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TITLE

Two-Photon Absorption Near Field Imaging of Non-Fluorescent Organic Nanoparticles

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ABSTRACT

We present here the first reported use of fiber aperture near-field optical microscopy (NSOM) for the purpose of characterizing directly the two-photon absorption (TPA) of non-emissive nanoparticles. It will be displayed how this empirically driven technique can provide per particle and per molecule assessment of the two-photon cross-section (TPACS) by extracting the non-linear optical (NLO) signal from that due to scattering and far-field effects. This is shown with the investigation of a known two-photon responsive porphyrin dimer, which has exhibited both severe fluorescence quenching and a multiple order of magnitude TPACS enhancement in aggregate, after self-assembly into uniform nanoparticles. A particular emphasis will be placed on the viability of this technique for the characterization of low-scatter optical limiting organic nanomaterials.

KEYWORDS

NSOM, two-photon, porphyrin dimer, organic nanoparticle

ARTICLE TEXT

1. INTRODUCTION

As attempts to develop functional condensed phase nanomaterials for non-linear optical (NLO) applications grow more sophisticated, it is critical that methods for directly probing the NLO structure-function relationship of assemblies be actualized. This is a particularly poignant concern for developing next generation

organic nanomaterials for applications like remote sensing, light harvesting and optical limiting [1-3]. Directly probing the NLO character of individual nanoscale assemblies is critical to determine how subtle changes in size, morphology and environment may enhance the response of a system. This is necessary for applications where optical limiting or light harvesting materials must coat or surface treat another functional device such as a CCD, remote sensor or inorganic solar array. In these instances it is uniformly required that the optically active coating diffract or scatter the non-absorbed light as little as possible and generate little or no fluorescence. This can be achieved readily by using organic nanomaterials which self-assemble and have well characterized optoelectronic properties at the interface of the particles. The viability of using two-photon excited fluorescence microscopy for probing directly the third order non-linear two-photon response of individual self-assembled nanomaterials has been displayed [4-6]. However, if a species experiences large quenching effects on assembly, quantitative two-photon fluorescence imaging poses a difficult prospect. This points instead to direct imaging of the multiphoton absorption. Though the possibility of true absorption imaging by NSOM has been displayed [7], here we show for the first time that two-photon absorption near-field imaging (TPA-NSOM) is a viable method for the quantitative inspection of non-fluorescing nanoscale materials. This allows for the investigation and identification of those morphologies which provide high NLO response but poorly detectable fluorescence. This study also presents a fast, empirical method for selecting particle/assembly regimes which provide significant enhancement factors in the solid state, a process beyond the ability of bulk TPA measurements.

Organic nanoassemblies in a variety of configurations, such as rods, macrocycles, molecular wires, ladders, and dendrimers, [4,8-11] have been shown to display enhanced NLO properties in ensemble over the individual building blocks. Previously, we have characterized an imidizoyl terminated porphyrin dimer (figure 1) which has been shown to possess a TPA cross-section enhancement factor of 90 when self assembled into a slipped cofacial macrocycle [8]. It is then possible to assemble different architectures that capture at least some of this ensemble enhancement, even if assembly is largely with random or uncontrolled orientation. A solvent transfer process and rapid deposition results in organic nanoparticles of uniform dimensions. TPA-NSOM provides direct imaging of these materials with a viable method for removal of scattering effects and optical edge resolutions < 15 nm. The method used to determine the two-photon cross-section enhancement of ~2.5 in the resultant nanoparticles readily provides images which can be assessed quantitatively for this empirically driven assembly and characterization regime.

2. EXPERIMENTAL

A femtosecond excitation source is used (Spectra-Physics Mai Tai) for this study, operated at 830 nm, 80 MHz and a pulse FWHM of 110 fs. Intensity is regulated using a variable neutral density filter. The excitation is coupled into a CDP-NSOM multiscopes with shear-force AFM, absorption and fluorescence detection capabilities. The probes use single mode fiber optic cable (F-SF Newport for 820 nm

signaling). The probes are pretreated with weak acid to hydrolyze and soften the cladding (0.1 M HCl) and pulled using a Sutter P-2000 CO₂ capillary puller optimized for a 13 deg. initial taper and low impact drawing. Tips are immediately submerged into a methanol ice bath to restrict cladding relaxation. Nominal aperture diameter is 30 nm from a non-metallated probe, as determined through from a fluorescent standard[REF]. The non-trivial far- and near-field scattering signal inherent to a non-metallated probe, which is linearly dependant on incident intensity, is removed after fitting from the non-linear component of the feature signals. Collection is done with a 2.5 nm pixel size. False redoubling to 1.25 nm and subsequent 3 pixel nearest neighbor averaging is performed on AFM and TPA-NSOM images using Nanoscope software. A 98 uM porphyrin dimer solution in 9:1 DMF/pyridine was added to Millipore purified water at a 1:20 ratio and shaken vigorously for 10 s. The resultant suspension was then vented for 30 seconds under a nitrogen flow and drop deposited on cleaved mica and vacuum dried for 30 minutes. Pixel size, averaging and probe dither give a 2.5 nm uncertainty in the AFM signal (x-y) and results in a nominal edge resolution of 5 pixels in the TPA-NSOM image.

3. RESULTS AND DISCUSSION

AFM scans of the assembled nanoparticles on a mica substrate (figure 1) show uniform porphyrin particles with consistent dimensions of 200 nm with heights ~10 nm. The features observed in the simultaneously collected NSOM image show a decrease in counts typically associated with absorption or scattering in most systems, and can be imaged with a resolution of 12.5 nm. For NSOM scattering images [12], this is typical of other systems with similar illumination and collection, but is one of the highest reported resolutions for optical absorption images[REF]. From peak averaging at a high incident flux the majority contribution for this signal appears as two-photon absorption from the nanostructure and is indicated in the extracted quadratic TPA signal given in figure 2. Quantitative polynomial extraction can be preformed on the observed intensity such that:

$$\iint I(x,y,i)dx dy = \iint s(x,y,z)I(x,y,i)dx dy + \iint t(x,y,z)I(x,y,i)^2 dx dy \quad (1)$$

and becomes in a pixilated environment with constant z (AFM value) and i (incident intensity):

$$\Delta I = s_z \sum_{x,y} I_{i,j} + t_z \sum_{x,y} I_{i,j}^2 \quad (2)$$

This is with **s** the cofactor for scattering, **t** the cofactor for TPA (linearly related to σ_2), and both **s** and **t** determined from polynomial fitting from equation (2) and shown in figure 2.

Several scans of an individual nanoparticle were made from 21 mW to 168 mW of incident power on the NSOM fiber optics, having relative intensities ranging from 1 to 8 (figure 3). Observation of the coupling efficiency for our system, through a pinhole with the probe 1 μm above contact, gives a 1.5 % throughput at the probe tip due to the extremely high optical bleed at the onset of taper and a some spot size/rejection at the fiber coupling point. Collection efficiency for absorption imaging is presumed near 100%. Correcting for scatter, PMT sensitivity at 830 nm and chromophore density, a TPACS of $2800 \pm 600 \text{ GM}$ (1 GM = $10^{-50} \text{ cm}^4\text{-second}/\text{photon}$) was determined for the porphyrin dimer using the following relationship given constant incident intensity:

$$\frac{(1-s) \iint I(x,y) dx dy}{\iint \frac{\rho}{M} N_A z(x,y) dx dy} = \sigma_2 / \text{molecule} \quad (3)$$

This is with ρ being an assumed density of 1.2 g/mL[13] and M the molar mass.

In solution, this dimer possesses a TPACS of 570 GM. As a self-assembled macrocycle with 19 dimer units, the TPACS per dimer was found to be two orders of magnitude higher. The TPACS enhancement in these particles is not as drastic as that found in the more sophisticated assembly of this structure. In the macrocycle the principle mode of enhancement was found to be related to a slipped co-facial imidizoyl-Zn association in conjunction with additional locally coordinated dimers resulting in a greatly enhanced transition dipole coupling in the system.[Ref] It is reasonable to assume, even given a random configuration, that some of the chromophores will find themselves in this or a similar environment. This leads to a modest particle ensemble TPACS enhancement factor of 5 for this assembly method as measured by our TPA-NSOM system.

The scattering signal appears low for this system, with S/N remaining constant at ~ 0.2 . This is specifically true when compared to other NSOM techniques in which scattering is the primary method for imaging from far field illumination. [REF] Several components of the system, including the apertured top-down illumination, may contribute to this low observed scattering and the 830 nm wavelength. The proximity of the excitation source, low aperture diameter, $< 5 \mu\text{m}$ thickness of the mica substrate and the close proximity of the collection aperture all may result in a low observed scattering, unlike other NSOM methods in which far-field excitation and near-field collection occur and systems where the collection is not in the direction of excitation. Additionally, far-field diffraction-type rings at $\lambda/2$ from center of object mass appear nominal, with intensities beginning below 1/10 noise level in the majority of line plots, further confirming the majority of signal is related to near-field excitation. These features of the system lead to a series of power dependant images by which scattering can be extracted via polynomial fitting and two-photon character determined from the non-linear component. Shown in figure 3 and table 1 are the NSOM transmission results for the study. It can be shown that the polynomial model used to determine scattering and TPA contributions reasonably matches with the line scan maxima observed in figure 3b.

4. CONCLUSIONS

Shown here for the first time is the viability of using TPA-NSOM for the observation of low-scatter systems in order to determine the exact TPA response of a non-fluorescing organic nanostructure. Through a straightforward assembly method of a known TPA material, exact per particle assessment of the NLO character can be extracted. This displays that even with scattering dominating at low intensities, where TPA becomes virtually unobservable, higher energy IR near-field excitation can provide direct observation of two-photon absorption for nanoparticles of 10 nm thickness with an optical feature resolution of less than 15 nm. TPA-NSOM makes possible a high throughput analysis of the per particle TPA for materials and their morphologies under ambient conditions even when a materials nanoscale fluorescence is difficult to observe. Through a similar empirically rigorous regime, it can be assumed that other organic material/assembly paradigms can be investigated for low scatter composite optical devices in the future. Only with the greatest understanding of individual particle behavior will the highest order of functionality be obtained in these materials, specifically sub-diffraction sized optical limiting organic particles. Additionally, in samples that do exhibit fluorescence, it may be possible to compare other TPEF analog fluorescence imaging techniques [9-10] to the Z-scan analog TPA-NSOM power dependency images, thereby clarifying discrepancies in the TPA cross-sections periodically observed by comparing the two methods.

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Figure 1. Topographic and near-field optical characterization of the porphyrin nanoparticle. Presented: (A) TPA-NSOM of single particle, FOV 1 μm with AFM inset, (B) AFM of uniform particles, FOV 4 μm with 3D inset, (C.) X- and Y- line selections displaying feature resolution, (D) 3D rendering of TPA-NSOM and (E) AFM for a single particle.

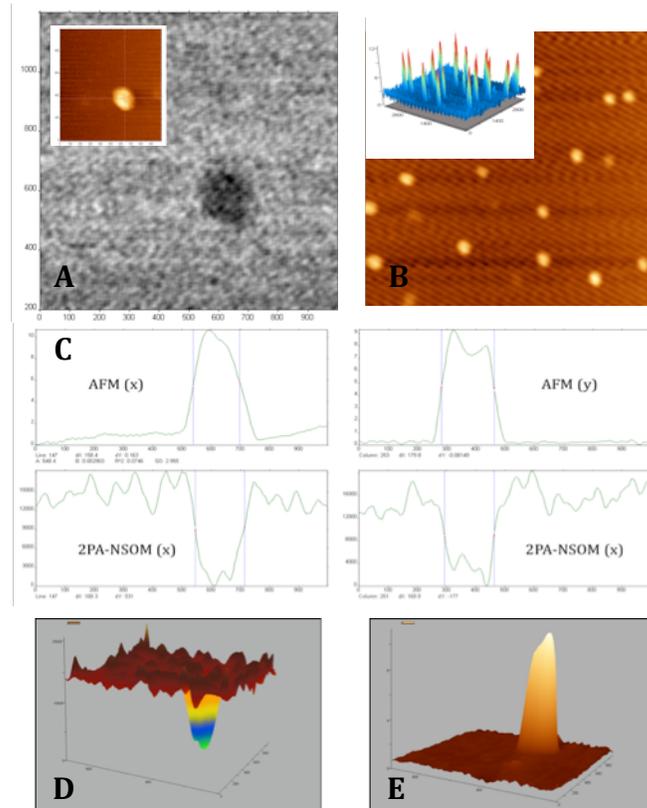


Figure 1.
Porphyrin dimer (1) and optical response per molecule.

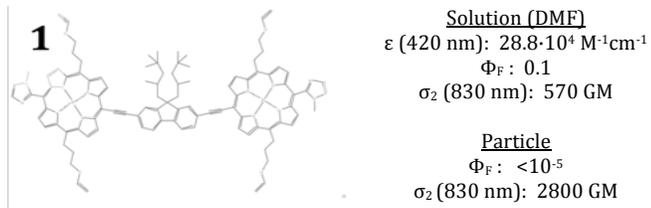


Table 1.

Summary of experimental results for quantitative TPA-NSOM

| I_{input} (mW) | Relative Power | I_{obs} (10^6 cps) | N (10^3 cps) | ΔI (cps) | S/N |
|----------------------------|-------------------|-----------------------------------|--------------------|---------------------|------|
| 168 | 8 | 5.03 | 4.53 | 19,166 | 4.23 |
| 147 | 7 | 4.43 | 4.51 | 14,389 | 3.19 |
| 126 | 6 | 3.80 | 3.95 | 10,896 | 2.76 |
| 105 | 5 | 3.17 | 3.62 | 6846 | 1.89 |
| 84 | 4 | 2.53 | 2.34 | 4339 | 1.86 |
| 61 | 3 | 1.83 | 1.86 | 2553 | 1.38 |
| 42 | 2 | 1.27 | 1.59 | 1185 | 0.74 |
| 21 | 1 | 0.63 | 1.15 | 305 | 0.26 |

I_{input} incident intensity coupled into fiber; I_{obs} median non-feature counts; N standard deviation of non-feature counts; ΔI median change in intensity at feature, less scattering counts.

Figure 2.

Power dependence determination of TPA and scattering components of nanoparticle images.

[A] Intensity dependence of image features. [B] Log-log plot showing degree of nonlinear character.

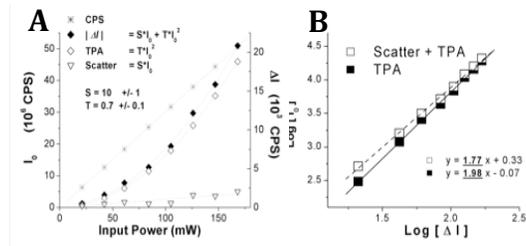


Figure 3.

Power dependant TPA-NSOM of a single porphyrin nanoparticle.

[A] TPA-NSOM, relative intensities from 1-8 adjusted for maximum contrast. [B] X-axis line plots adjusted to zero background, red lines indicating expected change in intensity based the signal polynomial (eqn. 2) given with linear scatter and non-linear two photon components.

