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Synthesis of Subphthalocyanines as Probes for the Accessibility of Silica Nanochannels

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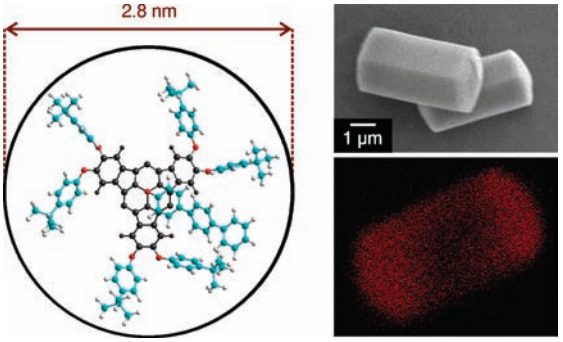
ABSTRACT



The synthesis of a new subphthalocyanine is reported. Its structural and photophysical properties are ideal for probing the accessibility of arrays of silica nanochannels.

Subphthalocyanines[1] (SubPcs) are lower homologues of phthalocyanines,[2] comprising a 14-π electron nonplanar aromatic macrocycle made of three diiminoisoindole units N-fused around a central boron atom.[3] Unlike the related planar phthalocyanines, SubPcs possess a peculiar conical structure which provides them with relatively high solubility and low tendency to aggregate. SubPcs exhibit a number of unique properties that allow a wide range of applications in fields such as nonlinear optics,[4] LEDs,[5] photovoltaics,[6] photodynamic therapy,[7] supramolecular chemistry,[8] as well as in photosynthetic models for studying energy- and electron-transfer processes.[9] SubPcs have also been employed as intermediates in the synthesis of unsymmetrically substituted phthalocyanines through a ring expansion reaction.[10]

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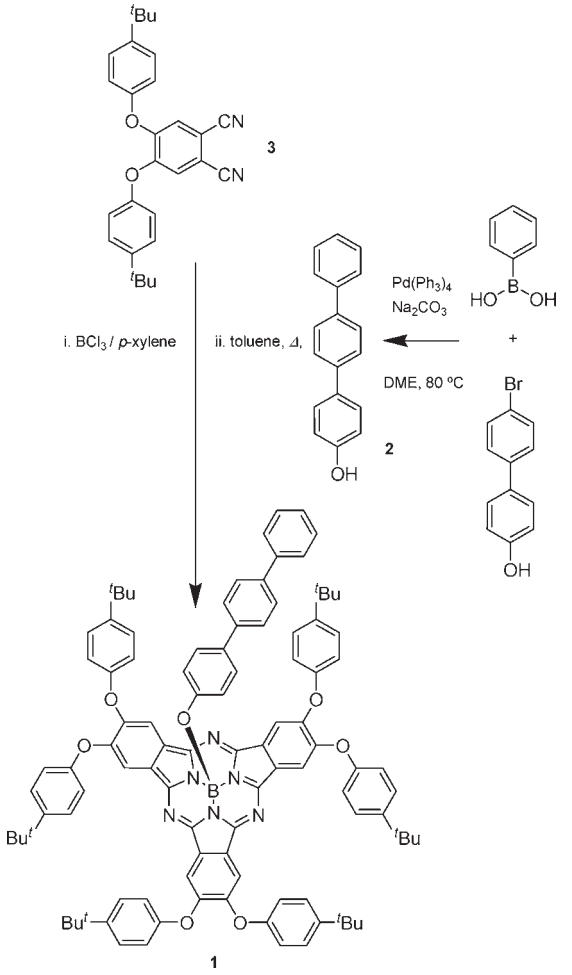
Scheme 1. Synthesis of SubPc **1**



Mesoporous silica with ordered pores[11] has become a versatile host material in various fields, including drug delivery[12] and catalysis.[13] These applications typically require functionalization of the mesoporous silica, giving rise to questions concerning the accessibility of the pores and the location of the functional groups.[14] The use of fluorescent probes and confocal laser scanning microscopy (CLSM) offers options for finding answers to these questions.[15] Arrays of silica nanochannels (ASNCs) have proven to be an ideal material for this purpose. ASNCs are hexagonally shaped fibers, each consisting of approximately 200 000 channels that run along the entire length of the particles.[16] Pore sizes of mesoporous materials are traditionally determined from nitrogen sorption data, often by means of the BJH method.[17] However, a pore size distribution does not necessarily provide unambiguous information about the accessibility of the pores.[18]

The adsorption of SubPcs in combination with CLSM imaging allows us to draw a correlation between the pore size distribution and the effective accessibility. We show that the frequently used evaluation of pore sizes by the BJH method fails to provide useful data on the pore accessibility.

Table 1. Structural Properties of ASNCs

	d_{DFT}[a] (nm)	V_{tot}[b] (cm^3/g)	V_P[c] (cm^3/g)	$V_{P(DFT)}$[d] (cm^3/g)
S-ASNCs	<2.0	0.24	0.23	0.23
M-ASNCs	2.6	0.57	0.52	0.54
L-ASNCs	3.2	0.75	0.70	0.71

[a] Average pore diameter determined by NLDFT. [b] Total pore volume. [c] Primary mesopore volume determined by the α_S-plot method. [d] Primary mesopore volume determined by NLDFT.

SubPc **1** (Scheme 1) was prepared in an overall yield of 21% by cyclotrimerization of 4,5-di(*p*-*tert*-butylphenoxy)-phthalonitrile[19] **3** in the presence of 1 equiv of BCl_3, followed by substitution of the axial chlorine atom by 1,1′:4′,1″-terphenyl-4-ol **2** in toluene.[20]

1,1′:4′,1″-Terphenyl-4-ol **2** was obtained in 55% yield by a Suzuki cross-coupling reaction between 4-bromo(1,1′-biphenyl)-4′-ol and phenylboronic acid in the presence of tetrakis(triphenylphosphine) palladium(0) as catalyst in DME by adapting a previously published procedure.[21] The synthesis of oxygenated subphthalocyanines such as **1** is still a challenge because BCl_3 tends to break the ether linkages.[22] This could be overcome by slowly adding substoichiometric amounts of BCl_3 to 4,5-di(*p*-*tert*-butylphenoxy)phthalonitrile (see Supporting Information).

To test the ability of SubPcs to discern pore sizes, we have synthesized ASNCs with different pore size distributions. We found the well-defined morphology of the ASNCs to be extremely sensitive to changes in the synthesis conditions and therefore decided to investigate possibilities for a postsynthetic pore size adjustment. Indeed, physisorption of dodecamethylpentasiloxane and subsequent calcination gave ASNCs with reduced pore sizes

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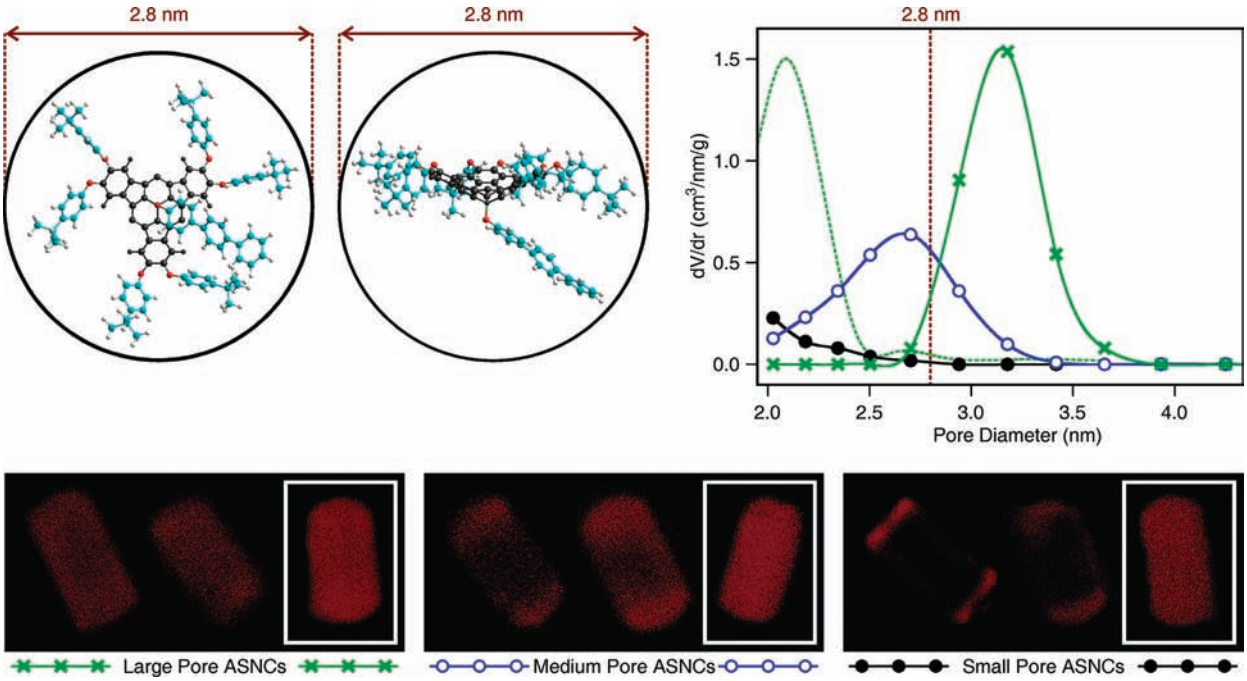

Figure 1. Top left: Estimation of the critical pore size for the inclusion of SubPc **1** in ASNCs. The SubPc macrocyclic core is highlighted in black for clarity. Top right: Pore size distributions of L-ASNCs (×, green), M-ASNCs (○, blue), and S-ASNCs (●, black) calculated from the nitrogen adsorption isotherms by a NLDFT model. The pore size distribution represented by the dashed green line has been calculated by the classical BJH method using the adsorption isotherm of L-ASNCs. Bottom: CLSM images of ASNCs after deposition of SubPc **1**. The outermost right image of each group (shown in a white frame) was obtained after deposition of SubPc **4**. Optical slices in the center of the particles were selected. The length of the particles is approximately 5 μm.

(Table 1) but still reasonably narrow pore size distributions (Figure 1).

Physisorption of SubPc **1** on large pore ASNCs (L-ASNCs) gave a uniform distribution throughout the L-ASNCs (Figure 1). This is in agreement with an assessment of the size of SubPc **1**, resulting in a critical pore diameter of 2.8 nm. The pore size distribution, calculated by a NLDFT (nonlocal density functional theory) model,[23] of L-ASNCs is positioned almost entirely at values larger than 2.8 nm. The average pore diameter of medium pore ASNCs (M-ASNCs) is 2.6 nm. Intuitively, one would therefore expect that SubPc **1** cannot enter the pores. CLSM images of the SubPc **1** distribution show that this is only partially true. Luminescence can be observed toward the center of the channels. According to the pore size distribution of M-ASNCs, there is a considerable fraction of pores with sizes larger than 2.8 nm, enabling SubPc **1** to access the pore body. Complete exclusion of SubPc **1** is only achieved if the entire pore size distribution is located in a range below the critical diameter of 2.8 nm. This is the case for small pore ASNCs (S-ASNCs). It is interesting to note that there seems to be an accumulation of SubPc **1** at the channel entrances of S-ASNCs as opposed to a uniform coverage of the external particle surface. We have also conducted reference experiments with the smaller SubPc **4** (Figure 2).[24] In this case, the critical pore diameter for inclusion into the nanochannels is 1.2 nm.

Contrary to the pore size distribution calculated by NLDFT, the pore size distribution of L-ASNCs determined by the classical BJH method indicates the presence of pores exclusively smaller than 2.8 nm (Figure 1), which would suggest a complete exclusion of SubPc **1**. This is a clear proof that the BJH method strongly underestimates the pore size of ASNCs. The NLDFT model, on the other hand, adequately describes the accessibility of the pores.

We have functionalized the external surface of L-ASNCs by reaction with 3-aminopropyltris(methoxyethoxyethoxy)silane (APTMEES) according to the method proposed by Gartmann and Brühwiler.[15] Subsequent labeling with fluorescein isothiocyanate (FITC) and CLSM imaging reveals that the labeled amino groups are indeed accumulated on the external particle surface. Figure 2A shows that, despite the presence of the FITC-labeled amino groups, the pores remain sufficiently accessible to allow the inclusion of SubPc **1**. An external surface area of 53 m^2/g was determined for L-ASNCs. Even in the event of quantitative grafting onto the external surface, the density of amino groups would remain in a reasonable range, that

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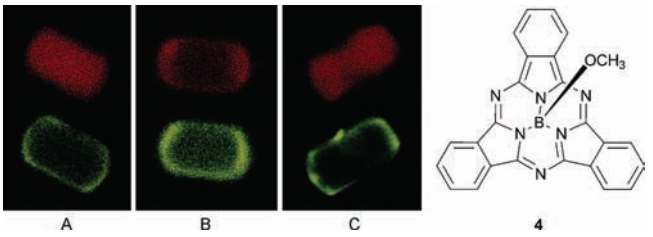

Figure 2. CLSM images of ASNCs after external surface functionalization with 100 μmol/g (A) or 500 μmol/g (B,C) of APTMEES and labeling with FITC, followed by physisorption of SubPc **1** (A,B) or SubPc **4** (C). The lower (green) images of each panel show the luminescence of the coupled FITC labels, whereas the upper (red) images were obtained upon excitation of the SubPc molecules at 543.5 nm. Optical slices in the center of the particles were selected.

is, close to one group per nm^2, in the case of 100 μmol of APTMEES per gram of L-ASNCs. Increasing the amount of APTMEES by a factor of 5, on the other hand, would produce a hypothetical density of more than 5 amino groups per nm^2. It can be assumed that, in this case, a considerable amount of amino groups is located on the pore surface close to the pore entrances, leading to pore blocking. CLSM images reveal that the distribution of SubPc **1** on such highly loaded particles indeed tends to be non-uniform (Figure 2B) with an accumulation of SubPc **1** at the pore entrances. However, the pores are apparently still large enough to enable penetration of SubPc **4** (Figure 2C).

In summary, a new SubPc was synthesized and used in combination with CLSM to probe the accessibility of ASNCs. Comparing the results of these studies to predictions based on pore size distributions calculated from the nitrogen adsorption isotherms revealed that an analysis by a model based on NLDFT adequately describes the accessibility of the pores. The classical BJH treatment was found to draw a misleading picture of the accessibility by considerably underestimating the pore size. The SubPc probe was further employed to investigate the effect of surface-grafted functional groups on the accessibility of the pores. The photophysical properties of the SubPc are compatible with those of the frequently used fluorescein labels, allowing independent imaging of the distribution of fluorescein-labeled functional groups and of the distribution of physisorbed SubPc.

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Supporting Information Available. Synthesis and characterization of SubPc **1**. Synthesis and functionalization of ASNCs. This material is available free of charge via the Internet at http://pubs.acs.org.