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High yield preparation of a novel tetrakis[ruthenium tris(bipyridine)]calix[6]arene derivative with good diastereomeric purity

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Abstract

In order to develop methodology for the selective preparation of complex molecular structures with potential photochemical or electron transfer functions, the diastereoselective synthesis of multiple ruthenium tris(bipyridine) complexes tethered to a central calix[6]arene core was investigated. Applying recently developed methodology, the resolved precursor *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ (98.6% ee) was efficiently reacted with a novel calix[6]arene derivative, to give the tetrakis[Ru(bpy)$_2$(bpy′)]calix[6]arene derivative (**9**) with almost complete retention of absolute stereochemistry at each of the four metal centres, as seen by the unusually strong molar circular dichroism (CD) spectrum. The synthesis of racemic **9** was also carried out, and demonstrated to have an inactive CD spectrum.
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1. Introduction

The redox and photophysical properties of ruthenium tris(bipyridine) complexes are well established,[1,2] and their use as photochemical molecular devices has been the subject of extensive investigation.[3–5] As the molecular architectures of these devices continue to increase in complexity, the photochemist must seek out new procedures that allow the controlled preparation of more and more complicated molecules in order to supply material for further study in this area, implying a need for increased selectivity. One fundamental area of control which has been only partially addressed is the low degree of stereocontrol inherent in the synthesis of ruthenium bis and tris(bipyridines). Von Zelewsky et al.[6,7] have made advances into this area through the use of the 'chirogen' ligand which

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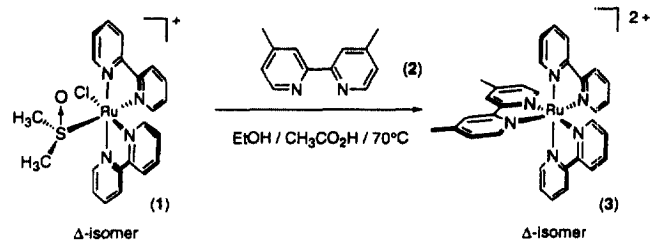
enables good diastereoselectivity to be attained. However, the products that arise must contain the chirogen ligand, which limits further modification of the structure. It is also of fundamental importance to note that the resolution of multiple chiral centre compounds is not readily achieved (e.g. chiral HPLC, co-crystallization with optically active compounds etc.), and for higher molecular weight structures, enantiomeric purity is practically impossible. A generally applicable, highly stereoselective methodology is therefore required. As part of our ongoing interest in the photochemical processes of ruthenium poly(bipyridine) complexes, we have recently developed a new synthesis, starting from a ruthenium bis(bipyridine) sulfoxide precursor.[8] If the sulfoxide complex is resolved into its enantiomers prior to reaction with a bipyridine nucleophile (using chiral HPLC techniques, see experimental section for details), almost complete retention of the absolute stereochemistry at the metal centre is observed. Thus, the reaction of *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ (**1**) (>99% ee) with 4,4′-dimethyl-2,2′-bipyridine proceeds in 97% yield, affording the Δ-isomer of the ruthenium tris(bipyridine) product (**3**) with an ee of 96.8% (see Scheme 1).[8]



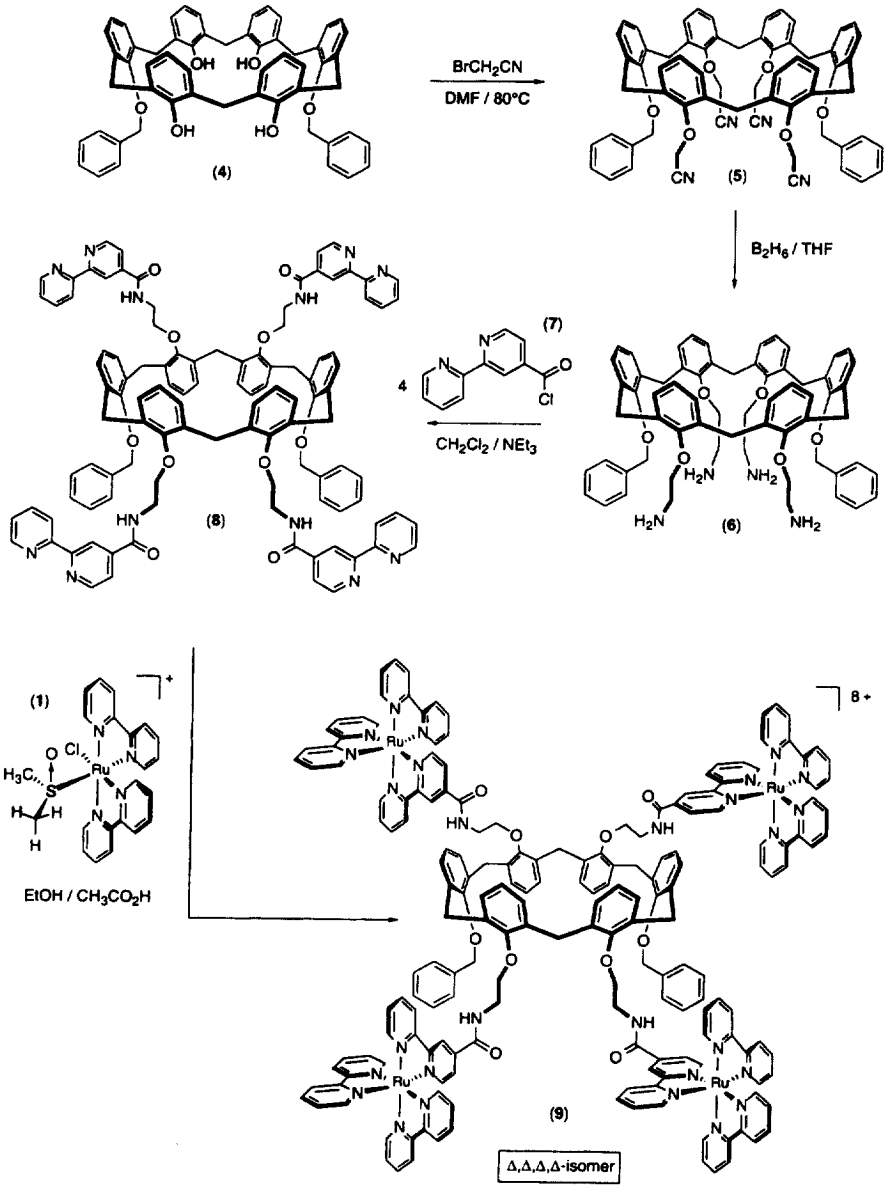
Scheme 1. Synthesis of an enantiopure ruthenium tris(bipyridine) complex (**3**), starting from resolved ruthenium bis(bipyridine) sulfoxide (**1**). Complete retention of the absolute configuration at the metal centre was observed

The high yield and selectivity afforded by this reaction seemed to us ideally suited for use in the preparation of more challenging structures which may act as photochemical devices, such as stereoregular polymers, or homochiral dendrimers. To the best of our knowledge, systems of this type which contain chiral ruthenium tris(bipyridine) building blocks have not yet been prepared. Racemic synthesis, followed by a resolution procedure is also non-viable for multi-centre molecules, as a result of the very difficult separation problems that would arise. In order to model the complexity of these systems, we chose to prepare the calix[6]arene (**9**), selectively derivatized on the lower rim, which has similar structural features to the above-mentioned classes of compound, i.e. a moderate level of flexibility and steric hindrance, and multiple reaction sites. The products of this reaction would enable us to evaluate the asymmetric formation of ruthenium tris(bipyridine) complexes in a multi-reaction process, and may also afford a product which is capable of acting as a chiral host for small neutral organic compounds, prior to carrying out photochemical processes on them. Indeed, simpler calix[4]arenes with bipyridine units attached to the lower rim have already been used to incorporate lanthanide ions, and their luminescence properties have been described,[9] as well as a luminescent pH sensor based on a *p-tert*-butylcalix[4]arene linked to one ruthenium tris(bipryridine).[10]

2. Results

The synthesis of the tetrakis[Ru(bpy)$_2$(bpy′)]calix[6]arene derivative (**9**) is shown in Scheme 2, which includes four novel calix[6]arene derivatives (**5**, **6**, **8**, and **9**). The conversion of the previously reported 39,42-bis(benzyloxy)calix[6]arene (**4**)[11] to the tetracyano product (**5**) was carried out with bromoacetonitrile in DMF at 80°C in 89% yield. This was subsequently reduced with diborane:THF

complex, affording the tetraamine (**6**) in 68% yield, which was then quenched with four equivalents of 2,2′-bipyridine-4-carbonyl chloride (**7**) in the presence of triethylamine, affording the tetrabipyridine calix[6]arene (**8**) in 55% yield. Reaction of this derivative with *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ (98.6% ee) (added in three equal portions in DMF at 0, 3 and 6 h) in EtOH:CH_3CO_2H at 75°C for 8 h in dark conditions led to the formation of **9** in 55% yield. This reaction was assumed to proceed with almost complete stereoretention at the metal centres, based on the subsequent observations.



Scheme 2. Synthesis of **9**

The formation of the highly symmetrical tetraruthenium complex was confirmed by ^{1}H NMR, and assignment of the signals to the individual protons of **9** was achieved by analysis of the COSY spectra (see Fig. 1). A singlet for the two benzylic CH_2 of the lower rim benzyloxy group is observed (4.6 ppm), and

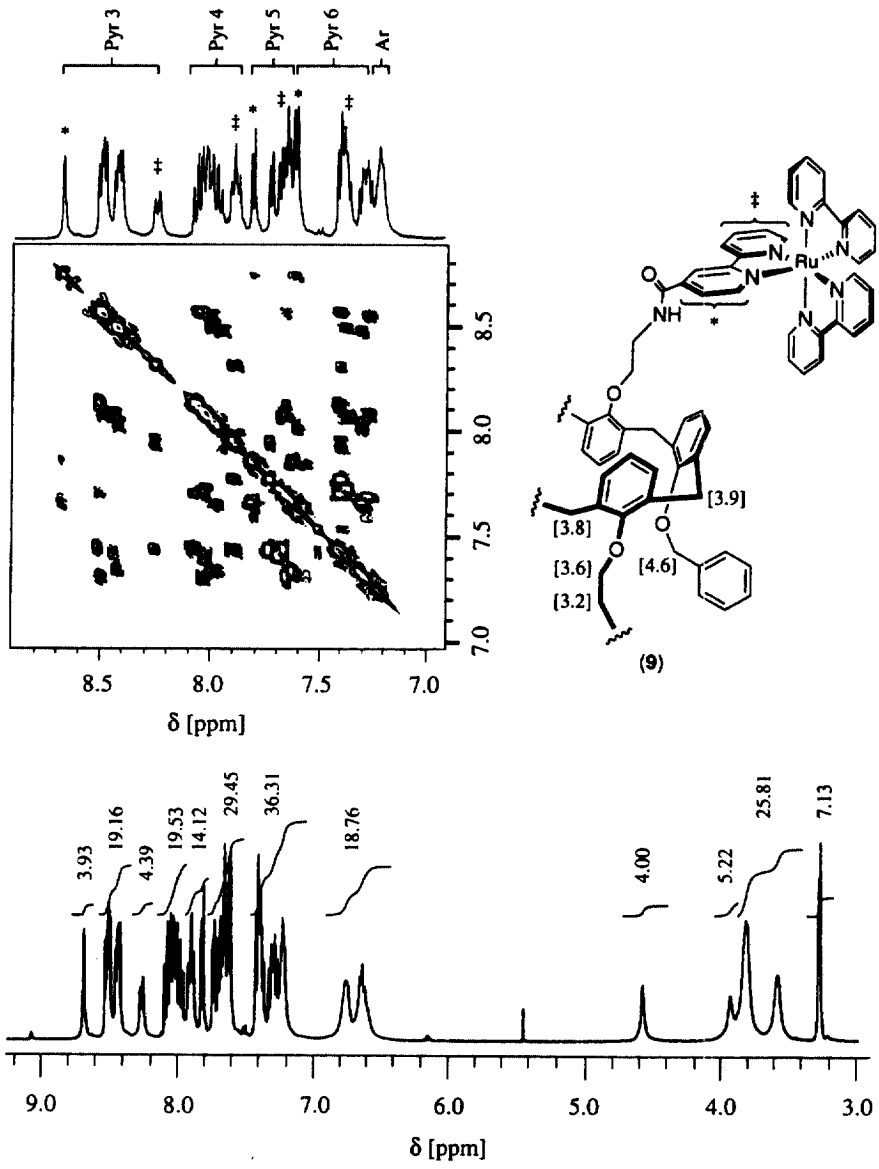


Figure 1. 400 MHz ^{1}H NMR (CD_3CN) and H–H COSY spectra of **9**. The numbers enclosed by square brackets indicate the chemical shift (ppm) for the adjacent protons

a 4:2 ratio for the CH_2 groups that link the arene groups in the ring (3.9 ppm and 3.8 ppm, respectively) is also observed. The flexibility of the calixarene ring is apparent from the broadness of these two signals. Indeed, variable temperature measurements for **9** showed a broadening of the peaks at 3.9 ppm and 3.8 ppm, although even at −40°C the conformation had not been completely 'frozen', demonstrating the conformational freedom that the calix[6]arene ring system possesses. All of the expected resonances were seen in the ^{13}C NMR spectrum of **9**, and the full assignments of these spectra are given in the experimental section.

The enantiomeric purity of the starting material **1** was determined by chiral HPLC analysis and CD spectroscopy, and the stereochemistry of the product assigned from the circular dichroism (CD) spectrum

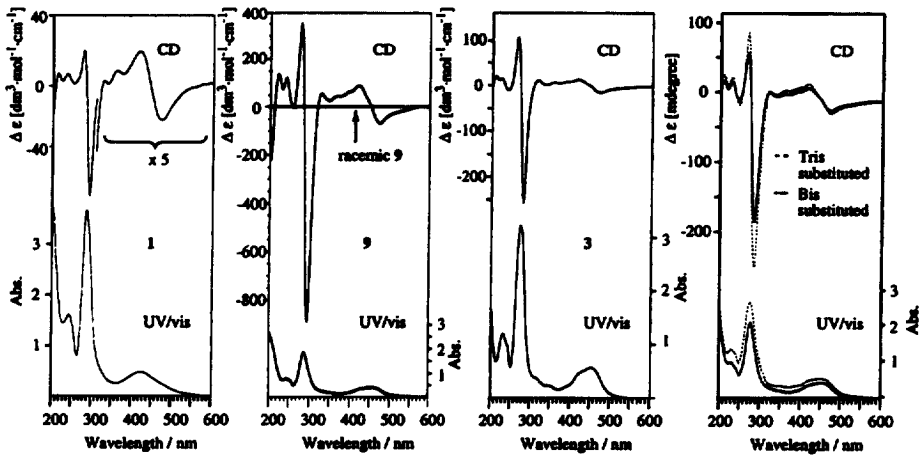


Figure 2. CD and UV/vis spectra for the resolved ruthenium bis(bipyridine) sulfoxide, **1**, for **9** and for enantiopure **3**. The CD spectrum of racemic **9**, as well as the tris- and bis-substituted products are also included for comparison purposes. Solutions of concentration 9×10^{-5} mol l^{-1}, 1×10^{-6} mol l^{-1} and 3×10^{-5} mol l^{-1} for **1**, **9** and **3**, respectively, were used when recording the CD spectra

(see Fig. 2). The CD spectrum shows unusually high activity for **9**, which has an extrema of ca. -900 dm^3 mol^{-1} cm^{-1} for the LC band centred around 280 nm, compared to the LC band (280 nm) of the starting sulfoxide complex **1**. This CD spectrum was assigned on the basis of an unambiguous assignment of the CD spectrum of **3**, for which both the CD spectrum and single crystal X-ray analysis were available.[8] Although the tetrasubstituted products could be isolated by normal HPLC techniques, attempts to resolve the Δ,Δ,Δ,Δ-product using chiral HPLC were completely unsuccessful. This may have been complicated by the conformational freedom of **9** and the by-products, which caused excessive broadening of the peaks under a variety of conditions. The synthesis of racemic **9** afforded a product which had similar ^{1}H NMR to the enantiopure material, but its CD spectrum was found to be completely inactive. The UV/vis of **9**, and the CD and UV/vis spectra of the bis- and tris-products are also shown in Fig. 2 for comparative purposes.

It is noteworthy that the enantioselective preparation of this complex avoided the formation of a very complex mixture of diastereomers that would prove very difficult, if not impossible, to separate. This was demonstrated when the synthesis of racemic **9** was carried out, starting from **8**. This precursor was reacted with either racemic $Ru(bpy)_2Cl_2$, or racemic *cis*-$[Ru(bpy)_2(DMSO)Cl]PF_6$, and in both cases, the CD spectra of the isolated tetraruthenium complexes showed no activity.

The evolution of **9** was also followed by non-chiral HPLC, and using this technique it was possible to observe the formation of the di-, tri- and tetra-substituted products (see Table 1). From these data we can see that the di-substituted product could be isolated as the major product during the initial stages of the reaction.

3. Discussion and conclusions

The preparation of multi-chiral centre high molecular weight compounds (e.g. polymers, dendrimers, etc.) affords special resolution problems, which are not easily overcome. Indeed, the simplest method involves the preparation of an enantiomerically pure product through the use of a completely diastereoselective process, thus removing the need for any resolution processes! In reality, attempts to achieve high enantiomeric purity products should rely on the highest possible level of stereocontrol that can

Table 1
The relative ratios of the tetrakis-, tris- and bis-derivatives, monitored by HPLC. Retention times using a Mightysil RP-18 column (33:67, 0.1 M $NaPF_6$ aq.:CH_3CN, with a flow rate of 0.5 ml min^{-1}, at room temperature). Products were detected by UV detector at 292 nm. Retention times are 11.4, 17.94 and 19.92 min, respectively

	Relative Ratio		
Time / h	Tetrakis derivative (9)	Tris derivative	Bis derivative
2	1.00	0.515	3.32
6	1.00	0.38	1.08
8	1.00	0.27	0.52

be achieved. The reaction of enantiopure Δ-[Ru(bpy)$_2$(DMSO)Cl]PF_6 with a bipyridine nucleophile has been found to proceed in high yield, with ca. 97% retention of the absolute chirality at the metal centre, making it a good candidate for the preparation of high enantiomeric purity poly chiral centre products. If we assume that the bipyridine units in the tetrakis(bipyridine) compound **8** can be treated independently, and that the formation of one ruthenium complex does not interfere with subsequent chiral centres (which is possible, due to the large, flexible nature of **8**), and using a stereoretention of 97% (based on the single reaction, see Scheme 1), then using a simple probability calculation, we can predict that the desired Δ,Δ,Δ,Δ-isomer will form in 88.5% [$(0.97)^4$]. Products containing only a single error will account for 10.9% [$4\times\{(0.97)^3\times(0.03)\}$] of the total yield of the tetra-substituted product. Thus, the fully Δ-product and the Δ,Δ,Δ,Λ-product account for 99.4% of the total tetra-substituted product. Although such a simple probability treatment cannot account for phenomenon such as cooperativity, etc., we can predict that our product contains ca. 90% of the desired product, and the only other contaminant of any significance will contain one erroneous stereocentre. This is in agreement with the very large extrema observed in the CD spectrum of **9**. Of course, such a statistical treatment can be extended to reactions which form multiple chiral centres. In general, an n-centre reaction, reacting with N% retention (in a non-cooperative fashion) affords the n-Δ product in [$100\times\{(N/100)^n\}$]% yield and the (n−1)Δ,Λ product in [$100\times n\times\{(N/100)^{n-1}\times((100-N)/100)\}$]% yield (in both cases, as a percentage of the total n-substituted product isolated). In order to achieve a good enantiomeric purity, the yield and N must be high. In our synthesis of **9**, the stereoretention upon the nucleophilic reaction of a bipyridine with *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF_6 has been extended to encompass a 'multicentre' reaction, and has been shown to afford the desired product in good yield, with an acceptable level of diastereoselectivity, without resorting to difficult resolution procedures. A conventional synthesis was also applied to the preparation of racemic **9**, and this gave a complex mixture of diastereomers, highlighting the advantages of the direct diastereoselective synthesis. The investigation of further reactions of other bipyridine nucleophiles with enantiomerically enriched ruthenium bis(bipyridine) sulfoxide complexes will be the subject of further reports from our laboratory.

4. Experimental

The reagents used in these studies were reagent grade or better, and were used without further purification. Solvents were purified according to published methods. Dimethyl sulfoxide (DMSO) were dried overnight over molecular sieves 4 Å, distilled and stored under argon.

Circular dichroism spectroscopy was performed on a JASCO J-720WI spectropolarimeter at 25°C in acetonitrile, or in the HPLC eluent ($NaPF_6$ aq.:CH_3CN mixed solvent). Concentrations of the solutions were determined by UV/vis measurements. Resolution of **1** was performed on a preparative scale using a recycling liquid chromatograph JAI LC-908 equipped with a preparative chiral column, Daicel Chiralcel OD-R (20 mm×250 mm). An aqueous solution of $NaPF_6$ (0.1 M) and acetonitrile was used as eluent, with a flow rate of 3 ml min^{-1}. The chromatograph was monitored at 292 nm with a UV detector. Monitoring the products of the synthetic reactions, and the degree of substitution of the separated fractions was performed using an analytical HPLC system (JASCO GULLIVER series) equipped with a Mightysil RP-18 column, with an HPLC pump PU-980, a 3-line Degasser DG-980-50, a UV/vis detector UV-970, and a column oven 860-CO, with a flow rate of 0.5 ml min^{-1}, at room temperature. Products were detected by UV detector at 292 nm. The eluent flow rate was 0.5 ml min^{-1} (33:67, 0.1 M $NaPF_6$ aq.:CH_3CN) and the chromatograph was monitored at 292 nm and recorded with a JASCO integrator 807-IT. Analytical thin-layer chromatography was performed with plastic backed silica sheets (Merck Kieselgel 60 F_{254}). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 400 spectrometer, operating at 399.65 and 100.40 MHz, respectively. Chemical shifts are reported relative to either the solvent reference or internal standard tetramethylsilane (TMS, 0.00 ppm) for ^1H NMR and solvent reference for ^{13}C NMR. Pulsed field gradient experiments were used for H–H correlation experiments, applying the VCOSYNH pulse sequence.

4.1. 39,42-Dibenzyloxy-37,38,40,41-tetrakis(cyanomethyloxy)calix[6]arene, 5

Potassium carbonate (1.2 g) and **4**[11] (1.6 g, 2 mmol) were stirred in a round bottom flask equipped with a reflux condenser in DMF (50 ml) under nitrogen for 10 min at 80°C. Bromoacetonitrile (0.56 ml, 8.8 mmol) was then slowly added dropwise to this solution over 10 min, and the reaction mixture was stirred for a further 2 h at 80°C. The DMF was removed under reduced pressure to give a yellow solid. This was dissolved in CH_2Cl_2 (80.0 ml), which was washed with 1 M HCl and then with water (2×20 ml), before being concentrated and dried in vacuo. Yield of **5**: 1.7 g, 89%. ^1H NMR ($CDCl_3$) 7.36 (bs, 10H, Ar–H), 6.9–6.7 (m, 18H, Ar–H), 4.82 (s, 4H, CH_2), 4.06 (s, 8H, CH_2), 3.96 (bs, 12H, CH_2). ^{13}C NMR ($CDCl_3$) 154.8, 153.6, 137.1, 134.2, 133.6, 129.9, 129.3, 128.6, 128.4, 128.1, 125.3, 124.1, 115.5, 75.6, 57.3, 31.1, 30.9. Anal. calcd $C_{65}H_{56}N_4O_6$: C, 78.92; H, 5.71; N, 5.66. Found: C, 78.71; H, 5.55; N, 5.65.

4.2. 39,42-Dibenzyloxy-37,38,40,41-tetrakis(aminoethyloxy)calix[6]arene, 6

A mixture of **5** (0.97 g, 1 mmol) and BH_3–THF (12 ml; 1 M solution) in dehydrated THF (50 ml) was stirred overnight at room temperature under a nitrogen atmosphere. The reaction mixture was then quenched with 1 M HCl and the solution evaporated to dryness under reduced pressure. The residue was dissolved in water, and 1 M aq. NaOH was used to raise the solution to pH 8. This was then extracted with CH_2Cl_2, which was separated, washed three times with water and then dried over anhydrous $MgSO_4$. The CH_2Cl_2 was removed under reduced pressure, and the residue was used in the next reaction step without further purification. Yield 68%. ^1H NMR (CD_3CO_2D) 7.8–6.8 (m, 28H, Ar–H), 5.18 (bs, 4H, CH_2), 4.4–3.2 (bm, 28H, CH_2). ^{13}C NMR (CD_3CO_2D) 155.7, 138.9, 136.6, 136.4, 136.3, 136.1, 135.9, 131.5–130.0, 129.9–126.5, 70.7, 41.7, 32.6–32.1. Anal. calcd $C_{65}H_{72}N_4O_6 \cdot DMF$: C, 75.74; H, 7.38; N, 6.49. Found: C, 75.06; H, 6.44; N, 5.11.

4.3. 39,42-Dibenzyloxy-37,38,40,41-tetrakis(2,2′-bypyridine-5-carboxamidoethyloxy)calix[6]arene, 8

2,2′-Bipyridine-5-carbonyl chloride **7** (1.0 g, 4.6 mmol) and **6** (1.0 g, 1 mmol) were added to a stirred solution of triethylamine (1.5 ml) in CH_2Cl_2 (60 ml) under a nitrogen atmosphere, and the mixture was then heated to reflux. After 3 h, TLC analysis (silica gel; $CHCl_3$:MeOH, 8:1, v/v) revealed that all of **6** had been consumed. The mixture was cooled to room temperature, and all the volatile components removed in vacuo. The resulting material was then dissolved in CH_2Cl_2 which was washed with water. The organic layer was then isolated, and the solvent evaporated. The crude sample was purified by column chromatography (silica gel; $CHCl_3$:MeOH, 8:1, v/v) which afforded **8** as a white powder (55% yield). ^{1}H NMR (CD_3CN) 8.66 (d, J=0.8 Hz, 4H, PyH-3), 8.40 (m, 12H, PyH-6, PyH-6′, NH), 8.13 (d, J=8 Hz, 4H, PyH-3′), 7.72 (t, 4H, PyH-4′), 7.58 (d, J=5.6 Hz, 4H, PyH-5), 7.40 (m, 4H, PyH-5′), 7.20–6.60 (m, 28H, Ar–H,), 4.86 (s, 4H, CH_2), 3.90–3.80 (m, 12H, CH_2), 3.60 (s, 8H, CH_2), 2.02 (bs, 4H, CH_2). ^{13}C NMR (CD_3CN) 167.8, 157.2, 155.6, 154.2, 150.3, 150.2, 149.7, 149.7, 143.2, 138.4, 137.5, 135.4, 135.2, 134.8, 129.2, 129.1, 128.8, 128.6, 128.4, 125.2, 125.0, 124.7, 121.9, 121.8, 121.4, 118.9, 75.6, 70.8, 40.7, 31.1, 30.7. Anal. calcd $C_{108}H_{92}N_{12}O_{10}\cdot H_2O$: C, 74.72; H, 5.46; N, 9.86. Found: C, 74.75; H, 5.57; N, 9.00.

4.4. 39,42-Dibenzyloxy-37,38,40,41-tetrakis(Δ-[Ru(bpy)$_2$(2,2′-bypridine-5-carboxamidoethyloxy)]-calix[6]arene octakis(hexafluorophosphate), 9

The calix[6]arene derivative **8** (0.17 g, 0.1 mmol) was suspended in a mixture of ethanol (40 ml) and glacial acetic acid (10 ml), and this mixture was heated to reflux under nitrogen. *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF_6, **1** (225 mg, 0.36 mmol), dissolved in a minimum amount of DMF, was added in three separate portions at 0, 3 and 6 h. The reaction was allowed to proceed for a total of 8 h, in dark conditions. After cooling to room temperature, the dark red solution was filtered through Celite® and the solvents removed under reduced pressure. The dark red residue was then dissolved in CH_3CN and chromatography was carried out on a Sephadex® LH-20 column (with CH_3CN as eluent), affording **9** as a glassy red solid in 0.22 g (50% yield), contaminated with a small amount of incompletely derivitized products. The tetrakis isomer was separated by preparative HPLC to give pure **9** for analytical purposes. ^{1}H NMR (CD_3CN) 8.70 (s, 4H, PyH-3), 8.53 (dd, J=8.4 Hz, 8H, PyH-3), 8.46 (dd, J=8.4 Hz, 8H, PyH-3), 8.28 (d, J=8.4 Hz, 4H, PyH-3), 8.11–7.83 (m, J=1.6 Hz, J=7.6 Hz, 24H, PyH-4), 7.84 (d, J=5.6 Hz, 4H, PyH-5), 7.76–7.63 (m, 28H, PyH-5, PyH-6, NH), 7.46–7.25 (m, 20H, PyH-6), 7.20 (m, 4H, Ar–H), 6.90–6.60 (m, 24H, Ar–H), 4.59 (s, 4H, CH_2), 3.94 (s, 4H, CH_2), 3.83 (s, 8H, CH_2), 3.60 (s, 8H, CH_2), 3.20 (s, 8H, CH_2). ^{13}C NMR (CD_3CN) 164.8, 158.7, 157.8, 157.7, 157.2, 153.3, 152.9, 152.6, 152.5, 143.1, 138.9, 138.8, 138.4, 135.6, 135.5, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 125.8, 125.5, 125.3, 125.2, 125.1, 122.4, 72.0, 41.3, 30.9, 30.8. Racemic **9** was prepared according to the same procedure, using either racemic **1**, or Ru(bpy)$_2Cl_2$ in the place of *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF_6. Anal. calcd $C_{188}H_{160}F_{48}N_{28}O_{10}P_8Ru_4$: C, 49.79; H, 3.56; N, 8.65. Found: C, 48.91; H, 3.50; N, 8.25.

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