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Two-Photon Accessed Excited State Absorption in bis(terpyridyl Osmium)-(Porphinato)Zinc

Description

Two-photon absorption properties of a (terpyridyl)osmium-(porphinato)zinc (OsPZnOs) are studied in bulk and waveguides. Integration of OsPZnOs ($d > 1300\text{GM}$) in waveguides showed enhanced nonlinear performance and potential for photonic applications.

Disciplines

Physical Sciences and Mathematics

Comments

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Abstract: Two-photon absorption properties of a (terpyridyl)osmium-(porphinato)zinc (OsPZnOs) are studied in bulk and waveguides. Integration of OsPZnOs ($\delta > 1300 \text{GM}$) in waveguides showed enhanced nonlinear performance and potential for photonic applications.

OCIS codes: (190.0190) Nonlinear Optics; (190.4710) Optical Nonlinearities in Organic Materials ; (190.7110) Ultrafast Nonlinear Optics ; (160.4330) Nonlinear Optical Materials.

1. Introduction

Chromophores that simultaneously have strong two-photon absorption (2PA) as well as strong and long-lived excited state absorptions (ESA) in the near IR have been shown to be promising candidates for all-optical switching applications, such as optical sensor protection.[1] To enhance the performance of the nonlinear absorbing chromophores, two paths have been exploited: Molecular engineering of nonlinear absorbers to increase the 2PA and ESA cross sections [2,3] as well as incorporating chromophores with microstructured optical devices like waveguides to enhance the nonlinear response benefited from increased energy density and interaction length [4]. In this report, we present the strong 2PA properties of a structurally engineered porphyrin-based material, (terpyridyl) osmium-(porphinato)zinc or OsPZnOs, and the further enhanced nonlinear response of OsPZnOs in waveguides.

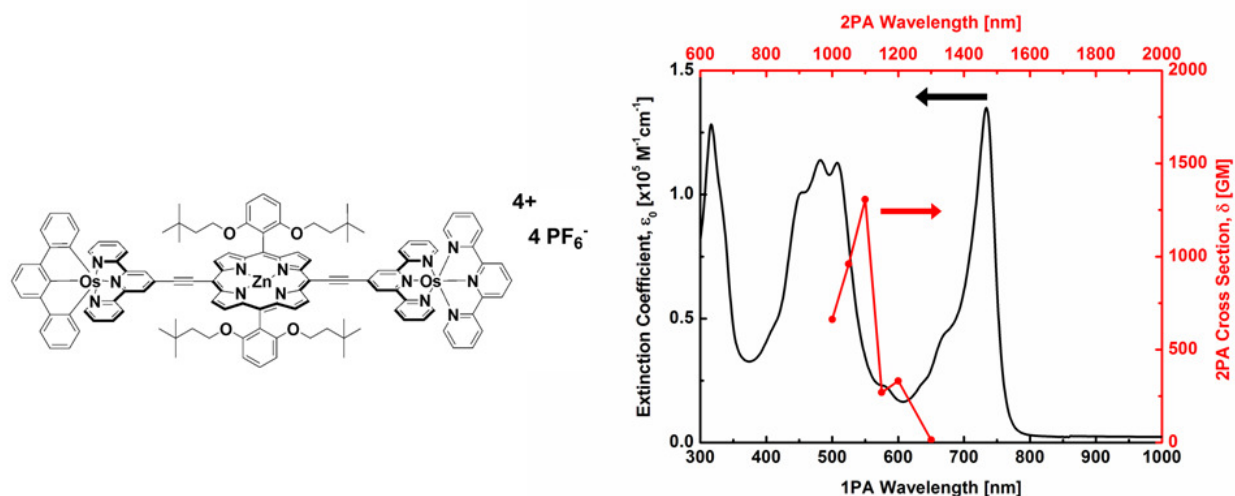


Fig. 1: (Left) Molecular structure of OsPZnOs. (Right) One-photon (black) and two-photon (red) absorption spectra of OsPZnOs in DMSO.

2. OsPZnOs as Promising Nonlinear Absorber

Porphyrin-based materials have been shown to possess interesting 2PA properties. These can be augmented by strong and long-lived ESA resulting from fast intersystem crossing from the two-photon-activated state to a metal-to-ligand charge-transfer excited triplet state. [1-3] The molecular structure of OsPZnOs, shown in figure 1, is comprised of two electronic-donating (D) terpyridyl osmium moieties, and one electronic-accepting (A) zinc porphyrin center. The three units are bridged by ethynyl π -linkers. For such D- π -A- π -D molecules, the ground state electron density is largely localized on individual donor and acceptor moieties, while, in the excited state, the strong coupling between donor and acceptor gives rise to delocalized electronic structure and extended conjugation length.[2,5] Essentially the ground state is three separate small particles-in-boxes while the excited state is one long particle-in-a-box. For OsPZnOs, such delocalization in the excited state leads to strong and spectrally broad excited

state absorption in the near IR[3]; furthermore, the conformational change between ground and excited state electronic structures as well gives rise to strong transition dipole moment that result in strong 2PA properties.[2,5] OsPZnOs has been previously reported with broad and extraordinary long-lived ($> 1 \mu\text{s}$) excited state absorptions in the near IR[3] and its D- π -A- π -D structure leads on to expect strong 2PA[5]. In this study, we performed a series of wavelength-dependent Z-scan measurements with femtosecond pulses on bulk material to illustrate the dispersion of 2PA cross sections.

3. Microstructure Enhanced Nonlinear Absorption of OsPZnOs

The two-photon absorption properties of OsPZnOs were measured by open-aperture z-scan with femtosecond pulses ($\tau_p \sim 65\text{-}75\text{fs}$) in the near IR. The sample of OsPZnOs was dissolved in DMSO at a concentration of $\sim 20\text{mM}$. OsPZnOs showed intensity-dependent 2PA absorption suggesting the existence of excited state absorptions or higher order nonlinearities. The magnitude of 2PA cross section ($\delta = \beta E_{ph}/N$, where N is the number of particles per unit volume and E_{ph} is the photon energy) is defined as the intercept value at zero intensity of the linear fits of the intensity-dependent 2PA. As shown in fig. 1, OsPZnOs has a 2PA resonance peaked around 1100nm with $\delta > 1300\text{GM}$. This value is significantly larger than those reported for other monomeric zinc porphyrins.[2,6] Moreover, the 2PA resonance of OsPZnOs overlapped with the weak terpyridinyl osmium absorption around 550nm, suggesting such enlarged 2PA cross sections may be due to charge transfer from osmium terminal donors..

The nonlinear performance of OsPZnOs was also tested with nanosecond-pulsed nonlinear transmission measurements. As shown in Fig. 2a, the nonlinear response of OsPZnOs at 1100nm was significantly enhanced in the waveguides (inner diameter = $10\mu\text{m}$ and pathlength = 18mm, conc = 0.21 mM) as compared to the measurement in bulk material. The wavelength dependence (Fig. 2b) of the enhanced response in the waveguide roughly follows the dispersion of 2PA cross sections of OsPZnOs. At 1100 nm, the peak of 2PA, the threshold is more than two orders of magnitude smaller than that observed in the bulk. The longer interaction length in the waveguide allows better thresholds and larger net suppression when comparing the nonlinear transmission experiments.

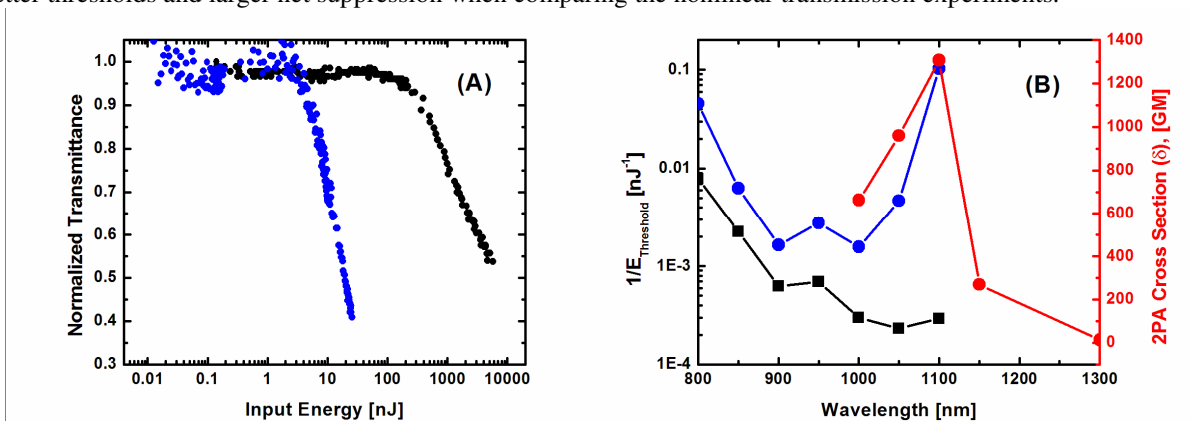


Fig. 2: The comparison of nonlinear response of OsPZnOs in capillary waveguides (blue) and bulk material (black). (Left) Nanosecond nonlinear transmission measurements at 1100nm. (Right) Wavelength-dependent nonlinear absorption thresholds in waveguides and bulk material versus the dispersion of 2PA coefficient of OsPZnOs (red).

4. Summary

OsPZnOs showed extraordinary nonlinear absorption capability as a result of the strong coupling of terpyridinyl osmium and porphyrin units. The nonlinear response of OsPZnOs was further enhanced via the incorporation of OsPZnOs with capillary waveguides and showed the potential of OsPZnOs as a promising nonlinear absorber in the near IR.

5. References

- [1] J. M. Hales, M. Cozzuol, T. E. O. Screen, H. L. Anderson, and J. W. Perry, *Opt. Express* **17**, 18478 (2009).
- [2] H. T. Uyeda, Y. Zhao, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, and M. J. Therien, *J. Am. Chem. Soc.* **124**, 13806 (2002)
- [3] T. V. Duncan, I. V. Rubtsov, H. T. Uyeda, and M. J. Therien, *J. Am. Chem. Soc.* **126**, 9474 (2004).
- [4] J. J. Butler, J. J. Wathen, S. R. Flom, R. G. S. Pong, and J. S. Shirk, *Opt. Lett.* **28**, 1689 (2003).
- [5] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, and C. Xu, *Science* **281**, 1653 (1998).
- [6] M. Drobizhev, Y. Stepenenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, and H. L. Anderson, *J. Phys. Chem. B* **109**, 7223 (2005).