Synthesis and spectral properties of mixed *meso*-metallocenylporphyrins

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A series of mixed porphyrins with different numbers of metallocenyl (ferrocenyl and cymantrenyl) and aryl (Ph and C_6F_5) groups at the *meso*-positions was obtained and characterized by ^1H NMR, electronic absorption, and mass spectra. The downfield shift of NH signals as well as the bathochromic shift of *Q*-bands can be attributed to a distortion of the porphyrin macrocycle upon the introduction of bulky *meso*-substituents.

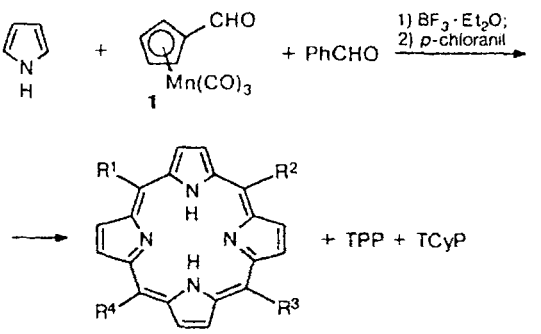
Key words: porphyrins, *meso*-metallocenylporphyrins; cymantrene, ferrocene, dipyrrolylmethanes; electronic absorption and ^1H NMR spectra.

Porphyrins containing fragments of sandwich compounds of transition metals, mainly metallocenes, have steadily attracted the attention of scientists.[1–6] Due to the specific geometric structure and reactivity of metallocenes, porphyrins of this type are promising objects for the synthesis of porphyrin-based systems with practically useful properties. Recently, we obtained the first representatives of a new class of metallocenylporphyrins, in which the organometallic substituent is directly linked to the macroheterocycle frame, namely, *meso*-tetracymantrenylporphyrin (TCyP, where Cy = $(CO)_3MnC_5H_4$), *meso*-tetraferrocenylporphyrin (TFcP, where Fc = $C_5H_5FeC_5H_4$), and *meso*-tetraruthenocenylporphyrin (TRcP, where Rc = $C_5H_5RuC_5H_4$).[7–9] The present paper describes the synthesis and spectroscopic properties of metallocenylporphyrins of mixed type containing various metallocenyl and aryl groups at *meso*-positions.

The condensation of pyrrole with an equimolecular mixture of formylcymantrene (**1**) and benzaldehyde catalyzed by $BF_3 \cdot Et_2O$ (Scheme 1) results in a mixture of six substituted porphyrins in 35% overall yield, which are observed as partially overlapping zones upon analytical chromatography of the reaction products on Silufol plates (ethyl acetate—hexane—Et_3N, 60 : 40 : 1).

The upper (easily eluted) and lower zones are tetraphenylporphyrin (TPP) and TCyP, respectively. According to electronic absorption and ^1H NMR spectra, the intermediate zone contains four mixed-type substituted porphyrins, which we were unable to separate chromatographically to individual components. However, an analysis of the ^1H NMR spectra of the intermediate zone and its separate fractions enriched with metallocenylporphyrins of various structures indicates that the reaction produces, along with TPP and TCyP, tricymantrenylphenyl- (**2**), 5,15-diphenyl-10,20-dicymantrenyl- (**3**), 5,10-diphenyl-15,20-dicymantrenyl- (**4**), and cymantrenyltriphenylporphyrins (**5**) in the ratio 1.3 : 3.1 : 1.0 : 1.6. The chemical shifts of NH protons for these compounds are −1.78, −2.15, −2.22, and −2.48 ppm, respectively.

Scheme 1



2–5

2: R^1 = Ph; R^2, R^3, R^4 = Cy **4**: R^1, R^2 = Ph; R^3, R^4 = Cy
3: R^1, R^3 = Ph; R^2, R^4 = Cy **5**: R^1, R^2, R^3 = Ph; R^4 = Cy

An analogous reaction of equimolecular amounts of compound **1** and pentafluorobenzaldehyde with pyrrole also occurs unselectively and gives a difficultly separable mixture of five porphyrins (overall yield 28%): four mixed-type metallocenylporphyrins and tetrakis(pentafluorophenyl)porphyrin (TPFPP). However, a different ratio of analogs of compounds **2–5** containing perfluorophenyl groups instead of phenyls is observed in this case, namely, 2.0 : 1.0 : 3.4 : 3.2. The chemical shifts of NH protons for these compounds are −1.83, −2.14, −2.30, and −2.61 ppm, respectively.

It could be expected that the method of synthesis of mixed porphyrins by the condensation of aldehydes with dipyrrolylmethanes in the presence of $BF_3 \cdot Et_2O$ would be more selective. Using this approach, we obtained the

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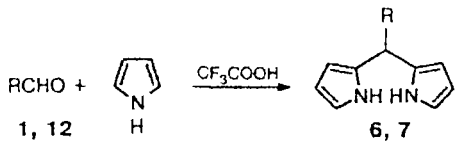
hitherto unknown cymantrenyldipyrrolyl- (**6**) and ferrocenyldipyrrolylmethanes (**7**) (Scheme 2), which were found to be stable even on prolonged storage.

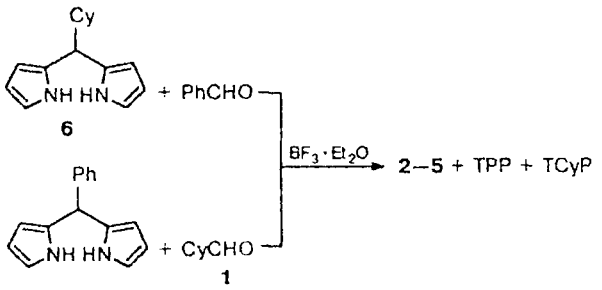
Scheme 2



1: R = Cy **6**: R = Cy
12: R = Fc **7**: R = Fc

However, the reaction of benzaldehyde with compound **6**, as well as the reaction of aldehyde **1** with dipyrrolyl(phenyl)methane, also results in a mixture of porphyrins **2**—**5**, along with TPP and TCyP (Scheme 3). In both cases, the ratio of mixture components are close and similar to the above ratio of the products of condensation of pyrrole with an equimolecular mixture of aldehydes.

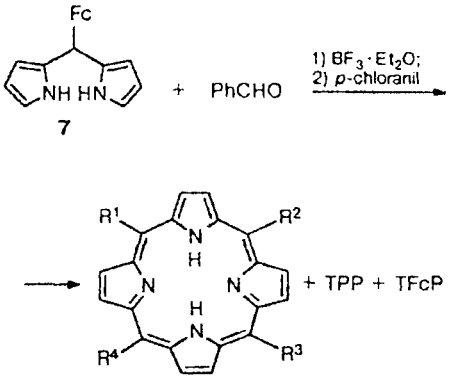
Scheme 3



An even lower selectivity is observed in the formation of porphyrins from benzaldehyde and compound **7** (Scheme 4). The ratio of yields of TFcP, triferrocenylphenyl- (**8**), 10,20-diferrocenyl-5,15-diphenyl- (**9**), 15,20-diferrocenyl-5,10-diphenyl- (**10**), ferrocenyltriphenyl- porphyrins (**11**), and TPP is 1.0 : 4.8 : 3.0 : 4.2 : 3.6 : 1.0 (overall yield 33%). Although we were unable to perform the preparative separation of porphyrins **8**—**11**, individual compounds **8** and **11** and a mixture of isomers **9** and **10** were isolated by TLC.

The reactions of dipyrrolyl(metallocenyl)methanes **6** and **7** with formylferrocene (**12**) and aldehyde **1**, respectively, were more successful in terms of obtaining mixed metallocenylporphyrins. These reactions occur more selectively, and the products formed can easily be separated by column chromatography. For example, the reaction of compound **6** with aldehyde **12** in CH_2Cl_2 in the presence of $BF_3 \cdot Et_2O$ gives preferentially 5,10-dicymantrenyl-15,20-diferrocenylporphyrin (**13**). The ratio of yields of TCyP, TFcP, compound **13**, tricymantrenylferrocenyl- (**14**), 5,15-dicymantrenyl-10,20-diferrocenyl- (**15**), and cymantrenyltriferrocenylporphyrins (**16**) is 0.5 : 1.0 : 26.0 : 6.0 : 12.0 : 13.0 (Scheme 5). Under the same conditions, the reaction of dipyrrolylmethane **7** with aldehyde **1** gives a mixture of TFcP and compounds **13**, **15**, and **16** enriched with the latter porphyrin; the ratio of the components is 6 : 1 : 5 : 20. A similar product ratio was obtained in the reaction of compound **7** with aldehyde **1** in MeCN catalyzed by CCl_3COOH. However, loss of selectivity is observed when this reaction is carried out in CH_2Cl_2. Conversely, the CCl_3COOH-catalyzed reaction of

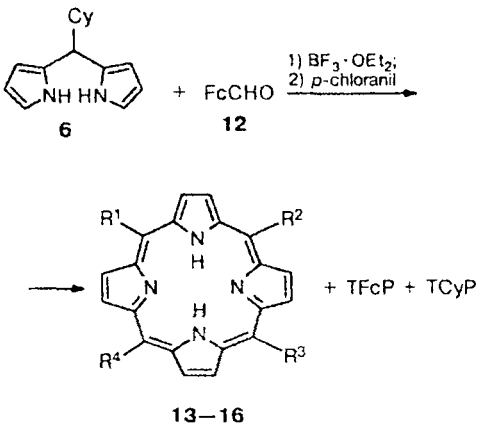
Scheme 4



8—**11**

8: R^1 = Ph; R^2, R^3, R^4 = Fc **10**: R^1, R^2 = Ph; R^3, R^4 = Fc
9: R^1, R^3 = Ph; R^2, R^4 = Fc **11**: R^1, R^2, R^3 = Ph; R^4 = Fc

Scheme 5



13—**16**

13: R^1, R^2 = Cy; R^3, R^4 = Fc **15**: R^1, R^3 = Cy; R^2, R^4 = Fc
14: R^1, R^2, R^3 = Cy; R^4 = Fc **16**: R^1, R^2, R^3 = Fc; R^4 = Cy

dipyrrolylmethane **6** with aldehyde **12** both in MeCN and in CH_2Cl_2 occurs with high selectivity and results almost exclusively in symmetrical 5,15-dicymantrenyl-10,20-diferrocenylporphyrin (**15**) in 9—11% yield.

The formation of mixtures of porphyrin with different structures in the condensation of aldehydes with dipyrrolylmethanes is usually explained by the acidic cleavage of the latter to the original fragments followed by statistical condensation.[10] However, we found that porphyrins are not formed in noticeable amounts on treatment of solutions of compounds **6** and **7** with $BF_3 \cdot Et_2O$, both in anhydrous and moist CH_2Cl_2, followed by the addition of *p*-chloranil. Furthermore, the addition of a strong hydride ion donor, $HSiEt_3$, to a solution of dipyrrolylmethane **6** or **7** in a CF_3COOH—$CHCl_3$ mixture, *i.e.*, the creation of conditions of ionic hydrogenation,[11] does not result in products of reduction of the previously assumed cationic intermediates,[10] at least within one day. Hence, either intermediates of higher degree of condensation than dipyrrolylmethanes mostly undergo cleavage into low-molecular components, as suggested by results[10] on the synthesis of tetraarylporphyrins with four different aryl groups, or the formation of low-molecular-weight components occurs by a different, possibly more complicated, mechanism.

The preferential formation of cymantrenyltriferrocenylporphyrin **16** in the reaction of dipyrrolylmethane **7** with aldehyde **1** in the presence of $BF_3 \cdot Et_2O$ made it possible to hope for a selective synthesis of this porphyrin under the same conditions by statistical condensation of pyrrole with formylcymantrene **1** in the presence of an excess of aldehyde **12**. In fact, the reaction of pyrrole with compounds **1** and **12** at a 4 : 1 : 3 ratio of the components, respectively, gives porphyrin **16** in 20% yield. However, in addition to compound **16**, the products also contained a mixture of dicymantrenyldiferrocenylporphyrins (10%), in which the content of *cis*-isomer **13** was *ca.* 90%, and even tricymantrenylferrocenylporphyrin **14** (2%). On the other hand, the yield of TFcP did not exceed 1%. Hence, the use of $BF_3 \cdot Et_2O$ as a catalyst favors the formation of porphyrins with cymantrenyl groups.

The series of mixed porphyrins that we obtained made it possible to find for the first time the effect of the number of bulky *meso*-substituents, in this case metallocenyl groups, on the parameters of NMR and electronic absorption spectra.

The transition from TPP to metallocenylporphyrins TCyP,[8] TRcP,[7] and TFcP,[7] as well as from TPFPP[12] to TCyP, is accompanied by a bathochromic shift of all absorption bands of the porphyrin chromophore in the electronic absorption spectra. In particular, the first long-wave *Q*-band for TPP (649 nm) is shifted by 40, 50, and 81 nm on the transition to TCyP (689 nm), TRcP (699 nm), and TFcP (730 nm), respectively. In the latter case, successive replacement of Ph groups in TPP with Fc fragments results in a gradual decrease in the effect of the metallocenyl *meso*-substituent on the shift of λ_{max} of this band. Such a significant bathochromic shift of the absorption bands of the porphyrin chromophore is usually due either to the expansion of the conjugated bond system[13—16] or to the distortion of the porphyrin cycle plane.[17—19] Since, due to steric reasons, *meso*-metallocenyl groups cannot be arranged at positions providing an efficient interaction with the π-system of the aromatic macroheterocycle, the observed spectral characteristics of metallocenylporphyrins are probably caused by distortion of the porphyrin cycle plane.

In parallel with an increase in the bathochromic shift of absorption bands of the porphyrin chromophore, the transition from TPP and TPFPP to metallocenylporphyrins is accompanied by a downfield shift of NH proton signals in the ^1H NMR spectra. The mean shift Δδ per replacement of one Ph group in TPP (δ NH −2.69) with an Fc or Cy moiety is 0.54 or 0.32 ppm, respectively.[7,8] Since the electronic nature of *meso*-substituents only slightly affects the position of signals of NH protons in the ^1H NMR spectra of aryl- and alkylporphyrins,[10,20,21] the strong downfield shift δ NH in the cases presented above is obviously also caused by a distortion of the porphyrin macrocycle on introduction of bulky metallocenyl fragments at the *meso*-positions of the macrocycle. A consequence of distortion of the porphyrin cycle is a decrease in the ring current in the conjugated system and in magnetic shielding of imine protons.

A similar spectral pattern is observed in the series of mixed porphyrins **13—16** containing two different metallocenyl groups. On transition from TCyP (δ NH −1.34)[8] to TFcP (δ NH −0.45),[7] successive replacement of $(CO)_3MnC_5H_4$ with $C_5H_5FeC_5H_4$ fragments, which make larger demands for space on their environment, results in an overall bathochromic shift of the NH signal by 0.9 ppm. On the other hand, the positions of proton signals of the cyclopentadienyl rings of the corresponding organometallic fragments in the ^1H NMR spectra of TCyP,[8] TFcP,[7] and compounds **13—16** virtually do not change, despite the considerable difference in the nature of electronic effects of these substituents. The increase in the number of ferrocenyl groups on transition from TCyP to TFcP is accompanied by a bathochromic shift of the *Q*-bands in the electronic absorption spectra, which also indicates an increase in the porphyrin cycle distortion upon replacement of Cy groups in TCyP with Fc ones. However, the difference in the electronic structures of these substituents manifests itself distinctly in the shift of the Soret band on transition from TCyP to TFcP. In contrast to the bathochromic shift of the *Q*-bands, the Soret band shifts to higher energies.

Thus, the data presented above show that the downfield shift of the signals of NH protons in the ^1H NMR spectra, as well as the bathochromic shift of the *Q*-bands in the electronic absorption spectra, can reflect the degree of distortion of the macrocycle plane

in porphyrins. This is also confirmed by some examples from the literature.[13,21–23] In the case of *meso*-metallocenylporphyrins, the degree of distortion increases in the series: cymantrene < ruthenocene < ferrocene.

The following facts provide additional confirmations of the conclusion that the porphyrin plane is deformed on the introduction of metallocenyl groups at *meso*-positions. As noted above, successive replacement of Ph groups in TPP with Fc and Cy fragments results in a gradual downfield shift of the NH signal in the ^{1}H NMR spectra. On the other hand, the introduction of one Fc or Cy fragment causes a downfield shift of the signal of β-protons closest to the metallocenyl group by 1.1 and 0.7 ppm, respectively, in the region characteristic of pyrrolic β-protons of the macrocycle. However, a further increase in the number of metallocenyl groups shifts the signals of these protons upfield. It appears difficult to explain the observed pattern in terms of electronic effects of the substituents.

It is known[24] that the distortion of the macrocycle plane increases both the acidity of NH protons and the basicity of N atoms of the porphyrin C_4H_2N fragments. Hence, it could be expected that the retention time of metallocenylporphyrins upon chromatography on both Al_2O_3 and SiO_2 would increase in the series TPP < TCyP < TRcP < TFcP. In fact, the R_f values for this porphyrin series mostly decrease in the anticipated order. For example, they are 0.88, 0.85, 0.11, and 0.15, respectively, on Al_2O_3 (Alufol, benzene).

Experimental

^{1}H NMR spectra were recorded on Bruker WP-200 SY and Bruker 400 HX spectrometers in $CDCl_3$ using $SiMe_4$ as the internal standard. Mass spectra were obtained on a Kratos MS-890 instrument (EI, ionizing voltage 70 eV; fast atoms bombardment spectra (FAB) in a *p*-nitrobenzyl alcohol matrix). Electronic absorption spectra (EAS) were recorded on a Specord UV-VIS spectrophotometer. The reactions were monitored by TLC on Silufol UV-254 and Alufol plates, as well as by electronic absorption spectra.

Synthesis of dipyrrolylmetallocenylmethanes (general procedure). A mixture of metallocenecarbaldehyde (5 mmol) and freshly distilled pyrrole (200 mmol) was stirred for 10 min in a stream of argon on a magnetic stirrer. CF_3COOH (0.5 mmol) was added, and the reaction was carried out until the aldehyde disappeared completely (30 min). The reaction mixture was then diluted with CH_2Cl_2, treated with 0.1 *N* aqueous NaOH to a neutral pH, washed with water, extracted with CH_2Cl_2, and dried with $MgSO_4$. The reaction product was crystallized from hexane by adding a small amount of benzene.

Dipyrrolylcymantrenylmethane (6). The raw product (1.5 g, yield 86%) was obtained as light-yellow crystals, m.p. 80–81 °C. MS (EI), *m/z*: 348 $[M]^+$. ^{1}H NMR, δ: 4.43 (m, 2 H, Cp); 4.51 (m, 2 H, Cp); 4.79 (s, 1 H, CH); 5.92 (m, 2 H, Pyrr); 6.10 (m, 2 H, Pyrr); 6.38 (m, 2 H, Pyrr); 7.64 (br.s, 2 H, NH). Found (%): C, 58.73; H, 4.0; Mn, 15.71; N, 8.24. $C_{17}H_{13}MnN_2O_3$. Calculated (%): C, 58.63; H, 3.76; Mn, 15.78; N, 8.04.

Dipyrrolylferrocenylmethane (7). The product (1.15 g, yield 70%) was obtained as orange-yellow crystals, m.p. 154–155 °C. MS (EI), *m/z*: 330 $[M]^+$. ^{1}H NMR, δ: 4.06 (m, 2 H, Cp); 4.08 (s, 5 H, CpH); 4.15 (m, 2 H, Cp); 5.19 (s, 1 H, CH); 6.00 (m, 2 H, Pyrr); 6.14 (m, 2 H, Pyrr); 6.64 (m, 2 H, Pyrr); 7.89 (br.s, 2 H, NH). Found (%): C, 68.69; H, 6.03; Fe, 16.98. $C_{19}H_{18}FeN_2$. Calculated (%): C, 69.11; H, 5.49; Fe, 16.91.

Synthesis of *meso*-metallocenylporphyrins from a mixture of aldehydes (general procedure). Freshly distilled pyrrole (2.8 mmol) was added in the dark in a stream of Ar to a solution of cymantrene- or ferrocenecarbaldehyde (1.4 mmol) and benzaldehyde or pentafluorobenzaldehyde (1.4 mmol) in anhydrous CH_2Cl_2 (150 mL), and the mixture was stirred on a magnetic stirrer for 20 min at ~20 °C. A solution of $BF_3 \cdot Et_2O$ (0.14 mmol) in CH_2Cl_2 was added, and stirring was continued for ~20 h. The porphyrinogens that formed were oxidized with *p*-chloranil (2 mmol) with refluxing for 2 h. The reaction mixture was filtered, neutralized with Et_3N, and concentrated. The isolation and additional purification of the porphyrins that formed were performed by column chromatography on SiO_2 (100–200 mesh; benzene or toluene as the eluents) followed by reprecipitation with pentane or hexane from concentrated solutions in $CHCl_3$.

In a similar way, porphyrins were synthesized from a mixture of cymantrene- or ferrocenecarbaldehydes with pyrrole at a molar ratio of the reagents 1.4 : 4.2 : 6.0, respectively.

Synthesis of mixed porphyrins from dipyrrolylmethanes (general procedure). A mixture of phenyldipyrrolyl-, cymantrenyldipyrrolyl-, or ferrocenyldipyrrolylmethane (3 mmol) and the required aldehyde (300 mL) in anhydrous CH_2Cl_2 or MeCN (200 mL) was stirred for 20 min on a magnetic stirrer at ~20 °C in a stream of argon. $BF_3 \cdot Et_2O$ or CCl_3COOH (0.15 mmol) was then added, and the mixture was stirred for 20 h in the dark in a stream of argon. *p*-Chloranil (9.3 mmol) was then added, and the mixture was stirred for an additional ~6 h. When CCl_3COOH was used as the catalyst, the reaction mixture was treated with 1 *N* HCl (100 mL), neutralized with a 10% solution of Na_2CO_3 (100 mL), washed with water, and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$.

The isolated individual porphyrins and their mixtures are nonmelting dark powders of various hues: compounds **2**–**5** and **8**–**11** are violet-green, while compounds **13**–**16** are dark-green.

5,10,15-Tricymantrenyl-20-phenylporphyrin (2). ^{1}H NMR, δ: −1.78 (s, 2 H, NH); 5.24 (m, 6 H, Cp); 5.81 (m, 6 H, Cp); 7.74 (m, 3 H, Ph); 8.15 (m, 2 H, Ph); 8.72 (d, 2 H, H(2), H(18), J = 4.7 Hz); 9.47 (d, 2 H, H(3), H(17), J = 4.8 Hz); 9.61 (s, 4 H, H(7), H(8), H(12), H(13)).

10,20-Dicymantrenyl-5,15-diphenylporphyrin (3). ^{1}H NMR, δ: −2.15 (s, 2 H, NH); 5.27 (m, 4 H, Cp); 5.88 (m, 4 H, Cp); 7.76 (m, 6 H, Ph); 8.18 (m, 4 H, Ph); 8.80 (d, 4 H, H(3), H(7), H(13), H(17), J = 4.8 Hz); 9.58 (d, 4 H, H(2), H(8), H(12), H(18), J = 4.8 Hz).

15,20-Dicymantrenyl-5,10-diphenylporphyrin (4). ^{1}H NMR, δ: −2.22 (s, 2 H, NH); 5.26 (m, 4 H, Cp); 5.86 (m, 4 H, Cp); 7.76 (m, 6 H, Ph); 8.10 (m, 4 H, Ph); 8.77 (s, 2 H, H(7), H(8)); 8.88 (d, 2 H, H(3), H(12), J = 4.6 Hz); 9.68 (d, 2 H, H(2), H(13), J = 4.5 Hz); 9.68 (s, 2 H, H(17), H(18)).

20-Cymantrenyl-5,10,15-triphenylporphyrin (5). ^{1}H NMR, δ: −2.48 (s, 2 H, NH); 5.26 (m, 2 H, Cp); 5.83 (m, 2 H, Cp); 7.75 (m, 9 H, Ph); 8.12 (m, 6 H, Ph); 8.70 (s, 4 H, H(7), H(8), H(12), H(13)); 8.76 (d, 2 H, H(3), H(17), J = 4.7 Hz); 9.68 (d, 2 H, H(2), H(18), J = 4.6 Hz). EAS (CH_2Cl_2) for a mixture of compounds **2**–**5**, λ_{max}/nm (A_{rel}): 434 (13.7), 530 (2.7), 575 (1.8), 606 (1.5), 667 (1).

5,10,15-Triferrocenyl-20-phenylporphyrin (8). ^{1}H NMR, δ: −1.1 (s, 2 H, NH); 3.95 (s, 15 H, CpH); 4.72 (m, 6 H, Cp); 5.36 (m, 6 H, Cp); 7.75 (m, 3 H, Ph); 8.19 (m, 2 H,

Ph); 8.41 (d, 2 H, H(2), H(18), J = 5 Hz); 9.63 (d, 2 H, H(3), H(17), J = 5 Hz); 9.75 (s, 4 H, H(7), H(8), H(12), H(13)). EAS (CH_2Cl_2), λ_{max}/nm (A_{rel}): 432 (19.2), 473 (2.8), 643 (1.5), 714 (1). MS (FAB), *m/z*: 939.2 $[M+H]^+$.

10,20-Diferrocenyl-5,15-diphenylporphyrin (9). ^{1}H NMR, δ: −1.65 (s, 2 H, NH); 3.65 (s, 10 H, CpH); 4.81 (m, 4 H, Cp); 5.48 (m, 4 H, Cp); 7.72 (m, 6 H, Ph); 8.16 (m, 4 H, Ph); 8.66 (d, 4 H, H(3), H(7), H(13), H(17), J = 4.9 Hz); 9.82 (d, 4 H, H(2), H(8), H(12), H(18), J = 4.9 Hz). EAS (CH_2Cl_2) for a mixture of compounds **9** and **10**, λ_{max}/nm (A_{rel}): 427 (15.7), 468 (2.9), 625 (1.3), 694 (1). MS (FAB), *m/z*: 831.2 $[M+H]^+$

15,20-Diferrocenyl-5,10-diphenylporphyrin (10). ^{1}H NMR, δ: −1.81 (s, 2 H, NH); 3.74 (s, 10 H, CpH); 4.83 (m, 4 H, Cp); 5.51 (m, 4 H, Cp); 7.74 (m, 6 H, Ph); 8.16 (m, 4 H, Ph); 8.63 (s, 2 H, H(7), H(8)); 8.70 (d, 2 H, H(3), H(12), J = 5 Hz); 9.80 (s, 2 H, H(17), H(18)); 9.92 (d, 2 H, H(2), H(13), J = 5 Hz). MS (FAB), *m/z*: 831.2 $[M+H]^+$.

20-Ferrocenyl-5,10,15-triphenylporphyrin (11). ^{1}H NMR, δ: −2.29 (s, 2 H, NH); 4.08 (s, 5 H, CpH); 4.79 (m, 2 H, Cp); 5.53 (m, 2 H, Cp); 7.75 (m, 9 H, Ph); 8.17 (m, 6 H, Ph); 8.73 (s, 4 H, H(7), H(8), H(12), H(13)); 8.61 (d, 2 H, H(3), H(17), J = 4.9 Hz); 9.95 (d, 2 H, H(2), H(18), J = 5 Hz). EAS (CH_2Cl_2), λ_{max}/nm (A_{rel}): 426 (17.3), 515 (2.5), 583 (1.8), 625 (1.4), 676 (1). MS (FAB), *m/z*: 723.2 $[M+H]^+$.

5,10-Dicymantrenyl-15,20-diferrocenylporphyrin (13). ^{1}H NMR, δ: −0.83 (s, 2 H, NH); 3.99 (s, 10 H, CpH); 4.80 (m, 4 H, CpFe); 5.28 (m, 4 H, CpMn); 5.36 (m, 4 H, CpFe); 5.78 (m, 4 H, CpMn); 9.38 (d, 2 H, H(3), H(12), J = 4.8 Hz); 9.43 (s, 2 H, H(7), H(8)); 9.67 (s, 2 H, H(2), H(13)); 9.74 (d, 2 H, H(17), H(18), J = 4.8 Hz). EAS (C_6H_6), λ_{max}/nm (A_{rel}): 445 (12.3), 500 (2.3), 643 (1.3), 712 (1). MS (FAB), *m/z*: 1083.5 $[M+H]^+$.

5,10,15-Tricymantrenyl-20-ferrocenylporphyrin (14). ^{1}H NMR, δ: −1.10 (s, 2 H, NH); 4.05 (s, 5 H, CpH); 4.83 (m, 2 H, CpFe); 5.29 (m, 6 H, CpMn); 5.37 (m, 2 H, CpFe); 5.78 (m, 6 H, CpMn); 9.42 (d, 2 H, H(3), H(17), J = 5.0 Hz); 9.46 (d, 2 H, H(8), H(12), J = 8.3 Hz); 9.48 (d, 2 H, H(7), H(13), J = 8.3 Hz); 9.77 (d, 2 H, H(2), H(18), J = 5.0 Hz). EAS (C_6H_6) λ_{max}/nm (A_{rel}): 448 (20.7), 495 (2.7), 533 (1.7), 695 (1.4), 702 (1). MS (FAB), *m/z*: 1101.5 $[M+H]^+$.

5,15-Dicymantrenyl-10,20-diferrocenylporphyrin (15). ^{1}H NMR, δ: −0.97 (s, 2 H, NH); 3.96 (s, 10 H, CpH); 4.75 (m, 4 H, CpFe); 5.22 (m, 4 H, CpMn); 5.29 (m, 4 H, CpFe); 5.73 (m, 4 H, CpMn); 9.33 (d, 4 H, H(3), H(7), H(13), H(17), J = 4.8 Hz); 9.66 (d, 4 H, H(2), H(8), H(12), H(18), J = 4.8 Hz). EAS (C_6H_6), λ_{max}/nm (A_{rel}): 446 (9.6), 498 (2.4), 647 (1.2), 715 (1). MS (FAB), *m/z*: 1083.5 $[M+H]^+$.

5,10,15-Triferrocenyl-20-cymantrenylporphyrin (16). ^{1}H NMR, δ: −0.67 (s, 2 H, NH); 4.00 (s, 15 H, CpH); 4.78 (m, 6 H, CpFe); 5.27 (m, 2 H, CpMn); 5.35 (m, 6 H, CpFe); 5.78 (m, 2 H, CpMn); 9.35 (d, 2 H, H(2), H(18), J = 4.2 Hz); 9.64 (d, 2 H, H(3), H(17), J = 6.7 Hz); 9.66 (d, 2 H, H(7), H(13), J = 6.7 Hz); 9.69 (d, 2 H, H(8), H(12), J = 4.2 Hz). EAS (C_6H_6), λ_{max}/nm (A_{rel}): 440 (15.8), 492 (2.5), 625 (1.2), 721 (1). MS (FAB), *m/z*: 1065.4 $[M+H]^+$.

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