J. Org. Chem. **2000,** *65,* 6841−6846 **6841**

Copper-Mediated Synthesis of Phthalocyanino-Fused Dehydro[12]- and [18]annulenes

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Received April 19, 2000

Cyclooligomeric phthalocyanines with the special feature of having a dehydroannulene core are described. Compounds **4a**,**b** and **5a**,**b** were prepared by an oxidative coupling mediated by copper from the corresponding diethynyl unsymmetrically substituted phthalocyanines **8a**,**b**, which are easily accessible from the corresponding diiodo compounds **6a**,**b** by a palladium−copper-catalyzed coupling. Appropriate conditions to selectively form cyclodimers and cyclotrimers using Glaser and Eglinton methodologies have been attempted. In this way, two compounds, **4a** and **5b**, each representative of a kind of oligomers, could be appropriately isolated and characterized by MALDI-MS. The UV−vis spectra of compounds **4a** and **5b** show a split Q-band shifted to the red with respect to the corresponding precursor **8a**,**b**. This can be interpreted, in light of previous results, as a consequence of intramolecular electronic coupling between the Pc subunits. Extensive formation of aggregates in chloroform can be also inferred from the spectra. No significant differences could be observed in the spectra by comparison with that of the open-chain analogue **11**, most probably due to a saturation phenomenon of the optical properties already pointed out in the literature for other alkynyl-linked open-chain dimers.

Introduction

Highly conjugated alkynyl linked compounds have been the focus of much synthetic effort, since acetylenic bridges, due to their role as conjugation extenders, have demonstrated a notorious ability to allow high excitonic and electronic coupling between chromophore units.[1]

With this aim, several porphyrin[1b,2] and phthalocyanine[3] alkynyl-substituted derivatives have been synthesized, some of which showed increased second-order nonlinear optical effects. In this context, our group has been interested for a long time in exploring the possibilities of phthalocyanines (Pcs) and related macrocycles as potential technological targets due to their intrinsic properties.[4]

On the other hand, the Glaser and Eglinton reactions[5] have been used to cyclooligomerize terminal alkynes, opening an entry in the world of dehydroannulenes, as Sondheimer pointed out already in 1962,[6] among other fascinating macrocycles.[7] However, it remains in the literature unclear whether it is possible to choose the appropriate conditions to selectively form cyclodimers, cyclotrimers, or mixtures of both and higher cyclooligomers. Thus, the use of the Glaser conditions gave dimers[8] or mixtures.[9] On the other hand, the use of the Eglinton reaction has led to dimers,[10] trimers[11] or mixtures.[6,11,12]

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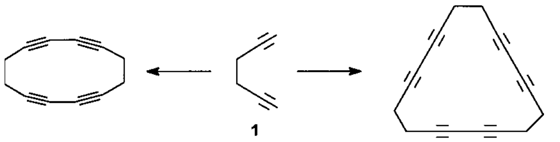
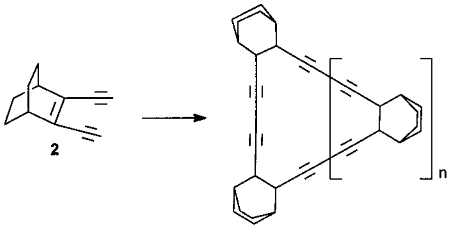
10.1021/jo0006019 CCC: $19.00

Some results are specially noteworthy. For example, hexa-1,5-diyne **1** afforded exclusively the cyclic dimer when subjected to Glaser conditions, whereas on Eglinton conditions it led to a mixture of cyclic trimer, cyclic tetramer, cyclic pentamer and linear dimer.[6,13] The enediyne **2** led to a mixture of dimer, trimer, tetramer and pentamer when heated at 70 °C under Eglinton conditions, but when the reaction was carried out at 50 °C the only cyclized product was the trimer.[11]



1



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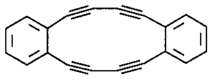


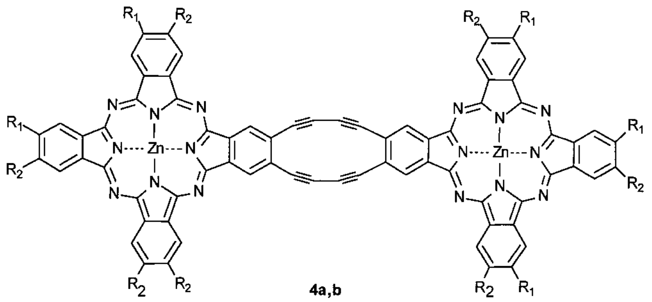
3

Recently, Bunz has described the structure elucidation and packing of the bisdiyne **3**.[10] Interestingly, the flat molecules of this compound are stacked parallel in the crystal and form columns. It is also well-known that phthalocyanines tend to build stacked co-facial arrangements that give rise to remarkable supramolecular properties such as electrical conductivity.[14]

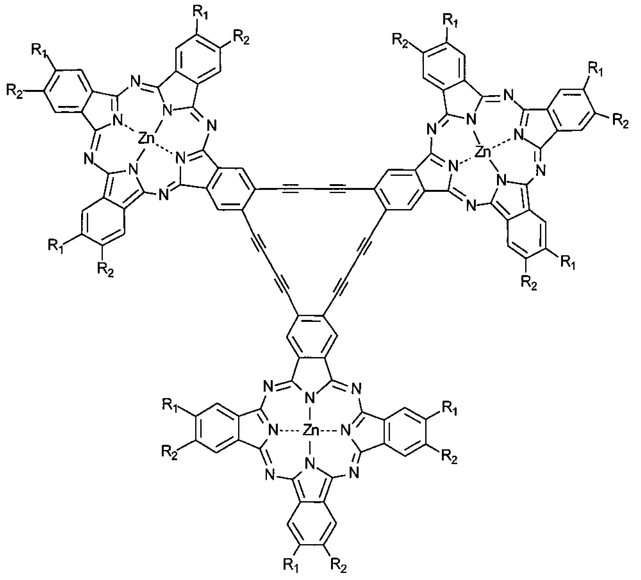
Thus, the combination of these previous two facts has led us to consider the possibility of subjecting dialkynyl-substituted Pcs to the Glaser and Eglinton conditions in order to obtain cyclooligomeric butadiynyl-substituted Pcs prone to build crystalline ladder structures with potential as building blocks of three-dimensional covalently linked organic networks.[15]

Very few examples of Pc-dimers covalently linked through alkynyl spacers can be found in the literature.[3]

In the present paper, we report on the preparation of tetradehydro[12]annulenes and hexadehydro[18]annulenes fused with phthalocyanine moieties, **4a**,**b** and **5a**,**b**, respectively.[16] The preparation involves a four-step pathway which includes three metal-mediated processes.



4a,b



5a,b

4a, 5a R$_1$= R$_2$= O*n-Bu*
4b, 5b R$_1$= ^{t}Bu, R$_2$= H

Results and Discussion

The statistical condensation of 4,5-dibutoxyphthalonitrile[17] with 4,5-diiodophthalonitrile[18] (in a 3:1 molar ratio) in the presence of a stoichiometric amount of zinc acetate dihydrate in dimethylaminoethanol (DMAE) (Scheme 1) gave a mixture of compounds from which the desired diiodo Pc, **6a**, could be isolated in 16% yield after several chromatographic purification steps. This compound was then subjected to a standard palladium–copper catalyzed coupling procedure with trimethylsilylacetylene in triethylamine (TEA) at room temperature for 15 h to afford the protected dialkynyl Pc **7a** in 71% yield, after column chromatography in neutral alumina (to avoid decomposition). **7a** was deprotected using TBAF/THF to yield the dialkynyl-substituted compound **8a** in 64%.[19]

In close analogy, the tri-*tert*-butyl-substituted Pc **6b** was obtained starting from 4-*tert*-butylphthalonitrile[20] and 4,5-diiodophthalonitrile (Scheme 1). After chromato-

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[13] Ojima, J.; Daimon, T.; Hiraiwa, N.; Higuchi, H.; Ueno, M.; Yamamoto, G. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2795, and literature cited therein.

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[15] The synthesis of single-crystalline polymeric materials represents a major challenge. See, for example: (a) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (b) Schlicke, B.; Schirmer, H.; Schlüter, A.-D. *Adv. Mater.* **1995**, *7*, 544. (c) Stupp, S. I.; Son, S.; Li, L. S.; Lin, H. C.; Keser, M. *J. Am. Chem. Soc.* **1995**, *117*, 5212.

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[18] Terekhov, D. S.; Nolan, K. J. M.; McArthur, C. R.; Leznoff, C. C. *J. Org. Chem.* **1996**, *61*, 3034.

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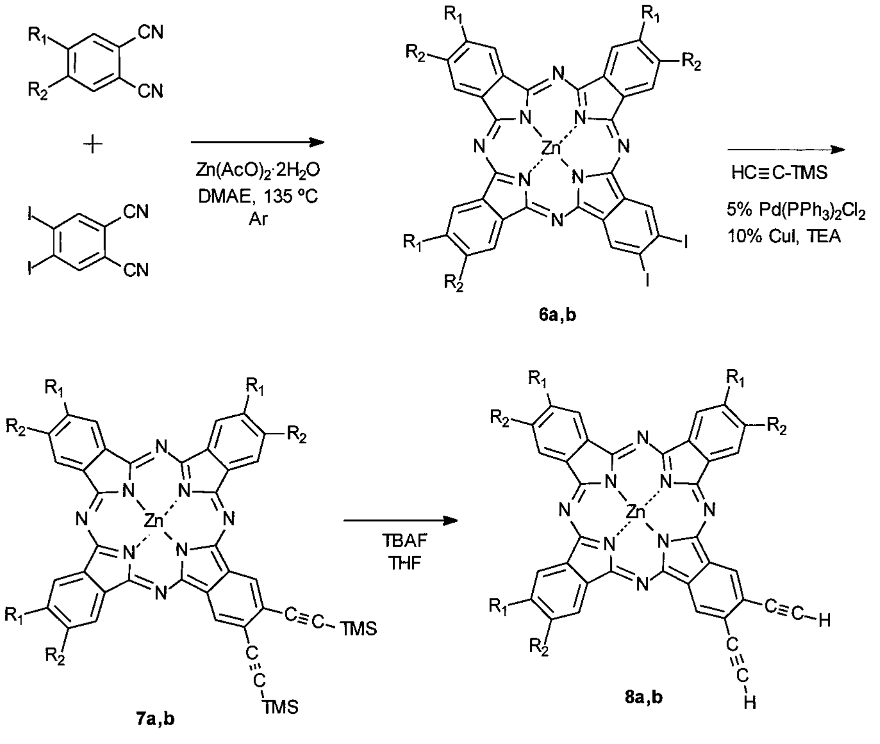
[20] Larner, B. W.; Peters, A. T. *J. Chem. Soc.* **1952**, 680.

Scheme 1. Synthesis of Diethynylphthalocyaninatozinc(II) Complexes 8a,b



6a, 7a, 8a R$_1$= R$_2$= O*n*-Bu
6b, 7b, 8b R$_1$= ^{t}Bu, R$_2$= H

graphic separation of the diiodo Pc **6b** from the statistical mixture (18% yield, as a mixture of 4 regioisomers), it was reacted with trimethylsilylacetylene as described above to yield 85% of **7b**, also as a regioisomeric mixture. Deprotection under standard conditions (TBAF, THF, rt) led to **8b** in 62% yield.

The reaction of compound **8a** with copper(II) acetate (Eglinton reaction) in methanol, pyridine, and ether at rt for 20 h[11] afforded a mixture of dimer **4a** and the trimer **5a** in an estimated (by MALDI-MS) 5:1 ratio with a global 52% yield. Due to their similarity, and the strong tendency to aggregation of these species, all efforts to separate them have been unsuccessful until now, even using size exclusion chromatography. On the other hand, when the reaction was carried out at a higher concentration of the reagents and under heating (70 °C) compound **4a** was obtained with 51% yield. No traces of higher cyclooligomers have been detected by MALDI-MS.

Compound **8b** underwent also self-condensation under the first reaction conditions described above for **8a** (i.e., at room temperature), affording a green solid which, after careful MALDI-MS analysis, happened to be a mixture of compounds **4b** and **5b** in an estimated 3:1 ratio in ca. 60% yield. As in the previous case, we were unable to separate them using different chromatography techniques. Similar results were obtained at higher concentration and temperature.

When **8a** and **8b** were subjected to the Glaser reaction [copper(I) chloride, oxygen, TEA at 70 °C] no identifiable products other than the corresponding starting material could be detected. However, when pyridine was added to the reaction mixture of **8b** with CuCl and TEA at 50 °C, trimer **5b** was formed as the only reaction product. The compound was isolated from the starting material **8b** by repeatedly washing with methanol/water 1:1 and then with methanol, in a 19% yield. However, **5a** could not be obtained under the same conditions. In this particular case only the starting material was recovered.

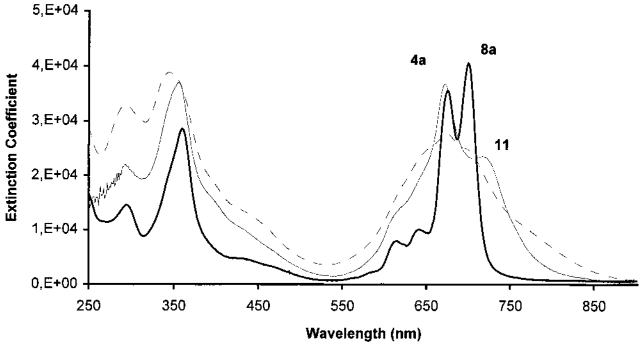
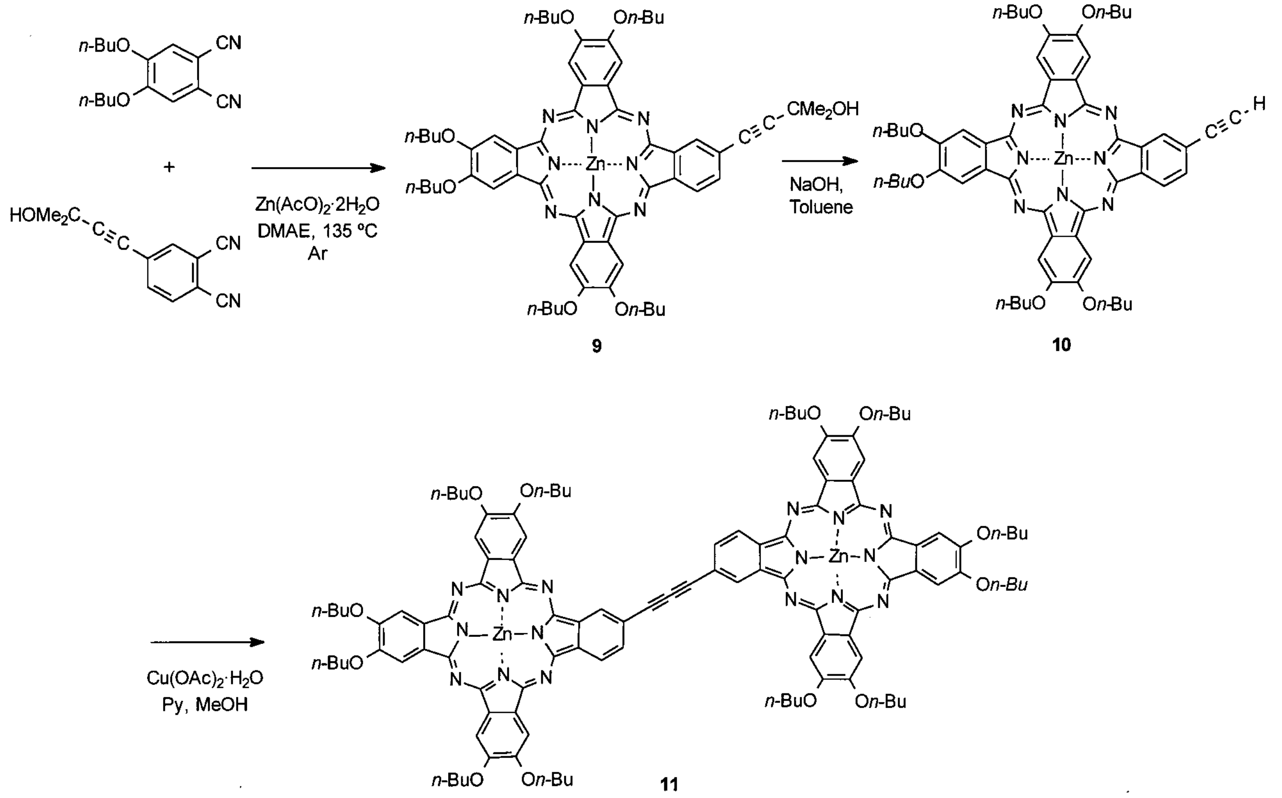


Figure 1. Electronic spectra in CHCl$_3$ of: **4a** (2.8×10^{-5} M) (thin line), **8a** (1.5×10^{-5} M) (solid line), and **11** (3.0×10^{-5} M) (dashed line).

The relative different behavior of both dialkynyl compounds **8a** and **8b** should be attributed to their distinct substitution patterns. The aggregation of compounds **4a**,**b** and **5a**,**b** in chloroform or benzene solution precludes the registration of useful ^{1}H NMR spectra. In both cases only broad signals corresponding to the aliphatic chains were observed.

The UV–vis spectrum of compound **4a** in CHCl$_3$ is shown in Figure 1. The optical features in CHCl$_3$ of this new chromophoric system differ remarkably from those of the unsymmetric parent terminal alkyne **8a** in the same solvent (Figure 1). The Soret (B) transition of **4a**

Scheme 2. Synthesis of Butadiynyl-Bridged Bisphthalocyaninatozinc(II) Complex 11



in the near-UV region of the spectrum span wavelength ranges of 300−450 nm, similar to that of compound **8a**. However, while diethynyl compound **8a** shows a clearly split Q-band (675 and 699 nm), typical of some unsymmetric metalled Pcs, homodimetallic binuclear Pc **4a** exhibits a remarkable broadening and redshift of this absorption. A new band centered at ca. 720 nm is clearly observed which extends to ca. 830 nm.[21] The bathochromic shift can be attributed to the enlargement of the π-conjugated system, with concomitant splitting of the Q-band probably as a consequence of intramolecular electronic coupling between the Pc subunits, in agreement with previous results obtained by us for related compounds.[3c] The broadening of the Q-band to the blue reveals the formation of aggregates in $CHCl_3$ solution.

For comparative purposes, we decided to synthesize compound **11**, an open-chain analogue (Scheme 2). This was achieved by statistical condensation of 4,5-dibutoxyphthalonitrile and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile[22] to give **9**, followed by removal of the protecting group with NaOH in boiling toluene and oxidative coupling of the resulting compound **10** under Eglinton conditions.

When the UV−vis spectrum of **11** is compared with that of **4a** (Figure 1), only minor differences can be pointed out. This can indicate that either the conjugation path is the same (each butadiynyl linker does not interact with the other) or, most probably, that there is a saturation phenomenon of the optical properties, as already pointed out by us for other alkynyl-linked open-chain dimers.[3d] Moreover, the broadening of the Q-band and the lower resolution of the bands in **4a** reveal also the existence of aggregates in $CHCl_3$ solution.

On the other hand, the UV−vis spectra of trimer **5b** and dimer **4b** (as a 3:1 mixture with **5b**) are practically identical and quite similar to that of **4a** with maxima at ca. 720 nm. Also in this case the most remarkable feature in comparison with starting material **8b** is the redshifting of the Q-band. For this reason, conclusions similar to that drafted above for **4a** can be inferred.

Although compound **3** is thermally unstable, exploding when heated,[10] the substituted derivatives are more stable, as previously stated.[8] This is also the case of compounds **4a** and **5b**. Thus, the heating of both compounds at 100 °C for 15 h did not alter significantly the UV−vis spectrum. Only after heating at 160 °C for 20 h can minor changes be observed.

In conclusion, we have achieved a simple method for the preparation of substituted annulene-phthalocyanines as an entry into the development of complex phthalocyanine-based molecules for functional materials. For this purpose, we set out to synthesize unsymmetric phthalocyanines equipped with two ethynyl substituents that can be considered versatile functionalized phthalocyanines for many synthetic purposes.

Experimental Section

23,24-Diiodo-2,3,9,10,16,17-hexabutoxyphthalocyaninatozinc(II) (6a). A mixture of 4,5-diiodophthalonitrile[12] (140 mg, 0.37 mmol), 4,5-dibutoxyphthalonitrile[11] (300 mg, 1.10 mmol), and zinc(II) acetate dihydrate (116 mg, 0.50 mmol) was refluxed in DMAE (4 mL) for 2 h under argon. The crude was washed by centrifugation with water/methanol (3:1) until the supernatants were colorless. Purification by column chromatography of the residue on silica gel, using a mixture of

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[21] Some differences in the maxima absorption positions were observed in the UV−visible spectra of **4a** and in that of a related compound recently described in ref 16. This is most probably due to the different substitution pattern of both compounds, meta and ortho, respectively.

[22] Maya, E. M.; Haisch, P.; Vázquez, P.; Torres, T. *Tetrahedron* **1998**, *54*, 4397.

hexane–dioxane (3:1), afforded 77 mg (16%) of **6a** as a green solid. Mp: >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.0–7.2 (m, 8 H, arom-Pc), 4.4–3.8 (m, 12 H, Pc-OCH_2), 2.2–1.9 (m, 12 H, Pc-OCH_2CH_2), 1.9–1.7 (m, 12 H, CH_2CH_3), 1.4–1.1 (m, 18 H, CH_3). FT-IR (KBr) ν: 2957, 1096, 1048 cm^{-1}. UV–vis (dioxane) λ_{max} (log ϵ): 688 (5.1), 674 (5.1), 612 (4.4), 356 nm (4.9). FAB-MS (NOBA) *m/z*: 1260–1266 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{56}H_{62}N_8O_6I_2Zn{\cdot}2H_2O$: C, 51.80; H, 5.12; N, 8.63. Found: C, 51.97; H, 5.34; N, 8.46.

2,3-Diiodo-9,16,23-tri-*tert*-butylphthalocyaninatozinc(II) (6b). A mixture of 4,5-diiodophthalonitrile (100 mg, 0.26 mmol), 4-*tert*-butylphthalonitrile[15] (150 mg, 0.82 mmol), and zinc(II) chloride (73 mg, 0.53 mmol) was refluxed in DMAE (4 mL) for 1 h under argon. The crude was washed by centrifugation with water/methanol (3:1) until the supernatants were colorless. Column chromatography of the residue (silica gel, petrol ether/dioxane 8:1) afforded 48 mg (18%) of **6b** as a bluish solid. Mp: >200 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.5–7.4 (m, 11 H, arom-Pc), 1.8–1.3 (several s, 27 H, CH_3). FT-IR (KBr) ν: 2963, 1489, 1330 cm^{-1}. UV–vis (CH_2Cl_2) λ_{max} (log ϵ): 688 (4.9), 674 (4.8), 611 (4.2), 352 nm (4.6). FAB-MS (NOBA) *m/z*: 996–1002 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{44}H_{38}N_8I_2Zn{\cdot}2H_2O$: C, 51.11; H, 4.09; N, 10.84. Found: C, 51.34; H, 4.20; N, 10.69.

23,24-Bis(2′-trimethylsilylethynyl)-2,3,9,10,16,17-hexabutoxyphthalocyaninatozinc(II) (7a). A mixture of phthalocyanine **6a** (61 mg, 0.048 mmol), $[Pd(PPh_3)_2Cl_2]$ (2 mg, 0.003 mmol), copper(I) iodide (4 mg, 0.021 mmol), and trimethylsilylacetylene (0.1 mL, 69 mg, 0.70 mmol) in TEA (4 mL) was stirred at rt for 15 h. After water addition, it was extracted with CH_2Cl_2. The organic phases were collected and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by chromatography (neutral alumina Brockmann III, hexane/dioxane, 4:1) to yield 41 mg (71%) of **7a** as a green powder. Mp: >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.0–7.5 (m, 8 H, arom-Pc), 4.2–3.9 (m, 12 H, Pc-OCH_2), 2.1–1.9 (m, 12 H, Pc-OCH_2CH_2), 1.9–1.7 (m, 12 H, CH_2CH_3), 1.4–1.1 (m, 18 H, CH_3), 0.57 (s, 18 H, SiCH_3). FT-IR (KBr) ν: 2958, 2149, 1249, 1096, 1048 cm^{-1}. UV–vis (dioxane) λ_{max} (log ϵ): 697 (5.1), 670 (5.1), 610 (4.4), 360 nm (4.9). FAB-MS (NOBA) *m/z*: 1200–1206 (isotopic pattern for $[M + H]^+$).

2,3-Bis(2′-trimethylsilylethynyl)-9,16,23-tri-*tert*-butylphthalocyaninatozinc(II) (7b). A mixture of phthalocyanine **6b** (54 mg, 0.057 mmol), $[Pd(PPh_3)_2Cl_2]$ (4 mg, 0.0057 mmol), copper(I) iodide (9 mg, 0.047 mmol), and trimethylsilylacetilene (0.2 mL, 138 mg, 1.4 mmol) in TEA (3 mL) was stirred at rt for 15 h under argon. After the solvent was distilled off, the crude was chromatographed (neutral alumina Brockmann III, petrol ether/dioxane 4:1) to yield 43 mg (85%) of a blue solid. Mp: >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.5–7.9 (m, 11 H, arom-Pc), 1.9–1.2 (several s, 27 H, CH_3), 1.0–0.9 ppm (several s, 18 H, SiCH_3). FT-IR (KBr) ν: 2962, 2146, 1485, 1261 cm^{-1}. UV–vis (CH_2Cl_2) λ_{max} (log ϵ): 699 (4.4), 674 (4.3), 614 (3.6), 353 nm (4.3). FAB-MS (NOBA) *m/z*: 936–941 (isotopic pattern for $[M + H]^+$).

23,24-Diethynyl-2,3,9,10,16,17-hexabutoxyphthalocyaninato zinc(II) (8a). TBAF (0.064 mL of a 1 M solution in THF, 0.064 mmol) was added dropwise to a solution of phthalocyanine **7a** (40 mg, 0.032 mmol) in THF (3.6 mL). After the mixture was stirred for 1 h at rt, the solvent was distilled off, and the residue was chromatographed (silica gel, petrol ether/dioxane 3:1), yielding 22 mg (64%) of **8a**. Mp: >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.0–7.5 (m, 8 H, arom-Pc), 4.2–3.9 (m, 12 H, Pc-OCH_2), 3.6 (broad signal, 2 H, C≡CH), 2.1–1.9 (m, 12 H, Pc-OCH_2CH_2), 1.9–1.6 (m, 12 H, CH_2CH_3), 1.4–1.1 (m, 18 H, CH_3). FT-IR (KBr) ν: 3313, 2976, 1092, 1046 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} (log ϵ): 693 (5.1), 668 (5.0), 608 (4.3), 358 nm (4.9). FAB-MS (NOBA) *m/z*: 1056–1063 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{60}H_{64}N_8O_6Zn{\cdot}2H_2O$: C, 65.84; H, 6.26; N, 10.24. Found: C, 66.45; H, 6.38; N, 10.41.

2,3-Diethynyl-9,16,23-tri-*tert*-butylphthalocyaninatozinc(II) (8b). TBAF (0.196 mL of a 1 M solution in THF, 0.196 mmol) was added dropwise to a solution of phthalocyanine **7b** (86 mg, 0.092 mmol) in THF (3.6 mL). After the mixture was stirred for 0.5 h at rt, the solvent was distilled off, and the residue was chromatographed (silica gel, petrol ether/dioxane 4:1), yielding 46 mg (62%) of a bluish product. Mp: >200 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.0–7.5 (m, 11H, arom-Pc), 3.6–3.0 (several s, 2H, C≡CH), 1.9–1.2 (several s, 27 H, CH_3). FT-IR (KBr) ν: 3312, 2955, 1487 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ϵ): 696 (5.3), 672 (5.2), 612 (4.6), 353 nm (5.1). FAB-MS (NOBA) *m/z*: 792–798 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{48}H_{40}N_8Zn{\cdot}2H_2O$: C, 69.44; H, 5.34; N, 13.50. Found: C, 69.63; H, 5.42; N, 13.24.

Reaction of Phthalocyanine 8a under Eglinton Conditions. Method A. Synthesis of 4a. A solution of copper(II) acetate monohydrate (34 mg, 0.17 mmol) in methanol (1.6 mL), pyridine (1.6 mL), and ether (0.2 mL) was added dropwise to a solution of **8a** (37 mg, 0.034 mmol) in methanol (0.5 mL) and pyridine (0.5 mL), and the mixture was heated at 70 °C for 0.5 h and then stirred at rt for 15 h under argon. The precipitate was separated by centrifugation and washed several times with methanol/water (1:1) and then with methanol to yield 19 mg (51%) of **4a** and as a green powder. Mp: >200 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.0–7.5 (m, 16 H, arom-Pc), 5.0–4.3 (m, 24 H, Pc-OCH_2), 2.5–0.5 (m, aliphatic chain). FT-IR (KBr) ν: 3345, 3342,1637, 1384, 1330 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} (log ϵ): 717 (sh), 671 (4.5), 624 (sh), 355 nm (4.6). MALDI-MS (ditranol) *m/z*: 2110–2117 (isotopic pattern for **4a** $[M + H]^+$). Anal. Calcd for $C_{120}H_{124}N_{16}O_{12}Zn_2{\cdot}2H_2O$: C, 67.06; H, 6.00; N, 10.43. Found: C, 67.36; H, 5.75; N, 10.70.

Method B. Synthesis of 4a and 5a as a Mixture. A solution of copper(II) acetate monohydrate (34 mg, 0.17 mmol) in methanol (2 mL), pyridine (2 mL) and ether (0.4 mL) was added dropwise to a solution of **8a** (17.2 mg, 0.02 mmol) in methanol (3 mL) and pyridine (0.6 mL), and the mixture was stirred at r.t. for 20 h under argon. The suspension was centrifugated and the precipitated washed several times with methanol/water (1:1). Finally, the product was filtered to yield 9 mg (52%) of **4a** and **5a** as a green powder. Mp: >200 °C. MALDI-MS (ditranol) *m/z*: 2110–2117 (isotopic pattern for **4a** $[M + H]^+$), 3166–3173 (isotopic pattern for **5a** $[M + H]^+$).

Reaction of Phthalocyanine 8b under Eglinton Conditions. Synthesis of 4b and 5b as a Mixture. A solution of copper(II) acetate monohydrate (17 mg, 0.085 mmol) in methanol (1 mL), pyridine (1 mL), and ether (0.2 mL) was added dropwise to a solution of **8b** (10 mg, 0.0126 mmol) in methanol (1.5 mL) and pyridine (0.3 mL), and the mixture was stirred at rt for 20 h under argon. The suspension was centrifugated and the precipitate washed with methanol/water (1:1); and then with methanol to yield 5.9 mg (60%) of **4b** and **5b** in a 3:1 estimated ratio (by MALDI-MS) as a green powder. Mp: >200 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.0–7.5 (m, 22 H, arom-Pc), 2.0–0.5 (several s, 54 H, CH_3). FT-IR (KBr) ν: 2955, 2203, 1638, 1399, 1371 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} (log ϵ): 720 (sh), 676 (4.7), 350 nm (4.8). MALDI-MS (ditranol) *m/z*: 1581–1587 (isotopic pattern for **4b** $[M + H]^+$), 2373–2380 (isotopic pattern for **5b** $[M + H]^+$).

Reaction of Phthalocyanine 8b under Glaser Conditions. Synthesis of 5b. A solution of copper(I) chloride (164 mg, 0.164 mmol) in pyridine (0.8 mL) was added dropwise to a solution of **8b** (20 mg, 0.025 mmol) in TEA (2 mL) and pyridine (0.4 mL). The mixture was heated at 50 °C for 25 h at air, and then it was stirred at rt for 17 h. The solvents were distilled off, and the residue was extracted with CH_2Cl_2/water. The organic phases were collected, dried and evaporated under reduced pressure. The residue was repeatedly washed with methanol/water (1:1) and then with methanol to yield 5.6 mg (19%) of **5b** as a green powder. Mp: >200 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.0–7.5 (m, 22 H, arom-Pc), 2.5–0.5 (several s, 54 H, CH_3). FT-IR (KBr) ν: 2957, 2203, 1637, 1363 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} (log ϵ): 720 (sh), 680 (4.7), 350 nm (4.8). MALDI-MS (ditranol) *m/z*: 2373–2380 (isotopic pattern for **5b** $[M + H]^+$).

2,3,9,10,16,17-Hexabutoxy-23-(3-hydroxy-3-methyl-1-butynyl)phthalocyaninatozinc(II) (9). A mixture of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile (128 mg, 0.61 mmol), 4,5-dibutoxyphthalonitrile (500 mg, 1.83 mmol) and zinc(I) chloride (0.61 mmol) was refluxed in DMAE (2 mL) overnight under argon. After water addition, the suspension was extracted with CH_2Cl_2, the organic phases were collected, dried and evaporated. Column chromatography of the residue (silica gel, CH_2Cl_2/EtOH 30:1) afforded 86 mg (13%) of **9**. Mp: >200 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.78 (s, 6 H, arom-Pc), 7.58 and 7.4 (2 × s, 3 H, arom-Pc), 4.67 and 4.43 (2 × m, 13 H, CH_2O, OH), 2.89 (m, 12 H, CH_2CH_2O), 1.91 (m, 12 H, CH_2-CH_3),1.30 (m, 24 H, CH_3). ^{13}C NMR (75 MHz, TFA-d_1) δ: 153.7, 150.5, 125.0, 118.7, 115.7, 115.0, 114.3, 111.2, 110.5, 107.5, 106.8, 97.5, 69.8, 29.7, 17.7, 11.1, 10.6. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 685 (5.1), 613 (4.4), 356 nm (5.0). FAB-MS (NOBA) *m*/*z*: 1091 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{61}H_{70}N_8O_7Zn{\cdot}4H_2O$: C, 62.97; H, 6.76; N, 9.64. Found: C, 62.58; H, 6.54; N, 9.61.

23-Ethynyl-2,3,9,10,16,17-hexabutoxyphthalocyaninatozinc(II) (10). A mixture of **9** (94 mg, 0.091 mmol) and NaOH (4 mg, 0.091 mmol) was refluxed in dry toluene (6 mL) under argon. The reaction was monitored by TLC. After disappearance of the starting material (4 h.), the solvent was distilled off and the residue was suspended in CH_2Cl_2 and washed with water. The organic phase was dried and evaporated. Column chromatography of the residue (silica gel, CH_2Cl_2/EtOH 100:1) afforded 74 mg (79%) of **10**. Mp: >200 °C. ^1H NMR (300 MHz, TFA-d_1) δ: 9.13, 8.69, 8.29 (3xm, 9 H, arom-Pc), 4.65 (m, 12 H, CH_2O), 3.7 (m, 1 H, $C{\equiv}CH$), 2.3 (m, 12 H, CH_2CH_2O), 1.9 (m, 12 H, CH_2CH_3), 1.3 (m, 18 H, CH_3). FT-IR (KBr) ν: 3500, 2885, 1280, 1092 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ): 681 (5.0), 613 (4.3), 356 nm (4.7). FAB-MS (NOBA) *m*/*z*: 1033 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{58}H_{64}N_8O_6$-$Zn{\cdot}2H_2O$: C, 65.07; H, 6.40; N, 10.47. Found: C, 65.37; H, 6.62; N, 10.33.

Bis[(23-ethynyl-2,3,9,10,16,17-hexabutoxyphthalocyaninato)zinc(II)]butadiyne (11). Compound **10** (10 mg, 0.009 mmol) and copper(II) acetate monohydrate (34 mg, 0.19 mmol) are stirred in pyridine (0.5 mL) and methanol (0.05 mL) at 55−60 °C for 4 h. The solvents were distilled off and the residue was suspended in CH_2Cl_2 and washed with water. The organic phase was dried and evaporated. Column chromatography of the green residue (silica gel, THF) afforded 8 mg (86%) of **11**. Mp: >200 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 8.5−8.0 (broad s, arom-Pc), 4.0 (m, 12 H, CH_2O), 1.9 (m, 12 H, CH_2 CH_2O), 1.5 (m, 12 H, CH_2), 1.0 (m, 18 H, CH_3). FT-IR (KBr) ν: 3440, 2957, 2931, 2617, 1604,1263 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 708 (sh), 677 (4.4), 344 nm (4.7). FAB-MS (NOBA) *m*/*z*: 2064 (isotopic pattern for $[M + H]^+$). Anal. Calcd for $C_{116}H_{126}N_{16}O_{12}Zn_2{\cdot}4H_2O$: C, 65.13; H, 6.31; N, 10.48. Found: C, 64.88; H, 6.47; N, 10.76.

Acknowledgment. This work was supported by CICYT and Comunidad de Madrid (Spain) through grants MAT-99-180 and 07N/0020/1998, respectively.

JO0006019