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5,5′-Diamino-2,2′-bipyridine: A Versatile Building Block for the Synthesis of Bipyridine/Catechol Ligands That Form Homo- and Heteronuclear Helicates

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Abstract: Herein we present an improved synthesis of 5,5′-diamino-2,2′-bipyridine (**1**) starting from the pyrrole-protected aminopyridine **4**. By standard reactions **1** can easily be transformed into the imine- or amide-bridged dicatechol–bipyridine ligands L^1-H_4 and L^2-H_4. Whereas ligand L^1 readily forms homodinuclear helicates $[(L^1)_3Ti_2]^{4-}$, the attempted formation of mono-, tri-, or even oligonuclear coordination compounds from this ligand did not work. However, the amide-connected ligand L^2 affords mononuclear ($[(L^2$-$H_4)PdCl_2]$, $[(L^2$-$H_4)_3Zn]^{2+}$), dinuclear ($[(L^2)_3Ti_2]^{4-}$), and heterotrinuclear coordination compounds ($[(L^2)_3Ti_2Zn]^{2-}$).

Keywords: coupling reactions · cryptands · helicates · N ligands · self-assembly

Introduction

During the last 15 years, helicates were investigated with the aim to understand the mechanisms of their formation as well as their structural features.[1] Helicates can be considered to be the "drosophila" of metallosupramolecular chemistry: important mechanistic aspects can very easily be studied and much knowledge can be gained by using them as simple model systems for more complex multinuclear supramolecular coordination compounds.[2] Although functionality is an important aspect in supramolecular chemistry,[3] only a few attempts have been made to study helicates owing to special reactivities or properties.[4]

Many publications on the formation of helicates have appeared during the last two decades, but only a few of them describe the formation of heteronuclear metal complexes. The chief problem is the incorporation of different metal binding units that are specific for different metal ions. Elegant approaches were described by Piguet and Lehn and their co-workers, in which binding sites with ligand units differing in their denticity were used.[5] We introduced a catechol/aminophenol ligand that can bind different metals owing to the different electronic properties of the binding sites.[6]

The present project developed as we first started to investigate bis(catecholimines) as ligands for helicate formation.[7] 5,5′-Diamino-2,2′-bipyridine (**1**) seemed to be the ideal building block to obtain bipyridine-bridged di(catecholimine) ligands L^1-H_4L^2-H_4 and their corresponding metal complexes.

Results and Discussion

An improved synthesis of 5,5′-diamino-2,2′-bipyridine (1): The preparation of 5,5′-diamino-2,2′-bipyridine (**1**) was previously described by Zhang and Breslow[8] and Janiak and co-workers;[9] both groups used nickel-mediated/catalyzed coupling reactions for the synthesis. However, when we applied the described conditions, they only worked in a few experiments and we were not able to reproduce the results on a regular basis. In a new approach, we have now prepared the diamine **1** using a dimethyl-substituted pyrrole as the

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protecting group for the amine.[10] This procedure provided the desired bipyridine **1** reproducibly in good yields and high purity.

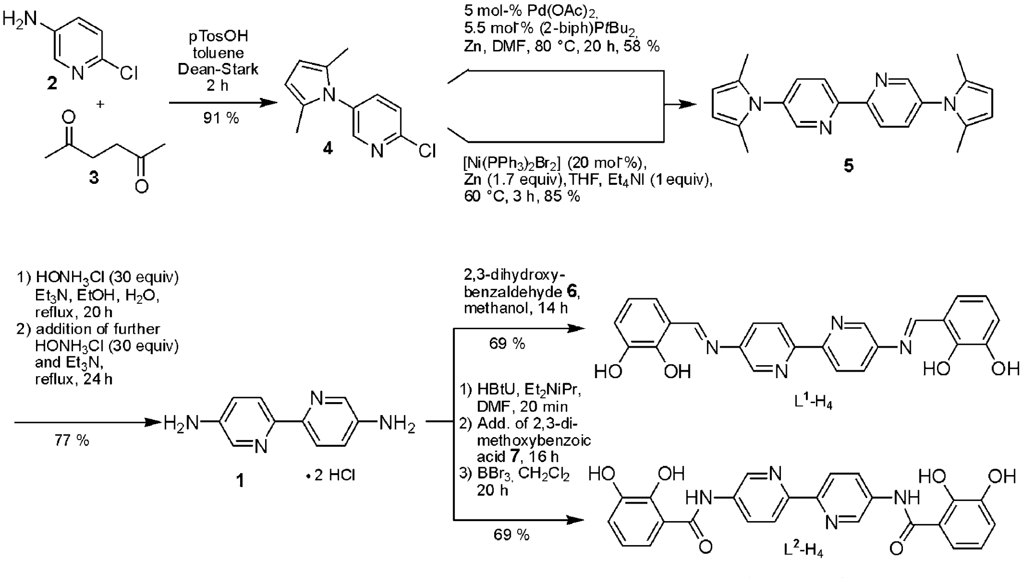
Compound **1** was synthesized starting from 2-chloro-5-aminopyridine (**2**). The amine group in **2** was protected as a pyrrole by reaction with 2,5-hexadione (**3**; Scheme 1). The resulting compound **4** could be homocoupled with zinc as reducing agent either in the presence of palladium(II) acetate and 2-biphenylbis(*tert*-butyl)phosphane ((2-biph)P*t*Bu$_2$) or with [Ni(PPh$_3$)$_2$Br$_2$] and tetraethylammonium iodide. The latter procedure is superior to the palladium-catalyzed coupling due to the much lower costs and the higher yield in the reaction. The resulting coupling product **5** was obtained in 85 % yield. The amine groups of **5** were deprotected by reaction with hydroxylamine in the presence of triethylamine. For a complete transformation, additional hydroxylamine had to be added after the reaction mixture had been refluxed for 20 h; the mixture was then heated for another 24 h. This procedure gave 5,5′-diamino-2,2′-bipyridine (**1**) as the bis-HCl adduct in 77 % yield (Scheme 1).

Synthesis of dicatechol/2,2′-bipyridine ligands L^1-H$_4$ and L^2-H$_4$: The preparation of the ligands L^1-H$_4$ and L^2-H$_4$ is straightforward. Condensation of 2,3-dimethoxybenzaldehyde (**6**) and 5,5′-diamino-2,2′-bipyridine (**1**) in methanol afforded the bisimine ligand L^1-H$_4$ in 69 %. The corresponding amide-connected ligand L^2-H$_4$ was also obtained in 69 % yield by initially generating an active ester of 2,3-dimethoxybenzoic acid **7** with hydroxybenztriazoluronium hexafluorophosphate (HBTU)[11] followed by addition of **1**. Finally, the methyl ethers were cleaved by reaction with BBr$_3$ to obtain the ligand L^2-H$_4$ in quantitative yield.

Formation of helicates of the imine-bridged ligand L^1-H$_4$:[12] Stirring of L^1-H$_4$ (3 equiv), [TiO(acac)$_2$] (2 equiv), and M$_2$CO$_3$ (M = Li, Na, K; 2 equiv) in DMF overnight led to red solutions which, after evaporation of the solvent, yielded M$_4$[(L^1)$_3$Ti$_2$] as red-orange solids. Analysis of the NMR spectroscopic data of these complexes revealed significant but expected differences to that of the free ligand L^1-H$_4$ (δ = 9.05 (s), 8.72 (s), 8.46 (d, J = 8.2 Hz), 8.00 (d, J = 8.6 Hz), 7.14 (d, J = 7.4 Hz), 6.97 (d, J = 7.4 Hz), 6.80 ppm (t, J = 7.4 Hz)), but also indicated the high degree of symmetry of dinuclear metal coordination compounds, since for example, the ^{1}H NMR spectrum of Na$_4$[(L^1)$_3$Ti$_2$] in [D$_6$]DMSO shows only half a set of signals for the bipyridine unit at δ = 8.46 (d, J = 2.4 Hz), 8.25 (d, J = 8.3 Hz), and 7.67 ppm (dd, J = 8.3, 2.4 Hz), and for the catecholates at δ = 7.08 (d, J = 7.7 Hz, 6 H), 6.41 (pseudo t, J = 7.7 Hz, 6 H), and 6.22 ppm (d, J = 7.7 Hz, 6 H). The imine protons are shifted to δ = 8.82 ppm (s, 6 H).

In addition, we were also able to obtain crystals of Na$_4$[(L^1)$_3$Ti$_2$] from DMF/diethyl ether which showed that its solid-state structure is similar to the one which was observed for the corresponding helicate having biphenyl as spacer instead of the bipyridine.[13] Three ligands L^1 and two titanium(IV) ions form a cylinder of approximately 2.1 nm length with the linear rigid ligands slightly twisting around the metal–metal axis (Figure 1a,b). Surprisingly one of the bipyridine units of the spacers possesses the nitrogen atoms orientated s-*trans* to each other, while the others are s-*cis* configured. The reason for this is presumably the packing of the crystal and its symmetry in the solid. The distance between the two Ti centers is 16.980 Å.

Two sodium cations are encapsulated in the interior of the helicate and are separated by 10.603 Å. Clearly, the alkali metal cations do not interact with the bipyridine nitrogen or imine nitrogen atoms but rather solely bind to the internal oxygen atoms of the catecholates (shown for one of the cations in Figure 1c). Three molecules of DMF coordinate to each of the sodium cations and lead to a sixfold coordination. Two further sodium cations bind to the termini of the



Scheme 1. Preparation of 5,5′-diamino-2,2′-bipyridine (**1**) and of bipyridine-bridged dicatechol ligands L^1-H$_4$ and L^2-H$_4$.

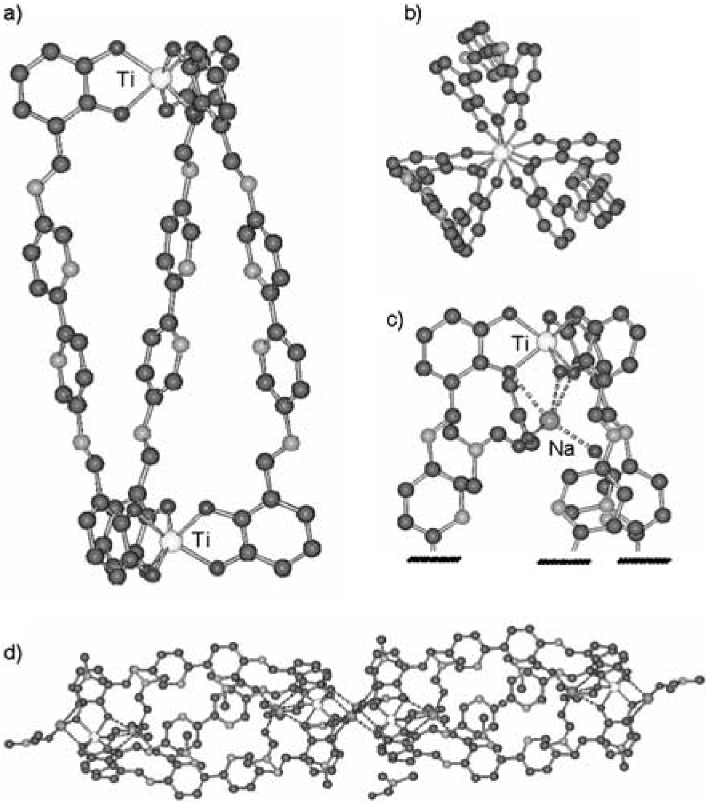


Figure 1. The structure of $[(L^1)_3Ti_2]^{4-}$ in the solid state; a) side view, b) top view, c) coordination geometry of encapsulated sodium cations, and d) formation of a polymeric strand in the solid state.

helicate and through DMF-bridging lead to an infinite polymer in the solid state (Figure 1 d) with alternating helicity of the helices in the polymer strand.

The bipyridine/catechol ligand L^1-H_4 was developed to form heteronuclear coordination compounds. As is schematically depicted in Figure 2, dinuclear complexes of the imine-bridged ligand L^1 possess a conformation that provides a cavity, which is too large to bind a single metal ion in the interior by coordination to more than one bipyridine unit. Repulsion of the lone pair at the imines and the "charge" at the catecholate oxygen atoms force the spacer in an "outward" orientation.

Based on this assumption we attempted to bind three metal complex units to the "outside" of the triple-stranded helicate $[(L^1)_3Ti_2]^{4-}$. Three equivalents of K_2PdCl_4 were allowed to react with $[(L^1)_3Ti_2]^{4-}$. However, the clean reaction (which was monitored by NMR spectroscopy in wet $[D_6]$DMSO) that was observed, unfortunately only resulted in the hydrolysis products **1**-$PdCl_2$ and $[(3\text{-formylcatecholate})_3\text{-}Ti]^{2-}$ (**8**; Scheme 2). Evidently, binding of dichloropalladium to the bipyridine moiety labilizes the imines, which leads to hydrolysis by reaction with residual water in the solvent. Similar imine hydrolysis is observed by direct reaction of K_2PdCl_4 with L^1-H_4.

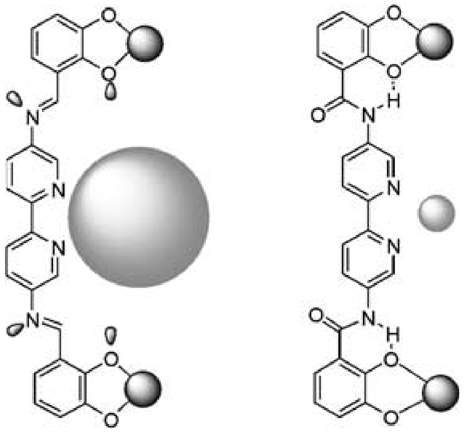
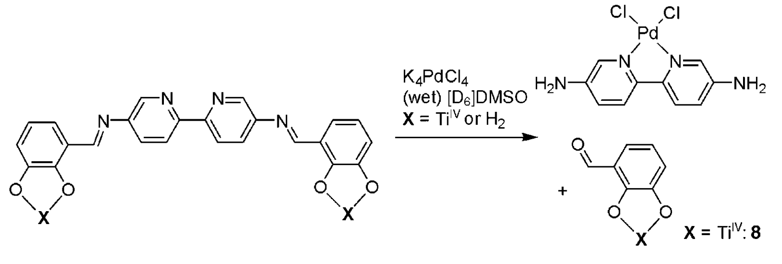


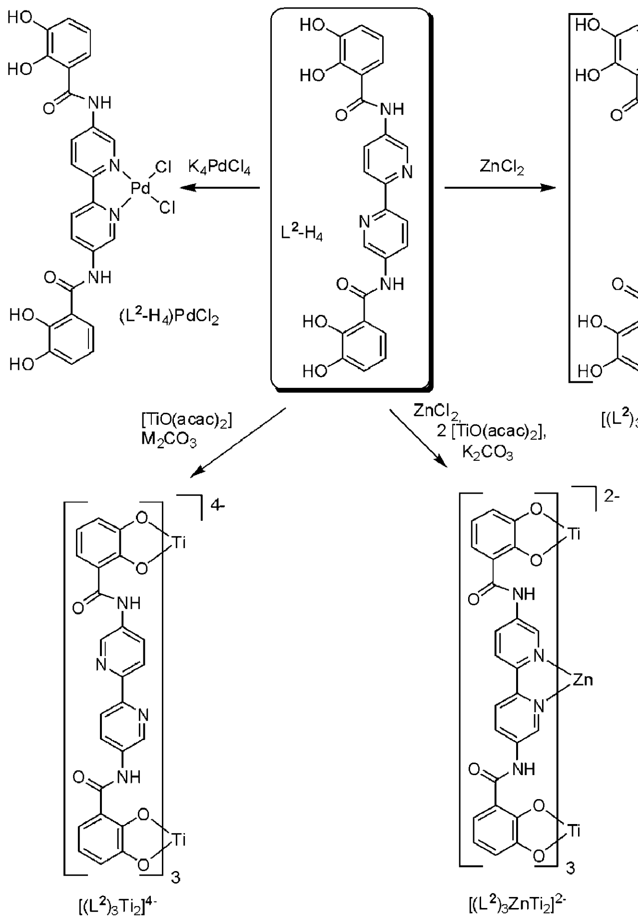
Figure 2. Preferred conformations at complexes of the ligands L^1 and L^2 and representation of the obtained internal space.



Scheme 2.

Formation of helicates of the amide-bridged ligand L^2-H_4: Following the concept shown in Figure 2, the complexes of the amide-bridged ligand L^2 should provide a cavity that is better preorganized for the incorporation of a single metal ion that can interact with all bipyridine moieties. Hydrogen bonding of the amides forces the bipyridine units to be orientated to the inside of the cavity. However, owing to the rigidity of the ligands and their linear orientation, the incorporated metal ions have to adopt a coordination geometry that is closer to trigonal prismatic than to octahedral. In addition, amides are more stable than the corresponding imines and less prone to hydrolysis.

Therefore, we tested ligand L^2-H_4 in a series of coordination studies (Scheme 3). In the reaction of L^2-H_4 with K_2PdCl_4 we obtained the desired mononuclear complex $[(L^2\text{-}H_4)PdCl_2]$ without hydrolysis of the spacer.[14] $[(L^2\text{-}H_4)PdCl_2]$ was characterized by its ^{1}H NMR spectrum, which showed, for example, a low-field shift of the protons in the 6- and 6′-position of the bipyridine unit to $\delta = 9.55$ ppm compared to the free ligand. Mass spectrometry revealed the molecular peak at *m*/*z* 638. Unfortunately, we were not able to use the complex $[(L^2\text{-}H_4)PdCl_2]$ as a ligand for the formation of triple-stranded helicates.



Scheme 3. Preparation of different complexes from ligand L^2-H_4.

Instead of the $PdCl_2$ fragment, other metals can be bound to the bipyridine unit to give tris(bipyridine) complexes. Thus, coordination studies were performed with three equivalents of L^2-H_4 and zinc(II) chloride to obtain the complex $[(L^2\text{-}H_4)_3Zn]^{2+}$ (Scheme 3). The peak of the dication can be observed by positive-ion ESI MS in methanol at *m/z* 719 (correct isotopic pattern). In the ^{1}H NMR spectrum of $[(L^2\text{-}H_4)_3Zn]Cl_2$ in [D$_6$]DMSO the catechol resonances are not shifted significantly. However, the signals of the bipyridine are now observed at $\delta = 9.03$ (s), 8.42 (d, $J = 8.7$ Hz), and 8.35 ppm (dd, $J = 8.7$, 2.4 Hz) (see Figure 3, c). Owing to the high polarity of the solvent, the NMR resonances could be averaged signals over different complexes of zinc with L^2-H_4 and the free ligand, which exchange in a fast equilibrium.

In addition to the bipyridine units, the catecholates can also be selectively addressed. Ligand L^2 forms dinuclear triple-stranded helicates $M_4[(L^2)_3Ti_2]$ with titanium(IV) ions in the presence of lithium, sodium, or potassium carbonate (Scheme 3).[15] As is shown in Figure 3b for $K_4[(L^2)_3Ti_2]$, the ^{1}H NMR signal of the amide proton is shifted to low field ($\delta = 12.44$ (Li), 12.50 (Na), 12.54 ppm (K)). This is due to the formation of a hydrogen bond from the amide to the catecholate oxygen atom upon metal coordination (see Figure 2). ESI MS showed the peaks of the dinuclear complexes, for example, at *m/z* 1473 $[Li_2H(L^2)_3Ti_2]^-$, 1572 $[Na_3(L^2)_3Ti_2]^-$, and 1575 $[K_3(L^2)_3Ti_2]^-$, respectively.

In $[(L^2)_3Ti_2]^{4-}$ a cavity is formed that provides a close to trigonal prismatic coordination site for cations. Metals with d^0 or d^{10} configuration do not possess an electronic preference for octahedral or trigonal-prismatic geometry.[16] Therefore, zinc(II) was used as a d^{10} metal ion. A complexation study of L^2-H_4 (3 equiv) was performed with $[TiO(acac)_2]$ (2 equiv) and $ZnCl_2$ (1 equiv) in the presence of potassium carbonate. Hereby, $K_2[(L^2)_3Ti_2Zn]$ was obtained as a red solid in quantitative yield. FT-ICR ESI MS showed the presence of the heterotrinuclear complex by a strong signal at *m/z* 761 corresponding to the dianion $[(L^2)_3Ti_2Zn]^{2-}$. As shown in Figure 3d, the ^{1}H NMR spectrum shows the signals of the amide NH group at $\delta = 11.48$ ppm (s), the resonances of the bipyridine at $\delta = 8.81$ (d, $J = 8.6$ Hz), 8.75 (d, $J = 8.6$ Hz), and 7.99 ppm (s), and the ones of the catechol unit at $\delta = 7.00$ (d, $J = 7.7$ Hz), 6.49 (t, $J = 7.7$ Hz), and 6.37 ppm (d, $J = 7.7$ Hz), respectively. Especially remarkable is the shift of the protons in the 6- and 6′-position of the bipyridine to $\delta = 7.99$ ppm, which is due to the fixation of this proton in the interior of the cavity close to the metal center.

Conclusion

Herein we presented a facile synthesis of 5,5′-diamino-2,2′-bipyridine (**1**), which is an important building block for the synthesis of multitopic ligands for the self-assembly of metallosupramolecular aggregates. For example, the dicatechol imine ligand L^1-H_4 forms triple-stranded dinuclear helicates with titanium(IV) ions; however, due to the lability of the imine bonds it cannot bind additional metal ions at the bipyridine moieties. Therefore, the corresponding amide-connected ligand L^2-H_4 was prepared and also tested in coordination studies to show the higher stability of the connecting units. During the course of this study we were able to obtain, for example, mononuclear $[(L^2)_3Zn]^{2+}$ and dinuclear $[(L^2)_3Ti_2]^{4-}$ in which the metal ions are bound either to the bipyridine or to the catecholate binding site, and we were also able to establish heterotrinuclear complexes

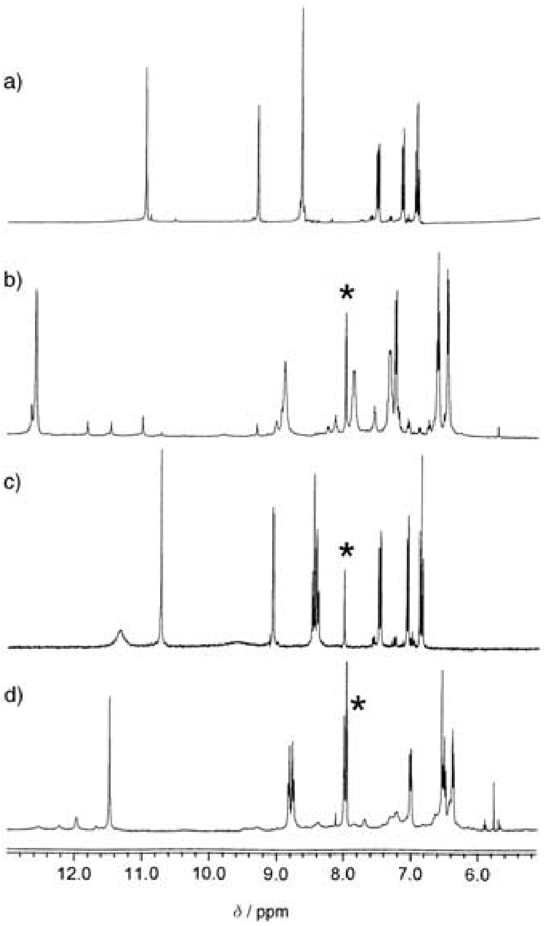


Figure 3. ^{1}H NMR spectra of a) L^2-H_4, b) $K_4[(L^2)_3Ti_2]$, c) $[(L^2$-$H_4)_3Zn]Cl_2$, and d) $K_2[(L^2)_3Ti_2Zn]$ in [D$_6$]DMSO (* = DMF).

$[(L^2)_3ZnTi_2]^{2-}$ in which both metal binding sites are involved in the coordination of the different metal ions. Further studies focussed on the formation of heterometallic coordination networks and the incorporation of metals into the cavity of the helicate are currently going on in our laboratories.

Experimental Section

NMR spectra were recorded on a Bruker DRX 500, WM 400, a Varian Inova 400, or a Unity 500 spectrometer. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV; FAB with 3-nitrobenzoic acid (3-NBA) as matrix) were taken on a Finnigan MAT 90, 95, or 212 mass spectrometer. FT-ICR ESI mass spectra were measured on a Bruker Bioapex II FTMS equipped with a 7 Tesla magnet. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Melting points: Büchi B-540 (uncorrected).

1-(2-Chloropyridine)-5-yl-2,5-dimethyl-1*H*-pyrrole (4):[10] 5-Amino-2-chloropyridine (**2**; 1.0 g, 7.8 mmol), 2,5-hexanedione (**3**; 1.1 mL, 9.4 mmol), and *p*-TsOH (15 mg, 0.08 mmol) were dissolved in toluene (15 mL) and heated in a Dean–Stark apparatus for 2 h. After the dark brown reaction mixture had been cooled, it was washed with saturated aqueous $NaHCO_3$ solution, five times with water, and with brine. After solution was dried over $MgSO_4$, the solvent was removed in vacuo. The dark residue was dried under high vacuum and was used for the coupling reaction without further purification (1.47 mg, 91 %). An analytically pure sample was obtained after column chromatography on silica gel with hexane/ethyl acetate/triethylamine (10/1/0.05 v/v) as eluent. m.p. 67–68 °C; ^{1}H NMR ($CDCl_3$, 500.1 MHz): $\delta = 8.29$ (d, $J = 2.7$ Hz, 1 H), 7.53 (dd, $J = 8.3$, 2.7 Hz, 1 H), 7.45 (d, $J = 8.3$ Hz, 1 H), 5.93 (s, 2 H), 2.04 ppm (s, 6 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): $\delta = 150.3$, 148.9, 138.1, 134.6, 128.8, 124.5, 107.0, 12.9 ppm; MS (CI, isobutane): *m/z* (%): 207.3 (100) [MH^+]; elemental analysis calcd (%) for $C_{11}H_{11}N_2Cl$ (206.67): C 63.93, H 5.36, N 13.55; found: C 64.07, H 5.41, N 13.56.

5,5′-Bis(2,5-dimethyl-1*H*-pyrrole)-2,2′-bipyridine (5): Bis(triphenylphosphane)nickel(II) bromide (0.74 g, 1 mmol), zinc powder (556 mg, 8.5 mmol), and tetraethylammonium iodide (1.28 g, 5 mmol) were suspended in absolute THF (20 mL). 1-(2-Chloropyridine)-5-yl-2,5-dimethyl-1*H*-pyrrole (**4**; 1.04 g, 5 mmol) dissolved in absolute THF (10 mL) was slowly added to this mixture by syringe. The resulting mixture was stirred for 3 h at 60 °C until TLC monitoring revealed complete consumption of the starting material. After that time concentrated ammonia (25 %, 20 mL), water (15 mL), and dichloromethane (60 mL) were added. After the mixture had been stirred for 15 min, the precipitate was filtered off and the organic layer was separated. The aqueous phase was further extracted with small portions of dichloromethane several times. The combined organic phases were washed with water and brine. After the organic phases had been dried over $MgSO_4$, the solvent was removed in vacuo. The residue was subjected to column chromatography on silica gel 60 using petroleum ether 40/60/ethyl acetate (9:1) containing 1 % of triethylamine as eluent to give the desired product (724 mg, 85 %). If necessary the product can be crystallized from 2-propanol. m.p. 215–216 °C; ^{1}H NMR ($CDCl_3$, 500.1 MHz): $\delta = 8.59$ (d, $J = 2.4$ Hz, 2 H), 8.58 (d, $J = 8.2$, 2 H), 7.71 (dd, $J = 8.2$, 2.4 Hz, 2 H), 5.97 (s, 4 H), 2.10 ppm (s, 12 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): $\delta = 154.3$, 148.5, 136.4, 135.8, 128.9, 121.3, 106.9, 13.0 ppm; MS (CI, *i*-butane): *m/z* (%): 342.2 (100) [MH^+]; elemental analysis calcd (%) for $C_{22}H_{22}N_4$ (342.22): C 77.16, H 6.48, N 16.36; found: C 77.56, H 6.57, N 16.32.

5,5′-Diamino-2,2′-bipyridine dihydrochloride (1):[8] 5,5′-Bis(2,5-dimethyl-1*H*-pyrrole)-2,2′-bipyridine (**5**; 1.19 g, 3.48 mmol), hydroxylamine hydrochloride (7.3 g, 105 mmol), triethylamine (4 mL), ethanol (25 mL), and water (10 mL) were heated under reflux for 20 h. After that time another portion of hydroxylamine hydrochloride (7.30 g, 105 mmol) and triethylamine (2 mL) was added. The solution was further heated under reflux for 24 h until TLC monitoring revealed complete consumption of the starting material. The reaction mixture was allowed to cool to room temperature before it was quenched by pouring it into ice-cold 1 N HCl (30 mL). Ethanol (50 mL) was added to the resulting suspension of a golden-yellow precipitate and the mixture was cooled to 0 °C and stirred at this temperature for 1 h. After that time the product was collected as a golden-yellow precipitate, washed with cold ethanol, and dried in high vacuum (690 mg, 77 %). ^{1}H NMR (D_2O, 500.1 MHz): $\delta = 8.59$ (m, 2 H), 8.02 (d, $J = 8.8$, 2 H), 7.75 ppm (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR (D_2O, 125.8 MHz): $\delta = 143.5$, 137.8, 132.8, 129.6, 124.0 ppm; MS (ESI, DMSO/MeOH): *m/z* (%): 187.3 (100) [MH^+].

***N*,*N*′-Bis[(2,3-dihydroxyphenyl)methylen]-2,2′-bipyridine-5,5-diamine (L^1-H_4)**: 5,5′-Diamino-2,2′-bipyridine dihydrochloride (**1**; 0.69 g, 2.68 mmol) was suspended in ethanol (50 mL), and triethylamine (approximately 5 mL) was added to form a clear solution. After addition of 2,3-dihydroxybenzaldehyde **6** (0.74 g, 5.36 mmol), the mixture was stirred for 72 h at room temperature. The precipitate was filtered off and was dried in vacuum (0.79 g, 69 %). M. p. 269 °C (decomp); ^{1}H NMR ([D$_6$]DMSO, 500.1 MHz): $\delta = 9.05$ (s, 2 H), 8.72 (s, 2 H), 8.46 (d, $J = 8.2$ Hz, 2 H), 8.00 (d, $J = 8.6$ Hz, 2 H), 7.14 (d, $J = 7.4$ Hz, 2 H), 6.97 (d, $J = 7.4$ Hz, 2 H), 6.80 ppm (t, $J = 7.4$ Hz, 2 H); ^{13}C NMR ([D$_6$]DMSO, 125.8 MHz): $\delta = 165.9$, 153.4, 149.8, 146.2, 144.9, 144.0, 129.3, 123.2, 121.3, 120.1, 119.4 ppm (one signal cannot be observed); MS (EI, 70 eV): *m/z* (%): 426 (100) [M^+]; elemental analysis calcd (%) for $C_{24}H_{18}N_4O_4 \cdot 1/4\,H_2O$: C 66.89, H 4.33, N 13.00; found: C 66.80, H 4.58, N 12.70.

***N*,*N*′-Bis(2,3-dimethoxybenzoate)-2,2′-bipyridine-5,5-diamine (L^2-Me_4)**: 2,3-Dimethoxybenzoic acid **7** (118 mg, 0.65 mmol) was dissolved in acetonitrile (25 mL), and HBTU (295 mg, 0.78 mmol) and diisopropylethylamine (244.6 μL = 184 mg, 1.43 mmol) were added. After 30 min at room temperature, a slightly yellow solution was formed. Then, bipyridine **1** (84 mg, 0.33 mmol) dissolved in acetonitrile (20 mL) and diisopropylethylamine (222.3 μL, 167 mg, 1.30 mmol, 2 equiv) were added. The solvent was removed after stirring overnight, to leave a yellow solid, which was dissolved in ethyl acetate and washed with aqueous NH_4Cl, $NaHCO_3$, H_2O, and brine. The protected ligand L^2-Me_4 was obtained after removal of the solvent (117 mg, 69 %). M. p. 247 °C (decomp); ^1H NMR ([D_6]DMSO, 400.0 MHz): $\delta = 10.61$ (s, 2 H), 8.95 (t, $J = 1.6$ Hz, 2 H), 8.34 (d, $J = 1.6$ Hz, 4 H), 7.24 (dd, $J = 7.7$, 1.9 Hz, 2 H), 7.20 (t, $J = 7.7$ Hz, 2 H), 7.16 (dd, $J = 7.7$, 1.9 Hz, 2 H), 3.88 (s, 6 H), 3.83 ppm (s, 6 H); ^{13}C NMR ($CDCl_3$, 125.8 MHz): $\delta = 163.2$, 152.4, 151.2, 147.1, 140.4, 134.9, 127.7, 125.9, 124.7, 122.8, 120.8, 116.0, 61.7, 56.1 ppm; MS (EI, 70 eV): *m/z* (%): 514 (100) [M^+]; elemental analysis calcd (%) for $C_{28}H_{26}N_4O_6$: C 65.36, H 5.09, N 10.89; found: C 64.89, H 4.88, N 10.53.

***N,N'*-Bis(2,3-dihydroxybenzoate)-2,2'-bipyridine-5,5-diamine (L^2-H_4)**: L^2-Me_4 (71 mg, 0.14 mmol) was dissolved in dichloromethane (20 mL) and cooled to 0 °C. At this temperature BBr_3 (0.13 mL, 285.6 mg, 1.40 mmol) was added. The yellow mixture was stirred overnight at room temperature and then methanol was added. The solvent was removed in vacuo and the residue was dissolved in ethyl acetate and washed with water. Removal of the solvent afforded L^2-H_4 (64 mg, quantitative). M.p. 261 °C (decomp); ^1H NMR ([D_6]DMSO, 400.0 MHz): $\delta = 10.86$ (s, 2 H), 9.20 (d, $J = 2.0$ Hz, 2 H), 8.55 (m, 4 H), 7.40 (dd, $J = 8.0$, 1.4 Hz, 2 H), 7.04 (dd, $J = 8.0$, 1.4 Hz, 2 H), 6.82 ppm (t, $J = 8.0$ Hz, 2 H); ^{13}C NMR ([D_6]DMSO, 125.8 MHz): $\delta = 167.5$, 147.1, 145.9, 144.7, 138.8, 136.4, 130.8, 121.9, 118.9, 118.5, 117.6 ppm (one signal cannot be observed); MS (EI, 70 eV): *m/z* (%): 458 (100) [M^+]; elemental analysis calcd (%) $C_{24}H_{18}N_4O_6$: C 62.88, H 3.96, N 12.22; found: C 62.57, H 4.27, N 11.79.

General procedure for the preparation of dinuclear complexes $M_4[(L)_3Ti_2]$ (M = Li, Na, K): Ligand L^1-H_4 (3 equiv), [$TiO(acac)_2$] (2 equiv), and the alkali metal carbonate (2 equiv) were mixed in DMF and stirred overnight. The solvent was removed in vacuo to obtain the complexes as red-orange solids which were purified by filtration over Sephadex LH 20.

$Li_4[(L^1)_3Ti_2]$: Yield: 69.5 mg (quantitative); ^1H NMR ([D_6]DMSO, 500.1 MHz): $\delta = 8.72$ (s, 6 H), 8.38 (d, $J = 2.4$ Hz, 6 H), 8.24 (d, $J = 8.4$ Hz, 6 H), 7.65 (dd, $J = 8.4$, 2.4 Hz, 6 H), 7.03 (d, $J = 7.7$ Hz, 6 H), 6.40 (pseudo t, $J = 7.7$ Hz, 6 H), 6.19 ppm (d, $J = 7.7$ Hz, 6 H); ^{13}C NMR ([D_6]DMSO, 125.7 MHz): $\delta = 165.3$, 162.8, 161.6, 152.1, 149.6, 143.2, 128.8, 121.1, 120.9, 119.6, 118.5, 116.8 ppm; ESI-MS (methanol): *m/z*: 688 $[M-2Li]^{2-}$, 685 $[M-3Li+H]^{2-}$, 456 $[M-3Li]^{3-}$, 454 $[M-4Li+H]^{3-}$; elemental analysis calcd (%) for $C_{72}H_{42}N_{12}Li_4O_{12}Ti_2 \cdot 9H_2O \cdot 2DMF$: C 55.14, H 4.39, N 11.54; found: C 55.08, H 5.02, N 11.85.

$Na_4[(L^1)_3Ti_2]$: Yield: 72.7 mg (quantitative); ^1H NMR ([D_6]DMSO, 500.1 MHz): $\delta = 8.82$ (s, 6 H), 8.46 (d, $J = 2.4$ Hz, 6 H), 8.25 (d, $J = 8.3$ Hz, 6 H), 7.67 (dd, $J = 8.3$, 2.4 Hz, 6 H), 7.08 (d, $J = 7.7$ Hz, 6 H), 6.41 (pseudo t, $J = 7.7$ Hz, 6 H), 6.22 ppm (d, $J = 7.7$ Hz, 6 H); ^{13}C NMR ([D_6]DMSO, 125.7 MHz): $\delta = 165.2$, 162.8, 161.2, 152.1, 149.5, 143.2, 129.1, 121.1, 120.7, 119.6, 118.8, 116.8 ppm; ESI-MS (methanol): *m/z*: 1431 $[M-Na]^-$, 704 $[M-2Na]^{2-}$, 693 $[M-3Na+H]^{2-}$, 462 $[M-3Na]^{3-}$, 455 $[M-4Na+H]^{3-}$; elemental analysis calcd (%) for $C_{72}H_{42}N_{12}Na_4O_{12}Ti_2 \cdot 4H_2O \cdot 4DMF$: C 55.45, H 4.32, N 12.32; found: C 55.46, H 4.67, N 11.89.

X-ray crystal structure analysis for $Na_4[(L^1)_3Ti_2]$: formula $C_{72}H_{42}N_{12}O_{12}Ti_2$-$Na_4 \cdot 12C_3H_7NO \cdot H_2O$, $M_r = 2350.10$, red crystal $0.30 \times 0.20 \times 0.10$ mm, $a = 15.586(1)$, $b = 20.796(1)$, $c = 38.513(1)$ Å, $\beta = 100.72(1)°$, $V = 12265.2(10)$ Å^3, $\rho_{calcd} = 1.273$ g cm^{-3}, $\mu = 2.21$ cm^{-1}, empirical absorption correction ($0.937 \leq T \leq 0.978$), $Z = 4$, monoclinic, space group *C*2/*c* (no. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 18878 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 10751 independent ($R_{int} = 0.042$) and 6630 observed reflections [$I \geq 2\sigma(I)$], 710 refined parameters, $R = 0.103$, $wR^2 = 0.295$, max. residual electron density 1.83(−0.55) e Å^{-3}, some of the DMF molecules show severe disorder, refinement with split positions did not improve the model, hydrogen atoms as part of water molecules could not be located, others calculated and refined riding.

The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating-anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[17] absorption correction SORTAV,[18] structure solution SHELXS-97,[19] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

CCDC-241101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

$K_4[(L^1)_3Ti_2]$: Yield: 76.0 mg (quantitative); ^1H NMR ([D_6]DMSO, 500.1 MHz): $\delta = 8.83$ (s, 6 H), 8.49 (d, $J = 2.0$ Hz, 6 H), 8.29 (d, $J = 8.4$ Hz, 6 H), 7.74 (dd, $J = 8.4$, 2.0 Hz, 6 H), 7.10 (d, $J = 7.7$ Hz, 6 H), 6.41 (pseudo t, $J = 7.7$ Hz, 6 H), 6.22 ppm (d, $J = 7.7$ Hz, 6 H); ESI-MS (methanol): *m/z*: 1479 $[M-K]^-$, 720 $[M-2K]^{2-}$, 701 $[M-3K+H]^{2-}$, 467 $[M-3K]^{3-}$; elemental analysis calcd (%) for $C_{72}H_{42}N_{12}K_4O_{12}Ti_2 \cdot 2H_2O \cdot 4DMF$: C 54.60, H 4.04, N 12.13; found: C 54.47, H 4.39, N 11.84.

$Li_4[(L^2)_3Ti_2]$: Yield: 16.2 mg (quantitative); ^1H NMR ([D_6]DMSO, 400 MHz): $\delta = 12.44$ (s, 6 H), 8.93 (s, 6 H), 7.64 (br, 6 H), 7.21–7.17 (m, 12 H), 6.58 (t, $J = 7.6$ Hz, 6 H), 6.42 ppm (d, $J = 7.6$ Hz, 6 H); negative-ion mode ESI MS**:** *m/z*: 1473 $[M-2Li+H]^-$; IR (drift, KBr): $\tilde{\nu} = 3409$, 1661, 1590, 1535, 1467, 1441, 1389, 1246, 1210, 1059, 844, 748, 679, 524 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{42}Li_4N_{12}O_{18}Ti_2 \cdot DMF \cdot 4H_2O$: C 55.20, H 3.52, N 11.16; found: C 55.21, H 3.28, N 11.04.

$Na_4[(L^2)_3Ti_2]$: Yield: 16.9 mg (quantitative); ^1H NMR ([D_6]DMSO, 400 MHz): $\delta = 12.50$ (s, 6 H), 8.90 (s, 6 H), 7.77 (d, $J = 7.3$ Hz, 6 H), 7.32–7.21 (m, 12 H), 6.59 (t, $J = 7.6$ Hz, 6 H), 6.44 ppm (d, $J = 7.6$ Hz, 6 H); negative-ion mode ESI MS: *m/z*: 1527 $[M-Na]^-$, 741 $[M-3Na+H]^{2-}$; IR (drift, KBr): $\tilde{\nu} = 3408$, 1659, 1588, 1532, 1465, 1439, 1386, 1285, 1245, 1208, 1056, 842, 745, 677, 522 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{42}N_{12}Na_4O_{18}Ti_2 \cdot DMF \cdot 12H_2O$: C 48.95, H 4.00, N 9.89; found: C 49.12, H 4.04, N 8.87.

$K_4[(L^2)_3Ti_2]$: Yield: 17.6 mg (quantitative); ^1H NMR ([D_6]DMSO, 400 MHz): $\delta = 12.54$ (s, 6 H), 8.86 (s, 6 H), 7.83 (br, 6 H), 7.33–7.26 (m, 6 H), 7.21 (d, $J = 7.6$ Hz, 6 H), 6.58 (t, $J = 7.6$ Hz, 6 H), 6.44 ppm (d, $J = 7.6$ Hz, 6 H); negative-ion mode ESI MS: *m/z*: 1575 $[M-K]^-$, 1537 $[M-2K+H]^-$, 768 $[M-2K]^{2-}$; IR (drift, KBr): $\tilde{\nu} = 3427$, 1660, 1587, 1531, 1464, 1439, 1386, 1283, 1244, 1208, 1055, 842, 744, 678, 522 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{42}N_{12}K_4O_{18}Ti_2 \cdot 2DMF \cdot 6H_2O$: C 50.11, H 3.67, N 10.49; found: C 49.98, H 3.89, N 10.01.

(L^2-H_4)$PdCl_2$: L^2-H_4 (15 mg, 0.033 mmol) and K_2PdCl_4 (10.7 mg, 0.033 mmol) were heated in DMF for 5 h to 70 °C. The solvent was removed in vacuo and the residue was washed with water and then dried to obtain 21 mg of a yellow solid in quantitative yield. ^1H NMR ([D_6]DMSO, 300 MHz): $\delta = 11.05$ (s, 2 H), 9.55 (d, $J = 2.5$ Hz, 2 H), 8.64 (dd, $J = 8.9$, 2.5 Hz, 2 H), 8.46 (d, $J = 8.9$ Hz, 2 H), 7.38 (dd, $J = 7.9$, 1.4 Hz, 2 H), 7.04 (dd, $J = 7.9$, 1.4 Hz, 2 H), 6.80 ppm (t, $J = 7.9$ Hz, 2 H); MS (EI, 70 eV): *m/z* (%): 638 (100) $[M]^+$; IR (drift, KBr): $\tilde{\nu} = 3434$, 2921, 1657, 1582, 1540, 1497, 1471, 1384, 1323, 1273, 1222, 840, 801, 741 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{18}N_4O_6PdCl_2$: C 45.34, H 2.85, N 8.81; found: C 44.89, H 3.10, N 9.28.

[(L^2-H_4)$_3$Zn]Cl_2: The ligand L^2-H_4 (15 mg, 0.033 mmol) and $ZnCl_2$ (1.5 mg, 0.011 mmol) were stirred overnight in DMF. Removal of the solvent afforded a yellow solid in quantitative yield (16.5 mg); ^1H NMR ([D_6]DMSO, 300 MHz): $\delta = 11.28$ (br, 6 H), 10.68 (s, 6 H), 9.56 (br, 6 H), 9.03 (s, 6 H), 8.42 (d, $J = 8.7$ Hz, 6 H), 8.35 (dd, $J = 8.7$, 2.4 Hz, 6 H), 7.43 (dd, $J = 7.9$, 1.5 Hz, 6 H), 7.02 (dd, $J = 7.9$ Hz, 1.5 Hz, 6 H), 6.81 ppm (t, $J = 7.9$ Hz, 6 H); IR (drift, KBr): $\tilde{\nu} = 3424$, 1656, 1532, 1477, 1388, 1261, 1219, 1058, 840, 739 cm^{-1}; positive-ion mode ESI MS (methanol): *m/z*: 719 $[M-2Cl]^{2+}$; elemental analysis calcd (%) for $C_{72}H_{54}N_{12}O_{18}Cl_2Zn \cdot 3DMF \cdot 2H_2O$: C 55.06, H 4.51, N 11.89; found: C 54.96, H 4.78, N 12.59.

$K_2[(L^2)_3Zn]Ti_2$: L^2-H_4 (15 mg, 0.033 mmol), [$TiO(acac)_2$] (5.7 mg, 0.022 mmol), K_2CO_3 (3 mg, 0.022 mmol), and $ZnCl_2$ (1.5 mg, 0.011 mmol) were mixed in DMF and stirred overnight. The solvent was removed and the residue washed with water and dried in vacuo to obtain a red solid in quantitative yield (17.6 mg). ^1H NMR ([D_6]DMSO, 400 MHz): $\delta = 11.48$ (s, 6 H), 8.81 (d, $J = 8.6$ Hz, 6 H), 8.75 (d, $J = 8.6$ Hz, 6 H), 7.99 (s, 6 H), 7.00 (d, $J = 7.7$ Hz, 6 H), 6.49 (t, $J = 7.7$ Hz, 6 H), 6.37 ppm (d, $J = 7.7$ Hz, 6 H); negative-ion mode ESI MS (methanol): *m/z*: 761 $[M-2K]^{2-}$; IR (drift, KBr): $\tilde{\nu} = 3440$, 1664, 1590, 1538, 1480, 1440, 1385, 1308, 1247, 1207, 1056, 848, 742, 679, 522 cm^{-1}; elemental analysis calcd (%) for

$C_{72}H_{42}K_2N_{12}O_{18}Ti_2Zn \cdot 3\,DMF \cdot 5\,H_2O$: C 50.89, H 3.85, N 10.99; found: C 50.76, H 4.01, N 11.02.

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