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Complexation of $Sc_3N@C_{80}$ Endohedral Fullerene with Cyclic Zn-Bisporphyrins: Solid State and Solution Studies

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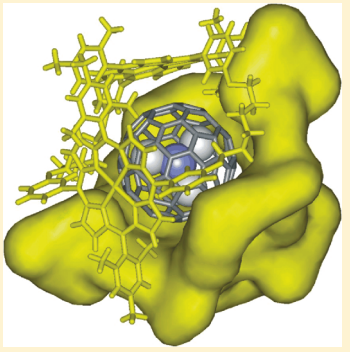
Supporting Information

ABSTRACT: We report the synthesis of two cyclic β-pyrrole unsubstituted *meso*-tetraphenyl bisporphyrins in which the porphyrin units are connected by two 2,3-hexadiynyl-1,6-dioxo or two hexyl-1,6-dioxo spacers, respectively. Both cyclic porphyrin dimers exist in solution as mixtures of two conformational isomers. In the solid state, the receptor with diynyl spacers forms a 1:1 complex with the icosahedral (I_h) isomer of the trimetallic nitride endohedral fullerene $Sc_3N@C_{80}$. In this complex the receptor adopts a scoop-shaped conformation having a dihedral angle of 87.25° between the two porphyrin planes. The hexyl spaced analogue, however, adopts a similar conformation upon encapsulation of one molecule of $Sc_3N@C_{80}$ in a self-assembled dimeric capsule. The capsular complexes pack in columns and render the fullerene units completely isolated. In toluene solution, ^{1}H NMR experiments indicate that the endohedral fullerene $Sc_3N@C_{80}$ is exclusively bound by the expanded isomer of both dimers. UV−vis and fluorescence titration experiments confirmed the existence of strong $\pi-\pi$ interactions between the fullerene $Sc_3N@C_{80}$ and the flexible bisporphyrin dimer with hexyl spacers. At micromolar concentration, the flexible receptor forms only a 1:1 complex with the endohedral fullerene with stability constant value of $K_a = 2.6 \pm 0.3 \times 10^5$ M^{-1}.



INTRODUCTION

Evidence of attractive fullerene−porphyrin interactions was first discovered in cocrystallates of fullerenes (C_{60} and C_{70}) with monoporphyrins.[1] Generally, in these solid state structures it was observed that the porphyrin formed 1:1 complexes with the fullerenes.[2] The fullerenes are sandwiched between two porphyrin units belonging to adjacent 1:1 complexes, and the porphyrin planes display either a parallel (cofacial) or tilted (zigzag) arrangement probably due to the maximization of intermolecular interactions in the packing of the lattice. More recently, the geometry of 1:1 inclusion complexes formed by cyclic dimers of porphyrins and fullerenes has also been investigated by X-ray crystallography and in solution.[3] For example, the inclusion complex of C_{60} with a cyclic free base porphyrin dimer **1**·H_4 having 1,3-butadiynyl spacers reveals a clamshell-like conformation for the receptor.[4] The porphyrin units are tilted with respect to each other providing a fullerene-bite angle of 52° between their planes. The authors stated that presumably the short distance between the two porphyrins of the dimer does not allow accommodating C_{60} in a parallel conformation of the receptor. On the other hand, Aida, Saigo, et al. reported that the elongated cyclic dimer **2**·Zn_2 with flexible hexyldioxo spacers (O-$(CH_2)_6$-O) forms a solid state inclusion complex with C_{60} that exhibits a perfect parallel arrangement of the porphyrin rings (dihedral angle of 0°).[5] The hexyldioxo spacers are in fact too long and have to fold in order to adjust the Zn-porphyrin-Zn-porphyrin to the ideal distance of 12.35 Å for sandwiching C_{60}. Surprisingly, none of the 15 solid state structures of 1:1 complexes involving endohedral C_{80} fullerenes and monoporphyrins retrieved from a search of the Cambridge Structure Database using "C_{80}" as the query for the compound names displayed the sandwich binding motif typically observed for C_{60}/C_{70} binding monoporphyrins. In addition and to the best of our knowledge, there are no examples reported of solid state structures of trimetallic nitride endohedral fullerenes bound to cyclic porphyrin dimers or any other type of molecular receptor.[6,7]

We undertook this work to evaluate the complexation properties of two cyclic bisporphyrin receptors with the icosahedral (I_h) isomer of C_{80} filled with scandium nitride ($Sc_3N@C_{80}$).[8] Herein we describe the synthesis of two new β-pyrrole unsubstituted cyclic Zn-porphyrins dimers **3**·Zn_2 and **4**·Zn_2 (Figure 1) having aryl groups in all *meso* positions and containing linker chains analogous to the ones previously reported by Aida

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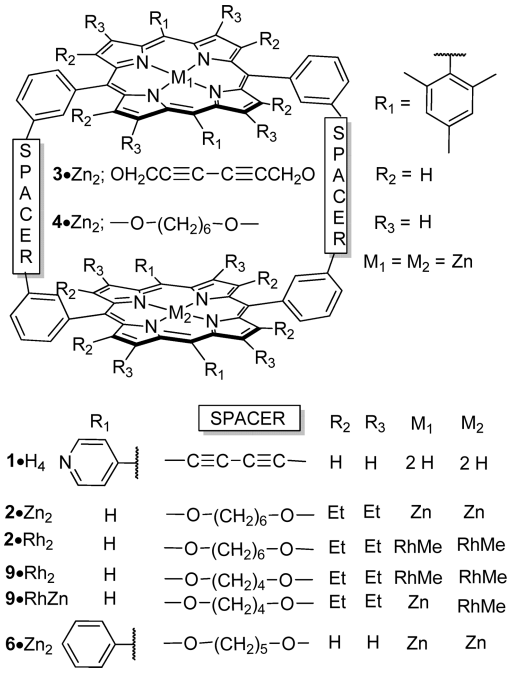


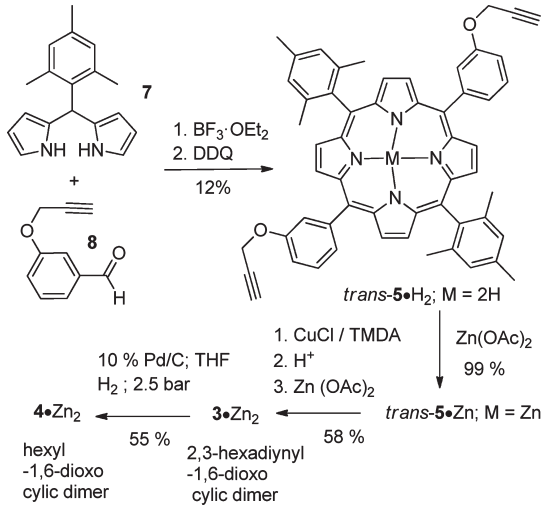
Figure 1. Line drawings of several cyclic bisporphyrin receptors.

and Saigo.[9] We report unprecedented results obtained in the solid state binding studies of the endohedral fullerene with these cyclic bisporphyrin receptors, as well as some spectroscopic and thermodynamic data of their interaction in solution. Molecular modeling studies suggested that the optimum distance between the Zn-porphyrin rings of a cyclic dimer in parallel arrangement and sandwiching one C_{60} molecule is 14.3 Å. This separation distance can be easily spanned by flexible hexyldioxo or pentyldioxo spacers (O-$(CH_2)_n$-O; n = 5 or 6) connecting the *meta* position of *trans*-phenyl-substituted porphyrins. It is well-known that pyrrole-β-substituted porphyrins experience an increase in π-basicity compared with their unsubstituted counterparts and tend to adopt a shallow concave conformation to avoid steric clashes between *meso* and β-pyrrolic substituents. Both effects are important for the stabilization of the supramolecular aggregates they form with fullerenes. Additionally, the β-pyrrole substituents surround the fullerene surface to establish weak CH-π interactions.[10]

We decided to use a non-β-pyrrole-substituted monoporphyrin bearing four *meso*-aryl substituents, *trans*-**5**, in the construction of the cyclic dimers used in this study. The incorporation of the *meso*-mesityl substituents was engineered as an alternative to the β-pyrrole substitution with the aim of retaining the π-basic properties of the porphyrin unit. Moreover, the facially encumbering methyl groups of the *meso*-mesityl substituents were expected to induce a shallow concave cavity on the porphyrin faces. We also envisaged that the *o*-methyl groups in the mesityl substituent could engage in CH-π interactions to increase the van der Waals contacts with the bound fullerene as β-pyrrole substituents ussually do.

In the course of this work the syntheses of cyclic bisporphyrin host **6**·Zn_2, possessing aryl substituents in the four *meso* positions and pentyldioxo linker chains, was published.[11] The synthetic procedure for **6** relied on a low yielding nontemplate macrocyclization reaction between a 5,15-bis[3′-(5-bromopentyl)phenyl]-10,20-diphenylporphyrin and *trans*-bis(3′-hydroxydiphenyl)-

Scheme 1. Synthesis of Cyclic Porphyrin Dimers 3·Zn_2 and 4·Zn_2 Used in This Study



diphenylporphyrin. Instead, we decide to approach the preparation of dimer **4** using the synthetic strategy described by Aida and Saigo in the preparation of cyclic bisporphyrin receptor **2**.[9]

RESULTS AND DISCUSSION

Synthesis. Porphyrins of the ABAB-type like *trans*-**5**·H_2 (Scheme 1) can be prepared by condensing a 5-aryl-substituted dipyrromethane with an aromatic aldehyde.[12] For the synthesis of monoporphyrin *trans*-**5**·H_2 we chose to condense 5-mesityldipyrromethane **7** with 3-propargyloxibenzaldehyde **8**. The use of sterically hindered 5-dipyrromethanes tends to reduce the scrambling in MacDonald-type 2 + 2 condensations and minimize the formation of the *cis*-A_2B_2-type porphyrin.[13] We applied the conditions described by Lindsey et al.[13] to the reaction of **7** with **8** and isolated *trans*-**5**·H_2 in 26% yield after two consecutive column chromatography purifications on silica. The treatment of *trans*-**5**·H_2 with zinc acetate using standard conditions afforded metalated *trans*-**5**·Zn in almost quantitative yield. After stirring a methylene chloride solution of *trans*-**5**·Zn, open to air, with a high molar excess of copper(I) chloride and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) during, 4 h we obtained, after the usual workup, a dark red solid.[14,9]

The ^{1}H NMR analysis of an aliquot of the reaction crude dissolved in $CHCl_3$-*d* indicated the presence of the proton signals expected for dimer **3**·Zn_2 with 2,3-hexadiynyl-1,6-dioxo spacers. Not unexpectedly, we also observed proton signals corresponding to ditopically coordinated TMEDA molecules included in the cavity of **3**·Zn_2.[9] The X-ray analysis of a crystal grown from the above $CHCl_3$-*d* solution confirmed the existence of the inclusion complex TMEDA⊂**3**·Zn_2 also in the solid state (Figure 2). In order to obtain the uncoordinated cyclic dimer **3**·Zn_2, we dissolved the reaction crude obtained from the Hay coupling in dichloromethane and added a few drops of 4 N HCl solution in dioxane to promote the complete demetalation of the porphyrin units. We obtained uncoordinated cyclic dimer **3**·Zn_2 in an overall yield of 58% after subsequent metalation of the free base porphyrin **3**·H_4 with zinc. Finally, the catalytic hydrogenation of **3**·Zn_2 using 10% Pd/C as catalyst and 2.5 bar of hydrogen

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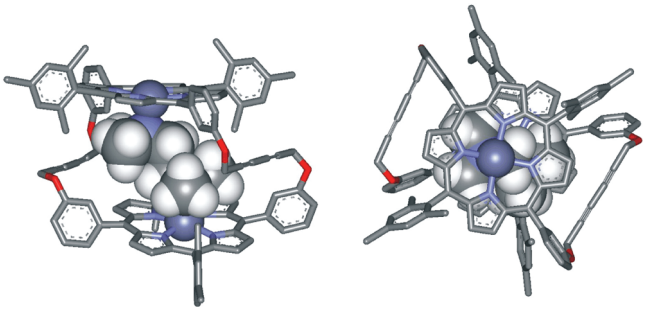

Figure 2. Side and top views of the TMEDA⊂**3**·Zn_2 complex. The bisporphyrin receptor is shown in stick representation, TMEDA and Zn atoms as CPK models. Hydrogen atoms of the receptor are omitted for clarity. Notice the adaptability of the cavity size to the ditopic binding of the diamine and the linearity of the 2,3-butadiynyl linkers.

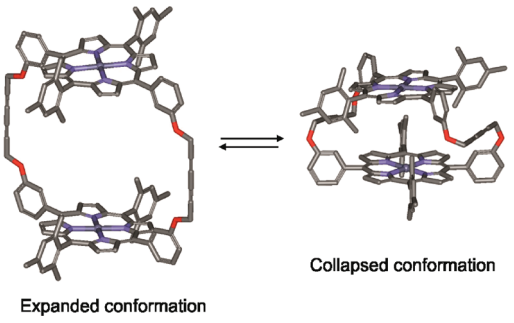

Figure 3. CAChe minimized structures of the two conformational isomers proposed for cyclic dimer **3**·Zn_2.

pressure afforded, after column chromatography purification, the flexible cyclic dimer **4**·Zn_2 with hexyldioxo spacers in 55% yield.

As a result of their conformational flexibility, both cyclic porphyrin dimers, **3**·Zn_2 and **4**·Zn_2, exist in solution as mixtures of the two conformational isomers.[15] The ^{1}H NMR spectrum of **3**·Zn_2 in $CHCl_3$-*d* showed two different sets of signals for the β-pyrrole protons. The major conformer showed two doublets resonating at δ = 8.80 and 8.50 ppm (J = 4.6 Hz) for the β-pyrrole protons (see Supporting Information). The minor conformer featured four doublets resonating at δ = 8.8, 8.74, 8.44, and 8.41 ppm (J = 4.6 Hz), respectively, for the β-pyrrole protons. Based on the number of proton signals observed in each set, we assigned an expanded conformation to the major isomer and a collapsed conformation to the minor one (Figure 3).

When dimer **4**·Zn_2 adopts the expanded conformation, it possesses two planes of symmetry, as well as a C_2 axis perpendicular to the porphyrin rings. Consequently, the four pyrrole units of each porphyrin ring experience the same magnetic microenvironment and the β-pyrrole protons resonate as two doublets. The minor isomer, however, having a collapsed conformation, features a C_2 axis but lacks one of the symmetry planes that are perpendicular to the porphyrin rings and renders the pyrrole rings in each porphyrin unit chemically nonequivalent. A 2D-ROESY experiment showed that the two conformers are involved in a slow chemical exchange process with respect to the chemical shift time scale of the ^{1}H NMR spectrum, and that is why resolved proton signals are observed for each conformer. The integration of the resolved proton signals allowed us to calculate a ratio of 80:20 for the conformational isomers in favor

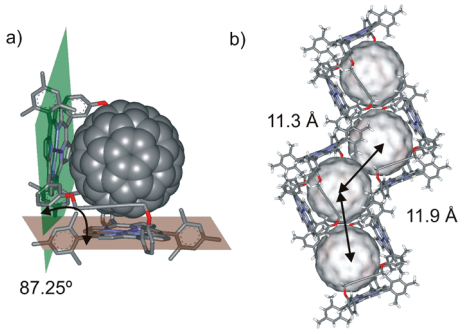

Figure 4. (a) Solid state structure of the $Sc_3N@C_{80}$⊂**3**·Zn_2 complex. Hydrogen atoms are omitted for clarity and the fullerene is shown in CPK representation. (b) Zigzag arrays of the $Sc_3N@C_{80}$⊂**3**·Zn_2 complexes in the crystal packing. C_{80} molecules are depicted as the van der Waals surface, and solvent molecular are omitted for clarity.

of the expanded one. Dimer **4**·Zn_2 containing fully saturated linker chains displays a completely analogous dynamic and conformational behavior with a similar isomer ratio.

Solid State Studies. To our delight, we were able to characterize the solid state structures of complexes formed by both cyclic dimers **3**·Zn_2 and **4**·Zn_2 with $Sc_3N@C_{80}$. The X-ray diffraction analysis of a single-crystal grown by slow evaporation from a *p*-xylene solution containing butadiynyldioxo linked cyclic receptor **3**·Zn_2 and 2 equiv of $Sc_3N@C_{80}$ revealed a 1:1 inclusion complex, $Sc_3N@C_{80}$⊂**3**·Zn_2. The asymmetric unit is made up of one cyclic receptor, one $Sc_3N@C_{80}$ endofullerene, and 2.5 *p*-xylene molecules. The shell of the endofullerene is disordered over three positions, and the included Sc_3N was modeled over five different positions. In the crystal structure, the receptor adopts a scoop-like conformation that fully includes the endohedral fullerene (Figure 4). The dihedral angle between the two pophyrin planes (four nitrogen mean plane) is 87.25°. The porphyrin rings show a reduced concavity to adapt to the convex surface of the fullerene. In each ring, two *trans-meso* carbon atoms are slightly outward from the four-nitrogen mean plane and the other two are inward. The displacement distances are in the range of 0.38−0.14 Å. The shortest separation between a carbon atom of C_{80} and the Zn-porphyrin centers is 2.961 Å. This value suggests the existence of strong $\pi-\pi$ interactions between the porphyrins and $Sc_3N@C_{80}$. Many hydrogen atoms of the substituents of the porphyrin rings are involved in CH-π interactions with the included guest. The crystal packing shows the formation of a zigzag chain of $Sc_3N@C_{80}$ and cyclic receptors forming a rod. Overall, it closely resembles the packing motif recently described for the C_{60}⊂**1**·H_4 complex.[4] The distances between the centers of adjacent $Sc_3N@C_{80}$ belonging to the same rod are 11.9 and 11.3 Å. This value is consistent with the outer diameter of C_{80}, suggesting that the adjacent endohedral fullerenes are in van der Waals contact with each other. This structure suggests potential uses of these complexes in organic photovoltaic (OPV) applications.

The closest fullerene belonging to a neighboring rod is at a distance of 14.35 Å. Adjacent rods pack to form layers that stack on top of each other. The 1:1 complexes of different layers are slightly tilted. Most likely, the uncovered π surface of the included $Sc_3N@C_{80}$ prefers to be involved in these interesting fullerene−fullerene interactions rather than forming $\pi-\pi$ interactions with the porphyrin rings of other 1:1 inclusion complexes. In fact, this binding behavior is completely in line with the

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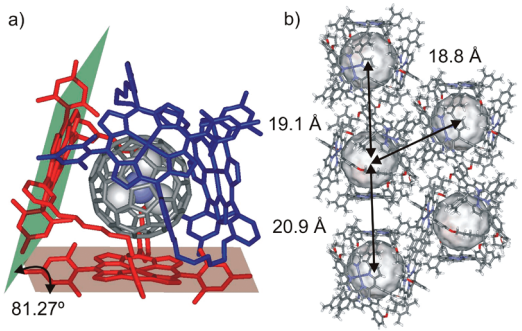

Figure 5. Solid state structure of the molecular capsule $Sc_3N@C_{80}\subset(\mathbf{4}\cdot Zn_2)_2$. Hydrogen atoms are omitted for clarity, the fullerene and the cyclic receptors are shown in stick representation with each bisporphyrin in a different color (red and blue), and the Sc_3N is depicted as a CPK mode. (b) Columnar arrangement of the molecular capsules in the packing of the crystal. $Sc_3N@C_{80}$ molecules are depicted as the van der Waals surface, and solvent molecular are omitted for clarity.

observations made in the solid state structures of the 1:1 complexes of monoporphyrin binding endohedral fullerenes. The binding motif of a fullerene sandwiched between two adjacent porphyrin rings which is common for C_{60}/C_{70} was never detected.

Surprisingly, the X-ray diffraction analysis of a single crystal grown from a *p*-xylene solution of the hexyldioxo linked cyclic receptor $\mathbf{4}\cdot Zn_2$ with 2 equiv of $Sc_3N@C_{80}$ revealed the formation of an unexpected 2:1 encapsulation complex. Two cyclic receptors self-assemble to form a supramolecular capsule that traps one molecule of $Sc_3N@C_{80}$ in its interior (Figure 5).

The complex possesses one C_2 symmetry plane, and the asymmetric unit contains one cyclic receptor and half of the encapsulated endohedral fullerene. Each monomer of the cyclic receptor in the 2:1 complex also adopts a scoop-shaped conformation similar to the one observed for the butadiynyl linked equivalent $\mathbf{3}\cdot Zn_2$ in the 1:1 complex. However, the dihedral angle between the two porphyrin planes (four nitrogen mean plane) decreases slightly to 81.27°. In this complex the porphyrin rings are almost completely planar. One of the hexyldioxo linker chains of the porphyrin dimer is disordered over two positions. The C_{80} shell is also disordered over two positions generated by the 2-fold axis while the Sc_3N, although highly disordered, is mainly located on two hypothetical planes that are perpendicular to the porphyrin rings of the dimer. The supramolecular capsules form a columnar arrangement through direct intermolecular interactions, as well as by the intermediacy of a *p*-xylene molecule sandwiched between two porphyrin units. The endofullerenes are placed at center to center distances in the range of 19−20 Å. It is worth noting that the encapsulation of the $Sc_3N@C_{80}$ in the 2:1 capsular complexes precludes the possibility of establishing direct $\pi-\pi$ interactions between adjacent fullerenes. The calculated volume for the cavity of the molecular capsule is 1053 Å^3, and the van der Waals volume of the included endohedral $Sc_3N@C_{80}$ is 698 Å^3, to yield a packing coefficient value of 0.66 for the resulting complex (Figure 6).[16] Moreover, the calculated volume of the interior of the C_{80} cage is 55 Å^3, and the van der Waals volume of the trapped Sc_3N is 41 Å^3, resulting in a second packing coefficient value of 0.75. Overall, the architecture of the capsule displays two different levels of reversible and irreversible molecular encapsulation with different packing coefficients and can be considered as another example of a "hetero bucky onion"[17]

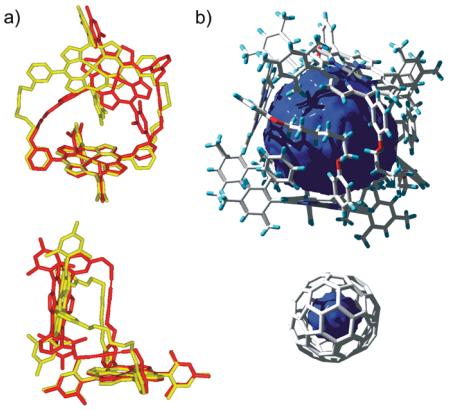

Figure 6. (a) Front and side views of the superimposed cyclic dimers (red, hexadiynyldioxo spaced $\mathbf{3}\cdot Zn_2$ and yellow, hexyldioxo spaced $\mathbf{4}\cdot Zn_2$) with the conformation adopted in the solid state on binding $Sc_3N@C_{80}$, hydrogen atoms are omitted for clarity. (b) Calculated volumes for the molecular capsule $(\mathbf{4}\cdot Zn_2)_2$ after removing the encapsulated $Sc_3N@C_{80}$ (top) and for $Sc_3N@C_{80}$ after deleting the included Sc_3N (bottom). The wide portals present in the capsule were locked with benzene molecules to fully close the cavity before performing the volume calculation using the Swiss-pdb software.[18]

In solution, Aida et al. reported the formation under stoichiometric control of similar 2:1 complexes between a methylrhodium cyclic bisporphyrin $\mathbf{9}\cdot Rh_2$ with much shorter -O(CH$_2$)$_4$-O- butyldioxo linkers and C_{60}/C_{70}.[17] The observation of this type of complexes was rationalized by the fact that the short spaced host $\mathbf{9}\cdot Rh_2$ must adopt a geometry in which the porphyrin units are tilted with respect to one another to accommodate the fullerenes in combination with an inherently large affinity of organorhodium porphyrin toward fullerenes. For the hybrid host $\mathbf{9}\cdot$RhZn only 1:1 complexes were observed with C_{60}. Also relevant is that 2:1 complexes have not been described in solution or in the solid state for the interaction of analogous hexyldioxo spaced metallo cyclic porphyrins $\mathbf{2}\cdot Zn_2$ and $\mathbf{2}\cdot Rh_2$ with C_{60}/C_{70}. We hypothesize that the larger volume of $Sc_3N@C_{80}$ in combination with its different electronic polarization contributes to the formation of the 2:1 complex $Sc_3N@C_{80}\subset(\mathbf{4}\cdot Zn_2)_2$.

Different single crystals from those described for $Sc_3N@C_{80}\subset(\mathbf{4}\cdot Zn_2)_2$ also grew from the same *p*-xylene solution. X-ray diffraction analysis demonstrated that they correspond to a solvate of $Sc_3N@C_{80}$.[19] The packing of the lattice shows that each $Sc_3N@C_{80}$ is surrounded by 12 molecules of *p*-xylene that establish $\pi-\pi$ and CH-π interactions plus six adjacent $Sc_3N@C_{80}$ molecules within a van der Waals interaction distance (Figure 7).

Solution State Studies. *^{1}H NMR Experiments.* We briefly studied the interaction of the cyclic bisporphyrins $\mathbf{3}\cdot Zn_2$ and $\mathbf{4}\cdot Zn_2$ with the endohedral fullerene $Sc_3N@C_{80}$ by means of ^{1}H NMR titration experiments (Figure 8). The addition of approximately 0.5 equiv of $Sc_3N@C_{80}$ to a 1 mM toluene-d_8 solution of either of the two dimers produced a noticeable upfield shift to the β-pyrrole protons but only to those assigned to the major isomer. On the contrary, the chemical shifts of the β-pyrrole protons of the minor isomer remained completely unaltered, although their intensity was clearly diminished compared to the ratio found for the free state of the receptor. Taken together, these observations indicate that the endohedral fullerene $Sc_3N@C_{80}$ is exclusively bound by the expanded isomer of the dimers, reinforcing our

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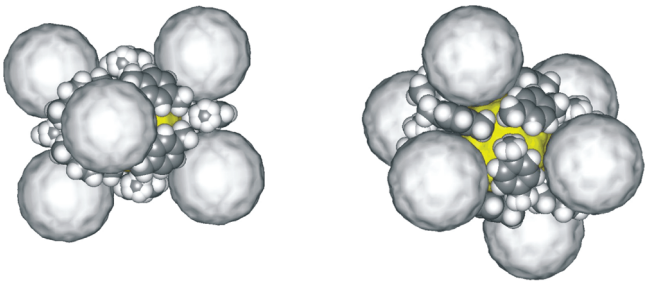

Figure 7. Top and side views of a section of the crystal packing of the solvate of $Sc_3N@C_{80}$. Solvent molecules are represented in CPK and the fullerene with van der Waals surface. The central fullerene is shown in yellow.

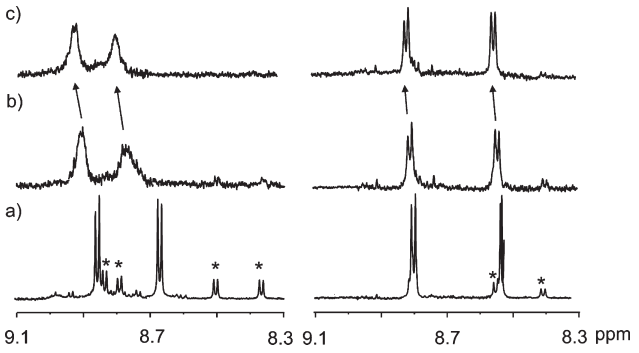

Figure 8. Changes in the region of the β-pyrrole protons during the ^{1}H NMR titration of $[\mathbf{4}\cdot Zn_2] = 9 \times 10^{-4}$ M (left) and $[\mathbf{3}\cdot Zn_2] = 9.1 \times 10^{-4}$ (right) with $Sc_3N@C_{80}$ in toluene-d_8: (a) 0 equiv, (b) ~0.5 equiv, and (c) ~ 1.2 equiv of $Sc_3N@C_{80}$ added. Minor proton signals corresponding to the collapsed isomer of the cyclic receptor are indicated with an asterisk.

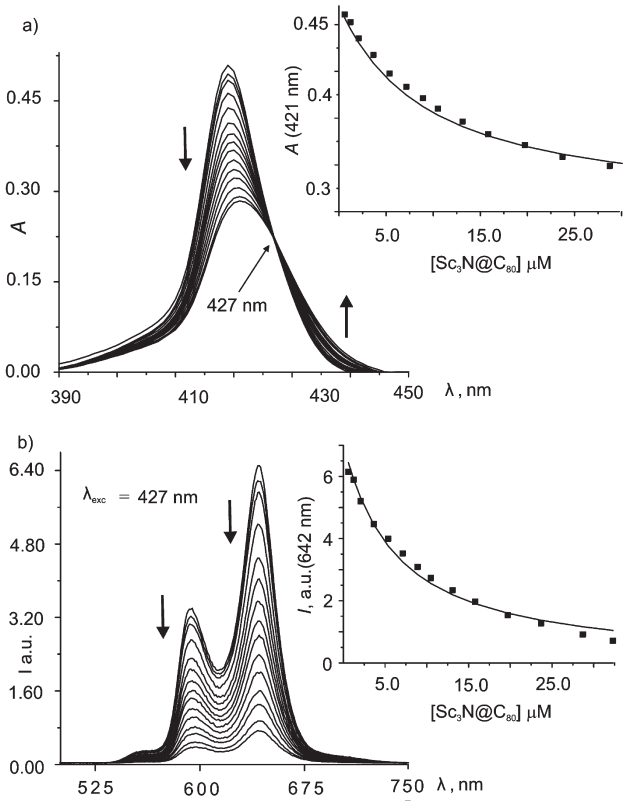

Figure 9. (a) UV−vis titration of $[\mathbf{3}\cdot Zn_2] = 9.13 \times 10^{-7}$ M with $Sc_3N@C_{80}$ in toluene and (b) corresponding fluorescence titration; 0−36 equiv of guest added. Insets: experimental data fitted to the theoretical isotherm for a 1:1 binding model. Changes in $\lambda = 421$ nm for the UV−vis data and $\lambda = 642$ nm for the fluorescence titration.

previous assignment of the two conformational isomers. Clearly, the selective consumption of the expanded isomer drives the conformers' equilibrium toward the production of additional free expanded cyclic dimer at the expense of the collapsed isomer, and this explains the observed reduction of the intensity for the proton signals. The chemical shift changes observed for the β-pyrrole protons of the expanded isomer are more pronounced for the complexation process of $Sc_3N@C_{80}$ with the hexyldioxo linker dimer $\mathbf{4}\cdot Zn_2$ than with the unsaturated parent compound $\mathbf{3}\cdot Zn_2$. In striking contrast, only the complexation of $Sc_3N@C_{80}$ with $\mathbf{4}\cdot Zn_2$ produced a significant broadening of the signals of the β-pyrrole protons that shift. This different behavior could be in principle assigned to the formation of a 1:1 complex with higher thermodynamic and kinetic stability between the $Sc_3N@C_{80}$ and $\mathbf{4}\cdot Zn_2$ than with $\mathbf{3}\cdot Zn_2$, as previously reported for related cyclic bisporphyrin binding with C_{60}/C_{70}.[3] However, the high association constant value determined for the 1:1 $Sc_3N@C_{80}\subset\mathbf{4}\cdot Zn_2$ complex (*vide infra*) together with the observation of the 2:1 complex $Sc_3N@C_{80}\subset(\mathbf{4}\cdot Zn_2)_2$ in the solid state suggests the existence in solution of intermediate exchange equilibria between the free receptor and complexes with different stoichiometries to be responsible for the broadening of the protons signals. However other dynamic processes like an oscillatory guest motion cannot be ruled out.[20,17] Unfortunately, the results derived from variable temperature ^{1}H NMR experiments were not sufficient to clarify this point. For both receptors, the addition of slightly more than 1 equiv of $Sc_3N@C_{80}$ induced additional downfield shifts of the β-pyrrole protons and in the case of $\mathbf{4}\cdot Zn_2$ the complete disappearance of the signals assigned to the collapsed isomer. For this receptor the pyrrole protons also became better defined at this point. Most likely, this is due to the predominance of the 1:1 complex in solution under these conditions.[21]

UV−vis and Fluorescence Experiments. To reduce the amount of fullerene $Sc_3N@C_{80}$ used in the binding experiments, we decided to use absorption and emission spectroscopies to probe the interaction with the cyclic dimer $\mathbf{4}\cdot Zn_2$. The titrations were carried out in toluene using constant micromolar concentrations of the dimers and adding incremental amounts of $Sc_3N@C_{80}$. Figure 9a and b depicts the changes in the absorption and emission spectra, respectively, obtained during the titrations of $\mathbf{4}\cdot Zn_2$ with $Sc_3N@C_{80}$. The fluorescent titrations were done by excitation at the isosbestic point (427 nm) observed in the UV−vis titration.[22] During the titration experiment the Soret band of $\mathbf{4}\cdot Zn_2$ experiences a red-shift of 5 nm with a decrease in intensity, indicating that the binding takes place through $\pi-\pi$ electronic interactions. The molar-ratio graphical method was used to derive a 1:1 stoichiometry for the complex formed in solution.[23] The nonlinear fit of the absorption titration data to a 1:1 complexation model allowed the calculation of the association constant value (K_a) for $Sc_3N@C_{80}\subset\mathbf{4}\cdot Zn_2$ as 2.3×10^5 M^{-1}. Fluorescence titration experiments also confirmed the existence of strong $\pi-\pi$ interactions between the fullerene $Sc_3N@C_{80}$ and the bisporphyrin dimer $\mathbf{4}\cdot Zn_2$.

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The steady state fluorescence of free **4**·Zn_2 was efficiently quenched by the incremental addition of $Sc_3N@C_{80}$, presumably via photoinduced electron transfer from the receptor to the fullerene. The fluorescence titration gave a K_a value of $2.9 \times 10^5\ M^{-1}$, which is acceptably close with the value from the absorption titration. The stability constant of the 1:1 complex $Sc_3N@C_{80}\subset$**4**·Zn_2 is 1 order of magnitude larger than for $C_{70}\subset$**4**·Zn_2.[24] Most likely, the greater size of $Sc_3N@C_{80}$ enables an increase in the aromatic surface interaction between the host and the guest although the different electronic polarization of the endohedral fullerene $Sc_3N@C_{80}$ might also contribute to the stronger binding.

CONCLUSIONS

In conclusion, we have synthesized two macrocyclic bisporphyrin receptors for the inclusion of fullerenes. We report that receptor **3**·Zn_2 with hexadiynildioxo spacers forms a 1:1 inclusion complex in the solid state with $Sc_3N@C_{80}$ in which the porphyrin units are not parallel-oriented but tilted. The crystal packing reveals a zigzag arrangement of the 1:1 complexes and that the fullerene guests are in van der Waals contact. The more flexible hexyldioxo spaced host **4**·Zn_2 produced a capsule-type 2:1 complex in the solid state. The $Sc_3N@C_{80}\subset$(**4**·Zn_2)$_2$ assembly can be considered as an evolved example of hetero "bucky onion" displaying two different levels of molecular encapsulation. The capsular complexes pack in columns and render the fullerene units completely isolated. Solution studies indicate the formation of inclusion complexes between the cyclic receptors and the endohedral fullerene that are stabilized through $\pi-\pi$ interactions. At micromolar concentration, using absorption and emission spectroscopies, we detected for the binding of $Sc_3N@C_{80}$ with **4**·$Zn_2$the exclusive formation of a 1:1 complex for which we calculated a stability constant value of $K_a = 2.6 \pm 0.3 \times 10^5\ M^{-1}$. To the best of our knowledge, this is the first report of solid state structures of an endohedral fullerene bound to molecular bisporphyrin receptors and the second one reporting binding studies in solution with synthetic molecular receptors.[25]

EXPERIMENTAL SECTION

General Methods. All commercial reagents, unless otherwise noted, were reagent grade and used without further purification. Solvents were of HPLC grade quality, obtained commercially and used without further purification. Anhydrous solvents were obtained from a solvent purification system (SPS). Pyrrole was freshly distilled under vacuum just prior to use. ^{1}H NMR spectra were recorded on a 400.1 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C {1H}) and a 500.1 MHz for ^{1}H NMR and 125.6 MHz for ^{13}C {1H} NMR spectrometers. UV−vis spectra were measured on a UV−vis spectrophotometer and the measurements of fluorescence were obtained on a luminescence spectrometer. High resolution mass spectra were obtained using a MALDI-TOF mass spectrometer. High performance liquid chromatography analyses were performed on a chromatograph equipped with a UV−vis detector. Analytical gel permeation chromatography (GPC) was carried out on a toluene (7.8 × 300 mm) column with 100% toluene. GPC purification was carried out on a column (19 × 300 mm) with 100% toluene. Flash column chromatography was performed with Silica gel.

*Synthesis of 2,2′-(Mesitylmethylene)bis(1H-pyrrole) (**7**)*[26]. A solution of 1.417 g (9.56 mmol) of mesitylaldehyde in 25.7 g (382 mmol) of freshly distilled pyrrole was degassed by flushing an argon flow for 20 min. Then, 0.136 g (0.956 mmol) of $BF_3\cdot(OEt)_2$ was added by syringe. The light brown mixture produced was stirred for 30 min under argon atmosphere. After this time, the solution was diluted with additional CH_2Cl_2 (50 mL) and immediately washed with 0.1 N NaOH (200 mg, 50 mL) and water (50 mL). The organic phase was dried and evaporated under reduced pressure at 40 °C afforded a brownish oil. The oil was triturated with cyclohexane yielding **7** as a white solid that was collected by filtration and washed with additional cyclohexane (0.32 g, 12.7%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 7.96 (bs, 2H, NH), 6.89 (s, 2H), 6.68 (s, 2H), 6.17 (q, 2H, J = 2.97 Hz), 6.03 (s, 2H), 5.93 (s, 1H, *meso*-H), 2.29 (s, 3H), 2.08 (s, 6H).

*Synthesis of 3-(Prop-2-ynyloxy)benzaldehyde (**8**)*[27]. To a solution of 2 g (16.38 mmol) of *m*-hydroxybenzaldehyde and 2.92 g (24.57 mmol) of propargyl bromide in dry CH_3CN (50 mL) were added 3.40 g (24.57 mmol) of K_2CO_3 and 0.216 g (0.819 mmol) of 18-crown-6. The solution was refluxed overnight under N_2. At the end of the reaction time a solid has appeared in the reaction mixture. The solid was collected and washed with CH_3CN. Compound **8** (2.6 g, 99%) was obtained after purification by flash column chromatography on silica of the filtered crude product. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 10.01 (s, 1H), 7.49 (m, 3H), 7.27 (m, 1H), 4.78 (d, 2H, J = 2.32 Hz), 2.57 (t, 1H, J = 2.32 Hz).

*Synthesis of Zn-5,15-bis(3-propargyloxyphenyl)-10,20-bis(1,3,5-trimethylphenyl)-porphyrin (trans-**5**·Zn).* A solution of 0.499 g (3.11 mmol) of 3-(prop-2-ynyloxy)benzaldehyde, **8**, and 0.823 g (3.11 mmol) of 2,2′-(mesitylmethylene)bis(1H-pyrrole), **7**, in 100 mL of $CHCl_3$ was purged with Ar for 10 min. Then 0.146 g (1.027 mmol) of $BF_3\cdot O(Et)_2$ was added. The solution was stirred at room temperature for 1 h, and then DDQ was added. The mixture was stirred at room temperature for an additional 1 h. The solvent was evaporated under diminished pressure. The residual solid was purified by column chromatography on silica gel with hexane/dichloromethane/triethylamine (50/50/1) as eluent. The third fraction collected was concentrated in vacuo to afford *trans*-**5**·H_2 as a purple solid (0.290 mg, 26%). This fraction was analyzed by HPLC (CH_3CN:H_2O-0.1%TFA 1 mL/min, 420 nm, sample dissolved in CH_3CN) eluting as a single peak with a retention time of 21 min. 0.270 mg (0.335 mmol) of *trans*-**5**·H_2 purple solid were treated with 0.614 g (3.35 mmol) of $Zn(OAc)_2$ in 40 mL of a CH_2Cl_2/CH_3OH (3/1): The resulting solution was covered with aluminum foil to protect it from light, and stirred at room temperature overnight. Then, the solvent was evaporated in vacuo and the metalated porphyrin, *trans*-**5**·Zn, (0.230 g, 85%) was obtained after purification of the crude by flash chromatography on neutral aluminum oxide using a gradient of CH_2Cl_2/THF (100:0 to 90:10) as eluent. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 9.00 (d, 4H, J = 4.73 Hz), 8.85 (d, 4H, J = 5.06 Hz), 7.93 (m, 4H), 7.67 (t, 2H, J = 7.76 Hz), 7.38 (dd, 2H, J = 8.44 and 2.30 Hz), 7.34 (s, 4H), 4.83 (t, 4H, J = 1.84 Hz), 2.69 (s, 6H), 2.58 (t, 2H, J = 2.36 Hz), 1.91 (s, 12H); HR-MS (MALDI) m/z calcd for $C_{56}H_{44}N_4O_2Zn$ (M^+) 868.2750, found 868.2740 (1 ppm); UV−vis (toluene) λ_{max} (ε, $M^{-1}\ cm^{-1}$) 423 (586731.92).

*Synthesis of TMEDA⊂**3**·Zn_2.* To 200 mL of CH_2Cl_2 solution containing 137 mg (0.157 mmol) of *trans*-**5**·Zn and 1.09 g (11.02 mmol) of copper(I) chloride was added 1.3 mL (11.02 mmol) of TMEDA. The mixture was stirred for 4 h under air and at room temperature. During this time the reaction mixture changes its color from fuchsia to green. At the end, the reaction mixture was washed with water, dried over Na_2SO_4, and evaporated to dryness. An aliquot of the crude product (0.219 g, 75%) was purified by preparative GPC (column in toluene, 1 mL/min; 420 nm; 1 mg/mL; inject 5 μL) with major peak eluting at 7.45 min and minor peak at 6.75 min. The peak at 6.75 min is assigned to polymers formed in the reaction The peak eluting at 7.45 min corresponds to the diacetylenic bisporphyrin complex TMEDA⊂**3**·Zn_2. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 8.64 (d, 8H, J = 3.30 Hz), 8.40 (d, 8H, J = 3.30 Hz), 8.01 (d, 4H, J = 6.84 Hz), 7.64 (t, 4H, J = 7.79 Hz), 7.25 (s, 8H), 7.12 (s, 4H), 6.91 (d, 4H, J = 7.31 Hz), 4.38

(s, 8H), 2.62 (s, 12H), 2.61 (s, 12H), 1.28 (s, 12H), −3.62 (s, 12H, CH_3 of coordinated TMEDA), −5.03 (s, 4H, CH_2 of coordinated TMEDA)

*Synthesis of Diacetylenic Bisporphyrin (**3**·Zn_2).* The reaction crude containing the acetylenic bisporphyrin coordinated with TMEDA, TMEDA⊂**3**·Zn_2, obtained above was dissolved in a minimum amount of CH_2Cl_2 and treated with few drops of a solution of HCl 4 N in dioxane. The resulting green mixture was stirred for 30 min and diluted with additional CH_2Cl_2. The organic phase was washed with water, dried, filtered, and evaporated to dryness. The obtained crude was purified by preparative GPC (toluene column, flow 6 mL/min, injections 20 mg/mL), collecting the second peak eluting at 7.31 min that corresponds to the pure diacetylenic bisporphyrin **3**·H_4 (0.180 g, 62%). A solution of 98 mg (0.061 mmol) of **3**·H_4 in 36 mL of a mixture of CH_2Cl_2/ CH_3OH (3:1) was treated with 0.40 g (1.217 mmol) of $Zn(OAc)_2$. The reaction mixture was covered with aluminum foil to protect it from light and stirred at room temperature overnight. The reaction can be monitored using alumina TLC plates and CH_2Cl_2/hexane (1/1) as eluent. At the end of the reaction, the solvent was evaporated and **3**·Zn_2 was obtained as a purple solid (62 mg, 58.6%) after purification of the crude by flash chromatography on neutral aluminum oxide using a gradient of CH_2Cl_2/THF (100:0 to 90:10) as eluent. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 8.80 (d, 8H, J = 4.74 Hz, H_2), 8.49 (d, 8H, J = 4.74 Hz, H_1), 7.81 (d, 4H, J = 7.30 Hz, H_4), 7.66 (s, 4H, H_3), 7.61 (t, 4H, J = 7.30 Hz, H_5), 7.33 (dd, 4H, J = 8.51 and 2.43 Hz, H_6), 7.18 (s, 4H, H_7), 6.79 (s, 4H, H_8), 4.78 (s, 8H, H_9), 2.48 (s, 12H, H_{10}), 1.77 (s, 12H, H_{11}), 0.76 (s, 12H, H_{12}), see Figure S4 for proton assignments; HR-MS (MALDI) m/z calcd for $C_{112}H_{84}N_8O_4Zn_2$ (M^+) 1732.5193, found 1732.5244 (3 ppm); UV−vis (toluene) λ_{max} (ε, M^{-1} cm^{-1}) 418 (789190.67).

*Synthesis of Bisporphyrin Cyclic Dimer (**4**·Zn_2).* To a 10 mL THF solution containing 38 mg of **3**·Zn_2 (0.023 mmol) was added 14 mg of Pd/C suspended previously in 4 mL of THF. The obtained suspension was stirred under H_2 at 2.5 bar during 15 h. The progress of the reaction was monitored using silica TLC plates and CH_2Cl_2/hexane (1/1) as eluent. After this time, the reaction was filtered over Celite to remove the catalyst and the organic solvent evaporated in "vacuo". The solid reaction crude was purified by column chromatography on neutral alumina using CH_2Cl_2 as eluent to yield **4**·Zn_2 as a purple solid (20 mg, 55%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C) δ (ppm) 8.77 (d, 8H, J = 4.67 Hz, H_2), 8.62 (d, 8H, J = 4.67 Hz, H_1), 7.79 (d, 4H, J = 7.27 Hz, H_4), 7.58 (t, 4H, J = 7.27 Hz, H_5), 7.48 (s, 4H, H_3), 7.26 (dd, 4H, J = 7.27 and 2.60 Hz, H_6), 7.24 (s, 4H, H_7), 7.17 (s, 4H, H_8), 4.01 (t, 8H, J = 6.23 Hz, H_9), 2.63 (s, 12H, H_{12}), 1.85 (m, 8H, H_{11}), 1.72 (s, 12H, H_{13}), 1.50 (m, 8H, H_{10}), 1.47 (s, 12H, H_{14}), see Figure S5 for proton assignments; HR-MS (MALDI) m/z calcd for $C_{112}H_{100}N_8O_4Zn_2$(M^+) 1748.6445, found1748.6248 (11 ppm); UV−vis (toluene) λ_{max} (ε, M^{-1} cm^{-1}) 419 (772176.67).

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra of *trans*-**5**·Zn, TMEDA⊂**3**·Zn_2, **3**·Zn_2, and **4**·Zn2. ROESY spectra of the mixture of conformational isomers for **3**·Zn_2 and **4**·Zn_2. General procedures used in the spectroscopic titrations and the mathematical analysis of the data obtained. Comments on the single crystal X-ray diffraction data and X-ray crystallographic files (in CIF format) for the complexes TMEDA⊂**3**·Zn_2, Sc_3N@C_{80}⊂**3**·Zn_2, Sc_3N@C_{80}⊂(**4**·Zn_2)$_2$, and the *p*-xylene solvate of Sc_3N@C_{80}. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Assuming a noncooperative binding process a value for the stability constant of the 2:1 complex can be statistically estimated as $K = K_m^2 = 4 \times 10^{10}$ M^{-2}. K_m is the microscopic binding constant value for the interaction of Sc_3N@C_{80} with **4**·Zn_2. The K_m was calculated from the UV−vis titration using a simple 1:1 binding model. The simulated speciation profiles considering the formation of both 1:1 and 2:1 complexes indicate that the 2:1 complex is formed at a negligible extent in the concentration range in which the UV−vis and fluorescence titrations have been performed. This result supports the simplification of the binding model used for the mathematical analysis of these titration data. On the contray, at 0.9 mM concentration and with 0.5 equiv of Sc_3N@C_{80} the speciation profile shows that [**4**·Zn_2] = 8.5 × 10^{-5}, [1:1] = 1.0 × 10^{-4} M, and [2:1] = 3.5 × 10^{-4} M and with 1 equiv [**4**·Zn_2] = 1.0 × 10^{-6}, [1:1] = 4.8 × 10^{-4} M, and [2:1] = 1.9 × 10^{-4} M.

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