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Formyl-Porphyrin and Formyl-Fullerenoporphyrin Building Blocks for the Construction of Multiporphyrin Arrays

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A fullerene derivative bearing a benzaldehyde unit has been prepared and used as starting material for the synthesis of a formyl-fullerenoporphyrin building block. Condensation of this aldehyde with pyrrole in $CHCl_3$ with $BF_3{\cdot}Et_2O$ as catalyst followed by *p*-chloranil oxidation yielded a pentaporphyrinic scaffold surrounded by four peripheral C_{60} subunits. By following a similar strategy, a bis-porphyrin building block bearing an aldehyde function was prepared and used for the construction of a nonaporphyrin array by reaction with pyrrole under typical porphyrin synthesis conditions. Whereas the ^1H NMR spectrum recorded at room temperature for the nonaporphyrin system is well defined, the signals recorded under the same conditions for the pentaporphyrin derivative surrounded by four peripheral C_{60} groups are broad. Indeed, the C_{60}-pentaporphyrin ensemble appears as a mixture of conformers which equilibrate slowly on the NMR time scale at room temperature.

Introduction

In the light of their particular electronic properties, C_{60} and porphyrins are perfectly suited building blocks for the construction of new photochemical molecular devices and artificial photosynthetic systems.[1] Indeed, numerous fullerene derivatives covalently bound to porphyrinic donor moieties have been described in the past few years.[1] Systematic investigations of their photophysical properties have revealed the occurrence of photoinduced electron transfer upon photo-excitation of the porphyrin moiety leading, in general, to quite short-lived charge-separated states.[1] With the aim of increasing the lifetime of the charge separated state, the synthesis of fullerene derivatives bearing multiporphyrinic donors has been achieved.[2–3] In such systems, the initial photoinduced electron transfer between the C_{60} unit and its neighboring porphyrin moiety can be followed by a charge shift from the first porphyrin moiety to the next one(s).[2] Therefore, the distance between the fullerene radical anion and the terminal porphyrin radical cation is quite long and the lifetime of the charge separated state is thus dramatically increased.[2] As far as the synthesis of fullerene-functionalized multiporphyrin arrays is concerned, most of them have been prepared by reaction of a preconstructed multiporphyrin derivative with C_{60} itself or a C_{60} derivative.[2] In contrast, the use of formyl-fullerenoporphyrin building blocks in porphyrin synthesis has been much scarcely considered.[3] This is mainly associated with the chemical reactivity of the fullerene moiety. Effectively, C_{60} derivatives react readily with radicals, various nucleophiles, carbenes, and participates as reactive 2π component in a variety of cycloaddition reactions.[4] Thus the range of reactions that can be used for the further transformations of fullerene-containing building blocks appears to be quite limited and the compatibility of C_{60} derivatives with reaction conditions classically used for porphyrin synthesis is not obvious. As a part of our research program on fullerene derivatives, we have already shown the potential of fullerene-benzaldehydes as starting materials for the construction of functionalized porphyrins.[5] More recently, we have reported a formyl-fullerenoporphyrin building block that has been used for the synthesis of a pentaporphyrinic core surrounded by four peripheral C_{60} subunits.[3] In this paper, we report a full account on the synthesis of this compound. In addition, we also show that the same synthetic strategy can be easily applied for the preparation of a nonaporphyrin array.

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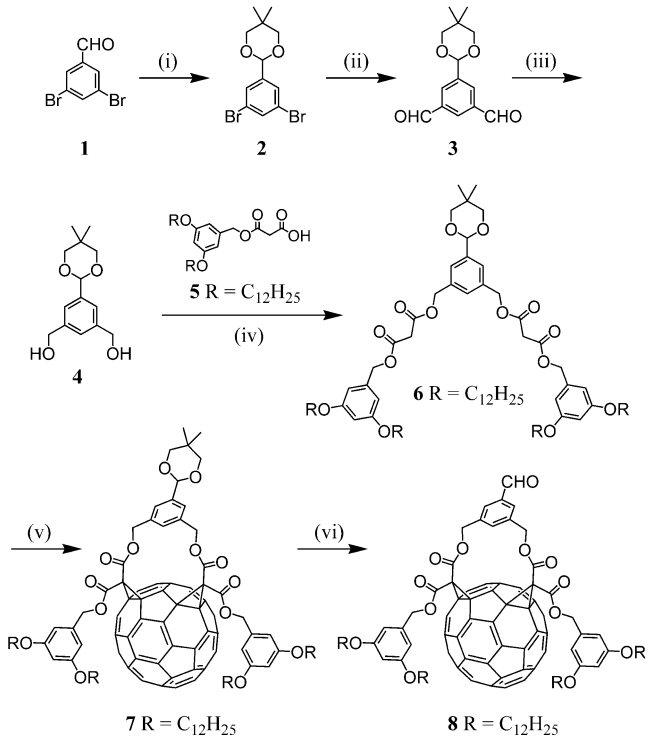
Results and Discussion

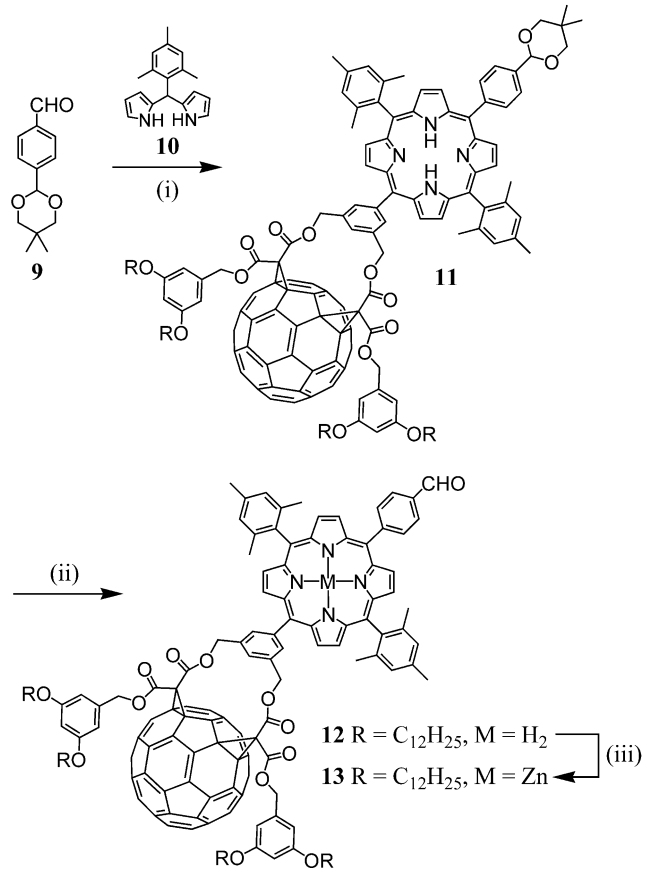
Preparation of the Formyl-Fullerenoporphyrin Building Block

The synthetic approach to prepare the formyl-fullerenoporphyrin derivative relies upon the construction of the

porphyrin unit from a fullerene-benzaldehyde precursor. This compound was obtained by taking advantage of the versatile regioselective reaction developed in the group of



Scheme 1. *Reagents and conditions:* (i) 2,2-dimethyl-1,3-propanediol, C_6H_6, *p*TosOH cat., Δ, Dean–Stark trap (97%); (ii) *t*BuLi (4 equiv.), THF, –78 to 0 °C, then DMF, –78 to 0 °C, then aq. 2 M HCl (58%); (iii) DIBAL-H, CH_2Cl_2, 0 °C (97%); (iv) DCC, DMAP, CH_2Cl_2, 0 °C to room temp. (72%); (v) C_{60}, DBU, I_2, toluene, room temp. (48%); (vi) CF_3CO_2H, H_2O, CH_2Cl_2, room temp. (93%).



Scheme 2. *Reagents and conditions:* (i) **8**, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), room temp. then *p*-chloranil, Δ (5%); (ii) CF_3CO_2H, CH_2Cl_2, room temp. (90%); (iii) $Zn(OAc)_2.2H_2O$, $CHCl_3$/MeOH (9:1), Δ (87%).

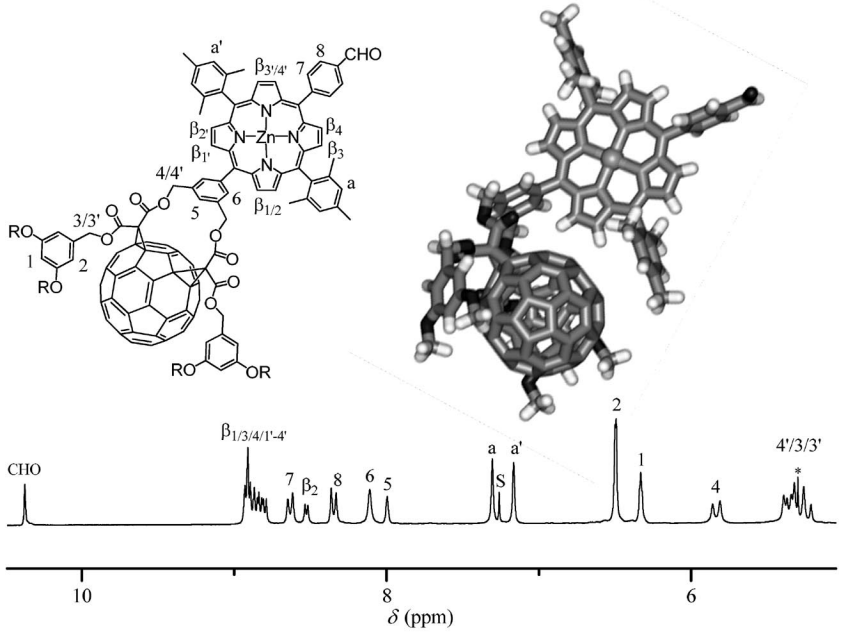
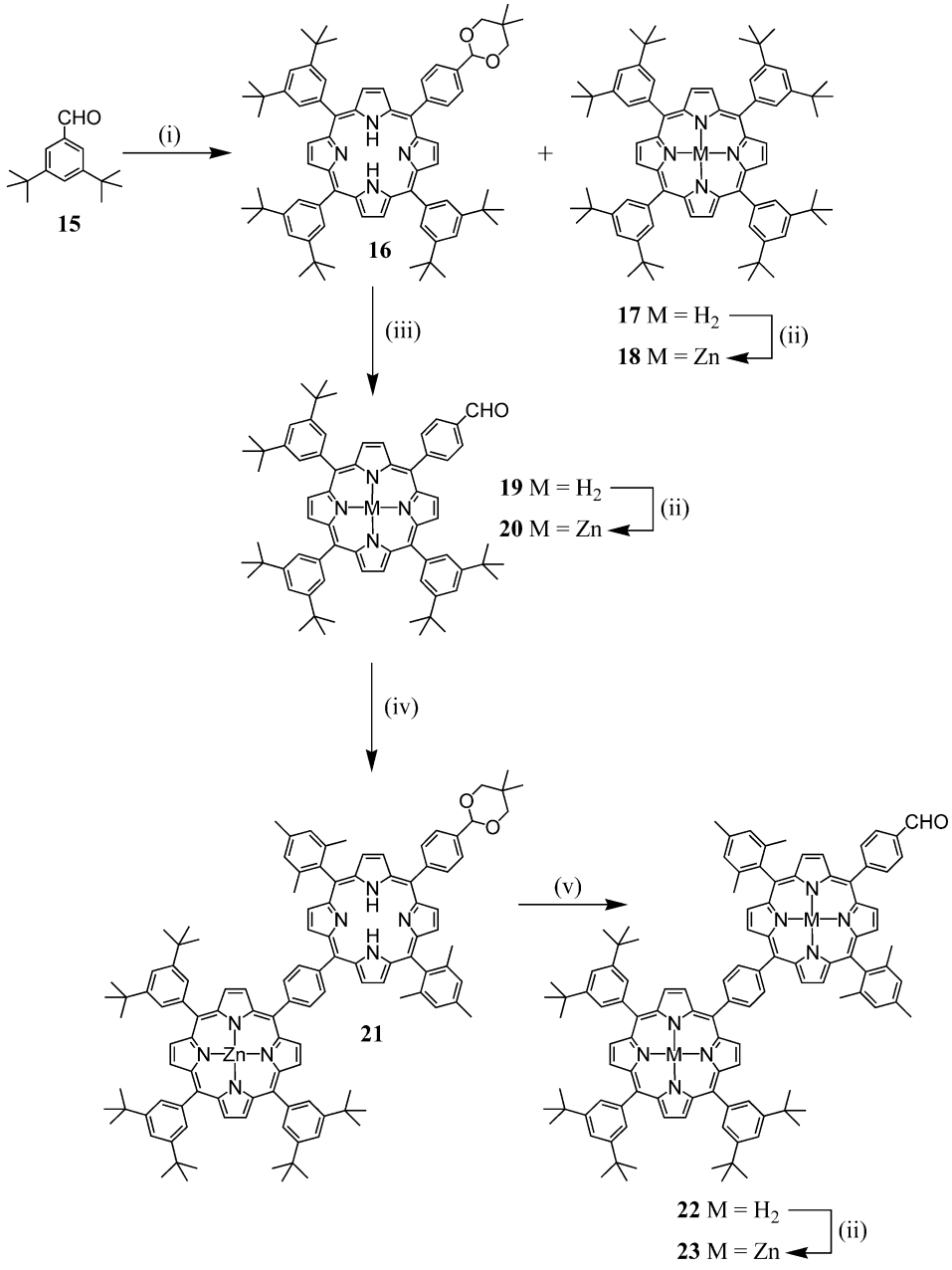


Figure 1. Calculated structure (molecular modeling was performed with Spartan (*Spartan 04 for Windows*, Wavefunction Inc., 1991–2003), the dodecyl chains have been replaced by methyl groups in the calculations) and ^1H NMR spectrum ($CDCl_3$, 300 MHz) of compound **13** (solvent peak: S, CH_2Cl_2 impurity: *). Unambiguous assignment was achieved on the basis of 2D-COSY and NOESY spectra recorded at room temperature in $CDCl_3$.

Diederich,[6] which led to macrocyclic bis adducts of C_{60} by a cyclization reaction at the C sphere with a bis-malonate derivative in a double Bingel[7] cyclopropanation. To this end, we have first prepared bis-malonate **6** bearing a protected aldehyde group (Scheme 1). Reaction of 3,5-dibromobenzaldehyde (**1**) with 2,2-dimethyl-1,3-propanediol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*TosOH) gave **2** in 97% yield. Treatment of **2** with an excess of *t*BuLi[8] in THF followed by quenching with *N*,*N*-dimethylformamide (DMF), and subsequent reduction of the resulting dialdehyde **3** with diisobutylaluminum hydride (DIBAL-H) afforded diol **4** in an overall 56% yield. *N*,*N*′-Dicyclohexylcarbodiimide (DCC)-mediated esterification[9] of **4** with the malonic mono-ester **5**[10] yielded bis-malonate **6**. It is worth noting that the 3,5-didodecyloxybenzyl groups introduced at this stage should prevent any solubility problems for the targeted pentaporphyrin surrounded by four peripheral C_{60} subunits. Indeed, this group has already proven to be an excellent solubilizing group for dendrimers bearing multiple peripheral fullerene moieties.[11] Treatment of C_{60} with **6**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the *cis-2* bis-adduct **7** in 48% yield. The relative position of the two cyclopropane rings in **7** on the



Scheme 3. *Reagents and conditions:* (i) **9**, pyrrole, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), room temp. then *p*-chloranil, Δ (**16**: 6% and **17**: 11%); (ii) $Zn(OAc)_2.2H_2O$, $CHCl_3$/MeOH (9:1), Δ (**18**: 97%; **20**: 92%; **23**: 99%); (iii) CF_3CO_2H, H_2O, CH_2Cl_2, room temp. (93%); (iv) **9**, **10**, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), room temp. then *p*-chloranil, Δ (17%); (v) CF_3CO_2H, H_2O, CH_2Cl_2, room temp. (93%).

C_{60} core was determined based on the molecular symmetry (C_s) deduced from the ^1H and ^{13}C NMR spectra. In addition, the orange-red color and the UV/Vis spectrum of **7** are fully consistent with those of previously reported analogous *cis-2* bis adducts.[12] Indeed, the colors and, accordingly, the absorption spectra of C_{60} bis adducts are highly dependent on the addition pattern and characteristic for each of the regioisomers.[13] It is also well-established that the 1,3-phenylenebis(methylene)-tethered bis-malonates produce regioselectively the C_s-symmetrical *cis-2* addition pattern at C_{60}.[6,12] Finally, treatment of **7** with CF_3CO_2H in CH_2Cl_2/H_2O, 1:1 afforded benzaldehyde **8**. It was obtained in 93% yield as an orange-red glassy product and its preparation was easily carried out on a gram scale.

The synthesis of compound **13** is depicted in Scheme 2. Compound **9**,[14] and dipyrromethane **10**[15] were prepared according to previously reported methods. Porphyrin **11** was obtained by using the reaction conditions developed by Lindsey for the synthesis of sterically hindered porphyrins.[16] A key feature of these conditions involves BF_3–ethanol co-catalysis. The condensation of **8** (1 equiv.), **9** (1 equiv.) and **10** (2 equiv.) was performed in $CHCl_3$ (commercial $CHCl_3$ containing 0.75% ethanol as stabilizer) at room temperature in the presence of $BF_3{\cdot}Et_2O$. After 4 h, *p*-chloranil (tetrachlorobenzoquinone) was then added to irreversibly convert the porphyrinogen to the porphyrin. The desired tetraphenylporphyrin **11** was subsequently isolated in 5% yield by tedious chromatographic separations. Treatment with CF_3CO_2H in CH_2Cl_2 gave aldehyde **12** in 90% yield. Finally, metalation of porphyrin **12** with $Zn(OAc)_2$ gave **13** in 87% yield.

The ^1H NMR spectra of **11**–**13** recorded at room temperature are in full agreement with their C_S symmetric structures imposed by the fullerene *cis-2* bis adduct subunit. As a typical example, the ^1H NMR spectrum of **13** is depicted in Figure 1. The characteristic features of the C_s symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis-2* bis adduct subunit are clearly observed.[12] Effectively, two AB quartets are observed for the two sets of diastereotopic benzylic CH_2 groups ($H_{3/3'}$and $H_{4/4'}$) and an AX_2 system is revealed for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring ($H_{5/6}$). Interestingly, the spectrum shows two sets of signals for the two mesityl groups indicating that they are non-equivalent. Indeed, molecular modeling studies on compound **13** show that the fullerene sphere is located to one side of the plane of its bridging phenyl ring. Therefore, due to the high barrier to rotation of this phenyl substituent on the porphyrin, the two mesityl groups are different. This in line with related fullerenoporphyrin derivatives prepared from aldehyde **8** for which variable-temperature NMR studies have confirmed the restricted rotation of the 3,5-substituted phenyl substituent on the porphyrin ring (free energy of the rotation $\Delta G^{\ddagger}$ = 18 to 20 kcal mol^{-1}).[5]

Preparation of the Formyl-Porphyrin Building Blocks

By following a similar synthetic route, we also prepared a bis porphyrin building block bearing an aldehyde function (Scheme 3). Compounds **16** and **17** were obtained from **9**, **15** and pyrrole according to a previously reported method.[17] Treatment of porphyrin **17** afforded reference Zn^{II}-porphyrin **18** as a crystalline purple solid. Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **18**. As shown in Figure 2, the aromatic porphyrin ring is nearly perfectly planar. It can also be noted that the central Zn atom lies on an inversion center. Close inspection of the packing revealed only intermolecular van der Waals interactions. Indeed, π-stacking interactions between the aromatic rings of neighboring molecules are completely prevented by the bulky *tert*-butyl groups. This is illustrated in Figure 2 which shows the dimer formed by two porphyrin molecules in the crystal lattice. Owing to the presence of the *tert*-butyl groups, the two neighboring aromatic porphyrin rings cannot give rise to any π-π interactions. Actually, the porphyrin-porphyrin distance is ca. 6.9 Å and the empty space resulting from this arrangement is filled by co-crystallized hexane molecules. Observation of the packing clearly illustrates how the 3,5-di-*tert*-butylphenyl groups prevent intermolecular π-π interactions. The latter observations explain also why the 3,5-di-*tert*-butylphenyl substituent is an excellent solubilizing group capable of preventing aggregation phenomena in solution.

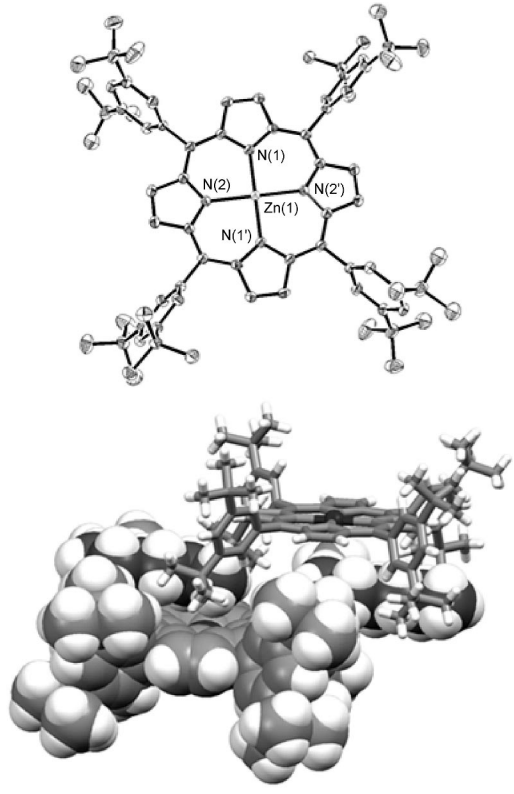


Figure 2. Top: ORTEP plot of the structure of **18**. Thermal elipsoids are drawn at the 50% probability level. The prime (′) characters in the atom labels indicate that these atoms are at equivalent position. Selected bond lengths and bond angles: Zn(1)–N(1): 2.029(3) Å; Zn(1)–N(2): 2.046(3) Å; N(1)–Zn(1)–N(2): 90.02(11)°; N(1)–Zn(1)–N(2′): 89.98(11)°. Bottom: stacking within the **18** lattice; the co-crystallized hexane molecules are represented in dark grey.

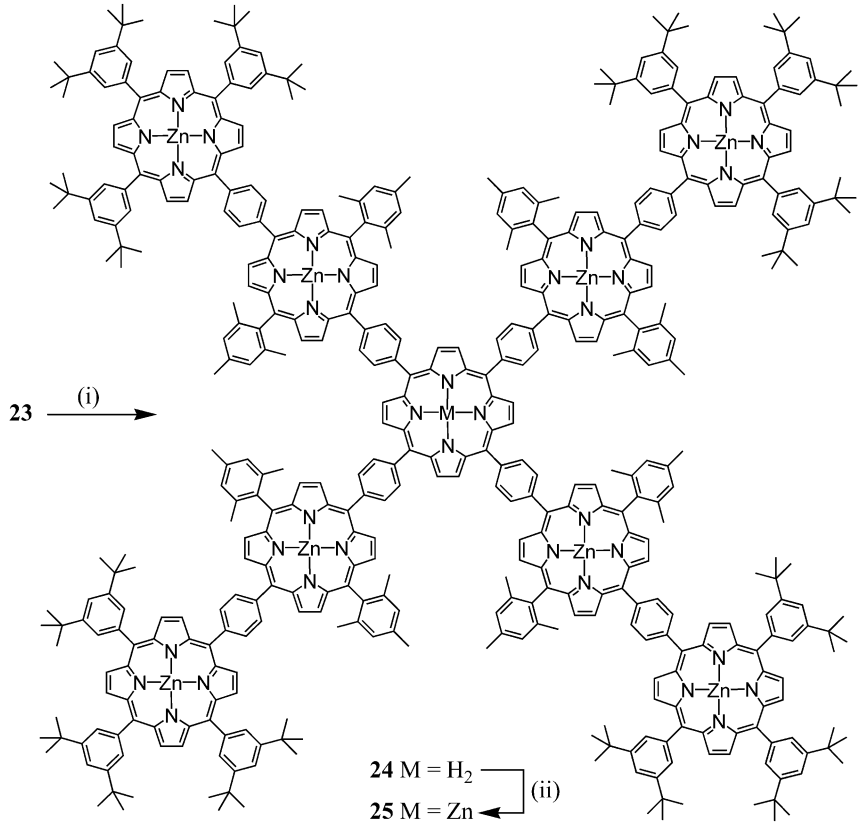
Treatment of **16** with CF_3CO_2H followed by metalation of the resulting **19** with $Zn(OAc)_2$ gave **20**. Reaction of **20** (1 equiv.), **9** (1 equiv.) and **10** (2 equiv.) in $CHCl_3$ in the presence of $BF_3{\cdot}Et_2O$ followed by *p*-chloranil oxidation gave bis-porphyrin **21** in 17% yield. Treatment with CF_3CO_2H in CH_2Cl_2/H_2O gave aldehyde **22** in 93% yield. Under these acidic conditions, the Zn^{II}-porphyrin subunit was demetalated. Indeed, the ^1H NMR spectrum of **22** recorded in $CDCl_3$ revealed two sets of signals at δ = –2.45 and –2.53 ppm for the porphyrinic NH protons of the two different free base porphyrin moieties. Finally, treatment of porphyrin **22** with $Zn(OAc)_2$ gave building block **23** in 99% yield.

Preparation of the Multiporphyrin Arrays

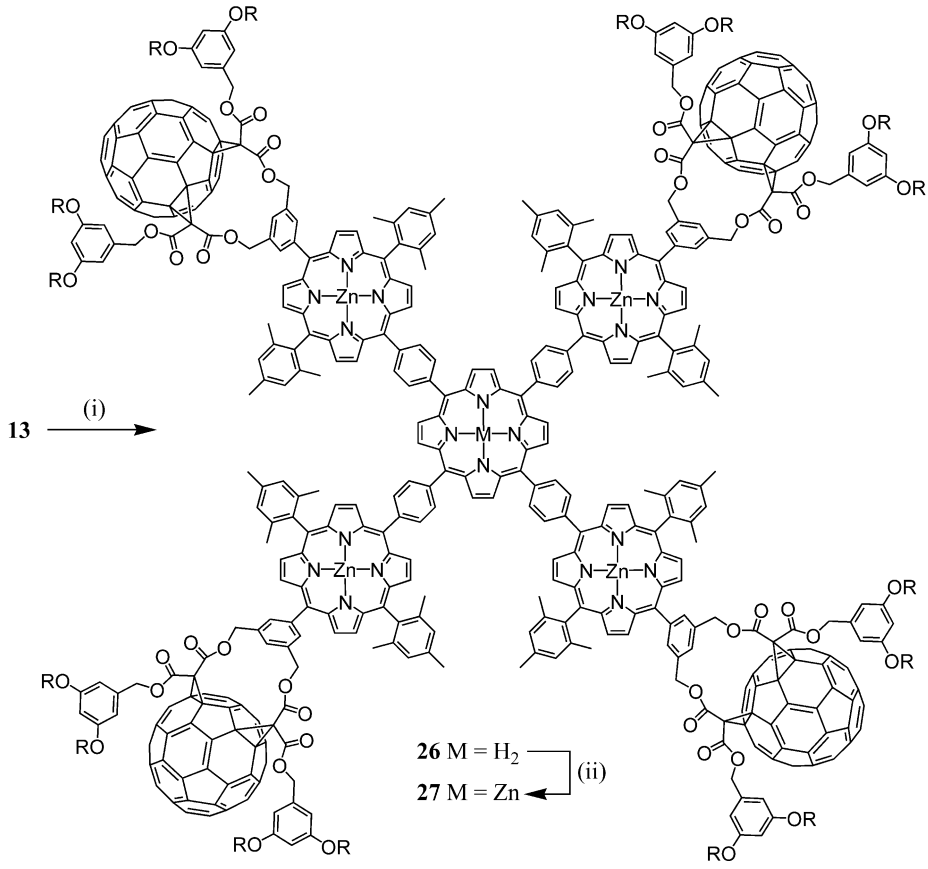
The preparation of multiporphyrins **24**–**27** from building blocks **13** and **23** is shown in Scheme 4 and Scheme 5. Nonaporphyrin **24** was obtained by reaction of **23** with pyrrole under typical Lindsey conditions. It is worth noting that partial demetallation of the Zn^{II}-porphyrins (< 5%) was observed under these conditions. This prompted us to fully metalate the resulting nonaporphyrin array by treatment with $Zn(OAc)_2$. Compound **25** was thus obtained in an overall 15% yield. Similarly, condensation of aldehyde **13** with pyrrole in $CHCl_3$ with $BF_3{\cdot}Et_2O$ as catalyst followed by *p*-chloranil oxidation yielded porphyrin **26** which was metalated with $Zn(OAc)_2$ to give **27**.

The spectroscopic characterization of **24**–**25** is straightforward and was achieved by NMR, UV/Vis, and mass spectrometry. As shown in Figure 3, the ^1H NMR spectra of nonaporphyrin **25** is in full agreement with its fourfold symmetrical structure. Effectively, a singlet is observed at δ = 9.82 ppm for the eight equivalent β-pyrrolic protons (β_9) of the central porphyrin core. All the expected signals for the four equivalent peripheral bis-porphyrin subunits are also clearly observed. Comparison with the ^1H NMR spectrum of its bis-porphyrin precursor (**23**) reveals dramatic changes in chemical shifts for the proton located close to the central aromatic porphyrin ring (β_{7-8}, and $H_{7/8/9}$) as a result of its ring current effect. Actually, a similar deshielding was also seen for protons β_{3-4} and $H_{5/6}$ when comparing the ^1H NMR spectra of bis-porphyrins **21**–**23** with those of porphyrins **19**–**20**.

The characterization of **26** and **27** was more complicated since these compounds appeared as mixtures of conformers in slow equilibrium on the NMR time scale at room temperature. As shown in Figure 4 for compound **27**, the ^1H NMR spectrum recorded at room temperature is very broad. Indeed, each of the terminal fullerene substituent can be located either on one or on the other side of its bridging phenyl group. Free rotation of the four substituents on the central porphyrin is therefore required to obtain a sharp symmetric NMR spectrum. Variable-temperature studies ($C_2D_2Cl_4$, 500 MHz) showed a perfectly reversible narrowing of all the peaks and a sharp spectrum was ob-



Scheme 4. *Reagents and conditions:* (i) pyrrole, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), room temp. then *p*-chloranil, Δ (20%); (ii) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (9:1), Δ (78%).



Scheme 5. *Reagents and conditions:* (i) pyrrole, $BF_3{\cdot}Et_2O$, $CHCl_3$ (containing 0.75% EtOH), room temp. then *p*-chloranil, Δ (57%); (ii) $Zn(OAc)_2{\cdot}2H_2O$, $CHCl_3$/MeOH (9:1), Δ (82%).

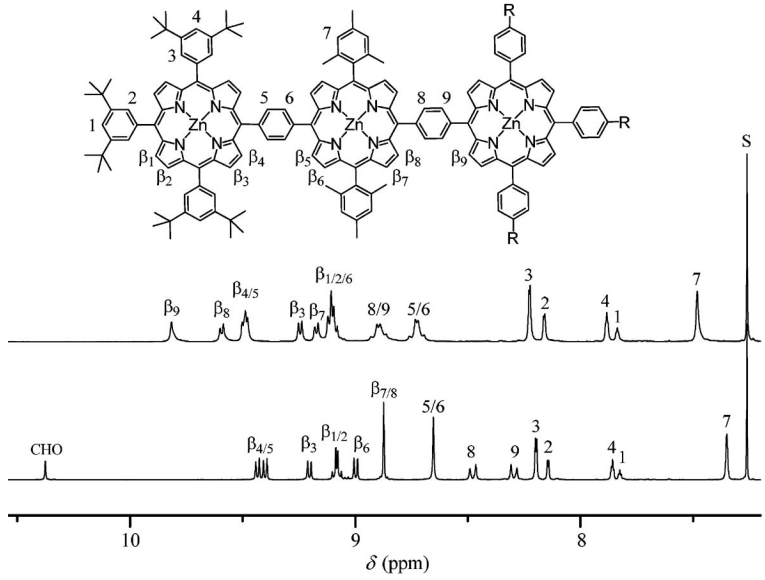


Figure 3. ^1H NMR spectra ($CDCl_3$, 300 MHz) of compounds **23** (bottom) and **25** (top) (solvent peak: S). Unambiguous assignment was achieved on the basis of 2D-COSY and NOESY spectra recorded at room temperature in $CDCl_3$.

tained at 383 K for both **26** and **27**. At this temperature, the dynamic exchange between the different atropisomers is fast on the NMR timescale, thus leading to a well resolved average spectrum. The spectrum of **27** recorded at 383 K is characterized by the diagnostic signals observed for its precursor **13**. The spectrum is also characterized by a singlet at δ = 9.82 ppm for the eight equivalent β-pyrrolic protons of the central porphyrin core. Close inspection of the

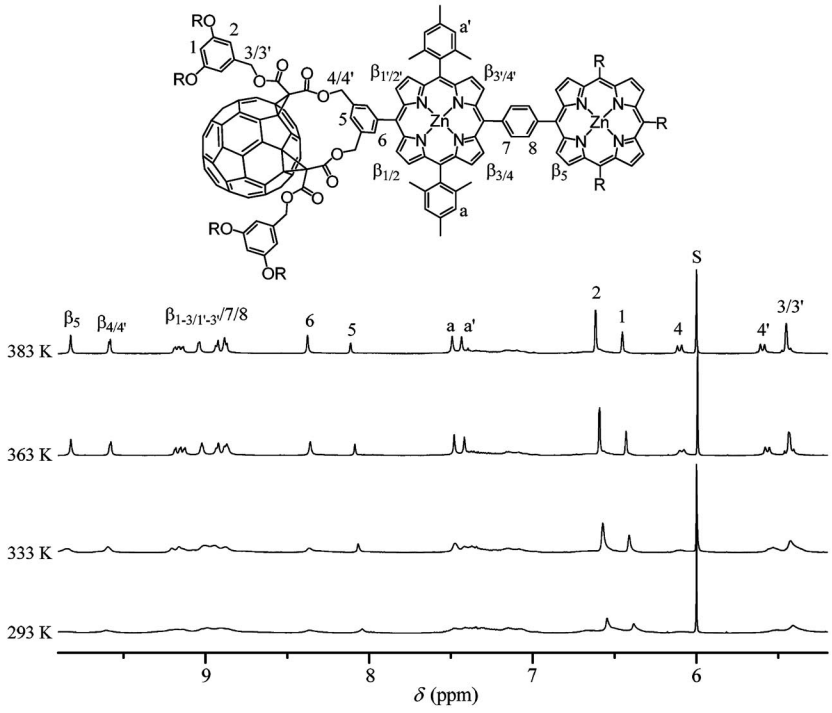


Figure 4. ^{1}H NMR spectra (500 MHz) of **27** recorded in $CDCl_2CDCl_2$ at different temperatures (solvent peak: S).

signals arising from the β-pyrrolic protons of the four equivalent peripheral porphyrin subunits suggests restricted rotation of the 3,5-substituted phenyl substituent on those porphyrin rings under these conditions ($C_2D_2Cl_4$, 383 K, 500 MHz). This is further confirmed by the non-equivalence of their two mesityl substituents. Effectively, two singlets are seen for the mesityl protons H_a and $H_{a'}$ as in the case of the spectra of compound **13** recorded at room temperature. Therefore, rotation of the 3,5-substituted phenyl substituent on the peripheral porphyrin ring is still not fast enough on the NMR timescale to explain the obtention of a sharp symmetric spectrum for **26** and **27** at high temperature. Actually, for both **26** and **27**, the dynamic exchange between the different atropisomers is an unambiguous signature of the restricted rotation of the *p*-phenyl substituents on the central porphyrin ring.

Conclusions

To sum up, we have shown that formyl-porphyrin derivatives **13** and **23** are versatile building blocks for the synthesis of multiporphyrin systems. The C_{60}-porphyrin conjugates **26** and **27** have also revealed unique conformational properties resulting from the symmetry of their 1,3-phenylenebis-(methylene)-tethered fullerene *cis-2* bis adduct subunits. Indeed, compounds **26** and **27** are, to the best of our knowledge, the first tetra(*p*-phenyl)porphyrins for which a high barrier to free rotation has been evidenced. Preliminary luminescence measurements reveal a dramatic quenching of the fluorescence arising from the pentaporphyrin core by the fullerene moieties in **27** thus suggesting the occurrence of intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and special emphasis is placed on the detection of long-lived charge-separated states.

Experimental Section

General: Reagents and solvents were purchased (quality: reagent grade) and used without further purification. Compounds **5**,[10] **9**,[14] **10**,[15] and **16**–**20**[17] were prepared according to the literature. THF was distilled from sodium benzophenone ketyl. Commercial $CHCl_3$ containing 0.75% EtOH was systematically used as solvent for the preparation of the porphyrins. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization was done by iradiation with UV light. Melting points were determined on an Electrothermal Digital Melting Point apparatus and are uncorrected. IR spectra (cm^{-1}) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 or a Bruker AV 500 with solvent peaks as reference. MALDI-TOF-mass spectra (*m*/*z*; % relative intensity) were carried out on a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer equipped with SCOUT™ High Resolution Optics, an X-Y multi-sample probe and a gridless reflector. Ionization was accomplished with the 337 nm beam from a nitrogen laser with a repetition rate of 3 Hz. All data were acquired at a maximum accelerating potential of 20 kV in the linear positive ion mode. The output signal from the detector was digitized at a sampling rate of 1 GHz. A saturated solution of 1,8,9-trihydroxy-

anthracene (dithranol, ALDRICH, EC 214-538-0) in CH_2Cl_2 was used as a matrix. Typically, a 1:1 mixture of the sample solution in CH_2Cl_2 was mixed with the matrix solution and 0.5 μL of the resulting mixture was deposited on the probe tip. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg (France).

Compound 2: A solution of **1** (8.65 g, 32.79 mmol), 2,2-dimethyl-1,3-propanediol (6.83 g, 65.58 mmol), and *p*TosOH (200 mg) in C_6H_6 (300 mL) was refluxed for 48 h using a Dean–Stark trap. The solution was then cooled to room temperature, washed with water, dried ($MgSO_4$), and the solvents evaporated. Rapid filtration through SiO_2 (CH_2Cl_2/hexane, 1:1) yielded **2** (11.47 g, 97%). Colorless crystals (m.p. 62 °C). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.81 (s, 3 H), 1.27 (s, 3 H), 3.63 (d, J = 11 Hz, 2 H), 3.78 (d, J = 11 Hz, 2 H), 5.32 (s, 1 H), 7.60 (d, J = 2 Hz, 2 H), 7.65 (t, J = 2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.7, 22.9, 30.1, 77.4, 99.4, 122.6, 128.1, 134.1, 141.9 ppm. $C_{12}H_{14}Br_2O_2$ (350.05): calcd. C 41.17, H 4.03; found C 41.01, H 4.07.

Compound 3: A 1.5 M *t*BuLi solution in pentane (43 mL, 64.5 mmol) was added dropwise within 30 min to a solution of **2** (5.0 g, 14.29 mmol) in dry THF (180 mL) at –78 °C under Ar. The resulting mixture was stirred at –78 °C for 2 h, then warmed slowly to 0 °C (1 h) and cooled to –78 °C. DMF (4.4 mL, 57.18 mmol) was added and after 30 min at –78 °C, the mixture was warmed slowly to 0 °C. A 2 M aqueous HCl solution was then added. The THF was evaporated and Et_2O was added. The organic layer was washed with a 2 M aqueous HCl solution, then with water, dried ($MgSO_4$) and the solvents evaporated. Column chromatography on SiO_2 (CH_2Cl_2) yielded **3** (2.06 g, 58%). Colorless crystals (m.p. 104 °C). IR ($CHCl_3$): $\tilde{\nu}$ = 1707 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.85 (s, 3 H), 1.30 (s, 3 H), 3.71 (d, J = 11 Hz, 2 H), 3.83 (d, J = 11 Hz, 2 H), 5.54 (s, 1 H), 8.31 (d, J = 2 Hz, 2 H), 8.38 (t, J = 2 Hz, 1 H), 10.13 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.6, 22.9, 30.1, 77.5, 99.6, 130.4, 132.5, 136.9, 140.9, 190.7 ppm. $C_{14}H_{16}O_4$ (248.28): calcd. C 67.73, H 6.50; found C 67.56, H 6.52.

Compound 4: To a solution of **3** (1.50 g, 6.04 mmol) in CH_2Cl_2 (200 mL) at 0 °C was added dropwise over 30 min a 1 M solution of DIBAL-H in hexane (18 mL, 18 mmol). The resulting mixture was stirred for 2 h. MeOH was then carefully added until no further gas evolution was observed, then an aqueous saturated NH_4Cl solution until the mixture became thick and a white solid started to form. Additional CH_2Cl_2 was added, and the resulting mixture was filtered. The solid was washed with CH_2Cl_2, and the combined organic fractions were dried ($MgSO_4$) and evaporated to afford **4** (1.52 g, 97%). Colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.81 (s, 3 H), 1.30 (s, 3 H), 3.66 (d, J = 11 Hz, 2 H), 3.78 (d, J = 11 Hz, 2 H), 4.67 (d, J = 6 Hz, 4 H), 5.40 (s, 1 H), 7.33 (d, J = 2 Hz, 2 H), 7.41 (t, J = 2 Hz, 1 H) ppm. $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.99; found C 66.81, H 8.11.

Compound 6: DCC (2.58 g, 12.53 mmol) was added to a solution of **4** (1.47 g, 5.83 mmol), **5** (6.89 g, 12.23 mmol) and DMAP (214 mg, 1.75 mmol) in CH_2Cl_2 (150 mL) at 0 °C. After warming slowly to room temperature (over 1 h), the mixture was stirred for 18 h, then filtered and the solvents evaporated to dryness. Column chromatography on SiO_2 (CH_2Cl_2/hexane, 5:1) yielded **6** (5.63 g, 72%). Colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 1749 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.81 (s, 3 H), 0.89 (t, J = 6 Hz, 12 H), 1.27 (m, 72 H), 1.44 (s, 3 H), 1.76 (m, 8 H), 3.49 (s, 4 H), 3.64 (d, J = 11 Hz, 2 H), 3.77 (d, J = 11 Hz, 2 H), 3.91 (t, J = 6 Hz, 8 H), 5.10 (s, 4 H), 5.37 (s, 1 H), 6.40 (t, J = 2 Hz, 2 H), 6.47 (d, J = 2 Hz, 4 H), 7.33 (br. s, 1 H), 7.47 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 21.8, 22.6, 23.0, 26.0, 28.4, 29.2, 29.3, 29.35, 29.6, 30.1, 31.8, 41.3, 65.6, 66.6, 67.1, 67.9, 77.5, 100.8, 101.1, 106.3, 125.9, 128.3, 135.7, 137.2, 139.4, 160.4, 166.1 ppm. $C_{82}H_{132}O_{14}$ (1341.94): calcd. C 73.39, H 9.91; found C 73.36, H 10.04.

Compound 7: DBU (0.4 mL, 2.77 mmol) was added to a solution of C_{60} (400 mg, 0.555 mmol), **6** (745 mg, 0.555 mmol), and I_2 (352 mg, 1.387 mmol) in toluene (800 mL) at room temperature under Ar. The resulting mixture was stirred for 12 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and the solvents evaporated. Column chromatography on SiO_2 (CH_2Cl_2/hexane, 8:3) yielded **7** (548 mg, 48%). Dark orange-red glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1749 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 259, 323, 375 (sh), 437 (sh), 467 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (s, 3 H), 0.89 (t, J = 6.5 Hz, 12 H), 1.27 (m, 72 H), 1.31 (s, 3 H), 1.73 (m, 8 H), 3.75 (AB, J = 11 Hz, 4 H), 3.85 (t, J = 6.5 Hz, 8 H), 5.09 (d, J = 13 Hz, 2 H), 5.24 (d, J = 12 Hz, 2 H), 5.33 (d, J = 12 Hz, 2 H), 5.46 (s, 1 H), 5.84 (d, J = 13 Hz, 2 H), 6.36 (t, J = 2 Hz, 2 H), 6.47 (d, J = 2 Hz, 4 H), 7.42 (br. s, 2 H), 7.49 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 21.8, 22.7, 23.1, 26.1, 29.2, 29.3, 29.4, 29.6, 30.2, 31.9, 49.0, 66.8, 67.2, 68.0, 68.6, 70.5, 77.6, 100.6, 101.5, 107.0, 123.4, 124.0, 134.4, 135.7, 136.1, 136.5, 136.8, 137.8, 139.1, 140.0, 141.0, 141.1, 142.3, 142.7, 143.1, 143.5, 143.7, 143.9, 144.1, 144.3, 144.5, 144.9, 144.95, 145.1, 145.3, 145.5, 145.7, 146.0, 147.2, 147.4, 148.6, 160.3, 162.5 ppm. $C_{142}H_{128}O_{14}$ (2058.57): calcd. C 82.85, H 6.27; found C 82.92, H 6.34.

Compound 8: A mixture of **7** (1.20 g, 0.58 mmol), CH_2Cl_2 (60 mL), CF_3CO_2H (30 mL) and H_2O (30 mL) was vigorously stirred at room temperature for 4 h. The organic layer was then washed with H_2O, dried ($MgSO_4$) and the solvents evaporated. A rapid filtration through SiO_2 (CH_2Cl_2) yielded **8** (1.064 g, 93%). Dark orange-red glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1749, 1702 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 323, 374 (sh), 437 (sh), 465 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.5 Hz, 12 H), 1.27 (m, 72 H), 1.73 (m, 8 H), 3.87 (t, J = 6.5 Hz, 8 H), 5.14 (d, J = 13 Hz, 2 H), 5.25 (d, J = 12 Hz, 2 H), 5.36 (d, J = 12 Hz, 2 H), 5.88 (d, J = 13 Hz, 2 H), 6.38 (t, J = 2 Hz, 2 H), 6.49 (d, J = 2 Hz, 4 H), 7.79 (s, 3 H) ppm. MALDI-TOF MS: 1973 (MH^+, calcd. for $C_{137}H_{119}O_{13}$: 1973.44). $C_{137}H_{118}O_{13}$ (1972.44): calcd. C 83.43, H 6.03; found C 83.55, H 6.24.

Compound 11: A 0.48 M solution of $BF_3{\cdot}Et_2O$ in $CHCl_3$ (1 mL, 0.48 mmol) was added to a solution of **8** (1.45 g, 0.735 mmol), **9** (162 mg, 0.735 mmol), **10** (389 mg, 1.47 mmol) in $CHCl_3$ (146 mL) at room temperature under Ar. The resulting mixture was stirred for 12 h. *p*-Chloranil (540 mg, 2.20 mmol) was then added and the mixture refluxed for 1 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and the solvents evaporated. Two successive purification steps by column chromatography on SiO_2 (CH_2Cl_2/hexane, 7:4) yielded **11** (85 mg, 5%). Brown-red glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1750 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 323 (sh), 419, 514, 547, 590, 647 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.61 (br. s, 2 H), 0.87 (t, J = 7 Hz, 12 H), 0.89 (s, 3 H), 0.93 (s, 3 H), 1,10–1.40 (m, 72 H), 1.65 (m, 8 H), 1.80 (s, 6 H), 1.88 (s, 6 H), 2.61 (s, 3 H), 2.67 (s, 3 H), 3.81 (t, J = 6.5 Hz, 8 H), 3.87 (d, J = 11 Hz, 2 H), 3.98 (d, J = 11 Hz, 2 H), 5.30 (d, J = 12 Hz, 2 H), 5.37 (m, 4 H), 5.77 (s, 1 H), 6.02 (d, J = 12 Hz, 2 H), 6.33 (t, J = 2 Hz, 4 H), 6.50 (d, J = 2 Hz, 4 H), 7.31 (s, 2 H), 7.24 (s, 2 H), 7.93 (d, J = 8 Hz, 2 H), 7.96 (br. s, 1 H), 8.18 (d, J = 1 Hz, 2 H), 8.29 (d, J = 8 Hz, 2 H), 8.61 (d, J = 5 Hz, 1 H), 8.70 (d, J = 5 Hz, 1 H), 8.72 (d, J = 5 Hz, 1 H), 8.76 (d, J = 5 Hz, 1 H), 8.77 (d, J = 5 Hz, 1 H), 8.82 (d, J = 5 Hz, 1 H), 8.83 (d, J = 5 Hz, 1 H), 8.89 (d, J = 5 Hz, 1 H) ppm. MALDI-TOF MS: 2680 (MH^+, calcd. for $C_{186}H_{165}N_4O_{14}$: 2680.37).

Compound 12: A mixture of **11** (85 mg, 0.58 mmol), CH_2Cl_2 (5 mL), and CF_3CO_2H (5 mL) was stirred at room temperature. After 16 h, the mixture was poured into water (100 mL) and the excess of acid neutralized by adding a saturated aqueous solution of Na_2CO_3. The organic layer was then washed with H_2O, dried (Na_2SO_4) and the solvents evaporated. A rapid filtration through SiO_2 (hexane/CH_2Cl_2, 1:1) yielded **12** (74 mg, 90%). Brown-red glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1751, 1701 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 323 (sh), 420, 514, 548, 591, 647 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.61 (br. s, 2 H), 0.86 (t, J = 7 Hz, 12 H), 1.10–1.40 (m, 72 H), 1.65 (m, 8 H), 1.80 (s, 6 H), 1.87 (s, 6 H), 2.61 (s, 3 H), 2.65 (s, 3 H), 3.81 (t, J = 6.5 Hz, 8 H), 5.30 (d, J = 12 Hz, 2 H), 5.37 (m, 4 H), 6.01 (d, J = 12 Hz, 2 H), 6.32 (t, J = 2 Hz, 4 H), 6.50 (d, J = 2 Hz, 4 H), 7.24 (s, 2 H), 7.31 (s, 2 H), 7.98 (t, J = 1 Hz, 1 H), 8.19 (d, J = 1 Hz, 2 H), 8.30 (d, J = 7 Hz, 2 H), 8.44 (d, J = 7 Hz, 2 H), 8.62 (d, J = 5 Hz, 1 H), 8.74 (d, J = 5 Hz, 1 H), 8.75 (s, 2 H), 8.77 (d, J = 5 Hz, 1 H), 8.79 (d, J = 5 Hz, 1 H), 8.91 (d, J = 5 Hz, 1 H), 10.40 (s, 1 H) ppm. MALDI-TOF MS: 2594 (MH^+, calcd. for $C_{181}H_{154}N_4O_{13}$: 2594.24). $C_{181}H_{154}N_4O_{13}$ (2593.23): calcd. C 83.03, H 5.99; found C 87.74, H 6.25.

Compound 13: A mixture of **12** (74 mg, 0.028 mmol) and zinc acetate dihydrate (30 mg, 0.14 mmol) in $CHCl_3$/MeOH, 9:1 (5 mL) was refluxed for 2 h and the solvents evaporated. Column chromatography on SiO_2 (CH_2Cl_2/hexane, 5:4) yielded **13** (66 mg, 87%). Brown-red glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1749, 1702 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 257, 323 (sh), 420, 550, 587 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 12 H), 1.10–1.40 (m, 72 H), 1.68 (m, 8 H), 1.77 (s, 6 H), 1.88 (s, 6 H), 2.65 (s, 3 H), 2.66 (s, 3 H), 3.83 (t, J = 6.5 Hz, 8 H), 5.24 (d, J = 12 Hz, 2 H), 5.35 (d, J = 12 Hz, 2 H), 5.37 (d, J = 12 Hz, 2 H), 5.83 (d, J = 12 Hz, 2 H), 6.33 (t, J = 1.5 Hz, 4 H), 6.50 (d, J = 1.5 Hz, 4 H), 7.17 (s, 2 H), 7.31 (s, 2 H), 8.00 (s, 1 H), 8.11 (s, 2 H), 8.35 (d, J = 7 Hz, 2 H), 8.53 (d, J = 5 Hz, 1 H), 8.63 (d, J = 7 Hz, 2 H), 8.80 (d, J = 5 Hz, 1 H), 8.83 (d, J = 5 Hz, 1 H), 8.86 (d, J = 5 Hz, 1 H), 8.88 (d, J = 5 Hz, 1 H), 8.90 (d, J = 5 Hz, 1 H), 8.92 (m, 2 H), 10.37 (s, 1 H) ppm. MALDI-TOF MS: 2658 (MH^+, calcd. for $C_{181}H_{152}N_4O_{13}Zn$: 2657.60). $C_{181}H_{152}N_4O_{13}Zn$ (2656.60): calcd. C 81.83, H 5.77; found C 81.52, H 5.69.

Compound 21: As described for **11**, with **20** (830 mg, 0.796 mmol), **9** (175 mg, 0.796 mmol) and **10** (421 mg, 1.59 mmol). Four successive purification steps by column chromatography on SiO_2 (CH_2Cl_2/hexane, 6:4) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **21** (231 mg, 17%). Purple glassy compound. UV/Vis (CH_2Cl_2): λ_{max} = 248, 306, 352, 418, 429, 515, 551, 590, 647 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.38 (br. s, 2 H), 0.97 (s, 3 H), 1.54 (s, 3 H), 1.63 (s, 18 H), 1.66 (s, 36 H), 2.00 (s, 12 H), 2.74 (s, 6 H), 3.90 (d, J = 11 Hz, 2 H), 4.03 (d, J = 11 Hz, 2 H), 5.80 (s, 1 H), 7.41 (s, 4 H), 7.90 (t, J = 2 Hz, 1 H), 7.93 (t, J = 2 Hz, 2 H), 7.99 (d, J = 8 Hz, 2 H), 8.22 (d, J = 2 Hz, 2 H), 8.27 (d, J = 2 Hz, 4 H), 8.37 (d, J = 8 Hz, 2 H), 8.73 (s, 4 H), 8.82 (d, J = 5 Hz, 2 H), 8.93 (d, J = 5 Hz, 2 H), 8.98 (d, J = 5 Hz, 2 H), 9.15 (d, J = 5 Hz, 2 H), 9.18 (d, J = 5 Hz, 2 H), 9.28 (d, J = 5 Hz, 2 H), 9.38 (d, J = 5 Hz, 2 H), 9.49 (d, J = 5 Hz, 2 H) ppm.

Compound 22: As described for **12**, with **21** (230 mg, 0.132 mmol). Column chromatography on SiO_2 (CH_2Cl_2/hexane, 6:4) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **22** (211 mg, 93%). Purple glassy compound. UV/Vis (CH_2Cl_2): λ_{max} = 250, 306, 352, 418, 430, 515, 550, 590, 648 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.53 (br. s, 2 H), –2.45 (br. s, 2 H), 1.55 (s, 18 H), 1.58 (s, 36 H), 1.93 (s, 12 H), 2.68 (s, 6 H), 7.35 (s, 4 H), 7.82 (t, J = 2 Hz, 1 H), 7.85 (t, J = 2 Hz, 2 H), 8.12 (d, J = 2 Hz, 2 H), 8.18 (d, J = 2 Hz, 4 H), 8.31 (d, J = 8 Hz, 2 H), 8.46 (d, J = 8 Hz, 2 H), 8.64 (s, 4 H), 8.78 (s, 4 H), 8.90 (d, J = 5 Hz, 2 H), 8.95 (d, J = 5 Hz, 2 H), 8.98 (d, J = 5 Hz, 2 H), 9.08 (d, J = 5 Hz, 2 H), 9.28 (d, J = 5 Hz, 2 H), 9.29 (d, J = 5 Hz, 2 H), 10.41 (s, 1 H) ppm. MALDI-TOF MS: 1601 (MH^+, calcd. for $C_{113}H_{115}N_8O$: 1601.21).

Compound 23: As described for **13**, with **22** (210 mg, 0.132 mmol) and zinc acetate dihydrate (480 mg, 2.19 mmol). Column chromatography on SiO_2 (CH_2Cl_2/hexane, 6:4) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **23** (228 mg, 99%). Purple glassy compound. UV/Vis (CH_2Cl_2): λ_{max} = 250, 308, 349 (sh), 418, 431, 550, 590 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 18 H), 1.59 (s, 36 H), 1.92 (s, 12 H), 2.69 (s, 6 H), 7.35 (s, 4 H), 7.83 (t, J = 2 Hz, 1 H), 7.86 (t, J = 2 Hz, 2 H), 8.14 (d, J = 2 Hz, 2 H), 8.20 (d, J = 2 Hz, 4 H), 8.29 (d, J = 8 Hz, 2 H), 8.48 (d, J = 8 Hz, 2 H), 8.65 (s, 4 H), 8.87 (s, 4 H), 9.00 (d, J = 5 Hz, 2 H), 9.07 (d, J = 5 Hz, 2 H), 9.09 (d, J = 5 Hz, 2 H), 9.20 (d, J = 5 Hz, 2 H), 9.40 (d, J = 5 Hz, 2 H), 9.43 (d, J = 5 Hz, 2 H), 10.38 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 21.7, 31.75, 31.8, 35.05, 35.1, 118.4, 119.8, 120.5, 120.7, 120.8, 122.6, 122.7, 127.8, 127.9, 129.6, 129.8, 131.2, 131.3, 131.8, 132.3, 132.35, 132.3, 132.5, 132.6, 132.65, 132.7, 132.8, 135.1, 135.4, 137.6, 138.9, 139.3, 141.8, 141.9, 142.3, 148.6, 148.65, 149.4, 149.5, 150.0, 150.2, 150.3, 150.4, 150.5, 150.6, 192.5 ppm. MALDI-TOF MS: 1727 (M^+, calcd. for $C_{113}H_{110}N_8OZn_2$: 1726.92). $C_{113}H_{110}N_8OZn_2$ (1726.92): calcd. C 78.59, H 6.42; found C 78.25, H 6.66.

Compound 24: As described for **11**, with **23** (39 mg, 0.022 mmol) and pyrrole (0.022 mmol). Two successive purification steps by column chromatography on SiO_2 (CH_2Cl_2/hexane, 4:5) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **24** (8 mg, 20%). Purple glassy compound. UV/Vis (CH_2Cl_2): λ_{max} = 248, 306, 352, 420, 439, 516, 551, 592, 648 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = –2.49 (br. s, 2 H), 1.58 (s, 72 H), 1.62 (s, 144 H), 2.09 (s, 48 H), 2.81 (s, 24 H), 7.48 (s, 16 H), 7.84 (t, J = 1.5 Hz, 4 H), 7.89 (t, J = 1.5 Hz, 8 H), 8.16 (d, J = 1.5 Hz, 8 H), 8.23 (m, 16 H), 8.71 (d, J = 8 Hz, 8 H), 8.74 (d, J = 8 Hz, 8 H), 8.88 (d, J = 8 Hz, 8 H), 8.92 (d, J = 8 Hz, 8 H), 9.09 (d, J = 5 Hz, 8 H), 9.11 (d, J = 5 Hz, 16 H), 9.16 (d, J = 5 Hz, 8 H), 9.24 (d, J = 5 Hz, 8 H), 9.48 (d, J = 5 Hz, 8 H), 9.71 (s, 8 H), 9.49 (d, J = 5 Hz, 8 H), 9.56 (d, J = 5 Hz, 8 H) ppm. MALDI-TOF MS: 7098 (M^+, calcd. for $C_{468}H_{446}N_{36}Zn_8$: 7097.97).

Compound 25: As described for **13**, with **24** (7 mg, 0.001 mmol) and zinc acetate dihydrate (3 mg, 0.014 mmol). Column chromatography on SiO_2 (CH_2Cl_2/hexane, 4:5) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **25** (5.5 mg, 78%). Purple glassy compound. UV/Vis (CH_2Cl_2): λ_{max} = 250, 308, 349 (sh), 420, 439, 551, 592 nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 72 H), 1.61 (s, 144 H), 2.09 (s, 48 H), 2.81 (s, 24 H), 7.48 (s, 16 H), 7.84 (t, J = 1.5 Hz, 4 H), 7.83 (t, J = 1.5 Hz, 8 H), 8.16 (d, J = 1.5 Hz, 8 H), 8.27 (d, J = 1.5 Hz, 16 H), 8.71 (d, J = 8 Hz, 8 H), 8.74 (d, J = 8 Hz, 8 H), 8.88 (d, J = 8 Hz, 8 H), 8.92 (d, J = 8 Hz, 8 H), 9.09 (d, J = 5 Hz, 8 H), 9.11 (m, 24 H), 9.17 (d, J = 5 Hz, 8 H), 9.24 (d, J = 5 Hz, 8 H), 9.49 (m, 16 H), 9.59 (d, J = 5 Hz, 8 H), 9.82 (s, 8 H) ppm. MALDI-TOF MS: 7161 (M^+, calcd. for $C_{468}H_{444}N_{36}Zn_9$: 7161.33). $C_{468}H_{444}N_{36}Zn_9$ (7161.33): calcd. C 78.49, H 6.25; found C 78.11, H 6.56.

Compound 26: As described for **11**, with **13** (66 mg, 0.025 mmol) and pyrrole (0.025 mmol). Two successive purification steps by column chromatography on SiO_2 (CH_2Cl_2/hexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **26** (38 mg, 57%). Brown-red glassy compound. IR (KBr):

$\tilde{\nu}$ = 1752 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 258, 325 (sh), 420, 434, 514, 548, 591, 647 nm. ^1H NMR (300 MHz, 373 K, $CDCl_2CDCl_2$): δ = –2.45 (br. s, 2 H), 0.95 (t, J = 7 Hz, 48 H), 1.20–1.40 (m, 288 H), 1.77 (m, 32 H), 2.04 (s, 24 H), 2.11 (s, 24 H), 2.80 (s, 12 H), 2.83 (s, 12 H), 3.95 (t, J = 6.5 Hz, 32 H), 5.45 (m, 16 H), 5.59 (d, J = 13 Hz, 8 H), 6.10 (d, J = 13 Hz, 8 H), 6.45 (t, J = 2 Hz, 8 H), 6.61 (d, J = 2 Hz, 16 H), 7.43 (s, 8 H), 7.48 (s, 8 H), 8.11 (s, 4 H), 8.37 (s, 8 H), 8.89 (br. s, 32 H), 9.03 (d, J = 4 Hz, 8 H), 9.13 (d, J = 5 Hz, 4 H), 9.17 (d, J = 5 Hz, 4 H), 9.55 (d, J = 4 Hz, 4 H), 9.69 (s, 4 H) ppm. MALDI-TOF MS: 10816 (M^+, calcd. for $C_{740}H_{614}N_{20}O_{48}Zn_4$: 10816.35).

Compound 27: As described for **13**, with **26** (32 mg, 0.003 mmol) and zinc acetate dihydrate (5 mg, 0.023 mmol). Column chromatography on SiO_2 (CH_2Cl_2/hexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX-1, toluene) yielded **27** (27 mg, 82%). Brown-red glassy compound. IR (KBr): $\tilde{\nu}$ = 1750 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 258, 325 (sh), 421, 436, 551, 592 nm. ^1H NMR (500 MHz, 381 K, $CDCl_2CDCl_2$): δ = 0.96 (t, J = 7 Hz, 48 H), 1.20–1.40 (m, 256 H), 1.46 (m, 32 H), 1.77 (m, 32 H), 2.05 (s, 24 H), 2.12 (s, 24 H), 2.80 (s, 12 H), 2.84 (s, 12 H), 3.96 (t, J = 6.5 Hz, 32 H), 5.45 (AB, J = 12 Hz, 16 H), 5.60 (d, J = 13 Hz, 8 H), 6.10 (d, J = 13 Hz, 8 H), 6.45 (s, 8 H), 6.62 (s, 16 H), 7.44 (s, 8 H), 7.49 (s, 8 H), 8.11 (s, 4 H), 8.38 (s, 8 H), 8.88 (m, 12 H), 8.93 (d, J = 7 Hz, 8 H), 9.04 (d, J = 4 Hz, 8 H), 9.14 (d, J = 4 Hz, 4 H), 9.16 (d, J = 4 Hz, 4 H), 9.19 (d, J = 4 Hz, 4 H), 9.59 (d, J = 4 Hz, 8 H), 9.82 (s, 8 H) ppm. MALDI-TOF MS: 10880.1 (M^+, calcd. for $C_{740}H_{612}N_{20}O_{48}Zn_5$: 10880.26). $C_{740}H_{612}N_{20}O_{48}Zn_5$ (10880.26): calcd. C 81.69, H 5.67; found C 81.67, H 5.69.

Crystal Structure Determination of 18: The dark purple-red crystal used for the diffraction study was produced by slow diffusion of hexane into a $CHCl_3$ solution of **18**. Data for crystal structure analysis were collected at 173 K on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[18] and refined against F^2 using the SHELXL-97 software.[19] The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as ridig atoms using SHELXL default parameters. Crystallographic data: formula: $C_{88}H_{120}N_4Zn$ (M = 1299.25 g·mol^{-1}); crystal system: triclinic; space group $P\bar{1}$; a = 9.4155(3) Å; b = 14.0964(7) Å; c = 15.4806(7) Å; α = 90.304(2)°; β = 94.869(2)°; γ = 104.485(2)°; V = 1981.42(15) Å^3; Z = 1; F(000) = 706; a total of 19200 reflections collected; 1.32° < θ < 27.50°, 9053 independent reflections with 6263 having $I > 2\sigma(I)$; 427 parameters; Final results: $R_1(F^2)$ = 0.0867; $wR_2(F^2)$ = 0.2550, Goof = 1.057.

CCDC-725947 (for **18**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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