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Abstract: A new approach for optical chemical sensor based on molecularly imprinted polymer (MIP) and localized surface plasmon resonance (LSPR) in plastic optical fibers (POFs), for the selective detection and analysis of 2,4,6-trinitrotoluene (TNT) in aqueous solution, has been developed. LSPR is excited in five-branched gold nanostars (GNS), suspended in an MIP specific for TNT (GNS-MIP), which assures the selectivity. This sensing layer has been deposited directly on two different POF platforms, i.e. tapered and not-tapered POF. Both sensors show better performance than a similar one previously proposed, in which the surface plasmon resonance (SPR) was excited in a thin gold layer at the surface of the POF in contact with the MIP layer (specific for TNT). In particular, in the sensor with a GNS-MIP sensing layer on the not-tapered POF the sensitivity was 8.5×104 nm/M, three times higher than in the gold layer sensor. In the sensor with GNS-MIP sensing layer on tapered POF the sensitivity increases further up to 8.3×105 nm/M, because the penetration depth of the evanescent field increases and the number of the interaction sites of TNT in the MIP involved in the generation of the signal increases accordingly.

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Sensitive detection of 2,4,6-trinitrotoluene by tridimensional monitoring of molecularly imprinted polymer with optical fiber and five-branched gold nanostars

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ABSTRACT

A new approach for optical chemical sensor based on molecularly imprinted polymer (MIP) and localized surface plasmon resonance (LSPR) in plastic optical fibers (POFs), for the selective detection and analysis of 2,4,6-trinitrotoluene (TNT) in aqueous solution, has been developed. LSPR is excited in five-branched gold nanostars (GNS), suspended in an MIP specific for TNT (GNS-MIP), which assures the selectivity. This sensing layer has been deposited directly on two different POF platforms, i.e. tapered and not-tapered POF. Both sensors show better performance than a similar one previously proposed, in which the surface plasmon resonance (SPR) was excited in a thin gold layer at the surface of the POF in contact with the MIP layer (specific for TNT). In particular, in the sensor with a GNS-MIP sensing layer on the not-tapered POF the sensitivity was 8.5×10^4 nm/M, three times higher than in the gold layer sensor. In the sensor with GNS-MIP sensing layer on tapered POF the sensitivity increases further up to 8.3×10^5 nm/M, because the penetration depth of the evanescent field increases and the number of the interaction sites of TNT in the MIP involved in the generation of the signal increases accordingly.

Keywords: chemical sensors, gold nanostars, localized surface plasmon resonance, molecularly imprinted polymer, trinitrotoluene, plastic optical fiber.

1. Introduction

Localized surface plasmon resonance (LSPR) is a very sensitive technique for determining small refractive index changes at the interface between a metal and a dielectric medium. Thus it can be a very useful tool for surface and nanostructured-surface interaction analysis and bio-sensing, in different areas of bio and chemical sensing, as reported in several recent review papers [1-4]. The signal, i.e. the change of the refractive index at the interface,

which is measured through the variation of the LSPR (in sensors employing metal nanoparticles) as well as of SPR (in sensors employing thin metal layers), is due to the adsorption/combination of the considered substance (i.e. the analyte) at the sensor surface.

In the present investigation, LSPR is applied as the transduction method to obtain a device with characteristics suitable for on line and remote sensing. As a proof of principle, 2,4,6-trinitrotoluene (TNT), a nitroaromatic explosive with low molecular mass (mw = 227.14), has been considered. LSPR sensors based on bio or synthetical receptors are commonly regarded as suitable for the analysis of medium or large molecular weight analytes, however several approaches have been proposed for the detection of low molecular mass substances too, mainly based on interaction reactions which give by-products inducing measurable refractive index changes at the surface of the optical device. A different approach is that of molecularly imprinted polymers (MIPs), synthetical porous solids that have been proved to change their refractive index when small molecules as for example nicotine [5] and TNT [6] are specifically adsorbed. MIPs are obtained by the molecular imprinting methods [7,8], and contain specific sites interacting with the molecule of interest according to a "lock and key" model. The high thermodynamic stability of the MIP-analyte adducts and their fast kinetics of formation make MIPs suitable receptors to be used in combination with SPR as transduction method. Additional favourable aspects for sensing in comparison to bioreceptors such as, for example, antibodies [9], include a better stability out of the native environment, a better reproducibility and a lower cost. Finally, MIPs, as other bioreceptors, are highly selective. In the case of the MIP for TNT here considered, it has been found to be very good, even against molecules of similar chemical structure [6].

Sensors based on SPR in plastic optical fiber present several advantages over silica fibers [5,6]. The use of a plastic optical fiber reduces the cost and the dimension of the device, with the possibility of easy integration of the SPR sensing platform with optoelectronic devices, such as LEDs and photodetectors, and electronic devices for data processing as well. Moreover, the multiple reflections of light occurring in the optical fiber allow to excite the sample to a large extent, so the detection sensitivity to the analytes can be excellent. An SPR platform in POF is an optimal approach for biosensors, the latter being usually based on very thin films or even monolayers of bio-receptors. The above platform has been found by us to be suitable also in the case of an MIP sensing layer [5,6]. However, this approach allows to monitor only the sites of MIP very near to the gold layer, in an almost two-dimensional way, due to the very thin penetration depth of the light. In other words, the signal (i.e. the local refractive index change, resulting in SPR variations) is produced by the interaction with only a limited number of sites. It can be imagined that metal nanoparticles would allow a larger interface between the metal and the dielectric, and a larger connection with the interaction sites, if the contact with MIP takes place in a tridimensional way, as it is when the metal nanoparticles are dispersed in the bulk of the dielectric medium. Actually this approach has been demonstrated to be effective in the case of an SPR sensor for dopamine [10], in which spherical gold nanoparticles were dispersed in a molecularly imprinted polymer deposited over a gold layer. Another example is a sensor for TNT [11] in which the use of spherical gold nanoparticles in an electrochemically polymerized MIP allowed impressively low detection limits to be reached.

In the present investigation, a particular kind of metal nanoparticles are used, i.e. five-branched gold nanostars

(GNS) [12, 13] instead of classical spherical gold nanoparticles [10,11], whose shape is shown in Figure 1 (trasmission electron microscopy image). The reason is that additional benefits are expected from the use of metal nanoparticles of this particular shape, besides the number and very thin dimensions of the branches, that increase the surface/mass ratio and the contact area with receptor holes in the MIP. In particular, they present multiple resonances [12] which are tunable and enter the near infrared range (maximum absorption in the 650-1600 nm range). This characteristics may both add flexibility to the sensor's design and increase its sensitivity. Finally, an interesting property of the POF platform is the easy preparation of tapered fibers, i.e. fibers with a zone of smaller diameter. Their implementation in SPR sensors has been demonstrated to considerably improve the sensor sensitivity in the case of SPR transduction [5,14], but as far as we know, it has never been applied to LSPR, even if in principle they should improve the sensitivity because they allow to interrogate a larger number of sites. Actually the presence of nanoparticles, which are a discontinuous layer, does not prevent the penetration of the electric field further inside the surrounding matrix.

2. **Material and methods**

2.1 **Sensing layer**

A. *Preparation of Five-Branched Gold Nanostars*

Gold nanostars were prepared according to a seed growth procedure previously published by some of us [12]. Briefly, a seed solution was prepared as follows. In a 20 mL vial, $HAuCl_4$ (5 mL, 5×10^{-4} M in water) was added to an aqueous solution of TritonX-100 (5 mL, 0.2 M). The mixture was gently hand-shaken and a pale yellow color was obtained. Then, a previously ice-cooled solution of $NaBH_4$ (0.6 mL, 0.01 M in water) was added. The mixture was gently hand-shaken and a reddish-orange color appears. The growth solution (10 mL) was prepared as follows. In a 20 mL vial, $AgNO_3$ (180 µL, 0.004 M in water) and $HAuCl_4$ (5 mL, 0.001 M in water) were added in this order to an aqueous solution of TritonX-100 (5 mL, 0.2 M). Then, an aqueous solution of ascorbic acid (170 µL, 0.0788 M) was added. The solution, after gentle mixing, became colorless. Soon after, the seed solution (12 µL) was added. The solution was gently hand-shaken and a pink color appeared and quickly changed to blue and became more intense. After 1 h at room temperature PEG_{2000}-SH was added in a concentration of 5×10^{-5} M. The mixture was stirred for 1h at room temperature, then the nanoparticles were ultracentrifuged for four cycles (13,000 rpm, 11 min) of elimination of the supernatant/redissolution of the pellet in 10 mL of bi-distilled water. These steps are required to eliminate excess PEG_{2000}-SH and TritonX-100. The pellet was dried under vacuum to obtain 0.6 mg of gold in the nanostars. Figure 1 shows TEM image and UV-Vis-nIR absorption spectrum of the GNS used in this paper.

B. *Prepolymeric mixture for MIP*

Divynilbenzene [1321-74-0] (DVB), 2,2'-azobisisobutyronitrile [78-67-1] (AIBN), 2,2-dichloro-N-[1,3-dihydroxy-1-4(4-nitrophenyl)propan-2-yl]acetamide [56-75-7] (CAP, chloramphenicol) were obtained from Sigma–Aldrich and used without any further purification. Methacrylic acid (MAA) [79-41-4] (Sigma–Aldrich cod. M0782) and

divinylbenzene (DVB) [1321-74-0] (Sigma–Aldrich cod. 414565) were purified with molecular sieves (Sigma–Aldrich cod 208604) prior to use in order to remove stabilizers. 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrobenzoic acid (TNBA) were synthesized as previously reported [6] (98% purity tested by HPLC). All other chemicals were of analytical reagent grade.

Stock solutions were prepared by weighing the solids and dissolving in ultrapure water (Milli-Q).

The prepolymeric mixture for MIP was prepared according to a classical procedure [6]. It is composed of trinitrotoluene (TNT) as template (20 mg), methacrylic acid as functional monomer (30 µl), DVB as cross-linker (665 µl) and AIBN as the radicalic initiator (15 mg). The reagents were at molar ratio 1 (TNT): 4 (MAA): 40 (DVB). The mixture was uniformly dispersed by sonication (visually homogeneous solution) and de-aerated with nitrogen for 10 min.

C. Sensor preparation by MIP with Gold Nanostars (GNS-MIP)

The pellet of gold nanostars was dispersed in 0.9 mL of prepolimeric mixture by sonication. The final concentration of the nanostars, expressed as mg of gold per mL of prepolimeric mixture, is 0.67 mg Au/mL. The polymeric film was prepared by dropping 100 µl of prepolymeric mixture on the optical platforms, and polymerizing at 70°C for about 16 h. The template molecule was extracted by washing with ethanol 10 times, leaving the imprinted sites free for successive template rebinding. Figure 2a shows schematically the sensing layer when it interacts with analytes.

2.2 Optical sensing platform based on POF

The fabricated optical sensor system has been realized removing the cladding of a plastic optical fiber (PMMA core of 980 µm and a fluorinated polymer cladding of 20 µm) along half circumference (D-type plastic optical fiber). The sample consisted in a plastic optical fiber without protective jacket embedded in a resin block, with the purpose of easing the polishing process. This was carried out with a 5 µm polishing paper. After 20 complete strokes following a "8-shaped" pattern in order to completely expose the core, a 1 µm polishing paper was used for another 20 complete strokes with a "8-shaped" pattern. The treated region was about 10 mm in length. The sensing layer (GNS-MIP) was deposited on the exposed POF core by dropping 100 µl of prepolymeric mixture on the gold layer, and polymerizing at 70°C for about 16 h. The template molecule was extracted by washing with ethanol 10 times, leaving the imprinted sites free for successive template rebinding. The POF platform with the MIP-GNS sensing layer is shown in Figure 2b. The plastic optical fiber has a PMMA core of 980 µm and a fluorinated polymer cladding of 20 µm. The refractive indexes of the materials, in the visible range of interest, are about 1.49 for PMMA, 1.41 for fluorinated polymer.

2.3 Optical sensing platform based on tapered POF

The optical platform based on tapered POF has been prepared as follows. The plastic optical fiber without protective jacket (the same of the section 2.2: PMMA core of 980 µm and a fluorinated polymer cladding of 20 µm), was heated at 150°C and stretched with a motorized linear positioning stage (Physik Instrumente (PI) M150.11) until the

taper ratio (i.e. the ratio between the maximum and minimum radius) reached 1.8. After this step the POF was embedded in a resin block, and polished as described in section 2.2. The modified region was about 10 mm in length. The sensing layer (MIP with suspended GNS) was deposited on the exposed tapered-POF core as described in section 2.2. Figure 3 shows this tapered-POF platform with the sensing layer.

2.4 Experimental setup

The experimental setup was arranged to measure the transmitted light spectrum and included a halogen lamp, illuminating the optical sensor systems (tapered POF or not-tapered POF platform with GNS-MIP sensing layer), and a spectrum analyzer. The employed halogen lamp (Model no. HL-2000-LL, manufactured by Ocean Optics) exhibits a wavelength emission range from 360 nm to 1,700 nm, while the spectrum analyzer detection range was from 200 nm to 850 nm. An Ocean Optics "USB2000+UV-VIS" spectrometer has been employed.

The spectrometer was finally connected to a computer. The LSPR curves along with data values were displayed on-line on the computer screen and saved with the help of advanced software provided by Ocean Optics.

2.5 TNT measurement procedure

The measurements were performed by dropping 100 µl of deionized water, or aqueous solution of the target molecule (TNT), over the resin block holding the modified plastic optical fiber, letting the drop to expand over the whole resin block. The transmission spectra were recorded after 5 min incubation. Between successive determinations the sensor was washed by repeatedly rinsing with water.

The experimentally obtained LSPR transmission spectra were normalized to the spectrum obtained with air as the surrounding medium when an MIP layer without GNS is placed on the optical platform (reference spectrum), for both the configurations (POF and tapered POF).

3. Results

The results reported in the following sections are relative to the two measurement configurations: POF and tapered POF platform, respectively.

3.1 MIP-GNS sensor based on POF platform

Figure 4 presents the LSPR transmission spectra, normalized to the reference spectrum, for different concentrations of TNT. It is important to stress that the localized surface plasmon resonance is excited when the GNS are suspended in the hydrated polymer phase (blue curve), as it happens when they are in direct contact with the POF [13]. This indicates that the light emerging from the fiber penetrates sufficiently in the polymer to interact with the GNS. Furthermore, it is evident from the above figure that two exploitable resonances take place, the insets showing the magnification of both of them. For the most sensitive one (first resonance) it is seen that, when increasing

concentrations of TNT interact with the molecularly imprinted polymer, the LSPR resonance changes and the resonance wavelength is shifted toward higher values (red shift).

3.2 MIP-GNS sensor based on tapered POF platform

Figure 5 presents the LSPR transmission spectra obtained with the tapered POF, normalized to the reference spectrum, for different concentrations of TNT and for two different substances with chemical structure similar to that of TNT: 2,4,6-trinitrobenzoic acid (TNBA in Fig. 5) and 2,2-dichloro-N-[1,3-dihydroxy-1-(4-nitrophenyl) propan-2-yl] acetamide (chloramphenicol, CAP in Fig. 5). In this case too two resonances are present, the first being the most sensitive one, as seen in the insets. There is evidence of plasmon resonance frequency shift only in presence of TNT, indicating the very good selectivity of the artificial receptors here considered. Figure 6 shows the resonance wavelength, versus the logarithm of the concentration of TNT, along with the Hill fitting to the experimental data [15] as shown in equation (1), in which the formal similarity of the Langmuir adsorption isotherm is stressed:

$$Hill\ equation: \Delta\lambda_{ex} = \frac{kc_{site}(K_f c)^h}{1+(K_f c)^h} \qquad (1)$$

$$\Delta\lambda_{ex} = k\left[\overline{AS}\right]$$

$$K_f = \frac{[\overline{AS}]}{[A][\overline{S}]}$$

$$c_{site} = [\overline{S}] + [\overline{AS}]$$

h is the Hill factor. In Figure 6 the results of not-tapered platform and of the platform composed of a gold layer over the not-tapered POF, in contact with MIP, as reported in a previous investigation [6], are compared with the results with tapered POF platform. The parameters used for estimating the continuous curves in Figure 6 are displayed in Table 1.

4. Discussion

The transmission spectra obtained with POF and tapered POF, shown in Figures 4 and 5, exhibit two transmission minima, at around 490 nm and 760 nm for POF (see Fig. 4), 400 nm and 720 nm for tapered POF (see Fig. 5), respectively. The dips are at lower wavelengths in the case of the tapered POF with respect to the not tapered one. Evidently the difference is due to the different shape of the waveguide in the two cases. The transmission minimum at the lower wavelength is much better defined in tapered POF than in POF, and its position depends on the TNT concentration more than that at around 720 nm, i.e. the sensitivity is much better. Also in the case of the not tapered POF, the first resonance (around 490 nm) undergoes a larger wavelength shift with the TNT concentration than the second one (around 760 nm), even if not well defined. The above considerations led to the choice of the first resonance, for both platforms, for the following comparative analysis.

For the sake of clarity, we briefly recall here the basic definitions for the sensitivity of plasmon resonance based

sensors. The sensitivity (S) can be defined by calculating the shift in resonance wavelength per unit change in refractive index (sensors with spectral interrogation). It is usually reported in nanometers of peak shift per Refractive Index Unit (nm/RIU):

$$S = \frac{\delta \lambda_{res}}{\delta n} \left[\frac{nm}{RIU} \right] \qquad (2)$$

For a biochemical optical sensor, the sensitivity is more conveniently defined as:

$$S = \frac{\delta \lambda_{res}}{\delta c} \left[\frac{nm}{M} \right] \qquad (3)$$

In other words, the sensitivity can be defined by calculating the shift in resonance wavelength per unit change in analyte concentration (nm/M) and calculating the slope of the regression line.

The above approach has been exploited to compare the performances of the proposed sensing platforms in the case of SPR based sensors for TNT detection characteristics from recent literature [6].

The regression line, obtained from the data reported above in the case of the GNS-MIP based sensor, with not-tapered POF, is reported below along with the regression line relative to the same MIP for TNT, but with SPR achieved through a gold layer interposed between the POF and the MIP layer, from ref. [6]:

$$GNS - MIP / POF \qquad \rightarrow \lambda_{ex} = 8.5(3) \cdot 10^4 \, c_{TNT} + 495.4(1) \qquad R^2 = 0.998$$

$$MIP \; on \; gold \; layer / POF \qquad \rightarrow \lambda_{ex} = 2.7(8) \cdot 10^4 \, c_{TNT} + 758.5(7) \qquad R^2 = 0.925$$

It is evident that the sensitivity is noticeably improved in the sensor based on gold nanostars suspended in the polymer with respect to the previously proposed sensor based on a thin gold layer [6], namely three times higher. As a consequence and because of the lower noise in the blank, the lower detection limit (LOD) is much better, being 2.4×10^{-6} M instead of 5.1×10^{-5} M (detection limit evaluated from twice the standard deviation of the blank), i.e. twenty times lower.

This indicates that the configuration based on GNS suspended in the polymer is much more sensitive to the refraction index variation than the thin layer of gold, probably because of the three dimensional structure of the nanostars. This allows the metal surface to be directly in contact with a larger number of combination sites in the polymer than the bidimensional gold layer. This could be confirmed by the fact that the third parameter of the Hill equation, kc_{site}, is higher in the case of gold nanostars suspended in polymer than in the case of the gold layer as seen in Table 1.

A further improvement in the sensitivity is obtained using the tapered POF, as reported in Table 1. The introduction of the tapered region before the SPR sensing region (see Figure 3) helps to reduce the incidence angles of the guided rays in the fiber close to the critical angle of the unclad uniform tapered region (sensing region). This is obtained by choosing the minimum allowed value of the radius of the output end of the taper so that all the rays remain guided in the uniform core sensing region [14]. After propagating through the uniform region, the rays enter the second taper

(after SPR sensing region, see Figure 3) which reconverts the angles of these rays into their initial values, so that they can propagate up to the output end of the fiber. Thus, the sensing probe has the minimum diameter such that no ray leaks out and a majority of rays are bound to propagate close to the critical angle, thereby increasing the penetration depth of the evanescent field to almost the maximum value [14]. Most of the previous investigations about the tapered optical fibers involve the SPR phenomenon, while in the present investigation LSPR is considered. Actually it has been found that the effect of the tapered fiber in the GNS-MIP based sensor considered in the present investigation is even higher than that reported by similar MIP on gold film layer [5] at the same taper ratio, 1.8. This is most probably due to the increased penetration depth of the evanescent field, involving a larger number of interaction sites of TNT in the GNS-MIP to generate a signal. This is seen from Table1, in which the third parameter of the Hill equation, kc_{site}, is much higher in the case of the sensor based on tapered fiber. Thus the sensitivity is noticeably improved with respect to the GNS-MIP sensor based on not-tapered POF platform.

Table 1 reports the experimentally measured performance parameters, in the linear range, for the tapered fiber sensor. In the linear range, the sensitivity is 8.3×10^5 [nm/M] for MIP-GNS on tapered POF platform, ten times higher than that of GNS-MIP on not-tapered POF, which is also reported in Table 1 for comparison. As a consequence the lower detection limit (LOD) is much better too, being 4.1×10^{-7} M instead of 1.2×10^{-6} M (GNS-MIP/POF).

The results obtained in the case of the not tapered fiber with MIP-gold layer and GNS-MIP are reported in Table 1. It is interesting to underline that the affinity constant is very similar, as expected as MIP is the same, while the parameter $k\,c_{site}$ is noticeably lower in the case of MIP-gold layer sensor, corresponding to the lower sensitivity.

Chemical Sensor System in POF for TNT	Sensitivity [nm/M]	LOD	Hill equation parameters
MIP on gold layer/POF [6]	2.7×10^4	5.1×10^{-5} M	K_f=4 10^4;kc_{site}=4;h=1
GNS-MIP/ POF	8.5×10^4	2.4×10^{-6} M	K_f=2 10^4;kc_{site}=7;h=1
GNS-MIP/tapered POF	8.3×10^5	4.1×10^{-7} M	K_f=4 10^4;kc_{site}=29;h=1

Table 1. Performance parameters for the MIP-GNS sensors with tapered and not-tapered POF platform, in the linear range. The parameters are compared with those for the same MIP for TNT, but with a gold layer interposed between the POF and the MIP layer previously obtained [6].

The parameters of the Hill equation are similar for the different platforms considered, only the maximum response value is different, corresponding to the different sensitivity, as discussed above. The parameter K_f, corresponding to the formation constant of the adduct polymeric site/template, is similar as expected considering that the imprinted polymer is the same. It is possible that a further improvement in sensitivity could be achieved by optimizing the polymer composition, in order to increase the affinity constant of the imprinted sites.

It must be recalled that an interesting characteristics of MIPs is their very high selectivity. The TNT-selective MIP prepared and used in this paper is identical to that previously employed for a POF sensor [6], which has been

proved to be selective even in the presence of molecules of very similar structure (TNBA and CAP). As seen in Figure 5 the selectivity is very good in GNS-MIP based sensors too, in which gold nanostars have been suspended in the prepolymeric mixture, before polymerization. In fact, concentrations of 2,4,6-trinitrobenzoicacid (TNBA) and chloramphenicol (CAP) as high as 10^{-4} M, three orders of magnitude larger then LOD of TNT (10^{-7} M), do not produce any shift of the resonance wavelength.

5. Conclusion

The experimental results indicate that the new sensor system based on the five-branched gold nanostars in MIP is suitable for highly sensitive TNT detection. The sensitivity of this new POF sensor is about three (not-tapered POF) or thirty (tapered POF) times the value of the POF sensor with an MIP layer on the planar gold film [6].

It has been found that it is possible to suspend the five branched gold nanostars prepared and purified as described in the prepolymeric mixture for MIP formation at a sufficiently high concentration to obtain a significant LSPR signal. This can be at least in part ascribed to the particular shape of the considered nano-objects. Furthermore, MIP maintains its selectivity even in the presence of suspended gold nanostars.

The proposed sensing platform is easy to implement, low cost and it opens the door to a new approach in the chemical optical fiber sensors field.

Acknowledgment

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Captions

Fig. 1 (a) TEM image of the same sample (acquired on a Jeol JEM-1200 EX II 140 instrument). (b) UV-Vis-nIR absorption spectrum of the five-branched GNS used in this work (sample is diluted 1:10 with bidistilled water and the spectrum is registered on a Cary6000i UV-Vis-nIR spectrophotometer equipped with a 1 mm glass cuvette)

Fig. 2 (a) Schematic representation of GNS-MIP sensing layer after the interaction of analyte (TNT). (b) Not-tapered POF platform with GNS-MIP sensing layer.

Fig. 3 (a) Tapered POF platform with GNS-MIP sensing layer. (b) Cross section view of sensing region.

Fig. 4 Not-tapered GNS-MIP/POF platform. LSPR transmission spectra, normalized to the reference spectrum, for different concentrations of TNT. Insets are the magnification of the indicated resonance wavelengths.

Fig. 5 Tapered GNS-MIP/POF platform. LSPR transmission spectra, normalized to the reference spectrum, for different concentrations of TNT and for two different analytes with chemical structure similar to that of TNT: CP and TNBA. Insets are the magnification of the indicated resonance wavelengths.

Fig. 6 Plasmon resonance wavelength variation as a function of TNT concentration. Continuous curves: Hill fitting to the experimental data (parameters as in Table 1). ◊: GNS-MIP/tapered POF platform. ▲: GNS-MIP/POF platform. *: MIP on gold layer/POF platform.
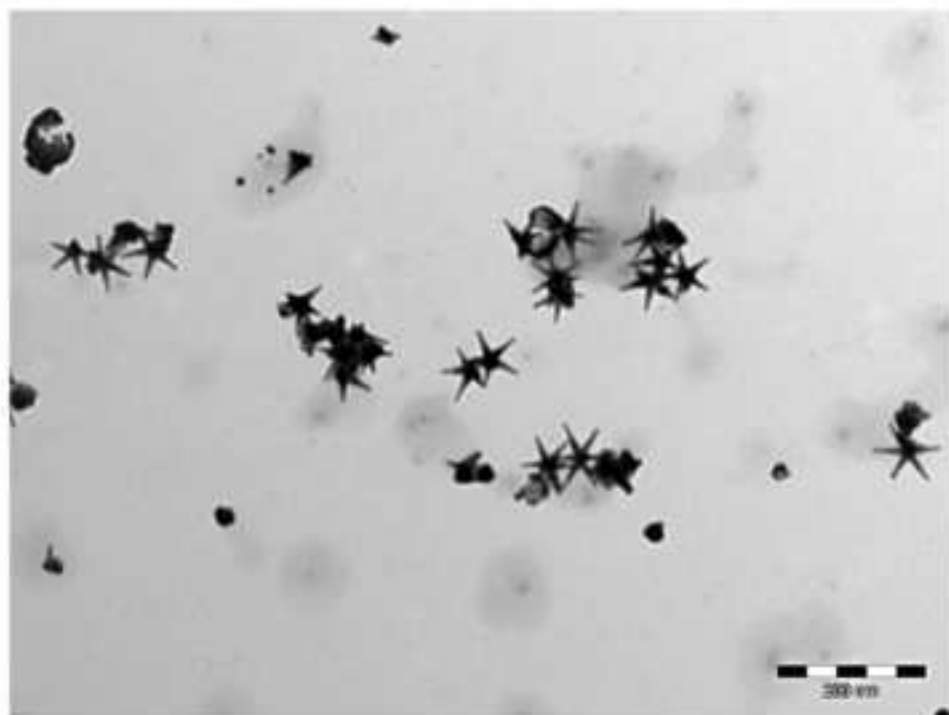
(a)
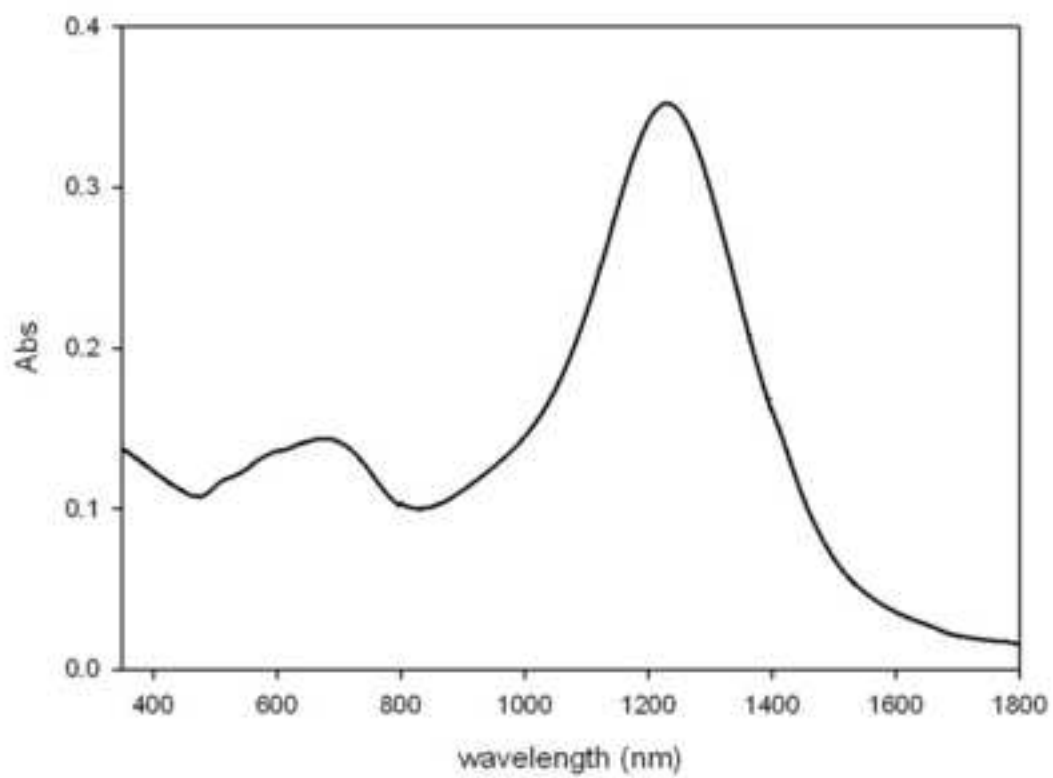
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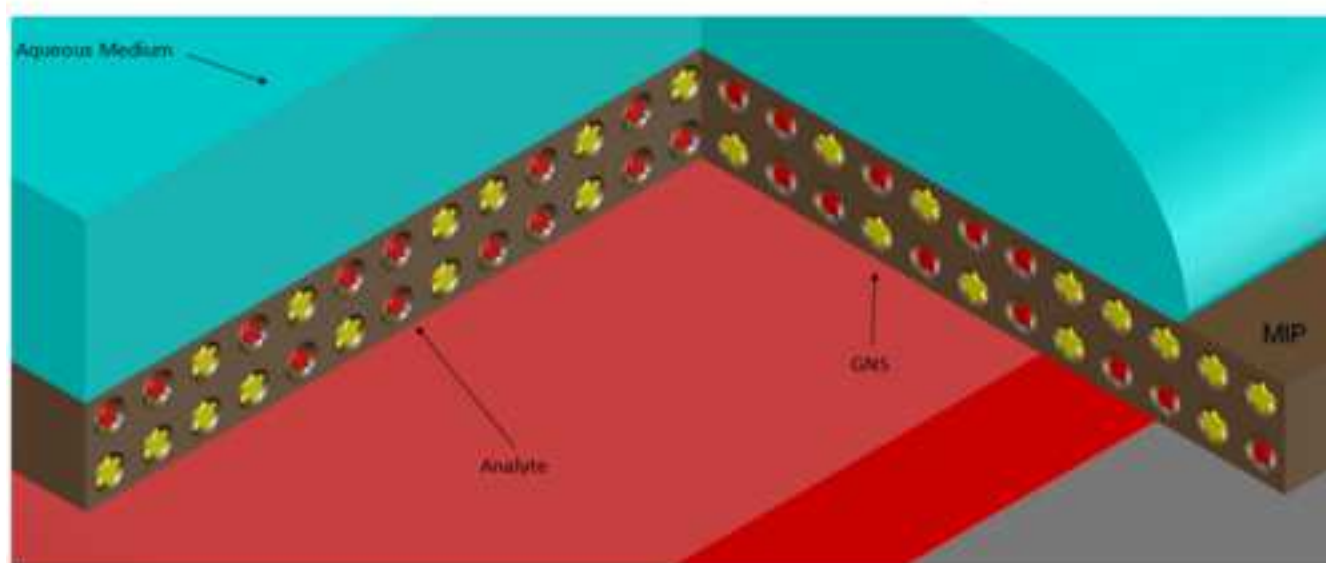
Figure2
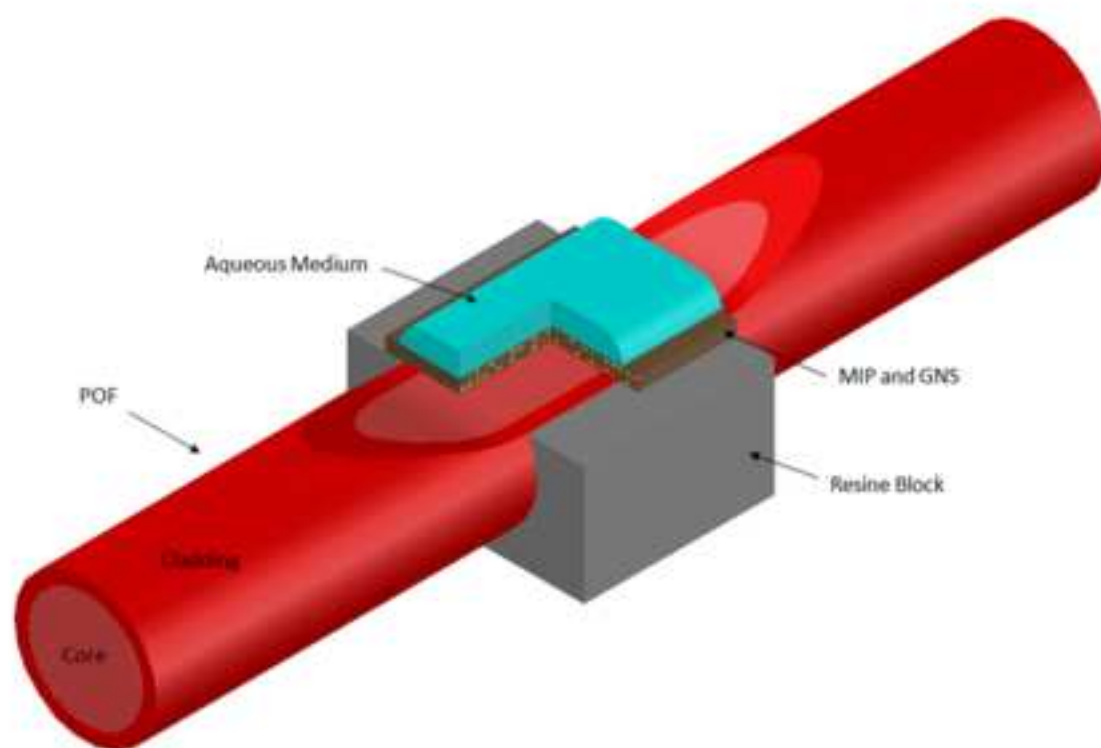**Click here to download high resolution image**

(a)

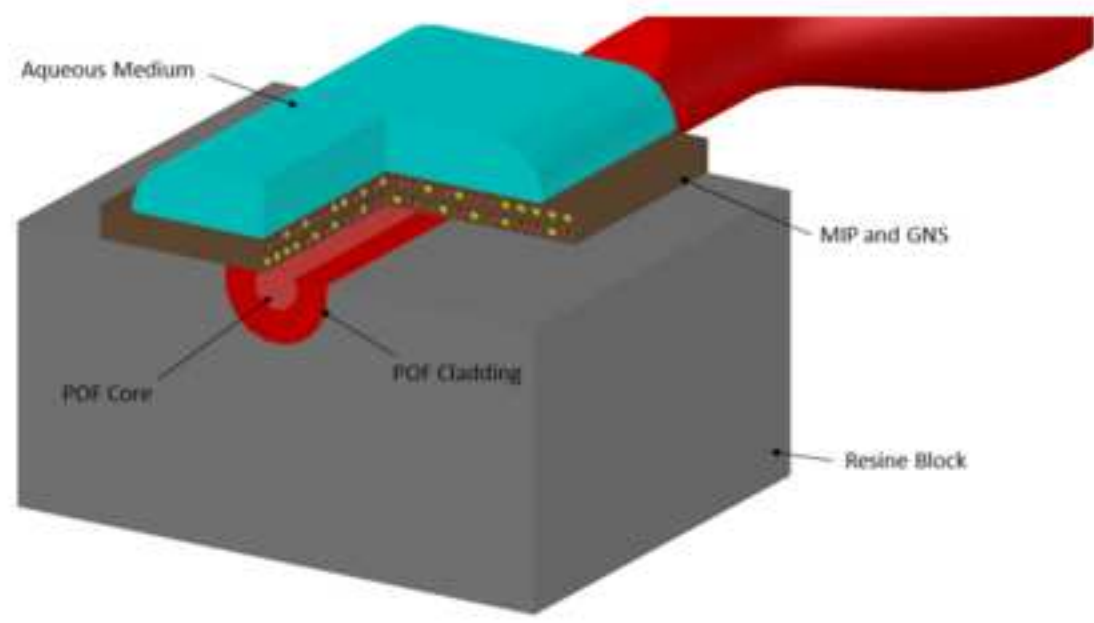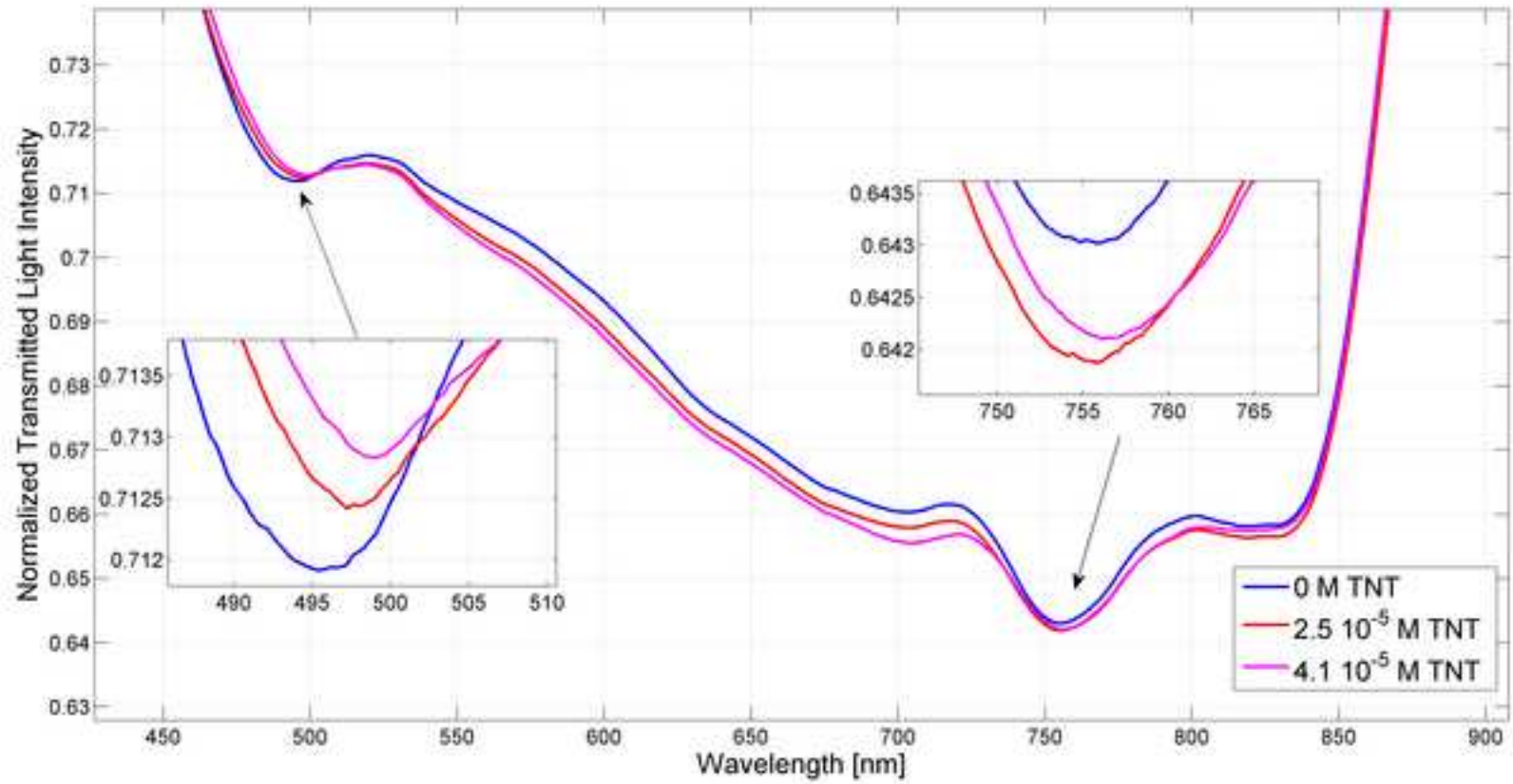(b)

Figure3
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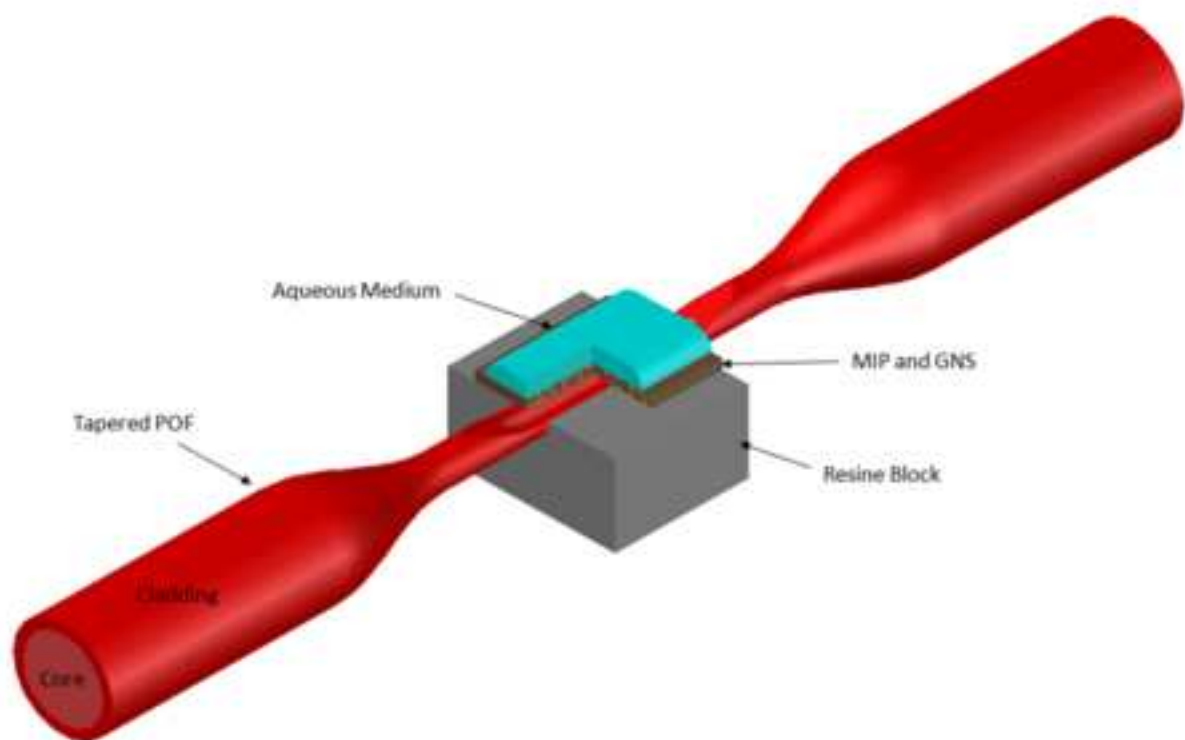
Aqueous Medium

MIP and GNS

Tapered POF

Resine Block

Cladding

Core

(a)

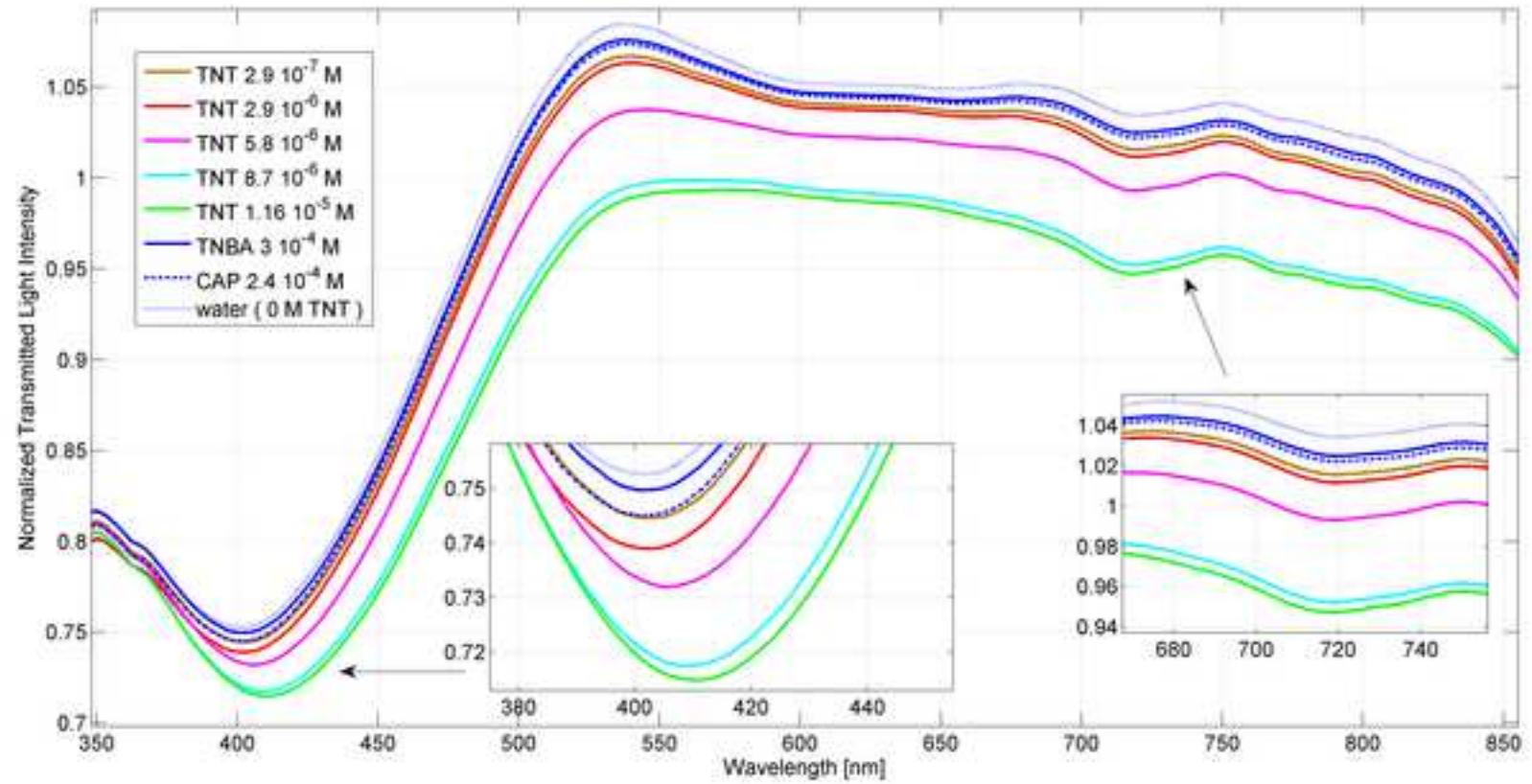Aqueous Medium

MIP and GNS

POF Core

POF Cladding

Resine Block

(b)

Figure4

Figure6
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