A [2]-catenane whose rings incorporate two differently metallated porphyrins†

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Received (in Strasbourg, France) 4th January 2001, Accepted 21st March 2001
First published as an Advance Article on the web 21st May 2001

A [2]-catenane made with Zn(II) and Au(III) porphyrin-incorporating marcrocycles has been synthesized using the transition metal templated technique, starting from either preformed Au or Zn porphyrin-containing macrocycles. The highest yield (11.5%) was obtained in the latter case. Removal of the copper(I) template metal afforded the free [2]-catenane, whose ^{1}H-NMR properties differ dramatically from those of the parent Cu(I) complex, suggesting a changeover in the molecular structure upon demetallation.

Molecular systems capable of showing intramolecular photo-induced electron transfer between donor and acceptor components have been the subject of intense interest since the early eighties.[1] One of our approaches to this topic has been the use of Zn(II) porphyrin donors in the excited state and Au(III) porphyrin acceptors in the ground state[2] in combination with the so-called mechanical bond found in catenanes and rotaxanes. Only relatively few porphyrin-containing catenanes[3] and rotaxanes[4] have been described in the literature. As shown schematically in Fig. 1, the compounds synthesized in our laboratory are either [2]-rotaxanes[5] made with a Au(III) porphyrin-containing macrocycle threaded onto a Zn(II) porphyrin-stoppered dumbbell [Fig. 1(a) and (b)] or a [2]-catenane,[6] made from macrocycles with *pendent* Zn and Au porphyrins [Fig. 1(c)].

A natural extension of this work was the preparation of the analogous Cu(I)-complexed [2]-catenate with macrocycles *incorporating* the Zn and Au porphyrins [Fig. 1(d)]. Here, we describe the different routes used for the preparation of the [2]-catenate [Cu**1**](PF$_6$)$_2$ (Fig. 2) and its demetallation to the [2]-catenane species.

† Electronic supplementary information (ESI) available: ^{1}H-NMR spectra (1D, 2D ROESY and COSY) of [Cu**1**](PF$_6$)$_2$ and [**1**]PF$_6$. See http:\\www.rsc.org\suppdata\nj\b1\b100275a\

The target Cu(I)-complexed [2]-catenate [Cu**1**](PF$_6$)$_2$ contains two different macrocycles. Therefore, two routes can be envisaged for its construction by the transition metal templated strategy;[7] these are shown in Fig. 3. Both involve the preparation of an intermediate precatenate species (**C**) or (**F**), in which either a Zn or Au porphyrin-containing macrocycle (**A**) or (**E**) is threaded onto chelate (**B**), as a result of copper(I) coordination. Formation of the second, interlocking macrocycle is achieved in the next step, by reaction of the preca-

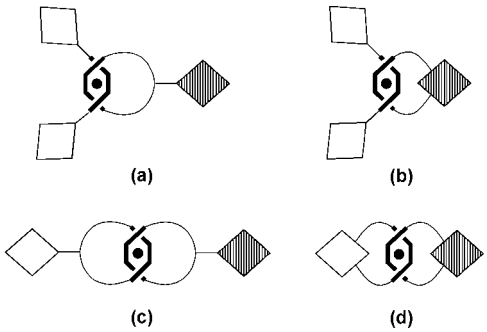
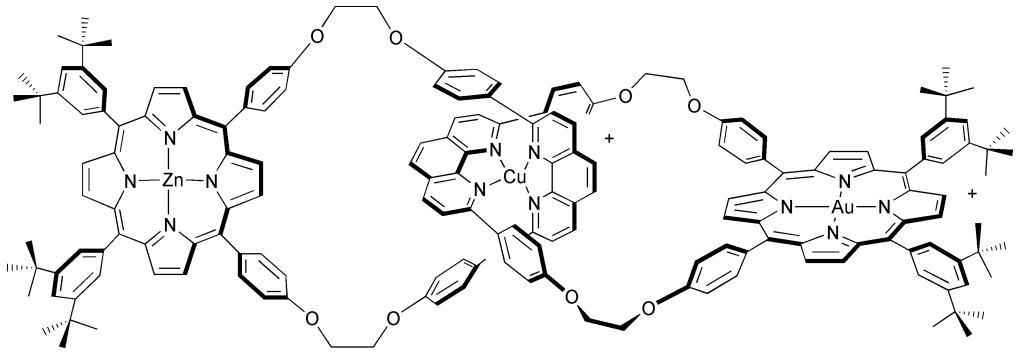


Fig. 1 Schematic representation of metal-complexed [2]-rotaxanes (a, b) and [2]-catenanes (c, d). The thick lines represent chelating fragments, the black disk is a metal cation, the open diamonds are Zn(II) porphyrins, and the hatched diamonds are Au(III) porphyrins.



[Cu**1**](PF$_6$)$_2$

Fig. 2 Chemical structure of [Cu**1**](PF$_6$)$_2$.

 DOI: 10.1039/b100275a

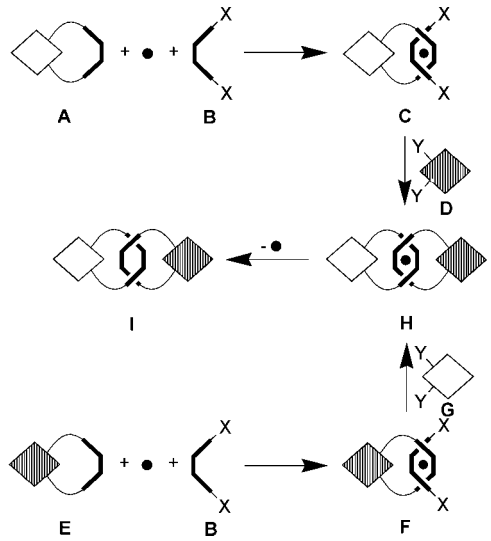


Fig. 3 Two strategies for the transition metal-templated synthesis of a [2]-catenane made with Zn and Au porphyrin-incorporating interlocked macrocycles. Symbols are as in Fig. 1. The black disk symbolises copper(I). See text for details.

tenate with the appropriate porphyrin, (**D**) in the case of (**C**), (**G**) in the case of (**F**), to produce the desired Cu(I)-complexed [2]-catenate (**H**). Finally, removal of the metal template affords the free catenane species (**I**).

The precursors of the target Cu(I) complexed [2]-catenate [Cu**1**]$(PF_6)_2$ are shown in Fig. 4. 5,10-Di(*p*-hydroxyphenyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrin **4** was obtained quantitatively by reaction of 5,10-di(*p*-anisyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrin **3**[5c] with BBr_3 in CH_2Cl_2 at −78 °C, and its zinc complex **5** was obtained in 79% yield by treatment of **4** with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing $CHCl_3/CH_3OH$. Free base-incorporating macrocycle **7** was prepared by combining 2,9-bis[*p*-(2-iodoethoxy)phenyl]-1,10-phenanthroline **2**[5c] and **4** in DMF at 55 °C in the presence of Cs_2CO_3, and was obtained in 28% yield after chromatography. Reaction of **7** with $Zn(OAc)_2 \cdot 2H_2O$ in refluxing $CHCl_3/CH_3OH$ afforded the zinc porphyrin-containing macrocycle **8** in 85% yield. Alternatively, this compound could be prepared directly from phenanthroline **2** and Zn porphyrin **5** under conditions similar to those described for **7**, and was obtained in 13% yield after chromatography.

The three steps of the most efficient route leading to the Cu(I) complexed [2]-catenate [Cu**1**]$(PF_6)_2$ are shown in Fig. 5.[7] Mixing of equimolar solutions of $[Cu(CH_3CN)_4]PF_6$ in acetonitrile and Zn porphyrin-containing macrocycle **8** in dichloromethane, followed by addition of phenanthroline derivative **2** in dichloromethane afforded in quantitative yield precatenate [Cu(**2**,**8**)]PF_6. Subsequently, this complex was combined with a stoichiometric amount of gold(III) 5,10-di(*p*-hydroxyphenyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrinate [**6**]PF_6 in DMF. The resulting solution was heated to 60 °C and treated portionwise with a suspension of Cs_2Co_3 in DMF. This procedure allows the relative instability of the present precatenate in basic media to be overcome.[8] Under these conditions, Cu(I) complexed [2]-catenate [Cu**1**]$(PF_6)_2$ was isolated in 11.5% yield after chromatography. The alternative route, which involves Au porphyrin-containing macrocycle [**9**]PF_6 and Zn porphyrin **5** as reactants afforded the same copper catenate in 5% yield. Demetallation leading to the free [2]-catenane species [**1**]PF_6, was carried out by treating the Cu(I) complex with 100 mol% KCN in a ternary mixture of $CHCl_3$/ CH_3CN/H_2O at 40 °C.[7] [2]-Catenane [**1**]PF_6 was obtained in 83% yield after chromatography (Fig. 6).

The target compounds [**1**]PF_6 and its Cu(I) complex were characterized by FAB-MS and ^{1}H-NMR spectroscopy. The FAB mass spectra in the positive mode show the molecular peak corresponding to singly charged species resulting from the loss of one PF_6^- anion, at *m*/*z* 3041.0 for the Cu(I) [2]-catenate, and 2832.2 for the free [2]-catenane. Peaks corre-

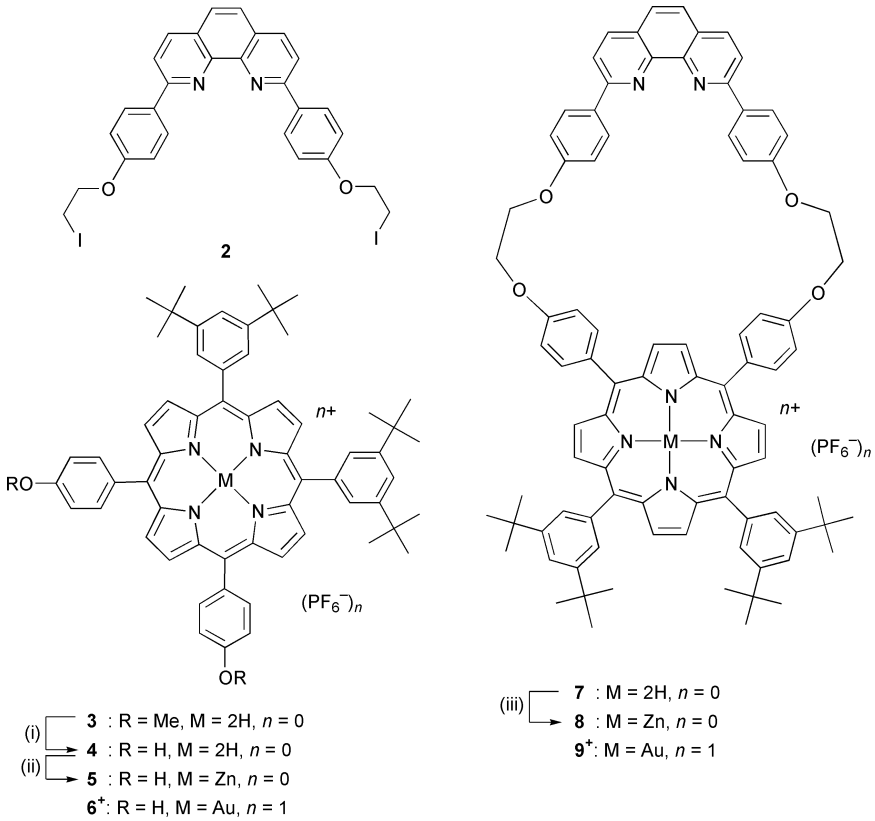


Fig. 4 Precursors to [2]-catenate [Cu**1**]$(PF_6)_2$. (i) BBr_3, CH_2Cl_2, −78 °C, 100%; (ii) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3/CH_3OH$, reflux, 79%; (iii) same as (ii), 85%.

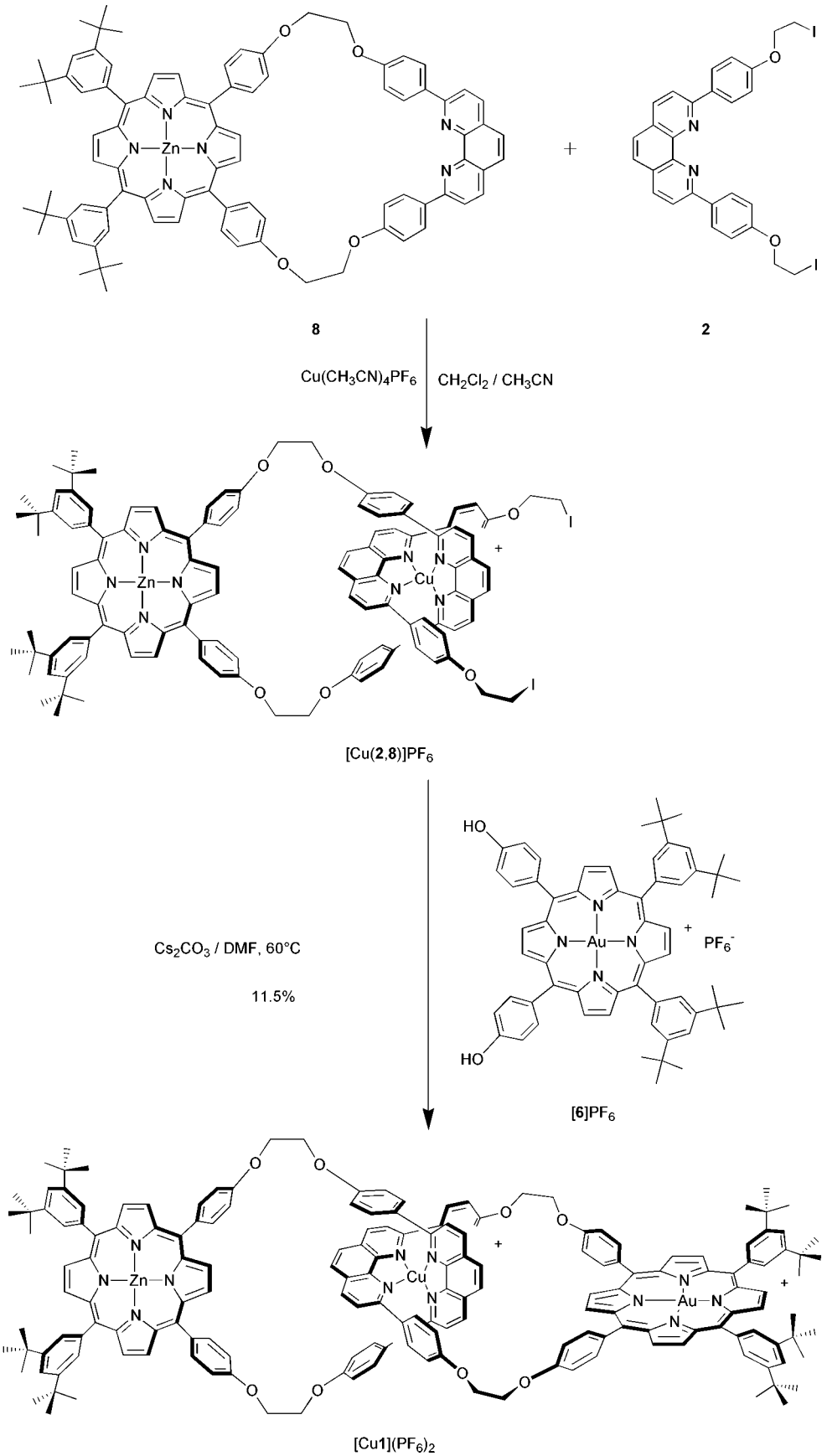


Fig. 5 Two-step preparation of Cu(I)-complexed [2]-catenate [Cu**1**]$(PF_6)_2$.

sponding to the Au porphyrin-containing macrocycle $\mathbf{9}^+$ and the protonated Zn porphyrin-containing macrocycle **8** are observed at *m*/*z* 1481.6 and 1349.5, respectively.

Fig. 7 shows a comparison of the room temperature ^{1}H-NMR spectra (low field region) of [Cu**1**]$(PF_6)_2$ [Fig. 7(a)] and [**1**]PF_6 [Fig. 7(b)]. Labelling of the protons is indicated in Fig. 6. The different signals were assigned using 2D ROESY experiments. To distinguish between protons belonging to the interlocked Zn and Au porphyrin-containing macrocycles, it was assumed, as observed previously, that the β-pyrrolic

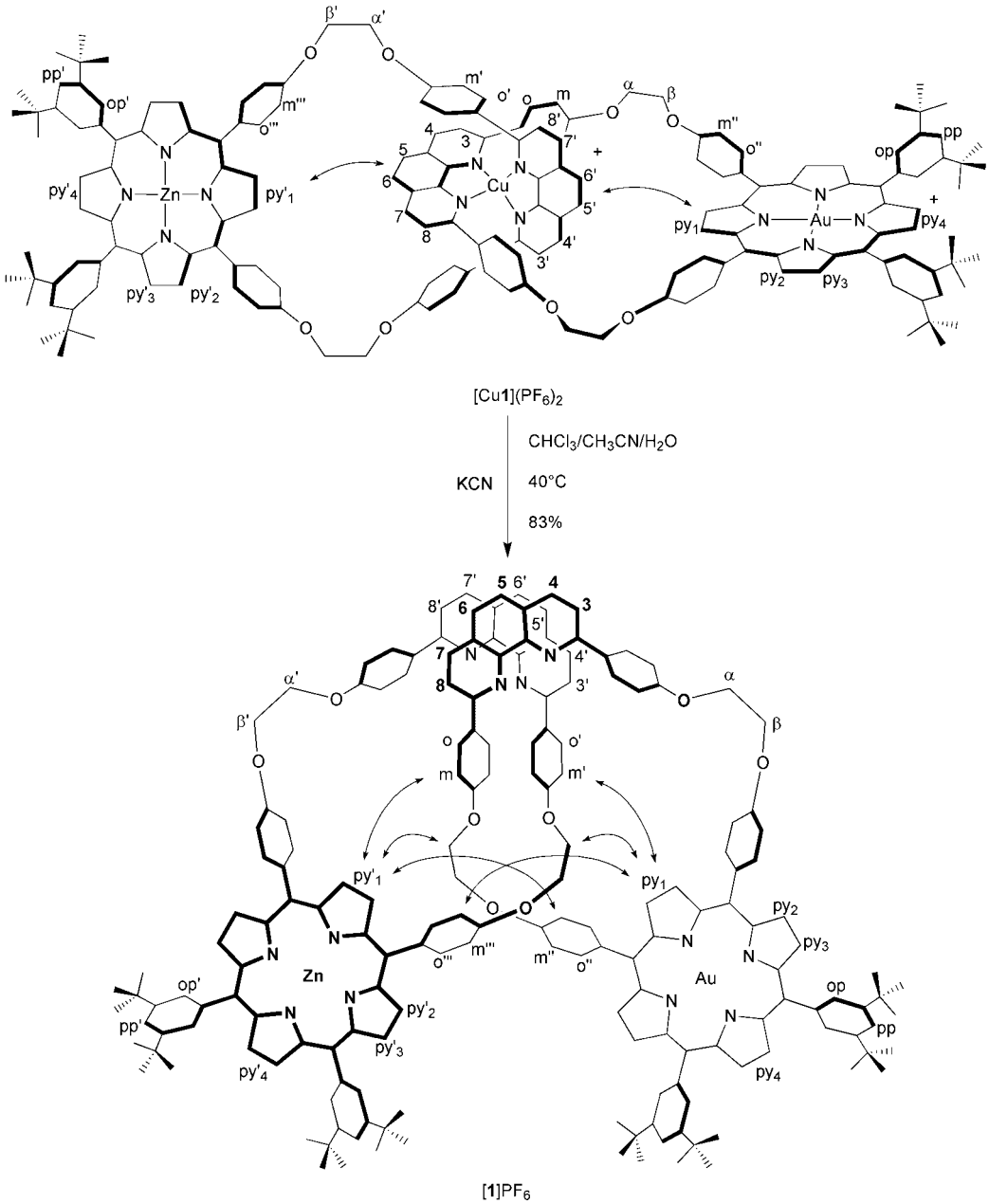


Fig. 6 Demetallation of [2]-catenate [Cu**1**]$(PF_6)_2$ to [2]-catenane [**1**]PF_6. Double bonds omitted for clarity. Double-headed arrows show selected ROESY correlations.

protons of the latter resonate at lower field than the former.[2b,9] This is in agreement with the strong withdrawing effect of gold(III). Typical of the mutual 'fit in' of the 2,9-diphenyl-1,10-phenanthroline chelates in the Cu(I) complexed [2]-catenate, are the upfield-shifted (6.4 ppm) signals of the *meta* protons (m and m′) belonging to the phenyl substituents, as compared to the other aromatic protons.[10] With the exception of the pyrrolic protons, which are the most sensitive to the nature of the porphyrinic metal, analogous protons of both macrocycles have similar chemical shifts. The spectrum of the free [2]-catenane [**1**]PF_6 is dramatically different from that of its parent Cu(I) complex. The signals of the pyrrolic protons move upfield, and the signals of protons o and o′, and m and m′ of the phenyl substituents belonging to the phenanthroline nuclei move downfield by 0.8 ppm. This latter shift is typically observed when passing from metallocatenates to free catenanes, and indicates that the phenyl substituent of a given phenanthroline chelate is no longer in the shielding field of the other phenanthroline upon removal of the metal template.[11] In addition to the above noted changes, the signals of the phenanthroline protons [3′–8′] of the Zn porphyrin-containing macrocycle are shifted upfield to a much greater extent than the corresponding protons [3–8] of the Au porphyrin-containing macrocycle. This is true, in particular, for the pairs 4′,7′ and 5′,6′, which undergo shifts of −0.82 and −0.66 ppm respectively.

2D ROESY maps of catenate [Cu**1**]$(PF_6)_2$ indicate dipolar couplings between protons py_1 of the Au porphyrin-containing macrocycle and protons 5′,6′ of the Zn porphyrin-containing macrocycle. The same is true for protons py'_1 and 5,6. These observations are in agreement with the structure depicted in Fig. 6. These correlations disappear in the case of catenane [**1**]PF_6, which shows only very weak cross peaks between protons of one macrocycle and protons of the other macrocycle, *e.g.*, py'_1 (py_1) and m (m′), m″ (m‴), or α (α′). VT ^{1}H-NMR spectra at temperatures down to −95 °C performed on the free catenane [**1**]PF_6 show only increasing broadening of the peaks, indicating that the molecule exists in many exchanging conformations.

The study of photoinduced electron transfer between the Zn porphyrin component in the excited state and the Au porphyrin component in the ground state by fast laser flash photo-

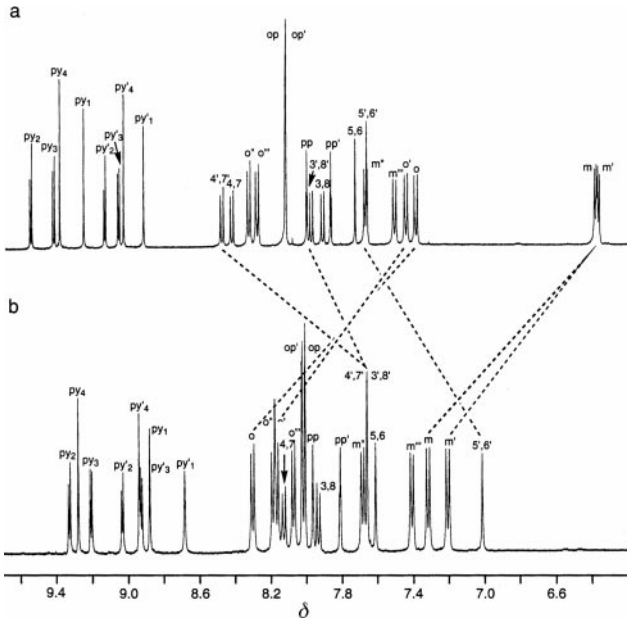


Fig. 7 ^{1}H-NMR spectra (500 MHz, CD_2Cl_2) of (a) [Cu**1**]$(PF_6)_2$ and (b) [**1**]PF_6. Atom numbering as shown in Fig. 6.

lysis techniques should allow more insight into the conformational properties of the [2]-catenane, as shown recently for a related [2]-rotaxane.[5c]

Experimental

General

^{1}H-NMR spectra were obtained on either Bruker AC200 (200 MHz), AC300 (300 MHz), Avance 400 (400 MHz), or ARX500 (500 MHz) spectrometers. Chemical shifts in ppm are referenced downfield from tetramethylsilane. Labels of the protons of the [2]-catenane and some of its precursors are provided in Fig. 6. Mass spectral data were obtained on a ZAB-HF (FAB) spectrometer. UV-visible absorption spectra were recorded with a Kontron-Uvikon 860 spectrophotometer. Elemental analyses were performed by the Service de Caracterisation of the Institut Charles Sadron (Strasbourg).

All reactions were performed under an atmosphere of argon, using standard Schlenk techniques. CH_2Cl_2 was distilled from P_2O_5 and DMF (analytical grade) was filtered through a pad of alumina prior to use. 2,9-Bis[*p*-(2-iodoethoxy)phenyl]-1,10-phenanthroline **2**,[5c] 5,10-di(*p*-anisyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrin **3**,[5c] gold(III) 5,10-di(*p*-hydroxyphenyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrinate [**6**]PF_6,[5c] macrocycle [**9**]PF_6,[5c] and [$Cu(CH_3CN)_4$] PF_6,[12] were prepared according to literature procedures.

Syntheses

5,10-Di(*p*-hydroxyphenyl)-15,20-di(3,5-di-*tert*-butylphenyl)-porphyrin 4. A solution of **3** (1.03 g, 1.13 mmol) in dry CH_2Cl_2 (170 mL) was added dropwise to a solution of BBr_3 (17 mL of a 1 M solution in CH_2Cl_2, 17 mmol) in CH_2Cl_2 (110 mL) at −78 °C. After 2.5 h stirring at −78 °C and 1 h at room temperature, the red solution was cooled to 0 °C, quenched with water (20 mL) and neutralized with aqueous Na_2CO_3. The organic layer was washed three times with water and evaporated to dryness to leave porphyrin **4** in pure form (0.995 g, quantitative). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.89 (s, 2H, $H_{py'1}$ or $H_{py'4}$), 8.87 (s, 2H, $H_{py'4}$ or $H_{py'1}$), 8.87 (br s, 4H, $H_{py'2}$ and $H_{py'3}$), 8.09 (d, 4H, ^3J = 8.4 Hz, $H_{o''}$), 8.07 (d, 4H, ^4J = 1.7 Hz, $H_{op'}$), 7.79 (t, 2H, ^4J = 1.8 Hz, $H_{pp'}$), 7.20 (d, 4H, ^3J = 8.4 Hz, $H_{m''}$), 5.13 (br s, 2H, O*H*′), 1.52 (s, 36H, CH'_3), −2.73 (br s, 2H, N*H*′). UV-visible (λ_{max}/nm): 421, 518, 554, 594, 649. Anal. Calc. for $C_{60}H_{62}N_4O_2$: C, 82.72; H, 7.17; N, 6.43%. Found: C, 82.27; H, 7.18; N, 6.30%

Zinc(II)5,10-di(*p*-hydroxyphenyl)-15,20-di(3,5-di-*tert*-butylphenyl)porphyrinate 5. A solution of **4** (0.174 g, 0.2 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.045 g, 0.2 mmol) in $CHCl_3/CH_3OH$ 2 : 1 (145 mL) was refluxed for 1 h. After evaporation of the solvents, the residue was dissolved in CH_2Cl_2, washed twice with water and the solution evaporated to dryness. Purification by chromatography (alumina, hexane/CH_2Cl_2 50 : 50) afforded **5** (0.147 g, 79% yield) as a purple solid. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 9.01 (s, 2H, $H_{py'1}$ or $H_{py'4}$), 8.99 (AB, 4H, $H_{py'2}$ and $H_{py'3}$), 8.98 (s, 2H, $H_{py'4}$ or $H_{py'1}$), 8.09 (d, 4H, ^3J = 8.5 Hz, $H_{o''}$), 8.09 (d, 4H, ^4J = 1.8 Hz, $H_{op'}$), 7.80 (t, 2H, ^4J = 1.8 Hz, $H_{pp'}$), 7.19 (d, 4H, ^3J = 8.5 Hz, $H_{m''}$), 5.14 (br s, 2H, O*H*′), 1.53 (s, 36H, CH'_3). UV-visible (λ_{max}/nm): 423, 551, 592. Anal. Calc. for $C_{60}H_{60}N_4O_2 \cdot H_2O$: C, 75.65; H, 6.56; N, 5.88%. Found: C, 75.88; H, 6.39; N, 5.84%.

Macrocycle 7. A solution of **2** (0.850 g, 1.26 mmol) and **4** (1 g, 1.15 mmol) in DMF (50 mL) was added dropwise to a stirred suspension of Cs_2CO_3 (1.87 g, 5.75 mmol) in DMF (750 mL) at 55 °C, over 24 h. After further stirring for 16 h at 55 °C, the solvent was evaporated under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed three times with H_2O, separated and evaporated to dryness. The crude product was purified by repeated chromatography (silica gel, hexane/CH_2Cl_2 50 : 50, then alumina, hexane/CH_2Cl_2 80 : 20), affording macrocycle **7** (0.412 g, 28% yield) as a purple solid. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 9.02 (d, 2H, ^3J = 5.1 Hz, $H_{py'2}$), 8.92 (d, 2H, ^3J = 5.1 Hz, $H_{py'3}$), 8.91 (s, 2H, $H_{py'4}$), 8.91 (s, 2H, $H_{py'1}$), 8.45 (d, 4H, ^3J = 8.9 Hz, $H_{o''}$), 8.27 (d, 2H, ^3J = 8.6 Hz, $H_{4'7'}$), 8.19 (d, 4H, ^3J = 8.6 Hz, $H_{o'}$), 8.10 (d, 4H, ^4J = 2 Hz, $H_{op'}$), 8.09 (d, 2H, ^3J = 8.4 Hz, $H_{3'8'}$), 7.81 (t, 2H, ^4J = 2 Hz, $H_{pp'}$), 7.74 (s, 2H, $H_{5'6'}$), 7.44 (d, 4H, ^3J = 8.6 Hz, $H_{m'}$), 7.26 (d, 4H, ^3J = 8.9 Hz, $H_{m''}$), 4.86 (t, 4H, ^3J = 3.9 Hz, $H_{\beta'}$), 4.53 (t, 4H, ^3J = 4.7 Hz, $H_{\alpha'}$), 1.50 (s, 36H, CH'_3), −2.68 (br s, 2H, N*H*′). FAB-MS: *m*/*z* 1287.7 (M + H$^+$).

Macrocycle 8. *Method A*. A solution of macrocycle **7** (0.375 g, 0.29 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.064 g, 0.29 mmol) in $CHCl_3/CH_3OH$ 2 : 1 (220 mL) was refluxed for 1 h. After evaporation of the solvents, the residue was dissolved in CH_2Cl_2, washed twice with water, and the organic layer evaporated to dryness. Purification by column chromatography (alumina, hexane/CH_2Cl_2 40 : 60) afforded macrocycle **8** (0.330 g, 85% yield) as a purple solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.126 (d, 2H, ^3J = 4.61 Hz, $H_{py'2}$), 9.039 (s, 2H, $H_{py'4}$), 9.038 (d, 2H, ^3J = 5.02 Hz, $H_{py'3}$), 9.029 (s, 2H, $H_{py'1}$), 8.445 (d, 4H, ^3J = 8.83 Hz, $H_{o''}$), 8.257 (d, 2H, ^3J = 8.43 Hz, $H_{4'7'}$), 8.194 (d, 4H, ^3J = 8.63 Hz, $H_{o'}$), 8.122 (d, 4H, ^4J = 1.81 Hz, $H_{op'}$), 8.082 (d, 2H, ^3J = 8.43 Hz, $H_{3'8'}$), 7.812 (t, 2H, ^4J = 1.81 Hz, $H_{pp'}$), 7.724 (s, 2H, $H_{5'6'}$), 7.426 (d, 4H, ^3J = 8.63 Hz, $H_{m'}$), 7.254 (d, 4H, ^3J = 9.64 Hz, $H_{m''}$), 4.854 (t, 4H, ^3J = 4.01 Hz, $H_{\beta'}$), 4.520 (t, 4H, ^3J = 4.21 Hz, $H_{\alpha'}$), 1.548 (s, 36H, CH'_3). FAB-MS: *m*/*z* 1350.6 (M + H$^+$).

Method B. A solution of **2** (1.17 g, 1.74 mmol) and **5** (1.625 g, 1.74 mmol) in DMF (76 mL) was added dropwise to a vigorously stirred suspension of Cs_2CO_3 (5.67 g, 17.4 mmol) in DMF (1.135 L) at 60 °C over 9 h. After further stirring for 2 days at 60 °C, the solvent was evaporated under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed three times with water and evaporated to dryness. The remaining solid was triturated with toluene and filtered on a millipore filter. Dissolution of the cake in CH_2Cl_2 afforded almost pure macrocycle **8**, that was further purified by chromatography (silicagel, 1% CH_3OH in CH_2Cl_2). Yield: 0.310 g (13%).

Precatenate [Cu(2,8)]PF_6. A solution of [$Cu(CH_3CN)_4$]-PF_6 (27.1 mg, 0.0727 mmol) in CH_3CN (6 mL) was transferred *via* cannula to a solution of macrocycle **8** (99.1 mg, 0.0733 mmol) in CH_2Cl_2 (34 mL). After 40 min stirring, a solution of

2 (49.3 mg, 0.0733 mmol) in CH_2Cl_2 (17 mL) was added *via* cannula to the reaction mixture. After stirring for 5 h, the solvents were removed *in vacuo*, leaving a quantitative amount of pure precatenate [Cu(**2,8**)]PF_6 as a red solid. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 9.14 (d, 2H, ^3J = 4.6 Hz, $H_{py'2}$), 9.06 (d, 2H, ^3J = 4.4 Hz, $H_{py'3}$), 9.03 (s, 2H, $H_{py'4}$), 8.94 (s, 2H, $H_{py'1}$), 8.52 (d, 2H, ^3J = 8.2 Hz, $H_{4,7}$), 8.45 (d, 2H, ^3J = 8.2 Hz, $H_{4',7'}$), 8.28 (d, 4H, ^3J = 8.2 Hz, $H_{o''}$), 8.12 (d, 4H, ^4J = 1.8 Hz, $H_{op'}$), 8.05 (s, 2H, $H_{5',6'}$), 7.91 (d, 2H, ^3J = 8.4 Hz, $H_{3,8}$ or $H_{3',8'}$), 7.89 (d, 2H, ^3J = 8.4 Hz, $H_{3',8'}$ or $H_{3,8}$), 7.86 (t, 2H, $H_{pp'}$), 7.81 (s, 2H, $H_{5,6}$), 7.49 (d, 4H, ^3J = 8.6 Hz, $H_{m''}$), 7.44 (d, 4H, ^3J = 8.8 Hz, H_o or $H_{o'}$), 7.43 (d, 4H, ^3J = 8.8 Hz, $H_{o'}$ or H_o), 6.30 (d, 4H, ^3J = 8.4 Hz, $H_{m'}$), 6.11 (d, 4H, ^3J = 8.6 Hz, H_m), 4.77 (br t, 4H, $H_{\beta'}$), 4.14 (br t, 4H, $H_{\alpha'}$), 3.89 (t, 4H, ^3J = 6.3 Hz, H_α), 3.33 (t, 4H, ^3J = 6.2 Hz, H_β), 1.55 (s, 36H, CH'_3).

Precatenate [Cu(2,9)](PF$_6$)$_2$. A solution of [Cu$(CH_3CN)_4$]PF_6 (38 mg, 0.103 mmol) in CH_3CN (5 mL) was transferred *via* cannula to a solution of macrocycle [**9**]PF_6 (170 mg, 0.104 mmol) in CH_2Cl_2 (10 mL). After 20 min stirring, a solution of **2** (70 mg, 0.104 mmol) in CH_2Cl_2 (6 mL) was added *via* cannula to the reaction mixture. After stirring for 2 h, the solvents were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and stirred overnight with a 5% aqueous solution of KPF_6. The organic layer was separated, washed with water, and evaporated to leave pure precatenate [Cu(**2,9**)](PF$_6$)$_2$ as a red solid (0.261 g, quantitative). ^{1}H-NMR (400 MHz, CH_2Cl_2): δ 9.55 (d, 2H, ^3J = 5.2 Hz, H_{py2}), 9.41 (d, 2H, ^3J = 5.2 Hz, H_{py3}), 9.38 (s, 2H, H_{py4}), 9.26 (s, 2H, H_{py1}), 8.52 (d, 4H, ^3J = 8.4 Hz, $H_{4,7}$ and $H_{4',7'}$), 8.33 (d, 4H, ^3J = 8.6 Hz, $H_{o''}$), 8.12 (d, 4H, ^4J = 1.8 Hz, H_{op}), 8.05 (s, 2H, $H_{5,6}$), 8.00 (t, 2H, ^4J = 1.8 Hz, H_{pp}), 7.88 (d, 2H, ^3J = 8.4 Hz, $H_{3',8'}$), 7.89 (d, 2H, ^3J = 8.4 Hz, $H_{3,8}$), 7.76 (s, 2H, $H_{5',6'}$), 7.66 (d, 4H, ^3J = 8.9 Hz, $H_{m''}$), 7.46 (d, 4H, ^3J = 8.6 Hz, $H_{o'}$), 7.40 (d, 4H, ^3J = 8.6 Hz, H_o), 6.33 (d, 4H, ^3J = 8.9 Hz, H_m), 6.12 (d, 4H, ^3J = 8.6 Hz, $H_{m'}$), 4.82 (t, 4H, ^3J = 3.8 Hz, H_β), 4.20 (t, 4H, ^3J = 4.3 Hz, H_α), 3.90 (t, 4H, ^3J = 6.39 Hz, $H_{\alpha'}$), 3.32 (t, 4H, ^3J = 5.9 Hz, $H_{\beta'}$), 1.54 (s, 36H, CH'_3).

[2]-Catenate [Cu1](PF$_6$)$_2$. *Method A*. To a solution of precatenate [Cu(**2,8**)]PF_6 (0.163 g, 0.0733 mmol) and gold porphyrin [**6**]PF_6 (97.5 mg, 0.0806 mmol) in DMF (10 mL) at 60 °C under argon, was added portionwise, *via* cannula, a suspension of Cs_2CO_3 (78.2 mg, 0.240 mmol) in DMF (12 mL) over 4.5 h. Heating and stirring were maintained overnight. The reaction was stopped 20 h after the end of the addition of Cs_2CO_3. The solvent was removed by rotary evaporation. The residue was taken up in CH_2Cl_2 (100 mL), washed with water, and stirred overnight with a 5% solution of KPF_6 in water (50 mL). The crude material was subjected to repeated column chromatography on alumina (CH_2Cl_2/CH_3OH 100 : 0.5–1 as eluent), and pure [Cu**1**](PF$_6$)$_2$ was isolated in 11.5% yield (26.8 mg). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 9.548 (d, 2H, ^3J = 5.08 Hz, H_{py2}), 9.420 (d, 2H, ^3J = 5.09 Hz, H_{py3}), 9.386 (s, 2H, H_{py4}), 9.253 (s, 2H, H_{py1}), 9.136 (d, 2H, ^3J = 4.47 Hz, $H_{py'2}$), 9.058 (d, 2H, ^3J = 4.47 Hz, $H_{py'3}$), 9.031 (s, 2H, $H_{py'4}$), 8.920 (s, 2H, $H_{py'1}$), 8.480 (d, 2H, ^3J = 8.32 Hz, $H_{4',7'}$), 8.424 (d, 2H, ^3J = 8.17 Hz, $H_{4,7}$), 8.330 (d, 4H, ^3J = 8.79 Hz, $H_{o''}$), 8.283 (d, 4H, ^3J = 8.63 Hz, $H_{o'''}$), 8.124 (d, 4H, ^4J = 1.85 Hz, H_{op} or $H_{op'}$), 8.122 (d, 4H, ^4J = 1.70 Hz, $H_{op'}$ or H_{op}), 8.004 (t, 2H, ^4J = 1.77 Hz, H_{pp}), 7.979 (d, 2H, ^3J = 8.32 Hz, $H_{3',8'}$), 7.915 (d, 2H, ^3J = 8.32 Hz, $H_{3,8}$), 7.870 (t, 2H, ^4J = 1.85 Hz, $H_{pp'}$), 7.733 (s, 2H, $H_{5,6}$), 7.673 (d, 4H, ^3J = 8.79 Hz, $H_{m''}$), 7.670 (s, 2H, $H_{5',6'}$), 7.512 (d, 4H, ^3J = 8.63 Hz, $H_{m'''}$), 7.447 (d, 4H, ^3J = 8.64 Hz, $H_{o'}$), 7.392 (d, 4H, ^3J = 8.64 Hz, H_o), 6.386 (d, 4H, ^3J = 8.79 Hz, H_m), 6.376 (d, 4H, ^3J = 8.78 Hz, $H_{m'}$), 4.821 (t, 4H, ^3J = 3.85 Hz, H_β), 4.780 (t, 4H, ^3J = 4.33 Hz, $H_{\beta'}$), 4.233 (t, 4H, ^3J = 4.23 Hz, H_α), 4.198 (t, 4H, ^3J = 4.08 Hz, $H_{\alpha'}$), 1.566 (s, 36H, CH_3 or CH'_3), 1.555 (s, 36H, CH'_3 or CH_3). FAB-MS: *m/z* 3041.02 [M − PF_6^-]$^+$, calc. 3042.1 (10%); 2896.07 [M − 2PF_6^- + e^-]$^+$, calc. 2897.17 (33%); 1545.5 [**9**$^+$ + Cu^+ + e^-]$^+$, calc. 1546.1 (13%); 1481.6 [**9**]$^+$, calc. 1482.6 (63%); 1448.6 [M − 2PF_6^-]$^{2+}$/2, calc. 1448.6 (61%); 1413.5 [**8** + Cu^+]$^+$, calcd. 1414.6 (23%); 1349.5 [**8** + H^+]$^+$, calc. 1351.0 (8%).

Method B. A solution of porphyrin **5** (95 mg, 0.102 mmol) and precatenate [Cu(**2,9**)](PF$_6$)$_2$ (0.261 g, 0.104 mmol) in DMF (20 mL) was added dropwise to a stirred suspension of Cs_2CO_3 (0.170 g, 0.52 mmol) in DMF (80 mL) at 50 °C at a rate of one drop every 30 s. After stirring for 16 h at 50 °C, the solvent was evaporated under reduced pressure, and the residue partitioned between CH_2Cl_2 and H_2O. The organic layer was washed three times with water, stirred with a 6.5% aqueous solution of KPF_6 and evaporated to dryness. The crude product was purified by repeated column chromatography (alumina, hexane/CH_2Cl_2 20 : 80) to afford [2]-catenate [Cu**1**](PF$_6$)$_2$ in 5% yield (14 mg) as a red solid.

[2]-Catenane [1]PF$_6$. A mixture of catenate [Cu**1**](PF$_6$)$_2$ (15.62 g, 4.904 μmol) and KCN (31.2 mg, 0.4791 mmol) in a ternary mixture of CH_3CN/$CHCl_3$/H_2O 5.5 : 1.5 : 1.5 (8.5 mL) was heated at 40 °C for 50 min. The reaction mixture was diluted with CH_2Cl_2, the organic layer washed twice with water, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (10 mL) and stirred for 8 h with a 5% solution of KPF_6 in water (10 mL). The product [**1**]PF_6 was purified by column chromatography on alumina (CH_2Cl_2 as eluent) and isolated in 83% yield (12.08 mg). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 9.329 (d, 2H, ^3J = 5.08 Hz, H_{py2}), 9.280 (s, 2H, H_{py4}), 9.209 (d, 2H, ^3J = 5.24 Hz, H_{py3}), 9.034 (d, 2H, ^3J = 4.63 Hz, $H_{py'2}$), 8.942 (s, 2H, $H_{py'4}$), 8.929 (d, 2H, ^3J = 4.62 Hz, $H_{py'3}$), 8.882 (s, 2H, H_{py1}), 8.686 (s, 2H, $H_{py'1}$), 8.304 (d, 4H, ^3J = 8.79 Hz, H_o), 8.188 (d, 4H, ^3J = 8.63 Hz, $H_{o''}$), 8.169 (d, 4H, ^3J = 8.78 Hz, $H_{o'}$), 8.128 (d, 4H, ^3J = 8.63 Hz, $H_{4,7}$), 8.075 (d, 4H, ^3J = 8.48 Hz, $H_{o'''}$), 8.027 (d, 4H, ^4J = 1.69 Hz, $H_{op'}$), 8.010 (d, 4H, ^4J = 1.70 Hz, H_{op}), 7.966 (t, 2H, ^4J = 1.77 Hz, H_{pp}), 7.935 (d, 2H, ^3J = 8.33 Hz, $H_{3,8}$), 7.813 (t, 2H, ^4J = 1.77 Hz, $H_{pp'}$), 7.686 (d, 4H, ^3J = 8.48 Hz, H_m), 7.661 (br s, 4H, $H_{3',8'}$ and $H_{4',7'}$), 7.613 (s, 2H, $H_{5,6}$), 7.409 (d, 4H, ^3J = 8.63 Hz, $H_{m'''}$), 7.318 (d, 4H, ^3J = 8.79 Hz, H_m), 7.208 (d, 4H, ^3J = 8.78 Hz, $H_{m'}$), 7.014 (s, 2H, $H_{5',6'}$), 4.979 (t, 4H, ^3J = 3.47 Hz, H_β), 4.880 (t, 4H, ^3J = 3.00 Hz, $H_{\beta'}$), 4.728 (t, 4H, ^3J = 3.70 Hz, H_α), 4.658 (t, 4H, ^3J = 3.85 Hz, $H_{\alpha'}$), 1.522 (s, 36H, CH_3), 1.494 (s, 36H, CH'_3). FAB-MS: *m/z* 2832.2 [M − PF_6^-]$^+$, calc. 2833.6 (31%); 1481.6 [**9**]$^+$, calc. 1482.6 (100%); 1350.6 [**8** + H^+]$^+$, calc. 1351.0 (18%).

Acknowledgements

We warmly thank Roland Graff, Jean-Daniel Sauer and Michelle Martigneaux for the high field ^{1}H-NMR spectra and Raymond Hueber for the FAB mass spectra. M. L. thanks the French Ministry of Education, Research and Technology and N. F. thanks the Japan Scholarship Foundation for fellowships.

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