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Synergistic Effect of Tetraaryl Porphyrins Containing Corannulene and Other Polycyclic Aromatic Fragments as Hosts for Fullerenes. Impact of C_{60} in a Statistically Distributed Mixture of Atropisomers

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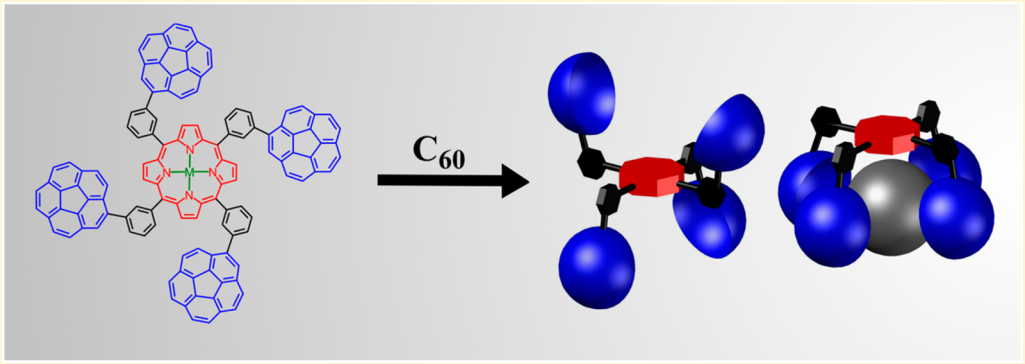
Supporting Information



ABSTRACT: Symmetric *meso*-tetraarylporphyrins bearing phenanthrene, pyrene, and corannulene moieties in meta positions have been synthesized in a straightforward procedure under microwave irradiation by quadruple Suzuki−Miyaura reactions. Their ^{1}H NMR spectra showed the typical pattern of four atropisomers distributed according to their statistical ratio not properly separable due to their fast isomerization. Their ability to bind buckminsterfullerene has been tested with the whole mixture, and different behaviors have been found, α_4 isomer corannulene-substituted porphyrins being the best hosts in the family.

Porphyrins are a vast family of naturally occurring macrocycles having multiple functions in living beings. Many applications have been developed[1] by using these astounding architectures, one of them being their use as hosts for fullerenes, especially for C_{60}, which is considered a very promising and potentially useful building block for new electronic devices.[2] The main approach in order to bind fullerenes by means of supramolecular forces has consisted of building structures with more than one porphyrin, yielding molecular tweezers, trimers, or strapped porphyrins leading to very high affinities.[3] However, there are not examples in which a single porphyrin shows binding abilities to C_{60} beyond cocrystallization,[4] except in the work of Ishizuka and Kojima et al.,[5] whose curved porphyrins were able to carry out such a task.

In our research regarding corannulene-functionalized molecules to act as fullerene hosts,[6] we decided to link this molecule to a porphyrin scaffold in order to add the association abilities of corannulene[7] to the porphyrin core. Additionally, other planar aromatic fragments were linked to the porphyrin core as well and tested for comparison purposes.

Compounds **2HP1** and **ZnP1** could be synthesized with the help of a microwave reactor with a modified method reported elsewhere.[8] From that point we reasoned that the Suzuki reaction from borylated polyaromatic fragments with known Schlenk techniques would lead to **2HP2a−c** and **ZnP2a−c** families (see Schemes S1−S3 in the Supporting Information for a description of all routes attempted); however, a great amount of homocoupling byproducts were obtained as well as non-negligible amounts of porphyrins with Pd in their cavity (Figures S57−S59 in the Supporting Information). This mixture leads to a very cumbersome chromatographic separations. Therefore, we turned to a synthetic route in which the pinacol boronate fragment was located in the porphyrin core and reacted with brominated polyaromatic fragments as depicted in Scheme 1. In order to obtain free base porphyrins, removal of the Zn atom was preferred. Additionally, all coupling reactions were carried out with microwave irradiation because the reaction times were significantly improved.[9]

New porphyrins were fully characterized by spectroscopic methods. All of them have the expected Soret bands around 430 nm and Q bands between 500 and 600 nm (Figures S67−S70 in the Supporting Information) in their absorption spectra. ^{1}H NMR spectra show clearly the presence of statistically distributed atropisomers,[10] especially for H_6 singlets (see the Supporting Information for the numbering of the system), as depicted in Figure 1. Attempts to separate each atropisomer individually, by both preparative methods and HPLC, were unfruitful, even though the HPLC chromatogram clearly

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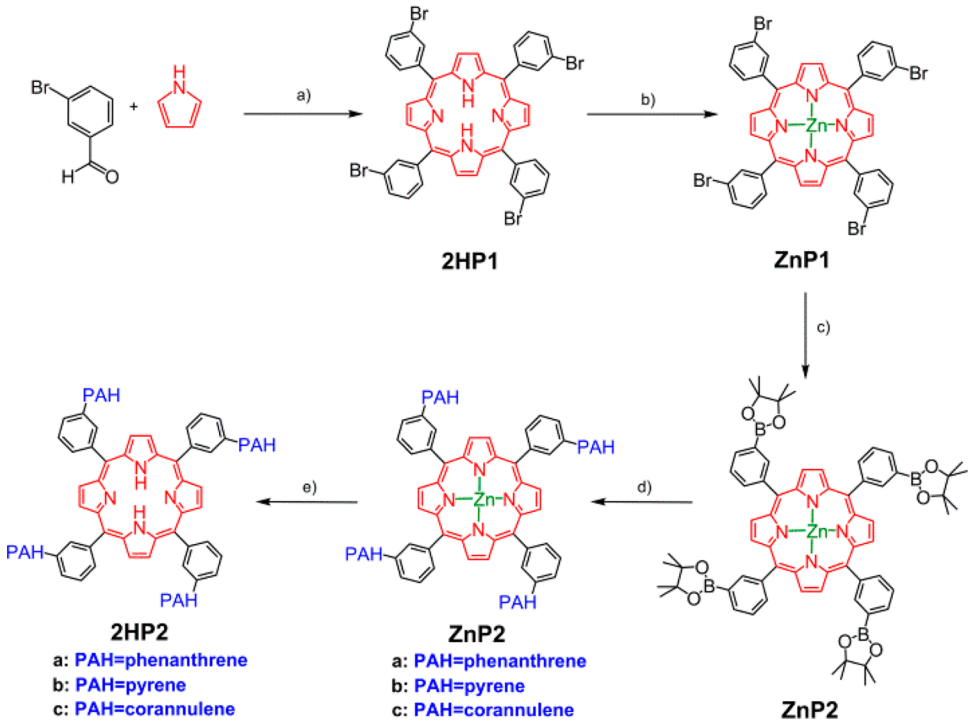
Scheme 1. Best Synthetic Route toward Porphyrin Targets[a]



[a]Reagents and conditions: (a) propionic acid, nitrobenzene, MW, 200 °C; (b) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$, MW, 120 °C; (c) B_2pin_2, [$PdCl_2$(dppf)], AcOK, dioxane, MW; (d) [$PdCl_2$(dppf)], ^tBuONa, toluene, MW; (e) CF_3CO_2H.

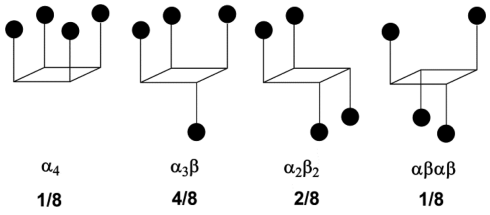


Figure 1. Schematic representation of the atropisomers and their statistical distribution.

showed four separate peaks. NMR tests of each fraction indicated the presence of the mixture, showing that isomerization occurred even at low temperature.[11]

Notwithstanding such limitations, we decided to analyze the ability of the whole mixture to bind C_{60} and, at the same time, to observe potential differences among all individual atropisomers. ^1H NMR was chosen to be the technique because, unlike UV/vis experiments, it is able to distinguish all isomers. This was complemented by mass spectrometry experiments. Before performing any titration, we first attempted to determine the stoichiometry of the adduct. Job plots were carried out for all compounds; however, only H_1 was observed as an average signal due to its inherent broadness, so that only the **2HP2** set could be properly analyzed (Figures S77−S79 in the Supporting Information). Surprisingly, all porphyrins showed 1:1 adduct formation and this was confirmed by MS (Figures S60−S66 in the Supporting Information). We assumed that this stoichiometry was maintained in **ZnP2** derivatives because only 1:1 adducts were located in all mass spectra. Titrations of phenanthrene and pyrene-substituted porphyrins **ZnP2a,b** and **2HP2a,b** provided several small chemical shift changes, indicating supramolecular association for some atropisomers. This was not expected, because it is known that compounds bearing these types of PAHs do not establish adducts with C_{60} due to their low shape complementarity;[12] this suggests that the host−guest formation is taking place due mainly to the porphyrin core.[13] On the other hand, corannulene derivatives, **2HP2c** and **Zn2P2c**, showed great chemical shift changes, except for one atropisomer. Interestingly, we observed the same pattern in all chemical shift changes, and especially for H_1, H_2, and H_6 hydrogens in all compounds. This suggests a similar behavior.

In order to assign signals for each atropisomer, we carried out computational studies[14] for the **2HP2** set of isomers and the optimized structures provided interesting features. Intramolecular association of PAH units at the same side is so preferred that it leads to deformation of the porphyrin, reaching a saddlelike conformation for the most stable isomers, $\boldsymbol{\alpha_4}$. On the other hand, $\boldsymbol{\alpha\beta\alpha\beta}$ isomers are the least stable and PAH moieties are not interacting among them. This lack of interaction could be the reason for the low stability. Thus, a quasi-planar porphyrin core as well as vague preorganization as host are observed, as seen in Figure 2 for **2HP2c**. The other atropisomers present intermediate situations and stabilities (Tables S1−S3 and Figures S80−S91 in the Supporting Information).

Theoretical NMR predictions for the H_6 proton signal in **2HP2c** gave, from lowest to highest field, the following order: $\alpha\beta\alpha\beta < \alpha_3\beta$(bottom) $< \alpha_3\beta$(outer) $< \alpha_2\beta_2 < \alpha_3\beta$(inner) $< \alpha_4$, as depicted in Figure 3.

From that starting point, we followed the evolution of singlet H_6 during titration with C_{60}. Simultaneously, the evolution of singlet H_2 proton (β-pyrrole) could be traced due to a great disruption observed upon addition of initial aliquots. It must be noted that these H_2 protons are all equivalent for $\boldsymbol{\alpha\beta\alpha\beta}$ and $\boldsymbol{\alpha_4}$ isomers, but there are two nonequivalent protons for $\boldsymbol{\alpha_3\beta}$ and

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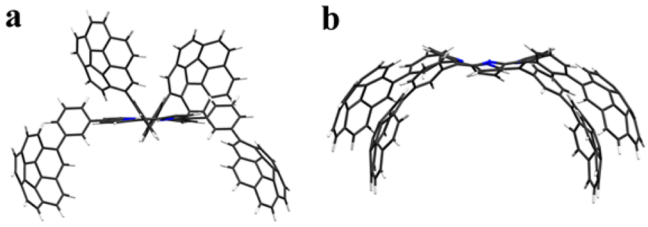

Figure 2. Optimized structures of (a) ***αβαβ*2HP2c** and (b) ***α*$_4$2HP2c**.

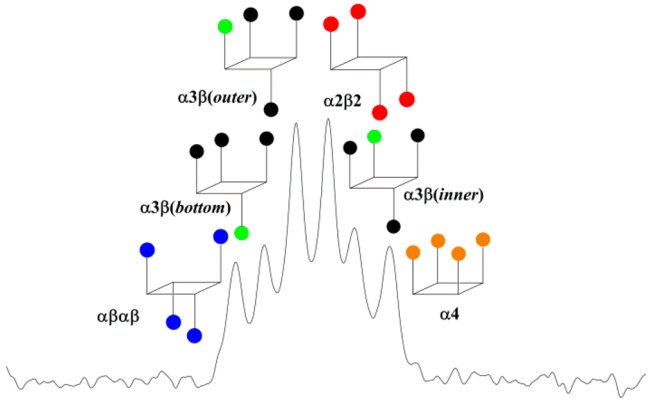

Figure 3. Simulated H_6 resonance in toluene of the **2HP2c** pattern and theoretical assignments with an integral ratio of 1:1:2:2:1:1.

***α*$_2$*β*$_2$** isomers. Additionally, this procedure was applied to **ZnP2c** to check similar behavior and reproducibility.

First of all, predicted ***α*$_3$*β*(bottom)** and ***α*$_3$*β*(outer)** H_6 chemical shift changes were followed and their curves fitted, yielding equal constants. However, ***α*$_3$*β*(inner)** H_6 could not be followed due to spectral overlap with ***α*$_2$*β*$_2$** H_6 during titration. Once those proton signals were located and determined, another atropisomer could be directly assigned, ***α*$_2$*β*$_2$**. Its H_6 signal is that left with a ratio of 2 (Figure 3). The titration for this atropisomer gave a very different constant (3-fold increase for **2HP2c** and 1 order of magnitude in **ZnP2c**). Thus, at this point, just two minor signals corresponding to ***αβαβ*** and ***α*$_4$** isomers were left to be matched with computational results. It was assumed that the theoretical assignment was correct due to the accuracy observed for the other predictions. Unfortunately, the H_6 proton for the ***α*$_4$** atropisomer could not be followed because it became broadened after the first addition. These findings are all gathered in Figure 4.

On the other hand, H_2 proton (*β*-pyrrole) evolution was followed as well in order to identify each signal in the course of titration experiments. Each chemical shift change observed was systematically subjected to a fitting process covering all possibilities until the association constants matched those previously estimated for H_6. Fortunately, signals corresponding to ***αβαβ*** and ***α*$_3$*β*** isomers, especially for **ZnP2c**, were located easily due to the lack of spectral overlap during titration. Spectral changes of the ***α*$_2$*β*$_2$** atropisomer (which, depending on FID processing, can be seen as one large broad signal or two resolved shifts) were also easily followed. A crossover with a broad chemical shift change that unexpectedly increased at the beginning of the titration was observed in the last additions. This new signal was accepted to come from the remaining ***α*$_4$** atropisomer; therefore, we carried out the same fitting procedure, resulting in a new association constant. This procedure is shown in Figure 5.[15]

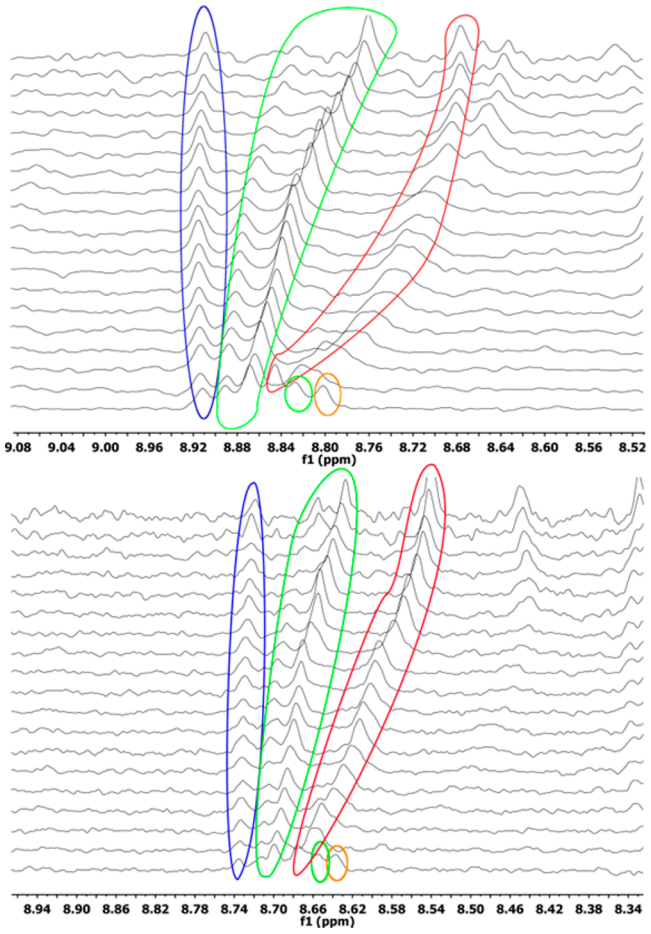

Figure 4. ^{1}H NMR showing H_6 chemical shifts in deuterated toluene of **ZnP2c** (up) and **2HP2c** (bottom) upon addition of aliquots of C_{60}. Colored domains enclose the assignments according to the pattern established in Figure 3. Note the overlap of the H_6 (inner) proton in the ***α*$_3$*β*** isomer with the H_6 proton in the ***α*$_2$*β*$_2$** isomer and the "disappearance" of the H_6 proton in the ***α*$_4$** isomer after the first addition.

This protocol was applied for phenanthrene- and pyrene-substituted porphyrins (**ZnP2a**, **ZnP2b**, **2HP2a**, and **2HP2b**), resulting in very similar findings, but less pronounced changes of chemical shifts were observed.

These results were not consistent with our initial assumptions, because we thought that ***αβαβ*2HP2c** ideally had a good preorganization in a double-tweezer mode and could lead to moderate association. However, we did not find chemical shift changes great enough to be measured in any of all ***αβαβ*** atropisomers. Furthermore, as stated previously, structures of optimized minima clearly showed that preorganization of this atropisomer to adapt a fullerene shape is not efficient, while other atropisomer preorganizations are much more efficient.

The best results were obtained for corannulene-functionalized porphyrins; especially **ZnP2c**. ***α*$_4$ZnP2c**, and ***α*$_2$*β*$_2$ZnP2c** showed the best association constants in the mixture of atropisomers, which are 22330 and 12140 M^{-1}, respectively. The presence of the metal favors supramolecular adduct formation.

As commented above, **2HP2** (free base) porphyrins possess averaged signals coming from internal hydrogens (H_1) and could be followed during titration experiments; therefore, an

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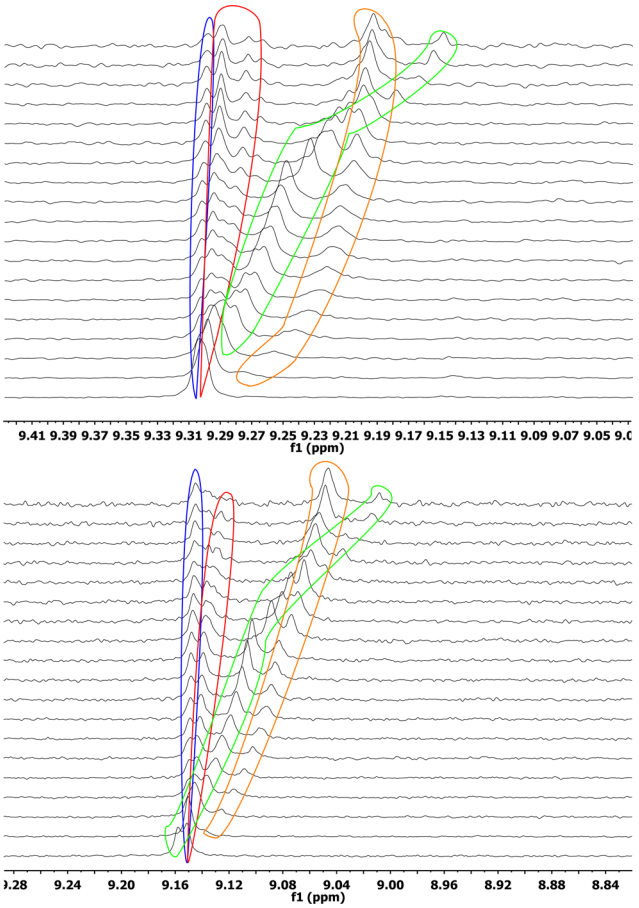

Figure 5. ^{1}H NMR showing H_2 chemical shifts in deuterated toluene of **ZnP2c** (top) and **2HP2c** (bottom) upon addition of aliquots of C_{60}. Colored domains enclose the assignments according to the pattern established in Figure 3. Note the crossover between the green and yellow domains.

average association constant could be given, leading to the conclusion that our corannulene-based porphyrins are very good hosts for C_{60} because their association constants are 1 order of magnitude greater than those bearing planar polycyclic hydrocarbons. In light of these findings, synergy between a porphyrin core and well-adapted corannulene groups to bind buckminsterfullerene is suggested. All of the estimated constants are gathered in Table 1.

In summary, a set of six tetrasubstituted porphyrins in meso positions with polycyclic aromatic hydrocarbons have been prepared very easily by using microwave irradiation. The existence of a statistically distributed mixture of atropisomers was identified by NMR and assigned with the help of a combination of titration experiments of the whole mixture with C_{60} and computational studies. Complexation studies were carried out, and a great difference was observed for each individual atropisomer, the best hosts being α_4 and $\alpha_2\beta_2$ porphyrins bearing corannulene as a substituent, whose crude estimated association constants were among the highest of those reported for single-porphyrin hosts. Theoretical calculations have suggested that preorganization of corannulene moieties in a tweezerlike fashion are crucial. This initial research has opened new possibilities to design more complex "picket fence" (α_4 atropisomer) porphyrins having multiple corannulene fragments with the objective to increase their affinity toward fullerenes thanks to a synergy between the porphyrin and nonplanar polycyclic hydrocarbon.

EXPERIMENTAL SECTION

All reagents were purchased from the usual vendors and used without further purification. Solvents were either used as purchased or dried according to procedures described elsewhere.[16] Microwave reactions were carried out with an Anton Paar Monowave 300 Reactor. Column chromatography was carried out using silica gel 60 (particle size 0.040−0.063 mm; 230−400 mesh) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254) and observed under UV light and/or dipping in anisaldehyde. NMR spectra were recorded on 400 and 500 MHz instruments. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced to TMS, using the solvent as an internal reference. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations used to indicate multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^{13}C{^{1}H} spectra for all porphyrin derivatives had to be recorded with the following acquisition parameters due to their fast relaxation: a 90° pulse, a relaxation delay of 5 ms, and an acquisition time of 250 ms. ^{1}H and ^{13}C assignments were performed by utilizing 2D NMR methods: band-selective HSQC and band-selective HMBC. High-resolution mass spectra were recorded with a MALDI-TOF system with an N_2 laser (337 nm, pulse energy 100 μJ, 1 ns). An acceleration voltage of 19 kV and a reflector positive mode were used. UV/vis absorption spectral wavelengths (λ) are reported in nanometers (nm), and molar absorption coefficient (ε) are reported in M^{-1} cm^{-1}. Corannulene and bromocorannulene were prepared according to literature procedures.[17]

General Method for Polyaromatic Boronate Ester Preparation. Bromoarene (0.4 mmol), bis(pinacolato)diboron (152 mg, 0.6 mmol), [$PdCl_2$(dppf)] (15 mg, 0.02 mmol), and AcOK (118 mg, 1.2 mmol) were mixed in a Schlenk flask under an inert atmosphere. A 2 mL portion of dry dioxane was added, and the mixture was degassed. Then, the mixture was refluxed overnight. Solvent was removed under vacuum before purification by column chromatography with SiO_2 gel and hexane/AcOEt as eluent (5/1 for 9-(pinacolatoboron)-phenanthrene (**1**), 20/1 for 1-(pinacolatoboron)pyrene (**2**) and 1-(pinacolatoboron)corannulene (**3**)). Yields were over 85%. Spectral data are in agreement with those published.[18]

2HP1. Pyrrole (277 μL, 4 mmol), 3-bromobenzaldehyde (468.0 μL, 4 mmol), propionic acid (12 mL, 160 mmol), and nitrobenzene (7 mL, 68 mmol) were mixed in a sealed reactor specifically designed for

Table 1. Summary of K_a of New Porphyrins vs C_{60} Estimated in Toluene-d_8

	ZnP2a	2HP2a	ZnP2b	2HP2b	ZnP2c	2HP2c
α_4	180	N/A[a]	790	1180	22330[b]	7700[b]
$\alpha_3\beta$	0[d]	0[d]	0[d]	540	1730	1820
$\alpha_2\beta_2$	240	130	690	1240	12140	5890
$\alpha\beta\alpha\beta$	0[d]	0[d]	0[d]	0[d]	0[d]	0[d]
average	N/A[c]	$(4.5 \pm 0.05) \times 10^2$	N/A[c]	$(4.6 \pm 0.05) \times 10^2$	N/A[c]	$(5.4 \pm 0.2) \times 10^3$

[a]Could not be estimated due to spectral overlap. [b]Determined from the $\Delta\delta$ change of H_2 β-pyrrole protons only. [c]Not measured (no average signal). [d]$\Delta\delta$ too low to allow a reasonable estimate of a constant.

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microwave irradiation. The mixture was stirred inside a microwave reactor at 200 °C for 15 min (a pressure of 5 bar was achieved). The resulting black crude product obtained after cooling to room temperature was taken up in MeOH (50 mL), precipitating a purple solid. The product was filtered in a Büchner funnel and washed thoroughly with more MeOH. The solid was collected, placed in an oven, and kept under reduced pressure (200 °C, 24 h, 50 mbar) to finally give pure **2HP1**, whose spectroscopic data agree with those reported[19] (0.295 g, 32% yield).

ZnP1. **2HP1** (0.250 g, 0.268 mmol) and $Zn(AcO)_2{\cdot}2H_2O$ (0.294 g, 1.34 mmol) were mixed in a sealed reactor specifically designed for microwave irradiation and dissolved in 12 mL of $CHCl_3$. The solution was stirred at 130 °C for 2.5 h (a pressure of 6 bar was achieved). Once the reaction was complete, solvent was removed in vacuo. The resulting solid was washed several times with water and dried to give a purple solid corresponding to **ZnP1** (0.203 g, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (s, 2H, H_2), 8.38 (s, 1H, H_6), 8.16 (br, 1H, H_{10}), 7.95 (d, J = 8.2 Hz, 1H, H_8), 7.64 (d, J = 8.2 Hz, 1H, H_9). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 150.0 (C_3), 144.5 (C_5), 137.1 (C_6), 132.9 (C_{10}), 132.1 (C_2), 130.9 (C_8), 128.0 (C_9), 110.0 (C_4). HRMS (MALDI-TOF): m/z 987.8010 $[M]^+$ (calcd 987.8026 for $C_{44}H_{24}Br_4N_4Zn$). UV/vis (toluene): λ 404 (ε = 17033), 424 (ε = 195165), 550 (ε = 10220), 588 (ε = 2308).

ZnP2. **ZnP1** (80 mg, 0.08 mmol), bis(pinacolato)diboron (122 mg, 0.48 mmol), [$PdCl_2$(dppf)] (12 mg, 0.016 mmol), and AcOK (94 mg, 0.96 mmol) were mixed in a reactor specifically designed for microwave irradiation inside a two-necked round-bottom flask in order to place the mixture under an inert atmosphere. A 1.8 mL portion of dry dioxane and 116 μL of dry pyridine were added, and the mixture was degassed before sealing the vial. Then, the mixture was stirred inside the microwave reactor at 150 °C for 2 h (a pressure of 3 bar was achieved). Solvent was removed under vacuum, and the resulting dark residue was redissolved in a $CHCl_3$/MeOH 95/5 mixture before the solution was quickly passed through a plug of SiO_2 gel. The deep red filtrate was concentrated to afford a purple solid (85 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (s, 2H, H_2), 8.66 (br, 1H, H_6), 8.31 (d, J = 7.5 Hz, 1H, H_{10}), 8.21 (d, J = 7.5 Hz, 1H, H_8), 7.76 (t, J = 7.5 Hz, 1H, H_9), 1.38 (s, 12H, H_{12}). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 150.3 (C_3), 142.5 (C_5), 140.5 (C_6), 137.1 (C_{10}), 133.9 (C_8), 132.1 (C_2), 127.8 (C_7), 126.1 (C_9), 121.1 (C_4), 84.1 (C_{11}), 25.1 (C_{12}). HRMS (MALDI-TOF): m/z 1180.5043 $[M]^+$ (calcd 1180.5047 for $C_{68}H_{72}B_4N_4O_8Zn$). UV/vis (toluene) λ 402 (ε = 17927), 425 (ε = 324268), 550 (ε = 16098), 590 (ε = 3049).

General Procedure for Quadruple C−C Cross Coupling. The porphyrin derivative (**2HP1**, **ZnP1**, or **ZnP2**; 0.02 mmol), PAH derivative (9-bromophenanthrene, 1-bromopyrene, bromocorannulene, **1**−**3**; 0.08 mmol), [$PdCl_2$(dppf)] (11.7 mg, 0.016 mmol), and ^{t}BuONa (23.1 mg, 0.24 mmol) were mixed in a reactor specifically designed for microwave irradiation inside a two-necked round-bottom flask in order to place the mixture under an inert atmosphere. A 2.2 mL portion of dry and degassed toluene and 30 μL of dry pyridine were added before sealing the vial. The mixture was then sonicated thoroughly and stirred vigorously inside the microwave reactor at 130 °C for 1 h (a pressure of 3 bar was achieved). After this time, solvent was removed under vacuum and the black residue was subjected to purification by column chromatography, yielding a pure purple solid corresponding with the expected product.

ZnP2a. Chromatography conditions: SiO_2 gel, hexane/AcOEt gradient elution (10/1−5/1−1/1 AcOEt). 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.20 (s, 2H, H_2), 8.85−8.75 (m, 1H, H_{17}), 8.75−8.65 (m, 1H, H_{20}), 8.50−8.41 (m, 1H, H_6), 8.41−8.35 (m, 1H, H_{23}), 8.35−8.27 (m, 1H, H_{10}), 8.05−7.96 (m, 2H, H_{12} + H_8), 7.96−7.86 (m, 2H, H_{14} + H_9), 7.73−7.51 (m, 4H, H_{16} + H_{21} + H_{15} + H_{22}). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 150.4 (C_3), 143.1 (C_5), 139.2 (C_7), 138.7 (C_{11}), 136.4 (C_6), 133.7 (C_{10}), 132.3 (C_2), 131.7 (C_{24}), 131.4 (C_{19}), 130.9 (C_{13}), 130.2 (C_{18}), 129.4 (C_8), 128.8 (C_{14}), 128.2 (C_{12}), 127.1−126.7 (C_9 + C_{15} + C_{16} + C_{21} + C_{22} + C_{23}), 123.1 (C_{17}), 122.6 (C_{20}), 121.1 (C_4). HRMS (MALDI): m/z 1380.4075 $[M]^+$ (calcd 1380.4104 for $C_{100}H_{60}N_4Zn$). UV/vis (toluene): λ 300 (ε = 38806), 400 (ε = 14179), 426 (ε = 211940), 552 (ε = 11642), 590 (ε = 4627).

ZnP2b. Chromatography conditions: SiO_2 gel, hexane/AcOEt gradient elution (5/1−1/1 AcOEt). 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.26−9.21 (m, 2H, H_2), 8.68−8.59 (m, 1H, H_{23}), 8.59−8.47 (m, 1H, H_6), 8.45−8.35 (m, 1H, H_{10}), 8.35−8.22 (m, 2H, H_{12} + H_{13}), 8.22−7.86 (m, 8H, H_{22} + H_8 + H_9 + H_{19} + H_{16} + H_{18} + H_{20} + H_{15}). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 150.4 (C_3), 143.3 (C_5), 139.5 (C_7), 137.6 (C_{11}), 137.0 (C_6), 133.6 (C_{10}), 132.2 (C_2), 131.6−130.7 (C_{26} + C_{17} + C_{21} + C_{14}), 129.8 (C_8), 128.9 (C_{24}), 128.1 (C_{12}), 127.8 (C_{22} or C_{16}), 127.5 (C_{22} or C_{16}), 126.7 (C_9), 126.0 (C_{19}), 125.4 (C_{23}), 125.2−124.8 (C_{13} + C_{15} + C_{18} + C_{20} + C_{25}), 121.0 (C_4). HRMS (MALDI): m/z 1476.4104 $[M]^+$ (calcd 1476.4104 for $C_{108}H_{60}N_4Zn$). UV/vis (toluene): λ 329 (ε = 36774), 347 (ε = 48548), 405 (ε = 20806), 428 (ε = 195161), 551 (ε = 12903), 591 (ε = 4839).

ZnP2c. Chromatography conditions: SiO_2 gel, hexane/AcOEt gradient elution (5:1−1:1 AcOEt $CHCl_3$). 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.18 (s, 2H, H_2), 8.74−8.65 (m, 1H, H_6), 8.42−8.31 (m, 1H, H_{10}), 8.28−8.21 (m, 1H, H_8), 8.21−8.11 (m, 2H, H_{24} + H_{12}), 8.00−7.90 (m, 1H, H_9), 7.90−7.72 (m, 7H, H_{14} + H_{15} + H_{17} + H_{18} + H_{20} + H_{21} + H_{23}). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 150.3 (C_3), 145.2 (C_{25} or C_{27}), 143.5 (C_5), 137.7 (C_7), 136.2 (C_6), 133.9 (C_{10}), 132.1 (C_2), 123.0 (C_{25} or C_{27}), 129.0 (C_8), 127.5 (C_{24}), 127.2−126.7 (C_9 + C_{14} + C_{15} + C_{17} + C_{18} + C_{20} + C_{21} + C_{23}), 126.2 (C_{12}), 120.9 (C_4). HRMS (MALDI): m/z 1668,4133 $[M]^+$ (calcd 1668,4104 for $C_{124}H_{60}N_4Zn$). UV/vis (toluene): λ 296 (ε = 146667), 400 (ε = 27407), 427 (ε = 438889), 551 (ε = 22037), 590 (ε = 4630).

General Procedure for Zn Removal. Zinc porphyrin derivatives (**ZnP2a**, **ZnP2b**, **ZnP2c**; 0.02 mmol) were dissolved in 2 mL of DCM. To the deep red solution was added 2 mL of CF_3CO_2H at once, and the mixture immediately turned green. The mixture was stirred at room temperature overnight. Then, it was diluted with 6 mL of DCM and a saturated solution of Na_2CO_3 in water was added portionwise with vigorous stirring until the evolution of gas ceased and the organic layer became deep red again. This layer was separated from the aqueous phase and washed three times with water. The solution was finally dried with anhydrous $MgSO_4$, filtered, and concentrated to afford the expected demetalated product as a purple solid.

2HP2a. From quadruple cross coupling of **1** and **2HP1**: chromatography conditions SiO_2 gel, hexane/AcOEt gradient elution (10:1−5:1−1:1 AcOEt); 73% yield. From demetalation of **ZnP2a**: quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.10 (s, 2H, H_2), 8.85−8.76 (m, 1H, H_{17}), 8.76−8.66 (m, 1H, H_{20}), 8.50−8.40 (m, 1H, H_6), 8.40−8.26 (m, 2H, H_{23} + H_{10}), 8.06−7.95 (m, 2H, H_{12} + H_8), 7.95−7.85 (m, 2H, H_{23} + H_8), 7.75−7.56 (m, 4H, H_{22} + H_{21} + H_{15} + H_{16}), −2.70 (br, 0.5H, H_1). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 142.4 (C_5), 139.4 (C_7), 138.6 (C_{11}), 136.4 (C_6), 133.9 (C_{10}), 131.7 (C_{24}), 131.4 (C_{13}), 130.9 (C_{19}), 130.2 (C_{18}), 129.6 (C_8), 128.9 (C_{14}), 128.2 (C_{12}), 127.0 (C_{23}), 126.8−126.7 (C_9 + C_{22} + C_{16} + C_{21} + C_{15}), 123.2 (C_{17}), 122.7 (C_{20}), 120.2 (C_4). HRMS (MALDI): m/z 1318.4946 $[M]^+$ (calcd 1318.4969 for $C_{100}H_{62}N_4$). UV/vis (toluene): λ 300 (ε = 35455), 400 (ε = 34364), 422 (ε = 250727), 517 (ε = 11091), 551 (ε = 5091).

2HP2b. From quadruple cross coupling of **2** and **2HP1**: chromatography conditions SiO_2 gel, hexane/AcOEt gradient elution (5:1−1:1 - AcOEt); 57% yield. From demetalation of **ZnP2b**: quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (s, 2H, H_2), 8.68−8.56 (m, 1H, H_{23}), 8.56−8.48 (m, 1H, H_6), 8.45−8.34 (m, 1H, H_{10}), 8.34−8.23 (m, 2H, H_{12} + H_{13}), 8.23−7.88 (m, 8H, H_{19} + H_9 + H_{16} + H_8 + H_{20} + H_{18} + H_{15} + H_{22}), −2.65 (br, 0.5H, H_1). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 142.5 (C_5), 139.8 (C_7), 137.4 (C_{11}), 137.0 (C_6), 133.7 (C_{10}), 131.6−130.7 (C_{26} + C_{17} + C_{21} + C_{14}), 130.2 (C_8), 128.9 (C_{24}), 128.1 (C_{12}), 127.9 (C_{22}), 127.6 (C_{16}), 126.9 (C_9), 126.1 (C_{19}), 125.3−124.9 (C_{13} + C_{15} + C_{18} + C_{20} + C_{23} + C_{25}), 120.2 (C_4). HRMS (MALDI): m/z 1414.4981 $[M]^+$ (calcd 1414.4969 for $C_{108}H_{62}N_4$). UV/vis (toluene): λ 333 (ε = 28462), 348 (ε = 35692), 405 (ε = 19846), 424 (ε = 93077), 517 (ε = 6923), 551 (ε = 4769).

2HP2c. From quadruple cross coupling of **3** and **2HP1**: chromatography conditions SiO_2 gel, hexane/AcOEt gradient elution (5:1−1:1 AcOEt $CHCl_3$); 47% yield. From demetalation of **ZnP2c**: quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.07 (s, 2H, H_2), 8.72−8.63 (m, 1H, H_6), 8.41−8.31 (m, 1H, H_{10}), 8.27−8.21 (m, 1H,

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H_8), 8.20−8.11 (m, 2H, H_{12} + H_{24}), 8.00−7.90 (m, 1H, H_9), 7.90−7.70 (m, 7H, H_{14} + H_{15} + H_{17} + H_{18} + H_{20} + H_{21} + H_{23}), −2.65 (br, 0.5H, H_1). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 142.8 (C_5), 141.5 (C_{25} or C_{27}), 138.2 (C_7), 136.3 (C_6), 135.9 (C_{11}), 135.5 (C_{10}), 134.1 (C_2), 131.1 (C_{25} or C_{27}), 129.5 (C_8), 127.7 (C_{24}), 127.6−126.8 (C_9 + C_{14} + C_{15} + C_{17} + C_{18} + C_{20} + C_{21} + C_{23}), 126.6 (C_{12}), 120.1 (C_4). HRMS (MALDI): m/z 1606,4985 $[M]^+$ (calcd 1606,4969 for $C_{124}H_{62}N_4$). UV/vis (toluene): λ 294 (ε = 131250), 404 (ε = 47000), 424 (ε = 279750), 516 (ε = 13000), 551 (ε = 6500).

General Procedure for Complexation Measurements. A 10^{-4} M solution of each compound in deuterated toluene was prepared, and a known volume was transferred to a NMR tube (500 μL). It was titrated by adding known portions of a stock solution of C_{60} (10^{-3} M) in deuterated toluene covering a wide range of amounts. A ^1H NMR spectrum was recorded at room temperature after each addition. Once all data were obtained, changes in chemical shifts ($\Delta\delta$) for selected protons (H_1, H_2. and/or H_6) were plotted as a function of guest molar fraction and the resulting curve was fitted by a nonlinear method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00454.

Overview of both synthetic methods, atom numbering, one- and two-dimensional NMR spectra of all new compounds, MS spectra, UV−vis spectra, details of association constant estimation, and computational calculations (PDF)

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Notes

The authors declare no competing financial interest.

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(14) See the Supporting Information for details about the computational model followed.

(15) Additional possibilities were also tested, implying other initial assignments for H_6 as reported by Sternhell et al. or Bernardou and Meunier et al.,[10a,b] but none of them were reasonable in our case, due mainly to inconsistencies in fitting of the curves and no reproducibility in comparison to H_2 chemical shift changes.

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