3N (0.31g, 3.1mmol) and CS_2 (0.23g, 3.1mmol) were added and stirred for 2 hours before increasing the solvent volume to 500mL. $CoCl_2.6H_2O$ (0.24g, 1.02mmol) was added and the mixture stirred for 15 hours under $N_{2(g)}$. The solution ws then evaporated to dryness, before being redissolved in CH_2Cl_2. It was washed four times with water, and then dried over $MgSO_4$. The CH_2Cl_2 was removed under reduced pressure. The resulting green powder was dried overnight *in vacuo*, before being recrystallized from CH_2Cl_2 and Et_2O (0.1g, 13% yield).

d**^{1}H NMR ($CDCl_3$, 300 MHz, 288K):** broad signals. 3.29 (12H, one broad signal rather than the expected triplet, -NHC**H_2**CH_2), 3.58 (24H, m [two indistinguishable triplets of similar chemical shift], -C**H_2**OC**H_2**-), 4.13 (12H, s, ArC**H_2**), 7.30 (30H, m, Ar**H**) **d ^{13}C NMR ($CDCl_3$, 75.5 MHz, 288K):** 47.0 (**C**H_2), 52.6 (**C**H_2), 68.6 (**C**H_2), 70.4 (**C**H_2),

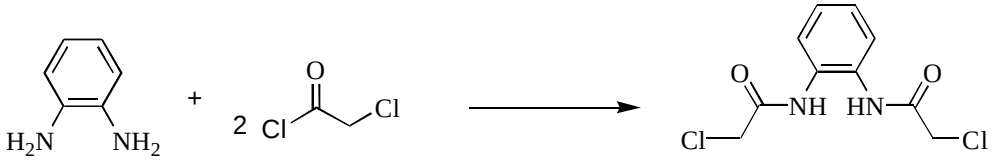
128.9 (Aρ**C**$^{2/3/4}$), 135.3 (Ar**C**^{1}), 208.6 (**C**S_2)

ESMS m/z: 1552.1 $[M]^+$, 1575.1 $[M+Na^+]^+$, 1591.2 $[M+K^+]^+$

Elemental analysis %:	**Calculated**	C	51.0	H	5.1	N	5.4
	Experimental	C	50.8	H	5.3	N	5.9

Cryptand 5b

Step 1 - 2-Chloro-*N*-[2-(2-chloro-acetylamino)-phenyl]-acetamide



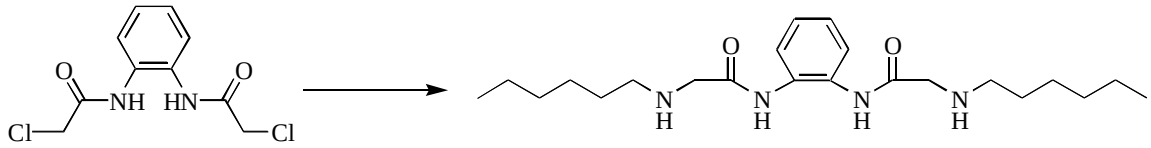
1,2-phenyldiamine (2.16g, 20.0mmol) was dissolved in $CHCl_3$ (50mL) and to this was added KOH (2.36g, 40.0mmol) in H_2O (20mL). Chloroacetyl chloride (4.52g, 40.0mmol) was dissolved in $CHCl_3$ (50mL) and added drop wise to the mixture with stirring. After 15 minutes the solid was filtered off and washed with Et_2O (20mL). Drying in *vacuo* yielded a pink solid.

Yield = 5.12g (98.1%)

^{1}H NMR (300MHz, DMSO-d_6) •: 8.67 (br, 2H, N*H*), 7.52 (d of d, ^{3}J = 6Hz, ^{4}J = 3Hz, 2H, Ar*H*), 7.32 (d of d, ^{3}J = 6Hz, ^{4}J = 3Hz, 2H, Ar*H*), 4.24 (s, 4H, CH_2Cl)

ESMS m/z: 283.1 $[M + Na^+]^+$

Step 2 - 2-Hexylamino-*N*-[2-(2-chloro-acetylamino)-phenyl]-acetamide



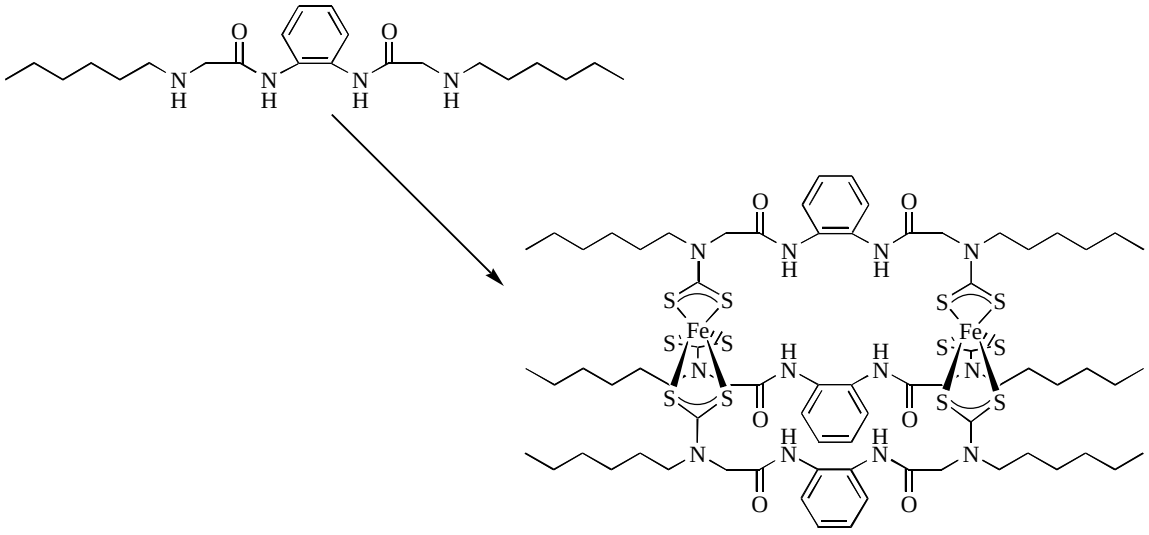
Hexylamine (20mL, excess) was heated to 40ºC and 2-chloro-*N*-[2-(2-chloro-acetylamino)-phenyl]-acetamide (4.24g, 16.6mmol) was added portion wise with stirring. The mixture was stirred for 12 hours. H_2O (200mL) was added and the product extracted into CH_2Cl_2 (4x50mL) and then washed again with H_2O (200mL) and dried over K_2CO_3. Filtration followed by solvent removal and heating at 40ºC in *vacuo* yielded a yellow oil.

Yield = 2.83g (63.0%)

^{1}H NMR (300MHz, $CDCl_3$) •: 9.42 (t, ^{3}J = 7Hz, 2H, CON*H*), 7.60 (d of d, ^{3}J = 6Hz, ^{4}J = 4Hz, 2H, Ar*H*), 7.17 (d of d, ^{3}J = 6Hz, ^{4}J = 4Hz, 2H, Ar*H*), 3.39 (s, 4H, COCH_2), 2.64 (t, ^{3}J = 8Hz, NHCH_2CH$_2$), 1.49 (m, 4H, NHCH$_2$CH_2), 1.29 (m, 12H, CH_2CH_2CH_2CH$_3$), 0.87 (t, ^{3}J = 7Hz, 12H, CH_3)

ESMS m/z: 391.4 $[M + H^+]^+$

Step 3 - Cryptand 5b



2-hexylamino-*N*-[2-(2-chloro-acetylamino)-phenyl]-acetamide (0.94g, 2.4mmol) was dissolved in THF:H_2O (2:1 v/v, 30mL) and KOH (0.27g, 4.8mmol) was added and stirred under $N_{2(g)}$ until dissolved. CS_2 (0.37g, 4.8mmol) was then added and the solution stirred for 30 minutes. $FeCl_3$ (0.29g, 1.6mmol) was added to the yellow solution and the mixture stirred for 15 hours. H_2O (100mL) was added with stirring, filtration followed by recrystallisation from DMSO/Et_2O followed by filtering and washing with EtOH (20mL) and Et_2O (20mL) yielded a black powder which was dried in *vacuo*.

Yield = 0.91g (65.6%)

UV/visible (DMSO) •/nm (•/10^3 $M^{-1}cm^{-1}$): 354 sh (10.4), 389 sh (15.0), 503 sh (4.3), 602 sh (2.3)

IR (Nujol®) •/cm^{-1}: 3214 (NH), 1676 (Amide I), 1518 (Amide II), 1482 (CN), 960 (CS_{as}), 644 (CS_s)

ESMS m/z: 1733.7 $[M + H^+]^+$, 866.7 $[M]^{2+}$

Elemental Analysis %:	Calculate	C	49.9	H	6.3	N	9.7		
Experimental	C	49.9	H	6.0	N	9.8			