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Christian G. Claessens[a]; Irene Sánchez-Molina[a]; Tomás Torres[a]
[a] Departamento de Química Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain

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Self-sorting among the diastereoisomers of a M_3L_2 subphthalocyanine capsule

Christian G. Claessens*, Irene Sánchez-Molina and Tomás Torres*

Departamento de Química Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain

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A new M_3L_2 homodimeric subphthalocyanine cage was self-assembled and characterised. 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 modelling studies demonstrate that dynamic chiral self-discrimination occurs when the cage compound is left enough time to reach equilibrium.

Keywords: subphthalocyanines; palladium complexes; capsules; metallosupramolecular chemistry; chiral self-discrimination

Introduction

The field of supramolecular self-assembly by coordination chemistry has seen a remarkable development over the last decade (*1*). 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 (*2*). 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 the presence or absence of a target molecule.

In this communication, we describe the synthesis (Figure 1) and characterisation of C_1 symmetric subphthalocyanine **1** (SubPc **3**) and its dimerisation into a set of M_3L_2 metallosupramolecular cages in the presence of a stoichiometric amount of (en)$Pd(NO_3)_2$. 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 (*3*). 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 six distinct diastereoisomeric cages, as illustrated schematically in Figure 2.

Subphthalocyanines are 14 π-electron non-planar aromatic macrocycles comprising three diiminoisoindole units *N*-fused around a central boron atom (*4*). 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 π-conjugated molecules such as fullerenes (*3b*). Moreover, they show very attractive photophysical and electrochemical properties, and have found applications as chromophores in nonlinear optics (*5*), organic light emitting diodes (OLEDs) (*6*), photovoltaic devices (*7*) and multicomponent donor–acceptor systems (*8*).

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. A triple Sonogashira cross-coupling reaction between 3-ethynylpyridine and SubPc **3** in the presence of catalytic amounts of CuI and $PdCl_2(PPh_3)_2$ in triethylamine as the solvent gave C_1 symmetric SubPc **1** in 65% yield.

SubPc **1** was characterised by NMR spectroscopy, MALDI-TOF mass spectrometry (MALDI-TOF MS) and UV spectrophotometry. The ^{1}H NMR spectroscopy of **1** in $CDCl_3$ 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 Sorett band at 350 nm. The MALDI-TOF MS shows a peak at 904.6 corresponding to $[M + H]^+$ 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)$Pd(NO_3)_2$ (1.5 equiv) in a 1:1:1 mixture water, methanol and acetonitrile at room temperature for 4 h followed by anion exchange with a 10-fold excess of ammonium hexafluorophosphate. The ^{1}H NMR spectrum of the resulting compound in CD_3CN showed an extremely complex pattern of signals in accordance with the presence of a mixture of various

*Corresponding authors. Email: christian.claessens@uam.es; tomas.torres@uam.es

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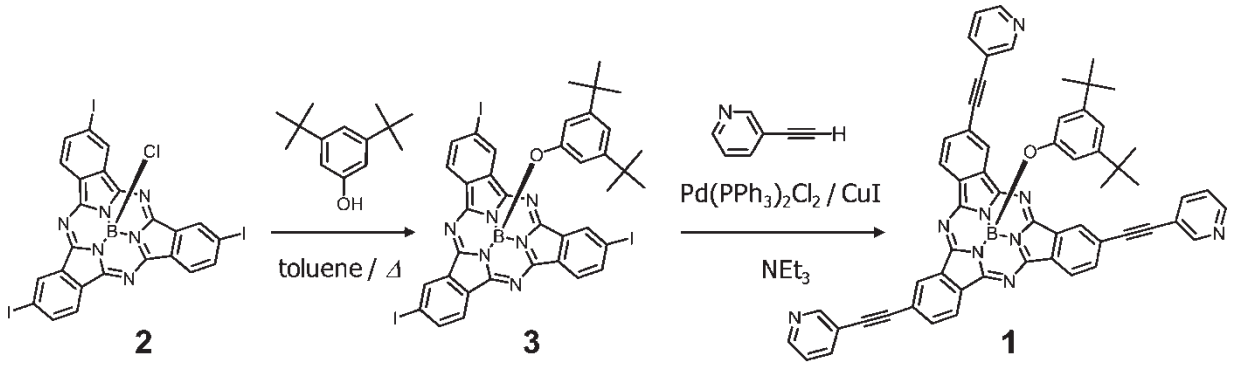

Figure 1. Synthesis of subphthalocyanine **1**.

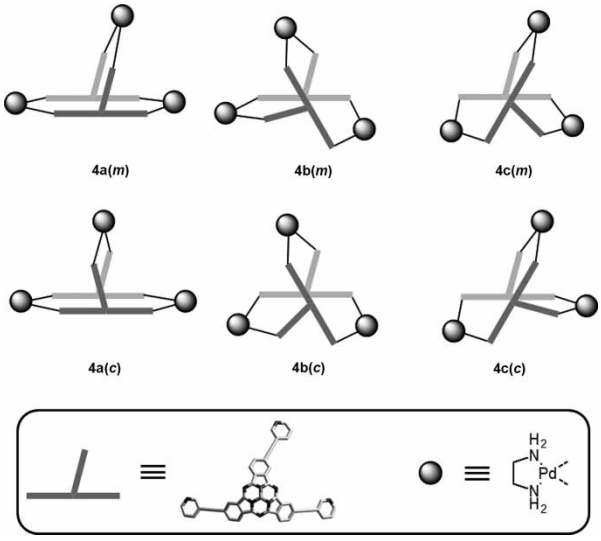

Figure 2. Schematic representation of the six possible diastereoisomers of cage compound **4** · $6PF_6$.

cage compounds. The presence of signals at approximately 9.0 ppm and the relative integral values of the various regions of the spectrum (i.e. aromatic *vs.* ethylenediamine protons) clearly demonstrated the presence of M_3L_2 cages in which the pyridine moieties are coordinated to Pd(II). The 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.

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 characterise. The ^{1}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 H***a***, H***f*** and H***g*** 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*)** · $6PF_6$, **4b(*m*)** · $6PF_6$, **4c(*c*)** · $6PF_6$ and **4b(*m*)** · $6PF_6$ were ruled out since they would give rise to much more complex patterns.

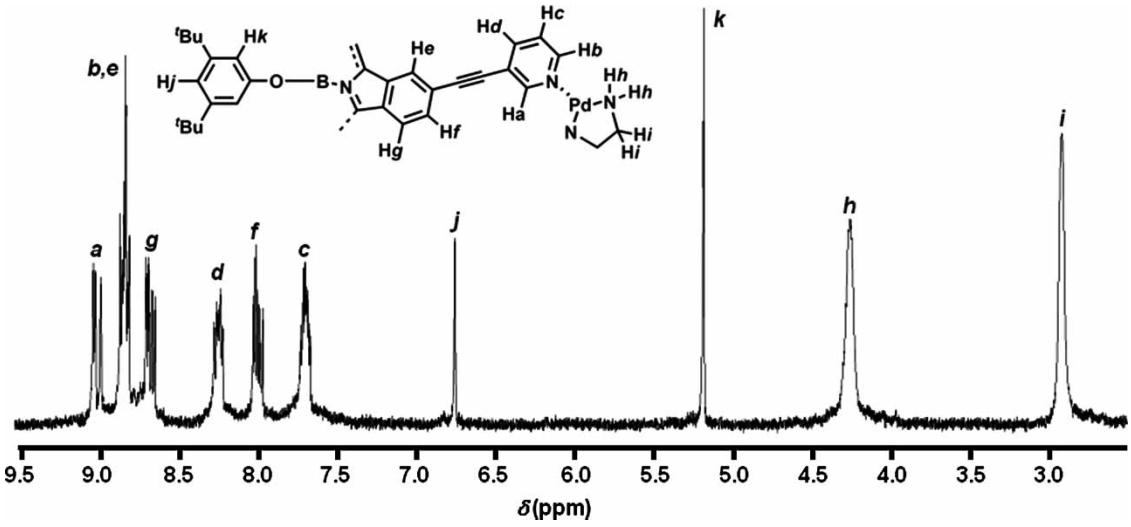

Figure 3. Portion of the ^{1}H NMR (500 MHz) spectrum in CD_3CN of cage compound **4a(*m*)** · $6PF_6$.

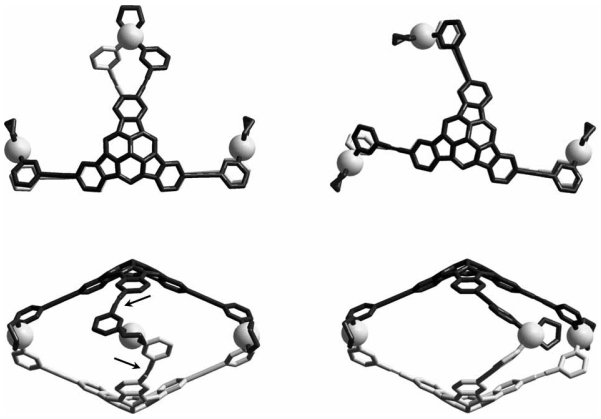

Figure 4. Tubular representation of the minimised structures (PM3 semi-empirical calculations) of **4a(*c*)** · $6PF_6$ (left) and **4a(*m*)** · $6PF_6$ (right). Axial groups and hydrogen atoms have been omitted for clarity. The arrows indicate the bent ethynyl bonds in **4a(*c*)** · $6PF_6$.

Cage **4a(*m*)** · $6PF_6$ is undoubtedly the only one fulfilling the symmetry requirement imposed by the NMR spectrum, but **4a(*c*)** · $6PF_6$, 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 centre. On the other hand, this spectrum is compatible with only one cage because a mixture of cages **4a(*c*)** · $6PF_6$ and **4a(*m*)** · $6PF_6$ should give rise to a mixture of different signals.

In order to determine which of the two diastereoisomers **4a(*c*)** · $6PF_6$ or **4a(*m*)** · $6PF_6$ is present after equilibrated self-assembly, we performed semi-empirical calculations at the PM3 level (Figure 4). These calculations showed that diastereoisomer **4a(*m*)** · $6PF_6$ was much more stable than **4a(*c*)** · $6PF_6$. For example, it can be clearly seen in Figure 4 that one of the ethynyl bond in **4a(*c*)** · $6PF_6$ is rather bent in order to allow the planar tetracoordination around one of the three palladium(II) centres. Thus, according to these considerations, the only isomer present in solution is **4a(*m*)** · $6PF_6$.

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

The UV–vis spectra were recorded with a Hewlett-Packard 8453 instrument. The IR spectra were recorded with a Bruker Vector 22 spectrophotometer. The MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. The NMR spectra were recorded with 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 aluminium sheets precoated with silica gel 60 F_{254} (E. Merck, Darmstadt, Germany). Subphthalocyanine **2** was synthesised according to a formerly described literature procedure (*9*, *10*).

*Synthesis of subphthalocyanine **1***

Under an argon atmosphere, 3-ethynylpyridine (50 mg, 0.484 mmol) was added to a mixture of triodo-3,5-di-*tert*-butyloxysubphthalocyanine **3** (131 mg, 0.134 mmol), palladium diphenylphosphine dichloride (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 × 20 mL) and the resulting organic phase was dried over Na_2SO_4. After removal of the solvent, the resulting solid was subjected to column chromatography on silica gel using acetone/hexane (3:2) as the eluent. After evaporation of the eluent, subphthalocyanine **1** was obtained as a purple solid, 90 mg (75%); m.p. >250°C; ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): $\delta = 9.03$ (br s, 3H, H***e***), 8.86 (m, 3H, H***a***), 8.81 (d, 2H, H***g***), 8.80 (d, 1H, H***g***), 8.62 (dd, 3H, H***b***), 8.04 (dd, 3H, H***f***), 7.91 (ddd, 3H, H***d***), 7.35 (dd, 3H, H***c***), 6.69 (t, 1H, H***j***), 5.20 (d, 2H, H***k***), 1.05 (s, 18H, H***w***); IR (KBr): $\nu = 2368$, 2198, 1601, 1437, 1299, 1156, 1065, 892, 822, 808, 756, 702, 635 cm^{-1}; UV–vis (MeCN): $\lambda_{max}(\log(\varepsilon)) = 585$ (4.8), 571 (sh), 543 (sh), 530 (sh), 349 (4.5), 335 (sh) nm; LSI-MS: *m/z* 904.6 $[M + H]^+$, 698.3 [M-3,5-di-*tert*-butylphenoxy]$^+$; MALDI-TOF: *m/z* 904.7 $[M + H]^+$, 698.5 [M-3,5-di-*tert*-butylphenoxy]$^+$. HR-LSIMS calcd for $C_{59}H_{42}N_9OB$: [M^+]: *m/z* 903.3605, found 903.3616; HR-LSIMS elemental analysis calcd (%) for $C_{59}H_{42}N_9OB$: 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$_6$*

Freshly prepared (en)$Pd(NO_3)_2$ (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_4PF_6 (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **4a(*m*)** · $6PF_6$ precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 40 mg (90%); m.p. >250°C; ^{1}H NMR (500 MHz, CD_3CN, 300 K): $\delta = 9.03$ (s, 2H, H***a***), 9.02 (s, 2H, H***a***), 8.98 (s, 2H,

H***a***), 8.86–881 (m, 12H, H***b*** and H***e***), 8.69 (d, 2H, H***g***), 8.68 (d, 2H, H***g***), 8.65 (d, 2H, H***g***), 8.27–8.22 (m, 6H, H***d***), 8.01 (d, 2H, H***f***), 8.00 (d, 2H, H***f***), 7.98 (d, 2H, H***f***), 7.72–7.67 (m, 6H, H***c***), 6.75 (br s, 2H, H***j***), 5.17 (s, 4H, H***k***), 4.25 (m, 12H, H***h***), 2.91 (m, 12H, H***i***), 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 cm^{1}; UV–vis (MeCN): $\lambda_{max}(\log(\varepsilon)) = 586$ (4.8), 569 (sh), 547 (sh), 536 (sh), 350 (4.5), 336 (sh) nm; ESI-MS: *m*/*z* 1443.0 $[M\text{-}2PF_6]^{2+}$, 913.7 $[M\text{-}3PF_6]^{3+}$, 649.4 $[M\text{-}4PF_6]^{4+}$, 490.2 $[M\text{-}5PF_6]^{5+}$, 384.7 $[M\text{-}6PF_6]^{6+}$; elemental analysis calcd (%) for $C_{124}H_{66}N_{24}O_2B_2Pd_3P_6F_{36}$: C 47.51, H 2.12, N 10.72; found C 46.96, H 2.43, N 11.17.

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