Synthesis of Polydendate Acyclic and Macrocyclic Polyamine Ligands Bearing 2,2'-Bipyridine or 2,2'-Bipyridine *N*,*N*'-Dioxide Moieties

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Abstract: The synthesis of various acyclic and macrocyclic complexing agents bearing bipyridine or bipyridine *N*,*N*-dioxide substituents is reported. These ligands, which possess three, four, or six pendant units, have been prepared by a general synthetic protocol starting from the mono(bromomethyl)-2,2'-bipyridine or mono(bromomethyl)-2,2'-bipyridine *N*,*N*'-dioxide derivatives and the corresponding amine in the presence of a mineral base. NMR and FAB-MS spectral data indicate that tripode **5** and hexapode **9**, respectively, form stable, highly colored and redox-active mono-and diiron(II) complexes.

Key words: podands, oligopyridines, multitopic ligands, iron complexes

The design of ligands bearing 2,2'-bipyridine (bpy) or analogous subunits has received considerable interest in the past twenty years or so.¹ The remarkable intrinsic properties of polypyridine transition-metal complexes, such as intense and well-defined absorption bands in the visible region, long-lived metal-to-ligand charge-transfer excited state obtained in high quantum yields, and a rich redox activity, make possible the sensitization of photoinduced electron- and/or energy-transfer processes.² Such highly desirable features have stimulated efforts to construct covalent assemblies having bpy subunits linked to macrocyclic and macrobicyclic structures, thereby producing photoactive hemi-cage or cage complexes. $^{3-5}$ The encapsulation of lanthanides⁶ and ruthenium⁷ using ligands built around bipyridine-based fragments has been achieved. In some cases, these complexes could not be obtained by the classical method of complexation [L + metal precursor] due to steric congestion around the complexation sites. However, the encapsulated metal complexes often could be obtained in two steps by first preparing the podand complex followed by subsequent closing of the pseudo-macrocyclic cavity by a cyclization reaction.⁸

Our recent work related to calixarenes modified with bpy subunits,⁹ and the study of their lanthanide complexes,¹⁰ prompted us to design polybipyridine ligands based on acyclic and macrocyclic polyamines. This work is motivated by the opportunity to construct or engineer ligands bearing more than six discrete coordination sites, with a preorganized cavity, that could offer improved stabilization of encapsulated lanthanide ions. The latter are known to be stabilized by eight or nine coordination sites.¹¹ The choice at the 5,5'-substituted bpy was deduced from previous work, where it has been shown clearly that high luminescence quantum yields could be obtained with europium while, for stereoelectronic reasons, the 6,6'-positions are less suitable.¹²

We report here the synthesis and complete characterization of polypodate ligands bearing three, four, or six bpy or bpy-N,N'-oxide fragments functionalized at the 5,5' position. While our work was in progress, the synthesis of a triazacyclononane ligand functionalized with bpy subunit was briefly described.¹³

The key starting material for these syntheses was 5-(bromomethyl)-5'-methyl-2,2'-bipyridine¹⁴ (1), obtained by radicaloid bromination of 5,5'-dimethyl-2,2'-bipyridine¹⁵ with *N*-bromosuccinimide (1 equiv) in the presence of 2,2'azobisisobutyronitrile as radical initiator. This synthesis appears to be the most convenient, with the use of one equivalent of NBS. Most of the dibromo derivative 2 can be removed by crystallization in CCl₄ while chromatography of the residue gives the monobromomethyl 1 and dibromomethyl 2 derivatives in, respectively, 34 and 25% isolated yield. Subsequent oxidation with 3-chloroperoxybenzoic acid afforded the corresponding *N*,*N*'-dioxide derivatives 3 and 4 in, respective1340134ly, 42 and 65% yield (Scheme 1).



For the synthesis of the 1,4,7-triazacyclononane derivative **5**, three equivalents of compound **1** in methanol are added dropwise to a 1:1 H₂O/MeOH mixture containing NaOH (3 equiv) and the triazamacrocycle (1 equiv). During the course of reaction, the pH becomes neutral and pure compound **5** is recovered by filtration after a couple of hours (74%). When applied to the other cyclic amines, this method gave lower yields of alkylated products.



Scheme 2

Consequently, additional ligands were prepared by a onepot reaction starting from 1 and the polyazamacrocycles (cyclen, hexacyclen) or with acyclic aromatic benzylic polyamines [1,3-bis(aminomethyl)benzene, 2,6-bis(ami-6,6'-bis(aminomethyl)-2,2'-bipyrnomethyl)pyridine, idine, 2,9-bis(aminomethyl)-1,10-phenanthroline] in the presence of sodium or potassium carbonate (excess), in anhydrous acetonitrile, under a controlled atmosphere (Schemes 2–4, Table 1). Ligands 10–13 were obtained in 27-58% yields after purification by alumina column chromatography. The commercially available polyamines in their protonated form (sulfate or chloride as counterion) or purified by recrystallization of their protonated form were neutralized before handling using a DOWEX ion-exchange resin.

Complexation Properties of Tripode 5 and Hexapode 9 with Iron(II) Salts

Polypyridine d⁶-transition metal complexes have been widely used as photosensitizers in catalytic systems [e.g. reduction of water to hydrogen or reduction of carbon dioxide to carbon monoxide].¹⁶ In some cases, the catalytically active species are generated by photolabilization of a ligand in organic or hydroorganic solvants.¹⁷ This limits the lifetime of the catalytic system and severely restricts potential applications of these systems. Moreover, iron tris(bipyridine) complexes have previously been utilized to catalyze thermal H₂O oxidation.¹⁸ Here also turnover numbers are restricted by instability of the complexes due



9

Scheme 3



Table 1. Selected Spectroscopic Data for Precursors and Polybipyridine Ligands.

Com- pound	Yield (%)	Molecular Formula	FAB ⁺ -MS (<i>m</i> -NBA)	¹ H NMR ^a δ , J	(Hz)			$UV-vis^{b}$ λ (nm) [ε (M ⁻¹ cm ⁻¹)]
			$[M+H]^+$	bpy-CH ₃	bpy-CH ₂	H _{6 or 6} -bpy	H _{6'or 6} -bpy	$(\pi \rightarrow \pi^*, bpy)$
3	42	$\mathrm{C}_{12}\mathrm{H}_{11}\mathrm{N}_{2}\mathrm{O}_{2}\mathrm{Br}$	295.0/297.0	2.43 (s, 3H)	4.64 (s, 2H)	8.54 (s, 1H)	8.32 (s, 1H)	260 (23,000)
4	65	$C_{12}H_{10}N_{2}O_{2}Br_{2}$	372.8/374.8/ 376.8	-	4.71 (s, 4H)	8.50 (d, 2H, ⁴ J	= 1.6)	256 (18,900)
5	74	$C_{42}H_{45}N_9$	676.0	2.34 (s, 9H)	3.62 (s, 6H)	8.56 (d, 3H, ${}^{4}J = 1.6$)	8.46 (d, 3H, ${}^{4}J = 1.4$)	285 (56,600)
6	60	$C_{42}H_{45}N_9O_6$	772.3	2.60 (s, 9H)	4.00 (s, 6H)	8.66 (s, 3H)	8.49 (s, 3H)	260 (54,100)
7	38	$C_{56}H_{60}N_{12}$	901.3	2.37 (s, 12H)	3.47 (s, 8H)	8.59 (d, 4H, ${}^{4}J = 1.6$)	8.46 (d, 4H, ${}^{4}J = 2.1$)	284 (76,000)
8	65	$C_{56}H_{60}N_{12}O_{6}$	1029.3	2.55 (s, 12H)	3.78 (s, 8H)	8.60 (s, 4H)	8.42 (s, 4H)	253 (73,500)
9	30	$C_{84}H_{90}N_{18}$	1351.6	2.38 (s, 18H)	3.52 (s, 12H)	8.49 (s, 6H)	8.46 (s, 6H)	285 (109,000)
10	58	$C_{56}H_{52}N_{10}$	865.3	2.31 (s, 12H)	3.62 (s, 8H)	8.64 (d, 4H, ⁴ <i>J</i> = 1.5)	8.43 (d, 4H, ${}^{4}J = 1.6$)	286 (81,300)
11	47	$C_{55}H_{51}N_{11}$	866.3	2.34 (s, 12H)	3.69 (s, 8H)	8.65 (d, 4H, ${}^{4}J = 1.6$)	8.44 (d, 4H, ${}^{4}J = 1.3$)	286 (83,400)
12	45	$C_{60}H_{54}N_{12}$	943.5	2.34 (s, 12H)	3.76 (s, 8H)	8.69 (d, 4H, ${}^{4}J = 1.2$)	$^{8.46}$ (d, 4H, $^{4}J = 0.6$)	286 (95,000)
13	27	$C_{62}H_{54}N_{12}$	967.5	2.37 (s, 12H)	3.82 (s, 8H)	8.75 (s, 4H)	8.47 (s, 4H)	286 (90,200)

to decoordination of the bpy ligands. The use of hemicage ligands might increase the chemical stability of these complexes. In order to test the ability of these ligands to form stable complexes we chose to complex tripode 5 and hexapode 9 with iron(II) salts. Low-spin mono- and dinuclear complexes were formed which could be studied by NMR, enabling us to explore the coordination properties of these new podands. Reaction of 5 and 9 with Fe(ClO₄)₂•6 H₂O in a dichloromethane/methanol mixture gave an instantaneous deep-violet color and precipitation. Based on analytical data, the resultant complexes were formulated as $[Fe(5)](ClO_4)_2$ and $[Fe_2(9)](ClO_4)_4$. The FAB-mass spectrum of the mononuclear $[Fe(5)](ClO_4)_2$ complex recorded in H3-nitrobenzyl alcohol exhibits an intense molecular peak at m/z = 930 [M + H], while a peak at $m/z = 1759 [M - ClO_4]$ is observed for the corresponding dinuclear $[Fe_2(9)](ClO_4)_4$ complex. No contamination from polymeric structures (or monomeric complex in the case of the dinuclear species) was observed. Both molecular peaks exhibit the expected isotopic profile and the mass spectra show peaks corresponding to the successive loss of perchlorate anions. In order to increase the solubility of these complexes, so as to facilitate ¹H NMR studies, the hexafluorophosphate salts were prepared. Reaction of 5 and 9 with one and two equivalents of $FeSO_4$ •7 H₂O, respectively, gave water-soluble, deep-violet complexes. After exchange of the counterion using an aqueous solu-

^a Performed in CD₃OD for **3**, in DMSO for **4**, in D₂O (*t*-BuOH as internal standard) for **6**, **8** and in CDCl₃ for **5**, **7**, **9–13**.

^b Measured in CH₃OH for 3, 6, in CH₃OH/H₂O ($1 \div 4$) for 4, 8 and in CH₂Cl₂ for 5, 7, 9–13, at r.t.

tion of KPF₆ and purification by chromatography, the complexes $[Fe(5)](PF_6)_2$ **14** and $[Fe_2(9)](PF_6)_4$ **15** were obtained in modest yield and characterized by ¹H NMR, FAB⁺, UV-vis spectroscopy, cyclic voltammetry, and elemental analysis.

Complexation of the metal rigidifies the ligands and induces drastic changes in the NMR shifts. In the case of $[Fe(5)](PF_6)_2$, the aromatic part of the spectrum is influenced by the iron center, and in particular the signals of the 6,6'-hydrogens (ortho from the coordinative nitrogens) are shifted downfield by $\Delta \delta = 0.57$ and 1.65 for each signal. This strong shielding is due to octahedral complexation of the bpy subunits forcing the H-atom ortho to the chelating N-atom to lie above the plane of a second bpy unit. In contrast, less pronounced shifts are observed for the signals of the other aromatic H-atoms.¹⁹ The CH₂-bpy signal, seen as a singlet in the free ligand at $\delta = 3.62$, is shifted to 4.18, but does not split into a clear AB pattern upon complexation. This is due to the fact that the CH₂ H-atoms are equivalent in the complex and do not point towards the chiral center of C_3 symmetry which has a helical twisting around the central 9N3 macrocycle/Fe axis. Splitting of the parent CH₂-bpy H-atom signals that span a macrobicycle or two bpy fragments into a well-defined AB pattern has been observed previously in macrobicyclic tris(bpy) cryptates²⁰ or in double-helicates generated by pseudo-tetrahedral copper(I) cations.²¹ Furthermore, the significant upfield shift of these CH_2 -bpy H-atoms (by ca. 0.6 ppm) indicates that they lie in the deshielding region of the bpy subunits. It is notable that a strong complexation effect is also found for the non-aromatic ring H-atoms which split into three well-defined multiplets [1:2:1 integration] with a significant upfield shift in the range of 0.2 to 0.9 ppm. This effect is due to steric crowding which distorts the flexible 9N3 polyazamacrocycle to such a degree that non-equivalence of these macrocyclic H-atoms is observed. As expected, no complexation effect was observed on the methyl H-atoms.

Identical effects are observed in the case of $[Fe_2(9)](PF_6)_4$, with the exception that one of the aromatic H-atoms is much more upfield shifted (ca. 3 ppm). Most probably, this effect is due to severe steric constraints which force one of the *ortho* H-atoms to reside very close to the shielding zone of one bpy unit, as can be inferred from examination of space-filling models of **15**. Looking closely at these models one can see clearly that the two metal ions are lodged on opposite sides of the plane defined by the hexaazacyclooctadecane macrocyclic ring, each ion being surrounded by three bpy units. This structural arrangement is illustrated in Scheme 5 for compound **15a**.



Scheme 5

The space-filling model of this geometrical arrangement shows that the coordination sphere provided by three alternating N-atoms of the ring and by three alternating bpy units is well suited for coordination of Fe(II). It can also be seen that an alternative geometrical arrangement exists for the iron(II) species which utilizes three contiguous bpy units on each side of the plane (**15b** in Scheme 5). This latter arrangement would not be suitable for a dinuclear complex, but should exclusively form the mononuclear species. These simple considerations and the well-defined NMR spectra exclude fluxional processes in solution and reflect the high stability of these complexes.

Both complexes exhibit a well-defined and intense metalto-ligand charge transfer UV-vis absorption band at low energy $\lambda_{max} = 503$ nm ($\varepsilon = 6,900 \text{ M}^{-1}\text{cm}^{-1}$) and $\lambda_{max} =$ 514 nm ($\varepsilon = 14$, 200 M⁻¹cm⁻¹), respectively, for **14** and **15**. The high-energy absorption bands are typical of ligandcentered transitions (Table 2). These electronic absorption spectra, measured in acetonitrile, compare well with the corresponding spectrum recorded for [Fe(bpy)₃]^{2+,22} Cyclic voltammetry shows that the mononuclear iron(II) complex **14** ($E_{1/2} = 1.08$ V) and the dinuclear iron(II) complex **15** ($E_{1/2} = 1.06$ V) are oxidized at the same potential, but at a value significantly higher than the corresponding [Fe(bpy)₃]²⁺ complex. As might be expected, both iron(II) centers are electronically isolated in **15**.

The synthetic protocol described herein provides access to a novel family of polydendate ligands bearing three, four, or six bipyridine or bipyridine N,N'-dioxide subunits covalently linked to acyclic and macrocyclic polyamines. Some of these ligands are suitable for the preparation of stable, low-spin, and redox-active iron(II) complexes. The presence in ligands **11**, **12**, **13** of a potential central coordinative bridging unit [pyridine, bipyridine, phenanthroline] is especially appealing for the future preparation of polynuclear transition-metal complexes exhibiting special properties, such as molecular recognition of cations.

UV-vis spectra: Shimadzu UV-260 or Perkin–Elmer Lambda 5. FT-IR spectra: Brucker IFS 25 spectrometer; KBr pellets. NMR spectra: at r.t.; Bruker-SY-200 or AC-200 (200.1 (¹H) or 50.3 MHz (¹³C)); δ (H) in ppm rel. to residual CHCl₃ in CDCl₃ (7.25), CD₃OD (3.30), acetone- d_6 (2.06), DMSO (2.6), D_2O (*t*-BuOH as internal standard) (4.8); δ (C) in ppm rel. to the solvent CDCl₃ (77.0). MS: FAB, positive mode ZAB-HF-VG-analytical apparatus in a H3-nitrobenzyl alcohol (*m*-NBA) or thioglycerol for **14**, **15**. Electrochemical studies were made by cyclic voltammetry with a conventional 3-electrode system using a BAS 50-W Instruments potentiostat. The working electrode was a highly polished platinum disc while the counter electrode was a Pt wire. A saturated calomel reference electrode was separated from the solution by a glass frit. Solutions contained the electrode-active substrate (ca. 10^{-3} M) and 0.1 M Bu₄NPF₆ as supporting electrolyte. All solutions were deoxygenated by purging with Ar prior to electrolysis.

Alumina (Merck), Na₂CO₃ (Prolabo), K₂CO₃ (Prolabo), hexacyclentrisulfate (Aldrich), 1,3-bis(aminomethyl)benzene (Aldrich), Fe(ClO₄)₂•6 H₂O (Aldrich), 3-chloroperoxybenzoic acid 50% dispersed in water (Lancaster) were used as received. CH₃CN used in the reactions was distilled over P₄O₁₀ under anhyd argon. Triazacy-clononane,²³ tetraazacyclododecane,²³ 2,6-bis(aminomethyl)pyridine,²⁴ 6,6'-bis(aminomethyl)-2,2'-bipyridine,²⁴ and 2,9-bis(aminomethyl)-1,10-phenanthroline²⁵ were prepared according to literature procedures.

5-(Bromomethyl)-5'-methyl-2,2'-bipyridine 1,1'-Dioxide (3):

A solution of *m*-CPBA (50% dispersed in water, 9.00 g, 25.7 mmol) in CHCl₃ (150 mL) was added dropwise over 3 h to a stirred cold solution of 5-(bromomethyl)-5'-methyl-2,2'-bipyridine (1) (2.26 g, 8.58 mmol) in CHCl₃ (500 mL). The mixture was stirred at r.t. for 3 d. The solution was filtered though an alumina column eluting with CHCl₃. After evaporation of the solvent, the precipitate was purified by chromatography (alumina, CH₂Cl₂/MeOH with a gradient of MeOH 0–5%) (alumina, CH₂Cl₂/MeOH 98:2, R_f 0.42). The recrystalization from CH₂Cl₂/hexane affording the pure white compound; yield: 1.06 g (42%).

$C_{12}H_{11}N_2O_2Br$	calcd	С	48.84	Η	3.76	Ν	9.49
(295.13)	found		48.62		3.59		9.40

¹H NMR (CD₃OD): δ = 8.54 (s, 1*H*), 8.32 (s, 1H), 7.58 (m, 4H), 4.64 (s, 2H, CH₂-Br), 2.43 (s, 3H, CH₃).

IR (KBr): v = 3034 (s), 2977 (m), 2920 (m), 1654 (m), 1604 (m), 1491 (s), 1445 (m), 1399 (s), 1282 (s)(v_{NO}), 1248 (s), 1208 (m), 1176 (s), 1134 (m), 1089 (m), 1047 (m), 1024 (s), 985 (m) cm⁻¹. UV-vis (MeOH): λ_{max} (ε , M⁻¹ cm⁻¹) = 260 (23,000), 223 (35,100) nm. MS (FAB): m/z = 295.0/297.0 (M + H)⁺, 279.0/281.0 (M – O + H).

5,5'-Bis(bromomethyl)-2,2'-bipyridine 1,1'-Dioxide (4):

A similar procedure was used to that for the preparation of **3**: *m*-CPBA (50%, 1.51 g, 4.38 mmol,), 5,5'-bis(bromomethyl)-2,2'-bipyridine (**2**) (0.5 g, 1.46 mmol), CHCl₃ (150 mL). After chromatography (alumina, CH₂Cl₂/MeOH with a gradient of MeOH 0–10%) (alumina,

Table 2. Selected Spectroscopic Data for the Iron Complexes

Compound	Yield (%)	Molecular Formula	FAB ⁺ -MS (thioglycerol)	UV-vis ^a λ (nm), [ε (M ⁻¹ cm ⁻¹)]	$\frac{E_{1/2} (V)}{\left[\Delta E_{p} (mV)\right]^{b}}$
		$[Fe (bpy)_3]^{2+}$		520 (8,050) ^c	+0.96 [80] ^c
14	91	$C_{42}H_{45}N_9FeP_2F_{12}\\$	876.4 (M-PF ₆) ⁺ 731.4 (M-2PF ₆)	503 (6,900), 292 (83,900), 252 (64,800)	+1.08 [93] -1.54 [88], -1.75 [72]
15	93	$C_{84}H_{90}N_{18}Fe_2P_2F_{24}$	1897.1 (M-PF ₆) ⁺ , 1752.1 (M-2PF ₆), 1607.1 (M- 3PF ₆), 1462.2 (M-4PF ₆)	514 (14,200), 296 (107,600), 249 (69,000)	+1.06 [93] -1.49 [64], -1.68 [85]

^a Measured in CH₃CN at r.t.

^b Determined in CH_3CN+n -Bu₄NPF₆ (0.1 M) using SCE as reference electrode, and ferrocene as internal reference, $E_{1/2} = +0.34$ V with a separation between anodic and cathodic peak potentials $\Delta E_p = 82$ mV. No compensation was made for internal cell resistance

^c According to ref. 22.

1344 Papers

 $CH_2Cl_2/MeOH$ 98:2, R_f 0.63), the analytically pure compound was obtained; yield: 0.358 g (65%).

$C_{12}H_{10}N_2O_2Br_2$	calcd	С	38.53	Η	2.69	Ν	7.49
(374.03)	found		38.29		2.41		7.29

¹H NMR (DMSO- d_6): $\delta = 8.50$ (d, 2H, ⁴J = 1.6 Hz), 7.66 (d, 2H, ³J =7.9 Hz), 7.49 (dd, 2H, ${}^{3}J = 8.0$, ${}^{4}J = 1.6$ Hz), 4.71 (s, 4H, CH₂-Br). IR (KBr): v = 3053 (s), 2976 (m), 1646 (m), 1604 (m), 1490 (s), 1433 (m), 1380 (s), 1277 (s)(v_{NO}), 1217 (s), 1180 (s), 1135 (m), 1047 (m), $1025 (s) \text{ cm}^{-1}$.

UV-vis (MeOH/H₂O 1:4): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 256 (18,900), 226 (39,200) nm.

MS (FAB): $m/z = 372.8/374.8/376.8 (M + H)^+$, 356.8/358.8/360.8 (M - O + H).

1,4,7-Tris[(5'-methyl-2,2'-bipyridin-5-yl)methyl]-1,4,7-triazacyclononane (5):

To a solution of 1 (0.59 g, 2.23 mmol) in MeOH (10 mL) at r.t. was added dropwise 1,4,7-triazacyclononane (0.085 g, 0.745 mmol) in water (5 mL) containing NaOH (0.09 g, 2.23 mmol) and MeOH (5 mL). After 10 min, a precipitate had formed, and the suspension was stirred until the pH approached neutrality (ca. 3 h). The white solid was filtered off, washed with water $(3 \times 10 \text{ mL})$ and Et₂O $(3 \times 25 \text{ mL})$, and dried under vacuum to give the pure product; yield: 0.365 g (74%).

$C_{42}H_{45}N_9$	calcd	С	74.64	Η	6.71	Ν	18	.65
(675.88)	found		74.41		6.51		18	.49
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H NMR (CDCl₃): $\delta = 8.56$ (d, 3H, ⁴J = 1.6 Hz), 8.46 (d, 3H, ⁴J 1.4 Hz), 8.24 (3 line-m, 6H), 7.72 (dd, 3H, ${}^{3}J = 8.1$, ${}^{4}J = 1.9$ Hz), 7.56 $(dd, 3H, {}^{3}J = 8.1, {}^{4}J = 1.9 \text{ Hz}), 3.62 (s, 6H, bpy-CH₂-N), 2.79 (s, 12H, 12H)$ N-CH2-), 2.34 (s, 9H, CH3).

¹³C-{¹H} NMR (CDCl₃): δ = 155.1, 153.6, 149.9, 149.5, 137.6, 137.3, 135.2, 133.1, 120.4, 120.3, 60.2, 55.5, 18.3.

IR (KBr): v = 2920 (m), 2802 (m), 1596 (m), 1553 (m), 1462 (s), 1360 (m), 1092 (m), 1026 (m) cm^{-1} .

UV-vis (CH₂Cl₂): λ_{max} (ε , M⁻¹ cm⁻¹) = 285 (56,600), 239 (41,500), 217 (22,700) nm.

MS (FAB): $m/z = 676.0 (M + H)^+$, 494.0 (M + H-CH₂-bpy-CH₃).

1,4,7-Tris[(5'-methyl-1,1'-dioxo-2,2'-bipyridin-5-yl)methyl]-1,4,7-triazacyclononane (6):

A stirred solution of anhyd CH₃CN (10 mL) containing 1,4,7-triazacyclononane (0.007 g, 0.053 mmol) and Na_2CO_3 (0.056 g, 0.530 mmol) was heated at 80°C. After 30 min, solid 3 (0.050 g, 0.169 mmol) was added to the mixture and the suspension was heated under reflux for 3 d. The solvent was removed under vacuum. The crude product was purified by chromatography (alumina, CH2Cl2/ MeOH with a gradient of MeOH 0 to 10%) (alumina, CH₂Cl₂/MeOH 94:6, $R_{\rm f}$ 0.51). Recrystallization of the precipitate by slow diffusion of hexane into a CH2Cl2/MeOH solution afforded the white analytically pure compound; yield: 0.024 g (60%).

 $C_{42}H_{45}N_9O_6$ •2 H_2O calcd C 62.44 Η 6.11 N 15.60 (771.88+36.03)found 5.94 15.20 62.26

¹H NMR (D₂O + *t*-BuOH): δ = 8.66 (s, 3H), 8.49 (s, 3H), 7.70 (m, 12H), 4.00 (s, 6H, bpy-CH₂-N), 3.12 (s, 12H, N-CH₂), 2.60 (s, 9H, CH_3).

IR (KBr): v = 3034 (s), 2977 (m), 2920 (m), 1654 (w), 1604 (w), 1491 (s), 1445 (m), 1399 (s), 1282 (s), 1248 (s), 1208 (m), 1176 (s), 1134 (m), 1089 (m), 1047 (m), 1024 (s), 985 (m) cm^{-1} .

UV-vis (MeOH): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 260 (54,100), 220 (87,100) nm. MS (FAB): $m/z = 772.3 (M + H)^+$, 756.3 (M – O + H), 740.4 (M – 2O + H), 724.3 (M - 3O + H).

1,4,7,10-Tetrakis[(5'-methyl-2,2'-bipyridin-5-yl)methyl]-1,4,7,10-tetraazacyclododecane (7):

A solution of 1,4,7,10-tetraazacyclododecane (0.056 g, 0.325 mmol) and Na₂CO₃ (0.344 g, 3.25 mmol) in anhyd CH₃CN (10 mL) was stirred 30 min at 80°C. Whereupon solid 1 (0.385 g, 1.46 mmol) was added to the mixture, which was heated under reflux for 1 d. The reaction was quenched with water and the organic product extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were dried (MgSO₄), the solvent was then removed under vacuum. The crude product was chromatographed (alumina, CH₂Cl₂/MeOH 99:1, $R_f = 0.25$), leading to the pure product; yield: 0.11 g (38%).

$C_{56}H_{60}N_{12}$	calcd	С	74.64	Н	6.71	Ν	18.65
(901.18)	found		74.53		6.68		18.61

¹H NMR (CDCl₂): $\delta = 8.59$ (d, 4H, ⁴J = 1.6 Hz), 8.46 (d, 4H, ⁴J = 2.1 Hz), 8.23 (4 line-m, 8H), 7.75 (dd, 4H, ${}^{3}J = 8.2$, ${}^{4}J = 1.9$ Hz), 7.56 $(dd, 4H, {}^{3}J = 8.2, {}^{4}J = 1.9 \text{ Hz}), 3.47 (s, 8H, bpy-CH₂-N), 2.72 (s, 16H,)$ N-CH2-), 2.37 (s, 12H, CH3).

¹³C-{¹H} NMR (CDCl₃): δ = 155.1, 153.7, 149.7, 149.5, 137.6, 137.3, 134.7, 132.9, 120.6, 120.4, 57.3, 53.2, 18.3.

IR (KBr): v = 2916 (m), 2796 (m), 1596 (m), 1553 (m), 1465 (s), 1365 (m), 1026 (m) cm⁻¹.

UV-vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 284 (76,000), 239 (56,400), 217 (31,200) nm.

MS (FAB): $m/z = 901.3 (M + H)^+$, 719.3 (M + H-CH₂-bpy-CH₃).

1,4,7,10-Tetrakis[(5'-methyl-1,1'-dioxo-2,2'-bipyridin-5-yl)methyl]-1,4,7,10-tetraazacyclododecane (8):

A similar experimental procedure as for the preparation of 5 was used: 1,4,7,10-tetraazacyclododecane (0.025 g, 0.146 mmol), 3 (0.175 g, 0.598 mmol), Na2CO3 (0.016 g, 1.460 mmol), CH3CN (10 mL). (alumina, CH₂Cl₂/MeOH, 94:6, R_f 0.43); yield: 0.096 g (65%).

 $C_{56}H_{60}N_{12}O_8 \cdot 2 H_2O$ calcd C 63.14 Η 6.06 Ν 15.78 (1029.18 + 36.03)found 63.05 5.98 15.57 ¹H NMR (D₂O + *t*-BuOH) δ = 8.60 (s, 4H), 8.42 (s, 4H), 7.74 (m,

16H), 3.78 (s, 8H, bpy-CH₂-N), 2.95 (s, 16H, N-CH₂), 2.55 (s, 12H, CH_3).

IR (KBr): v = 3048 (m), 2976 (m), 2926 (m), 2796 (m), 1646 (m), 1492 (m), 1453 (m), 1405 (m), 1354 (m), 1276 (s), 1252 (m), 1178 (m), 1079 (m), 1048 (m), 1026 (s) cm⁻¹

UV-vis (MeOH/H₂O 1:4): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 253 (72,900), 217 (126,600) nm.

MS (FAB): $m/z = 1029.3 (M + H)^+$, 1013.5 (M – O + H), 997.5 (M – 2O + H), 981.5 (M - 3O + H), 965.2 (M - 4O + H), 949.5 (M - 5O + H)H).

1,4,7,10,13,16-Hexakis[(5'-methyl-2,2'-bipyridin-5-yl)methyl]-1,4,7,10,13,16-hexaazacyclooctadecane (9):

solution of 1,4,7,10,13,16-hexaazaoctadecane (0.11 0.415 mmol) and $\mathrm{Na_2CO_3}$ (0.88 g, 8.3 mmol) in anhyd $\mathrm{CH_3CN}$ (10 mL) was stirred 30 min at 80 °C. Whereupon, solid 1 (0.765 g, 2.91 mmol) was added and the mixture was heated under reflux for 1 d. The reaction was quenched with water and the organic products were extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were dried (MgSO₄) and the solvent removed under vacuum. After short filtration over an alumina column using a mixture of CH2Cl2/MeOH 99:1, $R_{\rm f}$ 0.2, a twofold recrystallization in CH₂Cl₂/hexane led to the pure product; yield: 0.17 g (30%).

$C_{84}H_{90}N_{18}$	calcd	С	74.64	Η	6.71	Ν	18.65
(1351.75)	found		74.45		6.60		18.47

¹H NMR (CDCl₃): δ = 8.49 (s, 6H), 8.46 (s, 6H), 8.21 (d, 12H, ³J = 8.0 Hz), 7.60 (m, 12H), 3.52 (s, 12H, bpy-CH₂), 2.68 (s, 24H, N-CH₂-), 2.38 (s, 18H, CH₃).

¹³C NMR-{¹H} (CDCl₃): δ = 155.0, 153.4, 149.4, 149.3, 137.2, 137.1, 134.5, 132.9, 120.4, 120.2, 56.4, 52.4, 18.2.

IR (KBr): v = 2918 (w), 2790 (w), 1597 (w), 1554 (m), 1463 (s), $1049 (m) cm^{-1}$.

UV-vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 285 (109,000), 240 (79,000), 217 (43,500) nm.

MS (FAB): $m/z = 1351.6 (M + H)^+$, 1169.5 (M + H-CH₂-bpy-CH₃).

1,3-Bis[bis(5'-methyl-2,2'-bipyridin-5-yl)aminomethyl)]benzene (10):

To a mixture of 1,3-bis(aminomethyl)benzene (0.05 g, 0.367 mmol) and Na₂CO₃ (0.86 g, 8 mmol) in anhyd CH₃CN (10 mL), was added solid **1** (0.423 g, 1.6 mmol). This blend was heated at 80°C for 12 h, protected from moisture. The reaction was then quenched with water and the organic products extracted with CH₂Cl₂. After drying the organic layers (MgSO₄), the solvent was removed under vacuum followed by chromatography (alumina, EtOAc/hexane 9:1, R_f 0.4). The pure title compound was then obtained; yield: 0.183 g (58%).

$C_{56}H_{52}N_{10}$	calcd	С	77.75	Н	6.06	Ν	16.19
(865.106)	found		77.71		5.93		16.11

¹H NMR (CDCl₃): δ = 8.64 (d, 4H, ⁴*J* = 1.5 Hz), 8.43 (d, 4H, ⁴*J* = 1.6 Hz), 8.24 (4 line-m, 8H), 7.79 (dd, 4H, ³*J* = 8.2, ⁴*J* = 2.1 Hz), 7.52 (dd, 4H, ³*J* = 8.2, ⁴*J* = 1.8 Hz), 7.37 (s, 2H, H₆-Ar), 7.28 (br s, 3H, H-Ar), 3.62 (s, 8H, bpy-CH₂), 3.59 (s, 4H, Ar-CH₂-N), 2.31 (s, 12H, CH₃).

¹³C-{¹H} NMR (\overrightarrow{CDCl}_3): $\delta = 155.3$, 153.4, 149.5, 138.8, 137.2, 134.1, 133.1, 128.9, 128.5, 127.6, 120.4, 57.9, 55.1, 18.2.

IR (KBr): v = 2920 (m), 1706 (w), 1594 (m), 1552 (m), 1466 (s), 1359 (m), 1027 (m) cm⁻¹.

UV-vis (CH₂Cl₂): λ_{max} (ε , M⁻¹ cm⁻¹) = 286 (81,300), 241 (57,000), 217 (30,200) nm.

MS (FAB): $m/z = 865.3 (M + H)^+$, $681.2 (M - CH_2$ -bpy-CH₃), 500.2 (M - 2(CH₂-bpy-CH₃) + 2H).

2,6-Bis[bis(5'-methyl-2,2'-bipyridin-5-yl)aminomethyl]pyridine (11):

1 (0.422 g, 1.6 mmol) was poured into a stirring mixture of 2,6bis(aminomethyl)pyridine (0.05 g, 0.364 mmol) and Na₂CO₃ (0.78 g, 7.3 mmol) in anhyd CH₃CN (10 mL), and then heated at 80 °C for 12 h, protected from moisture. The reaction was quenched with water, the organic matter extracted with CH₂Cl₂, dried (MgSO₄), and the residue obtained after solvent evaporation was purified by chromatography (alumina, EtOAc, R_f 0.2). The pure desired product was obtained; yield: 0.15 g (47%).

C ₅₅ H ₅₁ N ₁₁	calcd	С	76.28	Н	5.94	Ν	17.79
(866.093)	found		76.05		5.74		17.54

¹H NMR (CDCl₃): δ = 8.65 (d, 4H, ⁴J = 1.6 Hz), 8.44 (d, 4H, ⁴J = 1.3 Hz), 8.24 (4 line-m, 8H), 7.81 (dd, 4H, ³J = 8.1, ⁴J = 2.1 Hz), 7.55 (dd, 4H, ³J = 8.1, ⁴J = 2.1 Hz), 7.39 (d, 2H, ³J = 7.0 Hz, H_{3.5}-pyr), 7.36 (d, 1H, ³J = 7.0 Hz, H₄-pyr), 3.77 (s, 4H, py-CH₂-N), 3.69 (s, 8H, bpy-CH₂), 2.34 (s, 12H, bpy).

¹³C-{¹H} NMR (CDCl₃): $\delta = 158.5$, 155.5, 153.5, 149.5, 137.5, 137.2, 134.1, 133.3, 121.3, 120.6, 59.7, 55.7, 18.4.

IR (KBr): *v* = 2918 (m), 1708 (w), 1595 (m), 1553 (m), 1461 (s), 1360 (m), 1030 (m) cm⁻¹.

UV-vis (CH₂Cl₂): λ_{max} (ε , M⁻¹ cm⁻¹) = 286 (83,400), 241 (55,000), 216 (30,700) nm.

MS (FAB): $m/z = 866.3 (M + H)^+$, $682.2 (M - CH_2 - bpy - CH_3)$.

6,6'-Bis[bis(5'-methyl-2,2'-bipyridin-5-yl)aminomethyl]-2,2'-bipyridine (12):

To anhyd CH₃CN (15 mL) containing 6,6'-bis(aminomethyl)-2,2'-bipyridine (0.05 g, 0.233 mmol) and Na₂CO₃ (0.5 g, 4.6 mmol) was added solid 1 (0.27 g, 1.0 mmol). After heating the mixture for 12 h at 80°C, water (10 mL) was added, and the organic compound was extracted with CH₂Cl₂. Flash chromatography (silica gel, CH₂Cl₂/ MeOH 95:5, $R_f 0.4$) afforded the pure compound; yield: 0.1 g (45%). calcd 76.41 Н 5.77 17.82 C60H54N12 C Ν (943.179)found 76.23 5.41 17.55

¹H NMR (CDCl₃): δ = 8.69 (d, 4H, ⁴*J* = 1.2 Hz), 8.46 (d, 4H, ⁴*J* = 1.2 Hz), 8.22 (m, 10H), 7.85 (dd, 4H, ³*J* = 8.1, ⁴*J* = 1.2 Hz), 7.78 (d, 2H, ³*J* = 8.1 Hz), 7.57 (dd, 4H, ³*J* = 8.1, ⁴*J* = 1.2 Hz), 7.48 (d, 2H, ³*J* = 8.1 Hz), 3.86 (s, 4H, bpy-CH₂-N), 3.76 (s, 8H, N(-CH₂-bpy)₄), 2.34 (s, 12H, CH₃).

¹³C NMR-{¹H} (CDCl₃): δ = 158.3, 155.4, 153.4, 149.5, 137.3, 134.0, 133.2, 122.8, 120.4, 119.4, 59.2, 55.2, 18.2.

IR (KBr): v = 2925 (m), 1707 (w), 1595 (m), 1571 (m), 1553 (m), 1467 (s), 1361 (m), 1027 (w) cm⁻¹.

UV-vis (CH₂Cl₂): λ_{max} (ε , M⁻¹ cm⁻¹) = 286 (95,000), 240 (58,000), 216 (34,000) nm.

MS (FAB): $m/z = 943.5 (M + H)^+$, 759.4 (M – CH₂-bpy-CH₃).

2,9-Bis[bis(5'-methyl-2,2'-bipyridin-5-yl)aminomethyl]-1,10-phenanthroline (13):

To anhydrous CH₃CN (10 mL) containing 2,9-bis(aminomethyl)-1,10-phenanthroline (0.03 g, 0.134 mmol) and K₂CO₃ (0.26 g, 1.35 mmol), was added solid **1** (0.156 g, 0.6 mmol). After heating the mixture for 12 h at 80 °C, water (10 mL) was added, the organic compound was extracted with CH₂Cl₂, and the organic layers were dried (MgSO₄). Chromatography (alumina, CH₂Cl₂/MeOH 99:1, $R_{\rm f}$ 0.15) gave the pure compound; yield: 0.035 g (27%).

C ₆₂ H ₅₄ N ₁₂ 967.202)	calcd found	С	76.99 76.57	Η	5.63 5.35	Ν	17.38 17.04
	-						

¹H NMR (CDCl₃): δ = 8.75 (s, 4H), 8.47 (s, 4H), 8.27 (m, 12H), 7.3 (d, 4H, ³*J* = 6.5 Hz), 7.73 (s, 2H), 7.57 (d, 4H, ³*J* = 6.5 Hz), 4.23 (s, 4H, phen-CH₂-N-), 3.82 (s, 8H, N-CH₂-bpy), 2.37 (s, 12H, CH₃).

¹³C NMR-{¹H} (CDCl₃): δ = 159.9, 155.4, 153.5, 149.7, 137.6, 137.4, 136.7, 134.1, 133.3, 127.9, 126.1, 122.2, 120.5, 60.3, 55.7, 18.3.

IR (KBr): v = 2923 (m), 1708 (w), 1595 (m), 1552 (s), 1466 (s), 1374 (m), 1027 (m) cm⁻¹.

UV-vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 286 (90,200), 239 (56,600), 230 (59,400) nm.

MS (FAB): $m/z = 967.5 (M + H)^+$, 785.4 (M – CH₂-bpy-CH₃).

To a solution of **5** (0.02 g, 0.029 mmol) in CH_2Cl_2 (5 mL) was added a solution of $Fe(SO_4)_2$ •7 H_2O (0.009 g, 0.032 mmol) in MeOH (5 mL). A deep-violet solution was instantaneously formed, and the mixture was stirred 3 h. After addition of KPF_6 (0.016 g, 0.087 mmol), slow evaporation of the solvent resulted in the precipitation of a crude red powder which was purified by column chromatography (alumina, CH_3CN) (alumina, $CH_3CN/H_2O/sat.$ aq KNO₃, 50:15:1, R_f 0.33). Recrystallization of the complex ($CH_3CN/toluene$) gave the titled compound as red needles; yield: 0.025 g (91%).

8.3 Hz), 8.29 (dd, 3H, ${}^{3}J = 8.3$, ${}^{4}J = 1.6$ Hz), 8.11 (dd, 3H, ${}^{3}J = 8.3$, ${}^{4}J = 1.6$ Hz), 8.11 (dd, 3H, ${}^{3}J = 8.3$, ${}^{4}J = 1.6$ Hz), 8.02 (s, 3H), 6.79 (d, 3H, ${}^{4}J = 1.6$ Hz), 4.18 (ls, 6H), 3.57 (m, 3H), 3.24 (m, 6H), 3.04 (m, 3H), 2.32 (s, 9H).

IR (KBr): v = 2824 (m), 1609 (m), 1470 (s), 1396 (m), 1109 (s) (PF₆), 1062 (m), 837 (m), 739 (s) cm⁻¹.

UV-vis (CH₃CN): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 503 (6,900), 292 (83,900), 252 (64,800) nm.

MS (FAB): $m/z = 876.4 (M - PF_6)^+, 731.4 (M - 2PF_6).$

$\label{eq:constraint} \begin{array}{l} \{1,4,7,10,13,16\mbox{-Hexakis}[(5'\mbox{-methyl-}2,2'\mbox{-bipyridin-}5\mbox{-yl})\mbox{methyl}] \\ 1,4,7,10,13,16\mbox{-hexaazacyclooctadecane} \\ \mbox{diiron(II) Hexafluoro-phosphate } [Fe_2(9)](PF_6)_4 \ (15): \end{array}$

To a solution of **9** (0.025 g, 0.018 mmol) in CH_2Cl_2 (5 mL) was added a solution of $\text{Fe}(\text{SO}_4)_2$ •7 H₂O (0.011 g, 0.040 mmol) in MeOH (5 mL). A deep-violet solution was instantaneously formed, and the mixture was stirred for 3 h. After filtration of the resulting solution over Celite, KPF₆ (0.020 mg, 0.108 mmol) was added and the solvent slowly removed under vacuum. The resulting precipitate was recovered by centrifugation, washed with water, and purified by chromatography (alumina, CH₃CN) (alumina, CH₃CN/H₂O/sat. aq KNO₃ 50;15;1, *R*_f 0.24). Recrystallization of the deep-red powder from an CH₃CN/toluene mixture, gave **15** as red needles; yield: 0.032 g (93%).

- ¹H NMR (CD₃CN): δ = 8.66 (d, 2H, ³J = 8.4 Hz), 88.64 (d, 2H, ³J = 8.4 Hz), 8.33 (m, 8H), 7.93 (m, 12H), 7.89 (s, 2H), 7.88 (s, 2H), 7.66 (s, 2H), 7.62 (s, 2H), 7.50 (s, 2H), 5.71 (s, 2H), 4.89 (m, 12H), 4.06 (m, 4H), 3.58 (m, 4H), 3.41 (m, 4H), 2.86 (m, 8H), 2.52 (m, 4H), 2.35 (s, 9H), 2.26 (s, 9H).
- IR (KBr): v = 2927 (m), 1631 (m), 1473 (s), 1396 (m), 1317 (w), 1110 (s, PF₆), 843 (s), 619 (m), 561 (m) cm⁻¹.
- UV-vis (CH₃CN): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 514 (14,200), 296 (107,600), 249 (69,000) nm.
- MS (FAB): $m/z = 1897.1 (M PF_6)^+$, 1752.1 (M 2PF₆), 1607.1 (M 3PF₆), 1462.1 (M 4PF₆).
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