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Synthesis and spectroscopic investigation of boronic esters of metal-free fluorinated and non-fluorinated phthalocyanines

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ABSTRACT

Phthalonitriles and metal-free phthalocyanines substituted with 2,3-dihydroxypropoxy and [2,3,5,6-tetrafluoro-4-(2,3-dihydroxypropoxy)]benzyloxy groups were synthesized. Their complexes with phenylboronic acid were prepared in THF at reflux in the presence of molecular sieves. The new compounds were characterized by using elemental analyses, FT-IR, UV–vis, ^{1}H NMR, ^{19}F NMR, ^{11}B NMR, and MALDI-TOF MS spectral data. Aggregation tendency of phthalocyanine complexes in relation to their concentrations were investigated by changes in their absorption spectra. Furthermore, photophysical and photochemical properties of metal-free phthalocyanines were investigated in ethanol and dichloromethane. The fluorescence quenching properties of synthesized phthalocyanines were investigated using 1,4-benzoquinone in dichloromethane.

1. Introduction

Phthalocyanines (Pcs) are well established and versatile macrocyclic compounds, which have found widespread applications ranging from industrial to biomedical fields [1]. Such applications are based on their chemical, physical, and optical properties. These properties vary with the central ion, its axial coordination or peripheral functionalities [2,3].

Organoboron derivatives are an important class of compounds due to their interesting properties such as fluorescence, photoconductivity, and electroluminescence. Moreover, they are also used as synthetic intermediates, functional molecules, ^{10}B carriers for neutron capture therapy, and biologically active compounds [4].

Considering the fact that increasing interest exists in boron chemistry, surprisingly few examples of boron–containing Pcs are known to date. Introducing carboranes, dodecaboranes, and boronic esters into Pc structures has profound effect on their applications in photodynamic therapy (PDT), boron neutron capture therapy (BNCT), coupling reactions, *etc.* [5–10].

Zorlu et al. [11] and Chin et al. [12] studied the solubility of phthalocyanine with glycerol groups. In addition, Özçelik et al. [13] prepared the boron esters with —OH side groups of phthalocyanines. Our aim in this study was to obtain boron complexes of phthalonitrile and phthalocyanines with having glycerol groups and to investigate the photophysical properties of these Pc complexes. In addition, the aggregation properties of the phthalocyanine compounds were investigated in a concentration range and in the presence of a surfactant (Triton-X 100). General trends were also described for fluorescence quantum yields and lifetimes of novel metal-free phthalocyanines in ethanol and dichloromethane (DCM). The fluorescence of the tetrasubstituted metal-free phthalocyanines complexes with phenylboronic acid was effectively quenched by 1,4-benzoquinone (BQ) in DCM.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality, obtained from commercial suppliers. The solvents were stored over molecular sieves (4 Å). 4-(2,3,4,5,6-Pentafluoro-benzyloxy) phthalonitrile [14] and 4-[(2,2-Dimethyl-[1,3]dioxolan-4-yl) methoxy)] phthalonitrile (**1**) [15] were synthesized as reported in the literature. Phenylboronic acid was used as commercially supplied. The progress of the reactions was monitored by TLC (SiO_2). Silica gel (Kieselgel 60, 200–400 mesh) was used in the separation and purification of compounds by column chromatography. All reactions were carried out under nitrogen atmosphere in dried solvents.

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2.2. Equipment

FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrometer; electronic spectra were recorded on a Scinco SD 1000 single beam diode-array ultraviolet-visible (UV-vis) spectrophotometer using 1 cm path length cuvettes at room temperature. Fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer. Mass spectra were measured on Bruker Microflex MALDI-TOF/MS with 2,5-dihydroxybenzoic acid (DHB) as the matrix. ^{1}H NMR, ^{19}F NMR, and ^{11}B NMR spectra were recorded on an Agilent VNMRS 500 MHz spectrometer using TMS as internal reference. Elemental analyses were performed on a Thermo Flash EA 1112.

2.3. Synthesis

2.3.1. 4-[2,3,5,6-Tetrafluoro-4-[(2,2-dimethyl-1,3-dioxolan-4-yl) methoxy]benzyloxy] phthalonitrile (2)

4-(2,3,4,5,6-Pentafluorobenzyloxy)phthalonitrile (1.000 g, 3.085 mmol) and solketal (0.407 g, 3.085 mmol) were stirred in DMF (15 mL) for three days at room temperature in the presence of K_2CO_3 (0.639 g, 4.628 mmol). The mixture was poured into ice-water (200 mL), extracted with chloroform (3 × 100 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The product was purified by column chromatography on silica gel using chloroform:ethyl acetate (1:4) as the eluent. Yield: 0.65 g (48%). Anal. calcd. for $C_{21}H_{16}F_4N_2O_4$; C, 57.80; H, 3.70; N, 6.42%. Found: C, 57.81; H, 3.68; N, 6.41%. IR: ν_{max}, cm^{-1} 3068 (Ar —CH), 2988–2885 (alkyl —CH), 2233 (C≡N), 1252 (C—O—C). ^{1}H NMR ($CDCl_3$): δ, ppm 7.75 (d, *J* = 8.3 Hz, 1H, Ar–H), 7.35 (s, 1H, Ar–H), 7.29 (d, *J* = 6.9 Hz, 1H, Ar–H), 5.19 (s, 2H, —OCH_2), 4.44 (m, 1H, —CH), 4.31–4.23 (m, 2H, —OCH_2), 3.94 (m, 2H, —OCH_2), 1.36 (s, 6H, –CH_3). ^{19}F NMR ($CDCl_3$): δ, ppm −143.77 (q, *o*-fluoro), −160.59 ppm (q, *m*-fluoro).

2.3.2. 4-(2,3-Dihydroxypropoxy)phthalonitrile (3)

4-[(2,2-Dimethyl-[1,3]dioxolan-4-yl)methoxy)]phthalonitrile (**1**) (2.580 g, 10 mmol) was stirred overnight in 20 mL of 80% solution of acetic acid at room temperature. The reaction mixture was evaporated to dryness under reduced pressure. The product was washed several times with cold ethanol, acetone, hexane, and diethyl ether and then dried *in vacuo*. Yield: 2.050 g (94%). Anal. calcd. for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62; N, 12.84%. Found: C, 60.59; H, 4.66; N, 12.88%. IR: ν_{max}, cm^{-1} 3373 (–OH), 3070 (Ar–H), 2939, 2886 (alkyl —CH), 2232 (C≡N), 1253 (C—O—C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ, ppm 7.96 (s, 1H, Ar–H), 7.68 (s, 1H, Ar–H), 7.41 (s, 1H, Ar–H), 4.54 (br, 2H, —OH), 4.14 (s, 1H, —CH), 4.03 (br, 2H, —OCH_2), 3.80 (br, 2H, —CH_2OH).

2.3.3. 4-[2,3,5,6-Tetrafluoro-4-[(2,3-dihydroxypropoxy)]benzyloxy] phthalonitrile (4)

According to the above procedure, 4-[2,3,5,6-tetrafluoro-4-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]benzyloxy]phthalonitrile (**2**) (0.200 g, 0.458 mmol) was treated with 20 mL of 80% solution of acetic acid for 16 h. The reaction solution was evaporated to dryness under reduced pressure. The white product was washed several times with hexane and dichloromethane, and then dried *in vacuo.* Yield: 0.173 g (90%). Anal. calcd. for $C_{18}H_{12}F_4N_2O_4$: C, 54.55; H, 3.05; N, 7.07%. Found: C, 54.52; H, 3.04; N, 7.06%. IR: ν_{max}, cm^{-1} 3352 (–OH), 3070 (Ar–H), 2972–2877 (alkyl —CH), 2233 (C≡N), 1253 (C—O—C). ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.78 (d, *J* = 8.5 Hz, 1H, Ar–H), 7.37 (s, 1H, Ar–H), 7.30 (d, *J* = 7.9 Hz, 1H, Ar–H), 5.21 (s, 2H, —OCH_2), 4.40–3.78 (m, 7H, glycerol moieties).

2.3.4. 4-[(2-Phenyl-1,3,2-dioxaborolan-4-yl)methoxy]phthalonitrile (5)

Compound **3** (0.218 g, 1.000 mmol) was dissolved in 20 mL of dry THF and then poured into the solution of phenylboronic acid (0.550 g, 4.500 mmol) in 50 mL dry of THF. The reaction solution was refluxed in a round bottom flask charged with 3 Å molecular sieve in order to remove the water released from the esterification. After 24 h at reflux, then the crude residue was washed with cold ethanol and crystallized from dichloromethane (30 mL) to give a white crystalline product. It was washed with cold diethyl ether and dried *in vacuo.* Yield: 0.220 g (72%). Anal. calcd. for $C_{17}H_{13}BN_2O_3$; C, 67.14; H, 4.31; N, 9.21%. Found: C, 67.19; H, 4.34; N, 9.26%. IR: ν_{max}, cm^{-1} 3070 (Ar–H), 2989, 2914 (alkyl —CH), 2230 (C≡N), 1352 (–B–O), 1249 (C—O—C), 701 (B–Ar). ^{1}H NMR ($CDCl_3$, 500 MHz): δ, ppm 7.79 (d, *J* = 7.9 Hz, 1H, Ar–H), 7.70 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.51 (t, *J* = 7.8 Hz, 2H, Ar–H), 7.39 (t, *J* = 7.8 Hz, 2H, Ar–H), 7.32 (s, 1H, Ar–H), 7.24 (m, 1H, Ar–H), 4.99–4.94 (m, 1H, —CH), 4.55 (t, *J* = 8.8 Hz, 2H, —OCH_2), 4.33–4.20 (m, 2H, —OCH_2). ^{11}B NMR (d-DMSO, 500 MHz): δ, ppm 31.5 (s, tricoordinated B). (MALDI-TOF): *m*/*z* 305.36 [M + 1]$^+$.

2.3.5. 4-[2,3,5,6-Tetrafluoro-4-[(2-phenyl-1,3,2-dioxaborolan-4-yl) methoxybenzyloxy] phthalonitrile (6)

Compound **6** was prepared according to the same procedure as described for the preparation of **5** by starting from **4** (0.396 g, 1.000 mmol) and phenylboronic acid (0.550 g, 4.500 mmol). Yield: 0.325 g (68%). Anal. calcd. for $C_{24}H_{15}BF_4N_2O_4$; C, 59.78; H, 3.14; N, 5.81%. Found: C, 59.34; H, 3.13; N, 5.78%. IR: ν_{max}, cm^{-1} 3079 (Ar–H), 2992–2904 (alkyl —CH), 2232 (C≡N), 1344 (–B–O), 1257 (C—O—C), 706 (B–Ar). ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 8.27 (d, *J* = 6.9 Hz, 1H, Ar–H), 7.78 (d, *J* = 8.8 Hz, 1H, Ar– H), 7.64 (t, *J* = 7.3 Hz, 2H, Ar–H), 7.54 (t, *J* = 7.8 Hz, 2H, Ar–H), 7.35 (d, *J* = 6.8 Hz, 1H, Ar–H), 7.28 (m, 1H, Ar–H), 5.20 (s, 2H, —OCH_2), 4.47–4.26 (m, 2H, —OCH_2), 4.18–3.98 (m, 2H, —OCH_2), 3.78 (m, 1H, —CH). ^{11}B NMR ($CDCl_3$ 500 MHz): δ, ppm 29.3 (s, tricoordinated B). (MALDI-TOF): *m*/*z* 482.015 [M]$^+$

2.4. General procedures for metal-free phthalocyanine derivatives (7 and 8)

A mixture of phthalonitrile derivatives (0.218 g, 1.000 mmol for **3** or 0.400 g, 1.000 mmol for **4**) and catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (15 μL) in 1-pentanol (2 mL) was heated and stirred at 145 °C for 24 h under nitrogen atmosphere. After cooling to room temperature the crude product precipitated after the addition of hexane. The solid was washed several times with chloroform, acetone, hexane, and diethyl ether and then dried *in vacuo.*

2.4.1. 2, 9(10), 16(17), 23(24)-Tetrakis-(2,3-dihydroxypropoxy) phthalocyanine (7)

Yield: 0.131 g (60%). Anal. calcd. for $C_{44}H_{42}N_8O_{12}$: C, 60.41; H, 4.84; N, 12.81%. Found: C, 60.42; H, 4.86; N, 12.85%. IR: ν_{max}, cm^{-1} 3375 (—OH), 3286 (N—H), 3068 (Ar–H), 2937, 2884 (alkyl —CH), 1254 (C—O—C). ^{1}H NMR (DMSO-d_6 500 MHz): 7.71-7.69 (d, 4H, Ar-H), 7.54–7.52 (d, 4H, Ar–H), 7.24 (br, 4H, Ar–H), 5.16 (br, 8H, –OH), 4.33-4.20 (m, 4H, –CH), 4.11-3.98 (m, 8H, –OCH_2), 3.80-3.72 (m, 8H,-CH_2OH), −3.05 (br, 2H, N—H). UV–vis (Ethanol): λ_{max}, nm (log ε, L mol^{-1} cm^{-1}): 343 (4.92), 618 (4.42), 674 (4.36). (MALDI-TOF): *m*/*z* 875.39 [M + 1]$^+$.

2.4.2. 2, 9(10), 16(17), 23(24)-Tetrakis-[2,3,5,6-tetrafluoro-4-[(2,3-dihydroxypropoxy)] benzyloxy]phthalocyanine (8)

Yield: 0.140 g (35%). Anal. calcd. for $C_{72}H_{50}F_{16}N_8O_{16}$: C, 54.48; H, 3.18; N, 7.06%. Found: C, 54.51; H, 3.16; N, 7.05%. IR: ν_{max}, cm^{-1} 3353 (–OH), 3290 (N—H), 3070 (Ar–H), 2937, 2957–2865 (alkyl