

Ethynyl porphyrins bridging bis(phosphine)platinum(II) centers: molecular models for conjugated organometallic porphyrin polymers

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Linear ethynylporphyrin-bridged platinum(II) complexes, $[X(R_3P)_2Pt-C\equiv C-Zn(por)-C\equiv C-Pt(PR_3)_2Y]$ [$Zn(por)$ is a non-ethynylated porphyrin **1a**] and related oligomers have been synthesized. Di- and tri-nuclear platinum centers are linked to different porphyrin arrays; the end groups $Pt(PR_3)_2X$ and $Pt(PR_3)_2Y$ ($R = n-Bu$ or Ph ; $X = Y = Cl$ or I ; $X = Cl$, $Y = I$) show that a ligand exchange $Cl \rightarrow I$ also occurs. The compounds containing PBu_3 as the ligand are more stable than the corresponding PPh_3 ones. The dinuclear platinum dimers containing one bridging porphyrin have been isolated and characterized by IR, UV/VIS, 1H NMR and MALDI (matrix assisted laser desorption/ionization) mass spectroscopies. The mixture of longer oligomers was separated from the crude reaction products and could be identified by MALDI. The *cis-trans* isomerization of the porphyrin complexes with respect to the platinum precursor complexes, *i.e.* *trans*- $[PtCl_2(PBu_3)_2]$, *cis*- $[PtCl_2(PPh_3)_2]$ and *trans*- $[PtH(Cl)(PPh_3)_2]$, was observed. The dimers and oligomers are expected to be model molecules for long chain organometallic polymers.

Introduction

The research on the synthesis, characterization and properties of porphyrins, and their derivatives, is always growing in the never-ending effort of finding new, unexpected features for these molecules. The biomimetic chemistry of ethyne-linked porphyrins has been investigated for the synthesis of light-harvesting arrays in the form of star-shaped pentamers¹ or linear ethynyl bridged trimers and oligomers.² The presence of ethyne, oligoethyne and multiple ethyne bridges between porphyrins is believed to allow dramatically high excitonic and electronic coupling between chromophore centers.³ The electronic structure and spectroscopic properties of a series of nickel porphyrin butadiyne-bridged complexes have been correlated recently with the aid of a density functional study.⁴ Many efforts have been devoted to the development of synthetic strategies that would lead to multiporphyrin arrays with extended conjugation,^{3,5-9} in order to achieve strong electronic communication between the porphyrins, a property most desired in the field of molecular electronics. The ethyne-linked porphyrins are obtained by oxidative coupling of the corresponding acetylenic precursors using $[Pd(PPh_3)_4]$ complex and copper(I) iodide as the catalysts⁵ or by the Pd-catalyzed cross coupling reaction of a porphyrin aryl iodide with a porphyrin aryl ethyne.^{1,7,10-12} New experimental conditions have recently been developed for the synthesis of ethyne- or butadiyne-linked porphyrin arrays, using copper-free Pd-catalyzed coupling reactions, which avoid the undesired insertion of copper into free base porphyrins.¹³ A quite remarkable property of porphyrin arrays in square configuration has recently been reported by the Lindsey group,¹⁴ the study of excited-state photodynamics is

important for the investigation of electron communication and energy transfer phenomena. Cyclic porphyrin oligomers can be prepared from the linear analogs by an elegant procedure that uses template molecules as the reaction promoters; a series of papers by Sanders and Anderson¹⁵ appeared on this special topic. These molecules with spacious open cavities are designed as enzyme mimics in catalytic reactions.¹⁶ Cyclic trimeric porphyrins linking bis(alkyneplatinum) spacers have also been proposed as hosts for aluminium(III) complex guests,^{17,18} in the framework of the catalytic activity of porphyrins. Multiporphyrin arrays of square configuration are obtained by the complexation of *cis* and *trans* square planar complexes of Pt^{II} and Pd^{II} with *meso*-dipyridylporphyrins.¹⁹ Infinite 3-D structures made of Pd-pyridyl-porphyrinato units peripherally connected by cadmium(II) centers have been reported,²⁰ as promising materials for infinite framework structure with peculiar electrical and optical properties.

Most of the outstanding perspectives for materials science are expected from (macro)molecules with exceptional NLO responses, that could be used in future generation optoelectronic devices for telecommunications, information storage and optical switches. Porphyrins are optimum candidates for such applications, because of their molecular and electronic structure. A conjugated porphyrin polymer, synthesized by the Glaser-Hay coupling of the *meso*-diethynylzinc porphyrin, was reported to show high third order susceptibility $\chi^3 = 7.3 \times 10^{-8}$ esu ($\chi^3 = 10.22 \times 10^{-16}$ m² V⁻²).²¹ An excellent research for the development of new chromophores with photophysical properties suitable for the realization of polymer-based optoelectronic devices has been performed by Therien and co-workers;²² electron withdrawing ($C\equiv CC_6H_4NO_2$, A) and

electron releasing ($C\equiv CC_6H_4NMe_2$, D) groups are linked to the zinc porphyrin, giving rise to the first order hyperpolarizability $\beta = 5000 \times 10^{-30}$ esu ($\beta = 7 \times 10^{-30}$ m² V⁻²). A theoretical study on these acetylene-linked porphyrins supports the exceptional large optical non-linearity and provides suggestions for other candidate chromophores;²³ for example two zinc porphyrin units [bearing the acceptor (A) and donor (D) groups respectively] bonded through an ethynyl bridge connection give rise to supramolecular chromophores that should show extremely large molecular first hyperpolarizabilities. Organometallic polymers where Pt or Pd is σ bonded to organic spacers, e.g. 1,4-diethynylbenzene (DEB) and 4,4'-diethynylbiphenyl (DEBP),²⁴ have been predicted to be good candidates for large χ^3 values. Some of these polymers, i.e. the Pt- and Pd-DEBP, have been successfully employed as sensitive membranes in humidity sensors (SAW, Surface Acoustic Wave, sensors),²⁵ and their responses are believed to depend on the peculiar ordering of the polymers backbone, even when spin deposited as thick layer films; this property has been studied and elucidated by NEXAFS (near-edge X-ray absorption fine structure) experiments.²⁶

In order to develop new macromolecules which might couple the optical and electrical properties of porphyrins with the characteristics of ordered polymeric systems, where the insertion of transition metals (Pt, Pd, Ni) between polyyne spacers can lead to a large conduction bandwidth,²⁷ we have studied the synthesis of linear Pt-linked porphyrin oligomers, which are the precursors of their related polymers.

Experimental

Instrumentation

The UV/VIS spectra were obtained using a Perkin-Elmer Lambda 16 spectrophotometer, NMR spectra on a Bruker AM400 spectrometer and FT-IR spectra on a Perkin-Elmer 1700 instrument. Matrix assisted laser desorption/ionization (MALDI) mass measurements were performed on a ReflexTM time-of-flight mass spectrometer system (Bruker-Franzen Analytik, Bremen, Germany), operating in the positive-ion linear mode. Ions formed by a pulsed UV laser beam (nitrogen laser, energy about 50 μ J, $\lambda = 337$ nm) were accelerated to 30 keV. The UV laser light was focused on to samples at a focal diameter of 100–300 μ m.

Materials

All solvents were reagent grade used without further purification; reactions were performed under argon using standard procedures. 2,8,12,18-Tetraethyl-5,15-diethynyl-3,7,13,17-tetramethylporphyrinatozinc(II) **1a** was synthesized according to literature procedures.²⁸

Synthesis

Porphyrin-bridged bis(tributylphosphine)platinum dimer dichloride 2a and oligomers 3a–14a. Complex **1a** (210 mg, 0.35 mmol) and *trans*-[PtCl₂(PBU₃)₂] (238 mg, 0.36 mmol) were separately dissolved in CH₂Cl₂ or CHCl₃ (15 or 5 ml respectively), previously degassed by bubbling argon for 30 min. Copper(I) iodide (5 mg, 26 μ mol) was added to the solution containing the platinum complex and the two solutions were mixed, maintaining the argon atmosphere. Diethylamine (20 ml) was inserted by a syringe and the reaction solution was then stirred under an argon atmosphere for 3 h at 60 °C in the dark. The reaction progress was monitored by UV/VIS measurements, following the disappearance of the absorbance due to **1a** (437 nm, CHCl₃) and the concomitant increase of a new band at 450 nm. The reaction goes to completion when only the band at 450 nm is detected. The crude material, obtained after solvent removal under reduced pressure, was washed with water (to eliminate

the ammonium salt [NH₂Et₂]Cl) and the residue products were separated by addition of *n*-hexane; two compounds were found. The more soluble product, which gives blue-purple crystals (yield 15%), is the porphyrin-bridged platinum dimer dichloride **2a**: λ_{max}/nm (*n*-hexane) 450 and 619; FTIR $\tilde{\nu}_{max}/cm^{-1}$ 2096 ($\nu_{C=C}$), 1526, 1512 (ν_{C-C}) and 303 (ν_{Pt-Cl}) (Nujol mull); MALDI; m/z 1857, [M – H]⁺ (C₈₄H₁₄₂Cl₂N₄P₄Pt₂Zn requires 1856); NMR δ_H (CD₂Cl₂) 0.80 (m, 36 H, CH₃ of Bu), 1.30 (m, 24 H, PCH₂CH₂CH₂CH₃), 1.60 (m, 24 H, PCH₂CH₂CH₂CH₃), 1.88 (t, 12 H, CH₂CH₃ of porphyrin), 2.06–2.20 (m, 24 H, PCH₂CH₂CH₂CH₃), 3.76 (s, 12 H, CH₃ of porphyrin), 4.02 (q, 8 H, CH₂CH₃ of porphyrin) and 9.85 (s, 2 H, *meso*).

The product almost insoluble in *n*-hexane appears to be a mixture of multiporphyrin oligomers (**5a–14a**): λ_{max}/nm (pyridine) 457, 497 and 705; MALDI m/z 4890, [M – H]⁺ (very low intensity peak) (C₂₅₆H₃₃₂Cl₂N₂₀P₆Pt₃Zn₅ requires 4889 **14a**), 4798, [M – H]⁺ (C₂₅₆H₃₃₂Cl₂N₂₀P₆Pt₃Zn₅ requires 4797 **13a**), m/z 4304, [M – H]⁺ (C₂₁₆H₂₉₄Cl₂N₁₆P₄Pt₃Zn₄ requires 4303 **12a**), 4212, [M – H]⁺ (C₂₁₆H₂₉₄Cl₂N₁₆P₄Pt₃Zn₄ requires 4211 **11a**), 3718, [M – H]⁺ (C₁₈₀H₂₆₀Cl₂N₁₂P₃Zn₃ requires 3717 **10a**), 3626, [M – H]⁺ (C₁₈₀H₂₆₀Cl₂N₁₂P₃Zn₃ requires 3625 **9a**), 3121, [M – H]⁺ (C₁₅₆H₂₀₆Cl₂N₁₂P₄Pt₂Zn₃ requires 3120 **8a**), 3029, [M – H]⁺ (C₁₅₆H₂₀₆Cl₂N₁₂P₄Pt₂Zn₃ requires 3028 **7a**), 2535, [M – H]⁺ (C₁₂₀H₁₇₆Cl₂N₈P₄Pt₂Zn₂ requires 2534 **6a**), 2443, [M – H]⁺ (C₁₂₀H₁₇₆Cl₂N₈P₄Pt₂Zn₂ requires 2442 **5a**); FTIR $\tilde{\nu}_{max}/cm^{-1}$ 2080 ($\nu_{C=C}$), 1539 (ν_{C-C}), 304 (ν_{Pt-Cl}) and 154 (ν_{Pt-I}) (Nujol mull).

Porphyrin-bridged bis(tributylphosphine)platinum dimer diiodide 4a. Complex **1a** (150 mg, 0.25 mmol) and *trans*-[PtCl₂(PBU₃)₂] (240 mg, 0.40 mmol) were dissolved in a solution of CH₂Cl₂ (20 ml) and NH₂Et₂ (20 ml), previously degassed by bubbling argon. Copper(I) iodide (5 mg, 26 μ mol) was added and the reaction was carried out under an argon atmosphere for 7 h at reflux. It was monitored with UV/VIS spectroscopy, as reported for **2a**. At the end the solvents were removed under dynamic vacuum and the crude residue [λ_{max}/nm (CH₂Cl₂) 453, 492 and 693] was separated by extraction with *n*-hexane. The soluble fraction (emerald green) gave the porphyrin-bridged platinum dimer diiodide **4a** (5% yield): λ_{max}/nm (*n*-hexane) 452 and 617; FTIR $\tilde{\nu}_{max}/cm^{-1}$ 2094 ($\nu_{C=C}$), 1538 (ν_{C-C}) and 158 (ν_{Pt-I}) (THF); MALDI m/z 2041, [M – H]⁺, C₈₄H₁₄₂I₂N₄P₄Pt₂Zn **4a** requires 2040; very low intensity peaks at m/z 1976, [M – H]⁺, corresponding to C₈₄H₁₄₄I₂N₄P₄Pt₂ (m/z 1975) **4a'** and at m/z 1949, [M – H]⁺, corresponding to C₈₄H₁₄₂Cl₂N₄P₄Pt₂Zn (m/z 1948) **3a**; NMR δ_H (CDCl₃) 0.85 (m, 36 H, PCH₂CH₂CH₂CH₃), 1.48 (m, 24 H, PCH₂CH₂CH₂CH₃), 1.65 (m, 24 H, PCH₂CH₂CH₂CH₃), 1.85 (m, 12 H, CH₂CH₃ porphyrin), 2.04–2.20 (m, 24 H, PCH₂CH₂CH₂CH₃), 3.80 (s, 12 H, CH₃ of porphyrin), 4.05 (q, 8 H, CH₂CH₃ of porphyrin) and 9.90 (br, s, 2 H, *meso*). The *n*-hexane insoluble fraction gave a mixture of oligomers [λ_{max}/nm (pyridine) 457, 497 and 705] which are only slightly soluble in the common solvents (pyridine, THF, CHCl₃). Since the mixture of oligomers could not be separated into single products, no further characterization was performed.

Porphyrin-bridged bis(triphenylphosphine)platinum dimer dichloride 2b. (i) Complex **1a** (200 mg, 0.34 mmol) was added to *cis*-[PtCl₂(PPh₃)₂] (380 mg, 0.47 mmol) and CuI (5 mg, 26 μ mol) in a solution of NH₂Et₂ (20 ml) and CH₂Cl₂ (20 ml). The mixture was deaerated with argon for 1 h, and kept under an argon atmosphere for 3 h at reflux. The reaction was monitored by UV/VIS spectroscopy (in CH₂Cl₂) until a single absorption band at 457 nm (and 632, 706 nm) was detected. The reaction was then carried on for 15 d (under the same conditions), with subsequent additions of **1a** (2 batches of 200 mg each) with the aim of getting a polymeric structure; no further reactivity was detected. Then, the reaction mixture was concentrated to dryness and the crude product washed several times with water and

dried again. By addition of THF, a green solution and an insoluble material were obtained and separated. The THF was evaporated and the residue crystallized from CH₂Cl₂-light petroleum (b.p. 30–50 °C) giving green-blue micro crystals (15% yield): λ_{\max}/nm (CH₂Cl₂) 455, 630 and 686; FTIR $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2090 ($\nu_{\text{C}\equiv\text{C}}$), 1588, 1543 ($\nu_{\text{C}\equiv\text{C}}$), 540 ($\nu_{\text{P}\text{--}\text{P}}$) and 320, 290 ($\nu_{\text{P}\text{--}\text{Cl}}$); MALDI m/z 1763 fragment from **2b** (m/z 2094) which lost 2Cl and 1PPh₃ moieties, *i.e.* [Pt(PPh₃)₂-C≡C-Zn(por)-C≡C-Pt(PPh₃)]; NMR δ_{H} (CD₂Cl₂) 1.80 (t, 12 H, CH₂CH₃ of porphyrin), 3.74 (s, 12 H, CH₃ of porphyrin), 4.00 (q, 8 H, CH₂CH₃ of porphyrin), 6.80–7.75 (br, m, 60H, PPh₃) and 9.8 (br, s, 2 H, *meso*).

The residue (30% yield), insoluble in THF, is slightly soluble in pyridine: λ_{\max}/nm (pyridine) 464, 501, 654 and 753; FTIR $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2100 ($\nu_{\text{C}\equiv\text{C}}$) and 1611 ($\nu_{\text{C}\equiv\text{C}}$); MALDI m/z 2338 corresponding to the fragment obtained from **3b** (C₁₄₄H₁₃₀Cl₂-N₈P₄Pt₂Zn₂ requires 2680) which lost 1Cl, 1Zn and 1PPh₃, *i.e.* [Pt(PPh₃)-C≡C-por-C≡C-C≡C-Zn(por)-C≡C-Pt(PPh₃)₂Cl + Na]⁺, and m/z 1197 attributed to the fragment obtained from **3b** which lost the two [Pt(PPh₃)₂Cl] moieties [H-C≡C-Zn(por)-C≡C-C≡C-Zn(por)-C≡C-H + Na]⁺ (cationization with alkaline cations is a phenomenon correlated with the MALDI mechanism).

(ii) The complexes *trans*-[PtH(Cl)(PPh₃)₂] (365 mg, 0.48 mmol) and **1a** (203 mg, 0.48 mmol) were dissolved in a solution of THF (25 ml) and NHET₂ (0.5 ml) previously deaerated with argon for 1 h. The reaction was carried out for 24 h at 70 °C. It was monitored by UV/VIS spectroscopy observing the evolution of the Soret band from λ_{\max} 437 to 455 nm (and 630, 686 nm) in CH₂Cl₂. When the reaction went to completion the solvent was removed under vacuum and the crude residue washed several times with water and dried under dynamic vacuum for 3 d. The dark green product mixture was dissolved in cool CH₂Cl₂; the solution was separated from the residue by vacuum filtration and the fraction soluble in CH₂Cl₂ recovered by rotary evaporation, to give a bright green solid **2b** (12% yield); FTIR, MALDI and ¹H NMR characterizations provided evidence for the formation of complex **2b**. The MALDI spectrum also showed m/z 2033, [M - H]⁺ (very low intensity peak) (C₁₀₈H₉₈Cl₂N₄P₄Pt₂ requires 2032) corresponding to compound **2b'**. The insoluble residue was characterized as reported in (i).

The molecular structures of dimers and oligomers are reported in Scheme 1 and Fig. 1.

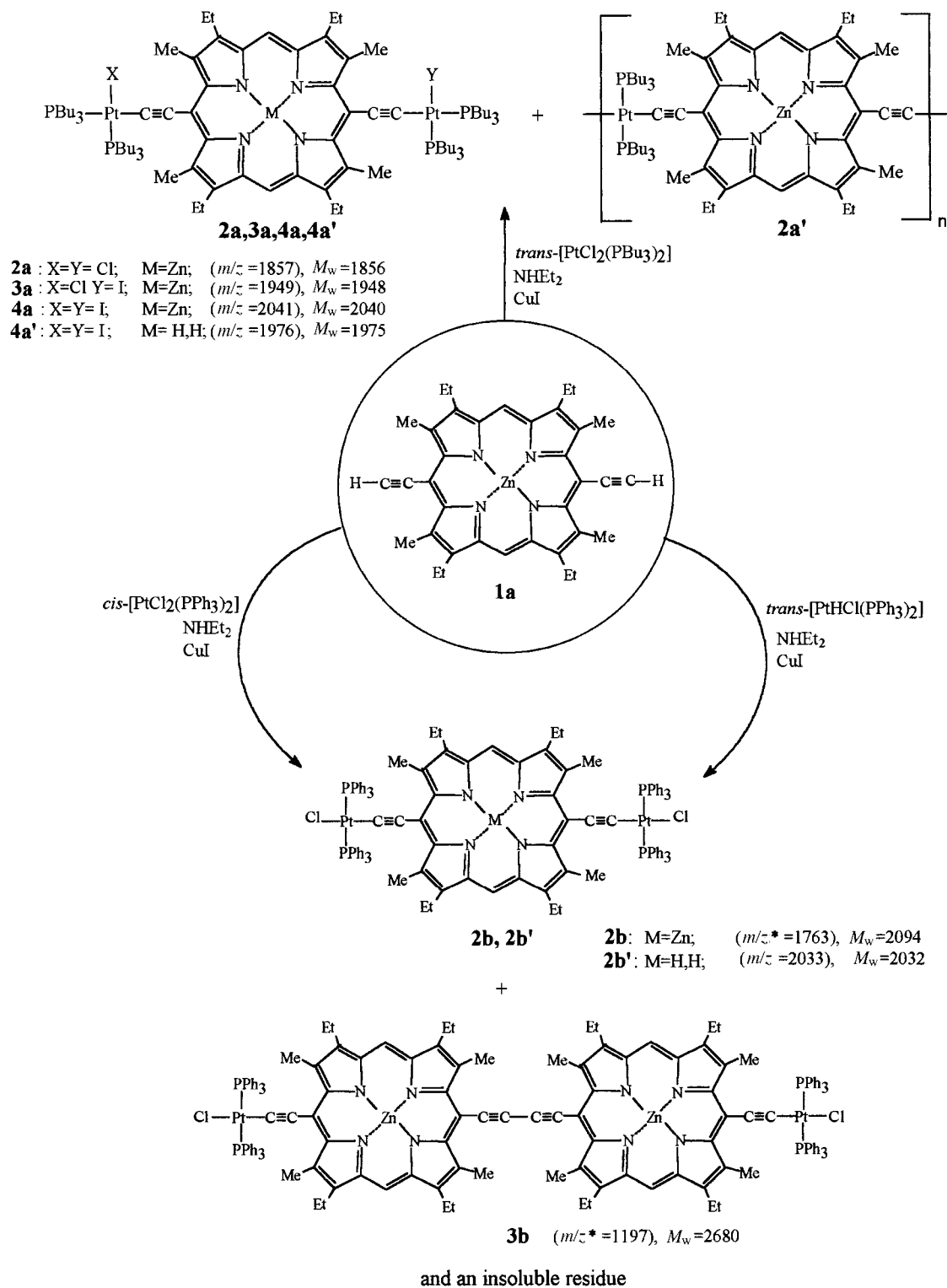
Results and discussion

In order to obtain model molecules and polymers with promising properties, such as electronic communication and large third order hyperpolarizability, we have tried to couple the contribution of the metal center (Pt) with the extended delocalization through the triple bonds and porphyrin ring in polymeric systems. The reactivity of bis(phosphine)platinum(II) complexes towards acetylenes in basic solvents is well known: mono- and bis-acetylides,²⁹ asymmetric bis-acetylides³⁰ and conjugated organometallic polymers³¹ can easily be obtained under mild conditions and with good yields.

The dehydrohalogenation reaction, originally introduced by Hagihara *et al.*,³¹ between metal (Ni, Pd, Pt) bis(phosphine) dichlorides and diacetylenes, readily allows the linkage metal-alkyne, leading to the formation of rigid-rod chains.^{31,32}

Copper free, Pd-mediated reactions are suitable for the synthesis of ethyne-linked arrays without σ -bonded Group X metals.¹³ In order to investigate the possible use of these reactions for the insertion of σ -bonded metal centers, we first used *trans*-[PtCl₂(PBu₃)₂] with **1a**; the tributylphosphine derivative has been chosen to obtain soluble polymers, as observed for organometallic polymers of Pt and Pd.²⁶ No coupling reaction has been observed between **1a** or its free base and *trans*-[PtCl₂(PBu₃)₂] in the presence of NHET₂. The presence of CuI

is necessary to catalyse this reaction: when the reaction was carried out on the free base porphyrin we obtained the corresponding copper porphyrinate as major product. The coordination of copper is an unfavourable process, because harsh conditions are necessary to remove this metal from porphyrin and because these compounds are not suitable for NMR characterization. We then used the zinc complex **1a** as starting material, since Zn can be easily removed or substituted with a different metal allowing one to explore the activity of different systems. The bathochromic shift of the Soret band observed during the progress of the reaction suggests an enhancement of the conjugation length,²¹ and was considered as a marker of reactivity. The TLC of the crude reaction products showed several spots with almost every common eluent, indicating the presence of different oligomers in the reaction mixture. Several attempts to perform chromatographic separation of oligomers failed, also resulting in their partial decomposition. To separate the more soluble fraction, the crude mixture was treated with *n*-hexane several times: the resulting solution left at 4 °C for 1 d yielded blue-purple crystals of the porphyrin-bridged platinum dimer **2a**, obtained from the reaction depicted in Scheme 1. A porphyrin platinum dimer analogous to **2a** has been reported among a series of porphyrin arrays studied for their linear and non-linear optical responses.³³ Dimer **2a** is a mixture of inseparable *cis/cis* and *trans/trans* isomers, with the *cis/cis* one being the major product. The ³¹P NMR spectrum shows two triplets centered at δ 4.75 and -2.10, with $J(\text{P-Pt}) = 1200$ and 1150 Hz respectively; the ³¹P resonance intensity ratio is roughly 7:3. The *cis-trans* structure isomerization was found by XPS investigations; the Cl 2p_{3/2} binding energy (198.3 eV) indicates the presence of a *cis* structure around Pt.³⁴ The ¹H NMR spectrum of **2a** confirms the proposed structure (Fig. 2). Further spectroscopic analyses have been performed by means of FTIR and MALDI techniques. The FTIR spectrum shows absence of the band at 3300 cm⁻¹ ($\equiv\text{C-H}$ stretching vibration), while the band at 2096 cm⁻¹ (C≡C stretching vibration) revealed that the coupling reaction had occurred. The band at 303 cm⁻¹ is characteristic of the Pt-Cl stretching mode, and a weak band at 154 cm⁻¹ is also present, indicating the possible presence of different ending side groups. The MALDI mass spectra (spectra run on sample dissolved in CHCl₃) confirms the presence of **2a** (Fig. 3) ($m/z = 1857$) as the major product, but reveals also the formation of the platinum dimer where one chlorine and one iodine are both linked to the metal (**3a**; $m/z = 1949$) in significant amount and of the platinum dimer **4a** (see Experimental section) in traces ($m/z = 2041$). Attempts to purify the mixture of oligomers slightly soluble in *n*-hexane by column chromatography were unsuccessful. The optical spectrum of the mixture (in pyridine) shows λ_{\max} 457, 497 and 705 nm; this shift and splitting of the Soret band are similar to those reported for the butadiyne linked porphyrin dimers³⁵ and strongly indicate the homo coupling between porphyrin units. In order to investigate the nature of the oligomeric products present in the fraction insoluble in hexane, we carried out a MALDI mass spectrometry analysis, performed by dissolving a very small amount of sample in THF. The spectrum (Fig. 4) shows a clear pattern of peaks which appear as a sequence of doublets separated by 586 units corresponding to **1a** without the ethynyl hydrogens. The presence of **2a** and **3a** is still quite evident; the separation is not exhaustive. However, complexes where the linear chain is expanded through the linking of zinc porphyrins in different arrays can be clearly detected; the ethyne-linked platinum oligomers are shown in Fig. 1. The substitution of chlorine with iodine at the head/tail end of the molecules is surprising, because it was never found under analogous reaction conditions leading to organometallic polymers where the organic spacers are diethynylbiphenyl²⁶ or anthracene and thiophene alkynyl chromophores;³² this feature indicated by MALDI spectra was confirmed and elucidated by XPS investigations.³⁴

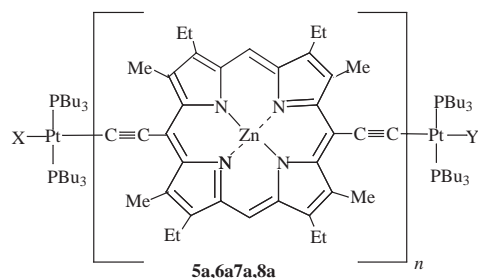


Scheme 1 Reaction pathways. * Indicates experimental MALDI fragmentation peak.

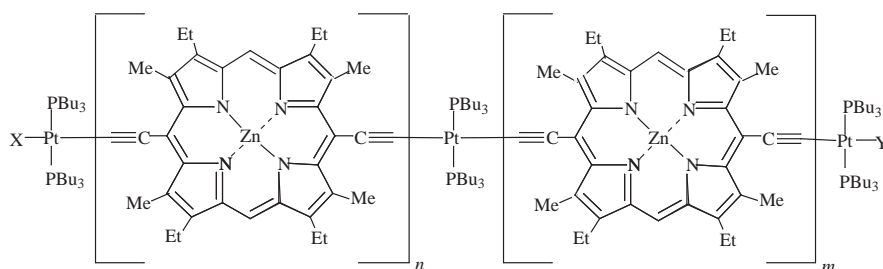
In order to investigate the possibility of improving the formation of polymeric products, the reaction of $trans$ -[PtCl₂(PBu₃)₂] and **1a** was then carried out for a longer time (6–8 h). In this case the main product is the porphyrin-bridged platinum dimer diiodide **4a** (Scheme 1): the compound is stable and can be purified by crystallization from *n*-hexane; after evaporation of the solvent, emerald green microcrystals are obtained. The Soret band of **4a** is found at 452 nm; the spectrum is quite similar to that of **2a**. The FTIR spectrum clearly shows the band at 2094 cm⁻¹, due to the stretching mode of the C≡C bond, and weak bands at $\nu < 200$ cm⁻¹ are indicative of Pt–I vibrations. A peculiar characteristic of this compound is the strong absorbance and the low resolution of the IR spectrum

which is characteristic of conducting materials. The MALDI spectrum shows the most intense peak at m/z = 2041, in accord with the proposed structure. A signal is also found at m/z = 1976, [M – H]⁺, corresponding to C₈₄H₁₄₄I₂N₄P₄Pt₂ (M = 1975) **4a'** (Scheme 1). Traces of **3a** are also revealed in the MALDI spectrum. The ¹H NMR spectrum of **4a** shows the same features as those of **2a**.

With the aim of investigating the influence of the different electronic effects of phosphine ligands on the chemical properties of the arrays, the synthesis of bis(triphenylphosphine)-platinum derivatives has been considered. The complexes studied were cis -[PtCl₂(PPh₃)₂] and the hydride $trans$ -[PtH(Cl)(PPh₃)₂]: on the basis of our previous research concerning



- $n = 2$ **5a**: X=Y=Cl ($m/z = 2443$); $M_w = 2442$
 6a: X=Cl, Y=I ($m/z = 2535$); $M_w = 2534$
 $n = 3$ **7a**: X=Y=Cl ($m/z = 3029$); $M_w = 3028$
 8a: X=Cl, Y=I ($m/z = 3121$); $M_w = 3120$



9a,10a,11a,12a,13a,14a

- $n = 1, m = 2$ **9a**: X=Y=Cl ($m/z = 3626$), $M_w = 3625$
 10a: X=Cl, Y=I ($m/z = 3718$), $M_w = 3717$
 $n = 2, m = 2$ **11a**: X=Y=Cl ($m/z = 4212$), $M_w = 4211$
 12a: X=Cl, Y=I ($m/z = 4304$), $M_w = 4303$
 $n = 2, m = 3$ **13a**: X=Y=Cl ($m/z = 4798$), $M_w = 4797$
 14a: X=Cl, Y=I ($m/z = 4890$), $M_w = 4889$

Fig. 1 Molecular structures of porphyrin-bridged bis(tributylphosphine)platinum dimers and oligomers.

reactions of these complexes with substituted alkynes,^{29,36} we expected the formation of platinum-monochloroacetylides, diacetylides and long chain polymers (analogous to **2a'**) in the case of $[\text{PtCl}_2(\text{PPh}_3)_2]$, and of the hydride $[\text{PtH}\{\text{C}\equiv\text{C}-\text{Zn}(\text{por})-\text{C}\equiv\text{C}-\text{H}\}(\text{PPh}_3)_2]$ **2a''** in the case of $[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$. The complex *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ can afford arrays where the porphyrin units are in a *cis* arrangement, so allowing a different charge interaction between Pt and porphyrin; furthermore the hydride **2a''** was expected to be the precursor of controlled building block reactions, which should afford Pt-containing porphyrin arrays of defined molecular structure.

However, the reactivity of these bis(triphenylphosphine)platinum complexes toward **1a** is somewhat more complicated and, to some extent, surprising. Both platinum precursor complexes, under different reaction conditions, afford the soluble porphyrin-bridged platinum dimer **2b** (Scheme 1), although some differences appear in the optical and IR spectra, which will be discussed. Compound **2b**, obtained from *trans*- $[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$, shows λ_{max} 455, 630, 686 nm (UV/VIS spectrum) and 2090 ($\nu_{\text{C}\equiv\text{C}}$), 540 (overtone of the P-C₃ deformation mode of PPh₃) and 320 cm^{-1} ($\nu_{\text{Pt}-\text{Cl}}$) in the FTIR spectra. The bands at 540 and 320 cm^{-1} are medium intensity. As previously described for PBu₃ derivatives, *cis*-*trans* isomerization might have occurred and **2b** could be a mixture of the two isomers,

since *cis*-bis(triphenylphosphine)platinum complexes are characterized by an intense band at 540 cm^{-1} . The ¹H NMR spectrum confirms that no hydrido complex was formed (no resonances at high field); the chemical shift values and the relative intensities of the resonances support the formation of **2b**. The splitting of the signal due to the *meso*-hydrogens suggests the presence of both *cis* and *trans* isomers. The MALDI spectrum shows a low intensity peak at $m/z = 2033$ corresponding to the molecular weight of **2b'**, that is demetalated **2b**. This is not surprising because, under the experimental conditions, that is in the presence of benzoic acid matrix, the demetalation of the porphyrin likely occurs. The oligomer **3b**, part of the reaction products, is soluble in hot CH₂Cl₂ or CHCl₃ and is crystallized from CH₂Cl₂-methanol. The optical spectrum of **3b** shows a red shift to λ_{max} 464 nm, which indicates a higher degree of π conjugation, with respect to **2b**, as reported for ethyne-linked porphyrin dimers⁴ and polymers.²¹ The FTIR spectrum of **3b** shows a feature quite similar to that of **2b**, and the ¹H NMR spectrum indicates a 2:30 ratio of the integrals for the *meso* and phenyl hydrogens, supporting one $[\text{Pt}(\text{PPh}_3)_2]$ moiety for every porphyrin unit. However, the MALDI mass spectrum does not show an ionic species at $m/z = 2681$, the $[\text{M} - \text{H}]^+$ ion corresponding to the expected peak for **3b**. The observed ionic species at $m/z = 2338$ is consistent with **3b** that lost

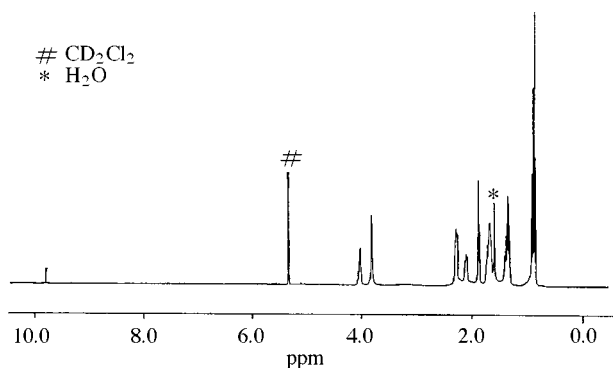


Fig. 2 Proton NMR spectrum of ethynyl porphyrin-bridged bis(tributylphosphine)platinum dimer **2a**.

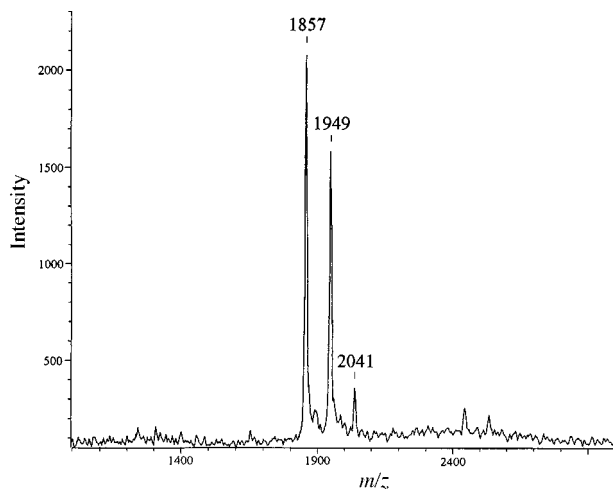


Fig. 3 The MALDI mass spectrum of platinum dimers **2a**, **3a** and **4a**.

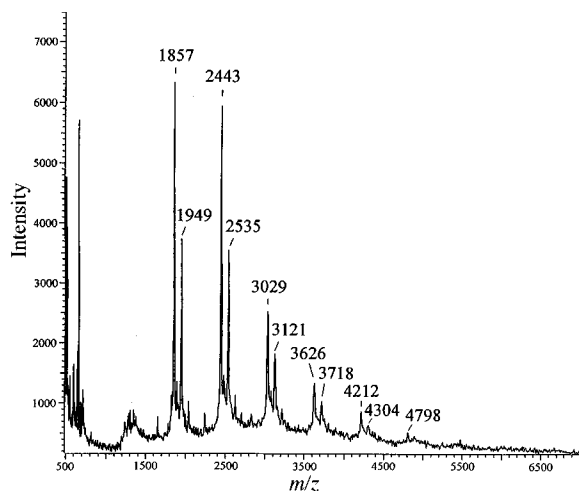


Fig. 4 The MALDI mass spectrum of ethynyl porphyrin-bridged bis(tributylphosphine)platinum oligomers.

chlorine, PPh_3 and Zn; this is not unusual for platinum(II) triphenylphosphine complexes, which undergo easy decomposition with release and recombination of PPh_3 with other species under ESI conditions.³⁷ However, the high intensity peak at $m/z = 1197$, corresponding to $[\text{H}-\text{C}\equiv\text{C}-\text{Zn}(\text{por})-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Zn}(\text{por})-\text{C}\equiv\text{C}-\text{H} + \text{Na}]^+$, can be considered a fingerprint of the original molecule.

The reaction of $\text{cis}-[\text{PtCl}_2(\text{PPh}_3)_2]$ with **1a** mainly affords **2b** and **3b**, although the reactivity of this complex is much lower (15 d are needed) and the yield of **3b** is favoured.

Conclusion

The synthesis and characterization of platinum(II) ethyne-linked porphyrin complexes and oligomers have been performed with the aim of finding convenient precursors for the preparation of extended π conjugated organometallic polymers which could give low band gap materials, suitable for applications in linear optics and photoluminescent devices.

The reactivity of the platinum complexes with diethynyl zinc porphyrin is extremely complicated, if compared with analogous reactions involving simple mono- and di-alkynes. However, dinuclear platinum molecules containing bridging ethynylporphyrins have been isolated, together with trinuclear platinum multiporphyrin arrays having a linear shape. Surprisingly, the tributylphosphine ligands lead to more stable and more easily characterizable compounds. All the complexes and oligomers were expected to be in *trans* or *cis* configuration, depending on the platinum precursor complex structures, *i.e.* $\text{trans}-[\text{PtCl}_2(\text{PBu}_3)_2]$, $\text{trans}-[\text{PtH}(\text{Cl})(\text{PPh}_3)_2]$ and $\text{cis}-[\text{PtCl}_2(\text{PPh}_3)_2]$. Isomerization occurs in a random way, leading to isomers, which can hardly be separated. However, in some cases, with the aid of XPS measurements,³⁴ some structures could be determined. Further work is now in progress in order to investigate optical properties of these dimers and oligomers, as well as their applications as sensitive membranes in sensor devices.

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