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Synthesis and characterization of a benzene-centered, phthalocyanine hexamer†

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The first benzene-centered, phthalocyanine hexamer has been synthesized by a dicobaltoctacarbonyl-catalyzed trimerization reaction of an ethynyl-bridged bisphthalocyanine and characterized by different spectrometric and spectroscopic techniques.

The construction of multi-chromophore molecular systems for materials science applications represents a quite attractive and challenging issue. In the past years a significant synthetic effort has been spent in the preparation of multi-porphyrin molecular architectures as building blocks for the construction of functional molecular systems such as molecular scale wires, switches and photovoltaic devices.[1]

Although phthalocyanines (Pcs),[2] porphyrin-related compounds, have shown to be interesting scaffolds for the preparation of molecular and supramolecular architectures,[3] the endeavour for the realization of multi-Pc molecular arrays has not been as large. Unfortunately, the step-wise approach necessary for the preparation of such complex molecular systems is limited considerably by the difficulty in preparing and purifying the unsymmetric Pc precursors.[4] Metal-mediated cross- and homo-coupling methodologies have been used with some success in the preparation of two-dimensional (2D) dimeric and trimeric Pc-containing structures.[5] Recently we have focused part of our work on the preparation of multi-Pc systems and related compounds possessing a three-dimensional (3D) topology.[3b,6]

In this communication we report on the synthesis and characterization of a novel 3D sterically-crowded multi-Pc system consisting of a central benzene ring substituted with six identical ZnPc units.‡

The ZnPc-containing persubstituted benzene **1** was prepared from the iodo-substituted ZnPc **2**, the last step involving a transition-metal-catalyzed trimerization reaction of the ethynyl-bridged bisphthalocyanine **3** (Scheme 1).

The first step towards the preparation of the ZnPc hexamer **1** consisted of the synthesis of the ZnPc dimer **3** in which two ZnPc units are connected *via* an ethynyl linkage. This dimer was prepared by a Pd(0)-catalyzed Sonogashira coupling reaction between the unsymmetrical iodo-substituted ZnPc **2** and the tri-*tert*-butylethynylphthalocyaninatozinc(II) in a 70% yield.[5b]

UV/vis analysis in THF of the symmetric ZnPc dimer **3** and its unsymmetrical parent **2** showed quite different electronic absorption profiles for the two compounds (Fig. 1).

In fact, whereas the iodo-substituted ZnPc **2** presents a single, sharp Q-band transition (672 nm) typical of mono-metalated Pcs,§ the ZnPc dimer **3** exhibits a split in the Q-band into two equally-intense peaks (705 and 671 nm), resulting from the extended π-conjugation of the ZnPc dimer.[5b]

The crucial synthetic step towards the preparation of the ZnPc-containing persubstituted benzene **1** involved a dicobaltoctacarbonyl-catalyzed trimerization reaction of the ZnPc-disubstituted ethyne **3**.

The cyclotrimerization of alkynes to give benzene derivatives has

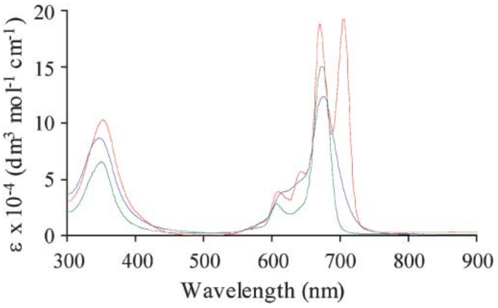
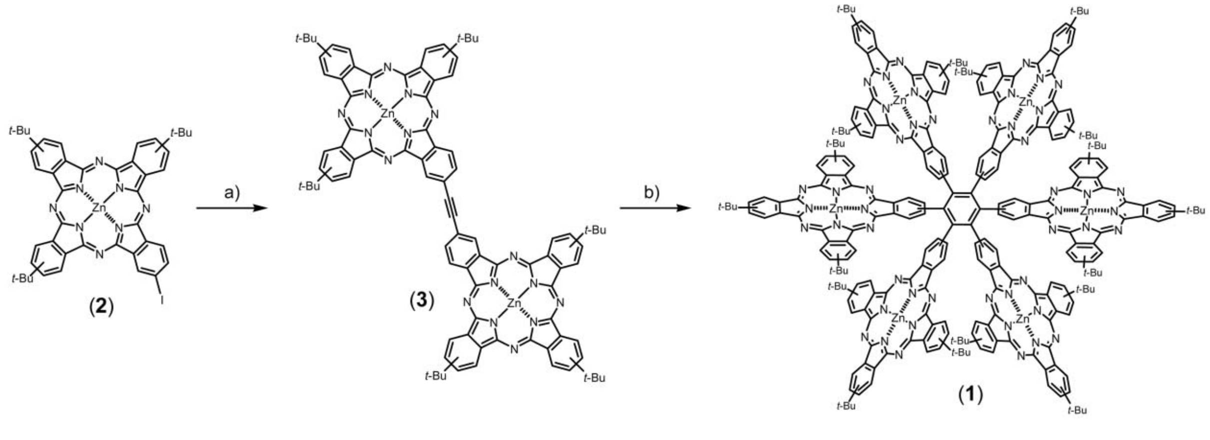


Fig. 1 UV/vis spectra (THF, conc. = 4 × 10^{-6} mol L^{-1}, T = 298 K) of ZnPc-containing hexasubstituted benzene **1** (blue line), iodo-substituted ZnPc **2** (green line) and ZnPc dimer **3** (red line).



Scheme 1 Synthesis of the ZnPc-containing persubstituted benzene **1**: a) tri-*tert*-butylethynylphthalocyaninatozinc(II), $Pd_2(dba)_3$, $AsPh_3$, piperidine, 35 °C, 6 h, 70%;[5b] b) $Co_2(CO)_8$, dioxane, reflux, 7 h, 16%. Abbreviation: dba = dibenzylydeneacetone.

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† Electronic supplementary information (ESI) available: experimental procedure, geometrical optimization, IR, UV/vis, MS and elemental analysis data for compound **1**. See http://www.rsc.org/suppdata/cc/b4/b411960f/

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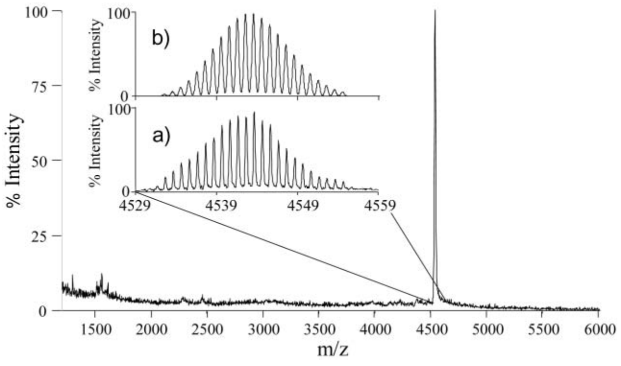

Fig. 2 Main graphic: MALDI-TOF MS spectrum (dithranol) of the ZnPc-containing hexasubstituted benzene **1**. Inset: a) isotopic resolution of the MALDI-TOF main peak; b) calculated isotopic pattern for **1**.

been known for almost three decades[7] allowing the facile access to highly substituted, and often sterically-crowded, benzenes[8] which are otherwise difficult to obtain by other modern synthetic techniques. However, it has never been used, to the best of our knowledge, for the synthesis of Pc-substituted benzenes.

The cyclotrimerization of the ZnPc dimer **3** takes place in dry dioxane catalyzed by $Co_2(CO)_8$ giving the multi-Pc benzene **1** in a 16% yield after purification by silica gel and size-exclusion column chromatographies. Although this yield could appear modest at first sight, one should take into account the high steric demand that this cyclotrimerization reaction presents which has to be overcome in order to form the final sterically-crowded product **1**.¶

The formation of the multi-Pc system was confirmed by a MALDI-TOF mass spectrometry (MS) experiment which showed a prominent peak at *m*/*z* 4543 whose isotopic profile matched almost perfectly with the calculated isotopic pattern for the ZnPc-persubstituted benzene **1** (Fig. 2).

Moreover, a MALDI-TOF MS–MS experiment was carried out in order to rule out the possibility that the main peak observed in the MALDI-TOF MS spectrum (*i.e.* *m*/*z* 4543) was the result of the supramolecular association of three molecules of the ZnPc dimer **3** (*i.e.* $[\mathbf{3}_3]^+$)‖ (see ESI, Fig. S2†). This experiment showed no fragmentation, thus clearly proving that this peak was due to a molecular ion and not to an ionic supramolecular ensemble.

UV/vis analysis of the ZnPc-persubstituted benzene **1** in THF presents a single, broad Q-band centered at 676 nm, whose optical absorption profile differs considerably from that of the ZnPc dimer **3**, resembling instead that of the iodo-substituted ZnPc **2** and the tri-*tert*-butylethynylphthalocyaninatozinc(II) (Fig. 1).

Taking into account that the profile of the ZnPc hexamer's Q-band absorption is concentration-independent and that the nature of the solvent (THF) rules out any intermolecular aggregation phenomenon, a possible explanation for the difference in the optical absorption profile between the persubstituted benzene **1** and its precursor **3** should be the conformational arrangement adopted by **1** in solution. In fact, in order to minimize the steric congestion of the system, the six tightly packed ZnPc units would adopt a tilted conformation with respect to the central benzene core (see ESI, Fig. S3†), as already seen for other sterically-crowded, persubstituted benzenes.[9] In such a conformation resembling a six-blade 'molecular propeller', electronic communication between the ZnPc units of the persubstituted benzene **1** should be significantly hampered. This may ultimately lead the ZnPc units to behave like independent, non-conjugated cromophores, thus giving rise to the single Q-band transition observed.

In conclusion, we have synthesized a novel Pc-containing hexasubstituted benzene (**1**) *via* a transition-metal-catalyzed trimerization reaction of an ethynyl-bridged ZnPc dimer (**3**). This reaction represents a quite elegant and facile method for the synthesis of sterically-crowded, benzene-centered multi-Pc systems otherwise difficult to obtain by other synthetic strategies. Considering the interesting topology of compound **1**, work is currently under way in our laboratories to prepare a new family of Pc-containing persubstituted benzenes bearing alternating donor and/or acceptor Pc units as promising second-order nonlinear optical (NLO) cromophores with octupolar characteristics.[10]

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Notes and references

‡ Recently, a persubstituted benzene system bearing six Pc units directly connected to the central aromatic ring through alkoxy (–OCH_2–) spacers has been communicated in a conference (ICPP-3, New Orleans, USA, July 11–16, 2004) by B. Isare, J. Sly, A. E. Rowan, R. J. M. Nolte and M. J. Cook (Proceedings in *J. Porphyrins Phthalocyanines*, 2004, **8**, 703).

§ Similarly to **2**, the tri-*tert*-butylethynylphthalocyaninatozinc(II) presents a single, sharp Q-band transition centered at 674 nm in THF.

¶ Mechanistic studies on the trimerization reaction have revealed that the mechanism is not a simultaneous [2 + 2 + 2] alkyne-concerted reaction at the transition-metal center, but rather a [4 + 2] reaction *via* the formation of a metallacyclopentadiene intermediate to which the third alkyne molecule is added.[11]

‖ The molecular ion $[\mathbf{1}]^+$ has the same chemical formula and consequently the same isotopic pattern distribution as the ionic supramolecular ensemble $[\mathbf{3}_3]^+$.

1 J.-S. Hsiao, B. P. Krueger, R. W. Wagner, T. E. Johnson, J. K. Delaney, D. C. Mauzerall, G. R. Fleming, J. S. Lindsey, D. F. Bocian and R. J. Donohoe, *J. Am. Chem. Soc.*, 1996, **118**, 11 181; H. A. M. Biemans, A. E. Rowan, A. Verhoeven, P. Vanoppen, L. Latterini, J. Foekema, A. P. H. J. Schenning, E. W. Meijer, F. C. de Schrijver and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1998, **120**, 11 054; J. Li, A. Ambroise, S. I. Yang, J. R. Diers, J. Seth, C. R. Wack, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1999, **121**, 8927; R. K. Lammi, A. Ambroise, T. Balasubramanian, R. W. Wagner, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 2000, **122**, 7579.

2 *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith and R. Guilard, eds., Academic Press, New York, 2003, vols. 15–20.

3 (*a*) H. Engelkamp, S. Middelbeek and R. J. M. Nolte, *Science*, 1999, **284**, 785; (*b*) A. de la Escosura, M. V. Martínez-Díaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte and T. Torres, *J. Am. Chem. Soc.*, 2003, **125**, 12 300.

4 M. S. Rodríguez-Morgade, G. de la Torre and T. Torres, in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith and R. Guilard, eds., Academic Press, New York, 2003, vol. 15, ch. 99.

5 (*a*) G. de la Torre, M. V. Martínez-Díaz, P. Ashton and T. Torres, *J. Org. Chem.*, 1998, **63**, 8888; (*b*) E. M. Maya, P. Vázquez and T. Torres, *Chem. Eur. J.*, 1999, **5**, 2004; (*c*) M. J. Cook and M. J. Heeney, *Chem. Eur. J.*, 2000, **6**, 3958; (*d*) E. M. García-Frutos, F. Fernández-Lázaro, E. M. Maya, P. Vázquez and T. Torres, *J. Org. Chem.*, 2000, **65**, 6841.

6 G. de la Torre, A. Gouloumis, P. Vázquez and T. Torres, *Angew. Chem., Int. Ed.*, 2001, **40**, 2895; C. G. Claessens and T. Torres, *Angew. Chem., Int. Ed.*, 2002, **41**, 2561.

7 K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 539.

8 C. D. Simpson, J. D. Brand, A. J. Berresheim, L. Przybilla, H. J. Räder and K. Müllen, *Chem. Eur. J.*, 2002, **8**, 1424.

9 R. E. Bauer, V. Enkelmann, U. M. Wiesler, A. J. Berresheim and K. Müllen, *Chem. Eur. J.*, 2002, **8**, 3858; X. Shen, D. M. Ho and R. A. Pascal, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 5798.

10 G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *J. Mater. Chem.*, 1998, **8**, 1641; G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *Chem. Rev.*, 2004, **104**, 3723.

11 N. E. Schore, *Chem. Rev.*, 1988, **88**, 1081.