Synthesis, optical and electrochemical properties of novel phenyl- and phenoxy-substituted subphthalocyanines

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ABSTRACT

Novel phenyl- and phenoxy-substituted subphthalocyanines bearing a halogen ion in the axial position were synthesised. The compounds obtained were characterised by ^{1}H, ^{13}C and ^{1}H–^{1}H nuclear Overhauser effect spectroscopy and high resolution mass spectrometry. The correlation between the position of the Q-band and the nature of axial or peripheral substituents was shown. Redox transitions of the compounds were characterised using cyclic voltammetry in *o*-dichlorobenzene. The redox potentials determined suggest a higher electron-donating ability of phenyl substituents compared to phenoxy groups. Absorption cross sections, quantum yields of fluorescence and intersystem crossing, lifetimes of excited states and non-linear optical properties were studied using UV–Vis spectroscopy, stationary and time-resolved fluorimetry, and a non-linear Z-scan technique.

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1. Introduction

Subphthalocyanines are cone-shaped 14 π-electron aromatic macrocycles which consist of three isoindole units around a central boron atom [1–3]. This peculiarity leads to the presence of intensive absorption and luminescence in the range of 500–600 nm. It results in the possibility of the application of subphthalocyanines in non-linear optics [2,4], organic light-emitting diodes [5], and organic photovoltaics [5,6]. There are two main approaches to changing subphthalocyanine structure: modification of the peripheral π-system [7–9] or changing axial ligands [10–14]. As was shown earlier for phthalocyanine complexes, introduction of aromatic peripheral substituents (phenyl or phenoxy groups) leads to interesting intermolecular π–π interactions, which have an influence on spectral and electrochemical properties of target complexes [15–17]. Furthermore, particular interest is focused on the electronic nature of phenoxy substituents, which can possess both electron-donating and electron-withdrawing properties [15,18].

The main purposes of the present study were to synthesise novel phenyl- and phenoxy-substituted subphthalocyanines with an axial halogen (chlorine or bromine) ion and to investigate the tuning of their optical and electrochemical properties upon changing peripheral or axial substituents.

2. Experimental

2.1. Chemicals and instruments

All reagents and solvents were obtained or distilled according to standard procedures. All reactions were monitored by TLC and UV/Vis until complete disappearance of the starting reagents unless otherwise specified. TLC was performed using Merck Aluminium Oxide F$_{254}$ neutral flexible plates. Electronic absorption (UV–Vis)

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spectra were recorded on a ThermoSpectronic Helios-α spectro-photometer using quartz cells (1 × 1 cm). MALDI-TOF mass spectra were taken on a VISION-2000 mass spectrometer with 2,5-dihydroxybenzoic acid (DHB) as the matrix. High-resolution MALDI mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument with DHB as the matrix.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400.13 and 100.61 MHz) and Bruker AVANCE 600 spectrometer (600.13 and 150.90 MHz) at room temperature. Chemical shifts are given in ppm relative to SiMe$_4$.

Fluorescence spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer. The spectroscopic measurements were carried out in DMSO using a 10 mm quartz cuvette. Time-resolved fluorescence measurements were performed on a time-correlated single photon-counting device (FluoTime 200, Pico-Quant) in DMSO using a 10 mm quartz cuvette. Emissions were collected through a monochromator at the maxima of fluorescence spectra. A picosecond laser with 80 ps pulse duration, 10 MHz frequency and a wavelength of 532 nm was used for fluorescence excitation. The fluorescence decays were fitted by PicoQuant's FluoFit software using a common multiexponential model:

$$I(t) = C + \sum_i A_i \exp(-t/\tau_i)$$

Experimental study of resonant non-linear absorption was carried out using an open-aperture single beam Z-scan technique [19]. We utilised the second harmonic generation light of mode-locked Nd:YAG laser operated in TEM00 mode with a pulse duration of 350 ps at a low repetition rate of 5 Hz (to prevent heating processes). The beam was tightly focused by a lens, the radius of the beam waist was 25–30 μm with the pulse energy 40 μJ. The peak intensity in the focus was 4.8×10^9 W/cm^2. All measurements were done in DMSO using a 5 mm quartz cuvette.

Electrochemical measurements were carried out with a μAuto-lab III (Metrohm Autolab B.V., Utrecht, Netherlands). Complexes (1–5 × 10^{-4} M) were dissolved in o-dichlorobenzene (o-DCB) containing 0.15 M tetrabutylammonium tetrafluoroborate (TBABF$_4$) and the measurements were performed under a nitrogen atmosphere in a conventional three-electrode cell using a Pt-disk procedure (BASi, West Lafayette, IN, USA), Pt-foil counter and a calomel reference electrode (SCE). The open-circuit potential of the working electrode when immersed in the solutions was in the region 0.2–0.3 V. At the end of measurements for every complex, ferrocene was added into the working solution as an internal reference and additional voltammograms were recorded. The scan rate of cyclic voltammetry (CV) measurements was varied from 0.02 to 1.00 V/s. All measurements were performed at room temperature (22 ± 2 °C).

2.2. Synthesis and identification
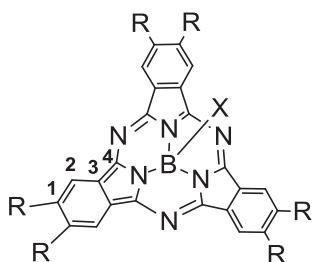
2.2.1. Preparation of hexaphenoxysubphthalocyanine boron chloride 2a

A mixture of 1,2-dicyano-4,5-diphenoxybenzene (150.0 mg, 0.48 mmol) and boron trichloride (0.23 mL, 1 M solution in CH$_2$Cl$_2$) were refluxed in o-DCB (4 mL) under argon for 30 min. The reaction mixture was cooled to room temperature and n-hexane was added. The precipitate was filtered, washed with n-hexane and then solved by toluene. Then the solvent was evaporated to give sub-phthalocyanine 2a as a purple powder. Additional portion of target complex can be obtained by evaporation of filtrate and subsequent washing with MeOH. Yield of 2a: (96.0 mg, 61%). UV–Vis (λ$_{max}$ (toluene)/nm (lg ε)): 347 (3.87); 573 (4.23). ^{1}H NMR δ$_H$ (400.13 MHz, THF-d$_8$) 7.06–7.08 (m, 12H, H$_{OPh}$); 7.19–7.22 (m, 6H, p-H$_{OPh}$); 7.39–7.43 (m, 12H, H$_{OPh}$); 7.52 (s, 6H, H$_{Ar}$). ^{13}C NMR δ$_C$ (100.61 MHz, THF-d$_8$) 113.85 (C$_3$); 115.63 (C$_4$); 119.12 (C$_{OPh}$); 119.87 (C$_{OPh}$); 124.76 (C$_{OPh}$); 125.87 (C$_2$); 130.75 (C$_1$); 131.10 (C$_{OPh}$). MS-MALDI-TOF m/z: 947 ([M−Cl]$^+$, 100%); 964 ([M−Cl + OH]$^+$, 46%); 982 ([M]$^+$, 35%); 1101 ([M−Cl + DHB]$^+$, 50%).

2.2.2. Preparation of hexaphenoxysubphthalocyanine boron bromide 2b

A mixture of 1,2-dicyano-4,5-diphenoxybenzene (50.0 mg, 0.16 mmol) and boron tribromide (7 μL) were refluxed in o-DCB (3 mL) under argon for 15 min. The reaction mixture was cooled to room temperature and n-hexane was added. The precipitate was filtered, washed with n-hexane and then solved by toluene. Then the solvent was evaporated to give subphthalocyanine 2b as a purple powder. Additional portion of target complex can be obtained by evaporation of filtrate and subsequent washing with MeOH. Yield of 2b: (41.0 mg, 75%). UV–Vis (λ$_{max}$ (toluene)/nm (lg ε)): 345 (3.90); 570 (4.35). ^{1}H NMR δ$_H$ (600.13 MHz, THF-d$_8$) 7.07–7.09 (m, 12H, H$_{OPh}$); 7.19–7.22 (m, 6H, p-H$_{OPh}$); 7.39–7.42 (m, 12H, H$_{OPh}$); 7.52 (s, 6H, H$_{Ar}$). ^{13}C NMR δ$_C$ (150.90 MHz, THF-d$_8$) 112.32 (C$_3$); 115.80 (C$_4$); 119.59 (C$_{OPh}$); 120.03 (C$_{OPh}$); 124.92 (C$_{OPh}$); 126.03 (C$_2$); 130.99 (C$_1$); 131.27 (C$_{OPh}$). MS-MALDI-TOF m/z: 964 ([M−Br + OH]$^+$, 20%); 947 ([M−Br]$^+$, 100%).

2.2.3. Preparation of hexaphenylsubphthalocyanine boron bromide 2c

A mixture of 1,2-dicyano-4,5-diphenylbenzene (100.0 mg, 0.36 mmol) and boron tribromide (16 μL) were refluxed in o-DCB (4 mL) under argon for 15 min. The reaction mixture was cooled to room temperature and n-hexane was added. The precipitate was filtered, washed with n-hexane and then solved by toluene. Then the solvent was evaporated to give subphthalocyanine 2c as a purple powder. Additional portion of target complex can be obtained by evaporation of filtrate and subsequent washing with MeOH. Yield of 2c: (55.0 mg, 50%). UV–Vis (λ$_{max}$ (toluene)/nm (lg ε)): 330 (4.45); 587 (4.75). ^{1}H NMR δ$_H$ (400.13 MHz, THF-d$_8$) 7.16–7.19 (m, 12H, o-H$_{Ph}$); 7.26–7.27 (m, 18H, m-H$_{Ph}$ and p-H$_{Ph}$); 8.05 (s, 6H, H$_{Ar}$). ^{13}C NMR δ$_C$ (150.90 MHz, THF-d$_8$) 115.44 (C$_3$); 116.34 (C$_4$); 129.20 (C$_{Ph}$); 129.37 (C$_{Ph}$); 130.59 (C$_{Ph}$); 136.81 (C$_2$); 139.33 (C$_1$); 146.65 (C$_{Ph}$). MS-MALDI-TOF m/z: 868 ([M−Br + OH]$^+$, 10%); 851 ([M−Br]$^+$, 100%).

3. Results and discussion

3.1. Synthesis and identification

Target subphthalocyanine complexes were obtained by a cyclotrimerisation reaction between substituted phthalonitriles 1 and boron trihalides. Initial phthalonitriles 1a and 1b were obtained from 4,5-dichlorophthalonitrile by nucleophilic substitution [20] and Suzuki cross-coupling [21] reactions, respectively.