Preparation of Donor-σ-Acceptor Molecules Using Arene−Ruthenium Chemistry

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Several donor-σ acceptor (D-σ-A) molecules with thioalkyl side chains have been prepared by ruthenium-activated nucleophilic aromatic substition (S_NAr) reactions. Selective substitution of chloride from cyclopentadienyl(1,4-dichlorobenzene)ruthenium by using piperazine derivatives as nucleophiles is addressed. This selectivity, in combination with further manipulation of the complexes, allows the preparation of unsymmetrically functionalized tetraalkyl-*p*-phenylenediamine (TAPD) units which are difficult to synthesize by traditional organic S_NAr conditions. Phenanthroline-assisted decomplexation of the product arene−RuCp systems under UV irradiation is described.

Introduction

The application of transition metals to facilitate nucleophilic aromatic substitution (S_NAr) reactions is playing an important role in a number of areas of organic[1] and materials chemistry research.[2−4] In materials chemistry, the preparation of triaryl-diether and polyphenylene oxide derivatives has been thoroughly studied,[2−4] but N-substituted phenylenediamine derivatives have attracted less attention.

N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD), a powerful and well-documented electron donor, has been known for a long time.[5] The application of TMPD derivatives as electron-donating molecules to prepare donor-σ-acceptor (D-σ-A) systems has attracted less attention probably because very few functionalized tetraalkyl-*p*-phenylenediamine (TAPD) derivatives are readily available.[6,7] Although several methods[8] for the construction of the arene−nitrogen bond to prepare TAPD derivatives can be found, most of these methods either suffer from nucleophile regiocontrol problems resulting from the presence of a benzyne intermediate,[9] the need for very high temperature and exotic equipment,[10] or the presence of specific functionality on the arene ring.[8] None of these methods shows a combination of good yields and high selectivity. More recently, palladium-based cross-coupling reactions have been reported that allow preparation of simple TAPDs,[11] but as far as we are aware this approach has not been successfully applied to the synthesis of multifunctional systems.

Recently, we have described methodology[6] for the preparation of TAPD derivatives by using arene−iron chemistry, and several D-σ-A molecules have been synthesized that show photoinduced electron-transfer character.[12] We are interested in preparing and studying such D-σ-A molecules in self-assembled monolayers (SAMs) on Au electrode to investigate their electrochemical properties, an area that has so far received little attention.[13] One of the problems that we have encountered with the used of arene−FeCp complexes is the poor yield and capricious nature of the preparation, from 1,4-dichlorobenzene, of complexes that serve as the starting materials for construction of the TAPD systems. Arene−ruthenium chemistry provides a useful alternative which often gives better yield with highly electron-deficient arenes,[14] such as 1,4-dichlorobenzene. S_NAr reactions of arene−ruthenium complexes have been reported[2b,c,4c] to proceed with good yields, and we report herein the use of arene−ruthenium chemistry in the synthesis of D-σ-A molecules that have alkylthiol side chains that may be employed for the formation of surface bound SAMs.

Results and Discussion

Numerous studies[15] have shown that spontaneous adsorption of long chain alkanethiols on gold surfaces leads to the formation of well-ordered SAMs, as a result of increased van der Waals interactions within the monolayers. The possibility of obtaining unsymmetrically substituted arenes by sequential chemoselective S_NAr

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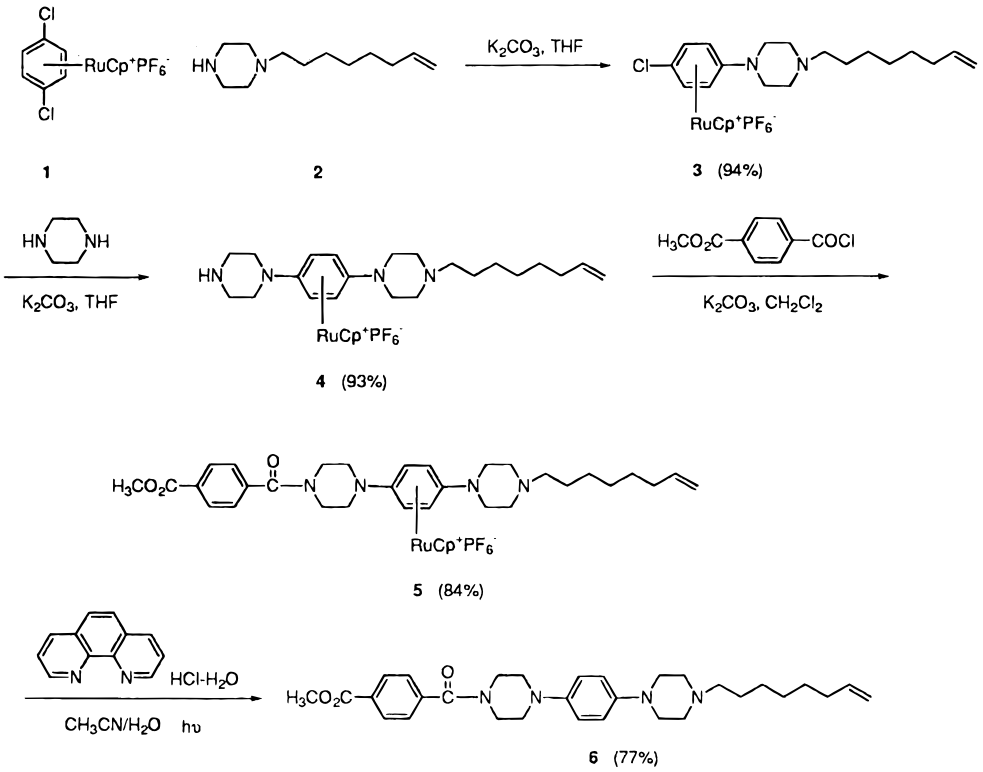
Scheme 1



reactions on a (1,4-dichlorobenzene)$FeCp^+$ complex is well precedented.[3,6] Here we describe the preparation of unsymmetrical phenylenediamine derivatives having long alkanethiol side chains by using (1,4-dichlorobenzene)$RuCp^+$ complex[16] **1**, in an effort to develop a more reliable protocol than is possible via the corresponding iron complexes. Our initial objective was the preparation of piperazine derivatives with an octyl side chain as the linker. 8-Bromo-1-octene reacted with piperazine[17] (2 equiv) to give **2** in 67% yield along with some di-N-alkylated piperazine (Scheme 1). No attempt was made to optimize the yield because this route did not ultimately afford the desired thiol derivatives (see later). Compound **2** (2 equiv) reacted with **1** in the presence of 1 equiv of K_2CO_3 to give **3** in 94% yield. When 1 equiv of **2** was used and the mole ratio of K_2CO_3 was increased to 5, the isolated yield of **3** was 92%, but a longer reaction time (106 h vs 40 h) was required. No double S_NAr product was detected from the ^1H NMR spectrum of either product. Following a second S_NAr reaction with piperazine, TAPD complex **4** was obtained with the secondary piperazine nitrogen available for further functionalization. Reaction of complex **4** with the acid chloride of monomethyl terephthalate gave the corresponding amide **5** with an electron acceptor incorporated into its structure. Earlier, we have reported[16d] that the ruthenium can be recovered as $[CpRu(CH_3CN)_3]^+PF_6^-$, the precursor of **1**, after decomplexation of the initial S_NAr product, in this case **5**, in CH_3CN under UV light irradation. Unfortunately decomplexation of **5** under these conditions required over 4 days for completion and gave low yield. Plausible reasons for this are that the more electron-rich ruthenium complex is more difficult to demetalate, and the piperazine rings of the product phenylenediamines can act as bidentate ligands and coordinate with the expunged ruthenium moiety. Photolytic decomplexation of **5** was achieved in good yield (77%) in the presence of 1,10-phenanthroline as a competing ligand.[6] Thus, we obtained the D-σ-A molecule **6** with an alkenyl side chain which is ready for functionalization. Two methods[18] have been reported for the conversion of alkenes to thioesters, which in turn can be reduced to thiols. Thioesterification of **6**, by using thioacetic acid under free radical conditions in the presence of AIBN, or by photochemical initiation, was unsuccessful. We also observed that neither **2** nor **3** would undergo radical addition to the terminal olefin to give the desired thioester, possibly as a result of interference of the radical pathway by the piperazine ring.

As a result of this lack of success we turned our attention to earlier functionalization of the olefin. 8-Bromo-1-octene reacted with thioacetic acid in the presence of a catalytic amount of AIBN as initiator to give **7** in 99% yield. N-Alkylation of piperazine, using 4−5 equiv of piperazine to avoid di-N-alkylation, afforded 1-(8-thiooctyl)-piperazine **9**. Presumably the initial product **8** was hydrolyzed during refluxing or workup. Compound **9** can be isolated by using a rapid workup process, but when **9** is exposed to air it is converted quantitatively to the disulfide **10**. We also prepared a piperazine derivative with a thioethyl side chain. By refluxing 4 equiv of piperazine with ethylene sulfide[19] in benzene, compound

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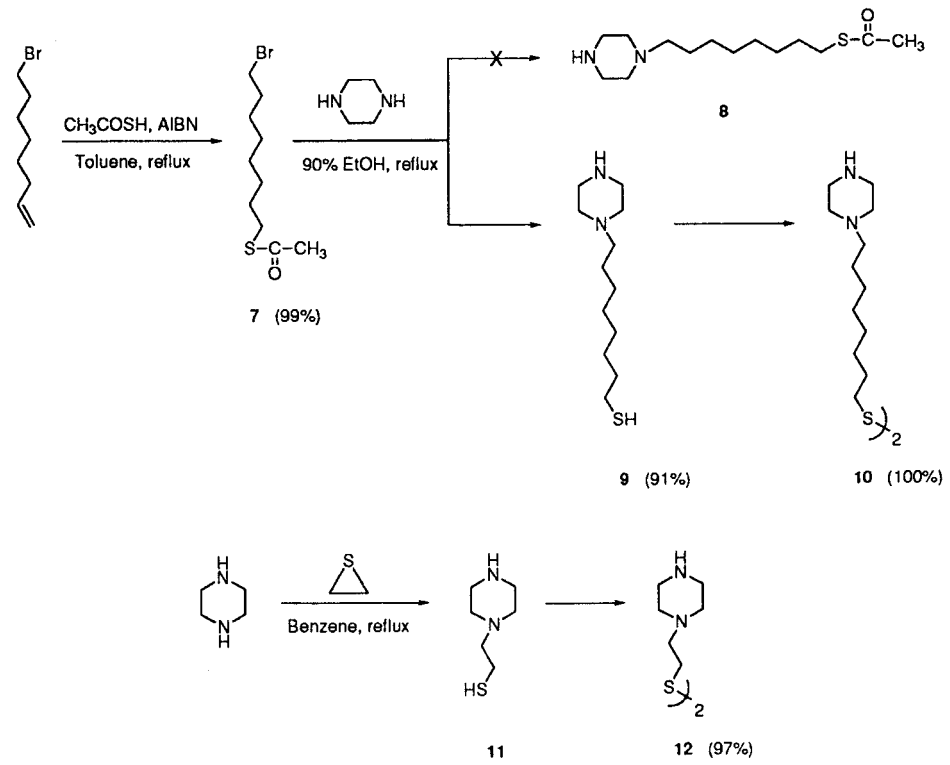
Scheme 2



11 was formed which then slowly oxidized to afford disulfide **12**, isolated in 97% yield. Disulfides **10** and **12** (Scheme 2) were used as starting materials for subsequent S_NAr reactions, as these are essentially protected thiols.[20] It is well established[15] that both thiols and disulfides can adsorb onto Au surfaces using a S−Au linkage, leading to the formation of highly ordered SAMs that show identical character.

For the S_NAr reactions, complex **1** (2 equiv) reacted with disulfides **10** and **12** in the presence of excess K_2CO_3 (10 equiv) in THF, to give **13** and **14** in 90% and 79% yield, respectively. Following a second S_NAr reaction with piperazine, two TAPD complexes **15** and **16**, differing in side chain length, were obtained in 95% and 91% yields. Treatment of complexes **15** and **16** with the acid chloride from monomethyl terephthalate gave the D-σ-A precursors **17** and **18**. Complex **16** was also coupled with a different acceptor molecule by reaction with the acid chloride of anthraquinone-2-carboxylic acid, to give complex **19** (Scheme 3).

The decomplexation of **18** was first performed in the presence of 6 equiv of 1,10-phenanthroline hydrochloride monohydrate in CH_3CN/H_2O. After 24 h irradiation under UV light, no **18** remained but very little product had been formed (less than 10%). By reducing the amount of 1,10-phenanthroline hydrochloride monohydrate to 3−4 equiv, the isolated yields of decomplexation of **18** and **19** were 58% and 47%. Phenanthroline-assisted decomplexation of **17** was not very effective, most likely as a result of slow decomposition of starting material and/or product under the slightly acidic conditions of the reaction. An alternative chelation reagent, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), was examined in an effort to improve the yield of decomplexation of **17** and **18**, and this afforded yields of 48% and 52%, respectively, but problems were encountered during the application of this method to **19**. Thus, it is important to study each method of decomplexation when utilizing this chemistry for the synthesis of a particular TAPD system.

For future electrochemical studies, **21** and **22** were further purified by TLC (Merck Neutral Al_2O_3 plate) with $CHCl_3$. We observed a significant difference in ^{1}H NMR spectra before and after chromatography, and we speculated that residual hydrochloric acid after workup leads to protonation of **21** and **22**. This caused a downfield shift for the ^{1}H NMR peaks of those protons close to the piperazine nitrogen(s). This speculation was confirmed by running the NMR spectrum of **10** in acetone-d_6 in the presence of CF_3CO_2H, which produced the expected downfield shifts in the ^{1}H spectra, depending on the amount of acid that was used. At ambient temperature the ^{1}H spectra of both the metal complexes and the free ligands exhibit considerable broadening of the piperazine ring signals, presumably due to slow rotation about the C−N bond as a result of the amide resonance. In addition, ^{13}C NMR spectra of **20**−**22** show severe broadening of the disulfide alkyl chain region due to slow conformational interconversion. Low-temperature spectroscopy in $CDCl_3$ was therefore employed to obtain the resolved spectra reported herein. We were unable to obtain well-resolved signals for the disulfide alkyl chain region of compounds **20**−**22**.

Because of the long reaction times required to prepare **13** and **14** (see Experimental Section), we have also examined a stepwise reaction between complex **1** and **10** (Scheme 4). By stirring **1**, disulfide **10** (1.2 equiv), and K_2CO_3 (1 equiv) in THF, complex **23** was isolated in 96% yield. Complex **14** was not detected in the product NMR spectrum, but its presence (≤5%) is not discounted. Complex **23** was then treated with **1** (1 equiv) in the

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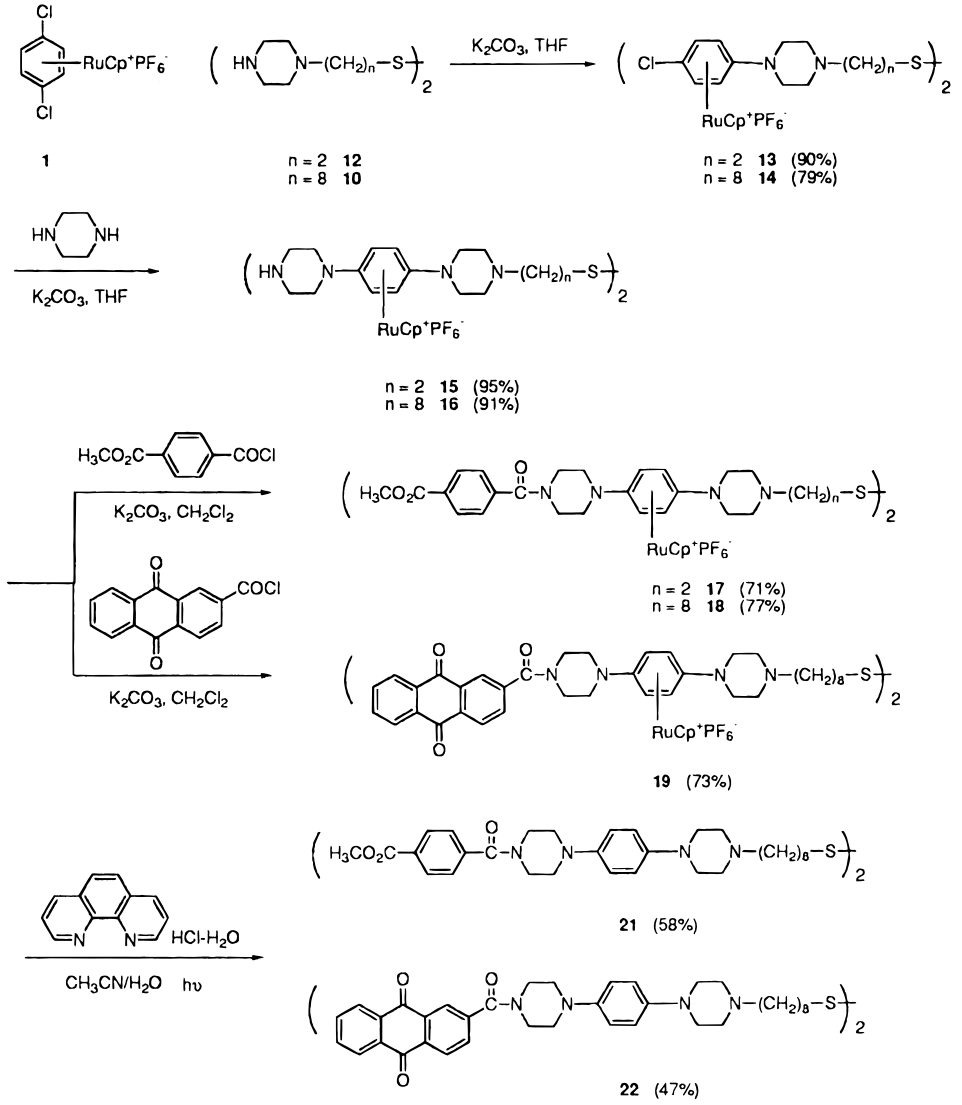
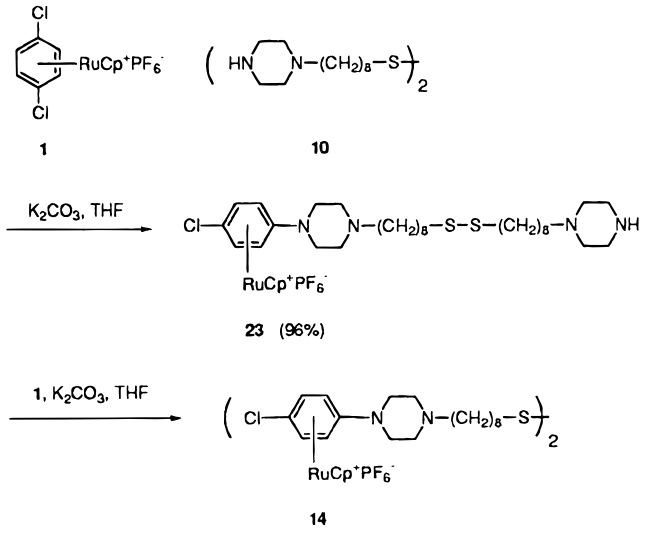
Scheme 3



Scheme 4



presence of excess K_2CO_3 (5 equiv) in THF at room temperature. After 13 days there still remained a significant amount of unreacted complex **1**. Similar results were observed by using CH_3CN as solvent or NEt_3 as base. At this time we do not have a reasonable explanation for this differential reactivity phenomenon.

Conclusions

We have illustrated the use of arene−ruthenium complexes to prepare D-σ-A molecules having thioalkyl side chains that will allow adsorption onto gold electrodes as a prelude to studying their electrochemical properties. These types of molecules are showing promise as unimolecular rectifiers,[21] and we therefore expect that our synthetic methodology can be used to prepare a broad range of potentially interesting materials. The $[RuCp]^+$ moiety activates 1,4-dichlorobenzene toward selective S_N-Ar reaction under mild conditions and protects the phenylenediamine during further functionalization without the risk of oxidation of this unit. The decomplexation of these derivatives in CH_3CN under UV irradiation is not straightforward due to complications involving metal chelation and possible photooxidation reactions of the phenylenediamine units. To circumvent this, we have found that phenanthroline-assisted decomplexation gave good yields, as was the case with the corresponding iron

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complexes.[6] TMEDA was also used as chelation reagent to coordinate the liberated metal and gave good results in some cases. We have applied these procedures to the synthesis of a series of D-σ-A molecules, the electrochemical and photoinduced electron-transfer studies of which will be reported in due course.

Experimental Section

General Procedures. All reactions were performed under an inert atmosphere (using dry, oxygen-free argon). All solvents used in the reactions were freshly distilled under nitrogen as follows: tetrahydrofuran and benzene from sodium/benzophenone, and methylene chloride and acetonitrile from CaH_2. Cyclopentadienyl(1,4-dichlorobenzene)ruthenium hexafluorophosphate **1** was prepared by the literature procedure.[16] Ethylene sulfide was purchased from Acros Chemical Co. and used as received. Demetalation was performed in a Rayonet apparatus (350 mm). Accurate masses (HRMS) are reported for the ^{102}Ru isotope unless otherwise noted. It is generally difficult to obtain accurate peak matching for the dimeric ruthenium complexes, owing to the presence of different isotope combinations (^{12}C, ^{13}C, ^{101}Ru, ^{102}Ru, etc.) at very close mass separations. On our instrument (Kratos MS25A) there is insufficient resolution under FAB conditions to allow accurate mass determination without significant error (>10 ppm). Where appropriate we include data for $^{102}Ru_2$ and $^{101}Ru^{102}Ru$ combinations.

1-(7-Octenyl)piperazine (2). A mixture of piperazine (2.05 g, 23.8 mmol, 2 equiv) and 8-bromo-1-octene (2.28 g, 11.9 mmol) in 38.5 mL of 90% ethanol was heated to reflux for 22 h. After removing the ethanol under reduced pressure, the residue was made strongly alkaline with 1 M NaOH, extracted with ether (5 × 50 mL), and dried over Na_2SO_4. The product was purified by flash chromatography on silica gel, 1:10:100, concentrated NH_3(aq):CH_3OH:$CHCl_3$ eluant, to give **2** (1.57 g, 67%). ^{1}H NMR (acetone-d_6) δ 5.85 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 4.90−5.06 (m, 2H), 2.81 (t, J = 4.9 Hz, 4H), 2.33 (br s, 4H), 2.27 (t, J = 7.2 Hz, 2H), 2.08 (m, 2H), 1.20−1.60 (8H); ^{13}C NMR (acetone-d_6) δ 139.5, 114.6, 59.7, 54.9, 46.1, 34.2, 29.6, 29.4, 27.9, 27.0; EI HRMS Calcd for $C_{12}H_{24}N_2$ 196.1939; found, 196.1941.

[(η5-Cyclopentadienyl)(η6-(1-chloro-4-(4-(octenyl)piperazino)benzene]ruthenium Hexafluorophosphate (3). Cyclopentadienyl(1,4-dichlorobenzene)ruthenium hexafluorophosphate (158 mg, 0.34 mmol) was stirred with K_2CO_3 (48 mg, 0.34 mmol) in THF (5 mL). Compound **2** (135 mg, 0.68 mmol, 2 equiv) was added, and the mixture was stirred at room temperature for 40 h. The solvent was removed, and 25 mL of ether was added. The precipitate was collected and washed with ether several times. Then the precipitate was redissolved in acetone and filtered, and the solvent was removed in vacuo to give the product (204 mg, 94%). ^{1}H NMR (acetone-d_6) δ 6.54 (d, J = 6.8 Hz, 2H), 6.18 (d, J = 6.8 Hz, 2H), 5.83 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 5.57 (s, 5H), 4.90−5.04 (m, 2H), 3.21 (br s, 4H), 2.58 (t, J = 5.2 Hz, 4H), 2.38 (t, J = 7.2 Hz, 4H), 2.06 (m, 2H), 1.20−1.60 (8H); ^{13}C NMR (acetone-d_6) δ 139.8, 126.3, 114.7, 101.7, 85.7, 81.2, 69.5, 58.8, 52.6, 47.9, 34.4, 29.6, 29.4, 27.9, 27.3; FAB HRMS Calcd for M − PF_6^- ($C_{23}H_{32}N_2$-ClRu) 473.1291; found, 473.1298.

[(η5-Cyclopentadienyl)(η^6-1-(piperazino)-4-(4-(octenyl)-piperazino)benzene]ruthenium Hexafluorophosphate (4). Complex **3** (105 mg, 0.17 mmol) was stirred with piperazine (58 mg, 0.68 mmol, 4 equiv) and K_2CO_3 (47 mg, 0.34 mmol, 2 equiv) in THF (4 mL) for 48 h at room temperature. The solvent was removed, and 25 mL ether was added. The precipitate was collected and washed with ether several times. The residue was dissolved in acetone and filtered, and the filtrate was evaporated in vacuo to give the product (105 mg, 93%). ^{1}H NMR (acetone-d_6) δ 5.87 (s, 4H), 5.83 (m, 1H), 5.50 (s, 5H), 4.90−5.05 (m, 2H), 3.10 (br, 4H), 3.01 (br s, 4H), 2.98 (br, 4H), 2.59 (t, J = 5.2 Hz, 4H), 2.39 (t, J = 7.2 Hz, 2H), 2.06 (m, 2H), 1.30−1.60 (8H); ^{13}C NMR (acetone-d_6) δ 139.8, 123.6, 123.0, 114.7, 77.4, 68.3, 68.1, 58.9, 52.9, 49.1, 48.4, 45.7, 34.4, 29.6, 29.4, 27.9, 27.4; FAB HRMS Calcd for M − PF_6^-($C_{27}H_{41}N_4Ru$) 523.2374; found, 523.2360.

[(η^5-Cyclopentadienyl)(η^6-1-(4-(4-(methoxycarbonyl)-benzoyl)piperazino)-4-(4-(7-octenyl)piperazino)benzene]-ruthenium(II) Hexafluorophosphate (5). The acid chloride from monomethyl terephthalate (81 mg, 0.45 mmol, 3 equiv) and K_2CO_3 (63 mg, 0.45 mmol, 3 equiv) were stirred in 4 mL of CH_2Cl_2. Complex **4** (100 mg, 0.15 mmol) in 6 mL of CH_2Cl_2 was added to the above solution, and the mixture was stirred at room temperature for 18 h. Then 50 mL of 1 M NaOH solution and 20 mL of CH_2Cl_2 were added, and the mixture was stirred for another 12 h. The organic phase was separated and washed with 1 M NaOH (3×), dried over Na_2SO_4, and evaporated to give complex **5** (105 mg, 84%).^{1}H NMR (acetone-d_6) δ 8.10 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 5.92 (s, 4H), 5.84 (m, 1H), 5.53 (s, 5H), 4.90−5.05 (m, 2H), 3.95 (s, 3H), 3.50−3.90 (br, 4H), 3.23 (brs, 4H), 3.10 (brs, 4H), 2.59 (t, J = 5.2 Hz, 4H), 2.38 (t, J = 7.2 Hz, 2H), 2.06 (m, 2H), 1.35−1.60 (8H); ^{13}C NMR (acetone-d_6) δ 169.2, 166.6, 141.1 139.8, 132.0, 130.3, 128.3, 123.3, 122.2, 114.7, 77.8, 69.3, 68.3, 58.9, 52.9 (2C), 52.6, 48.3 (2C), 34.4, 29.8, 29.6, 27.9, 27.4; IR (CH_2Cl_2) 1735, 1654 cm^{-1}; FAB HRMS Calcd for M − PF_6^- ($C_{36}H_{47}N_4O_3$-Ru) 685.2692; found, 685. 2666.

(1-(4-(4-(Methoxycarbonyl)benzoyl)piperazino)-4-(4-(7-octenyl)piperazino)benzene (6). To an acetonitrile/water (15 mL/1 mL) solution of the 1,10-phenanthroline−HCl·H_2O (60 mg, 0.256 mmol, 2 equiv) was added Ru complex **5** (105 mg, 0.126 mmol). The mixture was degassed for 30 min then irradiated under UV light for 28 h. Basic alumina (Brockman I) was added to the intense red solution. The solvent was removed, and the alumina/residue was dried in vacuo. This was placed atop a short basic alumina column, and the TAPD derivative was washed off by passing chloroform through the column. Any remaining phenanthroline was then removed by washing the chloroform eluant with 0.05 M HCl solution and water, and then the organic phase was dried over Na_2SO_4 and evaporated to give **5** (51 mg, 77%). ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 6.86 (s, 4H), 5.75 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 4.90−4.99 (m, 2H), 3.92 (s, 3H), 3.54 (br, 8H), 2.93−3.15 (br, 8H), 1.92−2.02 (m, 4H), 1.30−1.45 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 169.3, 166.2, 146.2, 143.8, 139.8, 138.5, 131.2, 129.8, 127.0, 119.1, 118.2, 114.6, 55.4, 52.3, 51.8, 50.2, 47.7, 42.1, 33.4, 28.5, 28.4, 26.6, 23.4; EI HRMS Calcd for M^+ ($C_{31}H_{42}N_4O_3$) 518.3257; found, 518.3237.

8-(Thioacetoxy)bromooctane (7). 8-Bromo-1-octene (1.17 g, 6.12 mmol) was dissolved in 15 mL of toluene. To this solution were added thioacetic acid (0.932 g, 12.24 mmol, 2 equiv) and AIBN (25 mg). The solution was then heated to reflux for 30 min. The mixture was cooled, quenched by addition of 30 mL of 1 M solution of $NaHCO_3$, and extracted with ethyl acetate. The organic phase was washed with 1 M $NaHCO_3$ (3×) and brine, dried over Na_2SO_4, and rotary evaporated to give **7** (1.62 g, 99%). ^{1}H NMR ($CDCl_3$) δ 3.40 (t, J = 6.8 Hz, 2H), 2.86 (t, J = 7.3 Hz, 2H), 2.32 (s, 3H), 1.85 (quint., J = 6.8 Hz, 2H), 1.56 (quint., J = 7.2 Hz, 2H), 1.21−1.45 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 195.6, 33.7, 32.6, 30.5, 29.3, 28.9, 28.7, 28.5, 28.4, 27.9; IR (neat) 1702 cm^{-1}; EI HRMS Calcd for MH^+ ($C_{10}H_{20}OSBr$) 267.0419; found, 267.0423.

1-(8-Mercaptooctyl)piperazine (9). A mixture of piperazine (572 mg, 6.64 mmol, 5 equiv) and 8-(thioacetoxy)bromooctane (355 mg, 1.33 mmol) in 16.5 mL of 90% ethanol was refluxed for 20 h. After removing the ethanol under reduced pressure, 30 mL of sat. $NaHCO_3$ solution was added, and the product was extracted with ether (4×), dried over Na_2SO_4, and evaporated to give **9** (279 mg, 91%). ^{1}H NMR (CD_3OD) δ 2.84 (t, J = 5.0 Hz, 4H), 2.49 (t, J = 7.2 Hz, 2H), 2.44 (br s, 4H), 2.33 (m, 2H), 1.30−1.65 (m, 12H); ^{13}C NMR (CD_3OD) δ 60.4, 54.9, 46.1, 35.3, 30.6, 30.2, 29.4, 28.7, 27.3, 25.1; EI HRMS Calcd for M^+ ($C_{12}H_{26}N_2S$) 230.1816; found, 230.1801.

Bis(8-piperazinooctyl) Disulfide (10). A mixture of piperazine (1.718 g, 19.9 mmol, 5 equiv), and 8-(thioacetoxy)-bromooctane (1.065 g, 3.99 mmol) in 40 mL of 90% ethanol was refluxed for 20 h. After removing the ethanol under reduced pressure, 30 mL of 1 M NaOH solution and 40 mL of ether were added. The mixture was stirred at room temper-

ature for 24 h, and the aqueous phase was separated and extracted with ether (4×). The combined ether extract was dried over Na_2SO_4 and evaporated to give **10** (0.832 g, 91%). ^{1}H NMR (CD_3OD) δ 2.83 (t, J = 5.0 Hz, 8H), 2.68 (t, J = 7.1 Hz, 4H), 2.44 (br s, 8H), 2.33 (m, 4H), 1.60−1.72 (4H), 1.20−1.55 (20H); ^{13}C NMR (CD_3OD) δ 60.4, 54.9, 46.0, 39.8, 30.6, 30.3, 30.2, 29.4, 28.7, 27.2; EI HRMS Calcd for M^+ ($C_{24}H_{50}N_4S_2$) 458.3477; found, 458.3470.

Bis(2-piperazinoethyl) Disulfide (12). A solution of piperazine (5.8 g, 67 mmol) in 40 mL of benzene was heated to reflux under Ar. A solution of ethylene sulfide (1 mL, 1.01 g, 16.8 mmol) in 20 mL of benzene was added via a dropping funnel over 15 min at reflux. The mixture was then refluxed for 2 h. The solvent was removed, and the product was purified by flash chromatography on silica gel, (5:20:75, concentrated NH_3(aq):CH_3OH:$CHCl_3$ eluant), to give **12** (2.38 g, 97%). ^{1}H NMR (acetone-d_6) δ 2.92 (t, J = 7.2 Hz, 4H), 2.80 (t, J = 4.6 Hz, 8H), 2.63 (t, J = 7.2 Hz, 4H), 2.42 (br, 8H); ^{13}C NMR (acetone-d_6) δ 59.0, 55.2, 46.7, 37.0; EI HRMS Calcd for MH^+ ($C_{12}H_{27}N_4S_2$) 291.1677; found, 291.1683.

Bis[2-[4-[η^6-(4-chlorophenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]ethyl] Disulfide Hexafluorophosphate (13). The procedure is the same as for compound **3**. Cyclopentadienyl(1,4-dichlorobenzene)ruthenium hexafluorophosphate (89 mg, 0.194 mmol. 2 equiv) was stirred with K_2CO_3 (135 mg, 0.97 mmol, 10 equiv) and disulfide **12** (28 mg, 0.097 mmol) in 4 mL of THF at room temperature for 17 days to give **13** (99 mg, 90%). ^{1}H NMR (acetone-d_6) δ 6.50 (d, J = 6.8 Hz, 4H), 6.13 (d, J = 6.8 Hz, 4H), 5.52 (s, 10H), 3.19 (t, J = 5.0 Hz, 8H), 2.94 (t, J = 7.2 Hz, 4H), 2.72 (t, J = 7.2 Hz, 4H), 2.62 (t, J = 5.0 Hz, 8H); ^{13}C NMR (acetone-d_6) δ 126.2, 101.6, 85.7, 81.1, 69.3, 57.9, 52.3, 47.7, 36.7; FAB HRMS Calcd for M − PF_6^- ($C_{34}H_{42}N_4S_2Cl_2Ru_2PF_6$) 988.9963; found, 988.9978.

Bis[8-[4-[η^6-(4-chlorophenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]octyl] Disulfide Hexafluorophosphate (14). The procedure is the same as for compound **3**. Cyclopentadienyl(1,4-dichlorobenzene)ruthenium hexafluorophosphate (94 mg, 0.205 mmol, 2 equiv) was stirred with K_2CO_3 (142 mg, 1.02 mmol, 10 equiv) and disulfide **10** (47 mg, 0.102 mmol) in 3 mL of THF at room temperature for 18 days to give **14** (105 mg, 79%). ^{1}H NMR (acetone-d_6) δ 6.52 (d, J = 6.8 Hz, 4H), 6.16 (d, J = 6.8 Hz, 4H), 5.55 (s, 10H), 3.19 (t, J = 5.1 Hz, 8H), 2.71 (t, J = 7.2 Hz, 4H), 2.54 (t, J = 4.8 Hz, 8H), 2.34 (t, J = 7.2 Hz, 4H), 1.20−1.75 (24H); ^{13}C NMR (acetone-d_6) δ 126.4, 101.6, 85.8, 81.2, 69.3, 58.8, 52.6, 47.9, 39.2, 30.6, 30.1, 29.8, 29.6, 28.0, 27.4; FAB HRMS Calcd for M − PF_6^- ($C_{46}H_{66}N_4S_2Cl_2RuPF_6$) 1157.1846; found, 1157.1820.

Bis[2-[4-[η^6-(4-piperazinophenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]ethyl] Disulfide Hexafluorophosphate (15). The procedure is the same as for compound **4**. Complex **13** (120 mg, 0.106 mmol) was stirred with piperazine (73 mg, 0.85 mmol, 8 equiv) and K_2CO_3 (58 mg, 0.43 mmol, 4 equiv) in 5 mL of THF at room temperature for 48 h to give **15** (125 mg, 95%). ^{1}H NMR (acetone-d_6) δ 5.87 (s, 8H), 5.49 (s, 10H), 3.11 (t, J = 5.0 Hz, 8H), 2.96−3.02 (m, 20H), 2.77 (t, J = 7.2 Hz, 4H), 2.69 (t, J = 5.0 Hz 8H); ^{13}C NMR (acetone-d_6) δ 123.6, 122.8, 77.4, 68.3, 68.2, 58.1, 52.7, 49.1, 48.3, 45.7, 36.8; FAB HRMS Calcd for M − PF_6^- ($C_{42}H_{60}N_8S_2Ru_2PF_6$) 1089.2130; found, 1089.2186.

Bis[8-[4-[η^6-(4-piperazinophenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]octyl] Disulfide Hexafluorophosphate (16). The procedure is the same as for compound **4**. Complex **14** (295 mg, 0.226 mmol) was stirred with piperazine (156 mg, 1.81 mmol, 8 equiv) and K_2CO_3 (125 mg, 0.90 mmol, 4 equiv) in THF (10 mL) for 52 h at room temperature to give the product (290 mg, 91%). ^{1}H NMR (acetone-d_6) δ 5.81 (s, 8H), 5.44 (s, 10H), 3.04 (br, 8H), 2.94 (br, 16H), 2.72 (t, J = 7.2 Hz, 4H), 2.54 (br, 8H), 2.34 (t, J = 7.2 Hz, 4H), 1.20−1.70 (24H); ^{13}C NMR (acetone-d_6) δ 123.6, 123.0, 77.4, 68.2, 68.0, 58.9, 52.9, 49.1, 48.4, 45.8, 39.2, 30.6, 30.1, 29.8, 29.6, 28.0, 27.5; FAB HRMS Calcd for M − PF_6^- ($C_{54}H_{84}N_8S_2Ru_2PF_6$) 1257.4013; found, 1257.3896.

Bis[8-[4-[η^6-(4-(4-(methoxycarbonyl)benzoyl)piperazino)phenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]ethyl] Disulfide Hexafluorophosphate (17). The procedure is the same as for compound **5**. Complex **15** (125 mg, 0.101 mmol), acid chloride from monomethyl terephthalate (110 mg, 0.61 mmol, 6 equiv), and K_2CO_3 (84 mg, 0.607 mmol, 6 equiv) gave **17** in 71% yield (112 mg). ^{1}H NMR (acetone-d_6) δ 8.10 (d, J = 7.8 Hz, 4H), 7.64 (d, J = 7.8 Hz, 4H), 5.91 (s, 8H), 5.51 (s, 10H), 3.95 (s, 6H), 3.60−4.00 (br, 8H), 3.22(br, 8H), 3.12 (br, 8H), 2.99 (t, J = 7.2 Hz, 4H), 2.77 (t, J = 7.2 Hz, 4H), 2.68 (br, 8H); ^{13}C NMR (acetone-d_6) δ 169.2, 166.6, 141.1, 132.0, 130.3, 128.3, 123.1, 122.2, 77.8, 69.2, 68.4, 58.1, 52.7 (3C), 48.3 (2C), 36.8; IR (CH_2Cl_2) 1731, 1655 cm^{-1}; FAB HRMS Calcd for M − PF_6^- ($C_{60}H_{72}N_8O_6S_2Ru_2PF_6$) 1413.2771; found, 1413.2764.

Bis[8-[4-[η^6-(4-(4-(methoxycarbonyl)benzoyl)piperazino)phenyl)(η^5-cyclopentadienyl)ruthenium(II)]-piperazino]octyl] Disulfide Hexafluorophosphate (18). The procedure is the same as for compound **5**. Complex **16** (130 mg, 0.09 mmol), acid chloride from monomethyl terephthalate (100 mg, 0.56 mmol, 6 equiv), and K_2CO_3 (77 mg, 0.56 mmol, 6 equiv) gave **18** in 77% yield (124 mg).^{1}H NMR (acetone-d_6) δ 8.11 (d, J = 8.2 Hz, 4H), 7.64 (d, J = 8.2 Hz, 4H), 5.92 (m, 8H), 5.53 (s, 10H), 3.95 (s, 6H), 3.50−3.90 (br, 8H), 3.23 (br s, 8H), 3.11 (br s, 8H), 2.77 (t, J = 7.2 Hz, 4H), 2.59 (t, J = 5.2 Hz, 8H), 2.39 (t, J = 7.2 Hz, 4H), 1.25−1.80 (24H); ^{13}C NMR (acetone-d_6) δ 169.2, 166.6, 144.1, 132.0, 130.3, 128.2, 123.3, 122.2, 77.8, 69.2, 68.2, 58.9, 52.9 (2C), 52.6, 48.3 (2C), 39.3, 30.6, 30.1, 29.8, 29.6, 28.0, 27.5; IR (CH_2Cl_2) 1731, 1644 cm^{-1}; FAB HRMS Calcd for M − PF_6^-+2H ($C_{72}H_{96}N_8O_6S_2{}^{102}Ru_2PF_6$) 1581.4653; found, 1581.4623, for ^{101}Ru^{102}Ru calcd 1580.4655; found, 1580.4606.

Bis[8-[4-[η^6-4-(anthraquinone-2-carboxy)piperazino)-phenyl)(η^5-cyclopentadienyl)ruthenium(II)]piperazino]-octyl] Disulfide Hexafluorophosphate (19). The procedure is the same as for compound **5**. Complex **16** (78 mg, 0.056 mmol), acid chloride from anthraquinone-2-carboxylic acid (84 mg, 0.333 mmol, 6 equiv), and K_2CO_3 (46 mg, 0.333 mmol, 6 equiv) gave **19** (76 mg, 73%). ^{1}H NMR (acetone-d_6) δ 8.24−8.34 (m, 8H), 7.93−7.99 (m, 6H), 5.86 (m, 8H), 5.49 (s, 10H), 3.60−3.95 (br, 8H), 3.22 (br, 8H), 3.04 (br, 8H), 2.71 (t, J = 7.2 Hz, 4H), 2.53 (br, 8H), 2.34 (t, J = 7.2 Hz, 4H), 1.20−1.70 (24H); ^{13}C NMR (acetone-d_6) δ 182.9, 182.8, 168.4, 142.3, 135.4 (2C), 134.7, 134.4, 134.2 (2C), 133.5, 128.2, 127.8 (2C), 126.4, 123.3, 122.2, 77.8, 69.2, 68.2, 58.9, 52.9 (2C), 48.3 (2C), 39.3, 30.6, 30.1, 29.8, 29.6, 28.0, 27.5; IR (CH_2Cl_2) 1686, 1646 cm^{-1}; FAB HRMS Calcd for M − PF_6^- ($C_{84}H_{96}N_8O_6S_2Ru_2PF_6$) 1725.4623; found, 1725.4666.

Bis[8-[4-(4-(4-(methoxycarbonyl)benzoyl)piperazino)-phenyl)]piperazino]ethyl] Disulfide (20). A solution of complex **17** (31 mg, 0.027 mmol) in CH_3CN/TMEDA (8 mL/4 mL) was degassed for 30 min and irradiated under UV light for 28 h. Basic alumina (Brockman I) was added to the solution. The solvent was removed, and the alumina/residue was dried in vacuo. This was placed atop a short basic alumina column, and the TAPD derivative was washed off by passing chloroform through the column. Further purification by TLC (Merck Al_2O_3 plate) with $CHCl_3$ afforded **20** (9 mg, 48%). ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 4H), 7.50 (d, J = 8.2 Hz, 4H), 6.89 (s, 8H), 3.95 (s, 6H), 3.90 (br, 4H), 3.50 (br, 4H), 3.16 (br, 12H), 3.02 (br, 4H), 2.93 (br, 4H), 2.81 (br, 4H), 2.72 (br, 8H), ^{13}C NMR ($CDCl_3$, −40 °C) δ 169.5, 166.6, 145.7, 144.8, 139.7, 131.1, 130.1, 127.2, 118.6, 117.9, 57.9, 53.3, 53.0, 51.0, 50.8, 49.9, 47.7, 42.2; IR (CH_2Cl_2) 1720, 1645 cm^{-1}; FAB HRMS Calcd for MNa^+ ($C_{50}H_{62}N_8O_6S_2Na$) 957.4131; found, 957.4172.

Bis[8-[4-[(4-(4-(methoxycarbonyl)benzoyl)piperazino)-phenyl)]piperazino]octyl] Disulfide (21). The procedure is the same as for compound **6**. Complex **18** (75 mg, 0.043 mmol) and 1,10-phenanthroline hydrochloride·H_2O (31 mg, 0.132 mmol, 3 equiv) gave **21** in 58% yield (28 mg) which was further purified by TLC (Merck Al_2O_3 plate) with $CHCl_3$ eluant. ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.1 Hz, 4H), 7.49 (d, J = 8.1 Hz, 4H), 6.88 (s, 8H), 3.93 (s, 6H), 3.90 (br, 4H), 3.52 (br, 4H), 3.16 (br, 12H), 3.00 (br, 4H), 2.67 (t, J = 7.2 Hz, 4H), 2.65 (br s, 8H), 2.42 (t, J = 7.2 Hz, 4H), 1.25−1.70 (24H); ^{13}C NMR ($CDCl_3$, −40 °C) δ 169.5, 166.6, 145.9, 144.7, 139.7, 131.0, 130.1, 127.2, 118.6, 117.8, 58.9, 53.4, 53.0, 50.9, 50.6, 47.7, 42.2, 38.7, 19.7, 29.6, 29.4, 29.2, 28.6, 27.7, 27.0; IR (CH_2Cl_2) 1728,

1644 cm^{-1}; FAB HRMS Calcd for MH^+ ($C_{62}H_{87}N_8O_6S_2$) 1103.6190; found, 1103.6181.

Bis[8-[4-[4-(anthraquinone-2-carboxy)piperazino)phenyl)]piperazino]octyl] Disulfide (22). The procedure is the same as for compound **6**. Complex **19** (65 mg, 0.035 mmol) and 1,10-phenanthroline hydrochloride·H_2O (33 mg, 0.14 mmol, 4 equiv) gave **22** in 47% yield (20 mg) which was further purified by TLC (Merck Al_2O_3 plate) with $CHCl_3$ eluant. ^1H NMR ($CDCl_3$) δ 8.38 (m, 8H), 7.85 (m, 6H), 6.90 (s, 8H), 3.98 (br, 4H), 3.57 (br, 4H), 3.15 (br, 12H), 3.05 (br, 4H), 2.68 (t, J = 7.2 Hz, 4H), 2.63 (br, 8H), 2.40 (t, J = 7.2 Hz, 4H), 1.32−1.67 (24H); ^{13}C NMR ($CDCl_3$, −30 °C) δ 182.7, 168.4, 145.8, 144.8, 141.0, 134.8, 133.9, 133.4, 133.2, 132.9, 128.2, 127.6, 125.8, 118.6, 117.9, 58.8, 53.2, 53.1, 50.9, 50.8, 49.9, 49.8, 49.7, 47.8, 42.3, 38.8, 29.9, 29.8, 29.6, 29.4, 29.2, 28.6, 27.6; IR ($CHCl_3$) 1684, 1637 cm^{-1}; FAB HRMS Calcd for MH^+ ($C_{74}H_{87}N_8O_6S_2$) 1247.6190; found, 1247.6144.

[8-[4-[η^6-(4-chlorophenyl)(η^5-cyclopentadienyl)ruthenium(II) hexafluorophosphate]piperazino]octyl][8′-piperazinooctyl] Disulfide (23). The procedure is the same as for compound **3**. Cyclopentadienyl(1,4-dichlorobenzene)ruthenium hexafluorophosphate (112 mg, 0.244 mmol) was stirred with disulfide **9** (135 mg, 0.294 mmol, 1.2 equiv) and K_2CO_3 (34 mg, 0.244 mmol) in 10 mL of THF at room temperature for 38 h to give **23** (206 mg, 96%). ^1H NMR (CD_3OD) δ 6.43 (d, J = 6.6 Hz, 2H), 6.05 (d, J = 6.6 Hz, 2H), 5.46 (s, 5H), 3.16 (t, J = 5 Hz, 4H), 3.10 (br, 4H), 2.60−2.70 (12H), 2.40−2.50 (m, 4H), 1.20−1.75 (m, 24H); ^{13}C NMR (CD_3OD) δ 126.3, 102.4, 86.3, 81.4, 70.2, 59.4, 59.2, 53.0, 51.4, 48.0, 44.8, 39.7, 30.4, 30.4, 30.2, 29.4, 28.4, 28.2, 27.5, 27.2; FAB HRMS Calcd for M − PF_6^- ($C_{35}H_{58}N_4ClS_2Ru$) 735.2828; found, 735.2835.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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