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Note

# A new phthalocyanine–ferrocene conjugated dyad

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## Abstract

The synthesis and optical properties of a new phthalocyanine–ferrocene conjugated dyad are reported. Using a Pd(0)-catalysed cross-coupling reaction, an unsymmetrical substituted metallophthalocyanine linked to a ferrocene subunit by an arylene–alkynylene spacer has been prepared. The electronic properties of this linearly π-conjugated compound and related ones were investigated by UV–visible spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Phthalocyanines; Ferrocene; Arylene–alkynylene; Pd(0)-catalysed cross-coupling

## 1. Introduction

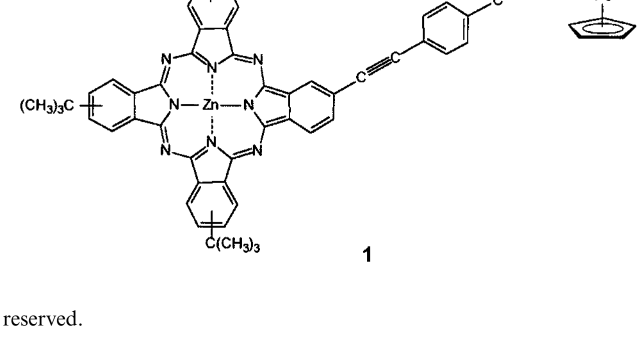
Phthalocyanines (Pcs) have been an area of increasing research for several years, due to their applicability in a variety of fields, such as liquid crystals, semiconductors, non-linear optics and electron transfer, among others [1]. Pcs are compounds of special interest for their unique redox [2] and photophysical properties. On the other hand, it is well known that ferrocene exhibits chemical stability and well defined electrochemical properties, and therefore it has been widely used in the construction of multicomponent systems [3].

Taking into account the particular electronic characteristics of phthalocyanines, ferrocene-bridge–phthalocyanine dyads combining two redox active centres should be an excellent model for studying intramolecular electron transfer processes.

Until now, only a few examples of covalently linked phthalocyanine–ferrocene systems have been reported [4,5], and most of them are not conjugated systems. Recently [5], we have reported on phthalocyanine–ferrocene dyads and triads in which both subunits are bound together through ethenyl spacers.

It is well known, that polyacetylene spacers operate as effective bridges for conducting electronic charge between redox active terminal units. Furthermore, it is possible to modulate the electronic coupling properties of such systems by introducing polycyclic hydrocarbons, as phenyl rings, along the wire between the two terminal units [6]. These linkers fulfil important requisites such as rigidity, linearity and synthetic versatility.

Following our interest in exploiting electronic and photonic interactions between individual subunits in multicomponent systems [7], we report herein the synthesis and optical properties of a new phthalocyanine–ferrocene conjugate consisting of an unsymmetrical substituted metallophthalocyanine linked to a ferrocene subunit by an arylene–alkynylene spacer.



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To the best of our knowledge this is the first phthalocyanine–ferrocene dyad in which the active centres are connected by a polyalkynyl spacer [8].

## 2. Results and discussion

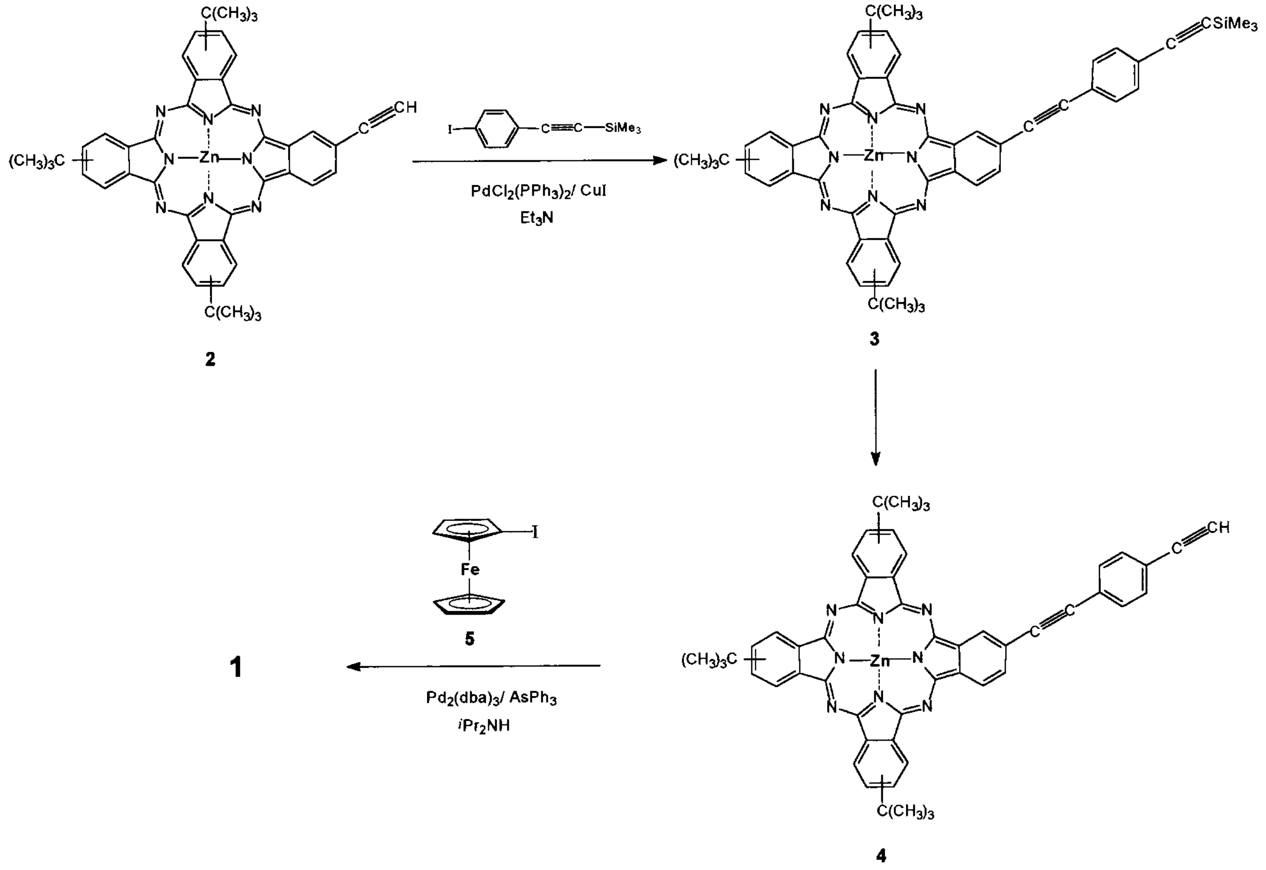
Phthalocyaninato zinc(II)-ferrocene dyad (**1**) has been prepared from ethynyl-Pc (**2**), previously described by us [9], in a three-step sequence (Scheme 1).

Thus (tri-*tert*-butyl-ethynylphthalocyaninato) zinc(II) (**2**) [9] (mixture of isomers) was reacted with 4-trimethylsilylethynyliodobenzene [10] using Sonogashira conditions [$PdCl_2(PPh_3)_2$, CuI] employing triethyl amine as base and affording the corresponding cross-coupling compound **3** in good yield. The $^1$H-NMR spectrum of this compound shows one singlet at $\delta$ 0.4 ppm for the trimethysilyl group and a large number of signals for the *tert*-butyl groups, pointing out the mixture of regioisomers that constitute compound **3**.

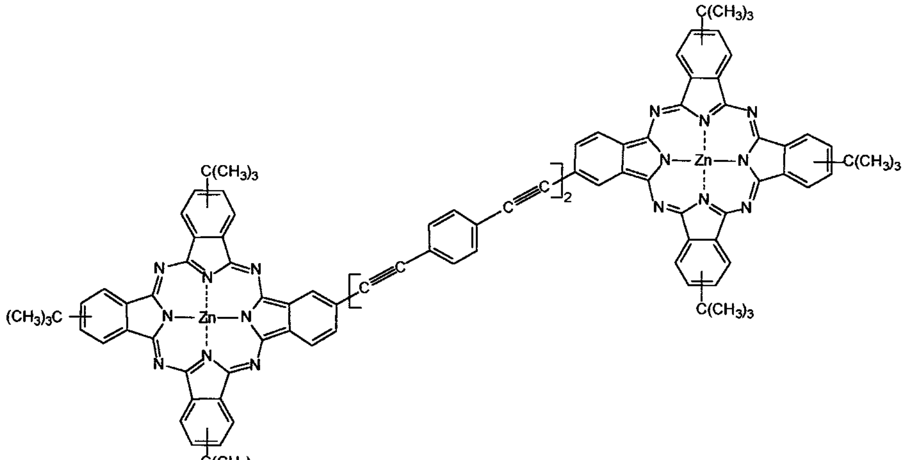
The trimethylsilyl group of compound **3** could be quantitatively removed by treatment with tetrabutyl ammonium fluoride in tetrahydrofurane solution affording the terminal alkyne **4**. In the $^1$H-NMR spectrum of **4** a new signal appears at 3.3 ppm corresponding to the proton of the terminal ethynyl group.

The synthesis of the metallophthalocyanine–ferrocene system **1** has been carried out following a modified Sonogashira procedure. The reaction between phthalocyanine **4** and iodoferrocene **5** using a catalyst formed by tris(dibenzylidenacetone)dippalladium(0) [$Pd_2(dba)_3$] and triphenylarsine ($AsPh_3$) in a freshly distilled and deaerated diisopropyl amine afforded compound **1** in moderate yield.

Although in the present case a copper-free palladium catalyst was used to perform the cross-coupling, in order to minimize the homocoupling reaction of the phthalocyanine **4**, compound **6** was always detected under the employed conditions. The isolation of ferrocene–metallophthalocyaninato dyad **1** from the reaction mixture was carried out by column chromatography. In this process compound **6** could also be isolated. In the $^1$H-NMR spectrum of **1**, it is possible to assign the signals corresponding to the ferrocene subunit, namely two multiplets centred at $\delta$ 4.2 and 4.6 ppm for the substituted cyclopentadienyl ring and a broad singlet at $\delta$ 4.4 ppm for the unsubstituted one.



Scheme 1.



**6**

The UV–visible spectra of compounds **1**, **2**, **4** and **6** are depicted in Fig. 1. The position of the Soret band (B band) in compounds **1** and **4** is quite similar to that of the parent ethynyl-phthalocianinato **2**. However, while the ethynyl-Pc **2** shows only a Q band at 684 nm, as is usual in metallated Pcs, compound **1** exhibits a split Q band (680 and 692 nm) somewhat shifted to the red. However, there are no remarkable differences between the UV–visible spectra of compounds **1** and **4**, thus indicating that the splitting is a consequence of the increasing conjugation of the Pc-system and not of an electronic coupling between the Pc and the ferrocene subunits. Taking into account this fact and references in the literature [4,5], it is possible to suggest that the ferrocenyl group is electronically independent in compound **1**.

The UV–visible spectrum of the homocoupling compound **6** also shows a split Q-band, as well as a broadening and red-shifting of this absorption with regard to compound **2**. This effect has been observed in

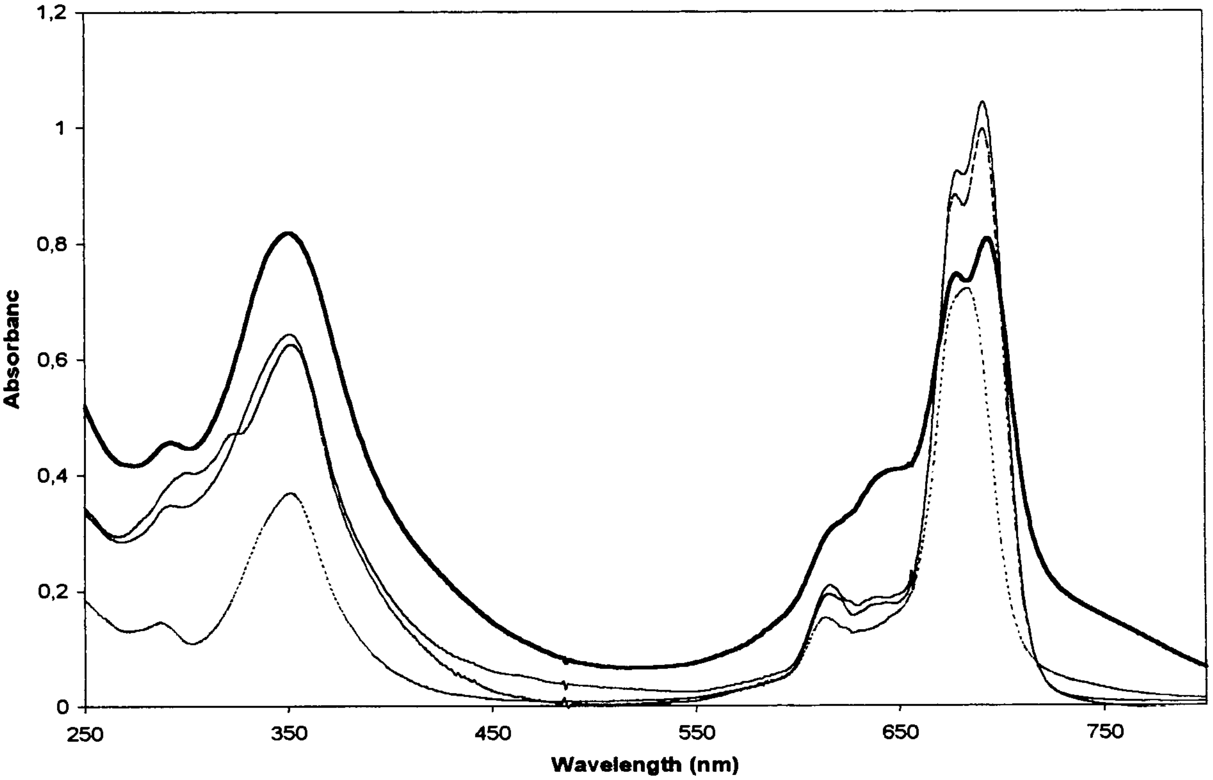
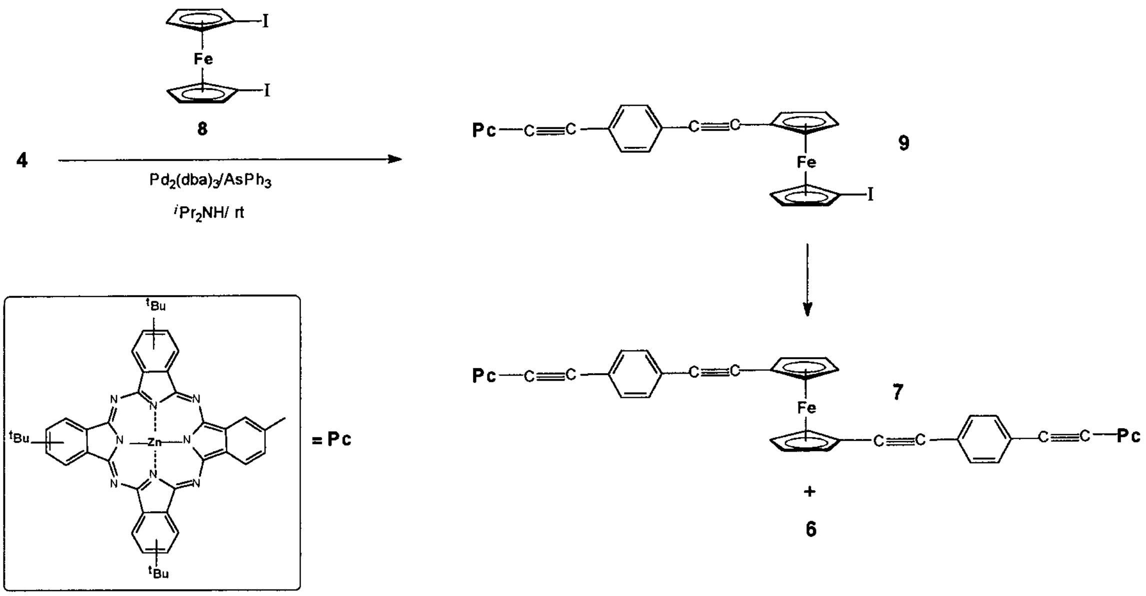


Fig. 1. Electronic spectra in $CHCl_3$ of **1** ($1.4 \times 10^{-5}$ mol dm$^{-3}$) (—), **2** ($2.9 \times 10^{-5}$ mol dm$^{-3}$) (···), **4** ($3.7 \times 10^{-5}$ mol dm$^{-3}$) (- - -), and **6** ($8.6 \times 10^{-5}$ mol dm$^{-3}$) (—).



Scheme 2.

other conjugated systems previously described by our group and it has been explained as the result of the extended conjugation of the system [9,11]. The close resemblance between the UV–visible spectra of **1** and **6**, the latter having a higher conjugation degree, suggests a saturation of the optical properties in the series. This effect had been already observed in related diethynylethene bisphthalocyaninato complexes [12].

Attempts to prepare triad **7** (Scheme 2) by reaction of diiodoferrocene (**8**) with two molar equivalents of phthalocyaninato **4** led to the monosubstituted compound **9** in moderate yield ($Pd_2(dba)_3$–$AsPh_3$, room temperature, 12 h, 48%) together with an important amount of unreacted diiododerivative **8** and compound **6**. The second cross-coupling reaction on the ferrocene seems to be more difficult, thus facilitating the formation of the dimer **6**. By performing the reaction under stronger reaction conditions ($Pd_2(dba)_3$–$AsPh_3$, 36 h rt and then 12 h 50 °C) compound **7** could be detected in the reaction mixture by mass spectrometry but the synthetic method is revealed to be inadequate.

## 3. Conclusions

A novel type of linearly π-conjugated molecular dyad, in which a Pc chromophore is linked to a ferrocene moiety by an arylene–alkynylene spacer has been prepared. UV–visible investigations did not reveal a significant interaction between the Pc and the metallocene. Electrochemical studies are now underway in order to detect potential electronic interactions between the two electroactive subunits.

## 4. Experimental

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer. The $^1$H-NMR spectra were obtained on a Bruker AC300. UV–visible spectra were recorded on a Perkin–Elmer Lambda 6 spectrometer using chloroform as solvent. The mass spectra were determined on a VG AutoSpec spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyser.

Reactions were performed under an atmosphere of dry nitrogen. Solvents were distilled prior to use from an appropiate drying agent. Chromatographic purification were performed on silica gel columns (Merck, 230–400 mesh) and aluminium oxide neutral (70–230 mesh) with the indicated eluents. 4-trimethylsilylethynyliodobenzene [10], 1,1′-diiodoferrocene [13] and (tri-*tert*-butyl-ethynylphthalocyaninato)zinc(II) (**2**) [9] were prepared according to literature procedures.

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

### *4.1. 1-Iodoferrocene*

This compound was synthesized using a modified literature procedure [14]. Ferrocene (0.5 g, 2.68 mmol) was stirred for 30 min in 2.5 ml of dry tetrahydrofurane and 2.5 ml of dry hexane under argon at rt and then cooled to 0 °C. A 1.5 ml volume of a 1.5 M solution of $^t$BuLi in pentane (2.23 mmol) was added dropwise during 30 min. The mixture was stirred another 90 min at this temperature and then was cooled to − 78 °C (dry ice/acetone bath). To this cooled solution was rapidly added a solution containing 1.06 g of iodine (4.17 mmol) dissolved in 20 ml of dry diethyl ether during 15 min. After the resulting mixture was stirred at − 78 °C for 1 h, it was allowed to warm slowly to rt, at which point 10 ml of water was added, and the solution stirred for additional 15 min. The mixture was extracted with $CH_2Cl_2$ (3 × 25 ml), washed with water, and brine and dried over $MgSO_4$. The product was purified by column chromatography in aluminium oxide using *n*-hexane as eluent. Yield 42%, orange needles. M.p. 45 °C. [lit. 44–45 °C].

$^1$H-NMR ($CDCl_3$): $\delta$ 4.1 (t, 2H), 4.2 (s, 5 H), 4.4 (t, 2H).

### 4.2. *Tri-tert-butyl-{ethynyl-2-phenyl-[4-ethynyl-2-(trimethylsilyl)]}phthalocyaninatozinc(II)* (***3***)

A mixture of (tri-*tert*-butylethynylphthalocyaninato) zinc(II) (**2**) (114 mg, 0.12 mmol) and 4-trimethylsilylethynyliodobenzene (39 mg, 0.12 mmol) was stirred under argon at 40 °C for 10 h, in freshly distilled and deaerated $Et_3N$ in the presence of $[Pd(PPh_3)_2Cl_2]$ (18 mg, 10%) and CuI (5 mg). The solution obtained was evaporated to dryness. The residue was extracted with $CH_2Cl_2$ and washed with water. The product was purified by chromatography (silica gel, toluene–isopropyl alcohol 100:1). Yield 76%, dark-blue powder. M.p. > 250 °C.

$^1$H-NMR ($CDCl_3$): $\delta$ 0.4 [s, 9H, $Si(CH_3)_3$], 1.4–1.6 (m, 27 H, $^t$Bu), 7.3–8.2 (m, 16H, ArH). UV–visible ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$ dm$^3$ mol$^{-1}$ cm$^{-1}$) 290 (4.92), 350 (5.05), 615 (4.62), 679 (5.25), 692 (5.32). IR (KBr) $\nu$ 2954, 2153 (C≡C), 1612 (C=N), 1087, 862, 834 cm$^{-1}$. FAB$^+$-MS (m-NBA) $m/z$ (%) 941 (100) $[(M+H)^+]$. Anal. Calc. for $C_{57}H_{52}N_8SiZn{\cdot}2H_2O$: C, 69.53; H, 5.68; N, 10.73. Found: C, 69.96; H, 5.77, N, 11.45%.

### 4.3. *Tri-tert-butyl-[ethynyl-2-phenyl-(4-ethynyl)] phthalocyaninatozinc(II)* (***4***)

An equimolecular amount of tetrabutyl ammonium fluoride in tetrahydrofuran solution (1 M) was added dropwise to a stirred solution of compound **3** (0.09 mmol) dissolved in anhydrous tetrahydrofurane during 10 min. After 15 min the solvent was removed and the residue was extracted with toluene. After drying the organic layer with sodium sulphate and evaporating the solvent, the product was purified by chromatography on silica gel using $CH_2Cl_2$ as eluent. Yield 99%, dark-blue powder. M.p. > 250 °C.

$^1$H-NMR ($CDCl_3$): $\delta$ 1.5–1.9 (m, 27 H, $^t$Bu), 3.3 (s, 1H, C≡CH), 7.4–8.6 (m, 16H, ArH). UV–visible ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$ dm$^3$ mol$^{-1}$ cm$^{-1}$) 352 (5.14), 615 (4.66), 678 (5.33), 692 (5.39); IR (KBr) $\nu$ 2953, 2153 (C≡C), 1611 (C=N), 1087, 831,746 cm$^{-1}$. FAB-MS (m-NBA) $m/z$ (%) 870 (100) $[(M+H)^+]$. Anal. Calc. for $C_{54}H_{44}N_8Zn{\cdot}3H_2O$: C, 70.16; H, 5.45; N, 12.12. Found: C, 70.60; H, 5.34, N, 11.75%.

### 4.4. *Tri-tert-butyl-2-ethynyl-[4-(ferrocenylethynyl) phenyl]phthalocyaninatozinc(II)* (***1***)

1-Iodoferrocene (80 mg, 0.25 mmol) was stirred in freshly distilled and deaerated diisopropylamine in the presence of $Pd_2(dba)_3$ (20 mg) and $AsPh_3$ (50 mg). Compound **4** (110 mg, 0.125 mmol) was then added and the mixture was stirred under argon atmosphere at 90 °C for 10 h. The green solution was evaporated to dryness, extracted with dichloromethane, and washed with water. The compound was purified by column chromatography (silica gel toluene–isopropyl alcohol 40:1). Yield 27% (35 mg), dark green powder. M.p. > 250 °C.

$^1$H-NMR ($CDCl_3$): $\delta$ 1.3–1.8 (m, 27 H, $^t$Bu), 4.18 (m, 2H, FcH), 4.35 (s broad, 5H, FcH), 4.61 (m, 2H, FcH), 7.6–8.9 (m, 16H, ArH). UV–visible ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$ dm$^3$ mol$^{-1}$ cm$^{-1}$) 351 (4.66), 616 (4.17), 680 (4.81), 692 (4.87). IR (KBr) $\nu$ 2923, 2212 (C≡C), 1635 (C=N), 1088, 802 cm$^{-1}$. Anal. Calc. for $C_{64}H_{52}N_8ZnFe{\cdot}3H_2O$: C, 69.35; H, 5.27; N, 10.11. Found: C, 69.56; H, 5.67, N, 10.45%.

### 4.5. *Bis-[(tri-tert-butylphthalocyaninato)zinc(II)]-1,4-bis-[phenyl-(4-ethynyl)]butadiyne* (***6***)

From the chromatographic separation performed above before isolation of compound **1**, product **6** was eluted. Yield 19% (20 mg), dark green powder. M.p. > 250 °C.

$^1$H-NMR ($CDCl_3$): $\delta$ 1.4–1.9 (m, 54H, $^t$Bu), 6.7–9.4 (m, 32H, ArH). UV–visible ($CHCl_3$) $\lambda_{max}$ (log $\varepsilon$ dm$^3$ mol$^{-1}$ cm$^{-1}$) 351 (4.3), 679 (4.1), 694 (4.2). IR (KBr) $\nu$ 2955, 2205 (C≡C), 1615 (C=N), 1046, 830, 741 cm$^{-1}$; HRMS-MALDI-TOF (dithranol) calc. for $C_{108}H_{86}N_{16}Zn_2$ 1734.580 (exact), found 1734.583.

## Acknowledgements

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