Parallelepipedic Passive Organic Optical Wave Guides: Laser Cutting, Controlling Guided Light Propagation Lengths and Out-Put Efficiency
6.1 Abstract

In this chapter we have exploited laser ablation/cutting technique to precisely control the longitudinal dimension of self-assembled organic nanotubes to create tailor-made lengths. Since these organic nanotubes show passive optical wave guiding tendency, the presented cutting technique is quite useful to exactly control the light propagation distance and to create multiple optical outputs. The estimated wave guiding efficiency (WGE) of a randomly selected tube with appropriate laser coupling is >47%. The efficiency of a tube is also dependent on its wall thickness, lengths and defect density. A tube not in contact with the substrate also guides the optical wave indicating its true wave guiding nature.

6.2 Introduction

Nanoscale optical wave guides are one of the important components of miniaturized nano-photonics devices. In particular, one dimensional (1D) organic solids are useful to manipulate and guide optical waves within the nano/submicro/micro domains, because the refractive index ($n$) of the organic solid ($n\sim1.6$) is usually higher than the surrounding air medium ($n=1$). Based on the type of light an 1D solid propagates, organic optical wave guides are classified into active- and passive-waveguides. In active wave guides, the molecular building block of the organic solid is electronically excited and the coupled exciton-polariton propagates to the output end as luminescence. Although this area is relatively young, a few excellent examples reported for
this type of exciton-polariton based active wave guides.\textsuperscript{10-23} On the other hand, passive organic wave guides function almost similar to commercial optical fibers and other dielectric-based guided wave structures, i.e., here the input light directly propagates along the organic medium to the output end. Chandrasekar and co-workers have recently reported for the first time on the passive wave guiding tendency of self-assembled organic submicrotubes and rods.\textsuperscript{26-30} The potential utility of the guided laser light along the submicrotubes to remotely excite a porphyrine nano-sheet positioned 20 microns away from the source laser was also demonstrated.\textsuperscript{28} Additionally, Raman scattering interaction of the propagating passive light with the molecular building blocks of the tube was used to pin-point nano/micro scale defect sites inherited during the self assembly process.\textsuperscript{28,29}

### 6.3 Results and Discussion

Importantly, to exploit organic optical waveguides as components for future nano-photonic device applications,\textsuperscript{1,2} it is imperative to precisely control the optical signal propagation distance from the input point to out point(s) of our choice. Additionally, it is essential to comprehend the correlation between transverse dimensionality of 1D organic nanostructures and the wave guiding propensity. Regrettably, though the science of self-assembled 1D organic nanostructures are known for a long time, still it is impossible to exactly control their growth length during self-assembly. To date, no experimental methods reported in the literatures on externally controlling the longitudinal dimensions of organic wave guiding solids (tube, rod and fiber), thereby precisely controlling optical wave propagation distance. Hence, performing length “cutting” operation on extended nano/micro scale organic solids is crucial step to assemble them as components in miniaturized organic nano-photonic devices.

**Figure 6.1** a) Confocal microscopy image of linear and curved parallelepipedic organic nanotubes. b) TEM image of tubes. c) SEM image displaying tapered open end of a tube (see dotted rectangle). d) Selected area electron microscopy image of a crystalline tube.
6.3.1 Optical Wave Guiding Studies:

In Chapter 4, fabrication and thorough characterization of self-assembled crystalline organic parallelepipedic nanotubes obtained from heterocyclic molecule \textit{L5} is presented (Scheme 6.1).\textsuperscript{31} We have found that the optical wave guiding tendency of these organic nanotubes is dependent on the tube transverse dimension i.e. height and width. In this chapter we would like to present three original general methodology on tuning organic waveguides towards photonic device applications: (i) submicro scale resolution laser cutting of organic parallelepipedic nanotubes at defined positions, ii) precise control of optical wave propagation distance along the nanotubes and generation of multiple optical outputs, and iii) estimation/control of the optical wave transmission efficiency. In this experiment, a combined laser confocal Raman/atomic force microscopy set-up was employed, the former to perform laser ablation/cutting operation and to do wave guiding experiments and the latter to investigate dimension of the ablated tube.

Building block molecule \textit{L5} forms parallelepipedic nanotubes upon slow evaporation conditions from THF/water on glass substrate.\textsuperscript{31} On the substrate some of the longer tubes bent and produced curved structures indicating their flexible nature\textsuperscript{28} (Fig. 6.1 a,b). A closer look at the tube ends revealed \textit{tapered} regions (Fig. 1c). The selected area electron diffraction (SAED) pointed out the crystalline nature of the tubes (Fig. 6.1 d). The solid state absorbance band of \textit{L5} showed that there is no possible molecular absorbance above \(\lambda \sim 420\) nm. Initially, to study the passive wave guiding behavior of these organic nanotubes, a confocal Raman/AFM microscope \textit{(back scattering mode)} was employed. A longer wavelength (\(\lambda\)) visible light (Ar\textsuperscript{+} 488 nm) was used for the optical waveguide experiments to circumvent any molecular electronic absorption and resultant fluorescence. Orthogonal direct laser illumination (Ar\textsuperscript{+} 488 nm; 100× objective; N.A. 0.95) at one of the open ends of a tube (tapered region) showed no output light at the opposite open end in the bright field image. Similar behavior was observed for irradiation performed at the other end and middle of the tube (Fig 6.2 a). The corresponding dark field images without and with 488 long pass edge filter (LPEF) presented in Fig 6.2 b and Fig 6.2 c, respectively also show similar trend. One can interpret this results in two ways: (i) the light is not coupled to the tube at the tapered ends possibly due to their much smaller transverse dimension (less than \(\lambda/2\)) in comparison to \(\lambda\) of the input light. (ii) the light can be
coupled in the middle of the tube and possibly confined within the tube with outcoupling due to tapered ends.

6.3.2 Laser Ablation/Cutting of Photonic Tubes:

To clearly understand the coupling of light with the tube and to observe any possible out coupled light in the bright and dark field images, a confocal Raman/AFM microscope (back scattering mode) set-up was employed to perform laser ablation or cutting on the tube at selected positions and AFM analysis of the ablated area as well. For tube cutting, a CW 488 nm Ar⁺ ion laser (40 mW) was point focused through 100× objective on the right side of the tube slightly away from the tapered area to burn the molecules using source laser heat (see cut 1; Fig. 6.2 d). Here the CW laser power is kept constant; hence the depth of cutting is dependent upon the laser ablation.

Figure 6.2 a) Bright field image of a tube illuminated with 488 Ar⁺ laser. b and c) the corresponding a dark field images without and with LPEF, respectively. d) The same tube ablated/cut with 488 Ar⁺ laser (see Cut 1); e and f) the corresponding dark field images without and with LPEF, respectively. g) The same tube ablated/cut with 488 Ar⁺ laser at the left side (see Cut 2); h and i) the corresponding dark field images without and with LPEF, respectively.
time. Afterwards, coupling of laser light to the left side (slightly away from the tapered area) or middle of the tube showed no perceptible out coupled light at the opposite end(s) in the bright and dark field images. Whereas the same dark field images with 488 LPEF showed weak and clear output signals at the ablated area (see arrow marks toward cut 1; Fig. 6.2 f). As expected coupling of laser light at cut 1 showed no out coupled light at the opposite end, indicating complete confinement of light within the tube due to tapered output ends. To verify further, the tube was again ablated at the opposite side (cut 2) slightly away from the tapered area (Fig. 6.2 g). Now coupling of laser light at cut 1, cut 2 and middle of the tube display out coupled light at the opposite laser ablated areas. But still the laser-tube coupling efficiency in the middle part of the tube was rather weak, which was apparent from the bright and dark field images (Fig. 6.2 g,h). These experiments demonstrate that the laser is not coupled to the tapered region and hence the tube was not able to act as a wave guide. When the laser was coupled away from the tapered end the tube shows wave guiding behaviour. To find a correlation between the tube transverse dimensions and laser-tube coupling tendency/propagation efficiency a selected tube was scrutinized by AFM technique.

**Figure 6.3** AFM images of (a) side and (b) top view of a laser ablated/cut tube at positions A (Cut 1), B (Cut 2) and C (Cut 3). H and W stand for height and width profiles, respectively. The corresponding depth profile of the cut regions are shown in the bottom figures.
As expected the height (H) and width (W) profiles were not same all over the tube, particularly at the tube ends. For example, the $H_x \times W_x$ ($x = 1-4$) profiles at four different regions ($x = 1-4$) varied in the range of $\sim 250 \text{ nm} \times \sim 2 \mu \text{m}$, $<570 \text{ nm} \times \sim 2.25 \mu \text{m}$, $\sim 633 \text{ nm} \times \sim 2.3 \mu \text{m}$, and $400 \text{ nm} \times \sim 2.1 \mu \text{m}$, respectively (see Fig. 6.3). The length of the tube was ca. 76 $\mu \text{m}$. Here, the variation of $H \times W$ transverse profile at the tapered tube ends arises during the growth process, for example Fig 6.1 c clearly shows that the top (W) and side walls (H) of the tapered region is not grown as much as the bottom wall (W), leading to a decrease of the tube height. To study transverse dimension (H and W) dependent wave guiding tendency of a tube, the same tapered tube was used. Here, the $\lambda$ of the laser line (488 or 532) is almost close to one of the transverse dimensions ($\lambda \leq H$) of the tube from A to B and it is around $\lambda/2 \geq H$ in the tapered regions 1 and $\lambda < H$ in region 4 (see Fig. 6.3 labels).

Initially two laser cuts (Cut-1 and Cut-2) were made by point illumination of

**Figure 6.4** a) A laser ablated tube [A (Cut 1) and B (Cut 2)] shown in Fig. 6.3 irradiated with 488 nm laser at B; (b) the corresponding dark field image; (c) PMT image of 532 nm wave guiding tubes displaying 29% output; d) Ablation of tube shown in Fig. 6.4a at position C (Cut 3), followed by irradiated with 488 nm laser at B; e) The corresponding dark field image; f) PMT image of a wave guiding tube with two out puts. The calculated optical transmission efficiency of tube 1 (from C to A) is ca. 35%. The red and blue circles stand for laser irradiation and output points, respectively.
488 nm light at positions A (H: 530 nm; W: 2.12 \( \mu \)m) and B (H: 540 nm; W: 2.35 \( \mu \)m) (see Fig. 6.3 and Fig. 6.4 a). AFM examination of a cut tube showed that the ablation was about 100 nm deep with the separation ca. 1 \( \mu \)m between the two pieces of a tube (Fig. 6.1). The optical wave guiding experiments on the tube was performed on laser confocal Raman/AFM microscope set-up (transmission mode) connected to a photomultiplier tube (PMT) (Scheme 6.1). Here a Nd:YAG 532 nm laser was bottom fix illuminated through a 5× objective at point A and the output light position of the output light signal was detected by scanning the entire area of the tube using a top 100× objective and sent to a photomultiplier (PMT) detector. Illumination of laser at point B (Cut-2) exhibited a clear output light at point A (Cut-1) (Fig. 6.4 a, b). The 3D mapping of the PMT counts clearly showed the output signal transmission efficiency at point B is ca. 29% (B/A). One should remember the fact that for calculating optical transmission efficiency the present light–tube coupling geometry is not appropriate since the source laser light couple to the tube in an orthogonal manner, which leads to unwanted scattering at the input point thus increasing optical loss. Hence to couple the light directly (longitudinal) to the tube (within the acceptance angle), another laser cut (Cut-3) was made at point C (H: 597 nm; W: 2.52 \( \mu \)m) there by producing two wave guiding tubes, 1 and 2 (see Figures 6.3 and 6.4 e). AFM profile analysis showed that the depth of cutting was ca. 75 nm.

**Figure 6.5** a and b) Bright and dark field images of a passive wave guiding tube ablated/cut with laser at tapered open ends, respectively. c and d) Bright and dark field images of the tube cut by laser into two sections to control the light propagation lengths and efficiency, respectively. The red and blue circles stand for laser irradiation and output points, respectively. e and f) Bright and dark field images of a bent tube displaying wave guiding tendency.
The separation between Tube 1 and 2 was ca. 1 μm (Fig. 6.3). Orthogonal illumination of 532 nm laser at point B showed remarkable propagation of light from point B to C and then to A. As expected the out coupled light intensity at point A was lower than the output at point C due to leakage at Cut-3. Nevertheless, the direct orientation of tubes 1 and 2 is an ideal geometry for improved estimation of optical transmission efficiency from tube 2. By ignoring the minor scattering losses at the coupling point C the estimated optical guiding effectiveness was >35% (A/C). Further to demonstrate the use of this technology to precisely control the light propagation length scale and to create multiple outputs along the wave guide, a 176 μm long was identified. At first, the tapered tip ends of the tube were removed by laser ablation. Subsequently, the tip polished tubular wave guide (Fig. 6.5 a,b) was exactly laser cut to create two wave guiding tubes of lengths 90 μm and 86 μm. Launching of laser light at the input clearly showed two output signals at a distance of 90 μm and 86 μm (Fig. 6.5 c,d). Similarly, a tips polished bent tube (bent angle of ~ 135°) also guide the input light to the output end confirming the true optical wave guiding tendency of the tubes (Fig. 6.5 e,f).

To prove light guiding tendency in a bent tube having acute turn, a tube forming a loop was laser polished to produce a U-shaped tube (Fig. 6.6 a). Laser

Figure 6.6 a) A tube forming a loop. b and c) U-shaped tube produced from the loop via laser ablation displaying passive wave guiding tendency even at acute turns. d and e) U-shaped tube laser ablated in the middle (cut 1) shows 2 out puts. f and g) U-shaped tube laser ablated at cut 2 shows 3 out puts. h and i) U-shaped tube laser ablated in the middle (cut 3) shows 4 out puts. The red and blue circles denote laser input and output points, respectively. An Ar+ 488 laser was used for laser ablation and wave guiding studies.
coupling at one of the ends of a tube showed clear output at the opposite end indicating an efficient propagation of guided laser light even at sharp turns (Fig. 6.6 b, c). Further to produce multiple optical outputs, the U shaped tube was laser ablated successively to create Cut-1, Cut-2 and Cut-3 (Fig. 6.6 d,f,h) and to emanate 2, 3 and 4 optical outputs, respectively (Fig. 6.6 e,g,i).

To rule out any substrate influence on the wave guiding tendency of tubes, it is important to demonstrate the wave guiding nature of an organic tube surrounded only by air medium (no substrate contact). For this experiment an AFM tip was used to lift a tube from the substrate and the cantilever carrying the tube was inverted and used for the optical wave guiding studies (Fig. 6.7). Note that during lifting, the tube surrounded by the air medium was broken and bent slightly. Orthogonal laser coupling one of the ends of the tube evidently showed guided light propagation to the respective opposite end (Fig. 6.7 b,c). This experiment clearly supported the true wave guiding character of the organic tube.

6.4 Conclusions

We have presented an innovative method to fabricate extended 1D organic solids with tailor made lengths using simple laser ablation/cutting technique. Additionally, we have also demonstrated the transverse dimension dependent optical wave guiding behaviour of parallelepipedic organic nanotubes. We have also established a better method to estimate optical transmission efficiency of wave guiding organic tubes using appropriate optical coupling geometry. It is also important to note that the optical

![Figure 6.7](image.jpg)

**Figure 6.7** a) A broken tube attached to an inverted AFM cantilever. b) and c) Optical wave guiding property of a bent tube surrounded by air. An Ar+ 488 laser was used for wave guiding studies. The red and blue circles denote laser input and output points, respectively.
transmission efficiency of the tubes is dependent upon the tube lengths, wall thickness and defects. The true wave guiding behaviour of a tube surrounded only by the air medium has also been demonstrated as well. This laser ablation methodology can be used to make tailor made nanophotonic organic wave guides with multiple outputs and to precisely control the guided optical wave propagation length scales.

References


