Synergistic effect of tetraaryl porphyrins containing corannulene and other polycyclic aromatic fragments as host for fullerenes. Impact of C_{60} in a statistically distributed mixture of atropisomers.

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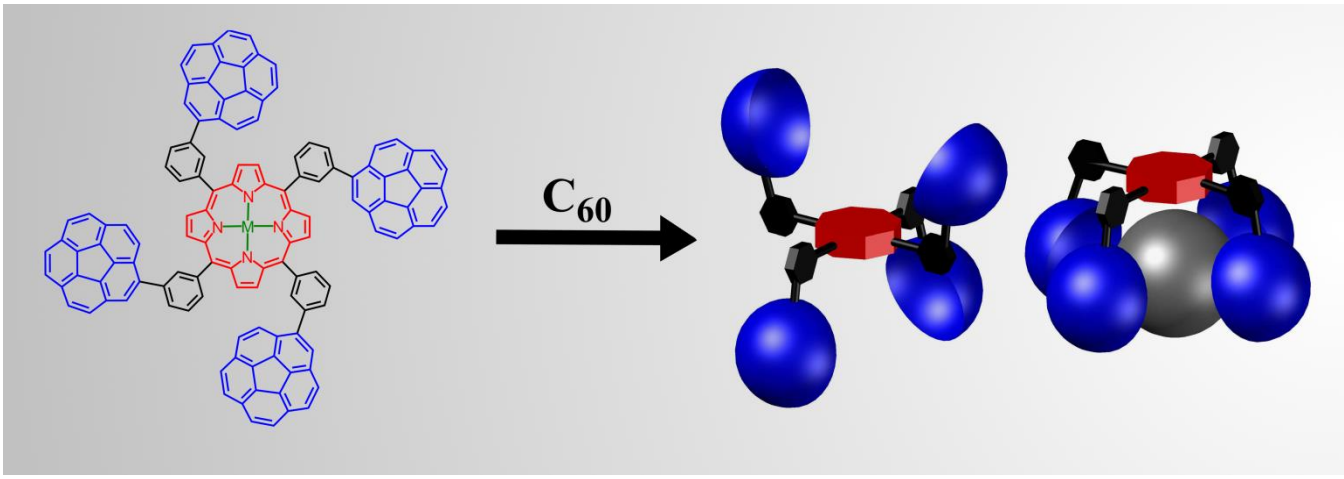


ABSTRACT: Symmetric *meso*-tetraaryl porphyrins bearing phenanthrene, pyrene and corannulene moieties in *meta* positions have been synthesized in a straightforward procedure under microwave irradiation by quadruple Suzuki-Miyaura reactions. Their ^{1}H NMR spectra showed the typical pattern of 4 atropisomers distributed accordingly 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, being α_4 isomer corannulene-substituted porphyrins the best hosts in the family.

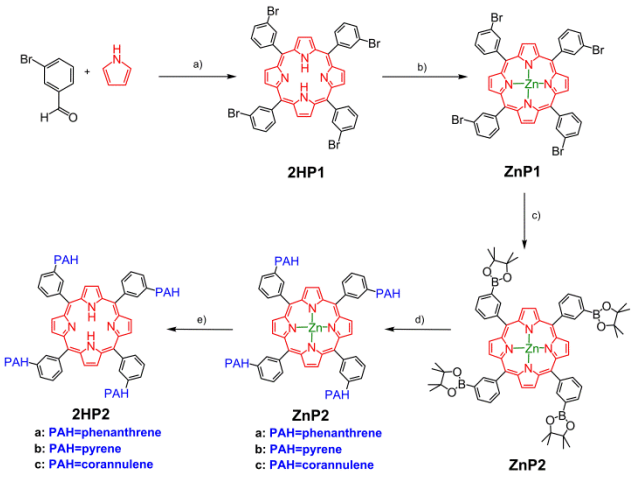
Porphyrins are a vast family of naturally occurring macrocycles having multiple functions in living beings. Many applications have been developed[1] by using these astounding architectures, being one of them their use as hosts for fullerenes, especially for C_{60}, which is considered a very promising 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 for the work of Ishizuma and Kojima *et al.*[5] whose curved porphyrins were able to do such task.

Under our research line regarding corannulene-functionalized molecules to act as fullerenes hosts,[6] we decided to link this molecule to a porphyrin scaffold in order to sum 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 Suzuki reaction from borylated polyaromatic fragments with known Schlenk techniques would lead to **2HP2a,b,c** and **ZnP2a,b,c** families (see Schemes S1-S3 for a description of all routes attempted), however a great amount of homocoupling by-products were obtained as well as non-negligible amount of porphyrins with Pd in their cavity (Figures S57-S59). This mixture leads to a very cumbersome chromatographic separations. So we turned to a synthetic route in which pinacol boronate fragment was located in the porphyrin core and reacted with brominated polyaromatic fragments as depicted in Scheme 1. In order to get free base porphyrins, removal of Zn atom was preferred. Additionally, all coupling reactions were carried out with microwave irradiation because reaction times were significantly improved.[9]

SCHEME 1 Best synthetic route towards porphyrin targets



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

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

though HPLC chromatogram showed clearly four separated peaks. NMR tests of each fraction indicated the presence of the mixture showing that isomerization occurred even at low temperature.[11]

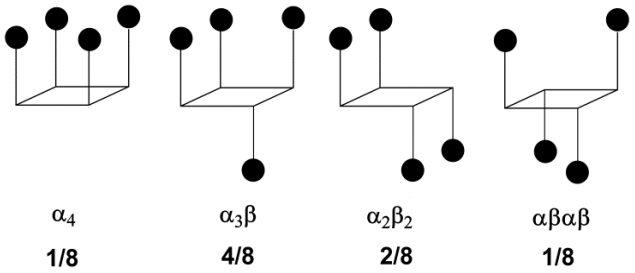


FIGURE 1 Schematic representation of the atropisomers and their statistical distribution.

Notwithstanding such limitation, 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. ^{1}H 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 firstly attempted to know 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 only **2HP2** set could be properly analyzed (Figures S77-S79). Surprisingly, all porphyrins showed 1:1 adduct formation and this was confirmed by MS (Figures S60-66). 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 little chemical shifts changes, indicating supramolecular association for some atropisomers. This was not expected because it is known that compounds bearing this type 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 **2HP2** set of isomers and the optimized structures provided interesting features. Intramolecular association of PAHs units at the same side is so preferred that leads to deformation of the porphyrin reaching a saddle-like conformation for the most stable isomers, α_4. On the other hand, $\alpha\beta\alpha\beta$ isomers are the least stable and PAHs 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).

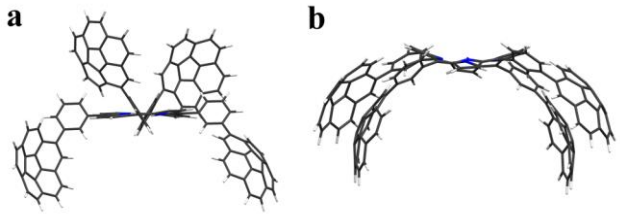


FIGURE 2 Optimized structures of: (a) **αβαβ2HP2c**; (b) **$\alpha_4$2HP2c**.

Theoretical NMR predictions for H_6 proton signal in **2HP2c** gave, from lowest to highest field, this order: αβαβ < $\alpha_3\beta$(bottom) < $\alpha_3\beta$(outer) < $\alpha_2\beta_2$ < $\alpha_3\beta$(inner) < α_4 as depicted in Figure 3.

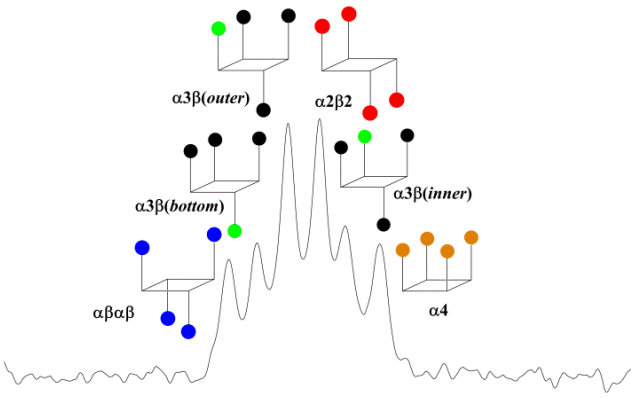


FIGURE 3 Simulated H_6 resonance in toluene of **2HP2c** pattern and theoretical assignments with an integral ratio of 1:1:2:2:1:1.

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 **αβαβ** and **α_4** isomers, but there are two nonequivalent protons for **$\alpha_3\beta$** and **$\alpha_2\beta_2$** isomers. Additionally, this procedure was applied for **ZnP2c** compound to check similar behaviors and reproducibility.

First of all, **$\alpha_3\beta$(bottom)** and **$\alpha_3\beta$(outer)** predicted H_6 chemical shifts changes were followed and their curves fitted yielding equal constants. However, **$\alpha_3\beta$(inner)** H_6 could not be followed due to spectral overlap with **$\alpha_2\beta_2$** H_6 during titration. Once located and determined those proton signals, another atropisomer could be directly assigned, **$\alpha_2\beta_2$**. Its H_6 signal is the one left with a ratio of 2, (Figure 3). The titration for this atropisomer gave a very different constant (three-fold increase for **2HP2c** and one order of magnitude in **ZnP2c**). So, 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 theoretical assignment was correct due to the accuracy observed for the other predictions. Unfortunately, H_6 proton for **α_4** atropisomer could not be followed because it got broadened after the first addition. These findings are all gathered in Figure 4.

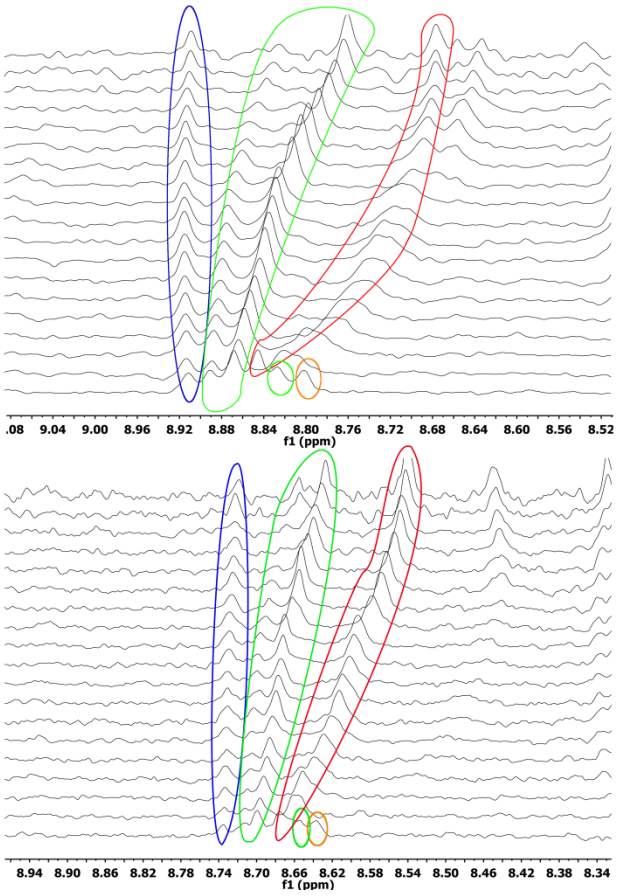


Figure 4: ^{1}H NMR showing H_6 chemical shifts in deuterated toluene of **ZnP2c** (up) and **2HP2c** (bottom) upon addition of aliquots of C_{60}. Colored domains enclose the assignments according to the pattern established in Figure 3. Note the overlap of H_6 (inner) proton in $\alpha_3\beta$ isomer with H_6 proton in $\alpha_2\beta_2$ isomer and the 'disappearance' of H_6 proton in α_4 isomer after the first addition.

On the other hand, H_2 protons (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 association constants matched those previously estimated for H_6. Fortunately, signals corresponding to $\alpha\beta\alpha\beta$ and $\alpha_3\beta$ isomers, especially for **ZnP2c**, were located easily due to the lack of spectral overlap during titration. Spectral changes of $\alpha_2\beta_2$ atropisomer (which, depending on FID processing, can be seen as one big broad signal or two resolved shifts) were also easily followed. A crossover with a broad chemical shift change that unexpectedly raised in the beginning of the titration was observed in the last additions. This new signal was accepted to come from the remaining α_4 atropisomer, so we carried out the same fitting procedure, resulting in a new association constant. This discussion is shown in Figure 5.[15]

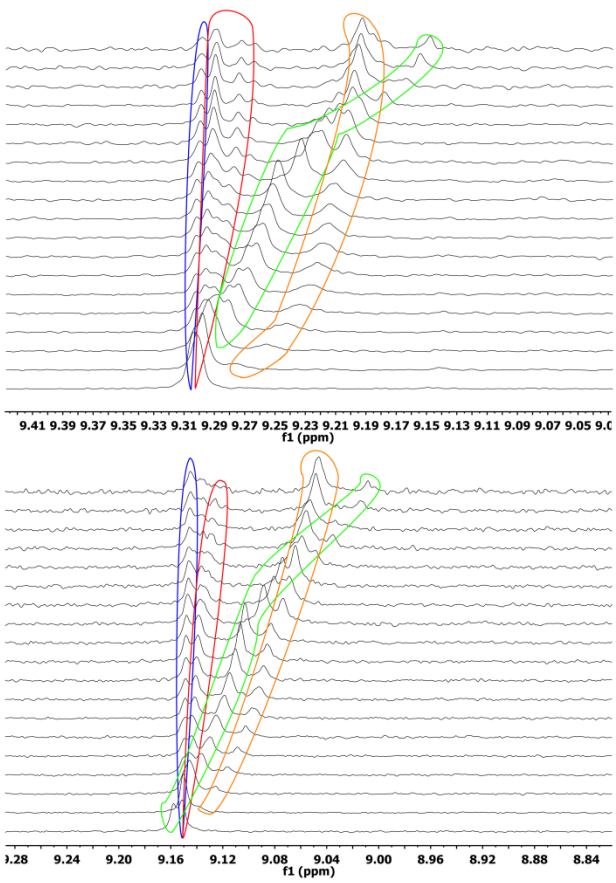


Figure 5: ^{1}H NMR showing H_2 chemical shifts in deuterated toluene of **ZnP2c** (up) and **2HP2c** (bottom) upon addition of aliquots of C_{60}.Colored domains enclose the assignments according to the pattern established in Figure 3. Note the crossover between green and yellow domains.

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 obserbed.

These results were not consistent with our initial assumptions, because we thought that **αβαβ2HP2c** ideally had a good preorganization in a double tweezer mode and could lead to moderate association. However, we did not find chemical shift changes big 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 fullerene shape is not efficient, while other atropisomers preorganizations are much more efficient.

The best results were obtained for corannulene-functionalized porphyrins, especially **ZnP2c**. **α_4ZnP2c** and **$\alpha_2\beta_2$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 average signals coming from internal hydrogens (H_1) and could be followed during titration experiments., so an average association constant could be given, concluding that our corannulene-based

porphyrins are very good host for C_{60} because their association constants are one order of magnitude better 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 constants estimated are gathered in Table 1.

TABLE 1. Summary of Ka of new porphyrins *vs* C_{60} estimated in toluene-d8.

	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]	$(4.5\pm0.05)10^2$	N/A[c]	$(4.6\pm0.05)10^2$	N/A[c]	$(5.4\pm0.2)\ 10^3$

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

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, being the best hosts, α_4 and $\alpha_2\beta_2$ porphyrins bearing corannulene as 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 tweezer-like 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 towards fullerenes thanks to a synergy between porphyrin and non-planar polycyclic hydrocarbon.

EXPERIMENTAL SECTION

All reagents were purchased from regular 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 were 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 in 400 MHz 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 solvents 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. $^{13}C\{^1H\}$ spectra for all porphyrin derivatives had to be recorded with the following acquisition parameters due to their fast relaxation: 90º pulse, relaxation delay of 5ms and acquisition time of 250ms. ^{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 N_2 laser (337 nm, pulse energy 100 μJ, 1 ns). Acceleration voltage of 19 kV and reflector positive mode were used. UV/Vis absorption spectra wavelengths (λ) are reported in nanometers (nm) and molar absorption coefficient (ε) are reported in $M^{-1}\cdot cm^{-}1$ units. Corannulene and bromocorannulene were prepared according to literature procedures.[17]

General method for polyaromatic boronate esters 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 inert atmosphere. 2 mL of dry dioxane were added and the mixture was degassed. Then, it was refluxed overnight. Solvent was removed under vacuum before a purification by column chromatography with SiO_2 gel, hexane/AcOEt (5:1 for 9-(pinacolatoboron)phenanthrene) (**1**), (20:1 for 1-(pinacolatoboron)pyrene (**2**) and 1-(pinacolatoboron) corannulene) (**3**). Yields over 85%. Spectral data are in agreement to 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 microwave irradiation. The mixture was stirred inside microwave reactor at 200 ºC for 15 minutes (a pressure of 5 bar was achieved). The resulting black crude obtained after cooling at room temperature was taken up and MeOH was added (50 mL), precipitating a purple solid. 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 ºC, 24 hours, 50 mbar) to finally get pure **2HP1** whose spectroscopic data agree with those reported[19] (0.295 g, 32% yield).

ZnP1: 2HP1 (0.25 0g, 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 ºC for 2.5 hours (a pressure of 6 bar was achieved). Once finished, solvent was removed in vacuo. The resulting solid was washed several times with water and dried to get 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{^{1}H} 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 put the mixture under inert atmosphere. 1.8 mL of dry dioxane and 116 μL of dry pyridine were added and the mixture was degassed before sealing the vial. Then, it was stirred inside microwave reactor at 150 ºC for 2 hours (a pressure of 3 bar was achieved). Solvent was removed under vacuum and the resulting dark residue was redissolved in a mixture of $CHCl_3$/MeOH 95:5 before quickly passing it 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{^{1}H} 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: Porphyrin derivative (**2HP1**, **ZnP1** or **ZnP2**) (0.02 mmol), PAH derivative (9-Bromophenanthrene, 1-Bromopyrene, Bromocorannulene, **1**, **2** or **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 put the mixture under inert atmosphere. 2.2 ml of dry and degassed toluene were added as well as 30 μL of dry pyridine before sealing the vial. The mixture was then sonicated thoroughly and stirred vigorously inside microwave reactor at 130 ºC for 1 hour (a pressure of 3 bar was achieved). After such time, solvent was removed under vacuum and the black residue was subjected to a purification by column chromatography yielding the 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** or **ZnP2c**) (0.02 mmol) were dissolved in 2 mL of DCM. To the deep red solution, 2 ml of CF_3CO_2H were added at once and the color turned immediately to green. The mix-

ture 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. It 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{^{1}H} 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{^{1}H} 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, 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{^{1}H} 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 equivalents. A ^{1}H NMR spectrum was recorded at room temperature after each addition. Once obtained all data, changes in chemical shifts (Δδ) 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

Synthesis 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 constants estimation and computational calculations are gathered in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interests.

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[13] Porphyrins **2HP1**, **ZnP1** and **ZnP2** were also tested to investigate their properties to bind Buckminsterfullerene, but both MS and ^{1}H NMR spectra gave negative results, indicating that PAHs subunits slightly contribute to form the adduct.

[14] See 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 was reasonable in our case due, mainly, to inconsistencies when fitting curves and no reproducibility when compared to H_2 chemical shift changes.

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