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Synthesis and Optical Properties of Regioisomerically Pure Alkynyl-Bridged Bis(phthalocyanines)

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Pb^{II} ethynyl- and butadiynyl-bridged bis(phthalocyaninates) **1a**–**d**, peripherally functionalized with *n*-butoxy moieties, have been synthesized by using Pd-catalyzed cross-coupling methodologies. Preliminary open-aperture Z-scan experiments with nanosecond pulses at 550 nm on solutions of Pb^{II} bis(phthalocyaninates) **1b** and **1d** show strong reduction of the transmission at high intensities, although an irreversible optical behaviour is observed at the experimental time scale.

Introduction

Phthalocyanines[1] (Pcs) have drawn considerable attention as molecular materials that give rise to outstanding electrical and optical properties.[2] Phthalocyanines are highly delocalized 18 π-electron aromatic molecules showing strong absorption in the visible region (ca. 700 nm). For this reason, Pcs have been largely used as dyestuffs for textiles and inks, but many other applications arise from their electronic delocalization and optical behaviour, namely, as antennas and electron-donor components in molecular dyads with long-lived photoinduced charge-separated states,[3] which can perform as light energy conversion systems,[4] and as non-linear optical materials.[5] Phthalocyanines exhibit other additional advantages as molecular materials for optical applications; they exhibit exceptional thermal, chemical and optical stability, synthetic versatility and can be easily processed to yield useful macroscopic arrangements. The architectural flexibility of phthalocyanines is well exemplified by the large number of metallic complexes described in the literature, as well as by the huge variety of substituents that can be attached to the phthalocyanine core. Furthermore, structural modifications such as the formal reduction of the number of isoindole units, the so-called subphthalocyanines,[6] or the formation of binuclear and trinuclear phthalocyanine derivatives, either fused[7] or linked through conjugated spacers,[8] alter the electronic structure of the macrocyclic core and, therefore, allow the fine tuning of the physical properties. Particularly, the nonlinear response of this type of macrocycles have shown to be sensitive to structural variations such as the nature of the central metal and the expansion or contraction of the π-conjugated system.[5]

Among all NLO properties, optical limiting (OL) is one of the most promising for practical applications in the protection of optical elements and sensors against damage by exposure to sudden high-intensity light. Optical-limiting materials must exhibit a decrease in transmittance at high intensity levels by means of nonlinear absorption and/or nonlinear refraction mechanisms. Phthalocyanines operate usually as *reverse saturable absorbers*,[9] that is, materials with an excited-state absorption cross-section (σ_{ex}) exceeding that of the ground state (σ_g). Metal phthalocyanines with heavy-metal atoms[9b,10] such as In, Sn, Pb usually display increased population of the triplet state through intersystem crossing, and thus, an enhanced triplet-triplet absorption, which usually brings about an improvement of the OL properties. Other structural factors that seem to increase the OL response are the introduction of axial ligands to decrease the aggregation phenomena,[9b,9e,11] the peripheral functionalization with either strong electron-donor or electron-withdrawing substituents[12] and the extension of the conjugation.[13] The elucidation of the influence of the electronic interaction between macrocycles on the nonlinear absorption of conjugated Pc-based binuclear systems is also an appealing task. Hanack et al. have recently reported on the OL properties of fused binuclear In^{III} phthalocyaninates, which showed lower performance than their monomeric counterpartners.[14] However, we have described the preparation and Z-scan measurements of highly conjugated ethynyl- and butadiynyl-bridged bis(phthalocyanines) containing Zn^{II} and Co^{II} cation;[15] these compounds have shown moderate cross-section ratios, but higher than the

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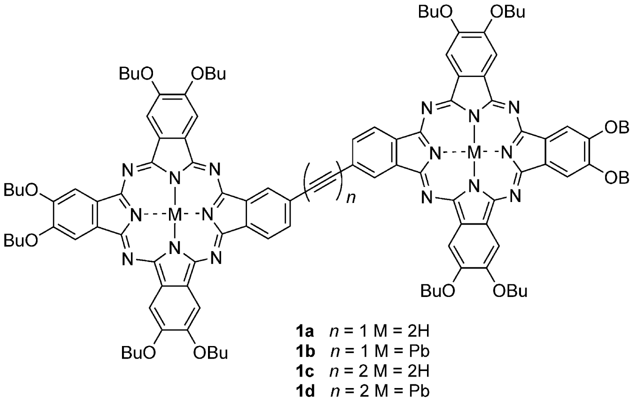
model monomeric phthalocyanines. For this reason, it is our aim to include electron-donor substituents at the periphery and heavy metal atoms in the central cavities of these binuclear structures, since this approach could render very efficient OL materials.

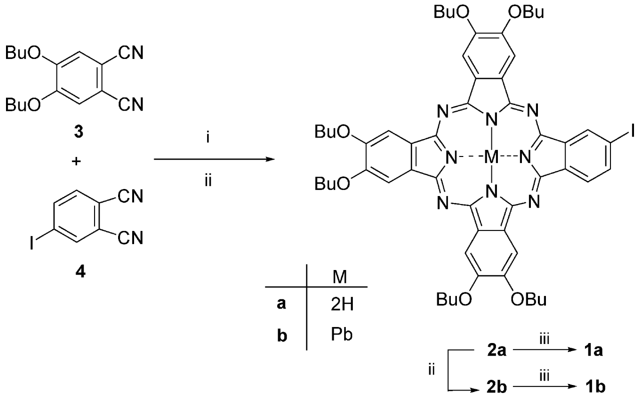
Herein, we report on the synthesis and characterization of new ethynyl- and butadyinyl-bridged bis(phthalocyaninates) **1a**–**d**, peripherally functionalized with strongly donor *n*-butoxy moieties. In order to optimize the yields in the preparation of these binuclear compounds, different synthetic approaches have been undertaken, starting from unsymmerically substituted (hexabutoxy)iodo- and or (hexabutoxy)alkynyl-functionalized mononuclear phthalocyanines (**2** and **3**, respectively) and making use of different Pd-catalyzed homo- and cross-coupling methodologies. It is worth mentioning that the attachment of six butoxy groups to each Pc core affords solubility to the system, electron richness for optical properties and precludes the formation of regiosomers, being this a structural advance with regard to other binuclear derivatives described previously by us.[15] Preliminary Z-scan experiments have been also performed on binuclear lead(II) complexes to validate the molecular design.



Results and Discussion

Synthesis and Characterization

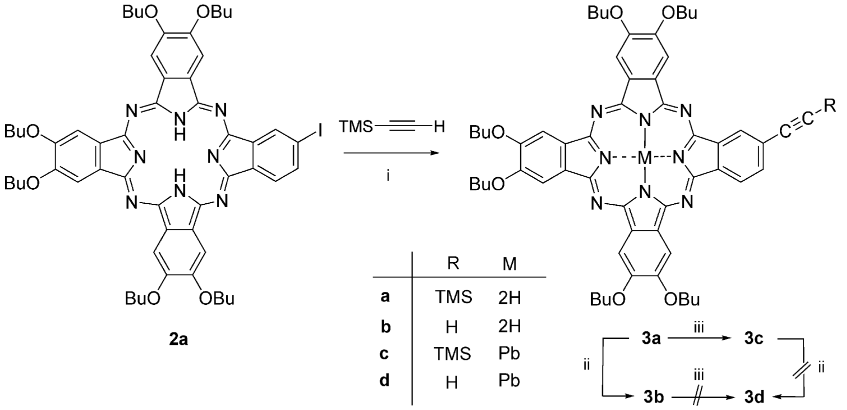
The synthesis of ethynyl- and butadyinyl-bridged Pb^{II} bis(phthalocyaninates) **1a**–**d** requires the preparation of adequately functionalized mononuclear compounds, namely monoiodophthalocyanine derivatives. Following reported procedures,[16] the first attempt on the synthesis of Pb^{II} monoiodophthalocyaninate **2b** (see structure in Scheme 1) involved the statistical condensation of 4,5-dibutoxyphthalonitrile (**3**)[17] and 4-iodophthalonitrile (**4**)[18] in a 3:1 ratio in the presence of different Pb^{II} salts (see Supporting Information, Scheme S1). However, the Pb^{II} phthalocyaninate was not formed in these conditions, so that we turned to the preparation of the free-base monoiodophthalocyanine **2a** that could be further metallated in a second step. Compound **2a** was prepared by statistical condensation of **3** and **4** in a 3:1 ratio in the presence of lithium metal and pentanol as solvent (Scheme 1). After acid treatment and chromatographic separation, the free-base **2a** was isolated in 12% yield. Metallation with $Pb(OAc)_2{\cdot}3H_2O$ afforded the lead(II) complex **2b** in *ca* 90% yield.



Scheme 1. i) Li/pentanol. ii) $Pb(OAc)_2{\cdot}3H_2O$, quinoline, THF. iii) $Bu_3SnC{\equiv}CSnBu_3$, $Pd(PPh_3)_4$, toluene.

The preparation of the ethynyl-bridged Pb^{II} bis(phthalocyaninate) **1b** was undertaken through double Stille-type coupling of monoiodophthalocyanine **2b** and bis(tributylstannyl)acetylene (Scheme 1). This double Pd-catalyzed ethynyl-aryl coupling gives the target binuclear compound **1b** in moderate yield (33%). With the goal in mind of improving the yield, we decided to carry out the cross-coupling between the free-base phthalocyanine **2a** and bis(tributylstannyl)acetylene, and to introduce the metal in both Pc-subunits in a second step. However, the reaction took place in lower yield (22%) than in the case of the coupling between Pb^{II} monoiodophthalocyaninate complex **2b** and bis(tributylstannyl)acetylene described above.

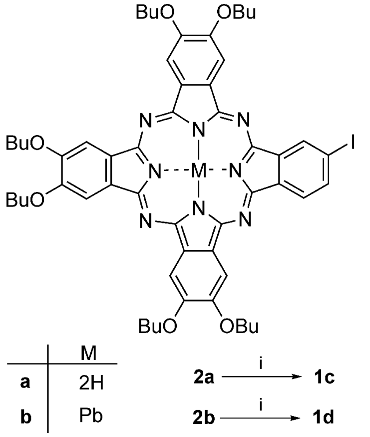
In order to improve the yields in compound **1b**, we explored a stepwise approach based on Sonogashira coupling between trimethylsilyl acetylene and Pb^{II} monoiodophthalocyaninate **2b** (see SI, Scheme S2). Deprotection of the resulting Pb^{II} ethynyl-functionalized phthalocyaninate and subsequent Sonogashira coupling with Pb^{II} monoiodophthalocyaninate **2b** would afford the target ethynyl-bridged binuclear complex **1b**. Moreover, the Pb^{II} ethynyl-functionalized phthalocyaninate would be the starting material for the preparation of the butadyinyl-bridged binuclear compound **1d** by means of a homocoupling reaction. Therefore, we reacted Pb^{II} phthalocyaninate **2b** with trimethylsilylacetylene in two different conditions, namely, catalytic amounts of $Pd(PPh_3)_2Cl_2$/copper(I) iodide and catalytic amounts of $Pd_2(dba)_3/AsPh_3$ in TEA (see SI, Scheme S2), but the phthalocyanine decomposed under both conditions. For this reason, we carried out the same cross-coupling reaction with the free-base monoiodophthalocyanine **2a** and trimethylsilylacetylene under Lindsey conditions $[Pd_2(dba)_3/AsPh_3]$[19] in the absence of Cu^I (Scheme 2) in order to avoid the introduction of this metal into the central cavity of the macrocycle, which had been previously observed in other Sonogashira couplings with free-base ethynyl phthalocyanines as substrates.[20] Trimethylsilylethynephthalocyanine **3a** was deprotected using



Scheme 2. i) $Pd_2(dba)_3$, $AsPh_3$. ii) TBAF/THF. iii) $Pb(OAc)_2\cdot 3H_2O$, quinoline, THF.

standard conditions (Scheme 2) to give **3b**. Since our main target is the preparation of the Pb^{II} complex **3d**, we tested the metallation of both free-base compounds, **3a** and **3b**. We did not succeed in the direct metallation of the ethynyl-containing phthalocyanine **3b**, but the treatment with $Pb(OAc)_2\cdot 3H_2O$ of the protected compound **3a** gave the lead(II) complex **3c** in 93% yield. However, the final deprotection of this molecule with TBAF led to demetallation of the macrocycle.

In our aim to prepare the ethynyl-containing Pb^{II} phthalocyaninate **3d**, we accomplished the Stille coupling of **2b** with tributylstannylacetylene, following Negishi conditions. However, when this reaction was carried out at 100 °C in toluene, using $Pd(PPh_3)_4$ as catalyst, the major compound happened to be the butadyinyl-bridged binuclear complex **1d**, which was isolated in 60% yield. In view of this result, we gave up the preparation of the ethynylphthalocyanine **3d** and tested different conditions to improve the yield in the target binuclear Pb^{II} complex **1d**. However, different attempts led to lower yields in **1d**. Finally, we also applied this one-pot procedure to the synthesis of metal-free binuclear compound **1c**, which is a synthetic intermediate of **1d** if both cavities are subsequently metallated with Pb^{II}. Cross-coupling between **2a** and tributylstannylacetylene afforded the metal-free butadyinyl-bridged complex in lower yield (56%) than that of the Pb^{II} binuclear complex **1d** (Scheme 3).



Scheme 3. i) $Bu_3SnC{\equiv}CH$, $Pd(PPh_3)_4$, toluene, 100 °C.

All the compounds were fully characterized by NMR, FTIR, MALDI-MS, and UV/Vis spectroscopy. The infrared spectra of the lead(II)-containing phthalocyanines exhibit the typical metal sensitive C–C stretching band at ≈ 1490 cm^{-1}, which correlates well with previous values reported for related Pb^{II} phthalocyaninates. The UV/Vis spectra of the binuclear Pb^{II} complexes **1b** and **1d** exhibited broadened Q bands in the visible region as compared to that of the mononuclear Pb^{II} phthalocyaninate **2b**. This broadening is associated to the extension of the π-conjugated system in these binuclear derivatives with regard to the mononuclear one. This explanation is consistent with the fact that both binuclear metal-free derivatives **1a** and **1c** show also broad Q bands in their UV/Vis spectra (Figure 1). ^1H NMR spectra of all binuclear compounds display also broad signals, especially for the aromatic protons, as a consequence of the aggregation between macrocycles at the experimental NMR concentrations.

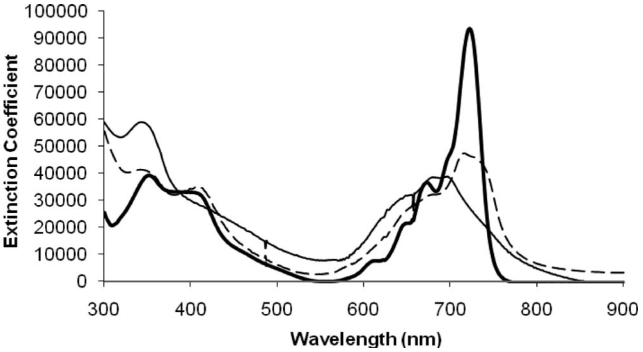


Figure 1. UV/Vis spectra in $CHCl_3$ of **2b** (bold line, c = 7.5 10^{-5} M), **1b** (thin line, c = 5.2 10^{-6} M) and **1d** (dashed line, c = 6.8 10^{-6} M).

Z-Scan Measurements

The open-aperture Z-scan experiment is a very convenient method to evaluate the optical limiting properties of materials. Optical limiting means a reversible decrease of transmittance of an optical system upon increase of the incident light intensity. Z-scan measures the total transmittance through the sample as a function of the incident laser intensity while the sample is gradually moved along the optical axis of a convex lens.

The most efficient mechanism to achieve OL is the sequential two-photon absorption, which involves the nonparametric optical pumping of low-lying electronic states of the material.[21] Under illumination, an initial photon is absorbed at the ground state level bringing the molecules to an excited state, which may absorb another photon at the same frequency. If the material has an excited state absorption cross-section larger than the ground state cross-section, and if the incident beam induces a significant population in the excited states, the effective absorption coefficient of the material increases and *reverse saturable absorption* occurs. To achieve a strong nonlinear absorption, both a large excited state absorption cross-section and a long excited state lifetime are required.

The open aperture Z-scan experiments (see Exp. Sect.) were performed using 7.0×10^{-3} M solutions of Pb^{II} ethynyl- and butadyinyl-bridged dimers **1b** and **1d**, measuring the sample transmission at 550 nm, where the linear absorption of both compounds is low (at the middle of the transmission window). One should mention that the spectra of both binuclear systems exhibit at this concentration similar absorption features than those displayed in Figure 1. Both compounds exhibited a reduction in the transmission (Figure 2) about the focus of the lens, which is indicative of positive nonlinear absorption, at quite low incident energies. However, there is an asymmetry in the Z-scan profiles of both dimers **1b** and **1d**: the transmission after the sample has passed through the focus is lower than it was initially at the same distance from the focal point before the focus. This behaviour may be associated to the formation of a photoproduct at high laser intensities, which displays a different optical performance than the parent compound. The nature of this photoproduct is yet to be determined.

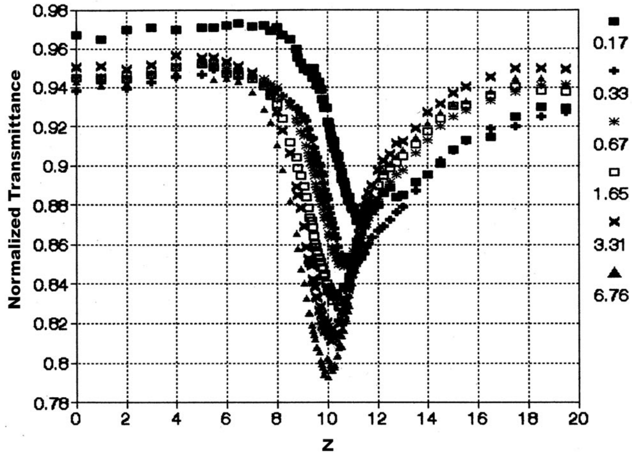


Figure 2. Open aperture Z-scan experiments on solutions of compound **1d** at different incident energies.

Conclusions

We have succeeded on the preparation for the first time of metal-free and Pb^{II} ethynyl- and butadyinyl-bridged dimers **1a–d**, following one-pot cross-coupling Pd-catalyzed approaches between monoiodophthalocyanines and either bis(tributylstannyl)acetylene or tributylstannylacetylene, which leads to the formation of two or three C–C bonds, respectively. Even though the lead(II) complexes **1b** and **1d** are the targets for optical limiting responses owing to the presence of the heavy-metal atom, the corresponding metal-free derivatives **1a** and **1c** are key intermediates and starting compounds for the incorporation of many other metals into the macrocyclic cavities and for the construction of extended supramolecular structures. Preliminar Z-scan experiments over the lead(II) complexes **1b** and **1d** show a strong reduction of the transmission at high intensities, but the concomitant formation of a photoproduct that makes the optical behaviour of these materials irreversible at the experimental timescale. This fact minimizes the applicability of these particular dimers in OL devices. The introduction of other different heavy-metal atoms into the macrocyclic structures will be pursued in order to obtain optically stable materials with enhanced OL responses.

Experimental Section

General: Column chromatography was carried out on silica gel 60 (Merck, 230–400 mesh, 60 Å), and TLC, on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Melting points were determined in a Büchi 504392-S equipment. IR spectra were recorded on a Bruker Vector 22 spectrophotometer using KBr disks. MALDI-TOF-MS spectra were determined on a Bruker Reflex III instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded with a Bruker AC-300 instrument. UV/Vis spectra were recorded with a Hewlett–Packard 8453 instrument. The apparatus for the Z-scan experiments has been described elsewhere.[11a] The laser source is an optical parametric oscillator (OPO) pumped by the third harmonic of a Nd/YAG laser with a pulse width of 2.5 ns. The laser was operated at 532 nm, with a pulse repetition rate of 10 Hz. The beam was spatially filtered to give a spatial profile that showed a correlation greater than 96% with a gaussian profile. The laser intensity was controlled by waveplate/polarizer combinations. The gaussian input beam was focused using approximately f/40 optics. The focal spot size, f/number and the beam quality as measured by M^2, were determined from knife edge scans at several positions along the beam path near the focus. The measured M^2 was approximately 1.1 at 530 nm. A diffraction limites gaussian beam would have $M^2 = 1$. The measured focal spot size was within about 10% of that expected for a gaussian beam at 550 nm. The sample was mounted on a translation stage and translated through the focus for the Z-scan experiments.

2,3,9,10,16,17-Hexabutoxy-23-iodophthalocyanine (2a): Lithium metal (10 mg, 1.43 mmol) in DMAE (3 mL) was heated at 70 °C until all the solid was dissolved. Then, 4,5-dibutoxyphthalonitrile (**3**) (186 mg, 0.68 mmol) and 4-iodophthalonitrile (**4**) (58 mg, 0.23 mmol) were added and the mixture was refluxed for 8 h under argon. After cooling, acetic acid (10 mL) was added and the mixture stirred for 1 h. The mixture was poured in water/methanol mixture (1:1, 50 mL), centrifugated and the supernatant removed. Several cycles of centrifugation/supernatant removal were done until colorless of the supernatants. The green solid was extracted with CH_2Cl_2 and washed with water. Purification by column chromatography of the residue on silica gel, using CH_2Cl_2 as eluent, yielded 25 mg (12%) of **2a** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3442, 2871, 1276, 1072 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.0 (m, 9 H, arom.), 4.4–4.0 (m, 12 H, OCH_2), 2.3–1.7 (m, 12 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.6–1.2 (m, 12 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.2–0.9 (t, 18 H, CH_3) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 1075–1072 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 697 (4.9), 669 (4.8), 641 (4.4), 610 (4.2), 441 (4.2), 347 nm (4.7). $C_{56}H_{65}IN_8O_6$ (1073.07): calcd. C 62.67, H 6.11, N 10.44; found C 63.54, H 6.29, N 10.99.

Pb^{II} (2,3,9,10,16,17-Hexabutoxy-23-iodophthalocyaninate) (2b): A mixture of **2a** (51.5 mg, 0.048 mmol) and $Pb(OAc)_2\cdot 3H_2O$ (50.8 mg, 0.134 mmol) under argon was heated at 130 °C in dry quinoline (1 mL) and dry THF (3 mL) for 3 h. The crude was washed by centrifugation with acetone/water (1:1) and water until the supernatants were colorless. The green solid was washed with hot methanol to yield 54 mg (88%) of **2b**; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3443, 2870, 1599, 1492, 1459, 1275, 1082 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.7–8.6 (m, 9 H, arom.), 4.5–4.4 (m, 12 H, OCH_2), 2.1–2.0 (m, 12 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.8–1.7 (m, 12 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.2–1.1 (t, 18 H, CH_3) ppm. MALDI-TOF [M + H^+] *m*/*z*: 1282–1276 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 722 (3.8), 673 (3.4), 352 nm (3.8). HRMS (MALDI-TOF) calcd. for $C_{56}H_{63}N_8O_6PbI$: 1278.3683, found 1278.3694.

2,3,9,10,16,17-Hexabutoxy-23-(trimethylsilylethynyl)phthalocyanine (3a): A mixture of phthalocyanine **2a** (18.3 mg, 0.017 mmol) $Pd_2(dba)_3$ (4.8 mg, 0.005 mmol), $AsPh_3$ (10.3 mg, 0.336 mmol) and (trimethylsiliyl)acetylene (0.05 mL, 34.5 mg, 0.35 mmol) in piperidine (5 mL) was heated at 30 °C for 17 h under argon. The solvent was removed under reduced pressure and the crude was purified by column chromatography (neutral alumina Brockmann III, dichloromethane) to yield 13.5 mg (76%) of **3a** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3445, 2960, 2146, 1491, 1261 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.2–7.0 (m, 9 H, arom.), 4.7–4.2 (m, 12 H, OCH_2), 2.3–1.7 (m, 12 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.6–1.2 (m, 12 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.2–0.9 (t, 18 H, CH_3), 0.6 (m, 9 H, $SiCH_3$) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 1045–1042 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 698 (5.0), 674 (5.0), 645 (4.6), 613 (4.4), 434 (4.4), 349 nm (4.80). HRMS (MALDI-TOF) calcd. for $C_{61}H_{74}N_8O_6Si$: 1042.5495, found 1042.5542.

2,3,9,10,16,17-Hexabutoxy-23-ethynylphthalocyanine (3b): TBAF (0.064 mL of a 1 M solution in THF, 0.064 mmol) was added dropwise to a solution of **3a** (15 mg, 0.014 mmol) in THF (2 mL). The mixture was stirred for 15 min at room temperature, the solvent was distilled off, and the residue was chromatographed (silica gel, hexane/dioxane, 2:1) to yield 8.6 mg (64%) of **3b** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3441, 3297, 2877, 2160, 1279, 1068 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.0 (m, 9 H, arom.), 4.6–4.2 (m, 12 H, OCH_2), 3.3 (s, 1 H, $C\equiv CH$), 2.3–1.7 (m, 12 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.6–1.2 (m, 12 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.2–0.9 (m, 18 H, CH_3) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 974–970 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 695 (4.9), 674 (5.0), 643 (4.6), 615 (4.5), 436 (4.40), 346 nm (4.8). $C_{58}H_{66}N_8O_6$ (970.5): calcd. C 71.73, H 6.85, N 11.54; found C 71.95, H 6.83, N 11.18.

Pb^{II} [2,3,9,10,16,17-Hexabutoxy-23-(trimethylsilylethynyl)phthalocyaninate] (3c): A mixture of phthalocyanine **3a** (12.5 mg, 0.012 mmol) and $Pb(OAc)_2\cdot 3H_2O$ (14 mg, 0.036 mmol) in a mixture of dry quinoline (3 mL) and THF (1 mL) was heated at 130 °C for 2 h under argon. The crude was washed by centrifugation with acetone/water (1:1) until the supernatants were colorless. The solid was washed with hot methanol to yield 14 mg (93%) of **3c** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 2957, 2147, 1492, 1274 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.7–7.0 (m, 9 H, arom.), 4.7–4.5 (m, 12 H, OCH_2), 2.3–2.0 (m, 12 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.9–1.5 (m, 12 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.3–1.1 (t, 18 H, CH_3), 0.4 (s, 9 H, $SiCH_3$) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 1251–1246 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 727 (5.2), 656 (4.5), 399 nm (4.8). $C_{61}H_{72}N_8O_6PbSi$ (1248.6): calcd. C 58.68, H 5.81, N 8.97; found C 58.74, H 6.00, N 8.82.

Bis(2,3,9,10,16,17-Hexabutoxyphthalocyanine-23-yl)ethyne (1a): A mixture of phthalocyanine **2a** (29.4 mg, 0.027 mmol), Pd $(PPh_3)_4$ (3.4 mg, 0.029 mmol) in dry and deaereated toluene (5 mL) was stirred under argon atmosphere. Then, 7 µL (0.013 mmol) of bis(tributylstannyl)acetylene was added and the reaction heated at 100 °C for 5 h. The solid obtained was purified by column chromatography (silica gel, CH_2Cl_2) to yield 6 mg (22%) of **1a** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3442, 2957, 2260, 1455, 1275, 1097 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.4 (m, 18 H, arom.), 3.9–3.2 (m, 24 H, OCH_2), 1.7–1.5 (m, 24 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.4–1.0 (m, 24 H, $\mathrm{CH_3}\mathit{CH_2}$), 0.9–0.7 (m, 36 H, CH_3) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 1919–1915 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 695 (4.3), 672 (4.3), 642 (4.2), 340 nm (4.4). HRMS (MALDI-TOF) calcd. for $C_{114}H_{130}N_{16}O_{12}$: 1915.0048, found 1914.999.

Bis[Pb^{II}(2,3,9,10,16,17-hexabutoxyphthalocyaninate-23-yl)]ethyne (1b): A mixture of phthalocyanine **2b** (10 mg, 0.0078 mmol), Pd $(PPh_3)_4$ (3 mg, 0.029 mmol) in dry and deaerated toluene (5 mL) was stirred under argon atmosphere. Then, 4 µL (0.0024 mmol) tributylstannylacetylene was added and the reaction heated at 100 °C for 17 h. Hexane was added and the solid obtained was washed with hexane to yield 3 mg (33%) of **1b** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3421, 2957, 2232, 2140, 1492, 1463, 1277, 1097 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.4 (m, 18 H, arom.), 4.7–4.5 (m, 24 H, OCH_2), 1.9–1.7 (m, 24 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.4–1.0 (m, 24 H, $\mathrm{CH_3}\mathit{CH_2}$), 0.9–0.7 (m, 36 H, CH_3) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 2330–2323 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 701 (4.6), 340 (4.8). $C_{114}H_{126}N_{16}O_{12}Pb_2$ (2326.7): calcd. C 58.85, H 5.46, N 9.63; found C 59.29, H 5.44, N 9.41.

Bis(2,3,9,10,16,17-hexabutoxyphthalocyanine-23-yl)butadiyne (1c): A mixture of phthalocyanine **2a** (31 mg, 0.029 mmol), Pd $(PPh_3)_4$ (3 mg, 0.029 mmol) in dry and deaerated toluene (5 mL) was stirred under argon atmosphere. Then, 30 µL (0.0024 mmol) tributylstannylacetylene was added. The mixture was heated at 100 °C for 10 h under argon. The crude was purified by column chromatography (silica gel, CH_2Cl_2) to yield 15.6 mg (56%) of **1c** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3442, 2925, 2240, 2150, 1277, 1069 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.2–7.5 (m, 18 H, arom.), 4.9–4.4 (m, 24 H, OCH_2), 2.1–1.9 (m, 24 H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.6–1.5 (m, 24 H, $\mathrm{CH_3}\mathit{CH_2}$), 1.3–1.2 (m, 36 H, CH_3) ppm. MALDI-TOF (dithranol) [M + H^+] *m*/*z*: 1945–1939 (isotopic pattern). UV/Vis ($CHCl_3$): λ_{max} (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 679 (4.9), 341 (5.0), 297 nm (5.0). $C_{116}H_{130}N_{16}O_{12}$ (1940.4): calcd. C 71.80, H 6.75, N 11.55; found C 71.43, H 6.63, N 11.92.

Bis[Pb^{II}(2,3,9,10,16,17-hexabutoxyphthalocyaninate-23-yl)]butadiyne (1d): A mixture of phthalocyanine **2b** (7.7 mg, 0.006 mmol), $Pd(PPh_3)_4$ (3.2 mg, 0.027 mmol) in dry and deaerated toluene (2 mL) was stirred under argon atmosphere. Then, 1.7 µL

(0.00013 mmol) of tributylstannylacetylene was added. The reaction was heated at 100 °C for 5 h. The crude was washed by centrifugation with acetone/water (1:1) until the supernatants were colorless. The solid compound was washed with hot MeOH to yield 4.3 mg (60%) of **1d** as a green solid; m.p. > 200 °C. IR (KBr): $\tilde{\nu}$ = 3442, 2925, 2245, 1490, 1458, 1261, 1094 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.7–7.4 (m, 18 H, arom.), 4.7–4.4 (m, 24 H, OCH$_2$), 1.7–1.5 (m, 24 H, CH$_2$), 1.4–1.0 (m, 24 H, OCH$_2$*CH$_2$*), 0.9–0.7 (m, 36 H, CH$_3$*CH$_2$*) ppm. MALDI-TOF (dithranol) [M + H$^+$] *m/z*: 2355–2346 (isotopic pattern). UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε/dm^3 mol^{-1} cm^{-1}): 726 (4.3), 406 (4.5), 339 nm (4.7). $C_{116}H_{126}N_{16}O_{12}Pb_2$ (2350.7): calcd. C 59.22, H 5.48, N 9.53; found C 59.97, H 5.70, N 9.79.

Supporting Information (see also the footnote on the first page of this article): General experimental part, synthetic schemes of the unsuccessful reactions and copies of the ^{1}H NMR and MALDI-TOF spectra of new compounds.

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