

Optical waveguiding and temperature dependent photoluminescence of nanotubulars grown from molecular building blocks



C. Maibohm^{a,*}, M. Rastedt^{b,1}, F. Kutscher^b, O.N. Frey^b, R. Beckhaus^b, H.-G. Rubahn^a, K. Al-Shamery^b

^a NanoSYD, MCI, University of Southern Denmark, Alision 2, 6400 Sønderborg, Denmark

^b Institute for Pure and Applied Chemistry and Center of Interface Science, Carl von Ossietzky University Oldenburg, Carl-von-Ossietzky-Straße 9–11, 26129 Oldenburg, Germany

ARTICLE INFO

Article history:

Received 2 September 2013

In final form 15 October 2013

Available online 23 October 2013

ABSTRACT

Optical waveguiding of blue light after UV-excitation is demonstrated in bundles of organic nanotubulars obtained via template assisted aggregation of the small π -conjugated non planar molecules 17*H*-Tetra-benzo[*a,c,g,i*]fluorene (17*H*-Tbf) and 17-Trimethylsilyltetra-benzo[*a,c,g,i*]fluorene (TMS-Tbf). The propagating blue light is strongly attenuated due to self-absorption. Vibronic spectra for both nanotubulars and macroscopic crystallites for temperatures between 5 and 300 K show a behavior of TMS-Tbf that resembles that of long chained molecules while 17*H*-Tbf resembles that of small organic molecules. For both molecular species crystallites and nanostructures have large average Huang–Rhys factors indicating strong phononic coupling promoted by the polycrystallinity of the samples.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Small conjugated organic molecules with semiconducting properties have been shown to have great potential as low cost active materials in photonic and optoelectronic devices. The optical and semiconducting properties of the molecules are defined by the charge transport efficiency along the π -conjugation of the backbone together with the overlap of π -orbitals between adjacent molecules and the collective properties of the crystal lattice [1–3]. For applications, these organic materials are either used as surface grown thin films or are transformed into well-defined nano scaled structures such as nanorods, nanobelts, nanoribbons, nanotubulars or nanofibers [2]. The optical properties of the organic material can be tuned to a certain extent by forming nanoaggregates [4]. Large scale tuning of the properties of the nanoaggregates can be achieved by changing the optoelectronic properties of the molecular building blocks [5,6], which allows for instance to grow nanoscale frequency doublers [7,8].

The quality of the nanoaggregates as well as their applicability in terms of device integration depends to a large extent on the fabrication method with which they are produced. Ordered arrays of crystalline nanofibers oriented parallel to the surface plane with extraordinary linear and nonlinear optical properties can be generated via vacuum epitaxial growth [9,10]. Since these nanoaggregates are mechanically weak due to the van-der-Waals bonding of the molecules inside the aggregates [11], device integration

becomes complicated and needs either sophisticated printing methods [12] or growth control on structured substrates [13].

A widely used method for fabrication of mutually well aligned 1D organic nanostructures that are oriented normal to the surface is micro- or nanoporous template assisted growth [14,17–19]. Here, dimensions and shapes of the nanostructures are controlled by the morphology of the implemented template. As in the case of surface grown nanoaggregates, the organic building blocks are held together by van-der-Waals forces making the structures mechanically flexible and their properties highly influenced by the individual molecule characteristics as well as the molecular packing. Depending on the material used, template pore diameter and the filling method (sol–gel, melt, solution filling or centrifugation) solid (nanorods) or hollow aggregates (nanotubulars) can be generated [2,14].

In the present paper we investigate temperature dependent optical properties of crystallites and template assisted grown nanotubulars derived from two organic molecules, namely 17*H*-Tetra-benzo[*a,c,g,i*]fluorene (17*H*-Tbf) and 17-Trimethylsilyltetra-benzo[*a,c,g,i*]fluorene (TMS-Tbf) [15,16]. Owing to their nanotubular structure these aggregates bear the potential to generate core–shell organic structures which opens up for specific tailoring of morphological, chemical and optical properties. Crystallites as well as nanotubulars exhibit especially at low temperature steady state photoluminescence resulting from transitions between the electronic ground state S_0 and the first excited singlet state S_1 , dominated by a progression of vibronic peaks. For both species of molecules and nanoaggregates the UV excited fluorescence spectra is dominated by the (0–1) transition which is centered at 475 nm for 17*H*-Tbf and at 460 nm for TMS-Tbf. As a route to possible applications of these new materials we investigate waveguiding

* Corresponding author. Present address: DTU Fotonik, Kgs. Lyngby, Denmark.

E-mail address: chmai@fotonik.dtu.dk (C. Maibohm).

¹ Present address: Next Energy, Oldenburg, Germany.

properties and determine experimentally attenuation constants of tubes that have been isolated on glass substrates.

2. Experimental section

17H-Tbf and TMS-Tbf molecules and crystallites were synthesized by a method described in detail in [15,16] and single crystals could easily be obtained by recrystallisation. Both species of molecules are semi planar butterfly shaped where the ‘wings’ of the butterfly are positioned above and below the plane of the fluorene middle part where they rapidly change positions so an asymmetric configuration is always present for the isolated molecules. Both molecules are shown in Figure 1 in a planar configuration. In the solid state the position of the ‘wings’ becomes fixed in one of the asymmetric configurations and the units stack together in a crystal structure that consists of rows of molecules promoted by face-to-face interactions [16].

Nanostructures of 17H-Tbf and TMS-Tbf were fabricated by template wetting with specific details described in [20] and results in the generation of polycrystalline nanotubulars, see Figure 2. The used templates were commercially available, anodic oxidized aluminum (AAO) foils (Whatman anodisc) with average pore diameters of 200 nm and average interpore distances of a few hundred nanometers. The porous membranes have a thickness of 60 μm , which is the maximum length of the fabricated nanoaggregates. In order to obtain scanning electron microscopy images as shown in Figure 2 the filled AAO templates were glued onto a carbon pad and dissolved in a NaOH solution and subsequently rinsed in DI water leaving the aggregates laying on the carbon pad. The remaining nanoaggregates were coated with 2 nm of an Au-Pd alloy for better conductivity. As seen, both the 17H-Tbf and the TMS-Tbf aggregates are hollow, with average diameters of 220 nm, lengths of 60 μm and wall thicknesses of 30 nm.

For the temperature dependent photoluminescence measurements the crystallite samples were prepared by drop casting an ethanol suspended crystallite solution onto a $1 \times 1 \text{ cm}^2$ piece of a Si wafer. In the case of nanotubulars those were extracted from the templates by dissolving it with NaOH and by filtering subsequent and rinsing with DI water. The nanotubulars were suspended in DI water after removal from the filter and were drop casted on a $1 \times 1 \text{ cm}^2$ piece of a Si wafer. In both cases the wafer piece was fixed to the sample holder with silver paste to ensure good thermal contact and mounted in a helium cold-finger cryostat. For excitation the 325 nm line of a HeCd cw laser was focused onto the sample. Fluorescence emission was collected and focused on the entrance slit of a monochromator (Acton SpectraPro-150) by a lens. Spectral intensities were measured by a cooled CCD array (Princeton Pixes 100) mounted on the monochromator. Samples for waveguiding experiments were prepared by drop casting nanotubulars from the DI water solution onto a glass slide and mounted in an epifluorescence microscope. An aperture was inserted in front of the mercury (Hg) excitation lamp to reduce the size of the excitation spot to about 7 μm , below the typical length of the

tubes. This made local excitation of the nanostructures possible. The excitation spot was moved along the nanostructure with high precision by moving the aperture in front of the lamp with fine adjustment screws. Fluorescence images were recorded at different positions by a CCD camera. Analyzed and scattered intensities from the end of the nanostructures at different excitation positions were collected and combined to form an attenuation curve (intensity as a function of distance between excitation and scattering spot).

3. Results and discussion

Figure 3 shows fluorescence images obtained after UV excitation of 17H-Tbf and TMS-Tbf crystallites as well as the corresponding nanostructures. All of these samples have been prepared by drop casting on a glass substrate. The fluorescence intensity is spatially inhomogeneous (Figure 3), which can be ascribed to several factors: (1) different amount of material along the nanopipe and (2) loss of fluorescing material, caused either by thermal degradation during the fabrication process or by photo-induced bleaching. A further note is that removal of the aluminum oxide template with NaOH might result in UV fluorescing residuals from the solvents and template. An enhanced fluorescence at the tip is also observed on some of the tubes in Figure 3c and d indicating that the nanotubulars support waveguiding. This will be further discussed in the waveguiding section.

At low temperatures both 17H-Tbf and TMS-Tbf crystallites show a progression of vibronic peaks similar to that observed in general for molecular crystals indicating a coupling between the C–C stretch vibrations and the electronic transitions. Since the value of the origin (0–0) at present is unknown, we tentatively allocate the spectral peaks to the series (0– n). We note, however, that even at 5 K the (0–0) band is suppressed and the (0–1) band therefore reveals highest intensity. With increasing temperature a broadening of the peaks is observed, see Figure 4.

Nanotubulars fabricated from TMS-Tbf were drop casted and investigated as described above. At low temperature the spectra show vibronic peaks which broaden with increasing temperature. The spectrum becomes featureless at 200 K, as seen in Figure 5. For comparison the spectra of crystallites and nanostructures, both at 5 K, are normalized and plotted together in Figure 5. It is seen that only the high energy tail of the spectra differs and is present at all temperatures showing only weak temperature dependent intensity behavior. This high energy tail could be caused by residual metal complexes from the dissolved AAO template.

In order to investigate the temperature dependence of the intensities of the individual transitions and positions all spectra were background corrected and fitted by GAUSSIAN distributions, taking into account the first 4 transitions. In the following we restrict ourselves to the (0–1) peak since it can be unambiguously identified for most of the temperature range and for all investigated substances and aggregates. Peak positions for the (0–1) transition for all 3 types of samples are listed in Table 1 and plotted in Figure 6 together with trend lines and estimated error bars for the fitted position. It is known from studies for films and aggregates of similar organic molecules such as *para*-hexaphenylene (p-6P) that in certain temperature ranges additional peaks or phase transition induced broadenings can occur, due to, e.g., polymorphism in the aggregates [21,22]. In the investigated samples only inhomogeneous broadening of the peaks was observed and no additional peaks were identified in the spectra or needed in the fitting process.

For 17H-Tbf crystallites the peaks are initially blue shifted from 5 K to 150 K and then red shifted from 150 K to 300 K similar to the case of p-6P powder, film, nanostructures [21] and small organic

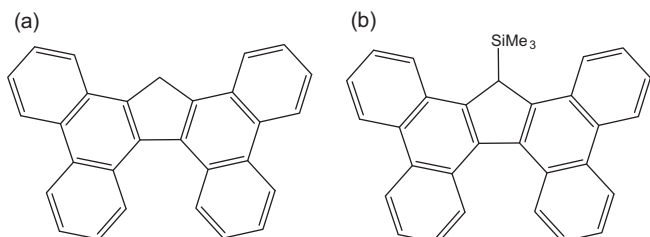


Figure 1. Molecular structures of (a) 17H-Tetrabenzo[*a,c,g,i*]fluorene (17H-Tbf) and (b) 17-Trimethylsilyltetrabenzo[*a,c,g,i*]fluorene.

Download English Version:

<https://daneshyari.com/en/article/5381272>

Download Persian Version:

<https://daneshyari.com/article/5381272>

[Daneshyari.com](https://daneshyari.com)