Supporting Information

Decoupling the synergistic effects in aromatic-porphyrin-fullerene systems

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General atom numbering

M = 2H, Zn
NMR spectra

2H-PTetraBr

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Figure S54: Expanded region of MS (MALDI-TOF) in DCTB of 2H-PTetraBpin [M]+.
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Figure S56: Expanded region of MS (MALDI-TOF) in DCTB of Zn-PTetraBpin [M]+.
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**Figure S58:** Expanded region of MS (MALDI-TOF) in DCTB of Zn-PTetraPyr [M]+.
Figure S59: Full MS (MALDI-TOF) in DCTB of 2H-PTetraPyr [M]⁺.

Figure S60: Expanded region of MS (MALDI-TOF) in DCTB of 2H-PTetraPyr [M]⁺.
Figure S61: Full MS (M ALDI-TOF) in DCTB of Zn-PTetraCor [M]^+.

Figure S62: Expanded region of MS (MALDI-TOF) in DCTB of Zn-PTetraCor [M]^+.

Figure S63: Full MS (MALDI-TOF) in: 1-Dithranol-negative, 2-Dithranol-positive, 3-DCTB-positive, 4-DCTB-negative of 2H-PTetraCor [M]^+. 
Complexation measurements

In order to estimate the association constants ($K_a$) of the compounds Zn-PTetraCor and 2H-PTetraCor with fullerenes, the dilution method was applied. A $10^{-4}$ M deuterated toluene solution of each compound was prepared, and a known volume was transferred to an NMR tube (500 μL). The titration was carried out by adding known portions of a stock solution of $C_{60}$ or $C_{70}$ ($10^{-3}$ M) in deuterated toluene to cover a wide range of equivalents. A $^1$H NMR spectrum was recorded at room temperature after each addition. Once all data had been obtained, the changes in the chemical shifts ($\Delta\delta$) of selected protons were plotted as a function of the molar fraction of the guest, and the resulting curve was fitted by a nonlinear method using the global analysis approach according to the following equations, depending on the type of equilibrium:¹

1:1 Equilibria

General expression for the equilibrium constant:

$$K_a = \frac{[HG]}{[H][G]}$$

eq.1

Changes upon NMR titration:

$$\Delta\delta = \Delta\delta_{HG}\left(\frac{[HG]}{[H]_0}\right)$$

eq.2

Figure S64: Expanded region of MS (MALDI-TOF) in DCTB of 2H-PTetraCor $[M]^+$. 
Where:

\([\text{HG}]\) is the concentration of the guest of the complex, and is calculated using the following equation:

\[
[\text{HG}] = \frac{1}{2} \left( [G_0] + [H_0] + \frac{1}{K_a} \right) - \sqrt{\left( [G_0] + [H_0] + \frac{1}{K_a} \right)^2 + 4[G_0][H_0]}
\]

\(\text{eq.3}\)

Where:

\([G_0]\) is the total concentration of the guest

\([H_0]\) is the total concentration of the host

\(\Delta \delta_{\text{HG}}\) is \(\Delta \delta\) at maximum complexation (100% supramolecular complex formation)

\(K_a\) is the estimated association constant for 1:1 equilibrium

\(\Delta \delta_{\text{HG}}\) and \(K_a\) for a 1:1 equilibrium were extracted using the non-linear curve fitting tool at the open access web portal [http://supramolecular.org](http://supramolecular.org) (accessed since 2016). Links to all the fittings of the data are provided below for every case.
Figure S65: $^1$H-NMR spectra of the titration of Zn-PTetraCor (10$^{-4}$ M) with variable concentrations of C$_{60}$ (10$^{-3}$ M) in toluene-d$_8$.

Figure S66: Nonlinear regressions for the results of the titration of Zn-PTetraCor (10$^{-4}$ M) with C$_{60}$ (10$^{-3}$ M) for selected protons (right plot: H$_6$ proton, left plot: H$_7$, 1:1 binding model).

For additional information see:

http://app.supramolecular.org/bindfit/view/c40ba3c1-1658-43b7-965e-17b2e510871b
Figure S67: $^1$H-NMR spectra of the titration of Zn-PTetraCor ($10^{-4}$ M) with variable concentrations of C$_{70}$ ($10^{-3}$ M) in toluene-d$_8$.

Figure S68: Nonlinear regressions for the results of the titration of Zn-PTetraCor ($10^{-4}$ M) with C$_{70}$ ($10^{-3}$ M) for selected protons (right plot: H$_6$ proton, left plot: H$_7$, 1:1 binding model).

For additional information see:

http://app.supramolecular.org/bindfit/view/1d6856af-192c-4e5a-9d53-f609627ac179
Figure S69: $^1$H-NMR spectra of the titration of 2H-PTetraCor (10^{-4} M) with variable concentrations of C_{60} (10^{-3} M) in toluene-d_8.

Figure S70: Nonlinear regressions for the results of the titration of 2H-PTetraCor (10^{-4} M) with C_{60} (10^{-3} M) for selected protons (right plot: H$_6$ proton, left plot: H$_7$, 1:1 binding model).

For additional information see:
http://app.supramolecular.org/bindfit/view/41c6686e-e06a-41fd-bc7c-ee6955080966
Figure S71: $^1$H-NMR spectra of the titration of 2H-PTetraCor ($10^{-4}$ M) with variable concentrations of C$_{70}$ ($10^{-3}$ M) in toluene-d$_8$.

Figure S72: Nonlinear regressions for the results of the titration of 2H-PTetraCor ($10^{-4}$ M) with C$_{70}$ ($10^{-3}$ M) for selected protons (right plot: H$_6$ proton, left plot: H$_7$, 1:1 binding model).

For additional information see:

http://app.supramolecular.org/bindfit/view/f3cbc3e0-aacf-4516-852f-a773e3b87783
Computational methods

Optimized geometries of porphyrin 2H-PTetraCor and the supramolecular assemblies C$_{60}$$@$2H-PTetraCor, C$_{70}$$@$2H-PTetraCor, (C$_{60}$)$_2$$@$2H-PTetraCor and (C$_{70}$)$_2$$@$2H-PTetraCor were obtained by DFT methods with the B97D3 functional, which contains the Becke-Johnson damping empirical dispersion correction and was provided by Grimme and collaborators. Pople’s split valence set 6-31G(d,p) was chosen as the basis set. Solvent corrections applied using the polarizable continuum model (PCM) using toluene ($\varepsilon=2.3741$).

The strategy to obtain the inclusion complexes C$_{60}$$@$2H-PTetraCor and C$_{70}$$@$2H-PTetraCor consisted of using the optimized structure of compound 2H-PTetraCor and manually placing the corresponding fullerene molecule halfway between the two corannulenes, rotating the single C-C bonds at the same time so that both PAH fragments matched with the fullerene surface. For the assembly C$_{70}$$@$2H-PTetraCor, several attempts were carried out by imposing different orientations on the fullerene C$_{70}$; only the most stable one was considered and is reported here. Once both 1:1 adducts were optimized, their structures were used as starting geometries for a second round of optimizations to obtain the complexes (C$_{60}$)$_2$$@$2H-PTetraCor and (C$_{70}$)$_2$$@$2H-PTetraCor by placing a second fullerene molecule following the same protocol described above.

All minima were confirmed by vibrational analysis to show no imaginary frequencies. The electronic energies of the optimized geometries were further evaluated using a more extended 6-31+G(d,p) basis set that includes diffuse functions.

Deformation energies were estimated by subtracting the electronic energy of the optimized porphyrin 2H-PTetraCor (H) from the electronic energy of the porphyrin in the optimized structure of the adduct (HG, i.e., C$_{60}$$@$2H-PTetraCor and C$_{70}$$@$2H-PTetraCor) according to eq. 4. For the supramolecular assemblies (C$_{60}$)$_2$$@$2H-PTetraCor and (C$_{70}$)$_2$$@$2H-PTetraCor) (HG$_2$), the subtraction was carried out from the porphyrin structure shown in the parent 1:1 inclusion complexes (HG) according to eq. 5:

$$E_{def} = E_{HG}(H) - E_{H}(H)$$  \hspace{1cm} \text{eq.4}$$E_{def} = E_{HG_2}(H) - E_{H}(H)$$  \hspace{1cm} \text{eq.5}

Where the subscripts denote the geometry used and the letter between parentheses corresponds to the molecular entity studied (porphyrin in all cases).

Interaction energies were calculated taking into account basis set superposition error (BSSE) with the Boys–Bernardi functional counterpoise scheme as follows (eq. 6):

$$E_{int}(HG) = E_{HG}^{HG}(HG) - E_{H}^{HG}(H) - E_{G}^{HG}(G)$$  \hspace{1cm} \text{eq. 6}

Where the subscripts denote the geometry used (inclusion complex in all cases) and the superscripts refer to the basis set (from the supramolecular assembly in all cases); H and G correspond to the host and guest molecular entities, respectively, and HG to the supramolecular adduct.
All the above-described computational methods were performed using the Gaussian 16 package.\textsuperscript{7}

Non-covalent interactions were obtained from the location critical points at which the reduced density gradient decreases to low electronic density values according to the scheme of Yang et al. with the help of the NCIPlot package.\textsuperscript{8} Calculations were performed with promolecular densities, and gradient isosurfaces were plotted with an isovalue of 0.3 a.u. and coloured on a blue-green-red scale according to the values of the sign of $\lambda_2$ (the second eigenvalue of the electron-density Hessian). Red indicates repulsion, green indicates weak attraction, and blue represents strong attraction. Graphics were visualized in Chimera\textsuperscript{9} with the help of Tangram NCIPlot GUI built by Insilichem Group.\textsuperscript{10}
C_{60}@2H-Pentacor (E = -7263.357726 a.u.)
(C_{60})_2@2H-PetaCor

(E = -9548.16104096 a.u.)
Figure S73: Plot of the reduced density gradient versus the electron density for the complex C_{60}@2H-PetraCor.
Figure S74: Non-covalent interaction isosurfaces for the assembly C₆₀@2H-PTetraCor.

Figure S75: Plot of the reduced density gradient versus the electron density for the complex C₇₀@2H-PTetraCor.

Figure S76: Non-covalent interaction isosurfaces for the assembly C₇₀@2H-PTetraCor
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