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Cobaltacarborane–phthalocyanine conjugates: Syntheses and photophysical properties

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ABSTRACT

Syntheses of two new cobaltacarborane–phthalocyanine conjugates, one anionic (Pc **6**) and one zwitterionic (Pc **7**), were accomplished via cyclotetramerization of the corresponding cobaltacarborane-substituted phthalonitriles (**4** or **5**) with excess phthalonitrile in quinoline. X-ray structures of two phthalonitrile precursors (**2** and **3**) were obtained and are discussed, and the absorption and emission properties of the two cobaltacarborane–phthalocyanine conjugates in several solvents were investigated. The anionic conjugate **6** exists mainly as a monomer in polar organic solvents and has fluorescence quantum yields in the region 0.2–0.3. The zwitterionic conjugate **7** aggregates in solution and displays lower quantum yields ~0.1 in organic solvents.

1. Introduction

Phthalocyanines (Pcs) containing boron-10 are attractive dual sensitizers for the photodynamic therapy (PDT) and the boron neutron capture therapy (BNCT) of tumors, due to their strong absorptions in the near-IR, their ability for generating singlet oxygen with high quantum yields and their tendency for selective accumulation within tumor tissues [1–4]. BNCT [5] and PDT [6] are localized cancer treatment modalities that involve the irradiation of sensitizer-rich tumors with low energy neutrons (in BNCT) or light (in PDT). The use of a single drug for both the BNCT and PDT of cancer has several advantages, since a dual treatment approach might lead to increased therapeutic efficacy due to the targeting of different cellular components and/or mechanisms of tumor cell destruction. We have recently reported the synthesis of boron-containing chlorins [7,8], tetrabenzoporphyrins [9] and phthalocyanines [10] for application as dual sensitizers in BNCT and PDT. Of these classes of compounds cobaltacarborane-containing Pcs show the strongest near-IR absorptions (>670 nm), which are able to utilize light having a deeper penetration power into most human tissues [11]. Several phthalocyanine-based molecules, for example AlPcS4 and Pc4, are currently undergoing clinical investigations for application in PDT [12]. On the other hand, only a few boron-containing phthalocyanines have been reported to date, because of their difficult syntheses and purification procedures. We have recently synthesized a series of anionic cobaltacarboranyl–phthalocyanines that show high solubility and exist as monomers in polar organic solvents [10]. Herein we report the syntheses of two new cobaltacarborane–phthalocyanine conjugates, one anionic and the other zwitterionic, and compare their solubility and photophysical properties.

2. Results and discussion

The synthetic route to cobaltacarborane–phthalocyanine conjugates **6** and **7** involves the nucleophilic attack of zwitterionic 3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{10}$) [13] by phenoxyl or pyridyl substituents situated on phthalonitriles **2** and **3**, followed by cyclotetramerization in the presence of excess phthalonitrile and zinc acetate (Scheme 1). The (4-hydroxyphenoxyl)phthalonitrile (**2**) was synthesized using two different methods: (1) by nucleophilic aromatic substitution of the nitro group of **1** followed by deprotection of the methoxy group using BBr_3 (in 33% overall yield), or (2) by direct nucleophilic substitution of 3-nitrophthalonitrile (**1**) using hydroquinone in 22% yield. 3-Pyridyloxyphthalonitrile (**3**) was prepared in 74% yield from the reaction of 3-nitrophthalonitrile (**1**) and 3-hydroxypyridine. The molecular structures of phthalonitriles **2** and **3** are shown in Fig. 1 and the crystal data are presented in Table 1. All CN triple bond distances fall within the range 1.147(2)–1.151(2) Å. The conformations of the two molecules are quite similar. The dihedral angle formed by the phthalonitrile ring and the phenol ring in **2** is 82.80(3)°, while the corresponding angle between the phthalonitrile and pyridine rings in **3** is 70.50(3)°. The phenolic OH group in **2** forms an essentially linear intermolecular O–H···N hydrogen bond with nitrile N1, having O···N distance 2.8137(17) Å.

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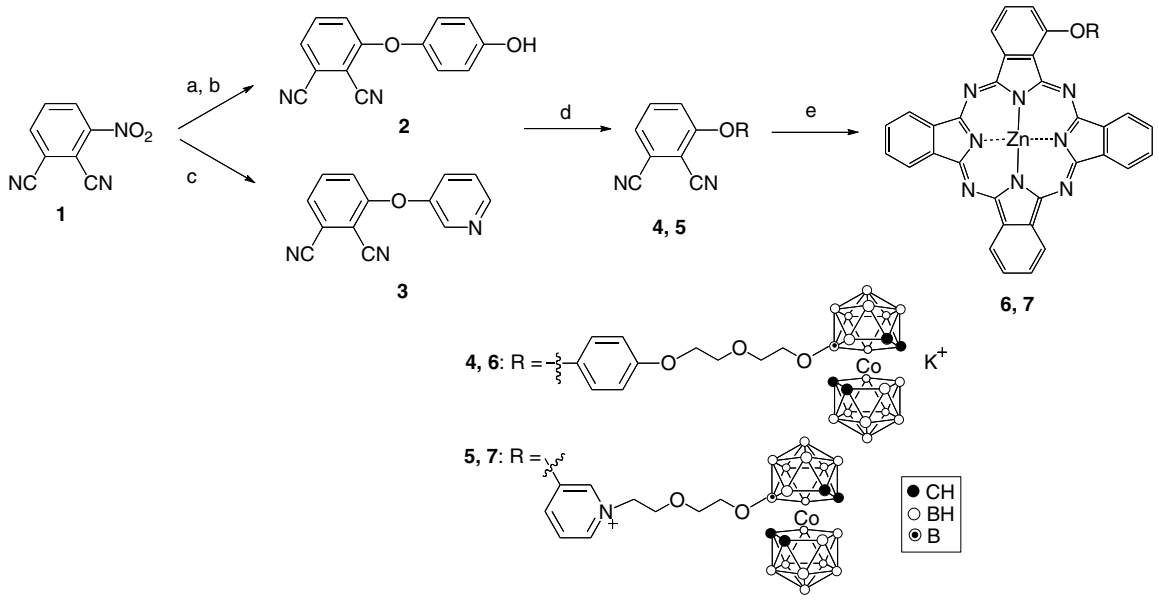

Scheme 1. Conditions: (a) 4-methoxyphenol, K_2CO_3, DMF, 90 °C (83%); (b) BBr_3, CH_2Cl_2, −80 °C (40%); (c) 3-hydroxypyridine, K_2CO_3, DMF, 90 °C (74%); (d) 3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{10}$), K_2CO_3, 50 °C, 24 h (94%); (e) 30 equiv. phthalonitrile, $Zn(OAc)_2$, quinoline, 220 °C, 1 h (1–8%).

Cobaltacarborane-containing phthalonitriles **4** and **5** were synthesized in 94% yield via a nucleophilic opening reaction of the dioxane ring of 3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{10}$) in the presence of anhydrous potassium carbonate, as previously reported [10]. Cyclotetramerization of phthalonitriles **4** and **5** with an excess (30 equiv.) of phthalonitrile in quinoline and in the presence of zinc acetate as template gave the target A_3B-type phthalocyanines **6** and **7** in 8% and 1% yields, respectively. The very low yield obtained for Pc **7** is mainly due to the instability of pyridyloxyphthalonitrile (**5**) under the high temperature reaction conditions, and the lower solubility of Pc **7** in common organic solvents due to its higher tendency for aggregation compared with Pc **6**. The observed low solubility of zwitterionic Pc **7** in comparison with anionic Pc **6**, is in agreement with our earlier investigations of cobaltacarborane–porphyrin conjugates [14–16].

The ^{1}H NMR spectra of compounds **6** and **7** in deuterated DMF show the macrocycle protons on the three identical isoindole subunits in the downfield region between 8 and 10 ppm, consistent with those observed for the di-substituted analogs [10]. The aromatic protons on the phenoxyl and pyridyloxyl rings are shifted upfield to 7–8 ppm. The aliphatic and dicarbollide protons appear in the range 3–5 ppm. Mass spectrometry (ESI) shows the mononegative molecular ion of Pc **6** at m/z 1095.4212 $[M-K]^-$. However, we were unable to obtain a clear mass spectrum with the expected isotopic patterns for Pc **7** due to its poor solubility in most organic solvents.

The absorption spectra of Pc **6** in acetone, DMF, DMSO and methanol show characteristic strong *Q* bands typical of monomeric Pcs with extinction coefficients larger than 10^5 L mol^{-1} cm^{-1}. Fig. 2 shows the absorption spectrum of Pc **6** in various solvents. As we have previously observed [10], the λ_{max} for the *Q* absorption band in DMSO (679 nm) was red-shifted by 7 nm compared with that in acetone (672 nm). In comparison with the anionic di-α-substituted cobaltacarboranyl–Pcs previously reported [10], Pc **6** shows 12–18 nm blue-shifted absorption and emission bands. In HEPES pH 7.4 solution Pc **6** showed a significant broader and weaker absorption, indicating aggregation of this compound in aqueous solution. On the other hand, the zwitterionic Pc **7** shows broader, weaker

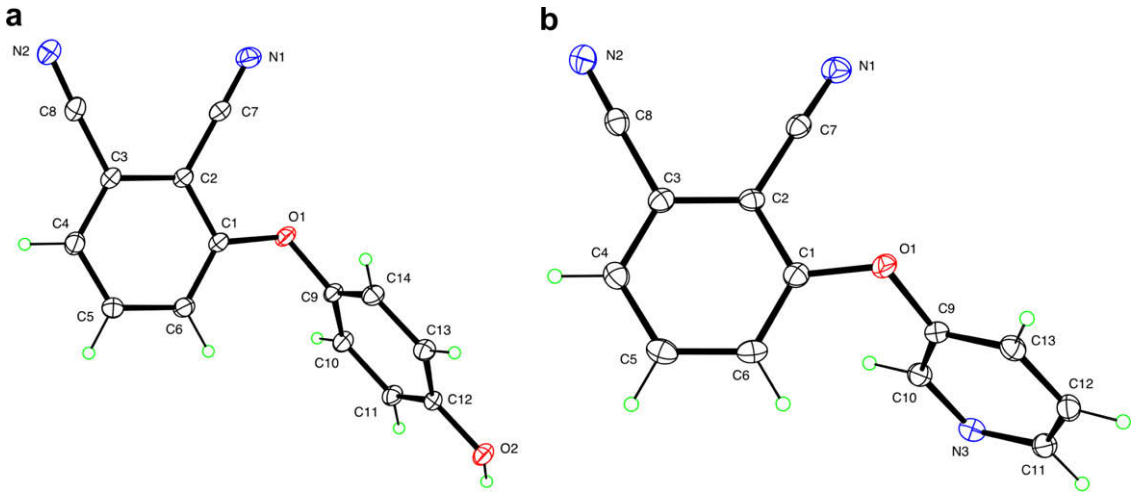

Fig. 1. Molecular structures of phthalonitriles (a) **2** and (b) **3**.

Table 1
Crystal data and structure refinement.

	2	3
Formula	$C_{14}H_8N_2O_2$	$C_{13}H_7N_3O$
CCDC deposition no.	CCDC 699696	CCDC 699697
Formula weight	236.22	221.22
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$
Cell dimensions		
a (Å)	17.586(2)	9.151(2)
b (Å)	11.7388(15)	10.401(2)
c (Å)	5.4751(5)	11.457(2)
β (°)	90	108.690(10)
V (Å^3)	1130.3(2)	1033.0(4)
Temperature (K)	90	90
Z	4	4
Crystal size	0.17 × 0.22 × 0.25	0.17 × 0.23 × 0.25
μ (mm^{-1})	0.096	0.095
θ_{max} (°)	35.0	30.0
Data collected	21256	13500
Independent data	2677	3018
Observed ($I > 2\sigma(I)$)	2361	2311
$[R_{(int)}]$	0.022	0.028
R	0.037	0.040
wR_2 $[I > 2\sigma(I)]$	0.096	0.097
Data/parameter	2677/166	3018/155
Residual density (e Å^{-3})	0.42, −0.24	0.33, −0.22

and red-shifted Q absorptions in acetone and DMSO compared with Pc **6**, due to its higher tendency for aggregation. Pc **7** has a major absorption at 681 nm in acetone and a corresponding 14 nm red-shifted absorption in DMSO. In HEPES pH 7.4 solution Pc **7** showed even a broader and weaker absorption. The emission spectra of Pcs **6** and **7** in acetone and DMSO show the same trend as their absorption spectra, as seen in Fig. 3. The spectroscopic properties of Pc **6** and **7** are summarized in Table 2. While Pc **6** emits at 684 nm in DMSO Pc **7** emits at 701 nm, a value similar to those observed for the anionic di-α-substituted cobaltacarboranyl–Pcs [10]. However, Pc **7** shows decreased intensity of emission in acetone and DMSO compared with Pc **6**. On the other hand Pc **6** has Stokes' shifts of 3–4 nm in polar organic solvents such as acetone, methanol and DMSO, while Pc **7** has larger Stokes' shifts of 8–10 nm in these solvents. Pc **6** has the largest fluorescence quantum yield [17] in DMSO (0.29), and the lowest in methanol (0.13). On the other hand Pc **6** has lower fluorescence quantum yields than Pc **7** in the corresponding solvent, the highest in DMSO and acetone (0.11), and the lowest in methanol (0.09). Quantum yields in the range 0.09–0.15 are typical for this type of compound [10,18]. Of all the cobaltacarborane-containing Pcs that we have tested to date, Pc **6** shows the largest fluorescence quantum yield in DMSO. We are currently investigating the biological properties of cobaltacarboranyl–Pcs, and their potential for application as dual sensitizers in the PDT and BNCT treatment of tumors.

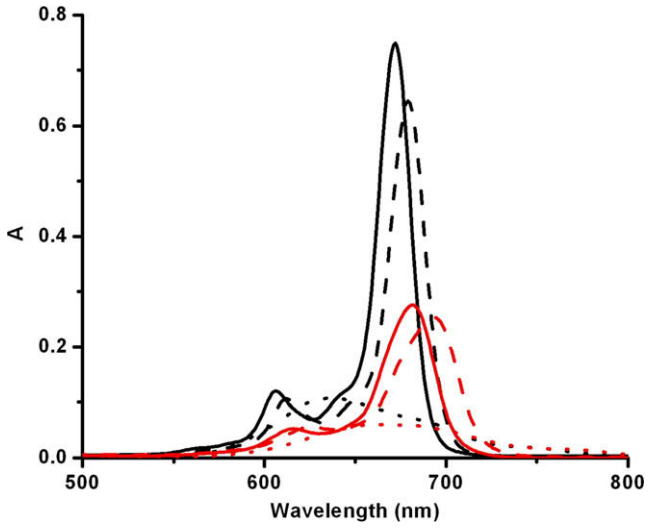

Fig. 2. UV–Vis spectra of Pcs **6** (black) and **7** (red) at 4.5 μM concentration in acetone (full line), DMSO (dash line), and HEPES pH 7.4 (dot line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Conclusions

Two new cobaltacarborane–phthalocyanine conjugates have been synthesized via the cyclotetramerization of the corresponding cobaltacarborane–phthalonitriles with excess phthalonitrile. The X-ray structures of phthalonitrile intermediates **2** and **3** are presented. While the anionic Pc **6** is highly soluble in polar organic solvents and only shows aggregation in aqueous solution, Pc **7** shows increased aggregation behavior in both polar organic solvents and in aqueous solution. Pc **6** has blue-shifted absorption and emission bands compared with di-α-substituted cobaltacarboranyl–Pcs but significantly higher fluorescence quantum yields (0.2–0.3) in polar organic solvents, while Pc **7** has decreased quantum yields of ~0.1. Both Pcs **6** and **7** might have application as dual sensitizers in the PDT and BNCT treatment of tumors.

4. Experimental

4.1. General

All reagents and solvents were purchased from commercial sources and used directly without further purification. Silica gel 60 (230 × 400 mesh, Sorbent Technologies) and alumina gel (50–200 μm, neutral, standard activity I, Sorbent Technologies) were used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using polyester backed TLC plates 254 (precoated, 200 μm) from Sorbent Technologies. NMR spectra were recorded on a DPX-250 or AV-400 Bruker spectrometers (250 MHz or 400 MHz for ^{1}H, 63 MHz or 100 MHz for ^{13}C). The chemical shifts are reported in δ ppm using the following deuterated solvents as internal references: CD_3COCD_3 2.04 ppm (^{1}H), 29.92 ppm (^{13}C); *d*-DMF 2.92 ppm (^{1}H), 34.89 ppm (^{13}C); CD_2Cl_2 5.32 ppm (^{1}H), 54.00 ppm (^{13}C); $CDCl_3$ 7.24 ppm (^{1}H), 77.23 ppm (^{13}C). Electronic absorption spectra were measured on a Perkin–Elmer Lambda 35 UV–Vis spectrometer. MALDI-TOF mass spectra were recorded on a Bruker ProFlex III mass spectrometer using dithranol as the matrix, and high resolution ESI mass spectra were obtained on an Agilent Technologies 6210 Time-of-Flight LC/MS. HPLC purification was carried out on a Dionex system equipped with a P680 pump and a UVD340U detector with a multi-step gradient elution; A: H_2O, B: acetonitrile; 85% B (0 min)–95% B (10 min)–100% B (20 min)–100% B (37 min) 85% B (40 min). A semi-preparative column Luna C_{18} 100 Å, 5 μm, 10 × 250 mm from Phenomenex, USA, was used.

4.2. Phthalonitrile (2)

4.2.1. Method A

3-Nitrophthalonitrile (**1**) (1.5 g, 8.7 mmol) and 4-methoxyphenol (1.6 g, 12.9 mmol) were dissolved in dry DMF (30 mL). Potassium carbonate (20 g, 14.5 mmol) was added in five portions. The reaction was heated at 90 °C for 2 h. The reaction mixture was cooled to room temperature, poured into ice water (500 mL), and the resulting precipitate was collected. The crude product was purified by alumina column chromatography using dichlorometh-

Table 2
Spectroscopic properties of phthalocyanine conjugates **6** and **7**.

	Solvent	DMSO	Methanol	Acetone	HEPES
6[a]	Absorption max (nm)	679 (m), 612	673(m), 608	672(m), 606	634(b)
	Emission max (nm)	684	678	677	–
	Stokes shift (nm)	4	3	4	–
	Q.Y.[c]	0.29	0.13	0.24	–
7[b]	Absorption max (nm)	693(m), 625	684(m), 621	681(m), 616	678(b)
	Emission max (nm)	701	694	691	–
	Stokes shift (nm)	8	10	10	–
	Q.Y.[c]	0.11	0.09	0.11	–

[a] Excited at 610 nm.
[b] Excited at 620 nm.
[c] Fluorescence quantum yield determined using ZnPc in 1-chloronaphthalene as standard; m, major; b, broad.

ane for elution to afford a white solid (1.8 g, 83%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.54 (t, J = 8.2 Hz, 1H, Ar-H), 7.39 (d, J = 7.6 Hz, 1H, Ar-H), 7.02–6.90 (m, 5H, Ar-H), 3.80 (s, 3H, Ar-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 161.53, 157.51, 146.70, 134.43, 126.47, 121.60, 119.69, 116.86, 115.34, 115.13, 112.78, 105.11 (Ar-C, CN), 55.59 (OCH_3). MS (MALDI-TOF) m/z 250.934 $[M+H]^+$, calcd. for $[C_{15}H_{11}N_2O_2]^+$ 251.082. The methoxy-protected phthalonitrile (1.0 g, 4 mmol) was dissolved in freshly distilled dichloromethane (25 mL) and the solution stirred at −80 °C. Boron tribromide (0.4 mL, 4.2 mmol) in dichloromethane (10 mL) was added dropwise over 10 min via an addition funnel. The reaction solution was kept at −80 °C for 1 h and then stirred at room temperature for 24 h. The reaction solution was slowly poured into 100 mL of ice water. The precipitate was collected, dissolved in 150 mL of ethyl acetate and extracted with 50 mL of 2 N NaOH solution. After neutralization with 1 N HCl and extraction with 150 mL ether, the organic layer was dried over anhydrous sodium sulfate. The crude product was purified by chromatography on a silica gel column using methanol/dichloromethane 1:9 for elution to afford a yellow solid (0.4 g, 40%).

4.2.2. Method B

Hydroquinone (1.0 g, 9 mmol) and potassium carbonate (1.6 g, 11.6 mmol) were dissolved in anhydrous DMF (30 mL) under argon. The solution was heated to 50 °C. 3-Nitrophthalonitrile (1 g, 5.8 mmol) dissolved in DMF (2 mL) was added via syringe. The reaction mixture was kept at 50 °C for 2 h and stirred at room temperature for two days. After evaporation of the solvent under vacuum, 1 N HCl (30 mL) was added to the residue and the precipitate was filtered and washed with water. The precipitate was dissolved in acetone (50 mL) and dried over anhydrous sodium sulfate. The crude product was purified by chromatography on a silica gel column using dichloromethane/methanol 95:5 for elution to afford a white solid (0.3 g, 22%). ^{1}H NMR (acetone-d_6, 250 MHz): δ 8.75 (br, 1H, OH), 7.79 (t, J = 4.3 Hz, 1H, Ar-H), 7.68–7.65 (m, 1H, Ar-H), 7.20–7.16 (m, 1H, Ar-H), 7.10–7.07 (m, 2H, Ar-H), 6.96–6.92 (m, 2H, Ar-H). ^{13}C NMR (acetone-d_6, 63 MHz): δ 162.59, 156.44, 147.18, 136.16, 127.83, 122.64, 121.14, 117.60, 117.38, 116.22, 113.87, 105.63 (Ar-C, CN). HRMS-ESI m/z 237.0655 $[M+H]^+$, calcd. for $[C_{14}H_9N_2O_2]^+$ 237.0658.

4.3. Phthalonitrile (3)

3-Nitrophthalonitrile (**1**) (1.5 g, 8.7 mmol) and 3-hydroxypyridine (1.5 g, 15.8 mmol) were dissolved in dry DMF (30 mL). Potassium carbonate (20 g, 14.5 mmol) was added to the solution in five portions. The reaction was heated at 90 °C for 4 h. The mixture was cooled down to room temperature, poured into ice water (500 mL), and the resulting precipitate was collected. The crude product was purified by column chromatography on alumina using methanol/dichloromethane 5:95 for elution to afford a pink solid (1.4 g, 74%). ^{1}H NMR (CD_2Cl_2, 250 MHz): δ *8.54–8.48* (m, 2H, Ar-H), 7.70–7.44 (m, 4H, Ar-H), 7.15–7.12 (m, 1H, Ar-H). ^{13}C NMR (CD_2Cl_2, 63 MHz): δ 160.16, 151.10, 147.58, 142.71, 135.29, 128.30, 127.86, 125.10, 121.16, 117.67, 115.43, 112.91, 106.84 (Ar-C, CN). MS (MALDI-TOF) m/z 221.946 $[M+H]^+$, calcd. for $[C_{13}H_8N_3O]^+$ 222.067.

4.4. Cobaltacarboranyl-phthalonitrile (4)

A mixture of phthalonitrile (**2**) (0.1 g, 0.41 mmol) and potassium carbonate (61.5 mg, 0.46 mmol) in acetone (50 mL) was refluxed at 50 °C under argon. After 20 min, 3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{10}$) (0.18 g, 0.43 mmol) [13] was added to

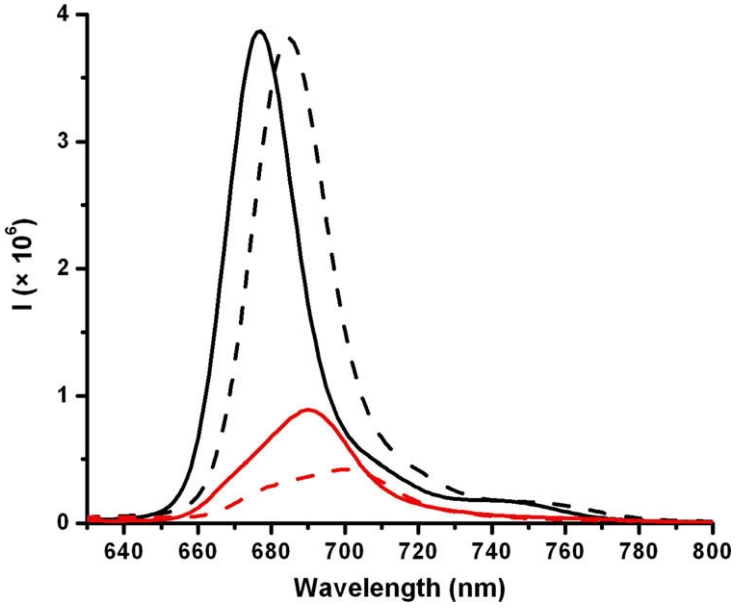

Fig. 3. Emission spectra of Pcs **6** (black) and **7** (red) at 0.4 μM concentration in acetone (full line) and DMSO (dash line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the mixture in 3 portions. The final mixture was heated for one day, then cooled to room temperature and the solvent removed under vacuum. The crude product was purified by silica gel chromatography using methanol/dichloromethane 5:95 for elution to afford a yellow solid (0.24 g, 94%). ^{1}H NMR (acetone-d_6, 400 MHz): δ *7.81–7.77* (m, 1H, Ar-H), 7.68–7.66 (m, 1H, Ar-H), 7.22–7.16 (m, 3H, Ar-H), 7.09–7.07 (m, 2H, Ar-H), 4.25 (br, 4H, OCH_2), 4.16 (t, J = 4.8 Hz, 2H, OCH_2), 3.82 (t, J = 4.8 Hz, 2H, OCH_2), 3.59 (s, 4H, CH), 3.00–1.50 (br, 34H, BH). ^{13}C NMR (acetone-d_6, 100 MHz): δ 162.39, 157.97, 148.14, 136.21, 127.94, 122.49, 121.36, 117.34, 117.13, 116.20, 113.83, 105.72 (Ar-C, CN), 72.85, 70.12, 69.27, 68.98 (OCH_2), 55.15, 47.22 (CH). HRMS-ESI *m/z* 646.3819 $[M-K]^-$, calcd. for $[C_{22}H_{36}B_{18}CoN_2O_4]^-$ 646.3812.

4.5. Cobaltacarboranyl-phthalonitrile (5)

A mixture of phthalonitrile (**3**) (0.1 g, 0.45 mmol) in acetone (50 mL) was refluxed at 50 °C under argon. 3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{10}$) [13] (0.2 g, 0.48 mmol) was added to the reaction solution in 3 portions. The reaction mixture was heated for one day, then cooled to room temperature and the solvent removed under vacuum. The crude product was purified by silica gel chromatography using methanol/dichloromethane 5:95 for elution to afford the title compound as a yellow solid (0.3 g, 94%). ^{1}H NMR (acetone-d_6, 250 MHz): δ *9.34–9.28* (m, 2H, Ar-H), 8.69–8.66 (m, 1H, Ar-H), 8.35–8.29 (m, 1H, Ar-H), 8.05–7.96 (m, 2H, Ar-H), 7.83–7.79 (m, 1H, Ar-H), 5.01 (t, J = 4.4 Hz, OCH_2), 4.13–4.06 (m, 4H, OCH_2), 3.94 (br, 2H, OCH_2), 3.64 (s, 4H, CH), 3.00–1.50 (br, 17H, BH). ^{13}C NMR (acetone-d_6, 63 MHz): δ 158.15, 155.06, 143.84, 138.80, 137.03, 131.24, 130.21, 124.39, 118.17, 115.76, 113.03, 108.84 (Ar-C, CN), 73.32, 69.75, 69.70, 63.08, 52.73, 47.35 (OCH_2, CH). HRMS-ESI *m/z* 631.3981 $[M-H]^-$, calcd. for $[C_{21}H_{36}B_{18}CoN_3O_3]^-$ 631.3815.

4.6. Cobaltacarboranyl-phthalocyanine (6)

Phthalonitrile (1.52 g, 12.0 mmol), anhydrous zinc(II) acetate (0.4 g, 2.0 mmol) and phthalonitrile (**4**) (67 mg, 0.1 mmol) were added to a 10 mL thick-wall Schlenk tube. The tube was dried by purge-and-refill with argon three times. Then 1.0 mL of freshly distilled quinoline was added and the solution was heated to 220 °C. After 1 h, the reaction mixture was cooled to room temperature. The precipitate was filtered and washed repeatedly with acetone and methanol. The dark green filtrate was concentrated under vacuum. The crude product was purified using a Sephadex LH-20 column and acetone for elution. The pure phthalocyanine was obtained by reverse phase HPLC using a Luna C_{18} semi-preparative column and water/acetonitrile as the mobile phase, with a multi-step gradient method. The pure product was collected and vacuum dried at 30 °C for 2 days to afford a dark bluish green solid (9.0 mg) in 8% yield based on the amount of **4** used. ^{1}H NMR (DMF-d_7, 400 MHz): δ *9.37–9.12* (m, 7H, Ar-H), 8.24–8.17 (m, 7H, Ar-H), 7.71 (d, J = 7.8 Hz, 1H, Ar-H), 7.59 (d, J = 9.0 Hz, 2H, Ar-H), 7.23 (d, J = 9.0 Hz, 2H, Ar-H), 4.31 (s, 2H, CH), 4.27 (s, 2H, CH), 4.21 (t, J = 4.7 Hz, 2H, OCH_2), 3.86 (t, J = 4.7 Hz, 2H, OCH_2), 3.70–3.68 (m, 2H, OCH_2), 3.64–3.62 (m, 2H, OCH_2). ^{13}C NMR (DMF-d_7, 100 MHz): δ 155.83, 154.38, 154.24, 154.00, 153.88, 153.53, 152.80, 152.73, 141.97, 139.38, 139.09, 131.31, 129.96, 128.41, 123.39, 123.02, 120.44, 120.26, 118.56, 116.65 (Ar-C), 72.59, 70.19, 69.23, 68.90 (OCH_2), 54.22, 47.21 (CH). HRMS-ESI *m/z* 1095.4212 [M-K]$^-$, calcd. for $[C_{46}H_{48}B_{18}CoN_8O_4Zn]^-$ 1095.4231. UV–Vis (acetone): λ_{max} (log ε) 672 (5.33), 606 (4.53) nm.

4.7. Cobaltacarboranyl-phthalocyanine (7)

The synthesis of this Pc was similar to that of Pc **6** described above and afforded a dark green solid in 1% yield. ^{1}H NMR (DMF-d_7, 400 MHz): δ *9.54–9.45* (m, 7H, Ar-H), 8.26–8.21 (m, 7H, Ar-H), 7.78 (m, 3H, Ar-H), 7.27–7.24 (m, 2H, Ar-H), 5.05 (s, 2H, OCH_2), 4.50 (s, 2H, CH_2), 4.39 (s, 2H, CH), 4.35 (s, 2H, CH), 4.03–4.02 (m, 2H, OCH_2), 3.95–3.92 (m, 2H, OCH_2). UV–Vis (acetone): λ_{max} (log ε) 682 (4.77), 616 (4.05) nm.

4.8. X-ray structures

The crystal structures of phthalonitriles **2** and **3** were determined, using data collected at low temperature with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. Details of data collection and refinement are given in Table 1. The H atoms for both structures were visible in difference maps, and were placed in calculated positions, except for the phenolic H atom of phthalonitrile (**2**), which was refined. Friedel equivalents were merged for refinement of the polar structure of **2**.

Acknowledgement

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Appendix A. Supplementary material

CCDC 699696 and 699697 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.037.

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