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Inclusion of C_{60} fullerene in a M_3L_2 subphthalocyanine cage†

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A C_3 symmetric subphthalocyanine (SubPc) M_3L_2 cage was shown to encapsulate C_{60} fullerene within its aromatic walls in acetone.

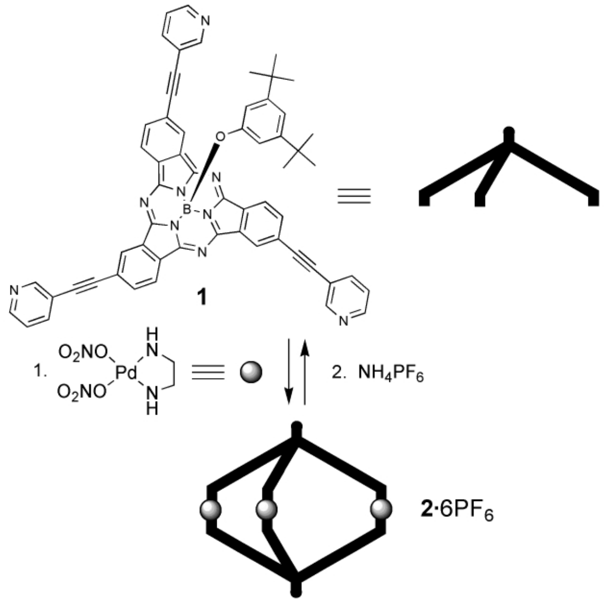
Very recently, concave–convex interactions between complementary geodesic polyarenes have attracted much attention as they are meant to play a determinant role in the formation of structures such as multiwall carbon nanotubes,[1] carbon onions[2] and fullerene peapods.[3] These types of interactions have been scarcely studied experimentally[4] since the synthesis of curved aromatic or π-conjugated systems is usually challenging or demanding. Subphthalocyanines[5] (SubPcs) represent one such curved aromatic system comprising a 14 π-electron core that is spatially accessible from its less hindered concave side. On the other hand, C_{60} fullerene was shown to interact with a small number of receptors such as calixarenes,[6] metallomacrocycles,[7] cyclodextrins,[8] cyclotriveratrilenes,[9] corannulenes[10] and other aromatic or π-conjugated systems.[11]

To the best of our knowledge, the full encapsulation of C_{60} was reported only once within a M_3L_2 calix[3]arene cage.[12] In this context, we thought that the C_3-symmetric concave face of subphthalocyanine would act as a good recognition site for a convex C_{60} molecule. Additionally, π–π interactions between these complementary π-extended surfaces are meant to provide further stabilization to the complex as well as to modulate the physical properties of these two photo- and electro-active compounds. We recently described the formation of a M_3L_2 subphthalocyanine cage[13] from a tris-3-pyridyl-substituted SubPc that was shown to self-assemble in a chiral self-discriminatory manner. In this communication we describe the synthesis and the dynamic behavior of a new M_3L_2 subphthalocyanine cage[14] that can encapsulate a C_{60} molecule within its larger cavity.

SubPc **1** (Scheme 1) was obtained in 70% yield by Sonogashira cross-coupling reaction between 3-ethynylpyridine and the corresponding triodo-SubPc precursor.[13] Cage compound $\mathbf{2}\cdot6NO_3$ was obtained by mixing at room temperature for 4 hours racemic SubPc **1** and 1.5 eq. of $(en)Pd(NO_3)_2$ in a 1:1:1 mixture of water, methanol and acetonitrile. The complex was isolated in 94% yield as its hexafluorophosphate salt $\mathbf{2}\cdot6PF_6$ by adding a ten-fold excess of NH_4PF_6 to the reaction mixture. The formation of the cage compound was supported by ESI-MS which showed prominent peaks at *m/z* = 913.7, 649.4, 489.6 and 384.7 corresponding to $[\mathbf{2}\cdot3PF_6]^{3+}$, $[\mathbf{2}\cdot2PF_6]^{4+}$, $[\mathbf{2}\cdot PF_6]^{5+}$ and $[\mathbf{2}]^{6+}$, respectively.

The ^1H NMR spectrum of $\mathbf{2}\cdot6PF_6$ in CD_3COCD_3 revealed the presence in solution of a mixture of two very similar sets of signals in a 2:1 ratio that evolves gradually to a 6:1 ratio over the course of *ca*. 40 days. These data are consistent with the formation, from chiral SubPc **1**, of two diastereoisomers, namely, a meso form [*M*,*P*] (**a**) and a racemic mixture [*MP*,*MP*] (**b**),[15] that slowly exchange until they reach a thermodynamic equilibrium (Fig. 1). It would be reasonable to assign the meso [*M*,*P*] cage (**a**) to the major isomer on the basis of previous results obtained with a smaller 3-pyridyl-based M_3L_2 SubPc cage[13] which self-assemble in a chiral self-discriminatory manner to give the corresponding meso form (only). In the case of $\mathbf{2}\cdot6PF_6$, due to the additional rotational freedom brought by the ethynylpyridyl linker in **1**, the self-assembly process does not proceed in such a specific manner. Assuming a first order kinetic law for the interconversion between the diastereoisomers **a** and **b**, the fitted kinetic values were found to be: $k_1 = 1.5 \times 10^{-6}\ s^{-1}$, $k_{-1} = 2.4 \times 10^{-7}\ s^{-1}$; these correspond to an equilibrium constant value, K_{eq}, of 6.1.

The fullerene complex $[C_{60} \subset \mathbf{2}]\cdot6PF_6$ was prepared by adding 5 equivalents of C_{60} to a previously equilibrated solution of $\mathbf{2}\cdot6PF_6$ in d_6-acetone. ^1H NMR spectrum at 500 MHz of this mixture revealed a broadening of the signals corresponding to the protons of the SubPc core and the 3-pyridyl groups while the signals corresponding to the *tert*-butyl groups' protons were not affected, indicating that the C_{60}-induced perturbation of the magnetic environment remains confined to the cavity of the M_3L_2 cage. Remarkably, the diastereoisomeric ratio (6:1) of the free cage did not change as complexation occurred. ^{13}C NMR spectrum of the same 1:5 mixture $\mathbf{2}\cdot6PF_6/C_{60}$ in CD_3COCD_3 showed (Fig. 2) a broadening of the signals and the appearance of a peak at 140.1 ppm that may be attributed to C_{60}. In sharp contrast, ^{13}C NMR spectrum of pure C_{60}



Scheme 1 Synthesis of the M_3L_2 subphthalocyanine cage $\mathbf{2}\cdot6PF_6$ from SubPc **1** and $(en)Pd(NO_3)_2$ followed by anion exchange with NH_4PF_6.

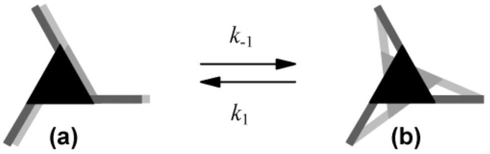


Fig. 1 Schematic representation of the equilibrium between meso form [*M*,*P*] (**a**) and racemic mixture [*MP*,*MP*] (**b**, only one enantiomer is represented for simplicity) of the cage $\mathbf{2}\cdot6PF_6$.

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† Electronic supplementary information (ESI) available: experimental procedures, NMR, IR, UV, and MS data for compounds **1**,$\mathbf{2}\cdot6PF_6$ and $[C_{60} \subset \mathbf{2}]\cdot6PF_6$. Details for the calculation of the kinetic and thermodynamic constants for the interconversion between the diastereoisomers of $\mathbf{2}\cdot6PF_6$. See http://www.rsc.org/suppdata/cc/b4/b401232a/

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in CD_3COCD_3 under the same conditions does not show any signal since fullerene is barely soluble in acetone (1 μg mL^{-1}).[16] Therefore, in the presence of the M_3L_2 subphthalocyanine cage **2**·$6PF_6$, fullerene experiences a one thousand fold solubility increase up to *ca*. 1 mg mL^{-1}. According to quantitative ^{13}C NMR experiments, the integration of the peak at 140.1 ppm, when compared to that of the signals corresponding to the cage's carbon atoms, is consistent with a 40% occupancy of the cages. The broadening is particularly pronounced in the case of the peaks corresponding to the carbon atoms of the SubPc core, *i.e*. C***e***, C***f***, C***g***, C***h***, C***i*** and C***j*** (Fig. 2). This substantiates that the C_{60} molecule is located preferentially in the center of the cavity as illustrated in Fig. 3. Further theoretical evidence comes from the ZINDO/1 optimized geometry of the adduct (Fig. 3), in which the shortest distance between the subphthalocyanine and the cage is *ca*. 3.1 Å between C***g*** or C***h*** carbon atoms and the closest C_{60} carbon atom.

Final evidence for the formation of the [$C_{60} \subset$ **2**]·$6PF_6$ complex was obtained from electrospray mass spectrometry in acetone that showed peaks at *m/z* = 1154.8, 829.7, 634.5 and 505.5 corresponding to [[$C_{60} \subset$ **2**]·$3PF_6$]$^{3+}$, [[$C_{60} \subset$ **2**]·$2PF_6$]$^{4+}$, [[$C_{60} \subset$ **2**]·PF_6]$^{5+}$ and [$C_{60} \subset$ **2**]$^{6+}$, respectively. Additional peaks corresponding to the free M_3L_2 subphthalocyanine cage were also observed in the same spectrum.[17]

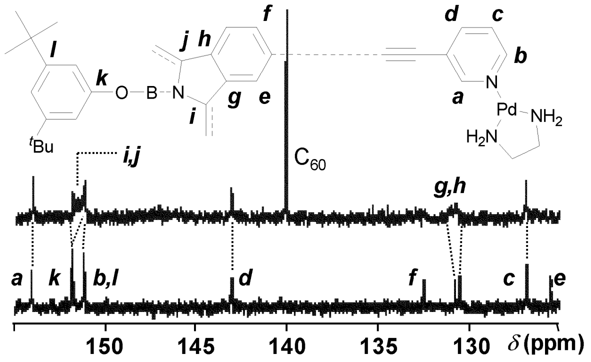

Fig. 2 Portion of the ^{13}C NMR spectra of (bottom) **2**·$6PF_6$ and (top) [$C_{60} \subset$ **2**]·$6PF_6$ showing the effect of C_{60} encapsulation on the aromatic carbon atom signals.

Fig. 3 Balls and cylinders representation of top (right) and side (left) views of the ZINDO/1 optimized geometry of the [$C_{60} \subset$ **2**]·$6PF_6$ complex. 3,5-Di-*tert*-butylphenoxy axial groups and hydrogen atoms were removed for clarity.

In conclusion, we have synthesized a larger 3-ethynylpyridyl-based subphthalocyanine coordination cage, proving that the original design[13] is robust enough to sustain chemical modifications. C_{60} fullerene was shown to encapsulate in this self-assembled cage possessing a complementary curved aromatic π-surface. Studies of the physical properties of the complex are under way.

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