Nonlinear optical studies of chiral organic waveguides and resonators

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Abstract: We study multiphoton processes in optical active organic microrods and microspheres made by self-assembly technique which are perspective for possible applications as active waveguides and whispering gallery mode microresonators.

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1. Introduction

Recently self-assembled microstructures fabricated of organic materials [1] with high luminescent yield and large value of nonlinear susceptibility have attracted a great deal of attention [2, 3]. The main advantage of their usage is a possibility of varying the shape of a microstructure and the spectral region of the photoluminescence (PL) by tuning HOMO-LUMO band gap which is perspective for numerous photonic applications.

In this work we report on the fabrication of microrods and microspheres composed of chiral binol [4] molecules carrying electron donor and acceptors groups. We study active waveguiding of nonlinear optical signal (multiphoton luminescence and second harmonic generation) in microrods and whispering gallery modes [5] in multiphoton luminescence spectrum in microspheres using nonlinear single-particle microscopy. Both types of the microresonators provide strong field localization and a possibility to manipulate the output nonlinear light intensity due to the large value of circular dichroism in a single microstructure.

2. Methods

The enantiomers R- and S-Binol [6] were prepared via Suzuki cross-coupling by reacting 4-formyl phenyl boronic acid and 1,1'-bi-2-naphthol (BINOL) derivatives namely R-or S-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthalene in 62% yields. The emission spectra of both enantiomers showed PL maxima at 485 nm in the solid state. For the self-assembly R- and S- compounds were sonicated for 30 s in $CHCL_3$:MeOH (2:1) mixture. Then 2-3 drops of the solution were dropcasted on clean cover glass and allowed to evaporate slowly to produce self-assembled microstructures. It is crucial to mention that for the microspheres formation molar concentration of about 6×10^{-6} M is needed. Following this procedure it becomes possible to fabricate microspheres 2-12 μm in diameter and microrods (width of 1 - 3 μm and length of 40 - 110 μm).

For optical studies two femtosecond laser systems (Avesta) were used (Ti-sapphire laser (60 fs pulse duration, 80 MHz repetition rate, mean power of 3-200 mW, 720 - 890 nm spectral range) and Ytterbium-doped solid-state femtosecond laser (TEMA-DUO) with fundamental wavelength of 1050 nm with 0.01-4 W mean power, repetition rate of 75 MHz and pulse duration of 200 fs). Nonlinear optical signal was detected by photomultiplier operating in photon counting mode and home-made spectrometer with 1 nm spectral resolution. Fundamental radiation was focused onto the sample by the objective Leica PL Fluotar L 63X (NA=0.7).

3. Results and Discussions

Observed waveguiding properties in binol microrods were studied by nonlinear microscopy setup providing polarization resolution and possibility to excite and detect nonlinear optical signal in different spatial points. For binol-microrods we have found quite a low loss ($I_{out}=I_{in}e^{Rd}$, d is a waveguide length, R - waveguiding loss coefficient in units of dB/μm) waveguiding for nonlinear optical signal (that is 0.12 dB/μm for the two-photon PL (2PL), second harmonic (SH) - 0.14 dB/μm and 0.22 dB/μm for three-photon PL (3PL), Fig. 1 (A - C)). These values of loss-coefficient are lower than for other nonlinear organic microrods, -wires and -ribbons [7, 8]. Furthermore this material provides bright multiphoton PL and SH and large value of nonlinear circular dichroism

(NLO-CD). We observed the possibility to modulate the waveguiding properties by 6-7% for multiphoton PL and 11% for SH due to the NLO-CD effect.
Also we studied the excitation of whispering gallery modes (WGM) in microspheres and typical 2PL spectrum for a single microresonator is shown in Fig. 1 (D) revealing WGMs with Q-factor of 250; inset shows optical image of a microsphere with boundary-localized blue-color 2PL due to WGMs excitation. Size dependence of free spectral range (FSR), Q-factor and mode volumes were measured. We also observed WGM splitting in 2PL spectrum for two microspheres with the diameter of 6 and 8 μm located close to each other due to energy transfer and coupling of microresonators which opens a path for the control over the resonant response.
All of these effects confirm strong light localization in binol microstructures. Simple fabrication method, high luminescent yield and rich possibilities for manipulating the microstructures' shape and optical properties can provide their wide usage in photonic devices, sensorics and energy storage components.

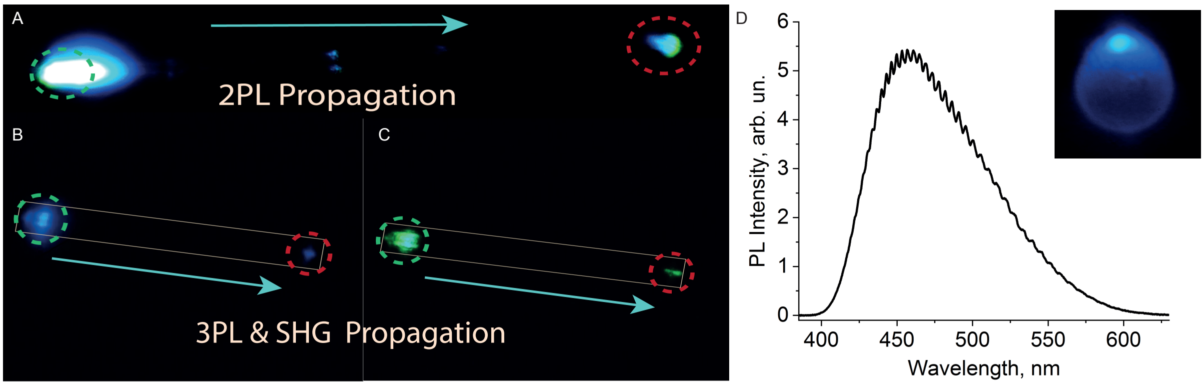

Fig. 1. A) 2PL waveguiding along the microrod, B) 3PL waveguiding along the microrod, C) SHG waveguiding along the microrod, D) WGM excitation in 10μm binol-microsphere (inset - optical image of 2PL distribution).

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