Synthesis of Subphthalocyanine-Based Stopcock for Zeolite L

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Dedicated to Professor Michael Hanack on the occasion of his 80th Anniversary

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The synthesis and characterization of a subphthalocyanine derivative, bearing a rigid three-phenylene tail on peripheral position, as stopcock for potential selective adsorption to the channel entrances of zeolite L, is described.

Keywords: Subphthalocyanines, energy transfer materials, zeolite L, stopcocks.

Introduction

Natural photosynthesis comprises light absorption by a photonic antenna system followed by directional energy transfer to the reaction center.[1] The construction and development of similar artificial systems, which transfer energy from electronically excited molecules to a specific reaction centre via unexcited neighbour molecules is one of the most important goals of the fast-growing field of supramolecular electronics.

Energy transfer materials can be prepared by sequentially incorporating different types of organic dyes in the channels of zeolite L, a microporous material well suited for the preparation of host-guest composites.[2] In these cases the entrances to the one-dimensional nanochannels of the zeolite L crystals are plugged with specific molecules called stopcocks composed of a rigid tail that can enter the channel and a head group that is too bulky to pass the pore opening. Upon selective excitation of the inner dyes, the energy travels via Förster Resonance Energy Transfer (FRET) to the stopcocks at the edges, which can now, for example transfer it to a photoelectronic or a photochemical device. Such artificial antenna materials are of particular interest in the design of sensitised organic solar cells.[3]

Phthalocyanines (Pcs),[3] bearing rigid tails either in the axial or peripheral positions were shown to be efficient stopcock molecules for energy transfer applications in artificial photonic antenna systems.[2,4] Thus, efficient energy transfer occurs from the photoexcited dyes within zeolite L channels to the ZnPc stopcock molecules. Subphthalocyanines (SubPcs)[5] are lower homologues of Pcs which are characterized by a 14-π electron non-planar aromatic macrocycle consisting of three diiminoisoindole units N-fused around a central boron atom. They have attracted much attention since their first synthesis by Meller and Ossko in 1972.[6] SubPcs have a particular cone-shaped structure in contrast with their related congeners the planar Pcs, and therefore a lower tendency to aggregate. SubPcs have found applications in many research fields like light-emitting diodes,[7] photovoltaics,[8] nonlinear optics,[9] supramolecular chemistry,[10] photosynthetic models,[11] and photodynamic therapy, among others.[12] The important photochemical advantage of this class of compounds is based on their strong light absorption in the visible region (500-700 nm) and their electronically rich π-conjugated system, which make them promising chromophores with potential applications in photosynthetic models for studying energy- and electron-transfer processes.[13]

We report herein the synthesis of new SubPc 1 as potential stopcock molecule for incorporation in zeolite L channels. Its structural formula is shown in Figure 1.

Figure 1. Structural formula of SubPc 1.

Experimental

All chemicals were purchased from Aldrich and used without further purification. 4,5-tert-butylphenoxyphthalonitrile
was prepared according to a published procedure. All reactions were followed by TLC employing aluminum sheets coated with silica gel 60 F254 (Merck). 1H NMR spectra were obtained using a Bruker Avance 300 spectrometer. UV-Vis spectra were recorded on a Hewlett Packard 8453 instrument. Photoluminescence was measured with a Perkin-Elmer LS50B. Infrared spectra (IR) were recorded on a Bruker Vector 22, employing solid samples (KBr pressed disks). MALDI-TOF mass spectrum was obtained in a Voyager-DE STR mass spectrometer.

Jgel (hexane-CHCl3 1:2) to yield 119 mg (40%) of a white solid. The crude product was purified by column chromatography on silica gel 60 F254 (Merck). After stirring for 15 min, dry K2CO3 (620 mg, 4.58 mmol) was added portionwise during 2 h with efficient stirring. The mixture was stirred under argon atmosphere for 24 h at room temperature, added to ice water (300 ml) thereafter. The precipitate was filtered off, washed with water, dried and recrystallized from methanol, obtaining 89 mg of a white solid. Yield: 82%. IR (KBr) vmax cm⁻¹: 2227, 1589, 1480, 1388, 1288, 1254, 1088, 848. 1H NMR (CDCl3, 298K) δppm: 7.74 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.44 (dd, J = 6.4 Hz, 2H), 7.32 (d, J = 2.4 Hz, 1H), 7.29 (dd, J' = 2.4, J = 8.8 Hz 1H), 7.29 (d, J = 8.8, 2H).

4-(4-Bromophenylphenoxy)phthalonitrile (4). In a typical procedure, a solution of 4-nitrophthalonitrile (500 mg, 2.88 mmol) and 4-bromo-4′-hydroxybiphenyl (720 mg, 2.9 mmol) in dry DMF (25 ml) was stirred under argon atmosphere. After stirring for 15 min, dry K2CO3 (620 mg, 4.58 mmol) was added portionwise during 2 h with efficient stirring. The mixture was stirred under argon atmosphere for 24 h at room temperature, added to ice water (300 ml) thereafter. The precipitate was filtered off, washed with water, dried and recrystallized from methanol, obtaining 89 mg of a white solid. Yield: 82%. IR (KBr) vmax cm⁻¹: 2227, 1589, 1480, 1388, 1288, 1254, 1088, 848. 1H NMR (CDCl3, 298K) δppm: 7.74 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8 Hz, 2H), 7.44 (dd, J = 6.4 Hz, 2H), 7.32 (d, J = 2.4 Hz, 1H), 7.29 (dd, J' = 2.4, J = 8.8 Hz 1H), 7.29 (d, J = 8.8, 2H).

4-(4-Biphenylphenoxy)phthalonitrile (3). A suspension of 4-(4-bromophenylphenoxy)phthalonitrile 4 (300 mg, 0.8 mmol), phenylboronic acid (133 mg, 1.09 mmol), tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.04 mmol) and Na2CO3 (1.5 mL of a 2 N aqueous solution) in dimethoxyethane (10 ml) was stirred under argon atmosphere overnight at 80°C. The suspension was cooled to room temperature and poured onto a 1 N NH4Cl solution (100 ml). The mixture was extracted with ethyl acetate (2×100 ml) and the combined organic extracts were washed with brine (20 ml), dried over Na2SO4 and evaporated in vacuo. The crude product was purified by column chromatography on silica gel gel (hexane-CHCl3, 1:2) to yield 119 mg (40%) of a white solid. m/z (MALDI-TOF) 372.1 [M+]. HR-MALDI-TOF-MS (Matrix: DCTB) calc. for C14H8BN2O [M+]: m/z: 1380.6588, found 1380.6632. IR (KBr) vmax cm⁻¹: 2923, 1720, 1508, 1458, 1383, 1398, 1215, 1173 (B-O), 823. 1H NMR (CDCl3, 298K) δppm: 8.72 (d, J = 9 Hz, 1H), 8.35 (s, 1H), 8.27-8.26 (m, 4H), 7.70-7.65 (m, 8H), 7.60 (d, J = 3 Hz, 1H), 7.58 (d, J = 3 Hz, 1H), 7.49-7.33 (m, 12H), 7.11-7.01 (m, 8H), 6.73 (d, J = 9 Hz, 2H), 5.23 (d, J = 9 Hz, 2H), 1.38-1.35 (m, 36H), 1.06 (s, 9H, CCH3 ax.). UV-Vis (CHCl3, λmax (lgε) nm: 573 (4.9), 516 (4.3), 356 (4.4), 282 (5.0).

Results and Discussion

SubPc 1 was prepared in 15% by cross cyclotrimerization of 4,5-di-(p-tert-butyloxynonyl)phthalonitrile[14] and 4-(4-biphenylphenoxy)phthalonitrile 3 in the presence of BCl3 (1 M solution in p-xylene), followed by substitution of the axial chlorine atom by tert-butoxyphenol (Scheme 1) in toluene.[15] 4-(4-Biphenylphenoxy)phthalonitrile 3 was obtained in 40% yield by Suzuki cross-coupling reaction between 4-(4-bromophenylphenoxy)phthalonitrile 4 and phenylboronic acid in the presence of tetrakis(triphenylphosphine) palladium as catalyst in DME.[16]

SubPc 1 was purified by silica gel column chromatography and characterized by 1H NMR spectroscopy, UV-Vis spectrophotometry, MALDI-TOF mass spectrometry, and FTIR spectroscopy. Compound 1 is soluble in both polar and non-polar organic solvents. SubPc 1 gave rise to a well-resolved 1H NMR spectrum in CDCl3 (Figure 2).

![Scheme 1. Synthesis of subphthalocyanine 1.](image-url)
All aromatic protons appear between 8.7-7.0 ppm, with the exception of the axial phenoxy ligand, whose signals are shielded at 5.3 ppm corresponding to the protons close to the aromatic SubPc ring.

The UV-Vis spectrum of SubPc 1 (Figure 3), recorded in chloroform (10^{-5} M), was found to be essentially non-aggregated and characterized by a sharp absorption band in the B-band region at around 350 nm, and in the Q-band region at 573 nm, together with a vibronic shoulder at around 515-520 nm. The bands are blue-shifted compared to those of Pcs owing to the smaller conjugated system (14 vs. 18 \pi electrons) and have lower absorption coefficients. The emission spectrum recorded at the excitation wavelength of 550 nm corresponding to the Q-band showed the expected mirror image with a maximum at 588 nm (Figure 3).

Currently, photophysical experiments are carried out with different potential donor molecules, well suited as donors for FRET experiments, that can be excited in a spectral range where the stopcock SubPc 1 has a very weak absorption (around 450 nm), and have emission spectra which overlap the SubPc absorption Q-band, giving rise to effective energy transfer.

In summary, we have described the synthesis of a novel SubPc dye 1 as potential stopcock molecule antenna for incorporation in zeolite L channels. The combination of the channel entrance of zeolite L with appropriate functionalized SubPc derivatives like 1 is expected to lead to valuable materials for optoelectronic applications.

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References

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