

# Homo- and hetero-dimetallic ethynyl- and butadiynyl-bridged bisphthalocyaninato complexes

Eva María Maya, Purificación Vázquez and Tomás Torres\*

Departamento de Química Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain

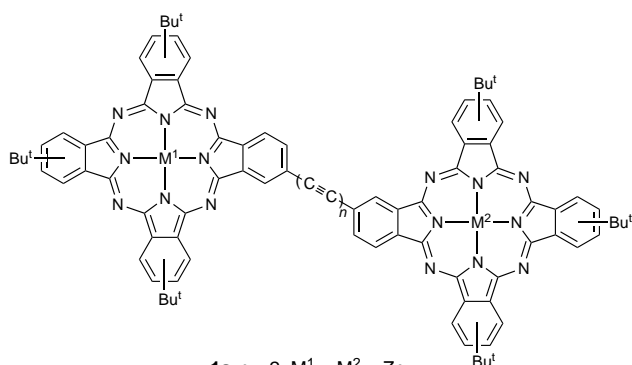
A new type of phthalocyanine-based chromophore system having two metallophthalocyanine rings bound together through ethynyl linkages has been synthesized.

Much effort has been expended in recent years to exploit electronic- and photonic-based cooperation between individual subunits of porphyrins.<sup>1</sup> However, despite the great interest of the related phthalocyanine (Pc) chromophore,<sup>2</sup> for example as a building block for the construction of new molecular materials, the effort devoted to preparing multiphthalocyanine arrays has not been as large. The main reason could be the difficulty of preparing unsymmetric Pcs,<sup>3</sup> necessary for a stepwise approach to building more complex Pc systems,<sup>4</sup> and in the purification of Pcs<sup>2</sup> in comparison with porphyrins. Non-conjugated binuclear Pcs, in which the two Pc nuclei are covalently bound *via* various kinds of linkage, have been reported.<sup>5</sup> However, to date very few examples of systems having phthalocyanine-to-phthalocyanine conjugated connections, namely planar binuclear phthalocyanines, have been described.<sup>6</sup>

Ethyne and oligoethyne bridges between chromophores have been recognized as ideal linkages, enabling unusually high excitonic and electron coupling between chromophore centres.<sup>7</sup> Recently, symmetric<sup>8</sup> and unsymmetric<sup>9</sup> Pcs having ethynyl functions have been described, but to the best of our knowledge the ethynyl linkage has not been used hitherto to assemble phthalocyanine systems with extended conjugation.

We are presently concentrating on the synthesis of Pcs and related compounds for nonlinear optics (NLO).<sup>10</sup> In this regard, the preparation of multiphthalocyanine arrays with extended conjugation represents an important goal.<sup>10b</sup>

Here the well-known metal-mediated cross- and homocoupling methodology is applied for the first time to the preparation of homo- and hetero-dimetallic ethynyl- and butadiynyl-bridged bis(phthalocyaninato)zinc and nickel complexes **1a,b** and **2a,b**.



- 1a**  $n = 2$ ,  $M^1 = M^2 = \text{Zn}$   
**b**  $n = 2$ ,  $M^1 = M^2 = \text{Ni}$   
**2a**  $n = 1$ ,  $M^1 = M^2 = \text{Zn}$   
**b**  $n = 1$ ,  $M^1 = \text{Zn}$ ,  $M^2 = \text{Ni}$

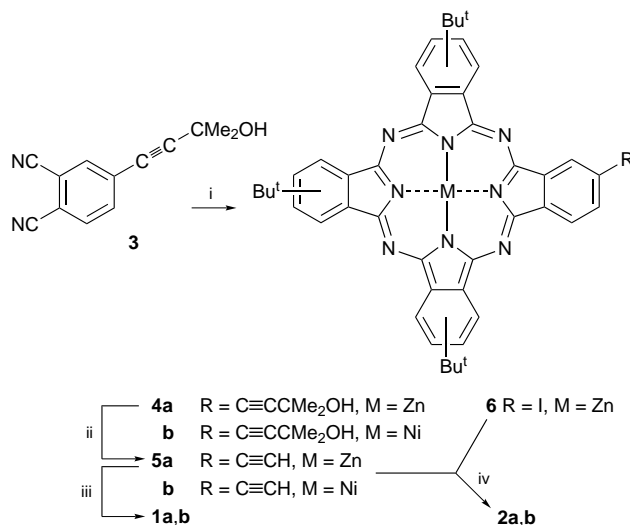
4-Iodophthalonitrile<sup>11</sup> was reacted with commercially available 2-methylbut-3-yn-2-ol in the presence of bis[triphenylphosphine]palladium(II) dichloride and copper(I) iodide<sup>11,12</sup> to

yield aryl alcohol **3**. The mixed condensation of this phthalonitrile with an excess of 4-*tert*-butylphthalonitrile in the presence of the corresponding metal(II) chloride afforded the corresponding zinc and nickel complexes **4a,b**<sup>†</sup> in moderate yield, as a statistical mixture of isomers in each case (Scheme 1). The protecting group was then removed by treatment with sodium hydroxide in toluene<sup>12</sup> to give ethynyl derivatives **5a,b**<sup>‡</sup> in good yields. Similarly, compound **6**<sup>‡</sup> was obtained by statistical mixed condensation of 4-iodophthalonitrile with 4-*tert*-butylphthalonitrile and zinc chloride, in low yield (*ca.* 20%) after chromatographic purification.

Oxidative homocoupling<sup>11</sup> of terminal alkynes **5a,b** in the presence of copper(II) acetate monohydrate in a mixture of dry pyridine and dry methanol led, after purification by chromatography on silica gel, to the homonuclear dimetallic complexes **1a,b**<sup>†</sup> in *ca.* 50% yield.

Cross-coupling of alkynes **5a,b** with monoiodophthalocyanine **6** in freshly distilled and deaerated piperidine, in the presence of a catalyst formed *in situ* by the addition of tris(dibenzylideneacetone)dipalladium(0) [Pd<sub>2</sub>(dba)<sub>3</sub>] and triphenylarsine<sup>1a,13</sup> afforded the corresponding homonuclear and heterodimetallic butadiynyl-bridged bis(phthalocyaninato) complexes **2a,b**<sup>†</sup> in *ca.* 40% yield, after chromatographic purification. The same cross-coupling was accomplished in lower yield and with longer reaction times (12 h) by using the catalytic system Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI<sup>8</sup> in freshly distilled and deaerated NEt<sub>3</sub> as solvent.

Fig. 1 shows the electronic absorption spectrum of butadiynyl-bridged bis(phthalocyaninato)zinc complex **1a**. The optical features of this new chromophoric system differ remarkably from that of the unsymmetric parent compound **5a**. The Soret (B) transition of **1a** occurring in the blue region of the spectra span wavelength ranges of 300–450 nm, similar to that



**Scheme 1** Reagents and conditions: i, 4-*tert*-butylphthalonitrile (3 equiv.), dimethylaminoethanol, reflux, MCl<sub>2</sub> (M = Zn, Ni); ii, toluene, NaOH; iii, CuOAc·H<sub>2</sub>O, 5% MeOH–pyridine, 55–60 °C, 90 min; iv, Pd<sub>2</sub>(dba)<sub>3</sub>, As(Ph<sub>3</sub>)<sub>3</sub>, piperidine, 35 °C, 4 h

of compound **5a** (maximum at 350 nm). However, while ethynyl compound **5a** exhibits only one Q-band at 684 nm, typical of metalated Pcs, dimer **1a** shows a splitting of this Q-band as well as a remarkable broadening and redshift of this transition, most probably resulting from the extended  $\pi$ -conjugation. § Thus in compound **1a** two intense bands appear at 675 and 709 nm, respectively. In addition, at higher concentrations, a shoulder centred at *ca.* 770 nm is observed which extends to *ca.* 820 nm. ¶

Fig. 2 shows the UV–VIS spectra of ethynylbis(phthalocyaninato)-zinc and -nickel complexes **2a,b**. The spectrum of **2a** is quite similar to that of **1a**, with the absorption maximum of the B-band slightly shifted to the blue (maximum at 344 nm), whereas the absorption maxima of the Q-bands appear slightly redshifted at 678 and 710 nm. In this case a broad band centred at 770 nm is also observed. The heterodimetallic compound **2b** shows only one intense absorption of the Q-band zone at 678 nm, with a shoulder at 713 nm.

The absorption coefficients of the Q-bands in **1** and **2** decrease, with regard to the mononuclear species **5**, due to increasing conjugation. The spectra are essentially unchanged down to  $5 \times 10^{-7}$  M. Compounds **1a,b** and **2a,b** show no sign of intermolecular aggregation in  $\text{CHCl}_3$  at concentrations below  $5 \times 10^{-5}$  M. At higher concentrations, however, intermolecular aggregation takes place in some cases.

The degree of intramolecular aggregation in solution and the extent of electronic coupling between the two halves of the binuclear molecules in unsymmetrically substituted derivatives are under investigation.<sup>15</sup>

This series of alkynyl-bridged bis(phthalocyaninato)metal compounds **1** and **2** represent a basis set of supramolecular chromophore systems for studying electron and excitation transfer processes. On the other hand, the stepwise synthetic procedure described will allow the preparation of systems with distinct central metals and different kinds of substituents, for example donor and acceptor, in each one of the Pc subunits for NLO purposes.<sup>10b</sup>

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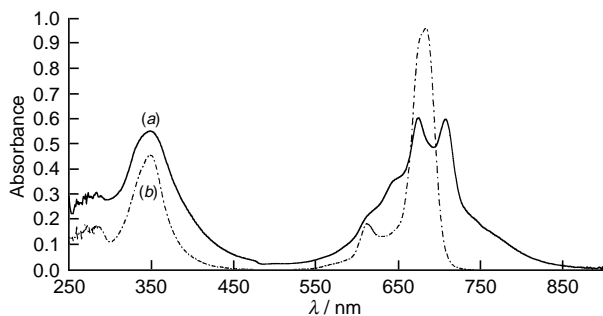


Fig. 1 Electronic spectra of (a) **1a** ( $1.1 \times 10^{-5}$  mol dm<sup>-3</sup>) and (b) **5a** ( $3.3 \times 10^{-6}$  mol dm<sup>-3</sup>) in  $\text{CHCl}_3$

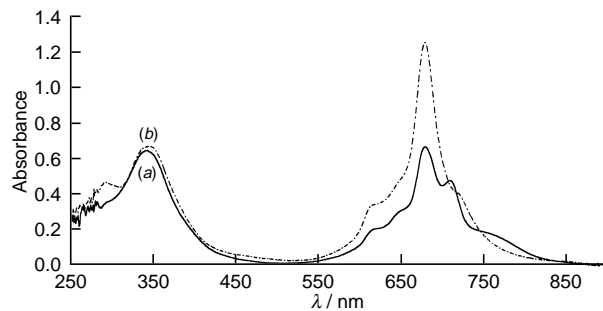


Fig. 2 Electronic spectra of (a) **2a** ( $3.6 \times 10^{-5}$  mol dm<sup>-3</sup>) and (b) **2b** ( $1.3 \times 10^{-5}$  mol dm<sup>-3</sup>) in  $\text{CHCl}_3$

## Footnotes

\* E-mail: tomas.torres@uam.es

† Elemental analysis and spectral data [FAB-MS, <sup>1</sup>H NMR ( $\text{CDCl}_3$ ), IR (KBr) and UV–VIS ( $\text{CHCl}_3$ )] for compounds **1–6** were consistent with assigned structures.

‡ Selected data (for UV–VIS see Figs. 1 and 2) for **1a**:  $m/z$  1539 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.5–7.2 (br signals, arom-H), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ]. For **1b**:  $m/z$  1525 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.4–7.1 (br signals, arom-H), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ]. For **2a**:  $m/z$  1514 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.4–7.0 (br signals, arom-H), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ]. For **2b**:  $m/z$  1507 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.5–7.2 (br signals, arom-H), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ]. For **3**:  $m/z$  211 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  4.0 (OH), 1.4 ( $\text{CH}_3$ );  $\delta_{\text{C}}$  115.2 (CN), 101.4 ( $\text{C}\equiv\text{C}$ ), 30.0 ( $\text{CH}_3$ ). For **4a**:  $m/z$  826 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  8.4–7.2 (br signals, arom-H), 4.0 (OH), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ], 1.4 ( $\text{CH}_3$ ). For **4b**:  $m/z$  820 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  8.2–7.3 (br signals, arom-H), 4.0 (OH), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ], 1.4 ( $\text{CH}_3$ ). For **5a**:  $m/z$  768 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.0–7.5 (br signals, arom-H), 3.4 ( $\text{C}\equiv\text{CH}$ ), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ];  $\nu_{\text{max}}/\text{cm}^{-1}$  3295, 2103 ( $\text{C}\equiv\text{C}-\text{H}$ ). For **5b**:  $m/z$  762 ( $\text{M} + \text{H}^+$ );  $\delta_{\text{H}}$  9.0–7.6 (br signals, arom-H), 3.4 ( $\text{C}\equiv\text{CH}$ ), 1.6 [br signals,  $\text{C}(\text{CH}_3)_3$ ];  $\nu_{\text{max}}/\text{cm}^{-1}$  3295, 2103 ( $\text{C}\equiv\text{C}-\text{H}$ ). For **6**:  $m/z$  870 ( $\text{M} + \text{H}^+$ ).

§ Tri-*tert*-butylethynyl- (**5a**) and tri-*tert*-butyliodo-phthalocyanine (**6**) have been recently prepared following a different procedure (ref. 9).

¶ Taking into account that compounds **1** and **2** are definitely a mixture of structural isomers, it could be considered that a higher ratio of one or more of these isomers might be the reason of the splitting of the Q-bands observed in the UV–VIS spectra (ref. 14). However, the magnitude of the splitting, the kind of substituents involved, the lack of splitting in the starting materials **5** and **6** (which are also mixtures of isomers) and preliminary results obtained for other symmetrically substituted dimers (ref. 15), suggest that the observed splitting is due, to a major degree, to the extended  $\pi$ -conjugation of the system.

¶ Similarly to **1a**, compound **1b** shows a broad absorption between 550 and 850 nm, with the only clear maximum at 670 nm. The Q-band of the parent compound **5b** appears at 673 nm.

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