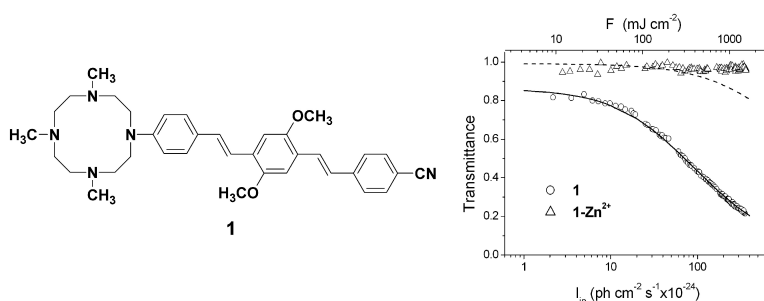


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Zinc-Induced Switching of the Nonlinear Optical Properties of a Functionalized Bis(styryl)benzene

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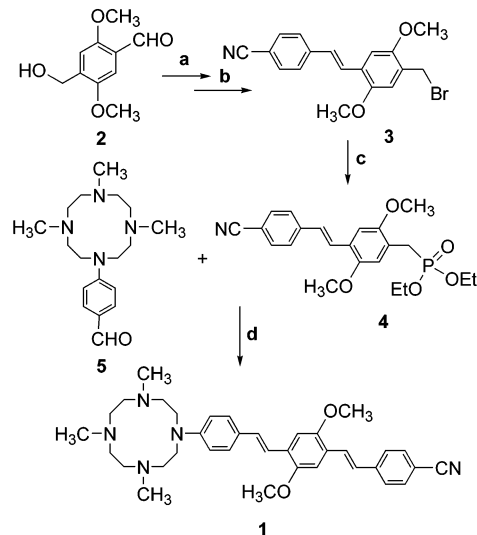
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Multiphoton absorption of π -conjugated molecules is an interesting nonlinear optical (NLO) property that has triggered an increasing interest because of its rapidly emerging prospects in the field of biophotonics and materials science. In this connection, the synthesis and study of multiphoton absorbing fluorophores with large cross sections, in particular two-photon (2PA) cross sections, is strongly pursued in view of applications that include three-dimensional fluorescence imaging,¹ optical power limiting,² and 3D optical data storage,³ to name only a few. Several molecular design principles have been proposed to enhance the nonlinear absorption within a variety of conjugated molecular structures. Among them, the bis(styryl)benzene (BSB) structure serves as an efficient conjugated bridge (π) for 2PA enhancement⁴ in which donor (D) and/or acceptor (A) substituents, in a symmetrical (D- π -D, A- π -A) or asymmetrical (D- π -A) arrangement, can be readily introduced at the central and side benzene rings. In the present work, a new A- π -D, BSB derivative (**1**, Scheme 1), in which the donor unit is a cyclen-based receptor for metal cations,⁵ was prepared and studied with the long-term objective to develop new zinc-specific probes operative within cells.⁶ We have found that, upon complexation with Zn^{2+} , the electronic properties of the cyclen ligand can be modified, thus allowing the control of the multiphoton absorption characteristics of the BSB derivative. Previously, the modulation of molecular NLO properties was reported for electrochemical⁷ and proton-transfer⁸ reactions.

The BSB **1** was synthesized by a four-step procedure starting from 4-hydroxymethyl-2,5-dimethoxybenzaldehyde **2**, which in turn was prepared from 1,4-dihydroxymethyl-2,5-dimethoxybenzene in 90% yield by selective oxidation of one hydroxyl function with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).⁹ A Wadsworth–Emmons coupling of **2** with 4-cyanobenzyl-diethylphosphonate¹⁰ in *N,N*-dimethylformamide (DMF) gave 4-[2-(4-hydroxymethyl-2,5-dimethoxyphenyl)-vinyl]-benzonitrile in 60% yield. Subsequent bromination with phosphorus tribromide gave 4-[2-(4-bromomethyl-2,5-dimethoxyphenyl)-vinyl]-benzonitrile **3** in 68% yield. Phosphonate **4** was obtained from **3** by a Michaelis–Arbuzov reaction in 82% yield. The Wadsworth–Emmons coupling reaction of **4** with **5**¹¹ gave BSB **1** in 69% isolated yield.

Figure 1 shows the absorption spectrum of **1** in CH_3CN without and in the presence of 2 equiv of $\text{Zn}(\text{ClO}_4)_2$ hexahydrate (**1-Zn²⁺**),¹² in which a clear shift to higher frequencies and a lower oscillator strength of the characteristic low-energy absorption band of BSBs,⁴ centered at 432 nm, can be observed. The difference between the two spectra, in particular the lower oscillator strength of the 532 nm transition for **1-Zn²⁺**, can be understood, at least partially, by considering that **1** is a push–pull molecular structure with the lowest excited state which is involved in a charge-transfer excitation from the cyclen unit (donor) to the cyano group (acceptor). Complexation with Zn^{2+} induces a higher localization of the electrons of the cyclen which, in turn, becomes a weaker

Scheme 1^a



^a Conditions: (a) 4-cyanobenzyl-diethylphosphonate, *t*-BuOK, DMF, 25 °C, 12 h, 60%. (b) PBr_3 , THF, 0–25 °C, 2 h, 68%. (c) Triethyl phosphite, 160 °C, 6 h, 82%. (d) *t*-BuOK, DMF, 25 °C, 12 h, 69%.

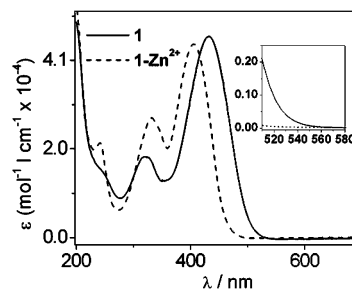


Figure 1. Absorption spectra of **1** and of **1-Zn²⁺** in CH_3CN .

donor. As a result, **1** changes its D- π -A characteristics to a more symmetrical A'- π -A character. This change can justify the variation of the linear absorption spectrum, recalling that for symmetrical BSBs one can predict,⁴ in that spectral region, the presence of two-photon-allowed electronic states which are not active in the linear spectrum.

Multiphoton absorption properties of **1** and **1-Zn²⁺** were obtained by nonlinear transmission measurements¹³ using 9 ns pulses of a Nd:YAG laser at the frequencies of 1064 and 532 nm. BSB **1** did not show any nonlinear absorption behavior at 1064 nm nor in the presence of an excess of metal cation. On the contrary, at 532 nm a definite nonlinear absorption performance was recorded for **1** in the absence of Zn^{2+} binding. Figure 2 shows the nonlinear transmission data at 532 nm of a 9.8×10^{-4} M solution of **1** in CH_3CN and of the same solution with 2 equiv of $\text{Zn}(\text{ClO}_4)_2$

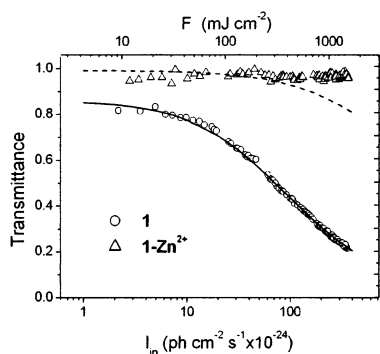


Figure 2. Nonlinear transmittance of **1** and **1-Zn²⁺** in CH₃CN at 532 nm. The solid line shows a model calculation for a sequential two-photon absorption process. The dashed line shows the same calculation but with a lower ground-state one-photon absorption cross section (see text).

hexahydrate. The on-off switching of the nonlinear transmittance, induced by Zn²⁺ coordination, is evident.

It has been recently reported,¹⁴ following theoretical studies, that multiphoton absorption phenomena may underlie different mechanisms for long (nanosecond) and short (femtosecond) laser pulses. In particular, long nanosecond pulses make possible a real population of excited states. Therefore, the usual large nonlinear optical response observed in this time regime can be related to sequential processes with absorption from excited states. Since we used nanosecond pulses for the nonlinear absorption measurements, we expect that excited-state absorptions are active in our system. Therefore the fitting, shown in Figure 2, was achieved by using a model for the dynamics of the excited states that was based on kinetic equations¹⁵ that could be written, and solved numerically,¹⁶ for one-photon, two-photon, and higher order absorptions. The model took into account that, at 532 nm, **1** has a weak linear absorption (see inset to Figure 1), which is indeed sufficient to drive the BSB toward an excited state. A good fitting has been obtained by considering the simplest excited-state process, namely, a one-photon excited-state absorption. The calculated curve, reported in Figure 2 for the nonlinear transmittance of **1**, gives a very satisfactory account of the experimental data by using 0.14 ns for the relaxation of the first excited state, a fast relaxation (1 ps) for the excited-state reached after the first excitation, a ground-state absorption cross section ($\sigma_{GS}^{(1)} = 1.26 \times 10^{-18} \text{ cm}^2$ equivalent to $\epsilon_{GS} = 330 \text{ mol}^{-1} \text{ l cm}^{-1}$ at 532 nm) obtained from the linear spectrum (see inset to Figure 1), and an absorption cross section for the one-photon excited state ($\sigma_{ex}^{(1)} = 8.0 \times 10^{-16} \text{ cm}^2$, $\epsilon_{ex} = 2.09 \times 10^5 \text{ mol}^{-1} \text{ l cm}^{-1}$) obtained from the fitting. A better knowledge of the relaxation time of the first excited state would make possible a better estimation of $\sigma_{ex}^{(1)}$.

To understand why the **1-Zn²⁺** complex shows a different behavior, one first observes that its linear absorption at 532 nm is much weaker than that of **1** (see inset to Figure 1). We therefore repeated the calculation, changing only the linear absorption ($\sigma_{GS}^{(1)} = 7.65 \times 10^{-20} \text{ cm}^2$, $\epsilon_{GS} = 20 \text{ mol}^{-1} \text{ l cm}^{-1}$). The calculated curve, reported in Figure 2 (dashed line), accounts for the experimental data up to $70 \times 10^{24} \text{ ph cm}^{-2} \text{ s}^{-1}$. This shows the importance of the linear absorption for the nonlinear behavior of **1-Zn²⁺** and strengthens the role of excited-state populations recalled above for nanosecond pulses. For the fitting at higher intensities, a $\sigma_{ex}^{(1)}$ value ($\sigma_{ex}^{(1)} = 8.0 \times 10^{-17} \text{ cm}^2$, $\epsilon_{ex} = 2.09 \times 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$) 1 order of magnitude lower than that previously used for **1** adequately accounts for the observed behavior up to the highest explored intensities.

In summary, we have shown how a large variation of the nonlinear transmission properties of a cyclen-based BSB could be

induced by a small change of the linear absorption spectrum upon Zn²⁺ binding. This result has been interpreted in the frame of a sequential two-photon process in which one photon is absorbed from the ground state and one photon is absorbed from an excited state.

The on-off switching of the nonlinear transmission characteristics of **1** induced by Zn²⁺ binding is, to our knowledge, a new phenomenon which holds promises in the field of bio-imaging since a high transmission in the nonlinear regime is recorded only when Zn²⁺ is present.

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Supporting Information Available: Details for the synthesis of **1** and NLO measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) 4-Cyanobenzyl-diethylphosphonate was prepared in 95% isolated yield from 4-cyanobenzyl bromide and triethyl phosphite, following the standard Michaelis–Arbuzov procedure.
- (11) The aldehyde **5** was prepared from *N*-phenyl-4,7,10-trimethyl-1,4,7,10-tetraazacyclododecane (Hirano, T.; Kikuchi, K.; Urano, Y.; Higuchi, T.; Nagano, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1052) through formylation with P₂O₃/Cl₄ in dry DMF (Downie, I. M.; Earle, J.; Heaney, H.; Shuhaibar, K. F. *Tetrahedron* **1993**, *19*, 4015).
- (12) Two-fold molar excess of Zn²⁺ over the cyclen ligand has been employed to ensure the full formation of the **1-Zn²⁺** complex.
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