Synthesis of Alkynyl-Linked Phthalocyanine Dyads: Push – Pull Homo- and Heterodimetallic Bisphthalocyaninato Complexes

Eva María Maya, Purificación Vázquez, and Tomás Torres*[a]

Abstract: Metallophthalocyanine dimers linked by butadiynyl and ethynyl bridges **3a – c** and **5a – c**, respectively, have been synthesized by metal-mediated coupling methodologies. The key to the synthesis of these chromophores was the ready availability of appropriately functionalized unsymmetrical phthalocyanines **2a – c** that bear a terminal ethynyl group. Following the same methodology, push – pull homo- and heterodimetallic ethynyl-bridged bisphthalocyaninato complexes **10a – c**, that contain electron-donor and electron-acceptor substituents in each of the two phthalocyanine subunits, have been also prepared.

Keywords: alkyne complexes · binuclear complexes · cross-coupling · heterodimetallic systems · phthalocyanines

Introduction

During the last decade a considerable amount of synthetic work has been devoted to the preparation and study of properties of covalently linked porphyrins and related macrocycles. Nonconjugated systems have been described in which the macrocycle units have been joined together by all kinds of linkages.[1] The goal of preparing multicomponent arrays requires methods for the linkage of large numbers of subunits. In this regard the metal-mediated cross- and homocoupling methodology of alkynes has shown to be highly efficient. Recently, considerable attention has been focused on the synthesis of conjugated porphyrin dimers and oligomers connected by ethynyl or butadiynyl bridges.[2] In this way, it has been possible to study the electronic- and photonic-based cooperation between the individual subunits of porphyrins.[2c,d, 3]

Despite the great scientific and technological interest in the related phthalocyanine (Pc) system,[4] the effort devoted to the preparation of multiphthalocyanine arrays has not been comparable. Nonconjugated Pc dyads, in which the two Pc cores are covalently linked by various kinds of bridges, have been reported.[5] However, very few examples in which the Pc subunits are connected through π-conjugated pathways have been described.[6] The first Pc dimeric system containing a butadiynyl bridge between the chromophores was synthesized by Leznoff and co-workers,[7a] by a method that employed only allows the preparation of homodimetallic bisphthalocyanines in low yield. More recently, we have reported an efficient method for the preparation of homo- and heterodimetallic ethynyl- and butadiynyl-bridged bisphthalocyaninato complexes by the use of metal-mediated coupling methodologies.[7b]

In this paper we report the preparation of these types of dimers as well as new ones which contain other metallic centers, such as cobalt. Additionally, new push – pull homo- and heterodimetallic bisphthalocyanine dyads that contain donor and acceptor substituents in each of the two Pc moieties are also described for the first time. These compounds provide interesting targets for investigations of their second-order nonlinear optical properties,[4b,d] since the electronic charge distribution can be tailored by varying the central metal and the peripheral substituents in each Pc subunit.

Results and Discussion

The key to the synthesis of ethynyl- and butadiynyl-bridged bisphthalocyaninato complexes by means of metal-mediated coupling was the ready availability of appropriately functionalized unsymmetrical phthalocyanines which bear a terminal ethynyl group, such as **2** (Scheme 1). Unsymmetrical Pcs are usually difficult to prepare[8] and their isolation from the complex reaction mixture became an important problem.[9] The preparation of compounds **2** was carried out in two steps from 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile[10] (Scheme 1).

Mixed condensation of the latter with 4-*tert*-butylphthalonitrile[11] (3 equiv) in the presence of the corresponding metal(II) salt afforded the unsymmetrical zinc-, nickel-, and cobalt-substituted complexes **1a – c**. These compounds, pro-

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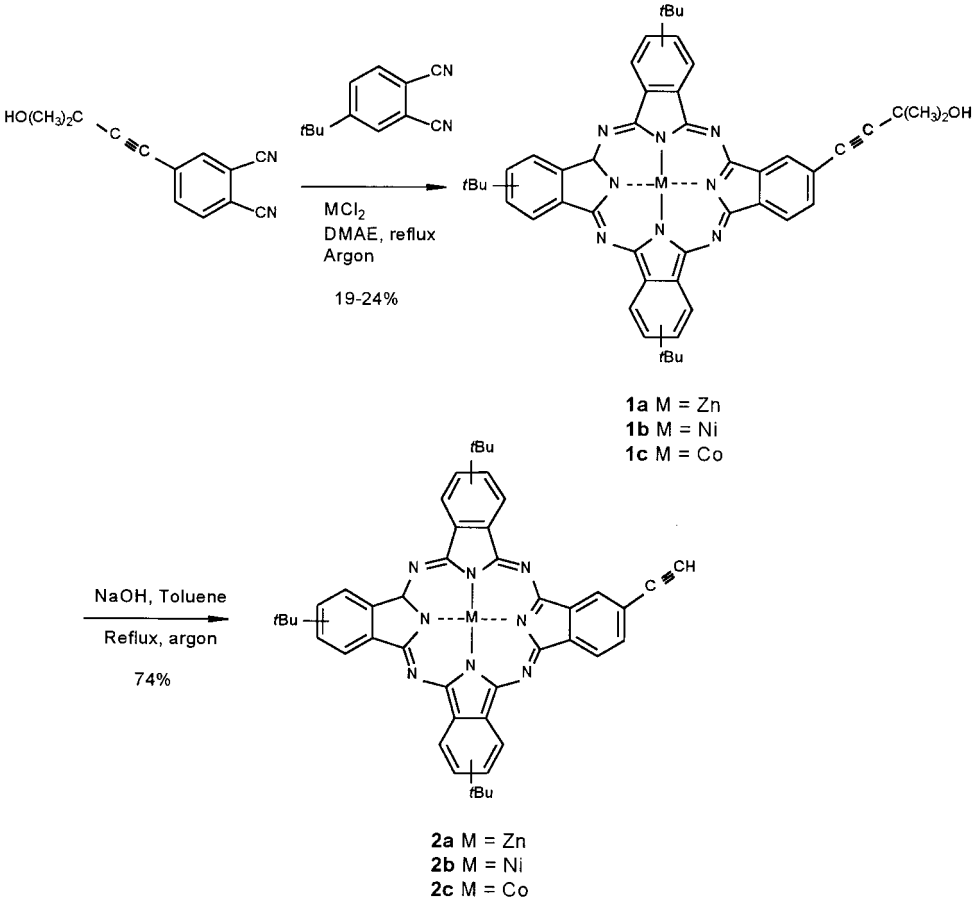


Scheme 1. Synthesis of ethynylphthalocyanines **2a–c**.

duced in moderate yields, were separated by column chromatograpy from the corresponding undesired tetra-*tert*-butylphthalocyanines formed in the statistical condensation. The -C(CH$_3$)$_2$OH protecting group of the ethynyl function in **1a–c** was then removed as acetone by treatment with sodium hydroxide in toluene to give the terminal alkynes **2a–c** in good yields.[12]

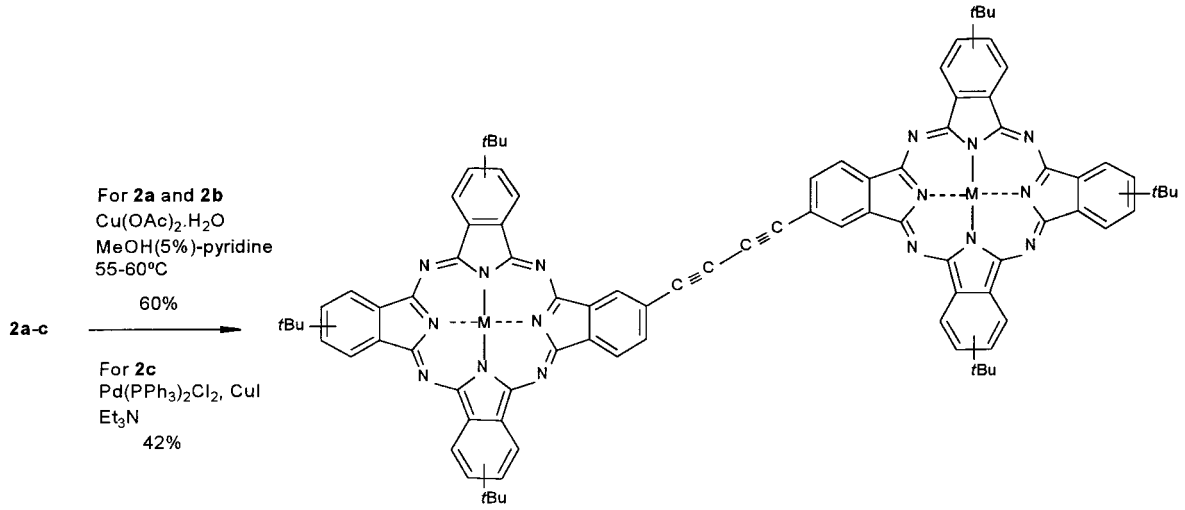
Homodimetallic butadiynyl-bridged bisphthalocyanines: The butadiynyl-bridged bis(tri-*tert*-butylphthalocyaninato)metal(II) complexes **3a,b** were synthesized by oxidative homocoupling of the terminal alkynes **2a,b** in the presence of a stoichiometric amount of copper(II) acetate monohydrate in a mixture of dry pyridine and dry methanol in ≈60% yield (Scheme 2).[13a,d] The homonuclear dimetallic complexes were isolated by column chromatography.

The dicobalt compound **3c** was, however, prepared in better yield (42%) from ethynyl Pc **2c** by the use of a catalytic amount of bis(triphenylphosphane)palladium(II) chloride and copper(I) iodide.[13b,c] Both the stoichiometric and catalytic coupling methods are only useful for metallated phthalocyanines. The use of free Pc bases as the substrate produced copper complexes to a greater or smaller extent by a metal insertion reaction.[10] These dimeric species are green, whereas the starting phthalocyanines are blue as a result of extended π conjugation.

The UV/Vis spectrum of the zinc dimer **3a** is depicted in Figure 1. The optical features of these new chromophoric systems differ remarkably from those of the unsymmetrical parent terminal alkyne **2a**. The Soret (B) transition of **3a** in the near-UV region of the spectrum spans wavelength ranges of 300–450 nm, similar to that of compound **2a**. However, while ethynyl compound **2a** shows only a Q band at 684 nm, as is usual for metallated Pcs, the homodimetallic binuclear Pc **3a** exhibits a split Q-band (675 and 709 nm) as well as a remarkable broadening and redshift of this absorption. In addition, at higher concentrations a shoulder centered at ≈770 nm is clearly observed which extends to ≈820 nm.

Since compound **3a** is a mixture of several isomers, it could be considered that a higher ratio of some of them might be the reason of the Q-band splitting observed in the spectrum.[14] However, the lack of splitting in the parent compound **2a** spectrum, which is also a mixture of isomers, the magnitude of the splitting taking into account the kind of peripheral substituents (*tert*-butyl groups), and our own experience with other kind of dimers, suggest that the observed splitting is mainly the result of extended π conjugation of the dyad. Few examples of intramolecular interactions between Pc subunits have been studied in homodimetallic binuclear phthalocyanine systems in which the Pc moieties are connected through π-conjugated systems.[6] In these cases, the Q band undergoes a shift to the red, which has been attributed to the enlargement of the π-conjugated system, with concomitant splitting of the Q band as a consequence of intramolecular electronic coupling between the Pc subunits. In the present case, it is not possible to conclude from the data available whether the electronic coupling between the two halves of the binuclear molecule is responsible for the splitting, taking into account

Abstract in Spanish: *Se han sintetizado dímeros de metaloftalocianina con los macrociclos unidos por puentes etinilo y butadiinilo **3a–c** y **5a–c**, utilizando metodologías de acoplamiento asistidas por metal. La clave para la síntesis de estos cromóforos ha sido la disponibilidad de ftalocianinas asimétricamente sustituidas con grupos etinilo terminales **2a–c**. Siguiendo esta misma metodología se han preparado bisftalocianinas homo- y heterodimetálicas de tipo push–pull **10a–c**, en las cuales las dos subunidades se encuentran conectadas por un grupo etinilo, que poseen sustituyentes electrón-dadores y electrón-aceptores en cada una de las unidades.*



Scheme 2. Synthesis of homodimetallic butadiynyl-bridged bisphthalocyaninato complexes **3a–c**.

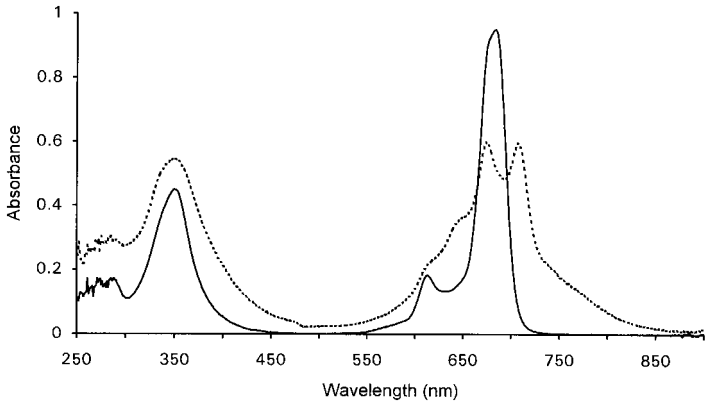


Figure 1. Electronic spectra of **2a** (1.4×10^{-6} mol dm^{-3}) (——) and **3a** (1.1×10^{-5} mol dm^{-3}) (••••) in $CHCl_3$.

that other effects, such as the degree of intermolecular aggregation in solution[15] or even the local asymmetry[16] of the molecules can also play an important role.

Figure 2 shows the electronic absorption spectra of the nickel and cobalt dimers **3b,c**. Although the Q bands undergo a remarkable broadening with regard to the parent compounds **2b,c**, in a manner similar to **3a**, these are not split, and the main absorption corresponds in both cases to that of the corresponding precursor ($\lambda \approx 670$ nm).

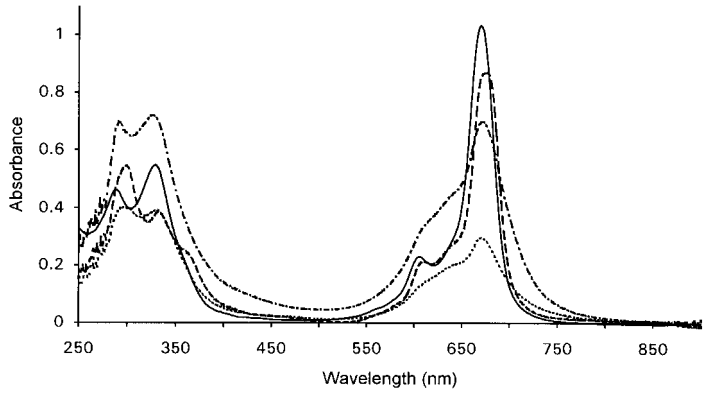


Figure 2. Electronic spectra of **2b** (2.18×10^{-6} mol dm^{-3}) (----), **2c** (3.04×10^{-6} mol dm^{-3}) (——), **3b** (6.5×10^{-6} mol dm^{-3}) (••••), and **3c** (1.1×10^{-5} mol dm^{-3}) (•–•–) in $CHCl_3$.

The apparently different behavior of **3b,c** in comparison with **3a** must be attributable to the nature of the central metal and it could be related to intermolecular aggregation phenomena in which the type of central metal is relevant.[15] Additionally, the structure of the new compounds have been determined by laser secondary ion mass spectometry (LSIMS) (molecular ions appear in all the cases), IR, and elemental analysis; NMR spectroscopy was not very informative.

Homo- and heterodimetallic ethynyl-bridged bisphthalocyanines: For the preparation of the ethynyl-bridged compounds, **5a–c**, a metal-mediated cross-coupling methodology of the alkynes **2a–c** with the iodophthalocyanine **4b** was used (Scheme 3).

Compound **4b** was prepared by the condensation of 4-iodophthalonitrile[13a] with 4-*tert*-butylphthalonitrile[11] (3 equiv) in the presence of zinc(II) chloride (1 equiv) (Scheme 4). The reaction yielded a statistical mixture of compounds (**4a–d**), and the ratios remained similar even if an excess of 4-*tert*-butylphthalonitrile (1:9 molar ratio) was used. All the reaction compounds were separated by column chromatography on silica gel and eluted with a mixture of petroleum ether and dioxane (4:1). Compounds **4a–d** are mixtures of the corresponding regioisomers.

Unsymmetrically substituted compound **4b** could also be prepared from the amino-tri-*tert*-butylphthalocyaninatozinc(II) complex by the Sandmeyer reaction.[12]

The cross-coupling reactions of **4b** and ethynyl compounds **2a–c** were carried out following a modified Sonogashira procedure. Thus, in order to reduce the reaction time and minimize the homocoupling reaction of the ethynyl substrates, a copper-free palladium catalyst was used, such as that

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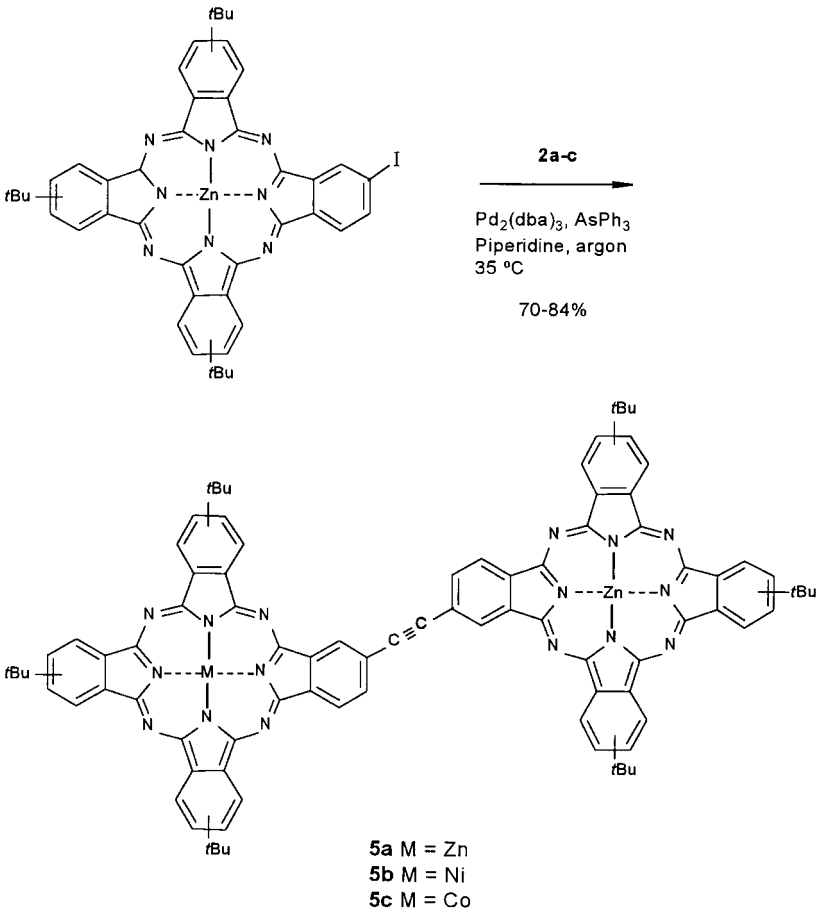
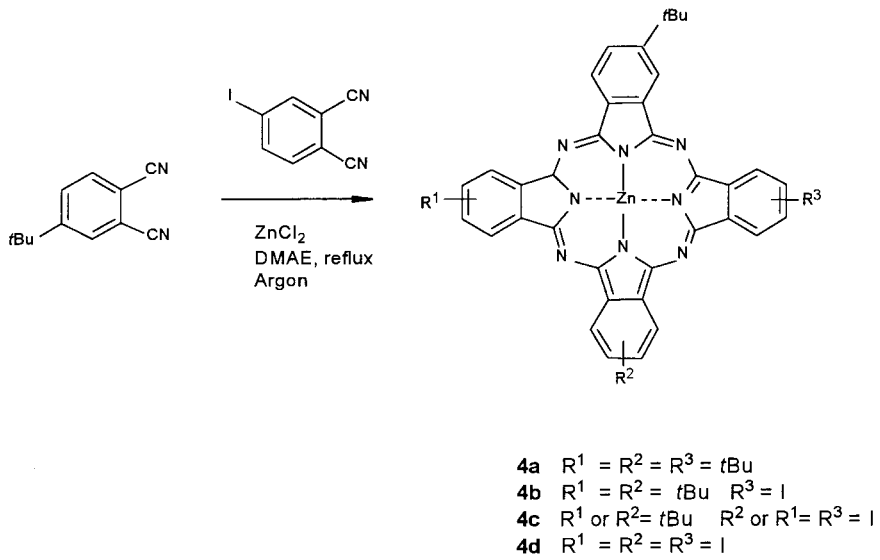


Scheme 3. Synthesis of homo- and heterodimetallic ethynyl-bridged bisphthalocyaninato complexes **5a–c**.



Scheme 4. Synthesis of iodo-tri-*tert*-butylphthalocyaninatozinc(II) (**4b**).

described by Lindsey and co-workers.[17] The utilization of the catalyst formed from tris(dibenzylidenacetone)dipalladium(0) ([$Pd_2(dba)_3$]) and triphenylarsane in a freshly distilled and deaerated piperidine solution of the reagents afforded the corresponding ethynyl-bridged bisphthalocyanines **5a–c** in good yields (76–84%). No homocoupling compounds were detected under these conditions. The change of the color of the reaction mixtures from blue to green in these couplings marks the formation of the dimer.

Compounds **5a–c** were characterized by UV/Vis, IR, and NMR spectroscopies, mass spectrometry (LSIMS), and elemental analysis. Figure 3 shows the UV/Vis spectra of ethynyl-bridged bisphthalocyanine **5a** and its precursors **2a** and **4b**. The spectrum of **5a** is quite similar to that of **3a** (Figure 1), the absorption maximum of the B band is slightly shifted to the blue, whereas the Q band appears slightly shifted to the red and split at 678 and 710 nm. Also in this case a broad absorption with low intensity at 770 nm is observed as in the case of **3a**. The same conclusions given above for the spectrum of **3a** can be applied to that of **5a**. Intramolecular electronic coupling between the two Pc subunits could take place, but it is not demonstrated.

As in the case where the butadiynyl-bridged dimers **3b,c**, which contain nickel and cobalt, respectively, were compared with the dizinc compound **3a**, the heterodimetallic ethynyl-bridged dimers **5b,c**, which contain the couples Ni/Zn and Co/Zn, respectively, display apparently different behavior in the UV/Vis spectrum in comparison with the homodizinc dimer **5a**.

Although the Q bands of **5b,c** undergo a remarkable broadening with regard to the parent compounds (Figures 4 and 5), the splitting is not resolved and the maximum of the absorption in both cases is similar to that of the corresponding precursors. Here, the nature of the central metal also plays an important role.[15]

Synthesis of push–pull ethynyl-bridged bisphthalocyanines: In connection with our work on the systems of Pcs and related compounds for nonlinear optics (NLO),[4b, 4d, 18] we were also interested in the preparation of different push–pull substituted bisphthalocyanines. The general approach to designing

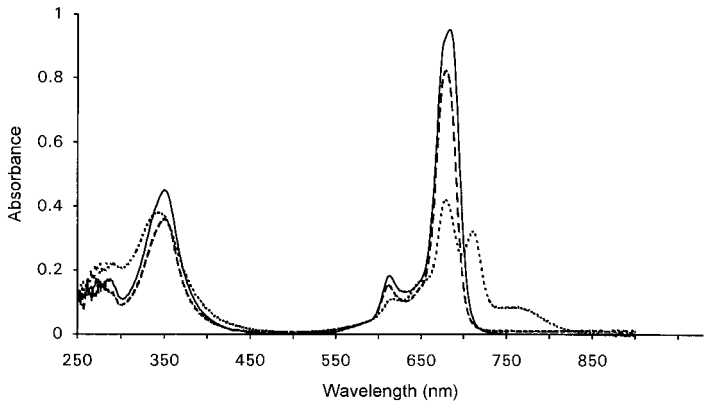


Figure 3. Electronic spectra of **2a** (1.4×10^{-6} mol dm^{-3}) (——), **4b** (1.9×10^{-6} mol dm^{-3}) (- - - -), and **5a** (3.6×10^{-6} mol dm^{-3}) (••••) in $CHCl_3$.

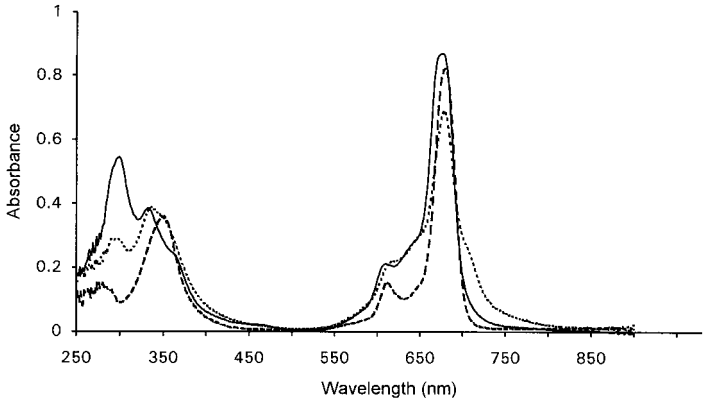


Figure 4. Electronic spectra of **2b** (2.18×10^{-6} mol dm^{-3}) (——), **4b** (1.9×10^{-6} mol dm^{-3}) (- - - -), and **5b** (3.3×10^{-5} mol dm^{-3}) (••••) in $CHCl_3$.

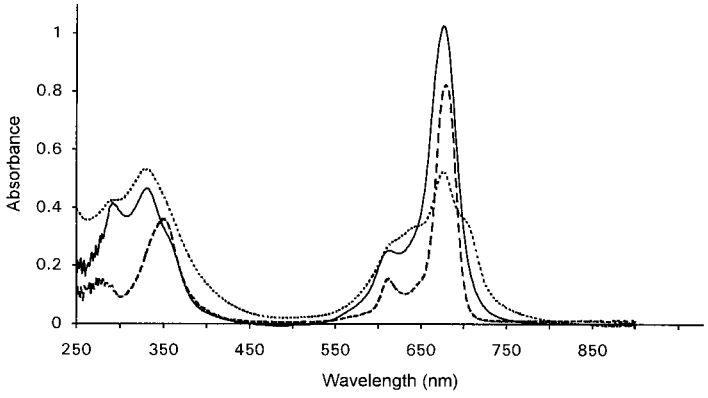


Figure 5. Electronic spectra of **2c** (1.4×10^{-6} mol dm^{-3}) (——), **4b** (1.9×10^{-6} mol dm^{-3}) (- - - -), and **5c** (1.3×10^{-5} mol dm^{-3}) (••••) in $CHCl_3$.

NLO-phores for second harmonic generation (SHG) has involved the coupling of both an electron donor (D) and electron acceptor (A) to an organic structure that provides electronic coupling between D and A.[19]

Thus, by the use of the metal-mediated cross-coupling methodology described above, we obtained push–pull dimeric systems **10a–c** from the reaction of the iodo compounds **8c** and **9b**, bearing alkylsulfonyl acceptor groups, with ethynyl-Pcs **2a,b**, containing alkyl donor substituents (Scheme 5).

The iodo Pcs **8c** and **9b** (Scheme 6) were prepared in two steps from 4-thiopropylphthalonitrile (**6**), which is readily accessible from 4-nitrophthalonitrile[20] by nucleophilic substitution with propylthiol in the presence of K_2CO_3.[21]

Oxidation of **6** with H_2O_2 in acetic acid[18b] afforded 4-propylsulfonylphthalonitrile (**7**). Mixed condensation of this compound with 4-iodophthalonitrile[13a] in a 3:1 molar ratio in the presence of the corresponding metal(II) acetate with a mixture of *o*-dichlorobenzene/dimethylformamide (3:1) or 2-ethoxyethanol as the solvent, afforded the corresponding mixtures of compounds **8a–d** and **9a–c**, respectively in a statistical distribution. Chromatographic separation on silica gel with CH_2Cl_2/isopropyl alcohol as the eluent allowed the isolation of **8c** from the mixture containing the compounds **8a–d**. On the other hand, the cobalt compound **9b** was isolated from the corresponding reaction mixture containing **9a–c** by chromatography with $CHCl_3$/isopropyl alcohol as the eluent.

Dimethylaminoethanol (DMAE) could not be used as the solvent in the previously mentioned reactions because of the decomposition of the alkylsulfonylphthalonitrile (**7**) under the reaction conditions used; this gave rise to a great number of purple compounds that were not identified.

Compound **8c** was then treated with the corresponding ethynyl Pc **2a,b** with $[Pd(PPh_3)_2Cl_2]$ as the coupling agent in the presence of catalytic amounts of CuI in diethylamine to afford the push–pull dimers **10a,b** in moderate yields (40–50%) (Scheme 5). The reaction was monitored by TLC until all starting blue Pcs were converted into the new green species. The dimer **10b** was obtained in the above-mentioned cross-coupling reaction as the only reaction product, whereas dimer **10a** was contaminated by small amounts of the butadiynyl-bridged dimer **3a**, as a result of the higher tendency of the ethynyl zinc-Pc **2a** to give homocoupling compounds.

In order to improve the yields of **10a,b**, the catalyst previously employed in the preparation of the related ethynyl-bridged dimers **5a–c**, $[Pd_2(dba)_3]$ and $AsPh_3$ in freshly distilled and deaerated piperidine, was then tested. In this way the yields were improved to reach levels of $\approx$80% (Scheme 5) and the homocoupling compounds were not observed. A similar method was used for the preparation of **10c** starting from **9b** and **2a**.

Dimers **10a–c** were purified by column chromatography on silica gel with CH_2Cl_2/isopropyl alcohol as the eluent. The ^{1}H NMR spectra of compounds **10a–c** at room temperature in chloroform do not provide any information about the structure of the dimers. All the aromatic protons appear as very broad signals, since compounds **10** are actually mixtures of structural isomers and because of aggregation phenomena that occur at the concentrations used for recording the spectra. No additional information was obtained when the spectra were recorded in $C_2D_2Cl_4$ at higher temperatures (90 °C). The compounds were characterized by UV/Vis and IR spectroscopies, mass spectrometry (FAB-MS), and elemental analysis.

Figure 6 shows the UV/Vis spectra of ethynyl-bridged bisphthalocyanine **10a** and its precursors **2a** and **8c**. As in the case of compound **5a**, the most remarkable change is the blue-shifting of the B band and the broadening of the splitting of the Q band, which is not well resolved and whose maximum

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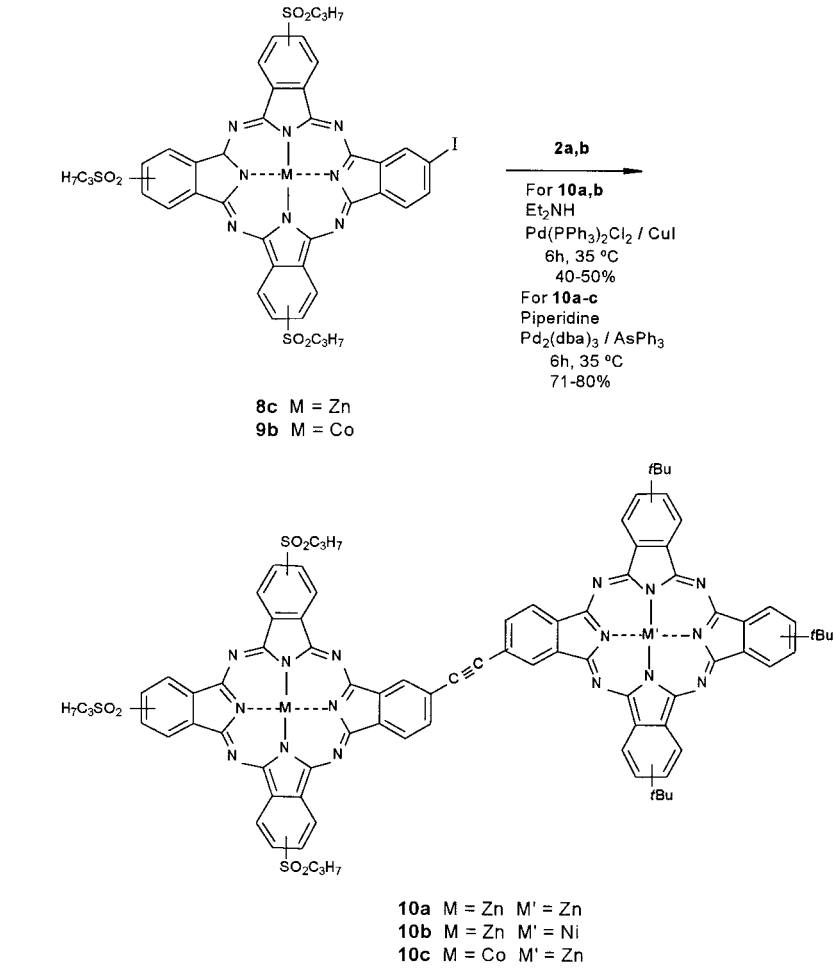
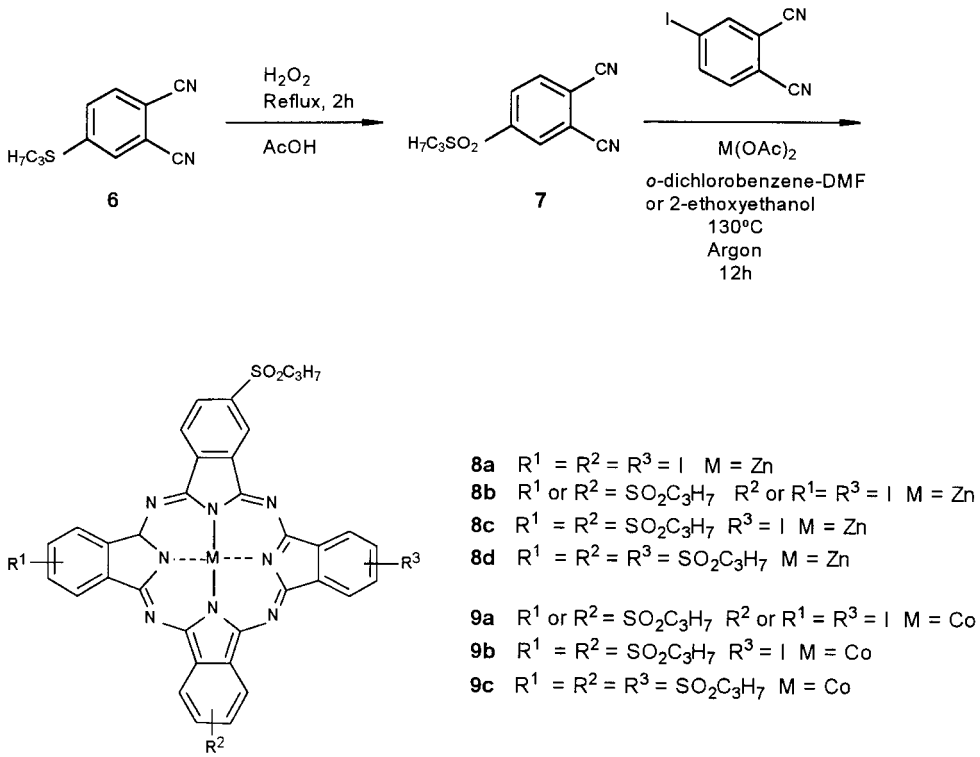


Scheme 5. Synthesis of push–pull homo- and heterodimetallic ethynyl-bridged phthalocyaninato complexes **10a–c**.



Scheme 6. Synthesis of iodo-tri-propylsulfonylphthalocyaninato complexes **8c** and **9b**.

appears slightly blue-shifted, although it is shifted more to the red than in the starting materials.

From a comparison of the Q-band spectra of compounds **5a** and **10a**, it is evident that in the latter compound the absorptions are shifted to shorter wavelengths as a consequence of the electron-withdrawing character of the alkylsulfonyl substituents.

Similar results are obtained for compounds **10b** and **10c** (Figure 7). However, in the case of **10b** a strong absorption at 627 nm is also observed which is most probably caused by intermolecular association.[22] We have recently reported aggregation in other kinds of related dimers.[15] A CPK model of push–pull compound **10c** is represented in Figure 8.

Conclusions

We have described for the first time several series of alkynyl-bridged bis(phthalocyaninato)-metal complexes. The stepwise synthetic methods used, based on common metal-mediated coupling methodologies, allow the preparation of homo- and heterodimetallic systems and the introduction of different kinds of substituents in each of the two Pc subunits. These dimers which display extended conjugation are interesting targets for the investigation of their NLO properties, especially the push–pull substituted dimers and heterodimetallic systems, which will be reported in due course, and for the investigation of their electron- and energy-transfer processes. However, the study described here indicates that these kinds of systems deserve much more additional work in order to provide new information on how central metals and substituents affect the electronic structure of phthalocyanine dimers; this

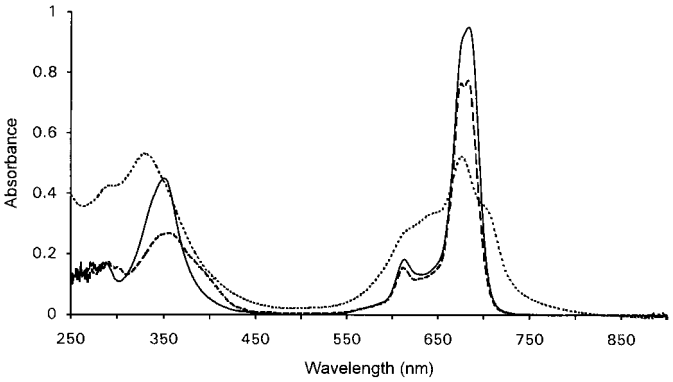


Figure 6. Electronic spectra of **2a** (1.4×10^{-6} mol dm^{-3}) (——), **8c** (6.5×10^{-6} mol dm^{-3}) (——), and **10a** (1.0×10^{-5} mol dm^{-3}) (••••) in $CHCl_3$.

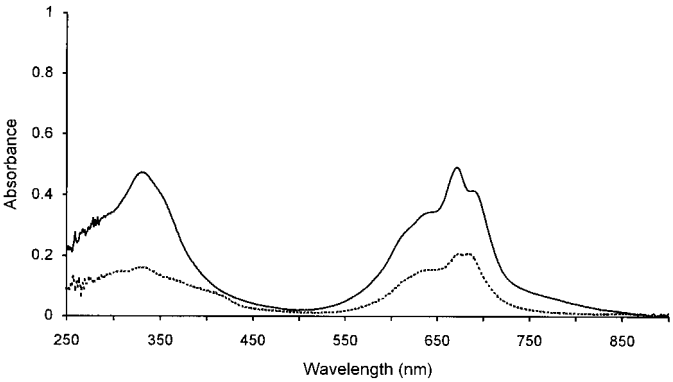


Figure 7. Electronic spectra of **10b** (3.5×10^{-6} mol dm^{-3}) (••••), and **10c** (1.51×10^{-5} mol dm^{-3}) (——) in $CHCl_3$.

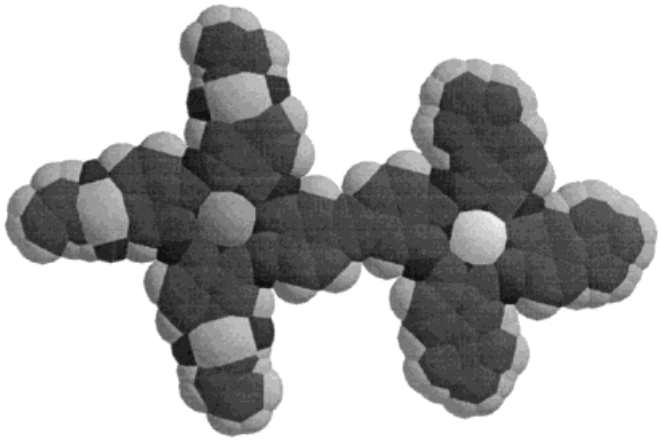


Figure 8. CPK model of compound **10c**.

might support a more fundamental understanding of the various modes of intramolecular interaction between the two Pc subunits. The relative orientation and motion in solution of the Pc moieties through the alkyne linkage (planarity of the systems) is also an important factor which must be taken into account, since it affects $\pi-\pi$ stacking interactions and aggregation phenomena.

Experimental Section

Melting points were determined on a Büchi 504392(S) apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AC200 (200 and 50 MHz, respectively). UV/Vis spectra were recorded on a Perkin–Elmer Lambda6 spectrophotometer. The mass spectra were determined on a VG AutoSpec spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400CHN elemental analyzer.

All tetrasubstituted phthalocyanines synthesized were obtained as a mixture of 2,9,16,23-, 2,10,16,24-, 2,9,17,24-, and 2,9,16,24-regioisomers.

[Tri-*tert*-butyl-(3-hydroxy-3-methyl-1-butynyl)phthalocyaninato]metal(II) (1a–c):

General procedure: A mixture of 4-*tert*-butylphthalonitrile[11] (400 mg, 2.17 mmol) and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile[10] (182 mg, 0.72 mmol) was refluxed in dimethylaminoethanol (DMAE) (1.5 mL) under argon for 12 h in the presence of the corresponding metallic salt MCl_2 (0.72 mmol). The mixture was concentrated under reduced pressure, the blue solid was extracted with CH_2Cl_2 and then washed with water. Compounds **1a–c** were separated from the corresponding tetra-*tert*-butylphthalocyaninate by chromatography (silica gel, CH_2Cl_2/isopropanol 100:1).

1a: Yield: 142 mg (24%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.4-7.2$ (br, arom H), 4.0 (s, 1H; OH), 1.6 [br, 27H; $C(CH_3)_3$], 1.4 (s, 6H; CH_3); IR (KBr): $\tilde{\nu} = 3495$ (OH), 2954 (CH), 2500 (C≡C), 1392, 1363 and 1331 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 684 (5.1), 613 (4.5), 351 nm (4.9); MS (FAB-*m*NBA): *m*/*z* (%): 827 (100) [*M*+H$^+$], 811 (31) [*M* − CH_3]$^+$, 771 (13); $C_{49}H_{46}N_8OZn \cdot 3H_2O$ (880.03): calcd C 66.79, H 5.95, N 12.73; found C 66.93, H 5.93, N 12.97.

1b: Yield: 128 mg (21%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.2-7.3$ (br, arom H), 4.0 (s, 1H; OH), 1.6 [br, 27H; $C(CH_3)_3$], 1.4 (s, 6H; CH_3); IR (KBr): $\tilde{\nu} = 3423$ (OH), 2955 (CH), 2599 (C≡C), 1394, 1363 and 1320 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 676 (5.0), 609 (4.4), 333 nm (4.7); MS (FAB-*m*NBA): *m*/*z* (%): 821 (100) [*M*+H$^+$], 805 (42) [*M* − CH_3]$^+$; $C_{49}H_{46}N_8ONi \cdot 2H_2O$ (856.33): calcd C 68.66, H 5.88, N 13.08; found C 68.44, H 5.88, N 13.44.

1c: Yield: 112 mg (19%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.0-7.3$ (br, arom H), 4.0 (s, 1H; OH), 1.6 [br, 27H; $C(CH_3)_3$], 1.4 (s, 6H; CH_3); IR (KBr) $\tilde{\nu} = 3425$ (OH), 2958 (CH), 2596 (C≡C),1394, 1363 and 1318 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 673 (5.2), 608 (4.6), 328 nm (4.9); MS (FAB-*m*NBA): *m*/*z* (%): 822 (100) [*M*+H$^+$], 806 (31) [*M* − CH_3]$^+$; $C_{49}H_{46}N_8OCo \cdot 2H_2O$ (857.33): calcd C 68.58, H 5.88, N 13.07; found C 68.25, H 6.26, N 12.80.

(Tri-*tert*-butyl-ethynylphthalocyaninato)metal(II) (2a–c):

General procedure: A mixture of [tri-*tert*-butyl-(3-hydroxy-3-methyl-1-butynyl)phthalocyaninato]metal(II) (**1a–c**) (0.145 mmol) and powdered sodium hydroxide (0.145 mmol) in dry toluene (3 mL) was refluxed under argon. The reaction was monitored by TLC until all the starting material had reacted. After the solvent was evaporated under reduced pressure, the product was extracted with CH_2Cl_2, washed with water, and then chromatographed (silica gel, CH_2Cl_2/isopropyl alcohol 20:1).

2a: Reaction time: 4 h. Yield: 82 mg (74%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.0-7.5$ (br, arom H), 3.4 (s, 1H; C≡CH), 1.6 [br, 27H; $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3495$ (C≡CH), 2954 (CH), 2103 (C≡CH), 1392, 1363, and 1330 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 684 (5.4), 612 (4.7), 350 nm (5.1); MS (FAB-*m*NBA): *m*/*z* (%): 769 (100) [*M*+H$^+$], 753 (26) [*M* − CH_3]$^+$; $C_{46}H_{40}N_8Zn \cdot H_2O$ (786.22): calcd C 70.09, H 5.37, N 14.22; found C 69.69, H 5.37, N 14.82.

2b: Reaction time: 24 h. Yield: 81 mg (73%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.0-7.6$ (br, arom H), 3.4 (s, 1H; C≡CH), 1.6 [br, 27H; $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3390$ (C≡CH), 2955 (CH), 2103 (C≡CH), 1390, 1365 and 1320 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 675 (5.5), 607 (4.8), 337 nm (5.1); MS (FAB-*m*NBA): *m*/*z* (%): 763 (100) [*M*+H$^+$], 747 (36) [*M* − CH_3]$^+$; $C_{46}H_{40}N_8Ni \cdot H_2O$ (781.58): C 70.69, H 5.42, N 14.34; found C 71.07, H 5.36, N 14.20.

2c : Reaction time: 4 h. Yield: 82 mg (74%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.0-7.3$ (br, arom H), 3.4 (s, 1H; C≡CH), 1.6 [br, 27H; $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3313$ (C≡CH), 2956 (CH), 2104 (C≡CH), 1394, 1363, and 1319 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 672 (5.4), 607 (4.7), 328 nm (4.9); MS (FAB-*m*NBA): *m*/*z* (%): 763 (100) [*M*+H$^+$], 747 (36) [*M* − CH_3]$^+$; $C_{46}H_{40}N_8Co \cdot 3H_2O$ (817.33): C 67.54, H 5.67, N 13.71; found C 67.74, H 5.46, N 13.63.

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Bis[(tri-*tert*-butylphthalocyaninato)metal(II)]butadiyne (3a–c):

*General procedure for **3a,b***:[13a,d] (Tri-*tert*-butylethynylphthalocyaninate)-metal(II) (**2a,b**) (0.025 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) were heated at 55–60 °C in a mixture of dry pyridine (1 mL) and dry MeOH (0.05 mL) under argon until all the starting material had reacted.

*Synthesis of **3c***: $[Pd(PPh_3)_2Cl_2]$ (3 mg) and CuI (6 mg), instead of $Cu(OAc)_2 \cdot H_2O$, in distilled Et_3N (1 mL) at room temperature were used.[13b,c] After the solvent was removed, the product was extracted with CH_2Cl_2, washed with water, and chromatographed (silica gel, CH_2Cl_2/MeOH 100:1).

3a: Reaction time 4 h. Yield: 12 mg (60%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.5-7.2$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3428$ (arC-H), 2955 and 2923 (CH), 2556 (C≡C), 1392, 1363 and 1330 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 709 (4.7), 675 (4.7), 350 nm (4.6); (FAB-*m*NBA): *m*/*z* (%): 1539–1535 (isotopic pattern) (100) [*M*+H$^+$], 1519 (20) [$M-CH_3]^+$; $C_{92}H_{78}N_{16}Zn_2 \cdot 5H_2O$ (1628.5): calcd C 67.81, H 5.44, N 13.76; found C 67.50, H 5.12, N 13.58.

3b: Reaction time 24 h. Yield: 11 mg (60%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C TMS): $\delta = 9.4-7.1$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3443$ (arC-H), 2962 and 2919 cm^{-1} (CH); UV/Vis ($CHCl_3$): λ_{max} (logε) = 671 (4.6), 332 nm (4.6); (FAB-*m*NBA): *m*/*z* (%): 1527–1523 (isotopic pattern) (100) [*M*+H$^+$]; $C_{92}H_{78}N_{16}Ni_2 \cdot 5H_2O$ (1614.5): calcd C 68.40, H 5.49, N 13.88; found: C 68.73, H 5.73, N 13.52.

3c: Reaction time 12 h. Yield: 8 mg (42%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.3-7.0$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3375$ (arC-H), 2961 and 2954 cm^{-1} (CH); UV/Vis ($CHCl_3$): λ_{max} (logε) = 672 (4.8), 326 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 1527–1525 (isotopic pattern) (100) [*M*+H$^+$]; $C_{92}H_{78}N_{16}Co_2 \cdot 4H_2O$ (1599.3): calcd C 69.04, H 5.42, N 14.01; found: C 69.43, H 5.27, N 13.81.

Tri-*tert*-butyl-iodophthalocyaninatozinc(II) (4b): A mixture of 4-*tert*-butylphthalonitrile[11] (400 mg, 2.17 mmol) and 4-iodophthalonitrile[13a] (183 mg, 0.72 mmol) was refluxed in DMAE (1.5 mL) under argon for 15 h in the presence of $ZnCl_2$ (100 mg, 0.72 mmol). The mixture was concentrated under reduced pressure, the blue solid was extracted with CH_2Cl_2 and then washed with water. The corresponding tri-*tert*-butyliodophthalocyaninato zinc(II) (**4b**) was separated from tetra-*tert*-butylphthalocyaninato zinc(II) (**4a**), di-*tert*-butyl-diiodophthalocyaninato zinc(II) (**4c**), and *tert*-butyl-triiodophthalocyaninato zinc(II) (**4d**) by chromatography (silica gel, petroleum ether/dioxane 4:1). The compounds were washed with hot MeOH after chromatography.

4b: Yield: 94 mg (15%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.7-7.5$ (br, arom H),1.6 [br, 27 H; $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3438$ (arC-H), 2995 (CH), 1392, 1363 and 1330 [$C(CH_3)_3$], 1091 cm^{-1} (C-I); UV/Vis ($CHCl_3$): λ_{max} (logε) = 679 (5.1), 612 (4.3), 351 nm (4.7); (FAB-*m*NBA): *m*/*z* (%): 871 (100) [*M*+H$^+$], 855 (24) [$M-CH_3]^+$; $C_{44}H_{39}N_8IZn \cdot H_2O$ (888.2): calcd C 59.44, H 4.61, N 12.61; found C 59.20, H 4.92, N 12.88.

4c: Yield: 60 mg (9%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9-8.5$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3434$ (arC-H), 2954 (CH), 1390, 1363 and 1329 [$C(CH_3)_3$], 1093 cm^{-1} (C-I); UV/Vis ($CHCl_3$): λ_{max} (logε) = 678 (5.2), 612 (4.4), 352 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 941 (100) [*M*+H$^+$], 925 (25) [$M-CH_3]^+$; $C_{40}H_{30}N_8I_2Zn$ (939.98) calcd C 51.01, H 3.21, N 11.90; found 51.09, H 3.30, N 11.77.

4d: Yield: 72 mg (10%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.5-8.0$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3430$ (arC-H), 2995 (CH), 1389, 1364, and 1330 [$C(CH_3)_3$], 1092 cm^{-1} (C-I); UV/Vis ($CHCl_3$): λ_{max} (logε) = 679 (5.2), 612 (4.5), 353 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 1010 (100) [*M*+H$^+$], 994 (11) [$M-CH_3]^+$; $C_{36}H_{21}N_8I_3Zn \cdot H_2O$ (1027.83): calcd C 41.99, H 2.25, N 10.88; found C 41.50, H 2.39, N. 10.86.

Bis[(tri-*tert*-butylphthalocyaninato)zinc(II)-zinc(II), zinc(II)-nickel(II), and zinc(II)-cobalt(II)]ethyne (5a–c):

General procedure: A mixture of (tri-*tert*-butylethynylphthalocyaninato)-metal(II) (**2a–c**) (0.025 mmol), tri-*tert*-butyliodophthalocianinatozinc(II) (**4b**) (22 mg 0.025 mmol), $[Pd_2(dba)_3]$ (8 mg), and $AsPh_3$ (18 mg) was stirred at 35 °C in freshly distilled and deaerated piperidine under argon until the starting phthalocyanines had reacted. The mixture was concentrated under reduced pressure. The green solid obtained was extracted with CH_2Cl_2 and washed with water. The bisphthalocyaninates were purified by chromatography (**5a** and **5b**: silica gel, CH_2Cl_2/isopropanol 40:1; **5c**: silica gel, toluene).

5a: Reaction time: 6 h. Yield: 26 mg (70%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.5-7.2$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3428$ (arC-H), 2957 (CH), 2550 (C≡C), 1391 and 1329 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 710 (4.7), 678 (4.7), 344 nm (4.6); (FAB-*m*NBA): *m*/*z* (%): 1515–1511 (isotopic pattern) (100) [*M*+H$^+$], 1499–1495 (isotopic pattern) (24) [$M-CH_3]^+$, $C_{90}H_{78}N_{16}Zn_2 \cdot 4H_2O$ (1586.5): calcd C 68.09, H 5.48, N 14.12; found C 68.26, H 5.74, N 13.87.

5b: Reaction time: 24 h. Yield: 28 mg (76%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.4-7.2$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3423$ (arC-H), 2955 (CH), 2597 (C≡C), 1393, 1363 and 1328 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 678 (4.3), 336 nm (4.0); (FAB-*m*NBA): *m*/*z* (%): 1509–1505 (isotopic pattern) (100) [*M*+H$^+$]; $C_{90}H_{78}N_{16}NiZn \cdot 5H_2O$ (1594.52): calcd C 67.73, H 4.92, N 14.05; found C 67.34, H 5.18, N 13.89.

5c: Reaction time: 14 h. Yield: 31 mg (84%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.1-8.5$ (br, arom H), 1.6 [br, $C(CH_3)_3$]; IR (KBr) $\tilde{\nu} = 3425$ (arC-H), 2960 (CH), 2550 (C≡C),1394, 1364 and 1319 cm^{-1} [$C(CH_3)_3$]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 700 (4.4), 676 (4.6), 622 (4.3), 329 nm (4.4); (FAB-*m*NBA): *m*/*z* (%): 1508–1506 (isotopic pattern) (100) [*M*+H$^+$], 1492–1490 (isotopic pattern) (55) [$M-CH_3]^+$; $C_{90}H_{78}N_{16}CoZn \cdot 4H_2O$ (1577.5): calcd C 68.44, H 4.98, N 14.19; found C 68.74, H 5.27, N 14.55.

4-Thiopropylphthalonitrile (6): A mixture of 4-nitrophthalonitrile[20] (3 g, 0.0173 mol) and propanothiol (1.58 g, 0.0208 mol) was stirred for 10 min in DMSO.[21] Then K_2CO_3 (2.8 g, 0.0208 mol) was added slowly. The reaction mixture was stirred under argon for 16 h. The product was extracted with CH_2Cl_2 and washed with a solution K_2CO_3 (5%). The brown oil obtained was purified by column chromatography (silica gel, CH_2Cl_2/hexane 2:1) to yield 2.3g (66%) of a gray solid. M.p. 61.9–62.3 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.63$ (d, J(H,H) = 8.3 Hz, 1 H; arom H), 7.53 (dd, J(H,H) = 8.3, J(H,H) 2.0 Hz, 1 H; arom H), 7.45 (d, J(H,H) = 2.0 Hz, 1 H; arom H), 2.99 (t, J(H,H) = 7.3 Hz, 2 H; SCH_2), 1.71 (m, 2 H; CH_2), 1.08 (t, J(H,H) = 7.4 Hz, 3 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 147.4 (C4), 133.1 (C6), 129.9 (C5), 129.8 (C3), 116.2 (C2), 115.5 (CN), 115.1 (CN), 110.6 (C1), 33.7 (SCH_2), 21.6 (CH_2), 13.3 (CH_3); MS (70 eV, EI): *m*/*z* (%): 202 (85) [*M*]$^+$, 173 (49) [$M^+ - CH_3CH_2$]; 159 (100) [$M^+ - CH_3CH_2CH_2$]; $C_{11}H_{10}N_2S$ (202.08): calcd C 64.04, H 5.85, N 13.28; found C 64.34, H 6.01, N 13.67.

4-Propylsulfonylphthalonitrile (7): 4-Propylsulfonylphthalonitrile (**6**, 2.3 g, 0.011 mol) was stirred with acetic acid under reflux. Then H_2O_2 (56 mL) was added slowly over a period of 15 min. The reaction was stirred at this temperature for 2 h.[22] The yellow solution was poured into water and the white solid obtained was filtered and washed with water. Yield: 2.05g (80%); m.p. 147.0–148.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.95 (d, J(H,H) = 8.1 Hz, 1 H; arom H), 8.45 (d, J(H,H) = 1.6 Hz, 1 H; arom H), 8.26 (dd, J(H,H) = 8.3, J(H,H) = 1.6 Hz, 1 H; arom H), 3.14 (m, 2 H; SO_2CH_2), 1.75 (m, 2 H; CH_2), 1.04 (t, J(H,H) = 7.3, 3 H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.3 (C4), 134.3 (C5), 132.7 (C6), 132.4 (C3), 123.3 (C1), 120.7 (CN), 120.3 (CN), 117.3 (C2), 57.7 (SCH_2), 16.3 (CH_2), 12.8 (CH_3); MS (70 eV, EI): *m*/*z* (%): 234 (11) [*M*]$^+$, 127 (100) [$M^+ - SO_2CH_3CH_2CH_2$]; $C_{11}H_{10}N_2SO_2$ (234.07): calcd C 56.40, H 4.30, N 11.96, S 13.68; found C 56.12, H 4.28, N 11.57, S 13.40.

Iodo-tri-propylsulfonylphthalocyaninatozinc(II) (8c): A mixture of 4-propylsulfonylphthalonitrile (**7**, 500 mg, 2.13 mmol) and 4-iodophthalonitrile[13a] (169 mg, 0.71 mmol) was stirred in a mixture of *o*-dichlorobenzene (1.5 mL) and DMF (0.5 mL) at 130 °C in the presence of zinc acetate monohydrate (155 mg). The mixture was heated for 12 h under argon atmosphere. The solvent was evaporated and the blue oil obtained was dissolved in CH_2Cl_2 and washed with water. The desired compound **8c** was isolated from a mixture of Pcs by columm chromatography (silica gel, CH_2Cl_2/isopropyl alcohol): the tri-iodo-propylsulfonylphthalocyaninatozinc(II) (**8a**) was obtained as the first eluted component with CH_2Cl_2/isopropyl alcohol (100:1). Then, a mixture 75:1 of these solvents was employed to separate the di-iodo-di-propylsulfonylphthalocyaninatozinc(II) (**8b**). Pc **8c** was obtained after increasing the polarity to 50:1. The last eluted component was the tetra-propylsulfonylphthalocyaninatozinc(II) complex **8d**.

8a: Yield: 19 mg (2.5%); m.p. >300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.40$ (d, J(H,H) = 1.6 Hz; arom H), 8.33 (dd, J(H,H) = 7.7,

J(H,H) = 1.56 Hz; arom H), 8.09 (s; arom H), 8.07 (d, J(H,H) = 7.1 Hz; arom H), 7.60 (s; arom H), 6.90 (s; arom H), 3.13 (t, J(H,H) = 7.9 Hz, 2H; SO_2CH_2), 1.83 (m, 2H; CH_2), 1.03 (t, J(H,H) = 7.3 Hz, 3H; CH_3); IR (KBr) $\tilde{\nu}$ = 3405 (arC-H), 2950(CH), 1300, 1250, 1140, 1090 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 683 (5.3), 675 (5.3), 612 (4.7), 353 nm (5.0); (FAB-*m*NBA): *m*/*z* (%): 1060 (100) [M+H$^+$], 952 (18) [$M^+ - SO_2C_3H_7$]$^+$; $C_{35}H_{19}N_8SO_2I_3Zn \cdot 2H_2O$ (1095.75): calcd C 38.35, H 2.12, N 10.23, S 2.91; found C 38.36, H 2.45, N 10.15, S 3.19.

8b: Yield: 72 mg (9%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.37 (d, J(H,H) = 1.0 Hz; arom H), 8.30 (d, J(H,H) = 7.7 Hz; arom H), 8.04 (d, J(H,H) = 7.7 Hz; arom H), 3.12 (t, J(H,H) = 7.8 Hz, 4H; SO_2CH_2), 1.76 (m, 4H; CH_2), 1.02 (t, J(H,H) = 7.4 Hz, 6H; CH_3); IR (KBr) $\tilde{\nu}$ = 3400 (arC-H), 2920 (CH), 1304, 1245, 1091 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 680 (5.3), 611 (4.6), 353 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 1043–1041 (isotopic pattern) (100) [M+H$^+$], 934 (20) [$M - SO_2C_3H_7$]$^+$; $C_{38}H_{26}N_8S_2O_4I_2Zn \cdot 2H_2O$ (1078.01): calcd C 42.34, H 2.94, N 10.23, S 5.84; found C 42.52, H 3.25, N 10.60, S 5.54.

8c: Yield: 60 mg (8%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.40 (d, J(H,H) = 1.2 Hz; arom H), 8.33 (dd, J(H,H) = 7.7, J(H,H) = 1.4 Hz; arom H), 8.07 (d, J(H,H) = 7.6 Hz; arom H), 7.60 (s; arom H), 6.90 (s; arom H), 3.10 (m, 6H; SO_2CH_2), 1.25 (m, 6H; CH_2), 1.03 (m, 9H; CH_3); IR (KBr) $\tilde{\nu}$ = 3400 (arC-H), 2940 (CH), 1731, 1305, 1255, 1141, 1092 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 682 (5.3), 672 (5.3), 609 (4.5), 352 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 1023–1021 (isotopic pattern) (100) [M+H$^+$]; 913 (23) [$M - SO_2C_3H_7$]$^+$; $C_{41}H_{33}N_8S_3O_6IZn \cdot 3H_2O$ (1076.2): calcd C 45.76, H 3.65, N 10.41, S 8.94; found C 45.77, H 3.37, N 10.05, S 8.87.

8d: Yield: 59 mg (8%); m.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.5 (s, arom H), 8.18 (d, J(H,H) = 1.3 Hz; arom H), 8.10 (dd, J(H,H) = 7.7, J(H,H) = 1.3 Hz; arom H), 7.6 (m; arom H), 7.56 (d, J(H,H) = 7.7 Hz; arom H), 3.10 (m, 8H SO_2CH_2), 1.76 (m, 8H;CH_2), 1.04 (m, 12H; CH_3); IR (KBr) $\tilde{\nu}$ = 3414 (arC-H), 2966 (CH), 1306, 1289, 1142, 1094 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 679 (5.5), 609 (4.7), 345 nm (4.9); (FAB-*m*NBA): *m*/*z* (%): 1003–1001 (isotopic pattern) (100) [M+H$^+$], 897–894 (isotopic pattern) (32) [$M - SO_2C_3H_7$]$^+$; $C_{44}H_{40}N_8S_4O_8Zn \cdot 4H_2O$ (1074): calcd C 49.18, H 4.50, N 10.43, S 11.93; found C 49.57, H 4.12, N 10.58, S 11.90.

Iodo-tri-propylsulfonylphthalocyaninatocobalt(II) (9b): A mixture of 4-propylsulfonylphthalonitrile (**7**, 500 mg, 2.13 mmol) and 4-iodophthalonitrile (180 mg, 0.71 mmol)[13a] was stirred in 2-ethoxyethanol (4 mL) at 135 °C in the presence of cobalt acetate dihydrate (177 mg, 0.71 mmol). The mixture was heated for 12 h under argon atmosphere. The solvent was evaporated and the blue oil was dissolved in CH_2Cl_2 and the solution was washed with water. The desired iodo-tri-propylsulfonylphthalocyaninatocobalt(II) (**9b**) was isolated from a mixture of Pcs by column cromatography (silica gel, $CHCl_3$/isopropyl alcohol). The di-iodo-di-propylsulfonylphthalocyaninatocobalt(II) (**9a**) was obtained as the first eluted component with $CHCl_3$/isopropyl alcohol (200:1). Then a mixture 100:1 of these solvents was employed to obtain compound **9b**. The last eluted component was the tetra-propylsulfonylphthalocyaninatozinc(II) complex (**9c**). The compounds were washed with hot MeOH after chromatography.

9a: Yield: 30 mg (4%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.16 (d, J(H,H) = 1.7 Hz; arom H), 8.11 (s, arom H), 8.09 (d, J(H,H) = 1.63 Hz; arom H), 7.50 (s, arom H), 3.10 (m, 4H; SO_2CH_2), 1.85 (m, 4H; CH_2), 1.05 (m, 6H; CH_3); IR (KBr) $\tilde{\nu}$ = 3456 (arC-H), 2967 (CH), 1294, 1139, 1094 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 667 (5.2), 607 (4.8), 306 nm (5.11); (FAB-*m*NBA): *m*/*z* (%): 1036 (100) [M+H$^+$], 928 (30) [$M^+ - SO_2C_3H_7$]$^+$; $C_{38}H_{26}N_8S_2O_4I_2Co \cdot 4H_2O$ (1107.55): calcd C 41.17, H 3.06, N 10.11; found C 41.56, H 3.19, N 9.80.

9b: Yield: 65 mg (9%); m.p. > 300 °C; ^{1}H RMN (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60 (s; arom H), 6.90 (s; arom H), 3.10 (m, 6H; SO_2CH_2), 1.82 (m, 6H; CH_2), 1.03 (m, 9H; CH_3); IR (KBr) $\tilde{\nu}$ = 3444 (arC-H), 2922 (CH), 1306, 1139, 1100 cm^{-1} (SO_2); UV/Vis ($CHCl_3$): λ_{max} (logε) = 666 (5.1), 604 (4.6), 327 nm (4.9); (FAB-*m*NBA): *m*/*z* (%): 1016 (100) [M+H$^+$], 908 (21) [$M - SO_2C_3H_7$]$^+$, $C_{41}H_{33}N_8S_3O_6ICo \cdot 2H_2O$ (1033.05) calcd C 47.60, H 3.60, N 10.84; found C 48.0, H 3.91, N 10.60.

9c: Yield: 38 mg (5%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.5–8.03 (m, arom H), 3.08 (m, 8H; SO_2CH_2), 1.70 (m, 8H; CH_2), 1.04 (m, 12H; CH_3); IR (KBr) $\tilde{\nu}$ = 3456 (arC-H), 2967 (CH), 1306, 1139, 1100 cm^{-1} ($-SO_2-$); UV/Vis ($CHCl_3$): λ_{max} (logε) = 667 (4.9), 602 (4.4), 328 nm (4.8); (FAB-*m*NBA): *m*/*z* (%): 996 (100) [M+H$^+$], 888 (20) [$M - SO_2C_3H_7$]$^+$; $C_{44}H_{40}N_8S_4O_8Co \cdot 4H_2O$ (1067.15): calcd C 49.43, H 4.49, N 10.48; found C 48.99, H 4.22, N 10.30.

[Tri-*tert*-butylphthalocyaninato metal(II)-tri-propylsulfonylphthalocyaninato metal(II)]ethyne (10a–c):

Method A: Tri-propylsulfonylphthalocyaninatozinc(II) (**8c**, 0.030 mmol) was stirred in freshly distilled and deaerated Et_2NH in the presence of [$Pd(PPh_3)_2Cl_2$] (1 mg) and CuI (0.6 mg). The (tri-*tert*-butylethynylphthalocyaninato)metal(II) (**2a** or **2b**, 0.030 mmol) was then added and the reaction was stirred under argon at 35 °C for 6 h (the reaction was monitored by TLC until all blue starting Pcs disappeared to form a new green species). The green solution obtained was evaporated to dryness. The residue was extracted with CH_2Cl_2 and the solution washed with water. The dimers were purified by chromatography (silica gel, CH_2Cl_2 /isopropyl alcohol 100:1).

Method B: (Tri-propylsulfonylphthalocyaninato)metal(II) (**8c** or **9b**, 0.030 mmol) was stirred in freshly distilled and deaerated piperidine in the presence of [$Pd_2(dba)_3$] (6 mg) and $AsPh_3$ (4 mg). The (tri-*tert*-butylethynylphthalocyaninato)metal(II) (**2a** or **2b**, 0.030 mmol) was then added and the mixture was stirred under argon at 35 °C for 6 h and then worked up as in Method A.

10a: Yield: 10 mg (41%, Method A), 19 mg (78%, Method B); m.p. > 300 °C; IR (KBr) $\tilde{\nu}$ = 3428 (arC-H), 2954 (CH), 2543 (C≡C), 1330, 1307, 1087 cm^{-1} [$C(CH_3)_3$, SO_2]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 677 (4.2), 343 nm (4.3); (FAB-*m*NBA): *m*/*z* (%): 1665–1661 (isotopic pattern) (100) [M+H$^+$], 1558–1553 (isotopic pattern) (27) [$M - SO_2C_3H_7$]$^+$; $C_{87}H_{72}N_{16}S_3O_6Zn_2 \cdot 5H_2O$ (1750.35): calcd C 59.64, H 4.72, N 12.80, S 5.47; found C 59.83, H 4.55, N 13.02, S 5.79.

10b: Yield: 12 mg (50%, Method A); 17 mg (71%, Method B); m.p. > 300 °C; IR (KBr) $\tilde{\nu}$ = 3420 (arC-H), 2952 (CH), 2540 (C≡C), 1330, 1307, 1087 cm^{-1} [$C(CH_3)_3$, SO_2]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 671 (4.2), 627 (4.18), 331 nm (4.2); (FAB-*m*NBA): *m*/*z* (%):1658–1655 (isotopic pattern) (100) [M+H$^+$]; $C_{87}H_{72}N_{16}S_3O_6NiZn \cdot 4H_2O$ (1726.36): calcd C 60.47, H 4.67, N 12.97, S 5.55; found C 60.66, H 4.52, N 13.12, S 5.89.

10c: Yield: 19 mg (80%, Method B); m.p. > 300 °C; IR (KBr) $\tilde{\nu}$ = 3434 (arC-H), 2945 (CH), 2356 (C≡C), 1311, 1256, 1139, 1089 cm^{-1} [$C(CH_3)_3$, SO_2]; UV/Vis ($CHCl_3$): λ_{max} (logε) = 690 (4.3), 672 (4.4), 638 (4.2), 330 nm (4.2); (FAB-*m*NBA): *m*/*z* (%): 1658–1656 (isotopic pattern) (100) [M+H$^+$], 1600–1598 (isotopic pattern) (24) [$M - t$Bu], 1550–1548 (isotopic pattern) (34) [$M - SO_2C_3H_7$]$^+$; $C_{87}H_{72}N_{16}S_3O_6ZnCo \cdot 4H_2O$ (1727.45): calcd C 60.43, H 4.66, N 12.96, S 5.55; found C 60.66, H 4.52, N 13.12, S 5.89.

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