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**Self-sorting among the diastereoisomers of a M3L2  
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Keywords:	subphthalocyanines, palladium complexes, capsules, metallosupramolecular chemistry, chiral self-discrimination



**BRIEF COMMUNICATION****Self-sorting among the diastereoisomers of a  $M_3L_2$  subphthalocyanine capsule**

Christian G. Claessens,<sup>a\*</sup> Irene Sánchez-Molina<sup>a</sup> and Tomás Torres<sup>a\*</sup>

<sup>a</sup>*Departamento de Química Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

**Abstract.** A new  $M_3L_2$  homodimeric subphthalocyanine cage was self-assembled and characterized. Among the six possible diastereoisomeric metallosupramolecular capsules attainable only one was shown to form under thermodynamic conditions. These results obtained on the basis of mass spectrometry, nuclear magnetic resonance and molecular modeling studies demonstrate that dynamic chiral self-discrimination occurs when the cage compound is left enough time to reach equilibrium.

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## INTRODUCTION

The field of supramolecular self-assembly by coordination chemistry has seen a remarkable development over the last decade.<sup>1</sup> Several works have dealt with the study of equilibrating systems of supramolecular entities. This field of chemistry has found applications in biological molecular recognition, dynamic materials, and catalysis.<sup>2</sup> Such systems rely on the reversible association between basic building blocks, spontaneously generating supramolecular libraries of structures that may equilibrate towards reduced sets of self-assembled entities in or without the presence of a target molecule.

<Figure 1>

In this communication we describe the synthesis (Figure 1) and characterization of  $C_1$  symmetric subphthalocyanine **1** (SubPc<sup>3</sup>) and its dimerization into a set of  $M_3L_2$  metallocsupramolecular cages in the presence of a stoichiometric amount of (en)Pd(NO<sub>3</sub>)<sub>2</sub>. It is noteworthy to mention that the related  $C_3$  symmetric precursor was shown to self-assemble very efficiently into a mixture of two equilibrating diastereoisomeric cages.<sup>4</sup> Our interest in the trispyridyl  $C_1$  symmetric precursor **1** came from the intrinsic asymmetry of the macrocycle that, theoretically, could self-assemble in the presence of Pd(II) to yield up to 6 distinct diastereoisomeric cages as illustrated schematically in Figure 2.

<Figure 2>

Subphthalocyanines are 14  $\pi$ -electron non-planar aromatic macrocycles comprising three diiminoisindole units *N*-fused around a central boron atom.<sup>3</sup> Their cone-shaped aromatic structure makes them very appealing concave building blocks for their use in the self-assembly of dimeric hollow capsules and the subsequent molecular recognition of complementary convex  $\pi$ -conjugated molecules such as fullerenes.<sup>4b</sup> Moreover, they show very attractive photophysical and electrochemical properties and have found applications as chromophores in nonlinear optics,<sup>5</sup> in OLEDs,<sup>6</sup> in photovoltaic devices<sup>7</sup> and in multicomponent donor-acceptor systems.<sup>8</sup>

## RESULTS AND DISCUSSION

Di-*tert*-butylphenoxy axially substituted SubPc **3** was obtained (Figure 1) in 75% yield by reacting 3,5-di-*tert*-butylphenol with the  $C_1$  isomer of chloroSubPc **2** in toluene at reflux for 16 h. Triple Sonogashira cross-coupling reaction between 3-ethynylpyridine and SubPc **3** in the presence of catalytic amounts of CuI and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in triethylamine as solvent gave  $C_1$  symmetric SubPc **1** in 65% yield.

SubPc **1** was characterized by NMR spectroscopy, MALDI-TOF mass spectrometry and UV spectrophotometry. <sup>1</sup>H NMR spectroscopy of **1** in CDCl<sub>3</sub> showed the expected complex pattern of signals in which each proton of the  $C_1$  symmetrical macrocycle gives rise to a different peak. The UV-vis spectrum of **1** shows the expected Q band at 584 nm and B or Soret band at 350 nm. MALDI-TOF mass spectrometry shows a peak at 904.6 corresponding to [M+H]<sup>+</sup> and a peak corresponding to the loss of the axial di-*tert*-butylphenoxy substituent at 698.5.

In a first instance we decided to employ the same conditions as for the successful self-assembly of the  $M_3L_2$  cage from the  $C_3$  counterpart of SubPc **1** by mixing SubPc **1** and stoichiometric amounts of (en)Pd(NO<sub>3</sub>)<sub>2</sub> (1.5 eq.) in a 1:1:1 mixture water, methanol and acetonitrile at room temperature for 4 hours followed by anion exchange with a ten-fold excess of ammonium hexafluorophosphate. <sup>1</sup>H NMR spectrum of the resulting compound in CD<sub>3</sub>CN showed an extremely complex pattern of signals in accordance with the presence of a mixture of various cage compounds. The presence of signals at ca. 9.0 ppm and the relative integral values of the various regions of the spectrum (ie. aromatic vs. ethylenediamine protons) clearly demonstrated the presence of  $M_3L_2$  cages in which the pyridine moieties are coordinated to Pd(II). Final evidence came from the ESI-MS spectra showing peaks at 913.6, 649.4, 489.6 and 384.6 corresponding to the loss of three, four, five and six hexafluorophosphate anions from the cage compound, respectively.

<Figure 3>

When the same self-assembly protocol was conducted at 60°C for 48 h, the resulting cage compound obtained after anion exchange was found to be much easier to characterize. The <sup>1</sup>H NMR spectrum showed well defined signals that could be assigned clearly to a cage compound with a fairly symmetrical structure (Figure 3). In Particular, each of the protons **Ha**, **Hf** and **Hg** gave rise to three sets of signals in perfect accordance with the presence of a plane of symmetry between the two coordinated subphthalocyanines. On the basis of this spectrum the four diastereoisomers **4b(c)**•6PF<sub>6</sub>, **4b(m)**•6PF<sub>6</sub>, **4c(c)**•6PF<sub>6</sub>, **4b(m)**•6PF<sub>6</sub> were ruled out since they would give rise to much more complex patterns. Cage **4a(m)**•6PF<sub>6</sub> is undoubtedly the only one fulfilling the symmetry requirement imposed by the NMR spectrum but **4a(c)**•6PF<sub>6</sub>, in spite of its lack of symmetry plane, could also give rise to a fairly uncomplicated spectrum since, locally, it is possible to draw two planes of symmetry and one inversion center. On the other hand, this spectrum is compatible with only one cage because a mixture of cages **4a(c)**•6PF<sub>6</sub> and **4a(m)**•6PF<sub>6</sub> should give rise to a mixture of different signals.

In order to determine which of the two diastereoisomers **4a(c)**•6PF<sub>6</sub> or **4a(m)**•6PF<sub>6</sub> is present after equilibrated self-assembly, we performed semi-empirical calculations at PM3 level (Figure 4). These calculations showed that diastereoisomer **4a(m)**•6PF<sub>6</sub> was much more stable than **4a(c)**•6PF<sub>6</sub>. For example, it can be clearly seen in Figure 4 that the ethynyl bond in **4a(c)**•6PF<sub>6</sub> is rather bent in order to allow the planar tetracoordination around one of the three palladium(II) center. Thus, according to these considerations, the only isomer present in solution is **4a(m)**•6PF<sub>6</sub>.

<Figure 4>

## CONCLUSIONS

The self-assembly process of  $C_1$  symmetric SubPc **1** was shown to be driven by the formation of a specific coordination architecture and demonstrates dynamic selection from a possible mixture of six different diastereoisomers. The *meso* diastereoisomer is the result of chiral self-discrimination between the enantiomers of SubPc **1** during its self-assembly.

## EXPERIMENTAL

### Materials and Methods

UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded with Bruker Vector 22 spectrophotometer. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a Bruker AC-300, Bruker AMX-300 and Bruker DRX-500 instruments. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and TLC was performed on aluminum sheets precoated with silica gel 60 F<sub>254</sub> (E. Merck). Subphthalocyanine **2** was synthesized according to a formerly described literature procedure.<sup>9,10</sup>

#### Synthesis of subphthalocyanine **3**:

Under an argon atmosphere, 3-ethynylpyridine (50 mg, 0.484 mmol) was added to a mixture of triodo-3,5-ditert-butylloxysubphthalocyanine (131 mg, 0.134 mmol), palladiumdiphenylphosphinedichloride (21 mg, 0.029 mmol) and copper iodide (5 mg, 0.029 mmol) in triethylamine (5 mL). The reaction was stirred under argon for 16 h and water (50 mL) was added. The resulting mixture was extracted with diethylether (3 x 20 mL) and the resulting organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the resulting solid was subjected to column chromatography on silica gel using acetone/hexane (3:2) as eluent. After evaporation of the eluent subphthalocyanine **1** was obtained as a purple solid, 90 mg (75%); m.p. > 250°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz): δ = 9.03 (br s, 3H, **He**), 8.86 (m, 3H, **Ha**), 8.81 (d, 2H, **Hg**), 8.80 (d, 1H, **Hg**), 8.62 (dd, 3H, **Hb**), 8.04 (dd, 3H, **Hf**), 7.91 (ddd, 3H, **Hd**), 7.35 (dd, 3H, **Hc**), 6.69 (t, 1H, **Hj**), 5.20 (d, 2H, **Hk**), 1.05 (s, 18H, **Hw**); IR(KBr): ν = 2368, 2198, 1601, 1437, 1299, 1156, 1065, 892, 822, 808, 756, 702, 635, cm<sup>-1</sup>; UV/Vis (MeCN): λ<sub>max</sub>(log(ε)) = 585 (4.8), 571 (sh), 543 (sh), 530 (sh), 349 (4.5), 335 (sh) nm; LSI-MS: *m/z*: 904.6 [M+H]<sup>+</sup>, 698.3 [M-3,5-ditertbutylphenoxy]<sup>+</sup>; MALDI-TOF: *m/z*: 904.7 [M+H]<sup>+</sup>, 698.5 [M-3,5-ditertbutylphenoxy]<sup>+</sup>. HR-LSIMS calcd for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>O<sub>3</sub>: [M<sup>+</sup>]: *m/z*: 903.3605, found 903.3616; HR-LSIMS elemental analysis calcd (%) for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>O<sub>3</sub>: C 78.40, H 4.68, N 13.95; found C 77.66, H 4.19, N 14.32.

#### Self-assembly of cage compound **4a(m)**•6PF<sub>6</sub>:

Freshly prepared (en)Pd(NO<sub>3</sub>)<sub>2</sub> (10 mg, 0.041 mmol) was added in one portion to a solution of subphthalocyanine **1** (25 mg, 0.028 mmol) in a mixture of water (1 mL), methanol (1 mL) and acetonitrile (1 mL). The resulting solution was stirred at 60°C for 48 h. After evaporation of methanol and acetonitrile, NH<sub>4</sub>PF<sub>6</sub> (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **4a(m)**•6PF<sub>6</sub> precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 40 mg (90%); m.p. > 250°C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K): δ = 9.03 (s, 2H, **Ha**), 9.02 (s, 2H, **Ha**), 8.98 (s, 2H, **Ha**), 8.86-8.81 (m, 12H, **Hb** and **He**), 8.69 (d, 2H, **Hg**), 8.68 (d, 2H, **Hg**), 8.65 (d, 2H, **Hg**), 8.27-8.22 (m, 6H, **Hd**), 8.01 (d, 2H, **Hf**), 8.00 (d, 2H, **Hf**), 7.98 (d, 2H, **Hf**), 7.72-7.67 (m, 6H, **Hc**), 6.75 (brs, 2H, **Hj**), 5.17 (s, 4H, **Hk**), 4.25 (m, 12H, **Hh**), 2.91 (m, 12H, **Hi**), 0.96 (s, 36H); IR(KBr): ν = 2345, 2218, 1720, 1621, 1480, 1453, 1381, 1304, 1263, 1223, 1182, 1155, 1115, 1074, 1061, 957, 846, 758, 715, 689 cm<sup>-1</sup>; UV/Vis (MeCN): λ<sub>max</sub>(log(ε)) = 586 (4.8), 569 (sh), 547 (sh), 536 (sh), 350 (4.5), 336 (sh) nm; ESI-MS: *m/z*: 1443.0 [M-2PF<sub>6</sub>]<sup>2+</sup>, 913.7 [M-3PF<sub>6</sub>]<sup>3+</sup>, 649.4 [M-4PF<sub>6</sub>]<sup>4+</sup>, 490.2 [M-5PF<sub>6</sub>]<sup>5+</sup>, 384.7 [M-6PF<sub>6</sub>]<sup>6+</sup>; elemental analysis calcd (%) for C<sub>124</sub>H<sub>66</sub>N<sub>24</sub>O<sub>2</sub>B<sub>2</sub>Pd<sub>3</sub>P<sub>6</sub>F<sub>36</sub>: C 47.51, H 2.12, N 10.72; found C 46.96, H 2.43, N 11.17.

## ACKNOWLEDGEMENT

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## REFERENCES

1. a) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. c) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. d) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. e) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. f) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351. g) Tranchemontagne, D. J.; Ni, Z.; O'Keefe, M.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5136.
2. a) Corbett, P. T.; Leclair, J.; Vial, L.; West, K. R.; Wietor, J.-L.; Sanders, J. K. M.; Otto, S. *Chem. Rev.* **2006**, *106*, 3652. b) de Bruin, B.; Hauwert, P.; Reek, J. N. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 2660.
3. a) Claessens, C. G.; Gonzalez-Rodriguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835-853. b) Torres, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 2834. c) De la Torre, G.; Claessens, C. G.; Torres, T. *Chem Commun.* **2007**, 2000.
4. a) Claessens, C. G.; Torres, T. *J. Am. Chem. Soc.* **2002**, *124*, 14522. b) Claessens, C. G.; Torres, T. *Chem. Commun.* **2004**, 1298.
5. a) De la Torre, T.; Torres, T.; Vázquez, P.; Agulló-López, F. *Chem. Rev.* **2004**, *104*, 3723. Claessens, C. G. b) González-Rodríguez, D.; Torres, T.; Martín, G.; Agulló-López, F.; Ledoux, I.; Zyss, J.; Ferro, V.; García de la Vega, J. M. *J. Phys. Chem. B* **2005**, *109*, 3800.
6. Díaz, D. D.; Bolink, H. J.; Cappelli, L.; Claessens, C. G.; Coronado, E.; Torres, T. *Tetrahedron Lett.* **2007**, *48*, 4657.
7. Gommans, H.; Gheyns, D.; Aernouts, T.; Giroto, C.; Poortmans, J.; Heremans, P. *Adv. Funct. Mater.* **2007**, *17*, 2653.
8. a) González-Rodríguez, D.; Claessens, C. G.; Torres, T.; Liu, S.; Echegoyen, L.; Vila, N.; Nonell, S. *Chem. Eur. J.* **2005**, *11*, 3881. b) Medina Martín, A.; Claessens, C. G.; Rahman, G. M. A.; Lamsabhi, A. M.; Mó, O.; Yáñez, M.; Guldi, D. M.; Torres, T. *Chem. Commun.* **2008**, 1759.
9. Claessens, C. G.; Torres, T. *Tetrahedron Lett.* **2000**, *41*, 6361.
10. Claessens, C. G.; Gonzalez-Rodriguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, *14*, 2547.

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3 **Captions to Figures**  
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6

7 **Figure 1.** Synthesis of subphthalocyanine **1**.  
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9 **Figure 2.** Schematic representation of the six possible diastereoisomers of cage compound **4**•6PF<sub>6</sub>.  
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11 **Figure 3.** Portion of the <sup>1</sup>H NMR (500 MHz) spectrum in CD<sub>3</sub>CN of cage compound **4a(m)**•6PF<sub>6</sub>.  
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13  
14 **Figure 4.** Tubular representation of the minimized structures (PM3 semi-empirical calculations) of  
15 **4a(c)**•6PF<sub>6</sub> (left) and **4a(m)**•6PF<sub>6</sub> (right). Axial groups and hydrogen atoms have been omitted for  
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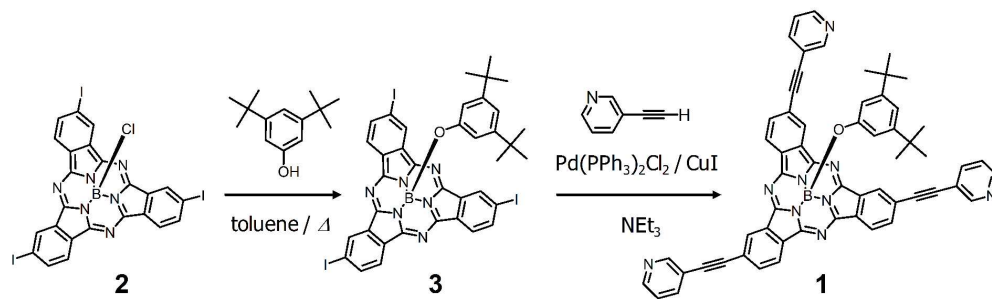


Figure 1

Synthesis of subphthalocyanine 1.  
241x98mm (600 x 600 DPI)

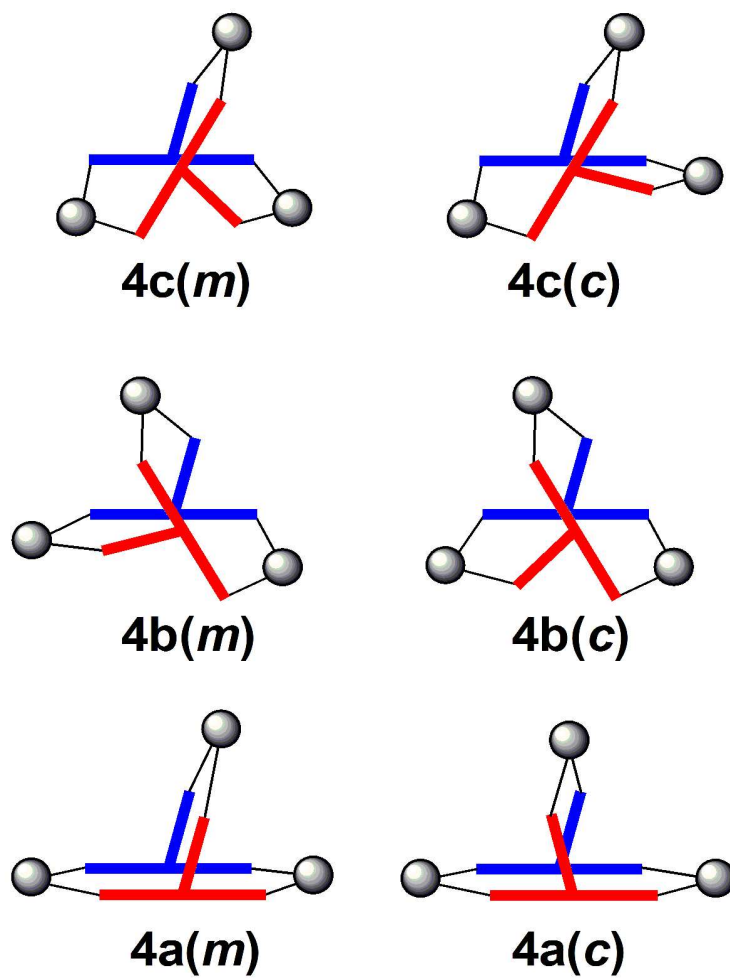


Figure 2

Schematic representation of the six possible diastereoisomers of cage compound  $4\text{Å}\square 6\text{PF}_6$ .  
102x161mm (600 x 600 DPI)

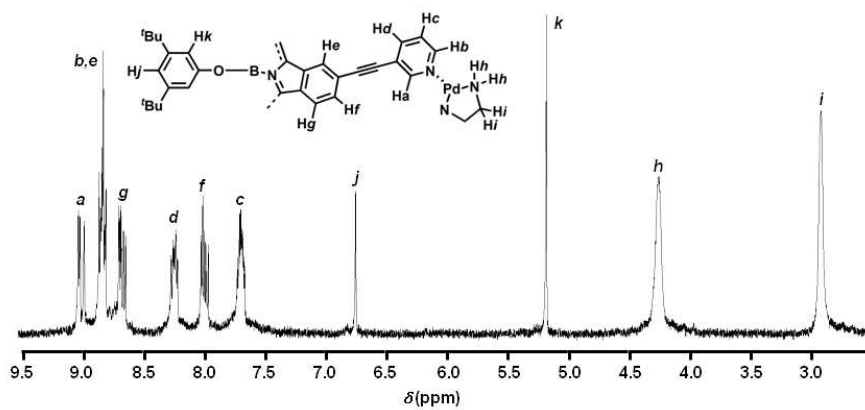
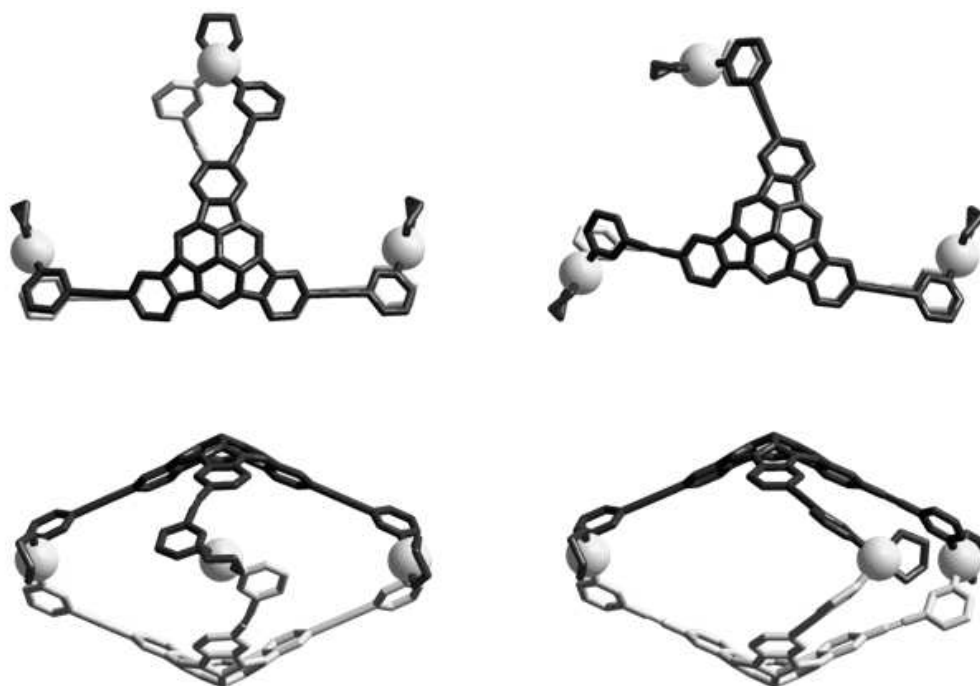


Figure 3

Portion of the <sup>1</sup>H NMR (500 MHz) spectrum in CD<sub>3</sub>CN of cage compound 4a(m)⊆6PF<sub>6</sub>.  
254x190mm (96 x 96 DPI)



**Figure 4**

Tubular representation of the minimized structures (PM3 semi-empirical calculations) of 4a(c)  $\square$  6PF6 (left) and 4a(m)  $\square$  6PF6 (right). Axial groups and hydrogen atoms have been omitted for clarity.

160x132mm (96 x 96 DPI)

Only

# REVISED VERSION

## BRIEF COMMUNICATION

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Christian G. Claessens,<sup>a\*</sup> Irene Sánchez-Molina<sup>a</sup> and Tomás Torres<sup>a\*</sup>

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In a first instance we decided to employ the same conditions as for the successful self-assembly of the  $M_3L_2$  cage from the  $C_3$  counterpart of SubPc **1** by mixing SubPc **1** and stoichiometric amounts of (en)Pd(NO<sub>3</sub>)<sub>2</sub> (1.5 eq.) in a 1:1:1 mixture water, methanol and acetonitrile at room temperature for 4 hours followed by anion exchange with a ten-fold excess of ammonium hexafluorophosphate. <sup>1</sup>H NMR spectrum of the resulting compound in CD<sub>3</sub>CN showed an extremely complex pattern of signals in accordance with the presence of a mixture of various cage compounds. The presence of signals at ca. 9.0 ppm and the relative integral values of the various regions of the spectrum (ie. aromatic vs. ethylenediamine protons) clearly demonstrated the presence of  $M_3L_2$  cages in which the pyridine moieties are coordinated to Pd(II). <sup>1</sup>H NMR spectrum of the same solution after several days at room temperature did not show any significant changes. Final evidence for capsule formation came from the ESI-MS spectra showing peaks at 913.6, 649.4, 489.6 and 384.6 corresponding to the loss of three, four, five and six hexafluorophosphate anions from the cage compound, respectively.

<Figure 3>

When the same self-assembly protocol was conducted at 60°C for 48 h, the resulting cage compound obtained after anion exchange was found to be much easier to characterize. The <sup>1</sup>H NMR spectrum showed well defined signals that could be assigned clearly to a single cage compound with a fairly symmetrical structure (Figure 3). Fast exchange between isomers, that would also give rise to a symmetrical <sup>1</sup>H NMR spectrum, was ruled out on the basis of former work on a  $C_3$  symmetrical version of the present capsule which diastereoisomers were shown to exchange on a much slower time scale than the NMR one.<sup>4b</sup> In Particular, each of the protons *Ha*, *Hf* and *Hg* gave rise to three sets of signals in perfect accordance with the presence of a plane of symmetry between the two coordinated subphthalocyanines. On the basis of this spectrum the four diastereoisomers **4b(c)**•6PF<sub>6</sub>, **4b(m)**•6PF<sub>6</sub>, **4c(c)**•6PF<sub>6</sub>, **4b(m)**•6PF<sub>6</sub> were excluded since they would give rise to much more complex patterns, these four isomers lacking any kind of symmetry element even locally as illustrated in Figure 2. Cage **4a(m)**•6PF<sub>6</sub> is undoubtedly the only one fulfilling the symmetry requirement imposed by the NMR spectrum but **4a(c)**•6PF<sub>6</sub>, in spite of its lack of symmetry plane, could also give rise to a fairly uncomplicated spectrum since, locally, it is possible to draw two planes of symmetry and one inversion center. On the other hand, this spectrum is compatible with only one cage because a mixture of cages **4a(c)**•6PF<sub>6</sub> and **4a(m)**•6PF<sub>6</sub> should give rise to a mixture of different signals.

In order to determine which of the two diastereoisomers **4a(c)**•6PF<sub>6</sub> or **4a(m)**•6PF<sub>6</sub> is present after equilibrated self-assembly, we performed geometry optimization at PM3 level (Figure 4). Diastereoisomer **4a(m)**•6PF<sub>6</sub> appeared to be more stable than **4a(c)**•6PF<sub>6</sub> at first sight. It can be clearly seen in Figure 4 that two of the six ethynyl bonds in **4a(c)**•6PF<sub>6</sub> are bent in order to allow the planar tetracoordination around one of the three palladium(II) center while all the other bond angles and distances in both diastereoisomers have standard values. Thus, according to these considerations, the most stable isomer and the only one present in solution should be **4a(m)**•6PF<sub>6</sub>.

<Figure 4>

## CONCLUSIONS

The self-assembly process of  $C_1$  symmetric SubPc **1** was shown to be driven by the formation of a specific coordination architecture and demonstrates dynamic selection from a possible mixture of six different diastereoisomers. The *meso* diastereoisomer is the result of chiral self-discrimination between the enantiomers of SubPc **1** during its self-assembly.

## EXPERIMENTAL

### Materials and Methods

UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded with Bruker Vector 22 spectrophotometer. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a Bruker AC-300, Bruker AMX-300 and Bruker DRX-500 instruments. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and TLC was performed on aluminum sheets precoated with silica gel 60 F<sub>254</sub> (E. Merck). Subphthalocyanine **2** was synthesized according to a formerly described literature procedure.<sup>9,10</sup>

### Synthesis of subphthalocyanine **3**:

Under an argon atmosphere, 3-ethynylpyridine (50 mg, 0.484 mmol) was added to a mixture of triodo-3,5-*tert*-butyloxysubphthalocyanine (131 mg, 0.134 mmol), palladiumdiphenylphosphinedichloride (21 mg, 0.029 mmol) and copper iodide (5 mg, 0.029 mmol) in triethylamine (5 mL). The reaction was stirred under argon for 16 h and water (50 mL) was added. The resulting mixture was extracted with diethylether (3 x 20 mL) and the resulting organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the resulting solid was subjected to column chromatography on silica gel using acetone/hexane (3:2) as eluent. After evaporation of the eluent subphthalocyanine **1** was obtained as a purple solid, 90 mg (75%); m.p. > 250°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz):  $\delta$  = 9.03 (br s, 3H, *He*), 8.86 (m, 3H, *Ha*), 8.81 (d, 2H, *Hg*), 8.80 (d, 1H, *Hg*), 8.62 (dd, 3H, *Hb*), 8.04 (dd, 3H, *Hf*), 7.91 (ddd, 3H, *Hd*), 7.35 (dd, 3H, *Hc*), 6.69 (t, 1H, *Hj*), 5.20 (d, 2H, *Hk*), 1.05 (s, 18H, *Hw*); IR(KBr):  $\nu$  = 2368, 2198, 1601, 1437, 1299, 1156, 1065, 892, 822, 808, 756, 702, 635, cm<sup>-1</sup>; UV/Vis (MeCN):  $\lambda_{\max}(\log(\epsilon))$  = 585 (4.8), 571 (sh), 543 (sh), 530 (sh), 349 (4.5), 335 (sh) nm; LSI-MS:  $m/z$ : 904.6 [M+H]<sup>+</sup>, 698.3 [M-3,5-*dtert*butylphenoxy]<sup>+</sup>; MALDI-TOF:  $m/z$ : 904.7 [M+H]<sup>+</sup>, 698.5 [M-3,5-*dtert*butylphenoxy]<sup>+</sup>. HR-LSIMS calcd for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>O<sub>3</sub>: [M<sup>+</sup>]:  $m/z$ : 903.3605, found 903.3616; HR-LSIMS elemental analysis calcd (%) for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>O<sub>3</sub>: C 78.40, H 4.68, N 13.95; found C 77.66, H 4.19, N 14.32.

### Self-assembly of cage compound **4a(m)**•6PF<sub>6</sub>:

Freshly prepared (en)Pd(NO<sub>3</sub>)<sub>2</sub> (10 mg, 0.041 mmol) was added in one portion to a solution of subphthalocyanine **1** (25 mg, 0.028 mmol) in a mixture of water (1 mL), methanol (1 mL) and acetonitrile (1 mL). The resulting solution was stirred at 60°C for 48 h. After evaporation of methanol and acetonitrile, NH<sub>4</sub>PF<sub>6</sub> (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **4a(m)**•6PF<sub>6</sub> precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 40 mg (90%); m.p. > 250°C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K):  $\delta$  = 9.03 (s, 2H, *Ha*), 9.02 (s, 2H, *Ha*), 8.98 (s, 2H, *Ha*), 8.86-881 (m, 12H, *Hb* and *He*), 8.69 (d, 2H, *Hg*), 8.68 (d, 2H, *Hg*), 8.65 (d, 2H, *Hg*),



8.27-8.22 (m, 6H, *Hd*), 8.01 (d, 2H, *Hf*), 8.00 (d, 2H, *Hf*), 7.98 (d, 2H, *Hf*), 7.72-7.67 (m, 6H, *Hc*), 6.75 (brs, 2H, *Hj*), 5.17 (s, 4H, *Hk*), 4.25 (m, 12H, *Hh*), 2.91 (m, 12H, *Hi*), 0.96 (s, 36H); IR(KBr):  $\nu = 2345, 2218, 1720, 1621, 1480, 1453, 1381, 1304, 1263, 1223, 1182, 1155, 1115, 1074, 1061, 957, 846, 758, 715, 689$   $\text{cm}^{-1}$ ; UV/Vis (MeCN):  $\lambda_{\text{max}}(\log(\epsilon)) = 586$  (4.8), 569 (sh), 547 (sh), 536 (sh), 350 (4.5), 336 (sh) nm; ESI-MS:  $m/z$ : 1443.0  $[\text{M}-2\text{PF}_6]^{2+}$ , 913.7  $[\text{M}-3\text{PF}_6]^{3+}$ , 649.4  $[\text{M}-4\text{PF}_6]^{4+}$ , 490.2  $[\text{M}-5\text{PF}_6]^{5+}$ , 384.7  $[\text{M}-6\text{PF}_6]^{6+}$ ; elemental analysis calcd (%) for  $\text{C}_{124}\text{H}_{66}\text{N}_{24}\text{O}_2\text{B}_2\text{Pd}_3\text{P}_6\text{F}_{36}$ : C 47.51, H 2.12, N 10.72; found C 46.96, H 2.43, N 11.17.

## ACKNOWLEDGEMENT

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## REFERENCES

1. a) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. c) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. d) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. e) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. f) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 351. g) Tranchemontagne, D. J.; Ni, Z.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 5136.
2. a) Corbett, P. T.; Leclaire, J.; Vial, L.; West, K. R.; Wietor, J.-L.; Sanders, J. K. M.; Otto, S. *Chem. Rev.* **2006**, *106*, 3652. b) de Bruin, B.; Hauwert, P.; Reek, J. N. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 2660.
3. a) Claessens, C. G.; Gonzalez-Rodriguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835-853. b) Torres, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 2834. c) De la Torre, G.; Claessens, C. G.; Torres, T. *Chem Commun.* **2007**, 2000.
4. a) Claessens, C. G.; Torres, T. *J. Am. Chem. Soc.* **2002**, *124*, 14522. b) Claessens, C. G.; Torres, T. *Chem. Commun.* **2004**, 1298.
5. a) De la Torre, T.; Torres, T.; Vázquez, P.; Agulló-López, F. *Chem. Rev.* **2004**, *104*, 3723. Claessens, C. G. b) González-Rodríguez, D.; Torres, T.; Martín, G.; Agulló-López, F.; Ledoux, I.; Zyss, J.; Ferro, V.; García de la Vega, J. M. *J. Phys. Chem. B* **2005**, *109*, 3800.
6. Díaz, D. D.; Bolink, H. J.; Cappelli, L.; Claessens, C. G.; Coronado, E.; Torres, T. *Tetrahedron Lett.* **2007**, *48*, 4657.
7. Gommans, H.; Gheyns, D.; Aernouts, T.; Girotto, C.; Poortmans, J.; Heremans, P. *Adv. Funct. Mater.* **2007**, *17*, 2653.
8. a) González-Rodríguez, D.; Claessens, C. G.; Torres, T.; Liu, S.; Echegoyen, L.; Vila, N.; Nonell, S. *Chem. Eur. J.* **2005**, *11*, 3881. b) Medina Martín, A.; Claessens, C. G.; Rahman, G. M. A.; Lamsabhi, A. M.; MÓ, O.; Yáñez, M.; Guldí, D. M.; Torres, T. *Chem. Commun.* **2008**, 1759.
9. Claessens, C. G.; Torres, T. *Tetrahedron Lett.* **2000**, *41*, 6361.
10. Claessens, C. G.; Gonzalez-Rodriguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, *14*, 2547.

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## Captions to Figures

**Figure 1.** Synthesis of subphthalocyanine **1**.

**Figure 2.** Schematic representation of the six possible diastereoisomers of cage compound **4**•6PF<sub>6</sub>.

**Figure 3.** Portion of the <sup>1</sup>H NMR (500 MHz) spectrum in CD<sub>3</sub>CN of cage compound **4a(m)**•6PF<sub>6</sub>.

**Figure 4.** Tubular representation of the minimized structures (PM3 semi-empirical calculations) of **4a(c)**•6PF<sub>6</sub> (left) and **4a(m)**•6PF<sub>6</sub> (right). Axial groups and hydrogen atoms have been omitted for clarity. The arrows indicate the bent ethynyl bonds in **4a(c)**•6PF<sub>6</sub>.

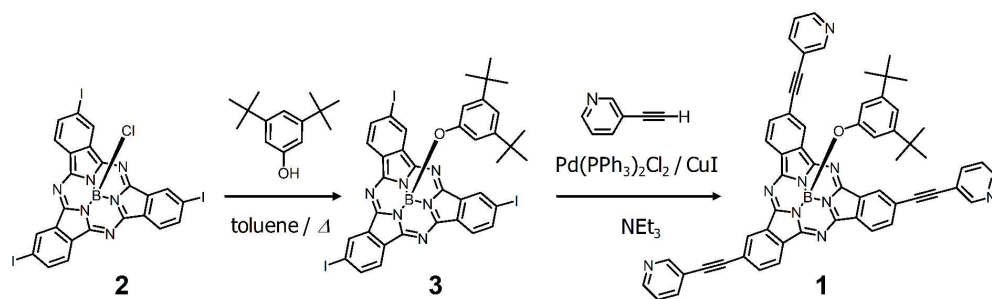
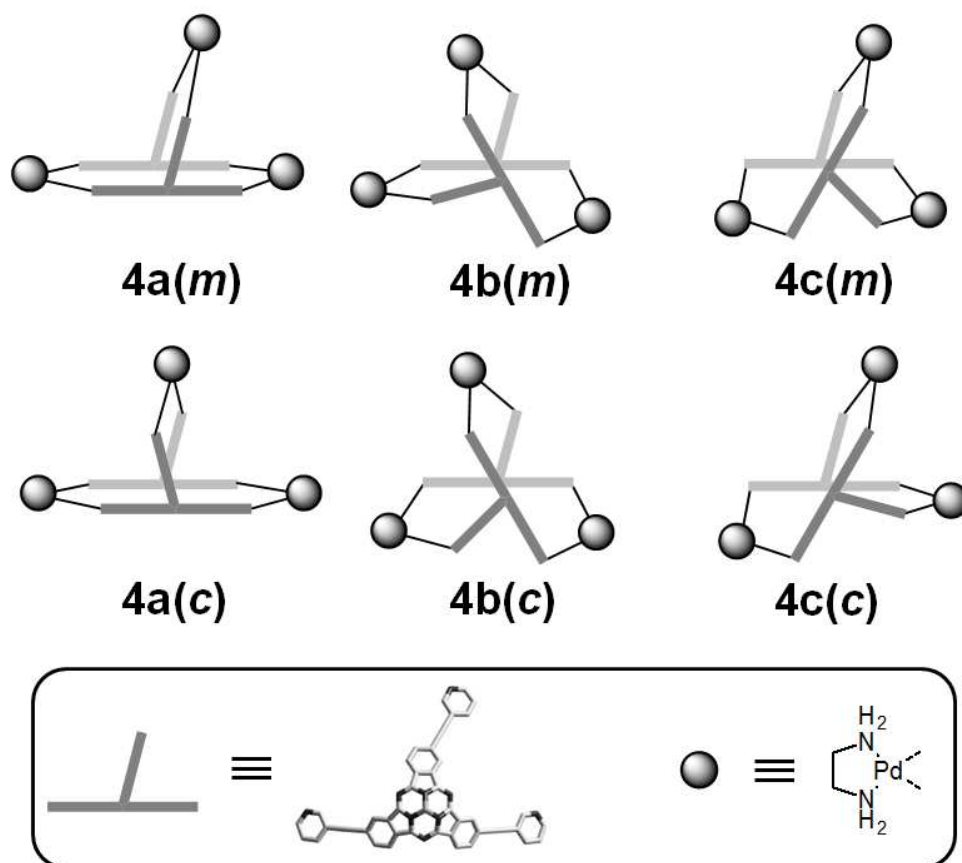


Figure 1

Synthesis of subphthalocyanine 1.  
241x98mm (600 x 600 DPI)



**Figure 2**

Schematic representation of the six possible diastereoisomers of cage compound  $4 \text{ @ } 6\text{PF}_6$ .  
211x205mm (96 x 96 DPI)

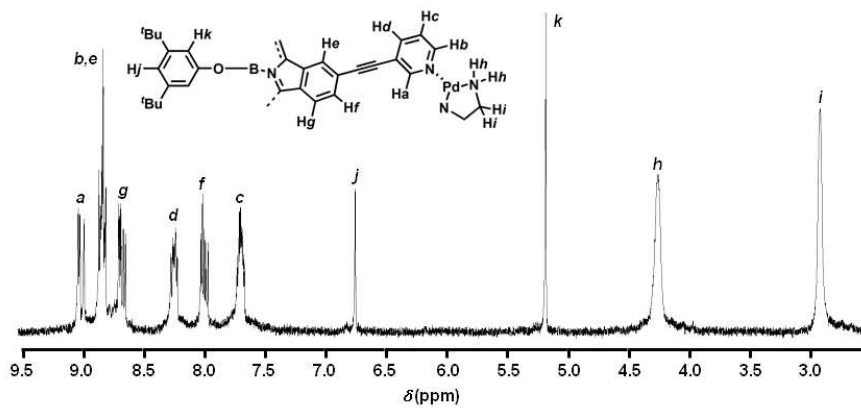
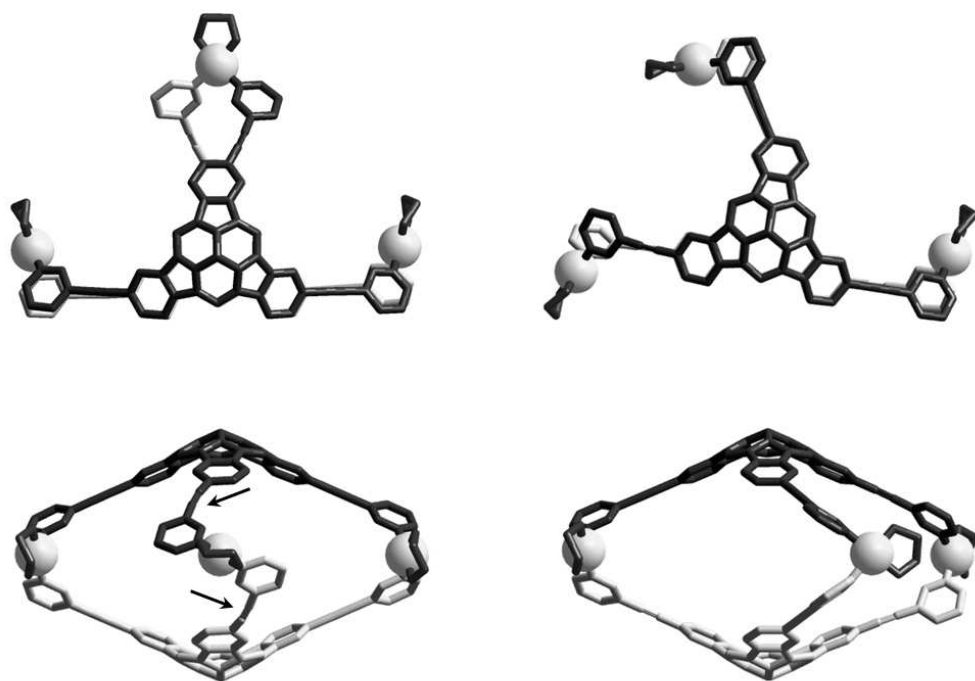


Figure 3

Portion of the <sup>1</sup>H NMR (500 MHz) spectrum in CD<sub>3</sub>CN of cage compound 4a(m) 6PF6.  
254x190mm (96 x 96 DPI)

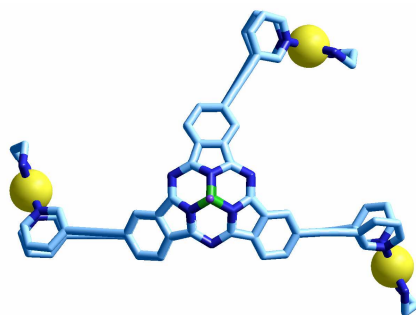


**Figure 4**

Tubular representation of the minimized structures (PM3 semi-empirical calculations) of 4a(c)-6PF6 (left) and 4a(m)-6PF6 (right). Axial groups and hydrogen atoms have been omitted for clarity. The arrows indicate the bent ethynyl bonds in 4a(c)-6PF6.

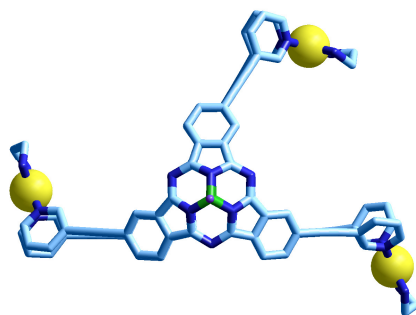
259x206mm (96 x 96 DPI)

Graphical Abstract



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## Graphical Abstract



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