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Highly Efficient NMR Enantiodiscrimination of Chiral Octanuclear Metalla-Boxes in Polar Solvent

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Summary: Self-assembly of 5,10,15,20-tetra(4-pyridyl)porphyrin (tpp-H_2) and 5,10,15,20-tetra(4-pyridyl)porphyrin-Zn(II) (tpp-Zn) tetradentate panels with the dinuclear p-cymene ruthenium clips $[Ru_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2(\mu\text{-}C_2O_4\text{-}\kappa O)Cl_2]$ and $[Ru_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2(\mu\text{-}C_6H_2O_4\text{-}\kappa O)Cl_2]$ (C_2O_4 = oxalato; $C_6H_2O_4$ = 2,5-dihydroxy-1,4-benzoquinonato) affords the cationic organometallic boxes $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-}tpp\text{-}H_2\text{-}\kappa N)_2(\mu\text{-}C_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{1}]^{8+}$), $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-}tpp\text{-}H_2\text{-}\kappa N)_2(\mu\text{-}C_6H_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{2}]^{8+}$), $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-}tpp\text{-}Zn\text{-}\kappa N)_2(\mu\text{-}C_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{3}]^{8+}$), and $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-}tpp\text{-}Zn\text{-}\kappa N)_2(\mu\text{-}C_6H_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{4}]^{8+}$). In solution, for all these complexes, a rapid and effective enantiodifferentiation was achieved in the presence of the NMR chiral solvating agent Λ-BINPHAT anion, only 0.05 to 0.10 equiv being necessary for complete baseline-to-baseline separation of some of the proton signals of the enantiomers. To add to this highly effective discrimination, all experiments were performed in the high-polarity solvent CD_3CN, a solvent traditionally not favorable for effective chiral ion-pairing phenomena.

Introduction

The $P \leftrightarrow M$ helical conversion in "double-rosette"-type supramolecular architectures[1] has been previously studied by NMR techniques as NMR has evolved in the last decades as one of the methods of choice for the detection of molecular chirality and the measurement of enantiomeric purity.[2] Recently, we have shown the cationic hexanuclear metalla-prisms $[(\eta^6\text{-arene})_6Ru_6(\mu_3\text{-tpt-}\kappa N)_2(\mu\text{-}C_2O_4\text{-}\kappa O)_3]^{6+}$ (arene = *p*-$Pr^iC_6H_4Me$, C_6Me_6; tpt = 2,4,6-tri(pyridine-4-yl)-1,3,5-triazine) and $[Cp^*{}_6M_6(\mu_3\text{-tpt-}\kappa N)_2(\mu\text{-}C_2O_4\text{-}\kappa O)_3]^{6+}$ (M = Rh, Ir) to possess such a helicity.[3] The helical chirality in these systems was further studied by ^{1}H NMR experiments in the presence of the anionic chiral NMR solvating agent BINPHAT.[4] Chiral hexacoordinated phosphate anions BINPHAT (bis(tetrachlorobenzenediolato)mono([1,1′]binaphthalenyl-2,2′-diolato)phosphate(V)) and its analogue TRISPHAT (tris(tetrachlorobenzenediolato)phosphate(V))[5] are effective NMR chiral solvating agents for organometallic substances, especially in halogenated solvents.[6] While efficient NMR enantiodifferentiation is indeed regularly achieved among ions in low-polarity solvents, it is not always the case in high-polarity solvents as a result of weaker electrostatic interactions. Cations and anions behave as dissociated ion pairs, and hence there is a sharp decrease in NMR split efficiency.[7] There are of course exceptions. For instance, water-soluble sulfonated calix[4]resorcarenes are effective NMR chiral solvating agents in water for cationic ammonium derivatives containing aromatic residues.[8] TRISPHAT and BINPHAT anions can discriminate metallo-organic, organometallic, and simple organic cations in very polar solvents (acetone, acetonitrile, dimethyl sulfoxide), but

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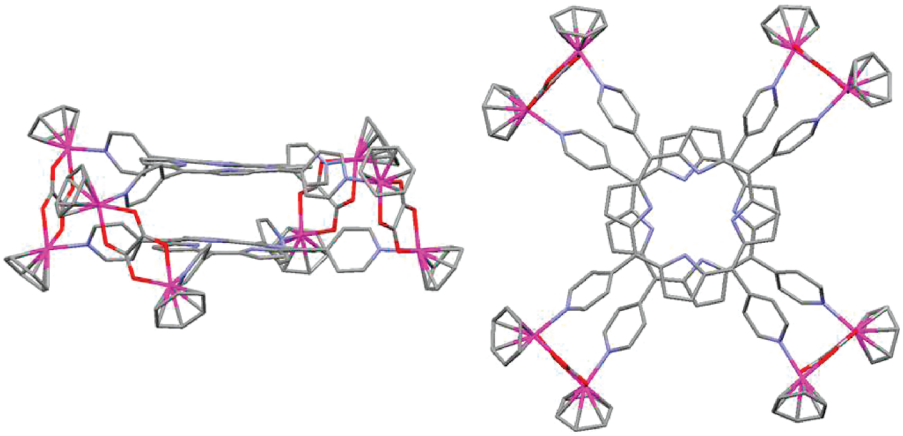
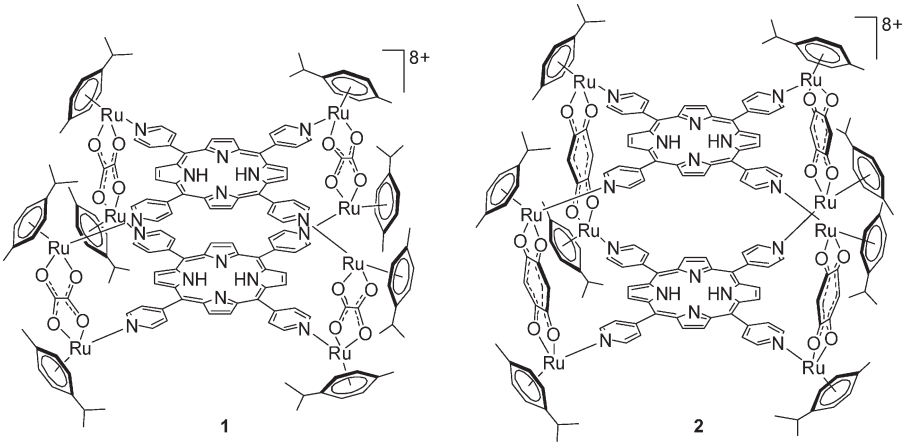
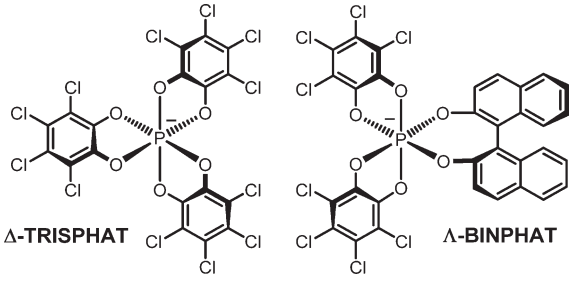


Figure 1. Side view and top view of one helical isomer of [**1**][CF_3SO_3]$_8$ (*M* enantiomer shown).[10]

Chart 1



one or more equivalents of NMR chiral solvating agents are usually required to obtain an effective NMR discrimination.[9]



The synthesis of porphyrin-containing octanuclear metalla-boxes (see Chart 1) was recently achieved using the same strategy as for the chiral cationic hexanuclear metalla-prisms [(η^6-arene)$_6$Ru$_6$(μ_3-tpt-κN)$_2$(μ-C_2O_4-κO)$_3$]$^{6+}$.[3a] In the solid state a chiral conformation was observed in the oxalato-bridged complex [Ru$_8$(η^6-*p*-Pr^{i}C$_6$H$_4$Me)$_8$(μ_4-tpp-H_2-κN)$_2$-(μ-C_2O_4-κO)$_4$][CF_3SO_3]$_8$ ([**1**][CF_3SO_3]$_8$) (tpp-H_2 = 5,10,15,20-tetra(4-pyridyl)porphyrin), for which a racemic mixture of two helical isomers was found in the crystal; see Figure 1.[10]

The more spacious metalla-box [Ru$_8$(η^6-*p*-Pr^{i}C$_6$H$_4$Me)$_8$(μ_4-tpp-H_2-κN)$_2$(μ-$C_6H_2O_4$-κO)$_4$][CF_3SO_3]$_8$ ([**2**][CF_3SO_3]$_8$), containing bridging 2,5-dihydroxy-1,4-benzoquinonato ligands, has shown diastereotopic protons in solution.[11] These observations encouraged us to further study the molecular chirality of this kind of octacationic metalla-box in solution. Herein we report that very low amounts (5−10 mol %) of enantiopure BINPHAT anion are sufficient for the enantiodiscrimination of these chiral supramolecular assemblies, this effective differentiation occurring moreover in polar CD_3CN as solvent.

Results and Discussion

As shown previously, the synthesis of the porphyrin-containing octanuclear metalla-boxes [Ru$_8$(η^6-*p*-Pr^{i}C$_6$H$_4$-Me)$_8$(μ_4-tpp-H_2-κN)$_2$(μ-C_2O_4-κO)$_4$]$^{8+}$ ([**1**]$^{8+}$)[10] and [Ru$_8$(η^6-*p*-Pr^{i}C$_6$H$_4$Me)$_8$(μ_4-tpp-H_2-κN)$_2$(μ-$C_6H_2O_4$-κO)$_4$]$^{8+}$ ([**2**]$^{8+}$)[11] is straightforward. Similarly for the metallo-porphyrin derivatives, addition of silver triflate to the dinuclear clips [Ru$_2$(η^6-*p*-Pr^{i}C$_6$H$_4$Me)$_2$(μ-C_2O_4-κO)Cl$_2$] or [Ru$_2$(η^6-*p*-Pr^i-C$_6$H$_4$Me)$_2$(μ-$C_6H_2O_4$-κO)Cl$_2$] (C_2O_4 = oxalato; $C_6H_2O_4$ = 2,5-dihydroxy-1,4-benzoquinonato) in the presence of

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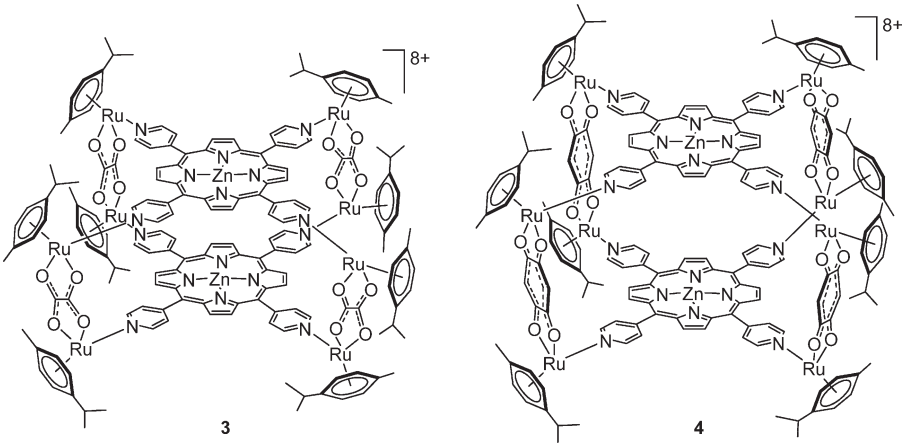
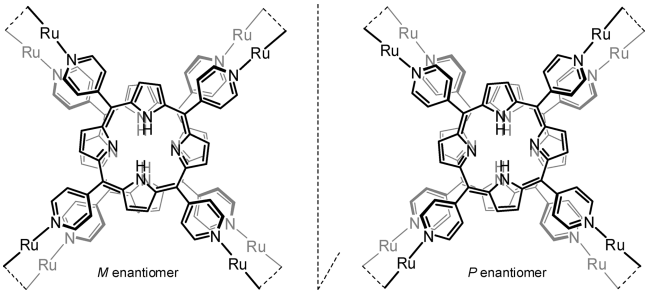
Chart 2



Scheme 1



5,10,15,20-tetra(4-pyridyl)porphyrin-Zn(II) (tpp-Zn) leads in excellent yield to the formation of the new octanuclear metalla-box cations $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-tpp-Zn-}\kappa N)_2(\mu\text{-}C_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{3}]^{8+}$) and $[Ru_8(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_8(\mu_4\text{-tpp-Zn-}\kappa N)_2(\mu\text{-}C_6H_2O_4\text{-}\kappa O)_4]^{8+}$ ($[\mathbf{4}]^{8+}$). These cationic rectangular boxes (see Chart 2) are isolated as their triflate salts and characterized by IR, NMR, and ESI-MS as well as by elemental analysis.

The ^{1}H NMR spectra in CD_3CN of **1**, **2**, **3**, and **4** display a similar signal pattern of the tpp and *p*-cymene protons. The *p*-cymene moieties give a doublet at $\delta \sim 1.6$ ppm and a septet at ~3.1 ppm for the protons of the isopropyl group, a singlet at ~2.4 ppm for the methyl group, and four doublets in the region 6.2−5.9 ppm for the aromatic protons. The tpp panels give between 9.5 and 7.0 ppm a total of six multiplets corresponding to the four pyridyl and two pyrrole protons of the tetrapyridyl porphyrin moieties. In complexes **2** and **4** an additional signal at $\delta \sim 6.2$ ppm corresponding to the benzoquinone protons is observed, while in **1** and **2** the N−H signal is observed at −6.90 and −6.96 ppm, respectively. This spectral pattern indicates that outer (H'_α and H'_β) and inner protons (H_α and H_β) of the pyridyl groups are nonequivalent, thus suggesting a tilt of the bimetallic clips and the presence of helical-type chirality.

As mentioned, in the solid state, a chiral conformation was observed in the oxalato-bridged complex $[\mathbf{1}][CF_3SO_3]_8$, for which a racemic mixture was found in the crystal.[10] A schematic representation of the helical enantiomers is presented in Scheme 1. To ascertain the occurrence of such conformations in solution, the ^{1}H NMR behavior of this and the other three cationic complexes was studied in the presence of the chiral solvating agent BINPHAT, which had been shown to be particularly efficient for the enantiodifferentiation of other metallaprismatic structures.[3a,3b]

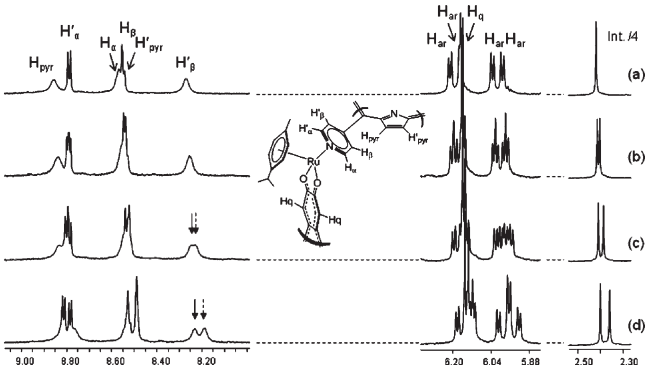


Figure 2. ^{1}H NMR spectra (parts, 500 MHz, CD_3CN) of $[\mathbf{2}][CF_3SO_3]_8$ and assignment of the pyridyl and pyrrole protons: (a) 0, (b) 0.05, (c) 0.1, and (d) 0.2 equiv of $[Bu_4N][\Lambda\text{-BINPHAT}]$.

Addition of 1.0 equiv of $[Bu_4N][\Lambda\text{-BINPHAT}]$ to a CD_3CN solution of $[\mathbf{1}][CF_3SO_3]_8$ at room temperature led to an immediate precipitation of the cationic complex, rendering the desired NMR detection impossible. After several attempts, it turned out that only 0.05 to 0.20 equiv of BINPHAT anion was necessary to induce splitting of some of the proton signals for $[\mathbf{1}][CF_3SO_3]_8$ and the other derivatives, under these conditions, the cationic complexes having a chance to remain soluble in CD_3CN. For $[\mathbf{1}][CF_3SO_3]_8$, the situation was still borderline: Precipitation appeared with 0.1 equiv of $[Bu_4N][\Lambda\text{-BINPHAT}]$ (as a solution in CD_2Cl_2), and the broadness of the tpp-H_2 and *p*-cymene protons allowed a decent yet partial split of the signals (see Supporting Information). However for $[\mathbf{2}][CF_3SO_3]_8$, for which precipitation occurred with a higher amount of the NMR agent (~0.35 equiv in CD_2Cl_2), an effective differentiation of the *p*-cymene and benzoquinone protons ($\Delta\delta$ 0.05 and 0.03 for H_{cymene} and H_q, respectively) was achieved with only 0.2 equiv of BINPHAT anion (Figure 2). The signals for the pyrrole protons are shifted to lower frequencies upon addition of BINPHAT.

The ^{1}H NMR spectrum of the metallo-porphyrin derivatives **3** and **4** showed sharp signals for all protons as compared to complexes **1** and **2**, containing no Zn(II) atom in the porphyrin core. Upon addition at room temperature of 0.1 equiv of $[Bu_4N][\Lambda\text{-BINPHAT}]$ (as a solution in CD_2Cl_2) to a CD_3CN solution of $[\mathbf{3}][CF_3SO_3]_8$ or $[\mathbf{4}][CF_3SO_3]_8$, an effective discrimination of the proton signals was observed.

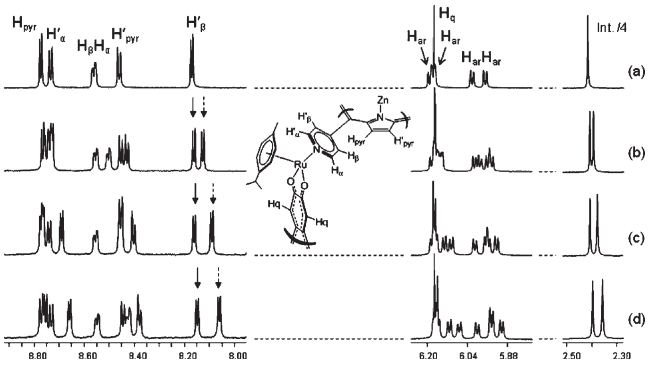


Figure 3. ^{1}H NMR spectra (parts, 500 MHz, CD_3CN) of [**4**][CF_3SO_3]$_8$ and assignment of the pyridyl and pyrrole protons: (a) 0, (b) 0.05, (c) 0.1, and (d) 0.2 equiv of [Bu_4N][Λ-BINPHAT].

For [**3**][CF_3SO_3]$_8$, precipitation occurred after addition of 0.2 equiv of [Bu_4N][Λ-BINPHAT] (see Supporting Information), while in [**4**][CF_3SO_3]$_8$ the precipitation started to become visible at approximately 0.35 equiv. Interestingly, in [**4**][CF_3SO_3]$_8$, only 0.05 equiv of [Bu_4N][Λ-BINPHAT] was needed to induce a baseline-to-baseline separation of almost all signals (Figure 3), these NMR experiments confirming that the complexes studied adopt chiral conformations in solution at room temperature. Strong electrostatic interactions[9c] as well as $\pi-\pi$ interactions[6g] are probably encountered in the high affinity observed between the octacationic metalla-box and the BINPHAT anion.

It is worth mentioning that, upon precipitation and for all cases, no selectivity was observed in solution among the diastereomeric salts as the 1:1 ratio remained. Two hypotheses can then be considered to explain the above result: (i) a configurational stability for the octanuclear metalla-boxes and an unselective precipitation or (ii) a configurational lability and a lack of supramolecular stereocontrol (Pfeiffer effect)[12] from the anion Λ-BINPHAT over the geometry of the cationic complexes.[1b,13] Unfortunately, due to the instability of the cationic derivatives at elevated temperature, variable-temperature NMR experiments, which would have possibly allowed a distinction of these two hypotheses, could not be performed.

In conclusion, the differentiation of these octanuclear metalla-boxes using Λ-BINPHAT as NMR solvating agent is quite astonishing. This is one of the strongest enantiodiscrimination observed by an anionic chiral solvating agent in a polar solvent to date.

Experimental Section

5,10,15,20-Tetrakis(4-pyridyl)porphyrin-Zn(II) (tpp-Zn) was purchased from Frontier Scientific, while [$Ru_2(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_2(\mu$-C$_2$O$_4$-κO$)$Cl$_2$] and [$Ru_2(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_2(\mu$-C$_6$H$_2$O$_4$-κO$)$Cl$_2$] were prepared according to published methods. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX 400 spectrometer using the residual protonated solvent as internal standard , while enantiodifferentiation experiments were performed on a Bruker AMX 500. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FTIR 1720 X spectrometer. Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. UV−visible absorption spectra were recorded on an Uvikon 930 spectrophotometer (10^{-5} M in acetone).

Synthesis of [3][CF_3SO_3]$_8$. [$Ru_8(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_8(\mu_4$-tpp-Zn-κN$)_2(\mu$-C$_2$O$_4$-κO$)_4$][CF_3SO_3]$_8$: A mixture of Ag(CF_3SO_3) (165 mg, 0.64 mmol) and [$Ru_2(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_2(\mu$-C$_2$O$_4$-κO$)$Cl$_2$] (202 mg, 0.32 mmol) in methanol (30 mL) is stirred at room temperature for 3 h, then filtered. To the red filtrate, tpp-Zn (109 mg, 0.16 mmol) is added. The solution is refluxed for 24 h, and then the solvent removed under vacuum. The residue is dissolved in dichloromethane (3 mL), and diethyl ether is added to precipitate the green solid.

[**3**][CF_3SO_3]$_8$: yield 298 mg (78%); IR ν (cm^{-1}) 3072 (w, CH aryl), 1520 (s, C=O), 1257 (s, CF_3); ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 9.28 (d, 8H, H$_{pyr}$), 9.22 (d, 8H, H′$_\alpha$), 8.97 (m, 16H, H$_\alpha$), 8.15 (d, 8H, H$_\beta$), 8.10(d, 8H, H′$_{pyr}$), 7.97 (d, 8H, H′$_\beta$), 6.15 (m, 24H, H$_{ar}$), 5.96 (m, 8H, H$_{ar}$), 3.13 (sept, 8H, C*H*(CH$_3$)$_2$), 2.36 (s, 24H, CH$_3$), 1.60 (m, 48H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ(ppm) 171.2 (*C*O), 153.7 (*C*H′$_\alpha$), 153.1 (*C*H$_\alpha$), 147.2 (*C*$_{pyr}$), 147.0 (*C*$_{pyr}$), 133.0 (*C*H′$_\beta$), 132.9 (*C*H$_\beta$), 114.6 (*C*CH(CH$_3$)$_2$), 101.8 (*C*$_{ox}$), 97.6 (*C*CH$_3$), 83.9 (*C*H$_{ar}$), 82.7 (*C*H$_{ar}$), 81.8 (*C*H$_{ar}$), 31.3 (*C*H(CH$_3$)$_2$), 21.9 (CH(*C*H$_3$)$_2$), 21.4 (CH(*C*H$_3$)$_2$), 17.6 (*C*H$_3$); ESI-MS 1048.7 [**3** + (CF_3SO_3)$_4$]$^{4+}$ and 1448.0 [**3** + (CF_3SO_3)$_5$]$^{3+}$; UV−visible (1.0×10^{-5} M, acetone, 298 K) λ_{max} 416 nm (Soret band, ε = 292 000 M^{-1} cm^{-1}), λ_{max} 510 nm (Q-band, ε = 78 000 M^{-1} cm^{-1}). Anal. (%): Calcd for $C_{176}H_{160}F_{24}Ru_8N_{16}O_{40}S_8Zn_2$: C 44.08, H 3.34, N 4.67. Found: C 43.91, H 3.12, N 4.50.

Synthesis of [4][CF_3SO_3]$_8$. [$Ru_8(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_8(\mu_4$-tpp-Zn-κN$)_2(\mu$-C$_6$H$_2$O$_4$-κO$)_4$][CF_3SO_3]$_8$: A mixture of $AgCF_3SO_3$ (86 mg, 0.34 mmol) and [$Ru_2(\eta^6$-*p*-Pr^{i}C$_6$H$_4$Me$)_2(\mu$-C$_6$H$_2$O$_4$-κO$)$Cl$_2$] (115 mg, 0.17 mmol) in methanol (60 mL) is stirred at room temperature for 3 h, then filtered. To the red filtrate, tpp-Zn (57 mg, 0.085 mmol) is added. The solution is refluxed for 24 h, and then the solvent removed under vacuum. The residue is dissolved in dichloromethane (3 mL), and diethyl ether is added to precipitate the red solid.

[**4**][CF_3SO_3]$_8$: yield 232 mg (81%); IR ν (cm^{-1}) 3073 (w, CH aryl), 1521 (s, C=O), 1257 (s, CF_3); ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.83 (d, 8H, H$_{pyr}$), 8.75 (d, 8H, H′$_\alpha$), 8.63 (d, 8H, H$_\beta$), 8.51 (d, 8H, H$_\alpha$), 8.20 (d, 8H, H′$_{pyr}$), 7.41 (d, 8H, H′$_\beta$), 6.20 (m, 16H, H$_{p\text{-cym}}$), 6.18 (s, 8H, H$_q$), 6.04 (d, 8H, H$_{p\text{-cym}}$), 5.97 (d, 8H, H$_{p\text{-cym}}$), 3.12 (sept, 8H, C*H*(CH$_3$)$_2$), 2.42 (s, 24H, C*H*$_3$), 1.54 (m, 48H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ (ppm) 185.2 (*C*O), 184.8 (*C*O), 154.0 (*C*$_{pyridyl}$), 152.8 (*C*H′$_\alpha$), 150.9 (*C*H$_\alpha$), 148.2 (*C*$_{pyrrole}$), 147.7 (*C*$_{pyrrole}$), 134.6 (*C*H′$_\beta$), 133.0 (*C*H$_\beta$), 132.8 (*C*H′$_{pyr}$), 132.5 (*C*H$_{pyr}$), 105.0 (*C*$_{ar}$), 99.9 (*C*$_{ar}$), 102.9 (*C*H$_q$), 84.9 (*C*H$_{ar}$), 84.5 (*C*H$_{ar}$), 83.4 (*C*H$_{ar}$), 82.9 (*C*H$_{ar}$), 32.4 (*C*H(CH$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$), 18.6 (*C*H$_3$); ESI-MS 1098.1 [**4** + (CF_3SO_3)$_4$]$^{4+}$; 1513.1 [**4** + (CF_3SO_3)$_5$]$^{3+}$; UV−visible (1.0×10^{-5} M, acetone, 298 K) λ_{max} 426 nm (ε = 360 000 M^{-1} cm^{-1}), λ_{max} 521 nm (ε = 46 000 M^{-1}cm^{-1}). Anal. (%) Calcd for $C_{192}H_{168}F_{24}Ru_8N_{16}O_{40}S_8Zn_2$: C 46.14, H 3.36, N 4.49. Found: C 45.97, H 3.30, N 4.29.

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Supporting Information Available: ^{1}H NMR spectrum (500 MHz, CD_3CN) of [**1**][CF_3SO_3]$_8$ and [**3**][CF_3SO_3]$_8$ in the presence of Λ-BINPHAT. MS spectra for complexes [**3**][CF_3SO_3]$_8$ and [**4**][CF_3SO_3]$_8$. UV−visible spectra of **1**−**4** in acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

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