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Synthesis of Triple-Stranded Complexes Using Bis(dipyrromethene) Ligands

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The reaction of an α-free, β,β′-linked bis(dipyrromethene) ligand with Fe^{3+} or Co^{3+} led to noninterconvertible triple-stranded helicates and mesocates. In the present context, a stable α-free ligand **2** has been developed and complexation of ligands **1** and **2** with diamagnetic Co^{3+}, Ga^{3+}, and In^{3+} has been studied. The triple-stranded $M_2\mathbf{1}_3$ (M = Ga, In) and $M_2\mathbf{2}_3$ (M = Co, Ga, In) complexes were characterized using matrix-assisted laser desorption ionization time-of-flight spectrometry, ^1H NMR and UV−vis spectroscopy, and X-ray crystallography. Again, the ^1H NMR analysis showed that both the triple-stranded helicates and mesocates were generated in this metal-directed assembly. Consistent with our previous finding on coordinatively inert Co^{3+} complexes, variable-temperature NMR spectroscopy indicated that the triple-stranded helicate and mesocate of labile In^{3+} did not interconvert in solution, either. However, the diastereoselectivity of the $M_2\mathbf{2}_3$ complexes was found to improve with an increase in the reaction temperature. Taken together, this study complements the coordination chemistry of poly(dipyrromethene) ligands and provides further insight into the formation of helicates versus mesocates.

Introduction

As a result of a fully conjugated bipyrrolic system, deprotonated dipyrromethenes (also known as dipyrrins) are known as useful monoanionic ligands that can, when coordinated with di- or trivalent metals, generate attractive uncharged complexes that have strong absorptions in the visible region.[1−5] As such, dipyrromethene complexes may serve as functional subunits of synthetic light-harvesting devices and, as a result, have drawn considerable attention in the last few decades.[6−8] In the pursuit of chromophoric supramolecular complexes, poly(dipyrromethene)s, which contain multiple dipyrromethene units connected by a linker, have been investigated as building blocks for the synthesis of nonpolar double-stranded helicates,[9−13] triangular helicates,[14,15] and oligomeric linear complexes.[16] However, these complexes were all constructed on the basis of tetrahedral coordination of the dipyrromethenes with a divalent metal. Curiously, neutral octahedral poly(dipyrromethene) complexes have rarely been reported,[17] even though mononuclear octahedral ones[3,4] and multinuclear double-stranded ones[9−13] have long been recognized. It is of interest to learn the requirements for a poly(dipyrromethene) ligand to form supramolecular architectures with octahedral geometry and to develop an efficient synthesis of ligands capable of generating such attractive three-dimensional supramolecules.

Recently, we reported the first examples of multinuclear octahedral bis(dipyrromethene) complexes, $Fe_2\mathbf{1}_3$ and $Co_2\mathbf{1}_3$, which are uncharged complexes with intensive UV−vis absorption.[17] The reaction of ligand **1** and Fe^{3+} (or Co^{3+}) gives both triple-stranded helicates and mesocates. In contrast, diastereoselective formation of helicates is normally

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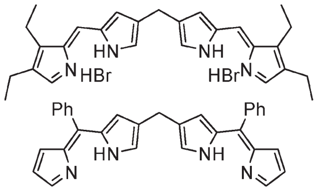
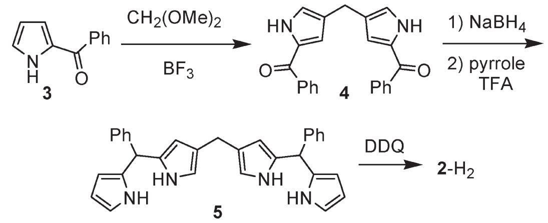


$\mathbf{1}$-$H_2 \cdot 2HBr$

$\mathbf{2}$-H_2

Figure 1. α-Free, *β*,*β*′-linked proligands $\mathbf{1}$-$H_2 \cdot 2HBr$ and $\mathbf{2}$-H_2.

Scheme 1. Synthesis of Proligand $\mathbf{2}$-H_2



observed in the well-reported studies of double-stranded complexes.[9−13] More intriguingly, the isolated helicates (or mesocates) did not convert to the corresponding diastereomeric mesocates (or helicates) even upon heating, suggesting that this complexation process is not simply under thermodynamic control, as is usually observed in a common metal-directed self-assembly. In order to examine whether this phenomenon is only a result of the well-known inertness of Co^{3+} complexes or is prevalent for other metal complexes, reactions of a stable ligand with metals, especially more labile ones such as Ga^{3+} and In^{3+}, need to be investigated. Unfortunately, because of the presence of four unsubstituted α positions, proligand $\mathbf{1}$-$H_2 \cdot 2HBr$ (Figure 1) is exceedingly unstable in solution, which severely limits its usefulness. In this study, we have designed and developed the synthesis of a novel α-free, *β*,*β*′-linked bis(dipyrromethene), $\mathbf{2}$-H_2, which is pretty stable in both solution and the solid state. Using the bis(dipyrromethene) ligands as models, we hoped our investigations could provide some insight into the self-assembled formation of helicate versus mesocate and provide direction for future ligand design.

Results and Discussion

Ligand Design and Preparation of the Complexes. The fully α-free, *β*,*β*′-linked ligand **1** was synthesized by condensing an α-free dialdehyde and fully α-free pyrrole.[17] To improve its stability and meanwhile to keep the α-unsubstituted character, a functional group might be introduced to the meso position of each dipyrromethene fragment. On the basis of the knowledge that an aryl group, especially an electron-withdrawing one at the meso position, can dramatically improve the stability of dipyrromethenes, we decided to introduce a phenyl group to these positions. Starting from *β*,*β*′-linked **4**, proligand $\mathbf{2}$-H_2 was readily synthesized by reduction, condensation, and oxidation (Scheme 1). It is noteworthy, however, that oxidation with dichlorodicyanoquinone (DDQ) produced not only the desirable $\mathbf{2}$-H_2 but also a small amount of the scrambled product 5-phenyldipyrromethene. An attempt at using the less reactive oxidant chloranil overnight failed to achieve conversion from **5** to $\mathbf{2}$-H_2. As anticipated, this bis(dipyrromethene) displayed very good stability.

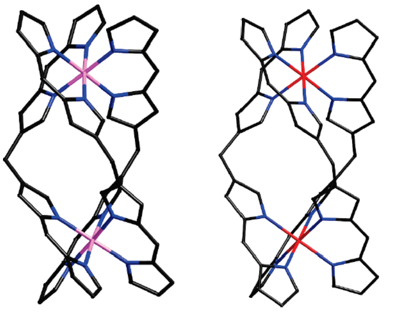


Figure 2. Stick model of the crystal structures of helicates $Co_2\mathbf{2}_3$ and $Ga_2\mathbf{2}_3$. Note: The helicates were a racemic mixture. Phenyl groups and hydrogen atoms have been omitted for clarity.

Table 1. Product Ratios at Different Reaction Temperatures[a]

	helicate/mesocate ratio					
reaction temperature (°C)	$Co_2\mathbf{1}_3$	$Ga_2\mathbf{1}_3$	$In_2\mathbf{1}_3$	$Co_2\mathbf{2}_3$	$Ga_2\mathbf{2}_3$	$In_2\mathbf{2}_3$
25	3:2	3:2	2:3	2:1	3:2	3:2
65	3:2	3:2	3:2	4:1	5:2	2:1
150	*b*	*b*	*b*	5:1	7:1	4:1

[a] The ratios were determined using ^1H NMR after chromatography. [b] Not measured because the proligand rapidly decomposed at this temperature.

Upon coordination with a diamagnetic trivalent metal in the presence of a few drops of NEt_3, both ligands **1** and **2** produced nonpolar triple-stranded complexes. To achive higher yields of the nonpolar products, methanol was used as the reaction medium for the complexation of ligand **2**. Under optimal conditions, the total yield of $Ga_2\mathbf{2}_3$ complexes (Figure 2) was almost double compared to that of $Ga_2\mathbf{1}_3$ complexes, while the yields of $In_2\mathbf{1}_3$ and $In_2\mathbf{2}_3$ complexes were very similar. Surprisingly, when $[Co(py)_4Cl_2]Cl$, which worked well with ligand **1**, was used, the expected complexes were generated in relatively low yields.

Both helicate and mesocate were generated in all of the reactions. Judging from integration of their ^1H NMR signal(s), the helicate/mesocate product ratios of diamagnetic $M_2\mathbf{1}_3$ (M = Co, Ga, In) complexes were essentially not affected by the metal ion used when the reaction was carried out at 65 °C (Table 1). Although the $Fe_2\mathbf{1}_3$ and $Co_2\mathbf{1}_3$ helicates and mesocates can be isolated on silica gel, the $Ga_2\mathbf{1}_3$ and $In_2\mathbf{1}_3$ complexes degraded under the same conditions. Alumina facilitated the separation of these complexes from the reaction mixture but was not effective enough to allow separation of the $M_2\mathbf{1}_3$ diastereomers. In the case of the $M_2\mathbf{2}_3$ complexes, the helicates and mesocates, unfortunately, have very similar R_f values on both silica gel and alumina and thus could not be separated from each other using common chromatography. However, carrying out the complexation of ligand **2** at 150 °C eventually led to the helicates as predominant products. In contrast, changing the reaction temperature of ligand **1** did not result in a significant change in the product ratio. Ligands **1** and **2** also produced triple-stranded complexes with paramagnetic metals such as Fe^{3+} and Mn^{3+}. The presence of two types of nonpolar complexes with very similar polarity on thin-layer chromatography (TLC) plates suggests that both helicates and mesocates were formed. Preliminary X-ray analysis showed that the crystals grown out of the product mixture had a helical structure, indicating

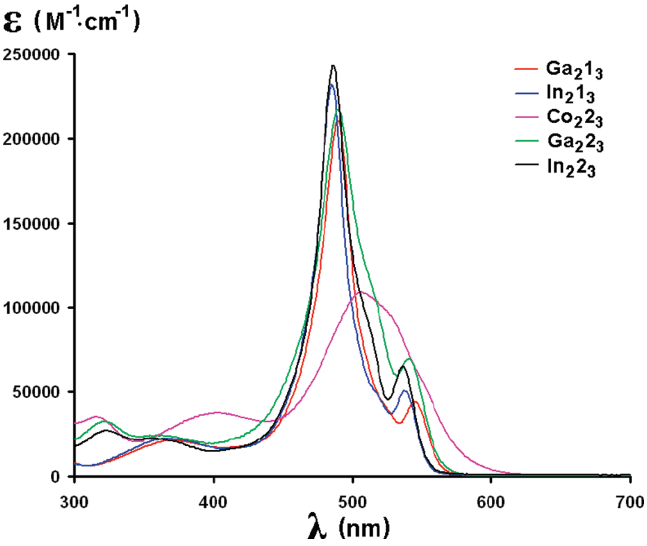
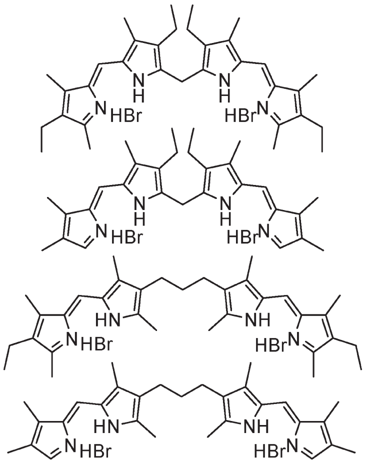


Figure 3. UV−vis spectra of $M_2\mathbf{1}_3$ and $M_2\mathbf{2}_3$ complexes. Note: The complexes were prepared at 65 °C and are a mixture of helicate and mesocate.

that the helicates again might be the major products in these cases. However, accurate helicate/mesocate ratios are still to be determined, and the properties of these complexes are under study.

Characterization of the Complexes. Using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix, matrix-assisted laser desorption ionization time-of-flight mass spectroscopy showed that all of the nonpolar complexes had a mass corresponding to M_2L_3 (L = **1**, **2**), indicating that they were triple-stranded. The ^{1}H NMR spectra of the diamagnetic $M_2\mathbf{1}_3$ and $M_2\mathbf{2}_3$ complexes are consistent with the fact that both the helicate and mesocate were generated from the same ligand and metal. Because a helicate has a D_3 point group and a mesocate has C_{3h} symmetry, the protons of the methylene linker are homotopic in a helicate and diastereotopic in a mesocate. Therefore, the singlet signal for the methylene group belonged to the helicate, while the two doublets, located at relatively higher field, represented the mesocate. In particular, the helicates and mesocates of Ga_2L_3 and In_2L_3 (L = **1**, **2**) can be unambiguously identified by the multiplicity of the methylene linker, but the two doublets merged into one broad peak in the case of the $Co_2\mathbf{2}_3$ mesocate. In 1,2-dichlorobenzene-d_4, a similar phenomenon was also observed for the $In_2\mathbf{2}_3$ mesocate.

Single crystals suitable for X-ray analysis were grown out of the product mixture prepared at 150 °C by vapor diffusion of hexane into a CH_2Cl_2 (or $CHCl_3$) solution (Table S1 in the Supporting Information). The crystal structures showed that, consistent with the observation using ^{1}H NMR, the predominant diastereomers were the helicates (Figure 3). In the solid state, the bis(*meso*-phenyldipyrromethene) $Co_2\mathbf{2}_3$ helicate had M−N bond lengths and N−M−N bond angles quite similar to those of the β-substituted $Co_2\mathbf{1}_3$ helicate.[17] The mean M−N bond length of the $Co_2\mathbf{2}_3$ helicate was 1.937 Å, also comparable to those of reported mononuclear complexes.[18] The twist angle of the $Co_2\mathbf{2}_3$ helicate is 103°, only 2° greater than that of the $Co_2\mathbf{1}_3$ helicate. The M−M distance is 7.765 Å for the $Co_2\mathbf{2}_3$ helicate, leading to a helical pitch of 27.1 Å. Similar to the cases of the $Co_2\mathbf{1}_3$ and $Co_2\mathbf{2}_3$ helicates, the mean Ga−N bond length of the $Ga_2\mathbf{2}_3$ helicate (2.051 Å) compares well to the reported bond lengths of 2.054 and 2.053 Å.[5] The twist angle of the $Ga_2\mathbf{2}_3$ helicate is 97°, smaller than those of the $Co_2\mathbf{1}_3$ and $Co_2\mathbf{2}_3$ helicates but close to that of the $Fe_2\mathbf{1}_3$ helicate.[17] The Ga−Ga distance is 8.038 Å. Consequently, the $Ga_2\mathbf{2}_3$ helicate owns a helical pitch of 29.8 Å.



6-H_2· 2HBr

7-H_2· 2HBr

8-H_2· 2HBr

9-H_2· 2HBr

Figure 4. Bis(dipyrromethene) hydrobromide salts **6**−**9**-$H_2 \cdot 2HBr$.

The primary UV−vis spectral features of the triple-stranded $M_2\mathbf{1}_3$ and $M_2\mathbf{2}_3$ complexes are intense absorption bands ($\varepsilon > 10^5\ M^{-1}\cdot cm^{-1}$) with maxima at around 500 nm (Figure 3). Compared to the corresponding mononuclear analogues, the major band of the dinuclear triple-stranded complexes has a similar pattern but a pronounced bathochromic shift of approximately 40 nm.[3−5,18] The strong similarity between the $M_2\mathbf{2}_3$ and $M_2\mathbf{1}_3$ complexes indicates that the substituent effect at the β or meso position on the ligand makes little difference to the optical properties of these complexes. Similar to the octahedral mononuclear complexes,[3−5,18] the absorption spectra of transition-metal complexes are characterized by a broad band with relatively weak absorbance, while the main spectral feature of main-group Ga^{3+} and In^{3+} helicates is a sharp, intense peak.

Scope of Bis(dipyrromethene) Ligands Capable of Generating Triple-Stranded Complexes. Both substituted α,α′- and β,β'-linked bis(dipyrromethene)s have been reported to form double-stranded helicates.[8,11] To survey their capability of generating neutral triple-stranded complexes, substituted ligands **6**−**9** (Figure 4) with different linker or α substituents were synthesized and examined. When ligands such as **6**−**8** were employed, neutral M_2L_3 complexes were not detected in any of the reactions. Interestingly, when β,β'-linked **9**, which has two α positions unsubstituted, was reacted with Co^{3+} or Fe^{3+}, a neutral species was generated; however, considerable degradation occurred during chromatography, and a pure sample, suitable for characterization, was not obtained. As evidenced by these facts, the size of the α substituents is crucial for the formation of homoleptic bis(dipyrromethene) triple-stranded complexes. Only ligands with the α position unsubstituted can generate

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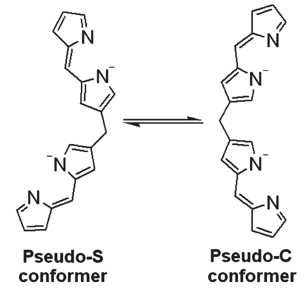
stable triple-stranded complexes with octahedral metals: this is consistent with the observations on mononuclear complexes.[3] Further, the failure of α-free α,α′-linked bis(dipyrromethene) ligand **7** suggests that the location of the linker is also critical. In contrast, the length of the linker seems to have no major effect. It is noteworthy, however, that the length of the linker is among the most important ligand features that affect the structure of the product. According to our previous work,[11] when $n = 0$ or $n > 4$ (n = number of carbon atoms in a linker), the ligand may favor the formation of mononuclear or even triangular complexes.[9,11,14]

Formation of Helicate versus Mesocate. Since the first discovery of a triple-stranded mesocate over a decade ago,[19] chemists have made significant progress toward understanding the formation of helicates versus mesocates.[20,21] Particularly, Albrecht and co-workers recognized that ligand linkers need to take either an asymmetric "S" or a symmetric "C" conformation in order to form D_3 helicates or C_{3h} mesocates and proposed an empirical *odd–even rule* on the basis of the self-assembly of a series of dicatechol ligands.[22–27] It was suggested that, because of the "zigzag" arrangement of the alkyl chains, a linker with an odd number of methylene units leads to the symmetric "C" structure of the ligand and thus facilitates the formation of mesocate, while one with an even number of methylene units makes the ligand take an asymmetic "S" conformation, which favors the helicate. However, obtaining both a triple-stranded helicate and mesocate from the same reaction in our study implies that an alkyl-linked ligand, upon coordination, can take either a pseudo-S or pseudo-C conformation through bond rotation (Scheme 2). Because the transition between the pseudo-S or pseudo-C conformers, of the methylene-linked ligands, does not usually involve much steric strain, these conformers interconvert rapidly under the reaction conditions. Presumably, even an ethylene-linked ligand may take a cis pseudo-C conformation and lead to mesocate. Therefore, the stereochemistry of the product(s) cannot be simply determined by the conformational preference of an alkyl linker.

In our previous study,[17] the isolated pair of bis(dipyrromethene) helicate and mesocate was found not to interconvert even upon heating. We suggested that severe steric overlap of the α hydrogen atoms in either a Bailar or a Ray-Dutt twist intermediate blocks the nondissociative interconversion. The same lack of interconversion was also observed for the current helicate/mesocate mixture in solution using variable-temperature ^{1}H NMR. Take the $In_2\mathbf{2}_3$ complexes for example, the temperature change over a range from room temperature to 155 °C did not lead to a change of the helicate/mesocate ratio, indicating even the more labile In^{3+} helicate and mesocate do not interconvert in solution (see the Supporting Information). We therefore conclude that the lack of interconversion is common for such triple-stranded helicates and mesocates.

Scheme 2. Interconversion between the pseudo-S and pseudo-C Conformations of Bis(dipyrromethene) Ligands



The fact that a pair of helicate and mesocate does not interconvert opens a door to improving the diastereoselectivity by changing the reaction conditions. To achieve this goal, both the reaction medium and temperature were varied for the complexation of ligand **2**. It turned out that the product ratio of ligand **2** with a trivalent metal did not change in various solvents such as chloroform, *N*,*N*-dimethylformamide (DMF), and methanol. However, the reaction temperature had a significant influence on the product ratio (Table 1). Surprisingly, decreasing the reaction temperature did not enhance the selectivity as it generally does. On the contrary, increasing the reaction temperature led to the predominant formation of helicates. It is noteworthy, however, in cases where a triple-stranded helicate can convert into the mesocate through either a dissociative or a nondissociative pathway, that the product ratio will eventually be governed by thermodynamic factors.

Conclusion

In summary, we have established the synthesis of a stable α-free, *β*,*β*′-linked bis(dipyrromethene) ligand. A survey on a series of bis(dipyrromethene) ligands showed that the size of the α substituents and the linker location of the bis(dipyrromethene) ligands is crucial. Coordinating with either group 13 or transition metals, α-free, *β*,*β*′-linked ligands generated both the triple-stranded helicate and mesocate. Although the diastereomers did not interconvert under the reaction conditions, the diastereoselectivity could be enhanced by increasing the reaction temperature. The triple-stranded bis(dipyrromethene) complexes have strong absorptions around 500 nm and can be, in principle, widely modified and exploited as self-assembling functional chromophores in the future.

Experimental Section

Materials and Instrumentation. Starting materials were purchased from commercial suppliers and used without further purification. Column chromatography was carried out using silica gel (particle size: 0.040–0.063 mm, 230–400 mesh) or alumina (particle size: 60–325 mesh, neutral, 6% H_2O added). The mass spectrometry (MS) and high-resolution MS (HRMS) spectra were measured on Kratos MS50 (electron impact, EI), Kratos Concept IIHQ (EI), or Bruker Esquire~LC (electrospray ionization, ESI) spectrometers. The mass of the

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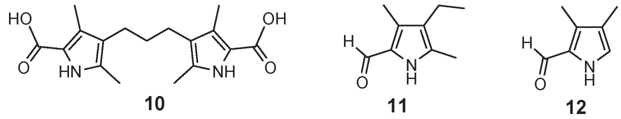
metal complexes was examined using MALDI-TOF in the presence of DCTB as the matrix on a Bruker Biflex IV instrument. Elemental analysis was performed on a Carlo Erba EA 1108 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded with Bruker 300 spectrometers, and chemical shifts are reported in ppm using the residual nondeuterated solvent as the reference standard. The melting points of crystalline compounds were measured with a Bristoline melting point apparatus and are uncorrected. The UV−vis spectra were measured on a Varian Cary 5000 spectrophotometer. X-ray crystallographic analyses were carried out on a Bruker X8 APEX diffractometer with graphite-monochromated Mo Kα radiation. Data were collected and integrated using the Bruker *SAINT* software package. The structures were solved by direct methods. All refinements were performed using the *SHELXTL* crystallographic software package of Bruker-AXS.

Preparation of Proligands. The α-free, *β*,*β*′-linked proligand **1**-H$_2$·2HBr was prepared following our recently reported method.[17] α,α′-Linked proligands **6**- and **7**-H$_2$·2HBr were prepared according to the reported procedures.[28,29]

4,4′-Methylenebis(1*H*-pyrrole-4,2-diyl)bis(phenylmethanone) (4). *β*,*β*′-Linked **4** was synthesized according to the method used for *β*,*β*′-linked diformyldipyrromethanes.[30] 2-Benzoylpyrrole **3** (1.7 g, 10 mmol) and dimethoxymethane (5 mmol) were dissolved in anhydrous acetonitrile (50 mL). The solution was cooled to 0 °C and subsequently treated with boron trifluoride diethyl etherate (10 mmol, 1.0 equiv). The reaction was allowed to proceed at 0 °C for 1 h before being quenched with NEt$_3$. After evaporation, the reaction mixture was separated by column chromatography on silica gel using ethyl acetate/hexanes (1:4) as the eluent. **4** was obtained as a white solid. Yield: 0.43 g, 12%. Mp: 211−213 °C. R_f (silica; ethyl acetate/hexanes, 1:2): 0.20. ^{1}H NMR (300 MHz, acetone-d_6): δ 10.85 (br s, 2H, NH), 7.86−7.83 (m, 4H, Ph-H), 7.61−7.46 (m, 6H, Ph-H), 7.12−7.10 (m, 2H, pyrrole-H), 6.76−6.75 (m, 2H, pyrrole-H), 3.76 (s, 2H, *meso*-CH$_2$). ^{13}C NMR (75 MHz, acetone-d_6): δ 184.5, 140.0, 132.3, 129.6, 129.5, 129.2, 127.0, 124.9, 119.6, 24.9. MS (EI): *m*/*z* 354 (M$^+$). Elem anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.95; H, 5.12; N, 7.90. Found: C, 77.61; H, 5.26; N, 7.76.

Bis{5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-3-yl}methane (5). **4** (0.10 g, 0.28 mmol) in MeOH (10 mL) was treated with excess NaBH$_4$ in several portions. Once the starting material was consumed, the solvent was removed and the organic residue was taken up in CH$_2$Cl$_2$ and washed with H$_2$O. Removal of CH$_2$Cl$_2$ provided a colorless liquid, which, subsequently, was dissolved in pyrrole (50 mL) and treated with trifluoroacetic acid (0.022 mL, 0.29 mmol) at room temperature. The reaction was allowed to proceed for 15 min before quenching with aqueous NaOH. After the reaction mixture was washed, dried, and separated on silica gel, **5** was obtained as a viscous oil. Yield: 0.11 g, 82%. R_f (silica, CH$_2$Cl$_2$): 0.45. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.60 (br s, 2H, NH), 9.20 (br s, 2H, NH), 7.29−7.15 (m, 10H, Ph-H), 6.68−6.65 (m, 2H, pyrrole-H), 6.45−6.43 (m, 2H, pyrrole-H), 6.00−5.97 (dd, J = 5.9 Hz, J' = 2.9 Hz, 2H, pyrrole-H), 5.76−5.67 (m, 2H, pyrrole-H), 5.67−5.66 (t, J = 1.8 Hz, 2H, pyrrole-H), 5.38 (s, 2H, pyrrole-H), 3.53 (s, 2H, *meso*-CH$_2$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 143.1, 133.2, 133.0, 129.1, 128.8, 127.3, 125.0, 117.7, 115.2, 108.7, 108.4, 107.5, 44.7, 25.4. MS (EI): *m*/*z* 456 (M$^+$). HRMS (EI). Calcd for $C_{31}H_{28}N_4$ (M$^+$): *m*/*z* 456.23140. Found: *m*/*z* 456.23116.

Bis{5-[phenyl(2*H*-pyrrol-2-ylidene)methyl]-1*H*-pyrrol-3-yl}methane (2-H$_2$). To a CH$_2$Cl$_2$ solution of **5** (0.1 g, 0.22 mmol) was added DDQ (0.1 g, 0.44 mmol). The reaction mixture was then stirred at room temperature for 3 h. After the solvent was removed under pressure, the product was isolated as a dark-brown solid by column chromatography. Yield: 0.045 g, 45%. Mp: 166−168 °C. R_f (silica; ethyl acetate/hexanes, 1:4): 0.59. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 12.64 (br s, 2H, NH), 7.69−7.68 (d, J = 1.1 Hz, 2H, pyrrole-H), 7.50−7.44 (m, 10H, Ph-H), 7.38−7.37 (m, 2H, pyrrole-H), 6.41 (d, J = 1.1 Hz, 2H, pyrrole-H), 6.39−6.37 (dd, J = 4.0 Hz, J' = 1.1 Hz, 2H, pyrrole-H), 6.30−6.29 (dd, J = 4.0 Hz, J' = 2.2 Hz, 2H, pyrrole-H), 3.59 (s, 2H, *meso*-CH$_2$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 153.9, 146.1, 142.2, 137.9, 136.9, 136.1, 134.7, 131.2, 129.5, 129.3, 128.1, 124.7, 114.1, 25.1. MS (EI): *m*/*z* 452 (M$^+$). HRMS (EI). Calcd for $C_{31}H_{24}N_4$ (M$^+$): *m*/*z* 452.20010. Found: *m*/*z* 452.19982.



10 11 12

Figure 5. Compounds **10**−**12**.

General Procedure for the Synthesis of Substituted *β*,*β*′-Linked Proligands 8 and 9. **10** (1 mmol) was dissolved in methanol (5 mL) and treated with HBr (33% in acetic acid, 1 mL) at room temperature. After the mixture was stirred for 1 h, **11** (or **12**) (2 mmol) was added. The solution was stirred for another 1 h before the addition of diethyl ether (50 mL). The proligand was obtained as a red powder after filtration (Figure 5).

1,3-Bis{5-[(4-ethyl-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-2,4-dimethyl-1*H*-pyrrol-3-yl}propane Dihydrobromide (8-H$_2$·2HBr). Yield: 83%. ^{1}H NMR (300 MHz, CDCl$_3$ with a few drops of CD$_3$OD): δ 6.97 (s, 2H, CH), 2.49 (s, 6H, CH$_3$), 2.45 (s, 6H, CH$_3$), 2.36−2.27 (m, 8H, CH$_2$), 2.17 (s, 6H, CH$_3$), 2.14 (s, 6H, CH$_3$), 1.53−1.42 (m, J = 7.7 Hz, 2H, *meso*-CH$_2$), 0.98−0.92 (t, J = 7.6 Hz, 6H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$ with a few drops of CD$_3$OD): δ 154.2, 152.3, 142.3, 141.6, 130.9, 127.7, 126.2, 125.7, 118.7, 29.8, 23.3, 16.9, 13.9, 12.3, 9.8, 9.6. Elem anal. Calcd for $C_{33}H_{46}Br_2N_4$: C, 60.19; H, 7.04; N, 8.51. Found: C, 59.53; H, 7.06; N, 8.38. HRMS (EI, [M − 2HBr + H]$^+$). Calcd for $C_{33}H_{45}N_4$: *m*/*z* 497.3644. Found: *m*/*z* 497.3650.

1,3-Bis{5-[(3,4-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-2,4-dimethyl-1*H*-pyrrol-3-yl}propane Dihydrobromide (9-H$_2$·2HBr). Yield: 80%, red solid. ^{1}H NMR (300 MHz, CDCl$_3$ with a few drops of CD$_3$OD): δ 7.45 (s, 2H, CH), 7.11 (s, 2H, CH), 2.50 (s, 6H, CH$_3$), 2.39−2.33 (t, J = 7.7 Hz, 4H, CH$_2$), 2.18 (s, 6H, CH$_3$), 2.17 (s, 6H, CH$_3$), 1.94 (s, 6H, CH$_3$), 1.52−1.46 (m, 2H, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$ with a few drops of CD$_3$OD): δ 156.4, 143.8, 141.9, 139.4, 129.0, 127.2, 126.7, 124.9, 120.9, 29.5, 23.4, 12.8, 10.0, 9.8, 9.6. HRMS (EI, [M − 2HBr + H]$^+$). Calcd for $C_{29}H_{37}N_4$: *m*/*z* 441.3018. Found: *m*/*z* 441.3009.

General Procedure for the Synthesis of Triple-Stranded M$_2$1$_3$ Complexes. The M$_2$**1**$_3$ complexes were synthesized at 65 °C following the method used for the preparation of the Fe$_2$**1**$_3$ and Co$_2$**1**$_3$ complexes.[17] After chromatography, on alumina, the complexes were isolated as a diastereomeric mixture.

Ga$_2$1$_3$. Yield: 38%. The helicate/mesocate ratio is approximately 3:2. R_f (alumina; CH$_2$Cl$_2$/hexanes, 1:1): 0.94. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 7.06 (s, helicate-CH and mesocate-CH), 6.77 (s, helicate-CH and mesocate-CH), 6.33 (s, helicate-CH and mesocate-CH), 6.23 (s, mesocate-CH), 6.21 (s, helicate-CH), 3.57 (s, *meso*-CH$_2$ of the helicate), 3.45−3.40 (d, J = 13.9 Hz, *meso*-CH$_2$ of the mesocate), 3.28−3.24 (d, J = 14.3 Hz, *meso*-CH$_2$ of the mesocate), 2.62−2.55 (q, J = 7.4 Hz, CH$_2$), 2.37−2.21 (m, CH$_2$), 1.17−1.11 (m, CH$_3$), 0.99−0.94 (t, J = 7.7 Hz, CH$_3$). MS (MALDI-TOF): *m*/*z* 1371.3 (M$^+$). HRMS (EI). Calcd for $C_{81}H_{91}N_{12}{}^{69}Ga_2$ ([M + H]$^+$): *m*/*z* 1369.6001. Found: *m*/*z* 1369.6035.

In$_2$1$_3$. Yield: 32%. The helicate/mesocate ratio is approximately 3:2. R_f (alumina; CH$_2$Cl$_2$/hexanes, 1:1): 0.94. ^{1}H NMR

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(300 MHz, CD_2Cl_2, 25 °C): δ 7.06 (s, helicate-CH and mesocate-CH), 6.86 (s, mesocate-CH), 6.85−6.84 (m, helicate-CH and mesocate-CH), 6.76 (s, helicate-CH), 6.55 (s, helicate-CH), 6.53 (s, mesocate-CH), 3.66 (s, *meso*-CH_2 of the helicate), 3.53−3.48 (d, J = 14.6 Hz, *meso*-CH_2 of the mesocate), 3.42−3.37 (d, J = 14.6 Hz, *meso*-CH_2 of the mesocate), 2.64−2.57 (q, J = 7.4 Hz, CH_2), 2.43−2.23 (m, CH_2), 1.17−1.12 (t, J = 7.5 Hz, CH_3), 1.04−0.99 (t, J = 7.7 Hz, CH_3). MS (MALDI-TOF): *m*/*z* 1460.6 (M^+). HRMS (EI). Calcd for $C_{81}H_{91}N_{12}{}^{115}In_2$ ($[M + H]^+$): *m*/*z* 1461.5567. Found: *m*/*z* 1461.5533.

General Procedure for the Synthesis of Triple-Stranded $M_2$2$_3$ Complexes. The proligand **2**-H_2 (50 mg, 0.11 mmol) was initially dissolved in a small amount of chloroform (2 mL) and then added to refluxing methanol (50 mL) (or DMF when the reaction was performed at 150 °C: only data of the former are shown in the following). While heating, $Co[(Py)_4Cl_2]Cl$ (or $Ga(OAc)_3$ or $InCl_3$) (0.8 mmol) was added to the solution, followed by the addition of a few drops of NEt_3. The mixture was stirred and heated at reflux for another 1 h before removal of the solvent. After chromatography on alumina, the complexes were obtained as diastereomeric mixtures.

$Co_2$2$_3$. Yield: 9%. The helicate/mesocate ratio is approximately 3:1. R_f (alumina; CH_2Cl_2/hexanes, 1:1): 0.83. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.53−7.39 (m, Ph-H of the helicate and mesocate), 6.69−6.67 (dd, J = 3.9 Hz, J' = 2.0 Hz, pyrrole-H of the helicate), 6.65−6.63 (dd, J = 4.2 Hz, J' = 1.3 Hz, pyrrole-H of the mesocate), 6.47 (d, J = 1.4 Hz, pyrrole-H of the helicate), 6.43 (d, J = 1.5 Hz, pyrrole-H of the mesocate), 6.32 (s, pyrrole-H of the helicate), 6.31−6.29 (dd, J = 3.5 Hz, J' = 2.0 Hz, pyrrole-H of the helicate), 6.28 (d, J = 1.8 Hz, pyrrole-H of the mesocate), 6.21 (d, J = 1.5 Hz, pyrrole-H of the helicate), 6.17 (s, pyrrole-H of the mesocate), 6.10 (d, J = 1.8 Hz, pyrrole-H of the mesocate), 3.44 (s, *meso*-CH_2 of the helicate), 3.26 (s, *meso*-CH_2 of the mesocate). MS (MALDI-TOF): *m*/*z* 1469.6 (M^+). HRMS (ESI). Calcd for $C_{93}H_{67}N_{12}{}^{59}Co_2$ ($[M + H]^+$): *m*/*z* 1469.4241. Found: *m*/*z* 1469.4236.

$Ga_2$2$_3$. Yield: 71%. The helicate/mesocate ratio is approximately 2:1. R_f (alumina; CH_2Cl_2/hexanes, 1:1): 0.83. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.51−7.34 (m, Ph-H of the helicate and mesocate), 6.80 (s, pyrrole-H of the helicate), 6.74 (d, J = 1.5 Hz, pyrrole-H of the helicate), 6.70 (d, J = 1.1 Hz, pyrrole-H of the mesocate), 6.61 (s, pyrrole-H of the mesocate), 6.56−6.54 (dd, J = 4.0 Hz, J' = 1.1 Hz, pyrrole-H of the helicate), 6.54−6.52 (dd, J = 4.0 Hz, J' = 1.5 Hz, pyrrole-H of the mesocate), 6.38 (d, J = 1.1 Hz, pyrrole-H of the helicate), 6.33 (d, J = 1.1 Hz, pyrrole-H of the mesocate), 6.24−6.22 (dd, J = 4.0 Hz, J' = 1.5 Hz, pyrrole-H of the helicate), 6.22−6.20 (dd, J = 4.4 Hz, J' = 1.8 Hz, pyrrole-H of the mesocate), 3.47 (s, *meso*-CH_2 of the helicate), 3.33−3.29 (dd, J = 14.3 Hz, *meso*-CH of the mesocate), 3.27−3.23 (dd, J = 14.0 Hz, *meso*-CH of the mesocate). MS (MALDI-TOF): *m*/*z* 1491.7 (M^+). HRMS (ESI). Calcd for $C_{93}H_{67}N_{12}{}^{69}Ga_2$ ($[M + H]^+$): *m*/*z* 1489.4123. Found: *m*/*z* 1489.4102.

$In_2$2$_3$. Yield: 34%. The helicate/mesocate ratio is approximately 2:1. R_f (alumina; CH_2Cl_2/hexanes, 1:1): 0.83. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.51−7.34 (m, Ph-H of the helicate and mesocate), 7.20 (d, J = 1.1 Hz, pyrrole-H of the mesocate), 7.06 (s, pyrrole-H of the helicate), 7.03 (d, J = 1.1 Hz, pyrrole-H of the helicate), 6.84 (s, pyrrole-H of the mesocate), 6.57−6.55 (dd, J = 4.4 Hz, J' = 1.1 Hz, pyrrole-H of the helicate), 6.54−6.53 (d, J = 1.1 Hz, pyrrole-H of the mesocate), 6.41−6.40 (d, J = 0.8 Hz, pyrrole-H of the helicate), 6.35−6.34 (d, J = 1.1 Hz, pyrrole-H of the mesocate), 6.31−6.29 (dd, J = 4.0 Hz, J' = 1.4 Hz, pyrrole-H of the helicate), 6.29−6.27 (dd, J = 4.2 Hz, J' = 1.6 Hz, pyrrole-H of the mesocate), 3.52 (s, *meso*-CH_2 of the helicate), 3.40−3.35 (dd, J = 14.3 Hz, *meso*-CH of the mesocate), 3.35−3.28 (dd, J = 14.3 Hz, *meso*-CH of the mesocate). MS (MALDI-TOF): *m*/*z* 1581.5 (M^+). HRMS (ESI). Calcd for $C_{93}H_{67}N_{12}{}^{115}In_2$ ($[M + H]^+$): *m*/*z* 1581.3689. Found: *m*/*z* 1581.3739.

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Supporting Information Available: X-ray crystallographic data in CIF format, NMR spectra, crystal data, and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.