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Heterodinuclear ruthenium(II) bipyridyl-transition metal dithiocarbamate macrocycles for anion recognition and sensing

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Abstract—New heterodinuclear ruthenium(II) bipyridyl-transition metal dithiocarbamate macrocycles have been prepared in good yields via metal directed self-assembly and shown to recognise anions. ^{1}H NMR anion titration studies reveal the nature of the bipyridyl amide metal dithiocarbamate spacer unit in the respective dinuclear metal macrocycle influences significantly the strength of chloride and bromide complexation in DMSO solutions. Luminescence spectroscopy was used to sense anions in polar organic solutions via notable emission enhancement and quenching of the respective ruthenium(II) bipyridyl groups in the receptors.

1. Introduction

Anionic species are well known to play numerous fundamental roles in biology and chemical processes and their detrimental effects as environmental pollutants is of growing concern.[1] In view of this, there is intense current interest being shown in the design and syntheses of receptors that are proficient at detecting anions in solution.[1,2] By incorporating redox- and photo-active transition metal inorganic signalling probes into various acyclic, macrocyclic and calixarene ligand frameworks, we have produced a series of selective spectral and electrochemical responsive reagents for anions.[2a,3] In an effort to construct new types of luminescent responsive receptors for anion recognition, we report here the synthesis of heterodinuclear ruthenium(II) bipyridyl-transition metal dithiocarbamate macrocycles using metal directed self-assembly.

2. Synthesis

We have exploited the positively charged ruthenium(II) bipyridyl moiety in the construction of a variety of acyclic and macrocyclic receptors for anion sensing.[2a,3] The preparation of these latter macrocyclic systems can be problematic as their synthesis requires high dilution conditions and often yields are moderate. These synthetic problems may be over come by applying metal directed self-assembly[4] in producing novel heterodinuclear ruthenium(II) bipyridyl-transition metal dithiocarbamate macrocyclic receptors.

Recently, the dithiocarbamate (dtc) moiety has proven to be a useful structural motif lending itself to the metal directed assembly of a range of structures including nano-sized resorcarene-based assemblies,[5] catenanes,[6] assorted macrocycles[7] and cyptands.[8] The dithiocarbamate ligand is simple to prepare via reaction of carbon disulfide with a secondary amine in the presence of base. Consequently, bipyridyl ligands were functionalised initially with secondary amines, and after chelation to the ruthenium(II) bis(bipyridyl) moiety, transition metal directed self-assembly using the dithiocarbamate ligand produced the target heterodinuclear macrocycles.

Reductive amination of 4,4′-diformyl-2,2′-bipyridyl **1** with butylamine afforded the bis amine **2** in 92% yield (Scheme 1). Condensation of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **3** with 2 equiv of *N*-butyl-ethane-1,2-diamine **4** produced the bis-amide-amine bipyridyl derivative **5** in quantitative yield (Scheme 2). Amide-amine bipyridyl compound **9** was similarly prepared by condensation of 4,4′-bis(chlorocarboxyl)-2,2′-bipyridine **3** with 2 equiv of a Boc-protected diamine (Scheme 3), which was obtained from 4-nitrobenzaldehyde (see Section 6).

Refluxing the appropriate bipyridyl amine derivative with *cis*-$Ru(bpy)_2Cl_2$ in aqueous ethanol solution followed by Sephadex column chromatography eluting with acetonitrile/methanol (95:5) and addition of excess NH_4PF_6 produced

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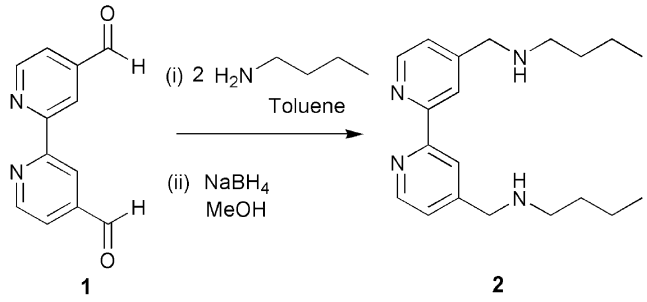

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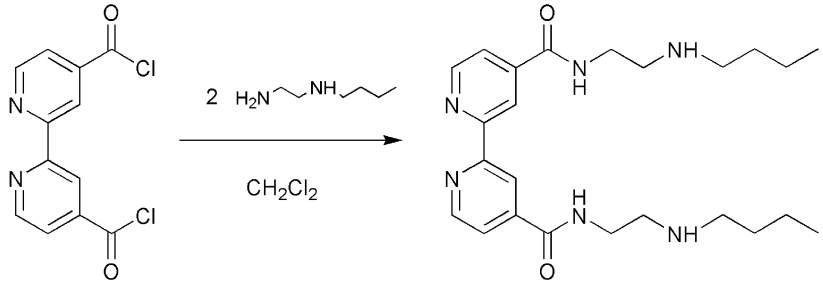
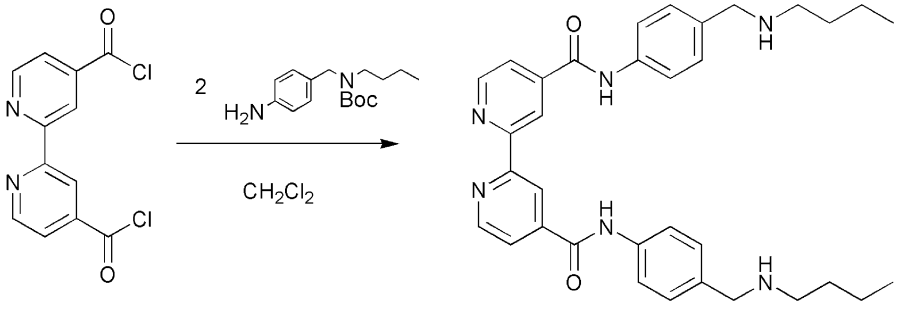
Scheme 1.



3 5

Scheme 2.



3 9

Scheme 3.

the respective ruthenium(II) complexes **10**–**12** in good yields (69–80%, Scheme 4).

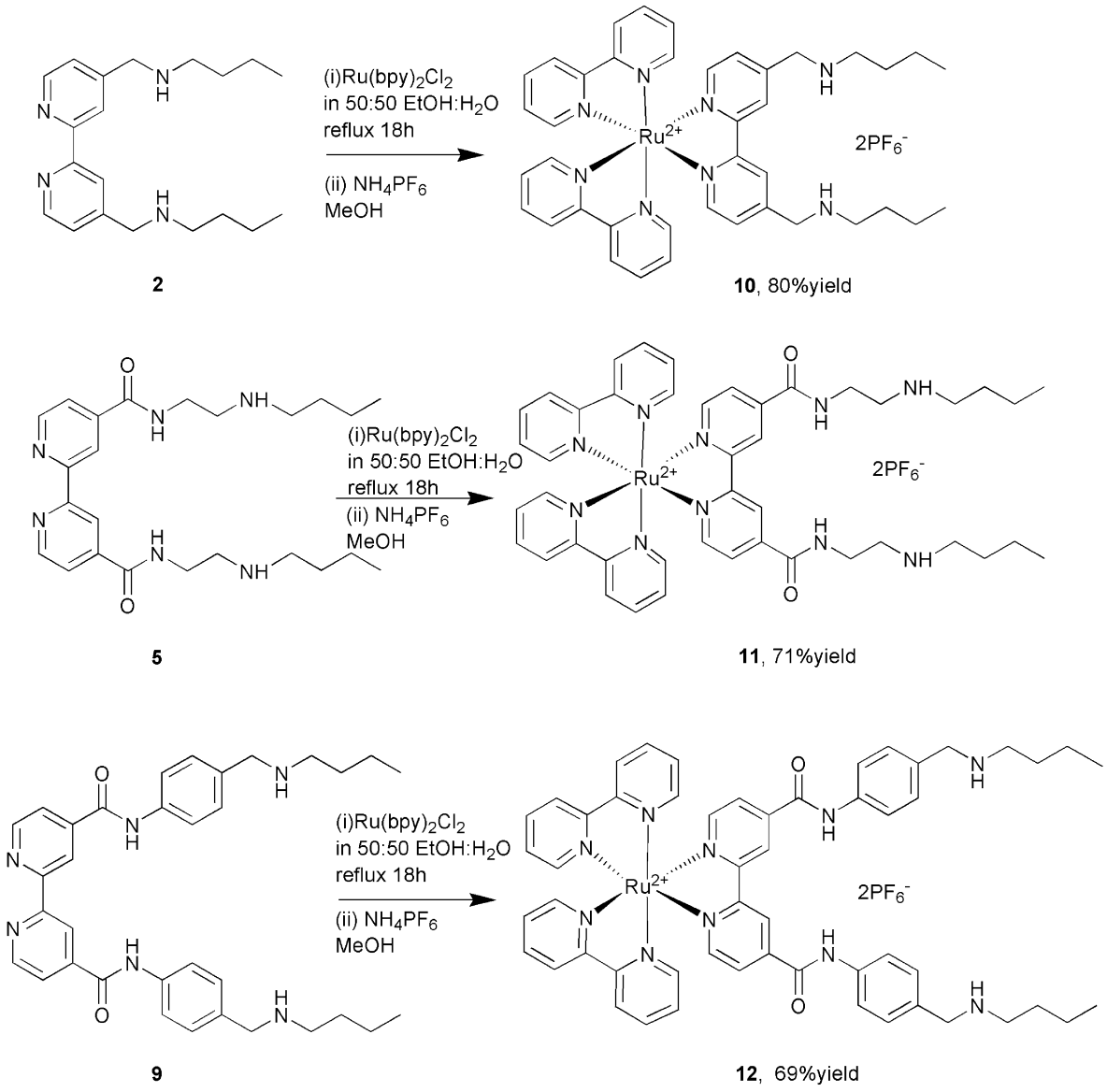
One-pot macrocyclisation with 2 equiv of carbon disulfide, KOH and transition metal acetate salt in acetonitrile/water (9:1) or THF/water (9:1) solutions gave the target heterodinuclear receptors **13**–**21** in good yields (48–95%, Scheme 5). These macrocyclic systems were characterised by ^{1}H NMR spectroscopy (for diamagnetic derivatives), electrospray mass spectrometry (ESMS) and elemental analysis (see Section 6). No evidence from ESMS was seen for dimeric or higher oligomeric structures.

3. Anion coordination studies

The interactions of anions with acyclic ruthenium(II) bipyridyl receptors **11** and **12** and their corresponding macrocycles **16**–**21** were investigated by a variety of spectroscopic techniques.

3.1. NMR titrations

Solubility problems at NMR concentrations dictated that all titration experiments were undertaken in d_6-DMSO. The addition of tetrabutylammonium anion salts to d_6-DMSO solutions of diamagnetic transition metal containing receptors, in general, resulted in significant downfield perturbations of the respective bipyridyl H_3 and amide receptor protons. EQNMR[9] analysis of the resulting titration curves suggested 1:1 receptor/anion stoichiometry in the majority of cases and the calculated stability constant values are shown in Table 1. Unfortunately with dihydrogen phosphate and acetate anions, precipitation problems during the titration experiment thwarted quantitative binding analysis for the majority of the receptors.



Scheme 4.

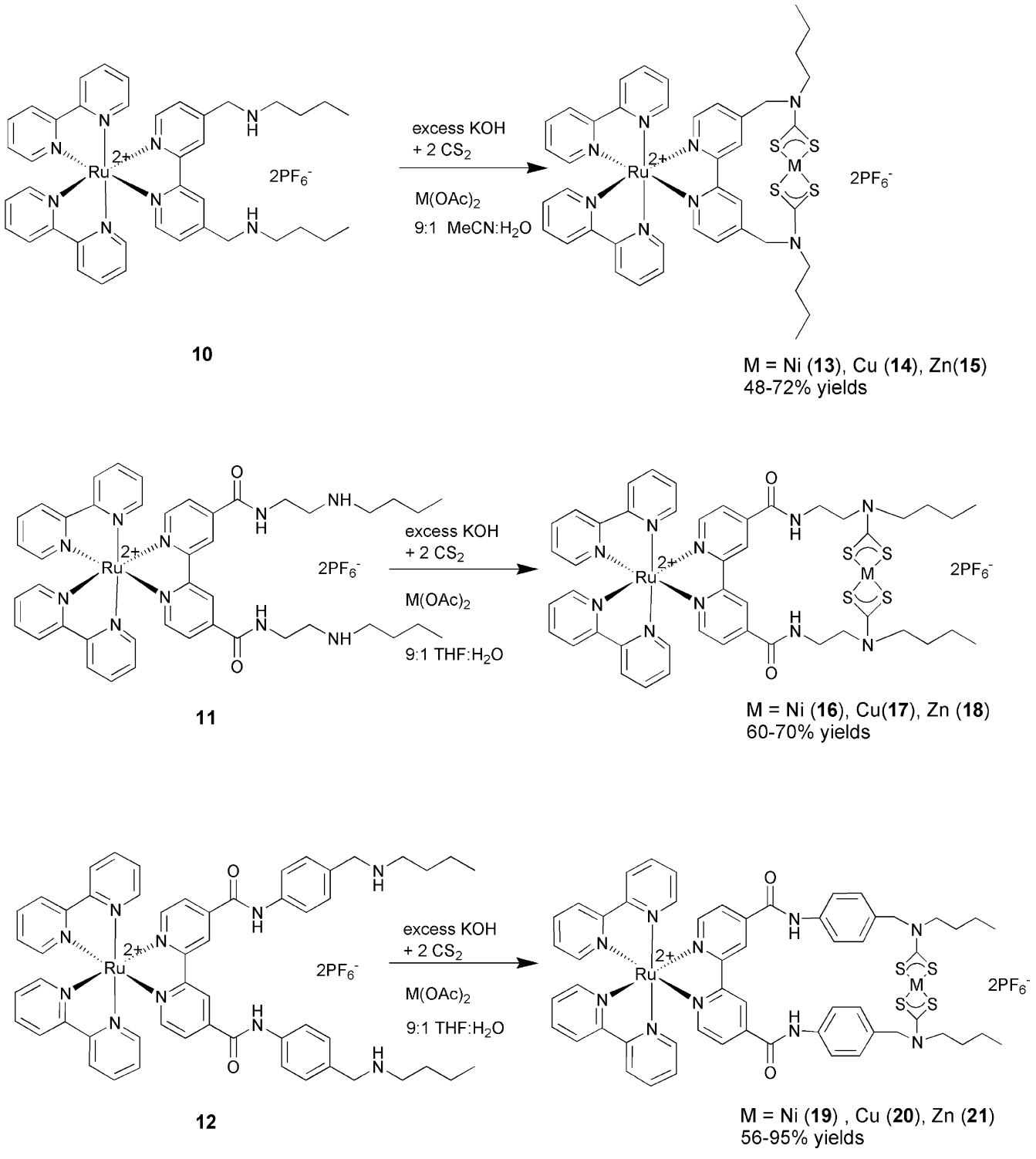
Table 1 shows that all three receptors containing ethyl spacer units connecting the ruthenium(II) bipyridyl amide unit to the respective secondary amine or transition metal dithiocarbamate complex **11**, **16** and **18** display the selectivity preference $Cl^- > Br^- > I^-$, which suggests the chloride anion is of complementary size to the receptors' cavity. These halide binding results contrast those of **19** and **21** where weak binding of all three halide anions is observed. Presumably, the aryl group containing macrocyclic cavity sterically hinders halide complexation. Acyclic receptor **12** complexes Br^- with similar strength to **11**, **16** and **18**. However, the stability of the Cl^- complex is significantly reduced in comparison.

3.2. UV–visible

The electronic spectral characteristics of the receptors are shown in Table 2, where as noted previously,[2a] the electron withdrawing characteristics of the amide groups causes a lower energy MLCT transition compared to the MLCT transition observed with $[Ru(bpy)_3]^{2+}$. The majority of the electronic transitions associated with the transition metal dithiocarbamate complexes are hidden beneath the ruthenium(II) bipyridyl absorptions. The addition of anions to acetonitrile solutions of the respective receptors resulted in small perturbations of the electronic spectrum. In some cases isosbestic points were observed (Fig. 1). However, attempts to determine quantitative binding data using Spectfit[10] proved problematic.

3.3. Luminescence spectroscopy

The ability of $[Ru(bpy)_3]^{2+}$ to act as a luminescent receptor unit is well established.[2] The emission spectra of all receptors displayed a single broad emission maximum which is red-shifted relative to $Ru(bpy)_3$ PF_6 (Table 3). Again the amide substituents on the bipyridyl motif can explain the energy decrease of the MLCT excited state. It is interesting to note that the relative emission intensities of the heterodinuclear macrocycles vary greatly depending



Scheme 5.

upon the nature of the transition metal dtc complex. The presence of redox-active transition metals nickel(II) **16** and copper(II) **17**, causes luminescence quenching of the $Ru(bpy)_3^{2+}$ units. Figure 2 shows that the emission intensity for zinc(II) dtc containing macrocycle **18** is much larger than that of acyclic ruthenium(II) bipyridyl receptor **11** and that emission quenching is clearly observed with **16** and **17** relative to **11**. The effects of addition of anions in the luminescence spectra of the receptors were investigated in acetonitrile for **11**, **16**–**18** and in DMSO for **12**, **19**–**21** due to solubility differences.

3.4. Emission binding studies in acetonitrile

The effect of anion addition on the emission spectra depended on the receptor in question. For **11** there was typically a marked increase in the intensity of the emission upon addition of chloride, bromide, iodide, and acetate with

Table 1. Anion stability constant values K (M^{-1}) in DMSO-d_6

	$M(dtc)_2$ M=	$H_2PO_4^-$	AcO^-	Cl^-	Br^-	I^-
11	—	1000	[a]	900	120	20
12	—	[b]	[a]	245	180	<10
16	Ni	[b]	990	1000	190	0
18	Zn	[a]	[b]	920	140	0
19	Ni	[b]	[b]	<10	<10	<10
21	Zn	[b]	[b]	<10	<10	<10

Errors estimated to be ≤10%, temp=298 K.
[a] EQNMR[8] could not fit data.
[b] Precipitation occurred.

Table 2. UV–visible characterisation data in CH_3CN at 1.25×10^{-5} M

Compound	MLCT		LC		MLCT	
	Wavelength (nm)	$\varepsilon/10^3$ M^{-1} cm^{-1}	Wavelength (nm)	$\varepsilon/10^3$ M^{-1} cm^{-1}	Wavelength (nm)	$\varepsilon/10^3$ M^{-1} cm^{-1}
$[Ru(bpy)_3]^{2+}$	244	27.2	287	79.8	450	14.3
10	245	180.0	287	75.6	454	75.2
11	246	20.6	288	46.8	451	8.2
13	245	45.9	288	72.9	454	14.0
14	245	24.2	287	53.3	454	11.0
15	245	41.6	288	89.6	454	17.5
16	246	49.7	288	79.5	456	12.6
17	244	28.7	287	55.2	445	10.5
18	254	41.0	286	75.8	455	12.6

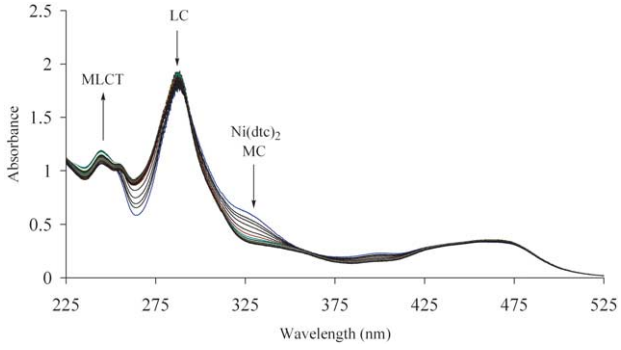


Figure 1. UV–visible titration of **16** and AcO^- in CH_3CN.

a concomitant hypsochromic shift in the emission λ_{max} (Table 4). For example, the addition of excess chloride to **11** caused a 47% increase in intensity and a 4.5 nm blue shift in the emission maximum (Fig. 3). The hypsochromic shift indicates that the MLCT state moves to higher energy in the presence of an anion. The MLCT $d\pi^*$ state has the electron formally residing on the bipyridine ligand, and this configuration is presumably less favourable when a negatively charged guest binds to the amide bipyridine group. The emission enhancement is probably due to the binding of an anion causing the receptor molecule to become more structurally rigid, by restricting its vibrational and rotational modes. This limits the pathways for radiationless decay, and hence increases the observed emission intensity.[11]

Table 3. Emission data in CH_3CN except for compounds marked '*' were in DMSO, 1.25×10^{-5} M, λ_{excit} at maxima of MLCT

Receptor	$M(dtc)_2$ M=	Wavelength (nm)	Intensity (arbitrary units)
$[Ru(bpy)_3][PF_6]_2$		597	56
20	—	603	214
21	—	631	87
22*	—	639	202
23	Ni	604	10
24	Cu	623	24
25	Zn	625	220
26	Ni	625	3
27	Cu	630	13
29	Zn	630	214
30*	Cu	635	119
31*	Zn	638	206

In contrast, macrocycle **18** displayed significant decreases in emission intensity on addition of anions. The luminescence quenching observed upon anion addition to the macrocyclic receptor is more difficult to explain. One possible cause of luminescence quenching is if the symmetry of the molecule is altered upon complexation, destabilising the ^{3}MLCT excited state. Thus the emission would be quenched, and an intensity decrease would be observed. This effect might also cause a change in the energy levels involved, which would be observed as a shift in the wavelength of the emission maximum.[12] Disappointingly, only small increases in

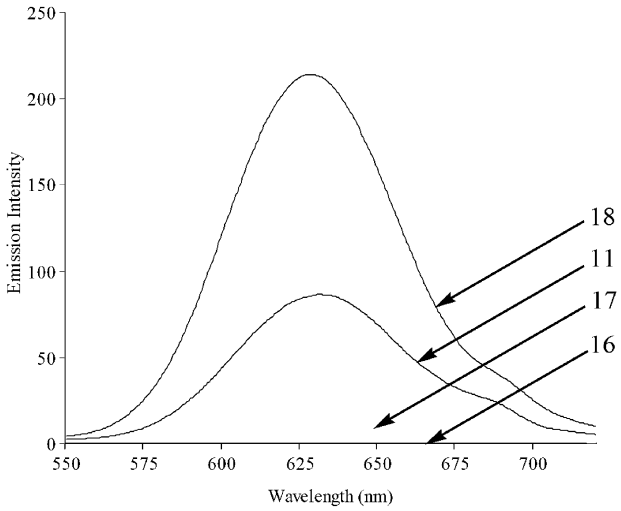


Figure 2. Emission spectra of **11** and **16–18** in CH_3CN, 1.25×10^{-5} M.

Table 4. Percentage change in emission maxima intensity in CH_3CN and change in wavelength maxima upon addition of excess anions

Anion	AcO^-	$H_2PO_4^-$,	Cl^-	Br^-	I^-
(11)	+64%	+39%	+47%	+38%	+7%
$\Delta\lambda_{max}$ (nm)	−12.5	−2.5	−4.5	−3.0	−3.0
(18)	−65%	−88%	−45%	−30%	−30%
$\Delta\lambda_{max}$ (nm)	−12.0	−2.0	−5.5	−4.5	−3.5

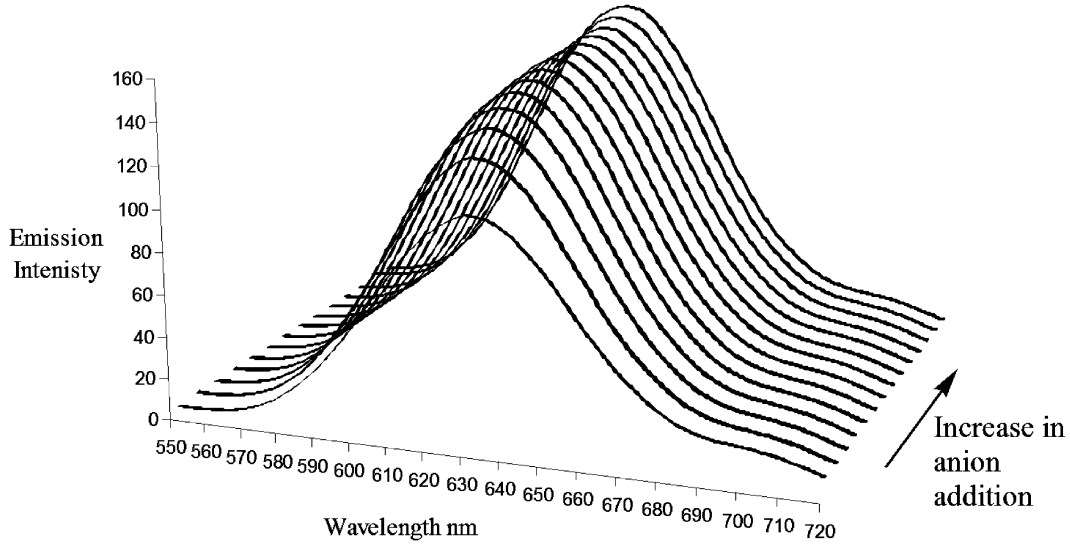


Figure 3. Luminescence titration of **11** with Cl^- in CH_3CN, 1.25×10^{-5} M.

emission intensity upon addition of anions to macrocycles **16** and **17** were observed.

Specfit[10] analysis of the titration data enabled stability constants to be determined (Table 5). The stability constants in acetonitrile for receptor **11** are all very high in this solvent and are quoted as log $\beta_1>6$, which is approaching the upper limit for log β_1 values by Specfit.[10] The halide anions (chloride, bromide and iodide) were all bound by receptor **11** with similarly large stability constants, whereas macrocycle **18** showed a selectivity trend $Cl^->Br^->I^-$, as seen in the ^1H NMR titration experiments. Stability constants for receptors **11** and **18** with dihydrogen phosphate could not be determined due to the complexity of the emission responses, and acetate was bound strongly by both receptors.

3.5. Emission binding studies in DMSO

The anion emission titration studies for receptors **12** and **19–21** were conducted in DMSO, due to their poor solubility in acetonitrile. Addition of anions to the ruthenium(II) receptor **12** in DMSO resulted in small increases in the emission intensity and slight hypsochromic shifts. However, the changes in the emission intensity in

Table 5. Stability constants determined by Specfit[10] in CH_3CN at receptor concentrations of 1.25×10^{-5} M (Temp=298 K)

	log β_1 **11**	log β_1 **18**
AcO^-	>6	>6
$H_2PO_4^-$	[a]	[a]
Cl^-	>6	5.72±0.07
Br^-	>6	5.04±0.04
I^-	>6	4.76±0.06

[a] Specfit[10] could not fit data.

DMSO were much less than those observed in CH_3CN for compound **11**. This is to be expected due to the competitive nature of DMSO.[13] Addition of anions to the macrocycles **19–21** caused only small decreases in emission intensity.

The only anion to cause significant changes in the emission spectra was dihydrogen phosphate. For this anion stability constants could be determined with a 1:1 stoichiometry and are given in Table 6. The zinc(II) macrocycle **21** displayed an enhanced binding affinity for dihydrogen phosphate compared to its acyclic analogue **12**.

Table 6. Stability constants determined by Specfit[10], in DMSO at receptor concentrations of 1.25×10^{-5} M (Temp=298 K)

	log β_1 **12**	log β_1 **21**
$H_2PO_4^-$	4.2±0.1	5.28±0.06

4. Electrochemical investigations

The electrochemical properties of **10**, **11** and copper(II) dtc containing receptors **14** and **17** were investigated using cyclic and square wave voltammetry with tetrabutylammonium tetrafluoroborate as supporting electrolyte. As expected the electrochemical data for **10** and **11** are similar to $Ru(bpy)_3^{2+}$, displaying four redox waves assigned to a metal centred Ru(II)/(III) oxidation and three ligand centred bipyridyl reduction processes (Table 7). The electrochemical properties of copper(II) dithiocarbamate complexes are well-documented undergoing reversible one-electron oxidation and reduction redox processes.[14–16]

The copper(II/III) couple in macrocycles **14** and **17** is compared to the copper(II/III) couple in the model compound, copper(II) diethyl dithiocarbamate ($Cu(Et_2dtc)_2$). The electrochemical investigations of **14** and **17** were limited to an electrochemical window of +1.25–0 V, in order to avoid decomposition of the macrocycles. Under more reducing conditions precipitation was observed and irreproducible results were noted. Thus assignment and study of the 2,2′-bpy reductions was rendered impossible (Table 7).

For all receptors the ruthenium(II/III) redox wave was observed at ~1.0 V. For **11** the first bipyridyl ligand centred reduction is assigned to the 4,4′-amide-substituted bipyridyl. The electron withdrawing amide group means that this bipyridyl group is easier to reduce than its neighbouring ones. The anodic shifts in the copper(II/III) couple for the ruthenium macrocycles **14** and **17** compared to $Cu(Et_2dtc)_2$ may be a result of the close proximity of the positively charged ruthenium(II) centre. All four systems investigated displayed quasi-reversible behaviour for both the ruthenium (II/III) couple and the copper(II/III) redox couples (for receptors **14** and **17**).

The addition of dihydrogen phosphate to receptor **10** caused a small cathodic shift for the first bipyridyl reduction wave (10 mV), but addition of acetate, chloride, bromide, and iodide caused little change (<5 mV). Addition of anions to **11** also caused modest cathodic shifts of ~10 mV for the first bipyridyl wave. The shift was approximately the same for addition of all anions, and little discrimination was shown. For both receptors **10** and **11**, no shifts were observed for the ruthenium(II/III) couple or the second and third bipyridyl reduction couples on the addition of anions. Electrochemical studies on $[Ru(bpy)_3][(PF_6)_2]$ showed no perturbations upon addition of anions to either the ruthenium(II/III) oxidation wave, or the bipyridyl reduction waves.

Cathodic shifts occur because the complexation of anions increases the negative charge density adjacent to the binding site.[17] This in turn inhibits the reduction of the redox centre and so a greater formal reduction potential is required to add more electrons. As noted in previous systems, the fact that no shifts were observed for the second or third bipyridyl reduction couples or for the ruthenium(II/III) couple lends support to the hypothesis that the binding of anionic guests is centred in the vicinity of the substituted bipyridyl groups in solution.

Electrochemical investigations of the macrocycles **14** and **17** and $Cu(Et_2dtc)_2$ upon addition of anions revealed no perturbations of the ruthenium(II/III) redox wave. However, significant cathodic shifts were observed in the copper(II/III) redox wave (Table 8). The addition of dihydrogen phosphate to macrocycle **14** resulted in a shift of 40 mV. This shift was considerably larger than the shift observed for $Cu(Et_2dtc)_2$ (<10 mV). Receptor **14** showed little interaction with acetate. However, the large cathodic shift in the copper(II/III) redox potential of $Cu(Et_2dtc)_2$ upon addition

Table 7. Electrochemical data for **10**, **11**, **14**, **17** in CH_3CN/0.1 M $TBABF_4$, $Ag/AgNO_3$ reference electrode

Complex	Ru(II/III) couple $E_{1/2}$/V	First 2,2′-bpy reduction $E_{1/2}$/V	Second 2,2′-bpy reduction $E_{1/2}$/V	Third 2,2′-bpy reduction $E_{1/2}$/V	Cu(II/III) couple $E_{1/2}$/V
$[Ru(bpy)_3]^{2+}$	+1.03	−1.61	−1.82	−2.12	—
10	+1.02	−1.60	−1.83	−2.12	—
11	+1.03	−1.51	−1.80	−2.10	—
14	+1.00	—	—	—	+0.29
17	+1.02	—	—	—	+0.20
$Cu(Et_2dtc)_2$	—	—	—	—	+0.19

$E_{1/2}=(E_{pa}+E_{pc})/2$.

Table 8. Cathodic shifts in Cu(II/III) redox wave upon addition of 5 equiv of anion in CH_3CN/0.1 M $TBABF_4$

Cu(II/III) couple ΔE (mV)	$Cu(Et_2dtc)_2$	**14**	**17**
$H_2PO_4^-$	<10	40	[a]
AcO^-	60	<10	[a]

[a] Precipitation occurred.

of acetate anions may imply there is a coordinative interaction between the copper(II) centre and the anion.

Unfortunately, no significant changes in oxidation potentials were observed on addition of bromide or iodide to **14** or **17**. At the concentrations used for the electrochemical experiments, addition of dihydrogen phosphate and acetate anions to receptor **17** caused precipitation, hindering further investigation.

5. Conclusions

A series of new 4,4′-amide-secondary amine substituted ruthenium(II) bipyridyl derivatives were prepared initially, which on applying metal directed self-assembly, using the dithiocarbamate ligand, produced novel heterodinuclear ruthenium(II) bipyridyl-transition metal dithiocarbamate macrocycles in good yields. A variety of spectroscopic and electrochemical techniques were employed to investigate their anion recognition and sensing capabilities. It is noteworthy that the nature of the spacer unit in the respective dinuclear metal macrocycles crucially dictates the strength of chloride and bromide binding in DMSO solutions with ethyl spacer containing macrocyclic receptors **16** and **18** forming much stronger complexes than the corresponding aryl linked systems **19** and **21**. Although UV–visible absorption spectroscopy proved largely insensitive to anion complexation, the luminescence spectra of the receptors were significantly perturbed on anion binding. Both anion complexation induced emission enhancement and quenching effects were noted, respectively, with **11** and **18**.

Voltammetric studies revealed modest anion induced cathodic shifts of the respective first bipyridyl reduction redox couple of acyclic receptors **10** and **11**, whereas a significant cathodic perturbation of the copper(II)/(III) dtc redox couple of **14** was noted with dihydrogen phosphate anion addition.

6. Experimental

6.1. General

NMR spectra were recorded on a Varian Mercury 300 or a Varian Unity Plus machine 500. FAB Mass spectrometry was carried out by the EPSRC mass spectrometry service, Swansea. Elemental analyses were performed by the Inorganic Chemistry Laboratory Microanalysis Service and electrospray mass spectrometry (ESMS) were performed on a Micromass ESI-TOF in the Inorganic Chemistry Department, University of Oxford. Fluorescence spectra were recorded on a Perkin Elmer Lamba 6 UV–visible Spectrometer. Measurements were conducted at 25 °C using a 1×1 cm rectangular quartz cuvette. UV–visible spectra were recorded on a PE Lamba 6 spectrometer. Electrochemical studies were performed on a Princeton Applied Research potentiastat/galvanostat model 273 using a glassy carbon working electrode, a platinum counter electrode and an $Ag/AgNO_3$ reference electrode (0.33 V ± 10 mV vs SCE). Kemet diamond sprays (1 μm and 0.25 μm) were used to polish the working electrode.

4,4′-Diformyl-2,2′-bipyridine **1**,[18] 4,4′-bis(carboxy)-2,2′-bipyridine **3**,[19] and 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **4**,[18] were prepared according to literature procedures.

6.1.1. 4,4′-Bis(butylaminomethyl)-2,2′-bipyridine, 2. 4,4′-Diformyl-2,2′-bipyridine (0.20 g, 0.9 mmol) and *n*-butylamine (0.13 g, 1.8 mmol) were dissolved in toluene (100 ml). The mixture was refluxed under nitrogen for 45 min using Dean–Stark apparatus and then the solvent was removed to yield an orange oil. This was dissolved in MeOH (100 ml) and a fivefold excess of $NaBH_4$ was cautiously added and stirred for 1 h under nitrogen. HCl (aq) (2 M) was added carefully until pH=1. The mixture was made basic (pH=11) by the addition of KOH (aq) (2 M). The product was extracted into CH_2Cl_2 (4×50 ml) and dried over K_2CO_3. Solvent removal and drying in vacuo yielded a yellow oil (0.27 g, 92%).

^{1}H NMR in $CDCl_3$ (δ/ppm): 0.85 (t, 6H, ^3J=7.2 Hz, CH_3), 1.30 (m, 4H, ^3J=7.2 Hz, CH_2CH$_3$), 1.45 (m, 4H, ^3J=7.2 Hz, CH$_2$CH_2CH$_3$), 2.58 (t, 4H, ^3J=7.2 Hz, NCH_2CH$_2$), 3.83 (s, 4H, bpyCH_2NH), 7.27 (d, 2H, ^3J=4.8 Hz, bpy-*H*5,5′), 8.27 (s, 2H, bpy-*H*3,3′), 8.56 (d, 2H, ^3J=4.8 Hz, bpy-*H*6,6′).

^{13}C NMR in $CDCl_3$ (δ/ppm): 14.67 (*C*H$_3$), 23.50 (*C*H$_2$), 32.23 (*C*H$_2$), 50.03 (*C*H$_2$NH), 53.43 (bpy*C*H$_2$), 120.71 (bpy-*C*), 123.27 (bpy-*C*), 139.01 (bpy-*C*), 149.34 (bpy-*C*), 150.77 (bpy-*C*).

ESMS: *m*/*z* 327.3 $[M+H]^+$.

6.1.2. 4,4′- Bis-[(2-butylamino-ethyl-carbamoyl] 2,2′-bipyridine, 5. *N*-Butyl-ethane-1,2-diamine (0.2 g, 1.7 mmol) was dissolved in CH_2Cl_2 (30 ml) under a nitrogen atmosphere. To this rapidly stirred solution, a solution of 4,4′-di(chlorocarbonyl)-2,2′-bipyridine **4** (0.24 g, 0.8 mmol) dissolved in CH_2Cl_2 (30 ml) was added dropwise. A white precipitate formed immediately, but the solution was stirred for a further 15 min to ensure completion of the reaction. The product was filtered, washed with H_2O (2×15 ml), Et_2O (2×15 ml) and dried in vacuo to give a highly insoluble white solid in quantitative yield (0.38 g).

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.82 (t, 6H, ^3J=3.9 Hz, CH_3), 1.28 (m, 4H, CH_2CH$_3$), 1.52(m, 4H, CH_2CH$_2$CH$_3$), 2.65 (m, 4H, NHCH_2CH$_2$CH$_2$CH$_3$), 2.81 (m, 4H, CH_2NH), 3.54 (m, 4H, CH_2NHCO), 7.88 (m, 2H, bpy-*H*5,5′), 8.76 (s, 2H, bpy-*H*3,3′), 8.83 (m, 2H, bpy-*H*6,6′), 9.14 (m, 2H, CON*H*).

ESMS: *m*/*z* 441.6 $[M+H]^+$, 463.6 $[M+Na]^+$.

6.1.3. Butyl-(4-nitro-benzyl)-amine, 6. 4-Nitrobenzaldehyde (2 g, 13 mmol) and *n*-butylamine (0.96 g, 13 mmol) were dissolved in toluene (100 ml). The mixture was refluxed under nitrogen for 45 min using Dean–Stark apparatus and the solvent was removed to yield an orange oil. This was dissolved in MeOH (100 ml) and a five-fold excess of $NaBH_4$ was added cautiously and stirred for 1 h under nitrogen. HCl (aq) (2 M) was added carefully until pH=1 and then NaOH (aq) (2 M) until pH=11. The product was extracted into CH_2Cl_2 (4×50 ml) and dried over K_2CO_3. Solvent removal and drying *in vacuo* yielded a yellow oil (1.76 g, 65% yield).

^{1}H NMR in $CDCl_3$ (δ/ppm): 0.81 (t, 3H, ^3J=7.2 Hz, CH_3), 1.19 (m, 2H, ^3J=7.2 Hz, CH_2CH$_3$), 1.40 (m, 2H, ^3J=7.2 Hz, CH_2CH$_2$CH$_3$), 3.11 (m, 2H, NHCH_2CH$_2$), 4.43 (s, 2H, ArCH_2), 7.30 (d, 2H, ^3J=7.8 Hz, Ar-*H*), 8.10 (d, 2H, ^3J=7.8 Hz, Ar-*H*).

ESMS: *m*/*z* 209.1 $[M+H]^+$.

6.1.4. Butyl-(4-nitro-benzyl)-carbamic acid *tert*-butyl ester, 7. Bis-(*tert*-butoxycarbonyl)anhydride (0.27, 1.2 mmol) was dissolved in 30 ml of dioxane. This was added, over 2 1/2 h, to butyl-(4-nitro-benzyl)-amine (0.2 g, 1.1 mmol) (which was dissolved in 30 ml of dioxane). The solution was stirred for 30 min, after which time the solvent was removed in vacuo giving a white semi-solid. H_2O (50 ml) was added and the product was extracted into CH_2Cl_2 (3×50 ml), dried with $MgSO_4$, filtered and reduced in vacuo leaving a clear, viscous oil (0.25 g, 74% yield).

^{1}H NMR in $CDCl_3$ (δ/ppm): 0.85 (t, 3H, ^3J=7.8 Hz, CH$_2$CH_3), 1.23 (m, 4H, ^3J=6.6 Hz, CH_2CH_2CH$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 3.14 (m, 2H, NBocCH_2CH$_2$), 4.46 (s, 2H, ArCH_2), 7.34 (d, 2H, ^3J=8.4 Hz, Ar-*H*), 8.13 (d, 2H, ^3J=8.1 Hz, Ar-*H*).

^{13}C NMR in $CDCl_3$ (δ/ppm): 13.95 (*C*H$_3$), 20.14 (*C*H$_2$), 28.52 ((*C*H$_3$)$_3$C), 30.5 (*C*H$_2$), 47.34 (*C*H$_2$), 67.24 (Ar*C*H$_2$N), 80.24 ((CH$_3$)$_3$*C*), 123.88 (Ar-*C*), 128.22 (Ar-*C*), 128.26 (Ar-*C*), 147.32 (Ar-*C*).

ESMS: *m*/*z* 331.2 $[M+Na]^+$.

6.1.5. (4-Amino-benzyl)- butyl-carbamic acid *tert*-butyl ester, 8. The nitro compound **7** (6.20 g, 0.018 mol) was reduced using Raney Nickel, 10 atm, 50 °C, 1 h in EtOH. The solvent was removed and the product purified by column chromatography on silica eluting with CH_2Cl_2 to give the amine (3.62 g, 72% yield).

^{1}H NMR in $CDCl_3$ (δ/ppm): 0.80 (t, 3H, ^3J=6.9 Hz, CH_3), 1.11 (m, 4H, ^3J=6.6 Hz, CH_2CH_2CH$_3$), 1.39 (s, 9H, CCH_3), 3.03 (br s, 2H, NH$_2$), 3.68 (m, 2H, NBocCH_2CH$_2$), 4.21 (s, 2H, ArCH_2), 7.15 (d, 2H, ^3J=8.1 Hz, Ar-*H*), 7.26 (d, 2H, ^3J=7.8 Hz, Ar-*H*).

^{13}C NMR in $CDCl_3$ (δ/ppm): 13.98 (*C*H$_3$), 20.16 (*C*H$_2$), 28.61 ((*C*H$_3$)$_3$C), 30.21 (*C*H$_2$), 45.85 (*C*H$_2$), 67.15 (Ar*C*H$_2$N), 79.27 ((CH$_3$)$_3$*C*), 115.08 (Ar-*C*), 128.10 (Ar-*C*), 129.33 (Ar-*C*), 146.14 (Ar-*C*).

ESMS: *m*/*z* 301.2 $[M+Na]^+$.

6.1.6. 4,4″ Bis-[(4-butylaminomethyl-phenyl)-carbamoyl]-2,2′-bipyridine, 9. (4-Amino-benzyl)- butyl-carbamic acid *tert*-butyl ester **8** (4.88 g, 1.7 mmol) was dissolved in CH_2Cl_2 (30 ml) under a nitrogen atmosphere. To this a solution of 4,4′-di(chlorocarbonyl)-2,2′-bipyridine (2.03 g, 8.0 mmol) dissolved in CH_2Cl_2 (30 ml) was added dropwise. An orange precipitate formed immediately, but the solution was stirred for a further 15 min to ensure completion of the reaction. The product was filtered, washed with H_2O (2×15 ml), Et_2O (2×15 ml) and dried in vacuo to give an orange solid (5.88 g, 96% yield). Interestingly during this reaction the amine protecting group (Boc) was removed to yield the free amine.

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.93 (t, 6H, CH_3), 1.22 (m, 4H, CH_2CH$_3$), 1.43 (m, 4H, CH_2CH$_2$CH$_3$), 3.15 (m, 4H, NHCH_2CH$_2$), 4.37 (s, 4H, ArCH_2), 7.20 (d, 4H, ^3J=7.8 Hz, Ar-*H*), 7.75 (d, 4H, Ar-*H*), 8.03 (d, 4H, ^3J=7.2 Hz, bpy-*H*5,5′), 8.94 (m, 4H, bpy-*H*6,6′ and CON*H*), 10.86 (s, 2H, bpy-*H*3,3′).

ESMS: *m*/*z* 565.7 $[M+H]^+$.

6.1.7. Ruthenium(II) (4,4′-bis(butylaminomethyl)-2,2′-bipyridine)bis(2,2′-bipyridine)-bis(hexafluorophosphate), 10. *cis*-Dichlorobis(2,2′-bipyridine)ruthenium(II) (0.12 g, 0.2 mmol) and 4,4′-bis-(butylaminomethyl)-2,2′-bipyridine **2** (0.09 g, 0.2 mmol) were dissolved in EtOH/H_2O (50:50) (50 ml) and refluxed for 18 h. The solvent was removed in vacuo leaving a shiny deep purple solid. The crude product was purified by column chromatography on Sephadex® LH-20, eluting with MeCN to remove excess $[Ru(bpy)_2Cl_2]$ and then 5% MeOH in MeCN to obtain the product. Solvent removal gave a deep purple shiny, flaky solid. It was noted that for this and all subsequent ruthenium compounds that there was a thin green band, between the purple of the *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) and the red of the product, attributed to a ruthenium(III) complex. The chloride counteranion was exchanged for hexafluorophosphate by dissolving the chloride salt in the minimum amount of MeOH and adding a saturated solution of NH_4PF_6 (aq). This gives the hexafluorophosphate salt as a precipitate, which can be removed by filtration, washed with H_2O, then Et_2O and dried under vacuum to yield a red solid (typically 90–94% conversion from the chloride salt). The red solid was isolated and dried under vacuum (0.16 g, 80% yield).

^{1}H NMR in CD_3CN (δ/ppm): 0.94 (t, 6H, ^3J=7.0 Hz, CH_3), 1.40 (m, 4H, ^3J=7.5 Hz, CH_2CH$_3$), 1.63 (m, 4H, ^3J=7.5 Hz, CH_2CH$_2$CH$_3$), 2.96 (m, 4H, ^3J=7 Hz, NCH_2CH$_2$), 4.22 (s, 4H, bpy*CH*$_2$NH), 7.44 (m, 6H, bpy-H_e and bpy-*H*5,5′), 7.75 (m, 6H, bpy-*H*6,6′ and bpy-H_f), 8.09 (t, 4H, ^3J=7.8 Hz, bpy-H_d), 8.52 (d, 6H, ^3J=7.8 Hz, bpy-H_c), 8.59 (s, 2H, bpy-*H*3,3′).

^{13}C NMR in CD_3CN (δ/ppm): 13.44 (*C*H$_3$), 20.04 (*C*H$_2$), 30.27 (*C*H$_2$), 48.83 (*C*H$_2$NH), 50.59 (bpy*C*H$_2$), 124.56 (bpy-*C*), 125.01 (bpy-*C*), 127.87 (bpy-*C*), 127.92 (bpy-*C*), 138.19 (bpy-*C*), 151.76 (bpy-*C*), 151.85 (bpy-*C*), 152.03 (bpy-*C*), 157.07 (bpy-*C*), 157.17 (bpy-*C*).

Elemental analysis: found: C 44.7%, H 4.8%, N 10.4%.

Calculated ($C_{40}H_{46}N_8RuP_2F_{12}\cdot 2H_2O$): C 45.0%, H 4.7%, N 10.5%.

ESMS: *m/z* 739.9 $[M-2PF_6]^+$, 884.9 $[M-PF_6]^+$, 1029.9 $[M]^+$.

6.1.8. Ruthenium(II) 4,4′- bis-[(2-butylamino-ethyl-carbamoyl] 2,2′-bipyridine bis(2,2′-bipyridine)-bis(hexafluorophosphate), 11. Procedure as for receptor **10**, using *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) (0.19 g, 0.36 mmol) and 4,4′-bis-[(2-butylamino-ethyl-carbamoyl] 2,2′-bipyridine **5** (0.16 g, 0.36 mmol) The hexafluorophosphate salt was then isolated (0.29 g, 71% yield).

^{1}H NMR in CD_3CN (δ/ppm): 0.96 (t, 6H, $^3J=7.2$ Hz, CH_3), 1.42 (m, 4H, $^3J=7.5$ Hz, CH_2CH$_3$), 1.66 (m, 4H, $^3J=7.0$ Hz, CH_2CH$_2$CH$_3$), 3.07 (t, 4H, $^3J=8.0$ Hz, NHCH_2CH$_2$ CH$_2$CH$_3$), 3.28 (t, 4H, $^3J=5.1$ Hz, CH_2NHCH$_2$CH$_2$CH$_2$), 3.71 (m, 4H, $^3J=7.0$ Hz, CONHCH_2), 7.44 (m, 4H, $^3J=5.7$ Hz, bpy-H_e), 7.73 (m, 6H, bpy-*H*5,5′ and bpy-H_f), 7.96 (d, 2H, $^3J=6.0$ Hz, bpy-*H*6,6′), 8.10 (m, 4H, $^3J=6.0$ Hz, bpy-H_d), 8.55 (m, 6H, bpy-H_c and 2CON*H*), 9.04 (s, 2H, bpy-*H*3,3′).

^{13}C NMR in CD_3CN (δ/ppm): 13.24 (*C*H$_3$), 19.74 (*C*H$_2$), 28.15 (*C*H$_2$), 37.41 (*C*H$_2$), 48.57 (*C*H$_2$), 48.92 (*C*H$_2$), 124.97 (bpy-*C*), 125.66 (bpy-*C*), 126.20 (bpy-*C*), 128.33 (bpy-*C*), 138.80 (bpy-*C*), 141.97 (bpy-*C*), 152.28 (bpy-*C*), 153.30 (bpy-*C*), 157.21 (bpy-*C*), 157.34 (bpy-*C*), 158.10 (bpy-*C*), 165.76 (*C*O).

Elemental analysis: found: C 43.2%, H 5.0%, N 11.1%.

Calculated ($C_{44}H_{52}N_{10}RuO_2P_2F_{12}\cdot 4H_2O$): C 43.5%, H 5.0%, N 11.5%.

ESMS: *m/z* 427.2 $[M-2PF_6]^{2+}$, 500.2 $[M-PF_6]^{2+}$, 573.2 $[M]^{2+}$.

6.1.9. Ruthenium(II) (4,4′ bis-[(4-butylaminomethyl-phenyl)-carbamoyl]-2,2′-bipyridine) bis(2,2′-bipyridine)-bis(hexafluorophosphate), 12. Procedure as for receptor **10** using *cis*-dichlorobis(2,2′-bipyridine)ruthenium (II) (0.85 g, 1.6 mmol) and 4,4′ bis-[(4-butylaminomethyl-phenyl)-carbamoyl]-2,2′-bipyridine **9** (1.25 g, 1.6 mmol) The product was isolated as a deep purple shiny, flaky solid. (1.40 g, 69% yield).

^{1}H NMR in CD_3CN (δ/ppm): 0.94 (t, 6H, $^3J=5$ Hz, CH_3), 1.39 (m, 4H, CH_2CH$_3$), 1.46 (m, 4H, CH_2CH$_2$CH$_3$), 3.05 (t, 4H, $^3J=7.8$ Hz, NHCH_2CH$_2$), 4.17 (s, 4H, ArCH_2NH), 7.32 (d, 2H, bpy-*H*5,5′), 7.56 (m, 4H, $^3J=5.4$ Hz, bpy-H_e), 7.77 (d, 2H, $^3J=5.4$ Hz, bpy-*H*6,6′), 7.88 (m, 4H, bpy-H_f), 7.96 (m, 4H, bpy-H_d), 8.19 (m, 8H, bpy-H_c and Ar*H*), 8.91 (m, 2H, bpy-*H*3,3′ and Ar*H*), 10.09 (br s, 1H, N*H*CO), 10.44 (br s, 1H, N*H*CO).

Elemental analysis: found: C 39.7%, H 4.1%, N 10.5%.

Calculated ($C_{54}H_{56}F_{12}N_{10}O_2P_2Ru\cdot 3H_2O$): C 49.0%, H 4.7%, N 10.6%.

MALDI: *m/z* 978.2 $[M-2PF_6]^+$, 1122.8 $[M-PF_6]^+$.

6.2. General method for synthesis of macrocycles, 13–15

The macrocyclic receptors were synthesised in a one pot reaction. To a stirred solution of the respective ruthenium (II) receptor **10** in 10 ml MeCN/H_2O mixture (9:1) was added an excess of KOH(aq) (1 M). Two equivalents of carbon disulphide were dropped into the solution and the mixture stirred for 10 min allowing formation of the potassium dithiocarbamate salt. This salt was not isolated but reacted in situ by the addition of 1 equiv of nickel, copper, or zinc (II) acetate. The mixture was stirred overnight. Addition of water precipitated the product. The mixture was stirred for a further 2 h before it was filtered and dried to give the macrocycles.

6.2.1. Nickel(II) macrocycle, 13. Procedure outlined above using receptor **10** (0.12 g, 0.1 mmol) and 1 equiv of nickel(II) acetate tetrahydrate. Red/brown solid (0.06 g, 48%).

^{1}H NMR in CD_3CN (δ/ppm): 0.87 (br m, 6H, CH_3), 1.32 (m, 4H, CH_2CH$_3$), 1.62 (br m, 4H, $^3J=7.5$ Hz, CH_2CH$_2$CH$_3$), (obscured by solvent, NCH_2CH$_2$), 5.69 (dd, 4H, $^3J=6.3$ Hz, $^4J=1.5$ Hz, bpyCH_2N), 7.43 (m, 6H, bpy-*H*6,6′ and bpy-H_e), 7.73 (t, 2H, $^3J=7.5$ Hz, bpy-H_f), 8.09 (m, 6H, bpy-*H*5,5′ and bpy-H_d), 8.55 (d, 4H, $^3J=7.5$ Hz, bpy-H_c), 8.99 (s, 2H, bpy-*H*3,3′).

Elemental analysis: found: C 39.9%, H 3.7%, N 8.8%.

Calculated ($C_{42}H_{42}N_8RuS_4NiP_2F_{12}\cdot 2H_2O$): C 39.6%, H 3.6%, N 8.8%.

ESMS: *m/z* 474.2 $[M-2PF_6]^{2+}$.

6.2.2. Copper(II) macrocycle, 14. Procedure outlined above using receptor **10** (0.12 g, 0.1 mmol) and 1 equiv of copper(II) acetate monohydrate. Brown solid (0.077 g, 62%).

NMR broad, paramagnetic.

Elemental analysis: found: C 38.3%, H 3.4%, N 8.6%.

Calculated ($C_{42}H_{42}N_8RuS_4CuP_2F_{12}\cdot 2H_2O$): C 39.6%, H 3.4%, N 8.8%.

ESMS: *m/z* 476.5 $[M-2PF_6]^{2+}$.

6.2.3. Zinc(II) macrocycle, 15. Procedure outlined above using receptor **10** (0.12 g, 0.1 mmol) and 1 equiv of zinc(II) acetate dihydrate. Red/brown solid (0.09 g, 72%).

^{1}H NMR in CD_3CN (δ/ppm): 0.85 (br m, 6H, CH_3), 1.25 (m, 4H, CH_2CH$_3$), 1.65 (br m, 4H, $^3J=7.5$ Hz, CH_2CH$_2$CH$_3$), 3.97 (m, 4H, $^3J=6.3$ Hz, NCH_2CH$_2$), 5.69 (dd, 4H, $^3J=6.3$ Hz, $^4J=1.5$ Hz, bpyCH_2N), 7.31 (d, 2H, $^3J=$ 4.2 Hz, bpy-*H*6,6′), 7.40 (m, 4H, $^3J=5.5$ Hz, bpy-H_e), 7.61 (t, 2H, $^3J=5.1$ Hz, bpy-H_f), 7.76 (dd, 4H, $^3J=20.0$ Hz, $^4J=4.5$ Hz, bpy-*H*5,5′), 8.05 (m, 4H, bpy-H_d), 8.50 (d, 4H, $^3J=7.5$ Hz, bpy-H_c), 8.69 (s, 2H, bpy-*H*3,3′).

Elemental analysis: found: C 43.5%, H 3.9%, N 8.8%.

($C_{42}H_{42}N_8RuS_4ZnP_2F_{12}$): C 42.0%, H 3.8%, N 8.5%.

ESMS: *m/z* 440.1 $[M-CS_2-2PF_6]^{2+}$, 478.0 $[M-2PF_6]^{2+}$, 955.2 $[M-2PF_6]^{+}$.

6.2.4. Macrocycles, 16–21. General procedure the same as for macrocycles **13–15**, but in a THF/H_2O (9:1) mix.

6.2.5. Nickel(II) macrocycle, 16. Procedure given above, using ruthenium receptor **11** (0.08 g, 0.08 mmol) and 1 equiv of nickel(II) acetate tetrahydrate. The product was isolated as red/brown coloured solid (0.03 g, 62% yield).

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.90 (t, 6H, $^3J=7.5$ Hz, CH_3), 1.29 (m, 4H, CH_2CH$_3$), 1.53 (m, 4H, CH_2CH$_2$CH$_3$), 2.94 (br m, 4H, NHCH_2CH$_2$CH$_2$CH$_3$), 3.10 (br m, 4H, CH_2NHCH$_2$CH$_2$CH$_2$), 3.60 (m, 4H, CONHCH_2), 7.74 (m, 4H, $^3J=4.5$ Hz, bpy-H_e), 7.84 (d, 4H, $^3J=4.5$ Hz, bpy-H_f), 7.84 (d, $^3J=5.4$ Hz, 2H, bpy $H5,5'$), 7.97 (d, 2H, $^3J=5.4$ Hz, bpy-$H6,6'$), 8.20 (m, 4H, $^3J=6.3$ Hz, bpy-H_d), 8.86 (d, 4H, $^3J=6.3$ Hz, bpy H_c), 9.15 (s, 2H, bpy-$H3,3'$), 9.25 (s, 2H, CONH).

Elemental analysis: found: C 40.4%, H 4.4%, N 9.8%.

Calculated ($C_{46}H_{50}F_{12}N_{10}O_2P_2RuNi\cdot H_2O$): C 40.3%, H 3.8%, N 10.2%.

ESMS: *m/z* 531.2 $[M-2PF_6]^{2+}$, 1207.1 $[M-PF_6]^{+}$.

6.2.6. Copper(II) macrocycle, 27. Procedure given above, using ruthenium receptor **21** (0.2 g, 0.18 mmol) and 1 equiv of copper (II) acetate monohydrate. The product was isolated as brown solid (0.14 g, 59% yield).

NMR broad, paramagnetic.

Elemental analysis: found: C 38.2%, H 4.1%, N 9.3%.

Calculated ($C_{46}H_{50}F_{12}N_{10}O_2P_2RuCu\cdot 3H_2O$): C 39.1%, H 4.0%, N 9.9%.

ESMS: *m/z* 533.6 $[M-2PF_6]^{2+}$.

6.2.7. Zinc(II) macrocycle, 18. Procedure given above, using ruthenium receptor **11** (0.2 g, 0.18 mmol) and 1 equiv of zinc (II) acetate dihydrate. The product was isolated as red/brown coloured solid (0.13 g, 55% yield).

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.85 (t, 6H, $^3J=7.5$ Hz, CH_3), 1.24 (m, 4H, CH_2CH$_3$), 1.65 (m, 4H, CH_2CH$_2$CH$_3$), 3.70 (br m, 4H, NHCH_2CH$_2$CH$_2$CH$_3$), 3.79 (br m, 4H, CH_2NHCH$_2$CH$_2$CH$_2$), 3.97 (m, 4H, CONHCH_2), 7.50 (br m, 4H, bpy-H_e), 7.72 (d, 4H, $^3J=4.5$ Hz bpy-H_f), 7.82 (d, 2H, bpy $H5,5'$), 7.95 (d, 2H, $^3J=5.7$ Hz, bpy-$H6,6'$), 8.18 (m, 4H, $^3J=7.5$ Hz, bpy-H_d), 8.84 (m, 4H, $^3J=6.3$ Hz, bpy H_c), 9.12 (s, 2H, bpy-$H3,3'$), 9.32 (s, 2H, CONH).

Elemental analysis: found: C 39.7%, H 4.1%, N 9.3%.

Calculated ($C_{46}H_{50}F_{12}N_{10}O_2P_2RuZn\cdot {}^3/_2H_2O$): C 40.1%, H 3.8%, N 10.2%.

ESMS: *m/z* 535.2 $[M-2PF_6]^{2+}$.

6.2.8. Nickel(II) macrocycle, 19. Procedure given above, using ruthenium receptor **12** (0.1 g, 0.07 mmol) and 1 equiv of nickel(II) acetate tetrahydrate. The product was isolated as red/brown coloured solid (0.095 g, 95% yield).

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.82 (t, 6H, $^3J=7.5$ Hz, CH_3), 1.20 (m, 4H, CH_2CH$_3$), 1.49 (m, 4H, CH_2CH$_2$CH$_3$), 3.29 (m, 4H, NBocCH_2CH$_2$), 4.77 (s, 4H, bpyCH_2), 7.30 (d, 2H, bpy-$H5,5'$), 7.55 (br m, 2H, bpy-H$_d$) 7.78 (m, 10H, Ar and bpy-H_c), 7.97 (br m, 2H, bpy-$H6,6'$), 8.19 (br m, 2H, bpy-H_e), 8.87 (br m, 2H, bpy-H_f), 9.38 (br s, 2H, CONH).

Elemental analysis: found: C 44.0%, H 4.1%, N 9.4%.

Calculated ($C_{56}H_{54}N_{10}O_2NiRuS_4P_2F_{12}\cdot 3H_2O$): C 43.9%, H 4.0%, N 9.2%.

MALDI: *m/z* for PF_6 salt, 1186.2 $[M-2PF_6]^{+}$, 1331.6 $[M-PF_6]^{+}$.

6.2.9. Copper(II) macrocycle, 20. Procedure given above, using ruthenium receptor **12** (0.1 g, 0.07 mmol) and 1 equiv of copper(II) acetate monohydrate. The product was isolated as brown solid (0.09 g, 91% yield).

NMR broad, paramagnetic.

Elemental analysis: found: C 43.7%, H 4.0%, N 8.8%.

Calculated ($C_{56}H_{54}N_{10}O_2CuRuS_4P_2F_{12}.3H_2O$): C 43.8%, H 3.9%, N 9.1%.

MALDI: *m/z* for PF_6 salt, 595.3 $[M-2PF_6]^{2+}$, 1191.6 $[M-2PF_6]^{+}$.

6.2.10. Zinc(II) macrocycle, 21. Procedure given above, using ruthenium receptor **12** (0.1 g, 0.07 mmol) and 1 equiv of zinc (II) acetate dihydrate. The product was isolated as red/brown coloured solid (0.058 g, 56%).

^{1}H NMR in DMSO-d_6 (δ/ppm): 0.84 (t, 6H, CH_3), 1.26 (m, 4H, CH_2CH$_3$), 1.66 (m, 4H, CH_2CH$_2$CH$_3$), 3.29 (m, 4H, NHCH_2CH$_2$), 5.01 (s, 4H, bpyCH_2), 7.33 (br m, 2H, bpyH-5,5′) 7.51 (br m, 2H, bpy-H_d) 7.74 (m, 10H, Ar and bpy-H_c), 7.89 (br m, 2H, bpy-$H6,6'$), 8.15 (m, 2H, bpy-H_e), 8.83 (m, 2H, bpy-H_f), 9.29 (br s, 2H, bpy-$H3,3'$), 10.75.(br s, 2H, NHCO).

Elemental analysis: found: C 43.6%, H 3.9%, N 9.0%.

Calculated ($C_{56}H_{54}N_{10}O_2ZnRuS_4P_2F_{12}\cdot 3H_2O$): C 43.7%, H 3.9%, N 9.1%.

MALDI: *m/z* for PF_6 salt, 607.2 $[M-2PF_6+H_2O]^{2+}$, 1193.4 $[M-2PF_6]^{+}$.

7. Protocol for ^{1}H NMR titrations

A solution of the receptor (500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in dueterated dimethyl sulfoxide. The initial ^{1}H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mol equiv was added in 20 μl. After each addition and mixing, the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of the displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by curve-fitting since the shape is indicative of the stability constant for the complex. The computer program EQMNR[9] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point. Typically these titrations experiments were repeated three times with at least fifteen data points in each experiment.

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