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Synthesis Of C3-Cyclotriveratrylene Ligands For Iron(II) and Iron(III) Coordination

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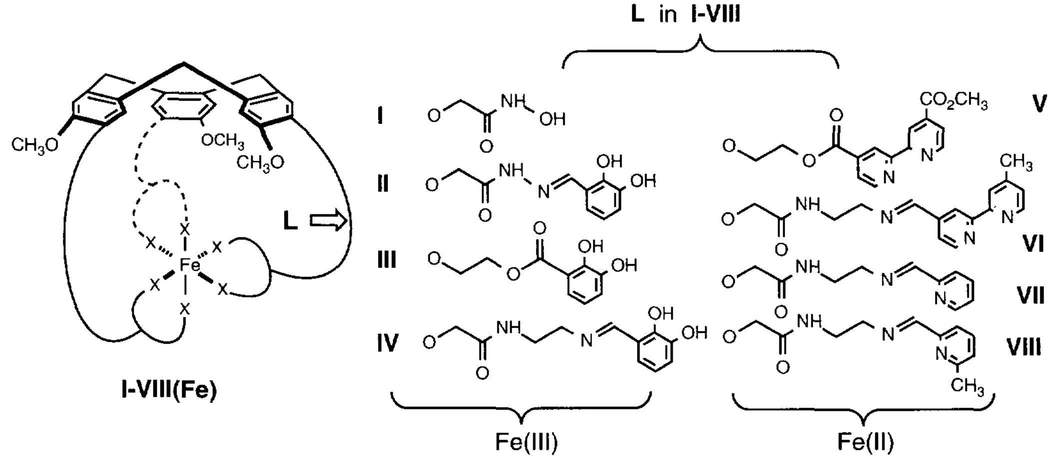
The design and synthesis of a new family of siderophores based on cyclotriveratrylene is described. The ligands consist of a C3-cyclotriveratrylene unit provided with three arms (spacers) ending with hydroxamate, catecholate, bipyridine, or iminopyridine units suitable for the octahedral coordination of transition metals and particularly for the complexation of iron(II) and iron(III).

The rigid, cone-shaped structure of cyclotriveratrylenes[1,2] and the availability of C3-functionalized derivatives make these compounds particularly attractive for the design of ligands capable of transition metal coordination, leading to complexes in which the metal would be accommodated in the cyclotriveratrylene cavity, or placed in close proximity of this cavity. Very recently, a few examples of such ligands and of their metal complexes have been described, in which the C3-cyclotriveratrylene unit is provided with three arms ending with phospite (for rhodium),[3] pyridine (for iron),[4] or thiol functions (allowing the complexation of iron-sulfur clusters).[5,6]

Scheme 1



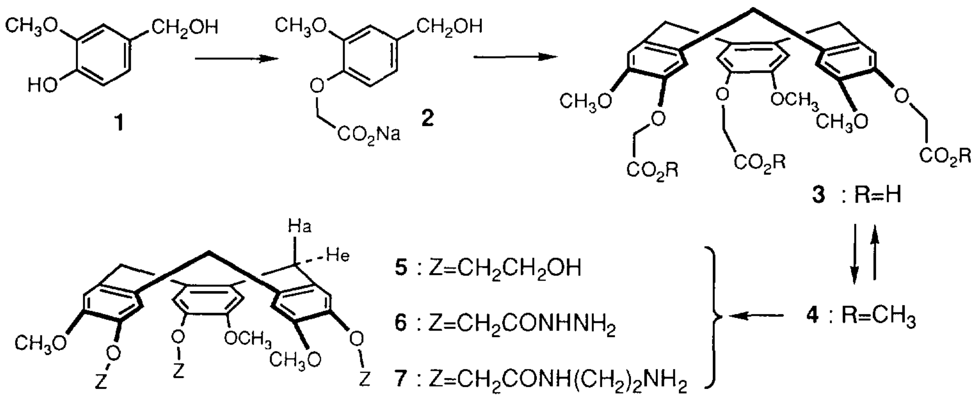
In this paper, we report recent work on the design and synthesis of a series of new ligands of this class (**I-VIII** in Scheme 1) provided with three hydroxamate, catecholate, bipyridine, and iminopyridine bidentate binding sites making them suitable for octahedral coordination of transition metals and particularly for iron(II) and iron(III). Natural and artificial molecules capable of binding iron (siderophores) are of considerable interest not only because they play (or can play) a role in biological processes that involve iron transport,[7] but also because one may expect that the electronic distribution at the iron center and hence its redox and magnetic properties can be finely tuned by the nature and geometry of the ligands thus giving access to supramolecular catalysts[8] or to molecular materials with interesting properties, e.g., spin crossover.[9]

The first part of this paper deals with the preparation of the key intermediates **3**-**7** consisting of a C3-cyclotriveratrylene subunit provided with three chains (spacers) ending with acid, ester, alcohol, hydrazide or amine functions, suitable for the attachment of the binding units. The second part describes the preparation of the ligands **I-VIII**, i.e., the preparation of the various binding units and their linking to the intermediates **3**-**7**. Although **3**-**7** and **I-VIII** are chiral, only racemic materials are considered here. The synthesis and relevant properties of iron complexes of **I-VIII** are only briefly mentioned here and full details will be described separately.

I - Key intermediates 3-7

The required racemic C3-cyclotriveratrylenes **3**-**7** were synthesized as indicated in Scheme 2. The construction of the C3-cyclotriveratrylene structure was satisfactorily achieved by cyclodehydration of the sodium salt **2** in 65% perchloric acid at room temperature, to give the triacid **3**. The starting material **2** was secured by condensation of vanillyl alcohol **1** with chloroacetic acid in the presence of 2 eq. of NaOH in ethanol. Triacid **3**, which is formed in ca. 45-50% yield, is almost insoluble in all common solvents (except in boiling acetic acid where it is slightly soluble) and is difficult to separate from the minor amounts of cyclic tetramer and pentamer which are also formed in the reaction.[10] Purification is better achieved via its tris(methyl ester) **4**, obtained by reaction of crude **3** with trimethyl orthoformate, and which is easily separated chromatographically from the other cyclic oligomers ; this procedure provides **4** in ca. 35-45% overall yield from **2**. Triester **4** is a crystalline solid (mp 193 °C) ; its hydrolysis to **3** is conveniently effected by reaction with $Bu_4N^+OH^-$ in methanol and the pure triacid is eventually obtained by crystallization from acetic acid.

Scheme 2

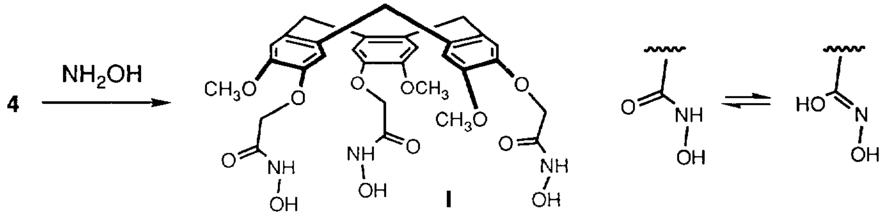


The conversion of **4** to the other derivatives **5**-**7** did not raise great difficulties. Triol **5** (mp 220 °C) was obtained in 57% yield by $LiAlH_4$ reduction of **4** in THF. On reaction with hydrazine hydrate, **4** yielded the tris(hydrazide) **6** (mp 236 °C) quantitatively, and, similarly, reaction of **4** with ethylenediamine (in excess) provided **7** (mp 200 °C). With the exception of **3** (insoluble) all these compounds were fully characterized by ^1H- and ^{13}C-NMR spectroscopy and gave elemental analyses in agreement with their expected structures. As the other cyclotriveratrylenes,[1] they exist in a rigid crown conformation, evidenced by the AX quartet of the methylene bridges in which the axial hydrogens (Ha), sterically congested at the top of the crown, resonate at ≈4.7 ppm, ca. 1.2 ppm downfield with respect to their equatorial partners (He) observed at ≈3.5 ppm (see experimental section).

II. Synthesis of ligands I-VIII

Tris(hydroxamate) ligand I. A number of natural and artificial siderophores contain three bidentate hydroxamic acid units suitable for the complexation of iron(III).[11] Ligand **I** which belongs to this category was obtained in high yield by reaction of the triester **4** with hydroxylamine in excess (Scheme 3). The resulting material was a high melting solid (mp > 240 °C with decomp.) which was isolated as a 1:1 complex of **I** and potassium acetate (from ^1H-NMR and elemental analysis, see experimental section). Its ^1H and ^{13}C-NMR spectra in dmso-d_6 showed extra peaks which probably correspond to tautomeric forms of the hydroxamic functions, as shown on the Scheme.

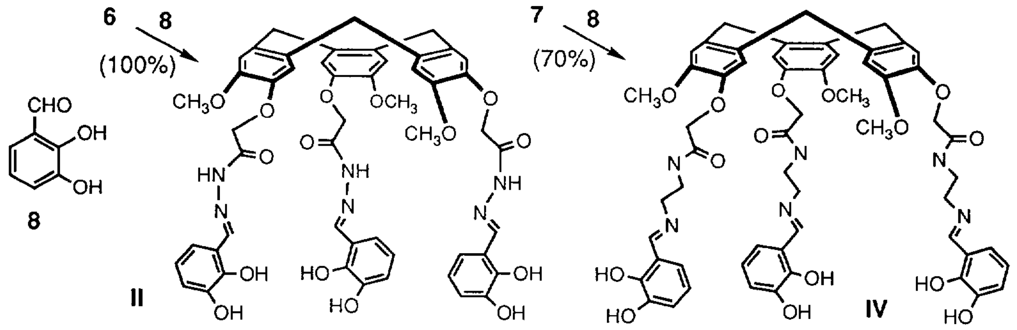
Scheme 3



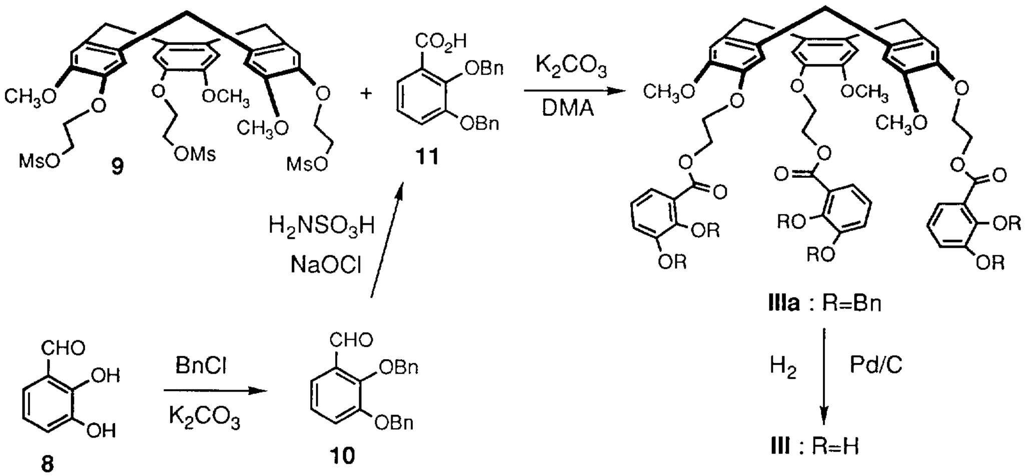
Catecholate ligands II-IV. Catecholate ligands are found in enterobactin and in other natural siderophores of iron(III), and have for this reason been used in the design of a variety of artificial analogues.[12] We prepared **II** and **IV** by reaction of 2,3-dihydroxybenzaldehyde **8** in excess with intermediates **6** and **7**, respectively. The reaction proceeded smoothly in refluxing acetonitrile and the desired compounds which crystallized off on cooling were isolated by simple filtration in excellent yield. These Schiff bases are high melting solids (mp > 240 °C, decomp.) which proved to be stable on standing in air and could be used without further treatment for the preparation of their metal complexes.

For the preparation of **III** (Scheme 5), the triol **5** was first converted into its trismesylate **9** which on reaction with the bis(O-benzyl) derivative of 2,3-dihydroxybenzoic acid **11**[13] in the presence of K_2CO_3 in dimethylacetamide (DMA) gave the protected ligand **IIIa** (71%). The cleavage of the benzyl ether groups of **IIIa** to regenerate the free catechol groups proved difficult and catalytic hydrogenolysis in a mixture of methanol, acid acetic and dichloromethane (to ensure solubilization) afforded a product which was used without further purification for the preparation of iron complexes.

Scheme 4



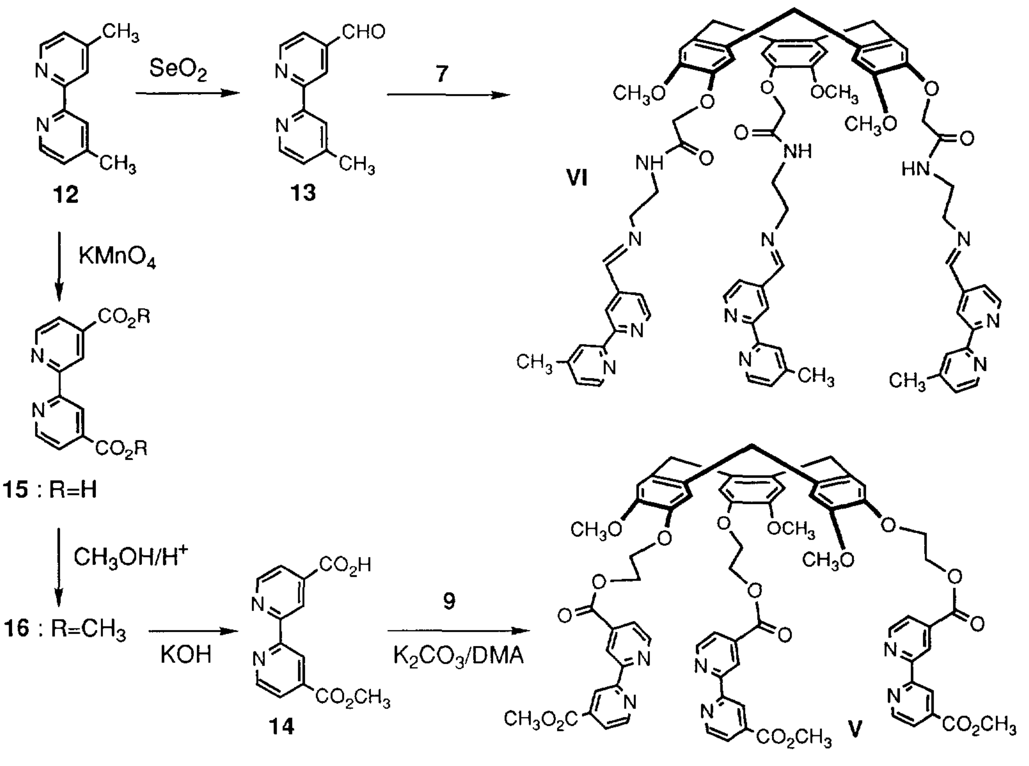
Scheme 5



Bipyridine ligands V and VI. Tris(bipyridine) systems are known to be effective for iron(II) complexation.[14] The synthesis of the C3-cyclotriveratrylene ligands **V** and **VI** required the preparation of the 4,4'-bisubstituted bipyridines **13** and **14** wich were both obtained from the commercially available 4,4'-dimethyl-2,2'-bipyridine **12** according to known procedures which were only slightly modified (Scheme 6). Thus, treatment of **12** with 1 eq. of SeO_2, according to Furue et al.,[15] provided the aldehyde **13**. For the preparation of **14** we first converted the methyl groups of **12** to the corresponding diacid **15** using $KMnO_4$ in a mixture of sulfuric and nitric acids as the oxidant.[16] The crude diacid, which is difficult to purify due to its insolubility, was converted[17] to its dimethyl ester **16** (methanol, H_2SO_4). The desired monoacid **14** was finally obtained in 40% yield by treatment of **16** with 1 eq. of KOH in a mixture of methanol and dioxane.

Then, reaction of the acid **14** with the trismesylate **9** was effected as described above for the synthesis of ligand **III**, affording **V** in 60% yield. Ligand **VI** (mp > 280 °C with decomp.) was obtained in 85% yield by reaction of the aldehyde **13** with the tris(amino) derivative **7** in refluxing acetonitrile.

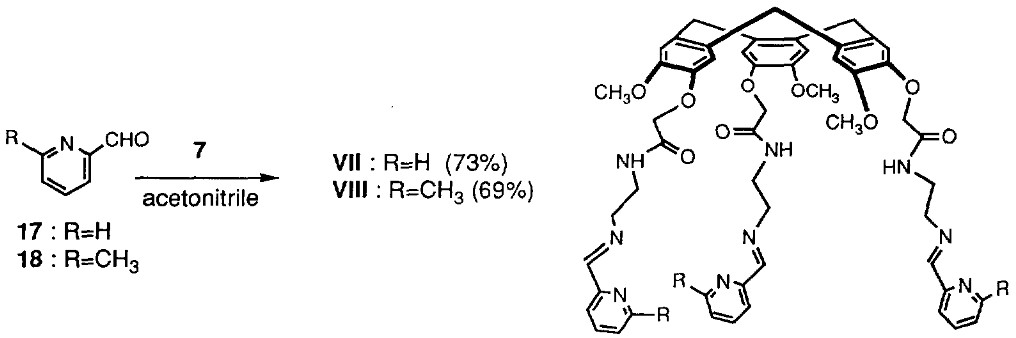
Scheme 6



Iminopyridine ligands VII and VIII. These ligands which are also suitable for iron(II) complexation[18] were prepared in a staightforward fashion by reaction of **7** with pyridine-2-carboxaldehyde **17** or its 5-methyl derivative **18** in refluxing acetonitrile (Scheme 7).

All ligands **I-VIII** gave NMR spectra in full agreement with their structures, and which showed that in these compounds the C3-cyclotriveratrylene ring adopts the usual conformationally rigid crown conformation. The iron(III) complexes of **I-IV** were prepared by mixing these ligands with $Fe(acac)_3$ in the presence of Et_3N in a suitable organic solvent (**I**, **III** : MeOH; **II** : DMF; **IV** : THF). The iron(II) complexes of **V-VIII** were similarly prepared from a Fe(II) salt under anaerobic conditions (**V-VII** : acetone/EtOH; **VIII** : MeOH). These complexes were isolated in the form of microcrystalline powder or, in some cases, as crystals suitable for X-ray diffraction studies. The crystal structure of the iron(II) complex of **VIII** (PF_6^- salt) was solved, confirming the structure of the ligand and its ability to bind iron in the way sketched in Scheme I above. Full details on this structure will be reported separately together with the magnetic and redox properties of these species.[19]

Scheme 7



17 : R=H
18 : R=CH_3

VII : R=H (73%)
VIII : R=CH_3 (69%)

Experimental Section

Chromatographic purifications were effected on Merck silica gel 60 (230-400 mesh). Melting points were measured on a Kofler hotbench or by DSC using a Perkin-Elmer DSC7 microcalorimeter. Unless otherwise stated, ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Bruker AC200 spectrometer ; due to the existence of tautomeric forms in equilibrium for compound **II**, the NMR spectra of this compound given below were recorded at high temperature, and the data therefore represent the fast-exchange averaged resonances of the various forms ; for some of the compounds, studied in dmso-d_6 solutions, the ^1H NMR spectra were recorded at 50-80 °C in order to shift upfield the signal of the residual water, which obscured some of the resonances of the compound (e.g., **7**, **IV**, **VI**, **VII** and **VIII**). Infrared spectra were taken on a Perkin-Elmer IRFT 1600 instrument. Combustion analyses were done by the Service Central d'Analyse du CNRS. Most of these cyclotriveratrylenes crystallize with inclusion of water (the presence of water is generally evidenced by NMR) and, in somes cases, of other species.[20] This circumstance often complicates the interpretation of the elemental analyses.

(4-Hydroxymethyl-2-methoxyphenoxy)acetic acid, sodium salt 2. To a stirred solution of chloroacetic acid (43.2 g, 0.46 mol) in 95% ethanol (340 mL), neutralized with 44.8 mL of 35% aqueous NaOH, were successively added 70 g of vanillyl alcohol (0.45 mol), 44.8 mL of 35% aqueous NaOH and sodium iodide (0.7 g). The mixture was refluxed for 5 h under argon, then cooled to room temperature and kept at 4 °C for 15 h. The resulting precipitate was filtered off, recrystallized from 200 mL of hot water and dried at 70 °C for 3 h to afford **2** (70.1 g, 66%). ^1H NMR (D_2O) : δ 3.79 (s, 3H, OCH_2), 4.39 (s, 2H, OCH_2), 4.47 (s, 2H, OCH_2CO_2), 6.74 (d, 1H, aromatic H, J = 8.3 Hz), 6.85 (dd, 1H, aromatic H, J = 8.3 and 1.8 Hz), 6.98 (d, 1H, aromatic H, J = 1.8 Hz) ; ^{13}C NMR (D_2O) : δ 56.2 (OCH_3), 64.9 (OCH_2), 68.8 ($O\underline{C}H_2CO_2$), 111.5, 113.5, 120.7, 136.3, 147.4, 149.7 (aromatic C), 175.6 (CO_2). Anal. Calcd. for $C_{10}H_{11}O_5Na{\cdot}H_2O$: C, 47.64; H, 5.20. Found : C, 47.8; H, 5.2.

(±)-2,7,12-Tris(methoxycarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 4. Alcohol **2** (10 g, 42.7 mmol) was added portionwise to 100 mL of 65% aqueous perchloric acid and the resulting solution was stirred at room temperature for 20 h. Then, 1 L of a chilled 1:9 acetic acid-water mixture was added dropwise. The resulting precipitate was collected by slow filtration through a sintered glass funnel and washed with acetic acid (200 mL) and water (200 mL). The still wet and acidic cake was added to a mixture of methanol (240 mL) and methyl orthoformate (120 mL), and the resulting suspension was refluxed for 5 h; the acid slowly dissolved while **4** precipitated. The reaction mixture was kept for 2 days at -20°C and the solid was collected by suction filtration. This material was dissolved in a 95:5 dichloromethane-methanol mixture (10 mL) and chromatographed over 500 g of silica gel by using dichloromethane-diethyl ether 9:1 (v/v) as the eluant, giving 3.3 g of pure triester **4** as a white crystalline powder, mp 193 °C (37%, first eluted, dried at 70 °C, 0.1 torr, for 5 h), followed by several fractions containing the tetraester and the pentaester derivatives. ^{1}H NMR (CDCl$_3$) : δ 3.50 (d, 3H, ArCH$_2$Ar, J = 13.8 Hz), 3.70 (s, 9H, CO$_2$CH$_3$), 3.87 (s, 9H, OCH$_3$), 4.58 (d, 3H, OCH$_2$, J = 16.2 Hz), 4.62 (d, 3H, OCH$_2$, J = 16.2 Hz), 4.69 (d, 3H, ArCH$_2$Ar, J = 13.8 Hz), 6.79 (s, 3H, aromatic H), 6.87 (s, 3H, aromatic H) ; ^{13}C NMR (CDCl$_3$) : δ 36.3 (ArCH$_2$Ar), 52.0 (OCH$_3$), 55.9 ($CO_2\underline{C}H_3$), 67.2 (OCH$_2$), 113.7, 117.6, 131.4, 134.0, 145.8, 148.6 (aromatic C), 169.8 (CO$_2$). Anal. Calcd. for $C_{33}H_{36}O_{12}$: C, 63.45; H, 5.81. Found : C, 63.3; H, 5.6.

(±)-2,7,12-Tris(hydroxycarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 3. A mixture of **4** (0.5 g, 800 mmol) and *t*-BuN$^+$OH$^-$ (4 mL, 3.2 mol) in methanol (8 mL) was refluxed under argon for 6 h (the solid was dissolved after 3 h), then acetic acid (8 mL) was added to the warm solution. The desired product crystallized off on cooling. After several hours at room temperature, it was collected by suction filtration, washed with water and dried under vacuum at 150 °C for 7 h. Yield 0.251 g (97%) of **3**, mp > 200 °C (dec), insoluble in usual solvents. Anal. Calcd. for $C_{30}H_{30}O_{12}\cdot 3\ H_2O$: C, 56.61; H, 5.70. Found : C, 56.7; H, 5.5.

(±)-2,7,12-Tris(2-hydroxyethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 5. To a stirred and warm suspension of lithium tetrahydridoaluminate (0.266 g, 7.01 mmol) in 25 mL of THF was added 1 g (0.4 mmol) of the triester **4**. After 4-h reflux under argon, the mixture was cooled in an ice-water bath and carefully hydrolyzed by 8 mL of ethyl acetate and 2 mL of water. Then 20 mL more of water were added and the mixture was acidified with 15 mL of 10% sulfuric acid. The THF was stripped off by a stream of argon, and the remaining precipitate was collected by suction filtration and washed with 10 mL of water. Recrystallisation from 320 mL of hot 95% ethanol gave 0.556 g (64%) of **5**, after drying at 120°C for 7 h, as a white crystalline powder, mp 220 °C. ^{1}H NMR (dmso-d$_6$) : δ 3.49 (d, 3H, ArCH$_2$Ar, J = 13.3 Hz), 3.60-3.71 (m, 6H, $C\underline{H}_2OH$), 3.70 (s, 9H, OCH$_3$), 3.83-4.03 (m, 6H, OCH$_2$C), 4.67 (d, 3H, ArCH$_2$Ar, J = 13.3 Hz), 4.75 (t, 3H, OH, J = 5.5 Hz), 7.04 (s, 3H, aromatic H), 7.07 (s, 3H, aromatic H) ; ^{13}C NMR (dmso-d$_6$) : δ 35.0 (ArCH$_2$Ar), 55.7 (OCH$_3$), 59.5 (CH$_2$OH), 70.3 (OCH$_2$), 113.8, 115.1, 132.0, 132.2, 146.4, 147.5 (aromatic C). Anal. Calcd. for $C_{30}H_{36}O_9$: C, 66.66; H, 6.71. Found : C, 66.0; H, 6.7.

(±)-2,7,12-Tris(hydrazinocarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 6. Hydrazine monohydrate (2.33 mL, 30 eq.) was added to a suspension of the triester **4** (1 g, 1.6 mmol) in 50 mL of THF, and the mixture was refluxed for 18 h under argon. The triester slowly dissolved and a precipitate began to form. The white crystalline solid was filtered off, washed with 50 mL of chloroform, and dried at 160 °C in vacuum for 5 h. Yield 1.05 g (97%) of pure **6**, mp 236 °C. ^{1}H NMR (dmso-d$_6$) : δ 3.48 (d, 3H, ArCH$_2$Ar, J = 13.5 Hz), 3.78 (s, 9H, OCH$_3$), 4.27 (s br, 6H, NH$_2$), 4.33-4.42 (m, 6H, OCH$_2$CO), 4.69 (d, 3H, ArCH$_2$Ar, J = 13.5 Hz), 7.02 (s, 3H, aromatic H), 7.10 (s, 3H, aromatic H), 8.89 (s br, 3H, CONH); ^{13}C NMR (dmso-d$_6$) : δ 35.1 (ArCH$_2$Ar), 56.0 (OCH$_3$), 68.2 (OCH$_2$), 114.0, 116.4, 131.8, 133.4, 145.9, 147.8 (aromatic C), 166.9 (NCO). Anal. Calcd. for $C_{30}H_{36}O_9N_6\cdot H_2O$: C, 56.07; H, 5.96; N, 13.14. Found : C, 55.8; H, 5.8; N, 13.1.

(±)-2,7,12-Tris(2-aminoethylcarbamoylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 7. Triester **4** (1 g, 1.6 mmol) was added to 65 mL (ca. 600 eq.) of ethylenediamine and the mixture was refluxed under argon for 48 h. After cooling to room temperature, the resulting pale yellow solution was poured into 500 mL of ice-water and stored et 4 °C for 15 h. The precipitate was collected by suction filtration, recrystallized from 25 mL of hot 95% ethanol, and dried over P$_2$O$_5$ for 5 h, yielding 0.95 g (84%) of **7** as a white crystalline powder, mp 200 °C. ^{1}H NMR (dmso-d$_6$, 50 °C) : δ 2.59 (t, 6H, C$\underline{H}_2$NH$_2$, J = 6.0 Hz), 2.86 (s br, 6H, NH$_2$), 2.98-3.24 (m, 6H, NHC$\underline{H}_2$), 3.49 (d, 3H, ArCH$_2$Ar, J = 13.5 Hz), 3.78 (s, 9H, OCH$_3$), 4.38 (d, 3H, OCH$_2$, J = 14.9 Hz), 4.41 (d, 3H, OCH$_2$, J = 14.9 Hz), 4.69 (d, 3H, ArCH$_2$Ar, J = 13.5 Hz), 7.03 (s, 3H, aromatic H), 7.11 (s, 3H, aromatic H), 7.70 (br t, 3H, CONH); ^{13}C NMR (dmso-d$_6$) : δ 35.1 (ArCH$_2$Ar), 41.1-41.9 (NCH$_2$), 55.9 (OCH$_3$), 69.1 (OCH$_2$), 113.9, 116.7, 131.9, 133.6, 145.8, 147.8 (aromatic C), 168.2 (CONH). Anal. Calcd. for $C_{36}H_{48}N_6O_9 \cdot 6.5\ H_2O$: C, 52.35; H, 7.44; N, 10.18. Found : C, 52.45; H, 7.2; N, 9.85.

(±)-2,7,12-Tris(ethoxymethanesulfonate)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene 9. Triol **5** (0.4 g, 0.74 mmol) was dissolved under argon with moderate heating in 8 mL of pyridine. The solution was cooled to -30 °C and 0.6 mL (7.75 mmol) of mesyl chloride was added dropwise. The orange coloured mixture was kept at 2 °C for 24 h, then it was poured into 30 mL of ice-water. The precipitate was collected by suction filtration and successively washed with 20 mL of water, 10 mL of 1 M aqueous HCl and 20 mL of water to give **9** as a whitish crystalline powder, after 1-h digestion in 30 mL of hot chloroform (0.421 g, 80%, mp 200 °C). ^{1}H NMR (dmso-d$_6$) : δ 3.20 (s, 9H, SO$_2$CH$_3$), 3.51 (d, 3H, ArCH$_2$Ar, J = 13.3 Hz), 3.72 (s, 9H, OCH$_3$), 4.06-4.29 (m, 6H, OCH$_2$), 4.47-4.52 (m, 6H, CH$_2$OMs), 4.70 (d, 3H, ArCH$_2$Ar, J = 13.3 Hz), 7.09 (s, 3H, aromatic H), 7.12 (s, 3H, aromatic H); ^{13}C NMR (dmso-d$_6$) : δ 34.9 (ArCH$_2$Ar), 36.9 (SO$_2$CH$_3$), 55.9 (OCH$_3$), 67.0-68.9 (OCH$_2$), 114.0, 115.5, 131.9, 133.0, 145.7, 147.6 (aromatic C). This relatively unstable trismesylate was used immediately for the next steps (conversion to ligand **IIIa** and **V**).

2,3-Dibenzyloxybenzaldehyde 10.[13] To a solution of 2,3-dihydroxybenzaldehyde (15 g, 108.6 mmol) in 135 mL of absolute ethanol were added 30 mL (252.2 mmol) of benzyl bromide and 20 g (144.7 mmol) of potassium carbonate. The mixture was refluxed under argon for 24 h, then it was concentrated under vacuum (rotatory evaporator). The wet residue was taken into 400 mL of ethyl acetate and 150 mL of water. The aqueous phase was extracted with 2×150 mL of ethyl acetate. The combined organic phases were washed with 3×150 mL of water (pH 6-7), dried over magnesium sulfate and evaporated to dryness to give a beige solid. The resulting solid was taken into 100 mL of 95% ethanol and collected by suction filtration. Column chromatography over 250 g of silica gel using dichloromethane-ethyl acetate 90:10 (v/v) as the eluant gave 23.2 g (67%, dried over P$_2$O$_5$) of **10**, which was used without further purification. ^{1}H NMR (CD$_2$Cl$_2$) : δ 5.21 (s, 4H, OCH$_2$), 7.10-7.54 (m, 13H, aromatic H), 10.26 (s, 1H, CHO).

2,3-Dibenzyloxybenzoic acic 11.[13] Benzaldehyde **10** (10 g, 31.4 mmol) was dissolved in 10 mL of acetone and the solution was diluted with 30 mL of water. To this heterogeneous mixture were added 4.27 g (44 mmol) of sulfamic acid and 3.73 g (33 mmol, portionwise over 3 min) of sodium chlorite (80% NaClO$_2$).The resulting solution was vigorously stirred at room temperature. After 1 h acetone was rotatory evaporated under vacuum and the residue was filtered on a fritted glass funnel. The solid was washed with absolute ethanol (10 mL), and recrystallized from hot 95% ethanol (70 mL), yielding 7.0 g (67%) of pure **11**, mp 124 °C (lit.[13] 124-124.5 °C). ^{1}H NMR (acetone-d$_6$) : δ 5.17 (s, 2H, OCH$_2$), 5.24 (s, 2H, OCH$_2$), 7.13-7.57 (m, 13H, aromatic H); ^{13}C NMR (acetone-d$_6$) : δ 71.7-78.2 (OCH$_2$), 118.7, 123.4, 125.1, 127.2, 128.7, 128.9, 129.0, 129.3, 129.5, 137.9, 138.2, 148.5, 153.5 (aromatic C), 166.8 (CO$_2$H). Anal. Calcd. for $C_{21}H_{18}O_4 \cdot H_2O$: C, 71.66; H, 5.43. Found : C, 71.6; H, 5.7.

4-Formyl-4'-methyl-2,2'-bipyridine 13.[15] A solution of 4,4'-dimethyl-2,2'-bipyridine **12** (5 g, 27.14 mmol) and selenium oxide (3 g, 27.04 mmol) in diglyme (60 mL), was refluxed for 6 h under argon. Then hot water (500 mL) was added and the insoluble selenium salts were removed by filtration and washed with 100 mL of hot water. After cooling to room temperature, the filtrate was treated with 20 mL of 2 M aqueous NaOH and washed with chloroform (4×300 mL). The combined organic layers were dried (MgSO$_4$) and concentrated under vacuum (rotatory evaporator) and the residual diglyme distilled under vacuum. The residue was taken into chloroform (40 mL) and evaporated to dryness. The crude solid material was dissolved in a minimum amount of dichloromethane (150 mL) and chromatographed on a silica gel column (ethyl acetate as the eluant) to give 2.16 g (40%) of **13** as a white powder. The product which contains some unreacted starting material (< 15%), was used without further purification. ^{1}H NMR (dmso-d$_6$) : δ 2.42 (s, 3H, CH$_3$), 7.33 (d, 1H, aromatic H, J = 4.8 Hz), 7.83 (dd, 1H, aromatic H, J = 4.9 and 1.45 Hz), 8.28 (s, 1H, aromatic H), 8.59 (d, 1H, aromatic H, J = 4.8 Hz), 8.78 (s 1H, aromatic H), 8.94 (d, 1H, aromatic H, J = 4.9 Hz), 10.2 (s, 1H, CHO).

2,2'-Bipyridyl-4,4'-bismethylcarboxylate 16. To a solution of potassium permanganate (45 g, 244 mmol) in 500 mL of water was added 5 g (27.14 mmol) of 4,4'-dimethyl-2,2'-bipyridine **12**. The mixture was refluxed until the solution became colourless (ca 7 h) and then filtered. The black precipitate was washed with warm water (100 mL) and the unreacted compound **12** was extracted with 2×200 mL of diethyl ether. The aqueous phase was cooled in an ice-water bath, acidified with 50 mL of 35% aqueous HCl and stored at 4 °C for 24 h. The resulting precipitate was collected by suction filtration and washed with 20 mL of water. The still wet and acidic solid was taken with methanol (150 mL) and 10 mL of concentrated sulfuric acid was added. The mixture was refluxed under argon for 20 h, then cooled to room temperature, poured into 200 mL of cold water, and stored at 4 °C. The precipitate was collected by slow filtration and recrystallized from 80 mL of hot ethyl acetate and dried at 100 °C under vacuum for 5 h, yielding 1.04 g (14%) of diester **16** as a white powder, mp 204 °C. ^{1}H NMR ($CDCl_3$) : δ 3.98 (s, 6H, OCH_3), 7.88 (dd, 2H, aromatic H, J = 4.9 and 1.55 Hz), 8.85 (d, 2H, aromatic H, J = 4.9 Hz), 8.94 (s br, 2H, aromatic H); ^{13}C NMR ($CDCl_3$) : δ 52.7 (OCH_3), 120.6, 123.2, 138.6, 150.1, 156.5 (aromatic C), 165.6 (CO_2). Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.77; H, 4.44; N, 23.50. Found : C, 61.85; H, 4.5; N, 23.6.

2,2'-Bipyridyl-4'-methylcarboxylate-4-carboxylic acid 14. Diester **16** (1 g, 3.67 mmol) was dissolved in a hot 1:1 dioxane-methanol mixture (100 mL). A solution prepared from 84-87% potassium hydroxide pellets (0.241 g, 3.67 mmol) in 30 mL of methanol was then added, and the reaction mixture refluxed for 6 h. The solvents were distilled off and the residue was taken with 150 mL of water, cooled in an ice-water bath, acidified with 40 mL of 1 M aqueous HCl and stored at 4 °C for 15 h. The precipitate is collected by slow filtration and then treated with hot ethyl acetate (200 mL). The insoluble undesired diacid was removed by suction filtration, and the filtrate concentrated under vacuum (rotatory evaporator). The solid residue was washed with warm chloroform (50 mL) and dried at 80 °C for 8 h to give **14** (0.3 g, 32%) as a slightly pink coloured crystalline powder, mp > 260 °C. ^{1}H NMR (dmso-d_6) : δ 3.96 (s, 3H, OCH_3), 7.88-7.93 (m, 2H, aromatic H), 8.84 (s br, 2H, aromatic H), 8.88-8.94 (m, 2H, aromatic H); ^{13}C NMR (dmso-d_6) : δ 52.6 (OCH_3), 119.1, 119.4, 122.7, 123.2, 136.1, 139.5, 150.3, 150.5, 155.2, 155.5 (aromatic C), 164.8, 165.7 (CO_2). Anal. Calcd. for $C_{13}H_{10}O_4N_2$, 0.25 H_2O; C, 59.43; H, 4.02; N, 10.66. Found : C, 59.65; H, 4.0.; N, 10.8.

(±)-2,7,12-Tris(hydroxyaminocarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene I. A solution prepared from 84-87% potassium hydroxide pellets (0.631 g, 9.61 mmol) in 4 mL of methanol was added at 35 °C under vigorous stirring to a solution of hydroxylamine hydrochloride (0.334 g, 4.81 mmol) in 4 mL of methanol. The mixture was cooled in an ice-water bath and a solution of the triester **4** (0.5 g, 0.8 mmol) in 10 mL of dichloromethane, was added, stirred for 1 h, and filtered under vacuum. The residual solid was then dissolved and stirred for 1 h in boiling aqueous 1 M acetic acid (50 mL). The solid was collected by suction filtration and washed with water, yielding 0.495 g (99%) of **I**, mp > 240 °C (decomp.). The ^{1}H NMR spectra of various samples of **I** prepared in this way always showed the presence of one equivalent of acetate ion. ^{1}H NMR (dmso-d_6) : δ 3.45 (d, 3H, $ArCH_2Ar$), J = 13.2 Hz) 3.76 (s, 9H, OCH_3), 4.36 (m, 6H, OCH_2), 4.69 (d, 6H, $ArCH_2Ar$, J = 13.2 Hz), 6.99 (s, 3H, aromatic H), 7.07 (s, 3H, aromatic H), 8.90 (s br, 3H, CONH), 10.63 (s br, 3H, NOH); ^{13}C NMR (dmso-d_6) : δ 55.9 (OCH_3), 67.5 (OCH_2), 113.9, 116.2, 131.6, 133.3, 145.8, 147.8 (aromatic C), 164.5 (CO). Anal. Calcd. for $C_{30}H_{33}N_3O_{12}\cdot 1.5\ H_2O\cdot AcOK$: C, 51.06; H, 5.22; N, 5.58. Found : C, 51.2; H, 5.2; N, 5.6.

(±)-2,7,12-Tris(2,3-dihydroxybenzhydrazonylcarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene II. To a solution of 2,3-dihydroxybenzaldehyde (0.611 g, 4.42 mmol) in 50 mL of acetonitrile, was added 0.5 g (0.74 mmol) of the tris-hydrazide **6**. The solution was refluxed under argon for 15 h. After cooling to room temperature, the precipitate was collected by suction filtration, washed with 50 mL of hot acetonitrile and dried at 150 °C under vacuum for 6 h, yielding **II** (0.785 g, 99.6%) as a beige crystalline powder, mp > 240 °C (dec). ^{1}H NMR (dmso-d_6, 110 °C) : δ 3.54 (d, 3H, $ArCH_2Ar$, J = 13.6 Hz), 3.76 (s, 9H, OCH_3), 4.70-4.77 (m, 9H, OCH_2 and $ArCH_2Ar$), 6.72 (t, 3H, aromatic H, J =7.7 Hz), 6.87 (dd, 3H, aromatic H, J =7.7 and 1.6 Hz), 6.93 (dd, 3H, aromatic H, J =7.7 and 1.6 Hz), 7.02 (s, 3H, aromatic H), 7.12 (s, 3H, aromatic H), 8.45 (s, 3H, CH=N); ^{13}C NMR (dmso-d_6, 140 °C) : δ 34.8 ($ArCH_2Ar$), 56.0 (OCH_3), 66.2 (OCH_2), 115.1, 117.1, 131.6, 133.4, 146.1, 148.0 (CTV aromatic C), 117.3, 118.5, 118.8, 119.4, 145.0, 145.4 (catechol aromatic C), 165.4 (broad signal, NCO and/or CH=N; two well resolved signal observed at room temperature at 164.8 and 168.8 ppm). Anal. Calcd. for $C_{51}H_{48}N_6O_{15}\cdot 3.5\ H_2O$: C, 58.45; H, 5.29; N, 8.01. Found : C, 58.2; H, 5.2; N, 8.2.

(±)-2,7,12-Tris(2-(2,3-dibenzyloxybenzoyloxy)ethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene IIIa. To a stirred solution of **11** (0.423 g, 1.27 mmol, 9 eq) in 7.5 mL of dimethylacetamide, under argon, was added 0.233 g (12 eq) of potassium carbonate. After 1 h, compound **9** (0.1 g, 0.141 mmol) was added, and the reaction mixture was stirred at room temperature for 45 h, then at 50°C for 3 h. After cooling to room temperature, 20 mL of chilled water was added and the mixture was kept overnight at 4 °C. The precipitate was filtrated off and washed with 20 mL of 2 M aqueous NaOH. Yield 0.139 g (71%) of **IIIa** as a beige solid which was deprotected to **III** without further purification. ^{1}H NMR (acetone-d$_6$) : δ 3.54 (d, 3H, ArCH$_2$Ar, J = 13.6 Hz), 3.65 (s, 9H, OCH$_3$), 4.25 (t br, 6H, CO$_2$CH$_2$), 4.49-4.56 (m, 6H, OCH$_2$), 4.77 (d, 3H, ArCH$_2$Ar, J = 13.6 Hz), 5.08 (s, 6H, OCH$_2$Bn), 5.19 (s, 6H, OCH$_2$Bn), 7.00-7.55 (m, 45H, aromatic H).

(±)-2,7,12-Tris(2-(2,3-dihydroxybenzoyloxy)ethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene III. To a solution of **IIIa** (0.03 g, 0.02 mmol) in 10 mL of dichloromethane was added a suspension of *ca.* 0.020 g of 10% palladium on charcoal in 5 mL of methanol and 2 mL of acetic acid as the catalyst. This mixture was stirred overnight under H$_2$ atmosphere. After adding 30 mL of acetonitrile, the catalyst was separated off through a celite padded funnel, and carefully washed with acetonitrile. The filtrate was evaporated under vacuum (rotatory evaporator) yielding 0.015 g (78%) of **III** as a beige crystalline powder which was used without further purification for iron complexation. ^{1}H NMR (dmso-d$_6$) : δ 3.49 (d, 3H, ArCH$_2$Ar, J = 13.2 Hz), 3.66 (s, 9H, OCH$_3$), 4.0-4.43 (m, 6H, CO$_2$CH$_2$), 4.55 (s br, 6H, OCH$_2$), 4.69 (d, 3H, ArCH$_2$Ar, J = 13.2 Hz), 6.65 (t br, 3H, aromatic H), 7.00 (d br, 3H, aromatic H), 7.04 (d br, 3H, aromatic H), 7.08 (s, 3H, aromatic H), 7.16 (s, 3H, aromatic H).

(±)-2,7,12-Tris(2-(2,3-dihydroxybenzimidoyl)-ethylcarbamoylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene IV. To a warm solution of the tris-amine **7** (0.1 g, 0.14 mmol) in 20 mL of acetonitrile, was added 0.12 g (0.85 mmol) of 2,3-dihydroxybenzaldehyde. The solution was refluxed under argon for 1 h. A yellow crystalline compound formed rapidly. The solid was collected by suction filtration and washed with diethyl ether, yielding 0.11 g (73%) of pure **IV** as a crystalline powder, mp > 280 °C (dec). ^{1}H NMR (dmso-d$_6$, 80 °C) : δ 3.44-3.51 (m, 9H, ArCH$_2$Ar and CONCH$_2$), 3.65-3.73 (m, 15H, OCH$_3$ and C=NCH$_2$), 4.39 (m, 6H, OCH$_2$), 4.66 (d, 3H, ArCH$_2$Ar, J = 13.3 Hz), 6.60 (t, 3H, aromatic H, J = 7.7 Hz), 6.79 (dd br, 3H, aromatic H, J = 6.2 Hz), 6.82 (dd br, 3H, aromatic H, J = 7.3 Hz), 6.99 (s, 3H, aromatic H), 7.08 (s, 3H, aromatic H), 7.74 (s br, 3H, CONH), 8.40 (s, 3H, CH=N); ^{13}C NMR (dmso-d$_6$) : δ 35.0 (ArCH$_2$Ar), 41.05 (NCH$_2$), 55.8 (OCH$_3$), 56.7 (CH$_2$N=), 114.0, 116.6, 131.9, 133.6, 145.9, 147.7 (CTV aromatic C's), 117.5, 117.6, 118.1, 121.9, 145.7, 151.3 (catechol aromatic C's), 167.0 (CH=N), 168.3 (NCO). Anal. Calcd. for $C_{57}H_{60}N_6O_{15}\cdot 5H_2O$: C, 59.06; H, 6.09; N, 7.25. Found : C, 59.1; H, 6.0; N, 7.3.

(±)-2,7,12-Tris(2-(4-carboxy-4'-methoxycarbonyl-2,2'-bipyridyl)-ethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene V. To a stirred solution of **14** (0.327 g, 1.27 mmol, 9 eq) in 7.5 mL of dimethylacetamide, under argon, was added 0.233 g (12 eq) of potassium carbonate. After 1 h **9** (0.1 g, 0.141 mmol) was added and the reaction mixture was stirred at room temperature for 45 h, then at 50°C for 3 h. After cooling to room temperature, the mixture was poured into 20 mL of chilled water. The precipitate was collected by suction filtration and recrystallized from 20 mL of hot 95% ethanol yielding 0.098 g (60%) of **V** as a whitish crystalline solid. ^{1}H NMR (dmso-d$_6$) : δ 3.51 (d, 3H, ArCH$_2$Ar, J = 13.7 Hz), 3.73 (s, 9H, CO$_2$CH$_3$), 3.95 (s, 9H, OCH$_3$), 4.27-4.44 (m, 6H, CO$_2$CH$_2$), 4.56-4.65 (m, 6H, OCH$_2$), 4.68 (d, 3H, ArCH$_2$Ar, J = 13.7 Hz), 7.05 (s, 3H, aromatic H), 7.13 (s, 3H, aromatic H), 7.63-7.87 (m, 6H, bipy aromatic H), 8.65-8.89 (m, 12H, bipy aromatic H).

(±)-2,7,12-Tris(2-(4-imidoyl-4'-methyl-2,2'-bipyridyl)-ethylcarbamoylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene VI. To a warm solution of the tris-amine **7** (0.1 g, 0.14 mmol) in 20 mL of acetonitrile, was added 0.168 g (0.85 mmol, 6 eq) of **13**. The solution was refluxed under argon for 0.5 h, then stirred at room temperature for 24 h. The precipitate was collected by suction filtration giving 0.15 g (85%) of pure **VI** as a yellowish crystalline powder, mp > 280 °C (dec). ^{1}H NMR (dmso-d$_6$, 80 °C) : δ 2.40 (s, 9H, CH$_3$), 3.36-3.56 (m, 9H, ArCH$_2$Ar and CONCH$_2$), 3.58-3.73 (m, 15H, OCH$_3$ and C=NCH$_2$), 4.30-4.48 (m, 6H, OCH$_2$), 4.59 (d, 3H, ArCH$_2$Ar, J = 13.7 Hz), 6.96 (s, 3H, aromatic H), 7.05 (s, 3H, aromatic H), 7.26 (d, 3H, aromatic H, J = 4.65 Hz), 7.59 (d, 3H, aromatic H, J = 4.7 Hz), 7.59 (t br, 3H, CONH), 8.21 (s, 3H, aromatic H), 8.36 (s, 3H, aromatic H), 8.51 (d, 3H, aromatic H, J = 4.65 Hz), 8.64 (s, 3H, N=CH), 8.69 (d, 3H, aromatic H, J = 4.7 Hz); ^{13}C NMR (dmso d$_6$) : δ 15.7 (CH$_3$), 35.0 (ArCH$_2$Ar), 40.7

($NHCH_2$), 55.8 (CH_3), 59.6 (NCH_2), 68.9 (OCH_2), 113.9, 116.4, 131.8, 133.4, 145.7, 147.6 (CTV aromatic C), 118.5, 121.2, 122.1, 125.1, 143.6, 148.0, 149.0, 149.6, 154.6, 156.0 (bipyridine aromatic C), 161.0 (N=CH), 168.1 (NCO). Anal. Calcd. for $C_{72}H_{72}N_{12}O_9 \cdot 8H_2O$: C, 62.06; H, 6.36; N, 12.06. Found : C, 62.1; H, 6.4; N, 12.0.

(±)-2,7,12-Tris(2-(2-pyridinimidoyl)-ethylaminocarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene VII. To a warm solution of the tris-amine **7** (0.1 g, 0.14 mmol) in 20 mL of acetonitrile, was added 0.81 µL (0.85 mmol, 6 eq) of 2-pyridinecarboxaldehyde. The solution was refluxed under argon for 0.5 h, then stirred at room temperature for 24 h. The precipitate was collected by suction filtration giving 0.1 g (73%) of pure **VII** as a crystalline powder (mp > 280 °C (dec) which turned yellow on standing in the air. ^1H NMR (dmso-d_6, 80 °C) : δ 3.36-3.62 (m, 9H, $ArCH_2Ar$ and $CONCH_2$), 3.64-3.88 (m, 15H, OCH_3 and $C{=}NCH_2$), 4.31-4.47 (m, 6H, OCH_2), 4.67 (d, 3H, $ArCH_2Ar$, J = 13.4 Hz), 6.99 (s, 3H, aromatic H), 7.07 (s, 3H, aromatic H), 7.38 (t br, 3H, aromatic H, J = 6.0 Hz), 7.51 (s br, 3H, CONH), 7.75-7.92 (m, 6H, aromatic H), 8.34 (s br, 3H, N=CH), 8.60 (d br, 3H, aromatic H, J = 4.3 Hz); ^{13}C NMR (dmso-d_6) : δ 35.1 ($ArCH_2Ar$), 40.7 (NCH_2), 55.9 (OCH_3), 59.3 (NCH_2), 68.9 (OCH_2), 114.0, 116.6, 131.9, 133.6, 145.7, 147.7 (CTV aromatic C), 120.6, 125.3, 136.9, 149.4, 154.0 (pyr aromatic C), 163.1 (N=CH), 168.2 (NCO). Anal. Calcd. for $C_{54}H_{57}N_9O_9 \cdot 5.5\ H_2O$: C, 60.33; H, 6.37; N, 11.72. Found : C, 60.3 H, 5.9; N, 11.8.

(±)-2,7,12-Tris(2-(6-methyl-2-pyridinimidoyl)-ethylaminocarbonylmethoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene VIII. To a warm solution of the tris-amine **7** (0.1 g, 0.14 mmol) in 20 mL of acetonitrile, was added a solution 0.105 g (0.85 mmol, 6 eq) of 6-methyl-2-pyridinecarboxaldehyde in 2 mL of acetonitrile. The solution was refluxed under argon for 0.5 h, then stirred at room temperature for 24 h. The precipitate was collected by suction filtration giving 0.1 g (69%) of pure **VIII** as a white crystalline powder (mp > 280 °C, dec) which immediately turned yellow in contact with air. ^1H NMR (dmso-d_6, 80 °C) : δ 2.48 (s, 9H, CH_3), 3.33-3.59 (m, 9H, $ArCH_2Ar$ and $CONCH_2$), 3.63-3.78 (m, 15H, OCH_3 and $C{=}NCH_2$), 4.31-4.47 (m, 6H, OCH_2), 4.65 (d, 3H, $ArCH_2Ar$, J = 13.6 Hz), 6.98 (s, 3H, aromatic H), 7.07 (s, 3H, aromatic H), 7.21-7.31 (m, 3H, aromatic H), 7.53-7.73 (m, 9H, CONH and aromatic H), 8.28 (s br, 3H, N=CH); ^{13}C NMR (dmso-d_6) : δ 23.8 (CH_3), 35.0 ($ArCH_2Ar$), 40.7 (NCH_2), 55.7 (OCH_3), 59.4 (NCH_2), 68.9 (OCH_2), 114.0, 116.5, 131.8, 133.5, 145.7, 147.7 (CTV aromatic C), 117.7, 124.4, 137.0, 143.4, 157.7 (pyr aromatic C), 163.2 (N=CH), 168.1 (NCO). Anal. Calcd. for $C_{57}H_{63}N_9O_9 \cdot 5H_2O$: C, 61.78; H, 6.64; N, 11.38. Found : C, 61.7; H, 6.2; N, 11.4.

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