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Supramolecular Chemistry



Self-sorting among the diastereoisomers of a M3L2 subphthalocyanine capsule

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BRIEF COMMUNICATION

Self-sorting among the diastereoisomers of a M₃L₂ subphthalocyanine capsule

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

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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.

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

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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 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 (SubPc³) and its dimerization into a set of M₃L₂ metallosupramolecular cages in the presence of a stoichiometric amount of (en)Pd(NO₃)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.⁴ 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 π -electron non-planar aromatic macrocycles comprising three diiminoisoindole units *N*-fused around a central boron atom.³ 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.^{4b} Moreover, they show very attractive photophysical and electrochemical properties and have found applications as chromophores in nonlinear optics,⁵ in OLEDs,⁶ in photovoltaic devices⁷ and in 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. Triple Sonogashira crosscoupling reaction between 3-ethynylpyridine and SubPc **3** in the presence of catalytic amounts of CuI and PdCl₂(PPh₃)₂ 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. ¹H NMR spectroscopy of 1 in CDCl₃ 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. MALDI-TOF mass spectrometry 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.

Supramolecular Chemistry

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(NO₃)₂ (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. ¹H NMR spectrum of the resulting compound in CD₃CN 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 ¹H 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 $4b(c) \cdot 6PF_6$, $4b(m) \cdot 6PF_6$, $4b(m) \cdot 6PF_6$ were ruled out since they would give rise to much more complex patterns. Cage $4a(m) \cdot 6PF_6$, 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 center. On the other hand, this spectrum is compatible with only one cage because a mixture of cages $4a(c) \cdot 6PF_6$ and $4a(m) \cdot 6PF_6$ should give rise to a mixture of different signals.

In order to determine which of the two diastereoisomers $4a(c) \cdot 6PF_6$ or $4a(m) \cdot 6PF_6$ is present after equilibrated self-assembly, we performed semi-empirical calculations at PM3 level (Figure 4). These calculations showed that diastereoisomer $4a(m) \cdot 6PF_6$ was much more stable than $4a(c) \cdot 6PF_6$. For example, it can be clearly seen in Figure 4 that the ethynyl bond in $4a(c) \cdot 6PF_6$ 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 $4a(m) \cdot 6PF_6$.

<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_{254} (E. Merck). Subphthalocyanine **2** was synthesized according to a formerly described literature procedure.^{9,10}

Synthesis of subphthalocyanine 3:

Under an argon atmosphere, 3-ethynylpyridine (50 mg, 0.484 mmol) was added to a mixture of triodo-3,5-di*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 Na₂SO₄. 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; ¹H NMR (CDCl₃, 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⁻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-diterbutylphenoxy]⁺; MALDI-TOF: *m/z*: 904.7 [M+H]⁺, 698.5 [M-3,5-diterbutylphenoxy]⁺; HR-LSIMS calcd for C₅₉H₄₂N₉OB: [M⁺]: *m/z*: 903.3605, found 903.3616; HR-LSIMS elemental analysis calcd (%) for C₅₉H₄₂N₉OB: 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) •6PF₆:

Freshly prepared (en)Pd(NO₃)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, NH₄PF₆ (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **4a**(*m*)•6PF₆ precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 40 mg (90%); m.p. > 250°C; ¹H NMR (500 MHz, CD₃CN, 300 K): δ = 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 (brs, 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): *v* = 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-2PF₆]²⁺, 913.7 [M-3PF₆]³⁺, 649.4 [M-4PF₆]⁴⁺, 490.2 [M-5PF₆]⁵⁺, 384.7 [M-6PF₆]⁶⁺; elemental analysis calcd (%) for C₁₂₄H₆₆N₂₄O₂B₂Pd₃P₆F₃₆: C 47.51, H 2.12, N 10.72; found C 46.96, H 2.43, N 11.17.

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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•6PF₆.
- **Figure 3.** Portion of the ¹H NMR (500 MHz) spectrum in CD₃CN of cage compound $4a(m) \cdot 6PF_6$.
- Figure 4. Tubular representation of the minimized structures (PM3 semi-empirical calculations) of $4a(c) \cdot 6PF_6$ (left) and $4a(m) \cdot 6PF_6$ (right). Axial groups and hydrogen atoms have been omitted for clarity.



4c(*c*)

4b(c)

4a(c)

4c(*m*)

4b(*m*)

4a(*m*)





Figure 2

Schematic representation of the six possible diastereoisomers of cage compound 4Â%6PF6.

102x161mm (600 x 600 DPI)



Figure 3

Portion of the 1H NMR (500 MHz) spectrum in CD3CN of cage compound $4a(m)\hat{A}\%$ 6PF6. 254x190mm (96 x 96 DPI)



Figure 4

Tubular representation of the minimized structures (PM3 semi-empirical calculations) of $4a(c)\hat{A}\%6PF6$ (left) and $4a(m)\hat{A}\%6PF6$ (right). Axial groups and hydrogen atoms have been omitted for clarity. 160x132mm (96 x 96 DPI)

REVISED VERSION

BRIEF COMMUNICATION

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

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

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Supramolecular Chemistry

 In a first instance we decided to employ the same conditions as for the successful self-assembly of the $M_{3}L_{2}$ cage from the C_{3} counterpart of SubPc 1 by mixing SubPc 1 and stoichiometric amounts of (en)Pd(NO₃)₂ (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. ¹H NMR spectrum of the resulting compound in CD₃CN 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 $M_{3}L_{2}$ cages in which the pyridine moieties are coordinated to Pd(II). ¹H 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 ¹H 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 ¹H 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.^{4b} 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*)•6PF₆, **4b**(*m*)•6PF₆, **4c**(*c*)•6PF₆, **4b**(*m*)•6PF₆ 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*)•6PF₆, 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*)•6PF₆ and **4a**(*m*)•6PF₆ should give rise to a mixture of different signals.

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<Figure 4>

CONCLUSIONS

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Under an argon atmosphere, 3-ethynylpyridine (50 mg, 0.484 mmol) was added to a mixture of triodo-3,5-di*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 Na₂SO₄. 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; ¹H NMR (CDCl₃, 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⁻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-3,5di*tert*butylphenoxy]⁺. HR-LSIMS calcd for C₅₉H₄₂N₉OB: [M⁺]: *m/z*: 903.3605, found 903.3616; HR-LSIMS elemental analysis calcd (%) for C₅₉H₄₂N₉OB: 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) •6PF₆:

Freshly prepared (en)Pd(NO₃)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, NH₄PF₆ (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **4a**(*m*)•6PF₆ precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 40 mg (90%); m.p. > 250°C; ¹H NMR (500 MHz, CD₃CN, 300 K): δ = 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 (brs, 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): v = 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-2PF₆]²⁺, 913.7 [M-3PF₆]³⁺, 649.4 [M-4PF₆]⁴⁺, 490.2 [M-5PF₆]⁵⁺, 384.7 [M-6PF₆]⁶⁺; elemental analysis calcd (%) for C₁₂₄H₆₆N₂₄O₂B₂Pd₃P₆F₃₆: C 47.51, H 2.12, N 10.72; found C 46.96, H 2.43, N 11.17.

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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•6PF₆.
- **Figure 3.** Portion of the ¹H NMR (500 MHz) spectrum in CD₃CN of cage compound $4a(m) \cdot 6PF_6$.
- **Figure 4.** Tubular representation of the minimized structures (PM3 semi-empirical calculations) of $4a(c) \cdot 6PF_6$ (left) and $4a(m) \cdot 6PF_6$ (right). Axial groups and hydrogen atoms have been omitted for clarity. The arrows indicate the bent ethynyl bonds in $4a(c) \cdot 6PF_6$.





Schematic representation of the six possible diastereoisomers of cage compound 4Å $\,$ 6PF6. 211x205mm (96 x 96 DPI) $\,$



Portion of the 1H NMR (500 MHz) spectrum in CD3CN of cage compound $4a(m)\hat{A}$ 6PF6. 254x190mm (96 x 96 DPI)





Figure 4

Tubular representation of the minimized structures (PM3 semi-empirical calculations) of $4a(c)\hat{A}$ 6PF6 (left) and $4a(m)\hat{A}$ 6PF6 (right). Axial groups and hydrogen atoms have been omitted for clarity. The arrows indicate the bent ethynyl bonds in $4a(c)\hat{A}$ 6PF6. 259x206mm (96 x 96 DPI)

Graphical Abstract



Graphical Abstract

