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Synthesis of 1-alkynyl(phthalocyaninato)iron(II) and -ruthenium(II) complexes

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Abstract

The preparation of dilithium[*trans*-bis(3,3-dimethyl-1-butynyl)phthalocyaninato]iron(II) (**IIIb**) is described. For comparison dilithium[*trans*-bis(phenylethynyl)phthalocyaninato]iron(II) (**IIIa**) was also made. Several 1-alkynyl(phthalocyaninato)ruthenium(II) compounds (**IVa,b**), of the first such species are reported. The products were obtained in high yields and characterized spectroscopically. The frequencies of the IR absorptions due to the stretching vibration of the C≡C bond are discussed.

1. Introduction

Some years ago we prepared bridged, stacked phthalocyaninosilicon, -germanium, and -tin compounds in which the acetylenic group (–C≡C–) was used as the bridging ligand [1]. These systems are regarded as model compounds for one-dimensional organic conductors [2]. A schematic drawing of these poly(*trans*-ethynyl)metallophthalocyanines is shown in Fig. 1(a). A series of *trans*-bis(1-alkynyl)metallophthalocyanines $\text{PcM}(\text{C}\equiv\text{C}-\text{R})_2$ [$\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{C}(\text{CH}_3)_3$], $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ (Fig. 1(b)) [3] as well as *trans*-bis-1-alkynyl(hemiporphyrizinato)germanium derivatives [3b] were also prepared, all by treating the phthalocyaninato(IVb)metal dichlorides with the appropriate alkynyl Grignard reagent. In the case of *trans*-bis-3,3-dimethyl-1-butynyl(hemiporphyrizinato)germanium, the structure was determined by an X-ray diffraction study [4].

In the last few years we have made and systematically characterized many low-dimensional bridged compounds $\text{MacM-L-MacM-L}\dots$, with $\text{Mac} =$, e.g., phthalocyanine (Pc), 1,2- and 2,3-naphthalocyanine (Nc) or tetrabenzoporphyrine (TBP), $\text{M} =$ transition metals, e.g., Fe, Ru, Os, Co, Rh, and $\text{L} =$, e.g., pyrazine, tetrazine, diisocyanobenzene or cyanide [5]. The isotype of bridged macrocyclic metal complexes

either with or without doping, exhibit good semiconducting properties. By appropriate substitution in the peripheral positions of the macrocycle these compounds can be made soluble in common organic sol-

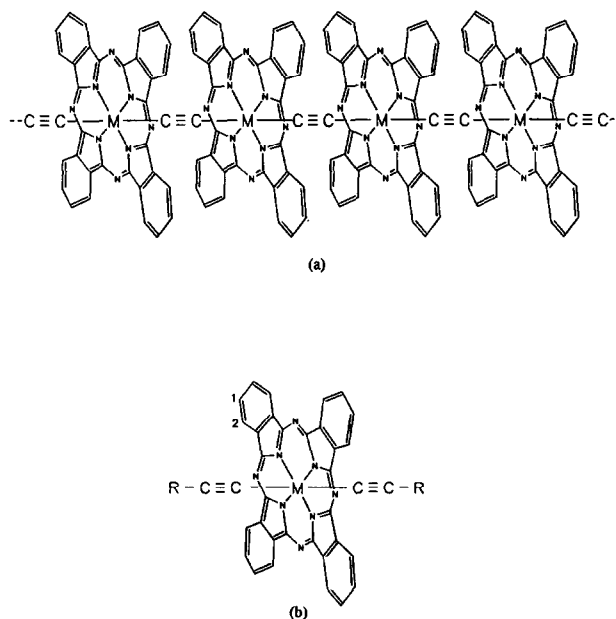


Fig. 1. (a) Poly(*trans*-ethynyl)metallophthalocyanine ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$); (b) *trans*-bis(1-alkynyl)metallophthalocyanine ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$).

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vents [6] and so used for producing Langmuir–Blodgett films [7] and also for non-linear optical materials [8].

In spite of the fact that so many of the bridged macrocyclic transition metal compounds mentioned above have been prepared and characterized, we have not yet been able to synthesize a phthalocyaninato-transition metal complex bridged with an acetylenic group to give rise to the type of structure shown in Fig. 1(a) with $M =$, e.g. Fe or Ru. For this type of (unknown) compound $[PcMC^2-]_n$ ($M =$ Fe, Ru), semi-conducting behaviour with a small band gap was predicted [9] or even metallic behaviour as indicated by EHMO calculations on a model polymer with tetraazaporphine (TAP) as macrocycle and iron(II) as a central metal atom [10].

The first phthalocyaninatoiron(II) complex with axial acetylenic substituents $Li_2[PcFe(C\equiv C-C_6H_5)_2] \cdot 7THF$ (**IIIa**) was reported by Taube *et al.* [11], and was obtained by treating phthalocyaninatoiron(II), $PcFe$ (**I**), with an excess of phenylethynyllithium, $LiC\equiv C-C_6H_5$ (**IIa**). The reaction between $PcFe(py)_2$ ($py =$ pyridine) and an excess of **IIa** led to $Li[PcFe(C\equiv C-C_6H_5)(py)] \cdot 4THF$ [11]. Another method of preparing 1-alkynyl (phthalocyaninato)iron(II) complexes was reported recently [12], involving reaction of $Na_2[PcFe] \cdot 5.5THF$ with 1-bromo-1-alkynes by oxidative addition to give the corresponding 1-alkynyl-iron(II)phthalocyanine complexes $Na[PcFeC\equiv C-R] \cdot nTHF$.

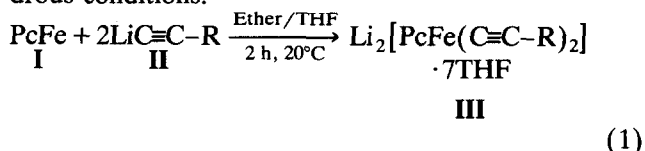
In this paper we describe attempts to synthesize acetylene-bridged macrocyclic transition metal compounds starting with the preparation and characterization of $Li_2[PcFe(C\equiv C-C(CH_3)_3)_2] \cdot 7THF$ (**IIIb**) with bisaxial metal–carbon (sp) bonds. The compound $Li_2[PcFe(C\equiv C-C_6H_5)_2] \cdot 7THF$ (**IIIa**) has also been synthesized, so that the stability of the iron–carbon σ bond with different substituents on the alkynyl C_{sp} atom of the bisaxial ligand could be examined. The influence of the size of substituents on the solubility of the complexes has been examined. Furthermore, we report for the first time on our attempts to prepare 1-alkynyl(phthalocyaninato)ruthenium(II) complexes (**IVa,b**) starting from phthalocyaninoruthenium(II), $PcRu$ (**V**).

2. Results and discussion

2.1. Synthesis and properties of dilithium[trans-bis(1-alkynyl)phthalocyaninato]iron(II) (**IIIa,b**)

High yields of dilithium[trans-bis(1-alkynyl)phthalocyaninato]iron(II) (**IIIa,b**) were obtained by a procedure analogous to that of Taube *et al.* [11] involving treatment of phthalocyaninatoiron(II), $PcFe$ (**I**), with an excess of the appropriate organolithium compound

(**II**) in ether/THF at room temperature under anhydrous conditions:



where $R = C_6H_5$ (**IIa/IIIa**) and $R = -C(CH_3)_3$ (**IIb/IIIb**).

The 1-alkynyl lithium compounds $LiC\equiv C-C_6H_5$ (**IIa**) and $LiC\equiv C-C(CH_3)_3$ (**IIb**) are soluble in THF, so that the excess of **IIa,b** can be removed by washing the dark blue microcrystalline product (**IIIa,b**) thoroughly with THF.

Both **IIIa** and **IIIb** are highly sensitive towards moisture and oxygen. Generally, a heterolytic cleavage of the iron–carbon σ bond occurs rapidly in protic solvents at room temperature to give $PcFe$ (**I**) and the corresponding alkyne, but when suitably stored the monomers **IIIa,b** show remarkable thermal stability. Compounds **IIIa** and **IIIb** are nearly insoluble in polar aprotic solvents such as THF, dioxane, DMF and benzene.

The (1-alkynyl)-iron compounds **IIIa,b** were characterized by elemental analyses, IR-spectroscopy and hydrolytic and thermal decomposition studies. It was not possible to investigate the complexes **IIIa,b** by NMR-spectroscopic methods because of their low solubility in common organic solvents, and also their low stability.

The IR spectra of **IIIa** and **IIIb** showed the absorption of the $C\equiv C$ bond (see Table 1). An additional absorption at 1070 cm^{-1} (in comparison with $PcFe$) is characteristic of hexacoordination for iron(II) in these complexes.

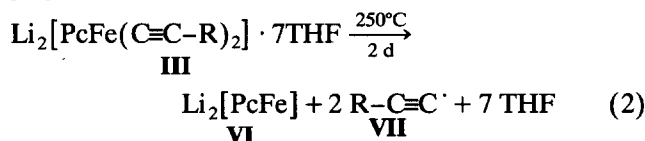
TABLE 1. The $C\equiv C$ stretching vibration frequencies $\nu(C\equiv C)$ of the 1-alkynyl complexes and the corresponding acetylenes. The corresponding data for several other IA- and IIA-metal-phenylethynyl complexes are also shown

Compound	$\nu(C\equiv C)$ [cm^{-1}]	Ref.
$H-C\equiv C-C_6H_5$	2110 ^a	
$Li[PcFe(C\equiv C-C_6H_5)py] \cdot 4THF$	2088 ^b	11
$Li_2[PcFe(C\equiv C-C_6H_5)_2] \cdot 7THF$	2080 ^c	
$Li[PcRuC\equiv C-C_6H_5] \cdot xTHF$	2062 ^b	
$LiC\equiv C-C_6H_5$	2036 ^c	15a
$NaC\equiv C-C_6H_5$	2018 ^b	15a
$KC\equiv C-C_6H_5$	2000 ^b	15a
$Ca(C\equiv C-C_6H_5)_2$	2036 ^b	15b
$Sr(C\equiv C-C_6H_5)_2$	2023 ^b	15b
$Ba(C\equiv C-C_6H_5)_2$	2017 ^b	15b
$H-C\equiv C-C(CH_3)_3$	2106 ^a	
$Li_2[PcFe(C\equiv C-C(CH_3)_3)_2] \cdot 7THF$	2077 ^c	
$Li[PcRuC\equiv C-C(CH_3)_3] \cdot xTHF$	2072 ^c	
$Li[PcRuC\equiv C-C(CH_3)_3] \cdot xTHF$	2065 ^b	

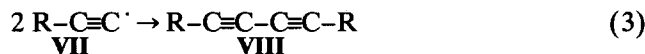
^a Neat. ^b Nujol. ^c KBr.

The hydrolysis of the monomers **IIIa,b** provides further evidence of their structure [11]. The compounds **IIIa** and **IIIb** were treated with aqueous HCl in THF in a sealed tube for 6 h at room temperature. The filtrate was analyzed by GLC. Phenylacetylene and 3,3-dimethyl-1-butyne were identified by comparison with authentic samples. The residue was identified as PcFe (I).

The thermal decomposition of **IIIa,b** takes place through a homolytic splitting of the iron–carbon σ bond, whereby reduced PcFe, $\text{Li}_2[\text{PcFe}]$ (**VI**), is formed [11]:



The resulting alkynyl radicals (**VII**) undergo dimerization:



The stable, white diynes **VIII** were characterized by IR, UV and ^1H NMR spectroscopy, as well as by mass spectrometry.

Besides the thermal decomposition experiments we obtained additional information on the number of solvent molecules per complex from the mass loss on heating of the compounds **IIIa** and **IIIb**, which were consistent with the formulae shown.

2.2. Reaction of 1-alkynyl lithium compounds (**IIa,b**) with phthalocyaninoruthenium(II), PcRu (**V**)

Ruthenium complexes of the type PcRuL_2 and $[\text{PcRuL}]_n$ are more stable than the well-studied iron derivatives towards oxidation of the central metal atom [$\text{M}^{\text{II}} \rightarrow \text{M}^{\text{III}}$] and they show a stronger complex stability due to the larger radius of the ruthenium ion. These facts led us to examine the 1-alkynyl(phthalocyaninato)-ruthenium(II) complexes (**IV**).

Reaction of PcRu (**V**) [13] in THF with $\text{LiC}\equiv\text{C}-\text{C}_6\text{H}_5$ (**IIa**) in ether, under the conditions used to prepare the (1-alkynyl)-iron compounds **IIIa** and **IIIb**, produced a purple microcrystalline powder. Owing to its quite high solubility in common organic solvents it was possible to obtain a ^1H NMR spectrum, and this showed that the product was a mixture of two complexes $\text{PcRu}(\text{thf})_2$ (**IX**) and a 1-phenylethynyl(phthalocyaninato)ruthenium(II) complex (**IVa**). To prove the identity of **IX**, this complex was prepared by reaction of PcRu (**V**) with an excess of THF at room temperature and the ^1H NMR spectra were compared.

To avoid the formation of $\text{PcRu}(\text{thf})_2$ (**IX**), a mixture of PcRu (**V**) and a large excess of $\text{LiC}\equiv\text{C}-\text{R}$ [$\text{R} = \text{C}_6\text{H}_5$ (**IIa**), $\text{C}(\text{CH}_3)_3$ (**IIb**)] in ether was initially

stirred for 1 h, then some THF was added and the solution stirred for 2 h (THF is necessary to remove the excess of the organolithium compounds **IIa** and **IIb**, which are both insufficiently soluble in ether). After filtration the residue was washed with ether and THF. The dark blue microcrystalline 1-alkynyl-(phthalocyaninato)ruthenium(II) complexes **IVa,b** are relatively stable, and the solubility in chloroform is sufficient to obtain ^1H NMR data.

The ^1H NMR spectra showed diamagnetic ring-current shifts such as are found in other PcRuL_2 complexes, e.g. $\text{PcRu}(\text{NC}-\text{C}_6\text{H}_5)_2$ [14]. The spectra consist of the usual two AA'XX' patterns (1-H: $\delta = 8.05\text{--}8.10$; 2-H: $\delta = 9.35\text{--}9.40$, in Pc, Fig. 1(b)) at low field, while the axial ligands are considerably shielded by the Pc ring system. The shorter the distance between the protons of the ligand and the centre of the metallo-phthalocyanine the larger is the shift of the resonances to higher field. The signals from protons of the phenylethynyl ligand in the complex **IVa** appeared at $\delta = 6.25$, 6.10 and 4.00, whereas in the case of the free ligand, phenylacetylene, they appear at $\delta = 7.50$, 7.30 (aromatic protons) and 3.00 (acetylenic proton). The ^1H NMR spectrum of **IVb** gave a signal at $\delta = -1.08$ from the protons of the tert-butyl group of the coordinated 3,3-dimethyl-1-butyne ligand, considerably shifted compared with that from the free ligand, which appears at $\delta = 1.20$. Integration of the spectra clearly shows that both the complexes **IVa,b** have a 1/1 $\text{PcRu}/\text{C}\equiv\text{C}-\text{R}$ stoichiometry. It is known that ruthenium(II) prefers an octahedral coordination sphere. Consequently, in addition to the 1-alkynyl ligand there is a further ligand, probably a solvent molecule (THF), coordinated at the central metal atom. But from the ^1H NMR spectra obtained it is not possible to decide what kind of ligand is in the sixth coordination site.

The IR spectra of **IVa,b** showed the characteristic absorption band of the $\text{C}\equiv\text{C}$ bond (see Table 1). The frequencies of the absorptions due to the $\text{C}\equiv\text{C}$ bond are discussed below. The different intensities of the bands at about 776 and 756 cm^{-1} showed that in these complexes the ruthenium(II) ion is hexacoordinated; in the case of analytically pure PcRu (**V**) these absorptions have equal intensities.

Analogous to the monomers $\text{Li}_2[\text{PcFe}(\text{C}\equiv\text{C}-\text{R})_2] \cdot 7\text{THF}$ (**IIIa,b**) the hydrolysis of the compounds **IVa,b** gave PcRu (**V**) and the corresponding acetylenes, which were analyzed by GLC-MS. This is further evidence for the presence of a ruthenium–acetylide σ bond.

We conclude that the reaction of PcRu (**V**) with $\text{LiC}\equiv\text{C}-\text{R}$ [$\text{R} = \text{C}_6\text{H}_5$ (**IIa**), $\text{R} = \text{C}(\text{CH}_3)_3$ (**IIb**)] leads to the compounds $\text{Li}[\text{PcRuC}\equiv\text{C}-\text{R}] \cdot x\text{THF}$ (**IVa,b**), whereas that of PcFe (**I**) gives $\text{Li}_2[\text{PcFe}(\text{C}\equiv\text{C}-\text{R})_2] \cdot 7\text{THF}$ (**IIIa,b**).

2.3. Discussion of the IR data

The IR spectra of the compounds $\text{Li}_2[\text{PcFe}(\text{C}\equiv\text{C}-\text{R})_2] \cdot 7\text{THF}$ (**IIIa,b**) and $\text{Li}[\text{PcRuC}\equiv\text{C}-\text{R}] \cdot x\text{THF}$ (**IVa,b**) showed a characteristic absorption band due to the stretching vibration of the $\text{C}\equiv\text{C}$ bond $\nu(\text{C}\equiv\text{C})$. The data are given in Table 1. The corresponding absorptions are also given for IA- and IIA-metal-phenylethynyl complexes [15] and for the free acetylenes.

All (1-alkynyl)transitionmetallophthalocyanines showed a decrease in $\nu(\text{C}\equiv\text{C})$ relative to the free acetylenes. This cannot be attributed to $d_{\pi}-p_{\pi}$ interactions (back donation), which would lead to a decrease in the $\text{C}\equiv\text{C}$ bond order. This assumption is supported by the $\nu(\text{C}\equiv\text{C})$ data of the IA- and IIA-metal-phenylethynyl compounds in which there cannot be π -interactions. These compounds show an even stronger decrease in $\nu(\text{C}\equiv\text{C})$ when compared with phenylacetylene (see Table 1).

The shift of frequencies of the absorption band due to the $\text{C}\equiv\text{C}$ bond depends only on the particular strength of the metal-carbon σ -interaction [16]. In the phenylacetylide anion the highest occupied σ orbital is weakly antibonding. Consequently, the high effective density of electrons at the carbon leads to a destabilization of the bonding MOs, and hence to a relatively low $\nu(\text{C}\equiv\text{C})$. In the formation of a covalent bond to the metal, electron density is transferred from the acetylide carbon to the metal. The higher the electronegativity and the valence of the coordinative bonded metal and the smaller the radius of the metal ion, the greater is the transfer of electrons from the acetylide carbon to the metal. This leads to a stabilization of the acetylide triple bond and consequently to an increase in $\nu(\text{C}\equiv\text{C})$.

In accordance with theory, the absorption band due to the $\text{C}\equiv\text{C}$ bond of the (1-alkynyl)-ruthenium compounds **Va** and **Vb** appears at lower frequency than that for the $\nu(\text{C}\equiv\text{C})$ absorption of the corresponding iron-acetylide complexes (**IIIa** and **IIIb**) since the ionic radius of iron(II) is smaller than that of ruthenium(II).

3. Experimental details

The IR spectra were recorded on a Bruker FT-IR IFS 48 and the ^1H NMR spectra on a Bruker AC 250. The analytical GLC was done with a Hewlett-Packard 5720 A (Carbowax 20 M) and the GLC-MS with a Hewlett-Packard 5890 A chromatograph linked to a Hewlett-Packard 5970 mass spectrometer. Elemental analyses were carried out with Carlo Erba Elemental Analyzers 1104 and 1106.

All organometallic reactions were conducted under dry argon, with exclusion of moisture and air, using anhydrous solvents. PcFe (**I**) [17] and PcRu (**V**) [13] were prepared as described previously. The 1-alkynyl-

lithium reagents **IIa** and **IIb** were prepared by reaction of the appropriate alkyne with *n*-butyllithium in ether at -78°C .

3.1. Dilithium[trans-bis(1-alkynyl)phthalocyaninato]iron(II) (**IIIa,b**)

3.1.1. General procedure

The 1-alkynyllithium compound **IIa** or **IIb** (25 mmol) in ether (45 ml) was added dropwise to a suspension of PcFe (**I**, 8.8 mmol) in THF (50 ml) at room temperature. The mixture was stirred for 1 h and filtered. The dark blue solid left on the filter was washed thoroughly with THF and dried under vacuum.

3.1.2. $\text{Li}_2[\text{PcFe}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)_2] \cdot 7\text{THF}$ (**IIIa**)

Yield: 5.0 g (44% based on PcFe). Anal. Found: C, 70.6; H, 6.3; N, 8.8. Calc.: C, 70.1; H, 6.6; N, 8.8%. IR (KBr): 690w, 733s, 755m, 783w, 905w, 1017w (sh), 1050m (sh), 1070m, 1098m, 1118s, 1163m, 1205w, 1285m, 1333s, 1419m, 1465w (sh), 1480m, 1508s, 2080w $\nu(\text{C}\equiv\text{C})$, 2870s, 2950s, 3044s cm^{-1} . Mass loss by thermal decomposition: Found, 39.00 (7.15 THF). Calc.: 39.83% (7 THF).

3.1.3. $\text{Li}_2[\text{PcFe}(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3)_2] \cdot 7\text{THF}$ (**IIIb**)

Yield: 4.5 g (41% based on PcFe). Anal. Found: C, 69.8; H, 7.2; N, 9.1. Calc.: C, 69.2; H, 7.3; N, 9.0%. IR (KBr): 733s, 757m, 783w, 883w (sh), 916w, 965w, 1008w (sh), 1070m, 1095m, 1120s, 1163m, 1205w, 1245w, 1284m, 1333s, 1420m, 1470m, 1513s, 2077w $\nu(\text{C}\equiv\text{C})$, 2834s, 2960s, 3057s cm^{-1} . Mass loss by thermal decomposition: Found, 40.40 (7 THF). Calc.: 40.40% (7 THF).

3.2. 1-Alkynyl(phthalocyaninato)ruthenium(II) complexes (**IVa,b**)

3.2.1. General procedure

PcRu (**V**, 0.16 mmol) was suspended in ether (5 ml). The appropriate 1-alkynyllithium compound **IIa,b** (5 mmol) in ether (30 ml) was added and the mixture was stirred for 1 h at room temperature. THF (15 ml) was then added, the mixture stirred for 2 h and filtered. The dark blue microcrystalline powder was washed thoroughly with ether and THF and then dried under vacuum.

3.2.2. $\text{Li}[\text{PcRuC}\equiv\text{C}-\text{C}_6\text{H}_5] \cdot x\text{THF}$ (**IVa**)

Yield: 115 mg. ^1H NMR (CDCl_3): δ = 9.36 (m, 8H) and 8.09 (m, 8H) (Pc-protons); 6.25 (m, 1H), 6.10 (m, 2H) and 4.00 (m, 2H) (coordinated phenylethynyl). IR (Nujol): 692w, 735s, 756m, 776w, 791w, 882w, 910w, 982m, 1066s, 1079m, 1123s, 1170s, 1248w, 1288m, 1328m, 1415m, 1489s, 2062w $\nu(\text{C}\equiv\text{C})$ cm^{-1} .

3.2.3. $\text{Li}[\text{PcRuC}\equiv\text{C}-\text{C}(\text{CH}_3)_3] \cdot x\text{THF}$ (**IVb**)

Yield: 100 mg. ^1H NMR (CDCl_3): $\delta = 9.32$ (m, 8H) and 8.04 (m, 8H) (Pc-protons); -1.08 (s, 9H) (coordinated 3,3-dimethyl-1-butynyl). IR (Nujol): 629m , 693w , 728s , 734s , 752m , 771w , 887w , 911w , 940w , 973w , 1005w , 1040w , 1065m , 1082w , 1122s , 1170m , 1204w , 1241w , 1287m , 1329m , 1414m , 1486s , $2065 \nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$.

3.2.4. $\text{PcRu}(\text{thf})_2$ (**IX**)

PcRu (**V**, 0.16 mmol) was stirred in THF (50 ml) for 2 h at room temperature. The dark blue solution was filtered and the solvent was evaporated. A purple microcrystalline powder was obtained in quantitative yield. ^1H NMR (CDCl_3): $\delta = 9.20$ (m, 8H) and 7.90 (m, 8H) (Pc-protons); -0.70 (m, 8H) and -1.60 (m, 8H) (coordinated THF-protons).

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