Sequential multiphoton absorption enhancement induced by zinc complexation in functionalized distyrylbenzene analogs†

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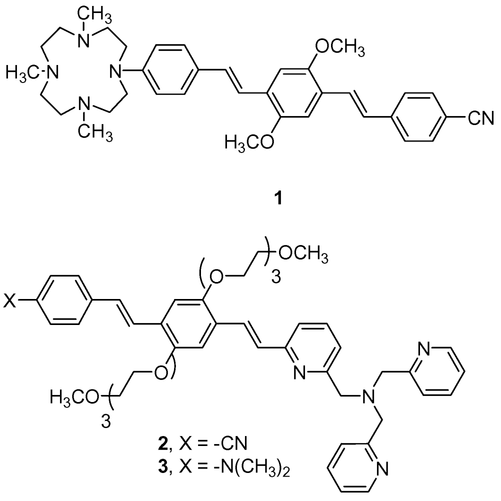
Functionalized distyrylbenzene analogs **2** and **3**, bearing a tris-(2-pyridylmethyl)amine-based receptor for Zn^{2+}, were synthesized by a Horner–Emmons–Wittig coupling reaction. It has been found that Zn^{2+} complexation induces changes in the linear absorption spectrum that enhance a nonlinear sequential two-photon absorption of nanosecond pulses at 532 nm. This absorption was also found to depend on the nature of the substituent at the side benzene ring of the styrylbenzene structure.

Introduction

Molecular switches represent key components for the control and processing of information for future technology.[1,2] Efficient schemes for molecular switching have been obtained through changes of optical or magnetic properties in a variety of molecular structures.[3–7] In particular, second- and third-order nonlinear optical (NLO) properties are becoming important issues for molecular switching: proton transfer reactions,[8] different redox states[9–11] and molecular aggregates[12] were used for NLO switching. We have shown that a functionalized distyrylbenzene (DSB) derivative exhibits the switching of its multiphoton absorption properties upon Zn^{2+} complexation.[13] A model fitting of the experimental data suggested to characterize the NL-absorbing process as a sequential two-photon absorption (S-2PA) event where a photon efficiently populates an excited state which, in turn, absorbs a second photon. S-2PA have been observed also for other classes of molecular structures, such as fullerenes,[14–16] phthalocyanines,[17–19] porphyrins[20] and porphyrazines[21] in which NL absorption derives from the activity of a triplet excited state. However, for these systems, the NLO properties cannot be controlled by an external agent, as for our functionalized DSB-based metal receptor[13] or for other medium-sensitive NLO probes that were recently reported in the literature.[22] S-2PA is operative with nanosecond pulses at relatively low laser intensity, if compared to other NL absorption phenomena, such as instantaneous two-photon absorption (I-2PA), because of the high polarizability of excited states involved in the sequential process. Recently, I-2PA was observed for DSB-based Mg^{2+} receptors with femtosecond pulses in the near infrared spectral region.[23] However, the importance of sequential processes, that must be taken into account for situations of quasi-resonance like those considered in this work, has been stressed also for I-2PA.[24] In the case of derivative **1** (Chart 1), in which a DSB was functionalized at one terminus with a cyclen ligand,[13] it has been shown that a large variation of its NL transmission characteristics could be induced by Zn^{2+} complexation. This result encouraged the preparation and study of chromophores **2** and **3** in which a styryl(vinylpyridyl)benzene (SVPB) structure is part of a tris(2-pyridylmethyl)amine-based receptor (TPMA), known for its Zn^{2+} binding characteristics and whose coordination chemistry has been studied in great detail.[25–28] We have found that, upon complexation with Zn^{2+}, **2** and **3** change their linear absorption, as in the case of **1**, thus allowing a control of their multiphoton absorption properties. It is worth noting that a variation in the linear absorption translates into a different excited state population and, therefore, into a different sequential multiphoton absorption. In the case of **2** and **3**, a higher NL transmission was recorded in the absence of



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2, X = -CN
3, X = -N(CH3)2

Chart 1 Molecular structures considered in this work.

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† Electronic supplementary information (ESI) available: Synthetic details and characterization for compounds **4**, **5**, **7**, **9–14**; NMR and IR spectra for **2** and **3**; ESI-MS for **2**, **3**, **2-Zn**$^{2+}$ and **3-Zn**$^{2+}$; titrations for stoichiometry and binding constant determination for **2-Zn**$^{2+}$ and **3-Zn**$^{2+}$. See DOI: 10.1039/b615076d

Zn^{2+}. In DSB **1**, instead, the same variation was found in the presence of Zn^{2+}. The effect that we observe for **2** and **3** is also opposite to that reported by Pond and coworkers[23] in which a lower I-2PA activity is observed upon Mg^{2+} complexation.

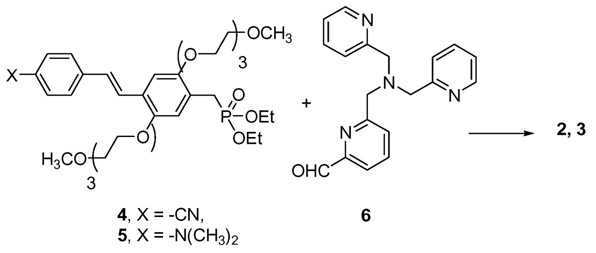
The results presented herein could also be of interest in view of understanding the mechanism of NL absorption changes induced by ion complexation in the frame of bio-imaging,[23,29–35] although other important factors, such as protonation equilibria or solvent effects,[36] should be considered.

Results and discussion

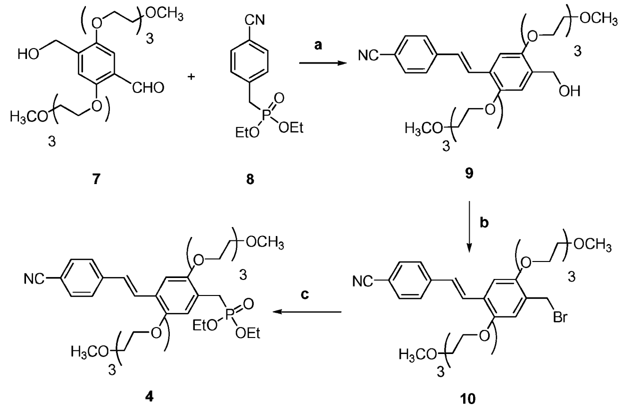
Synthesis

Compounds **2** and **3** (Chart 1), have an electron-donor amine or an electron-acceptor cyano substituent located at position 4 of the side benzene ring of the SVPB structure. It is reasonable to assume that complexation with Zn^{2+} induces a higher localization of the electrons of the TPMA receptor and, in particular, of the π electrons of the pyridine moiety which is part of the SVPB structure, thus making this pyridine ring a stronger acceptor. This change should, at least partially, affect the intramolecular charge distribution of the molecules both in their ground and excited states and could be useful for obtaining a variation of their NLO activity. In this connection, Pond and coworkers have demonstrated in a recent publication[23] that a similar design scheme can be employed for the development of NL molecular sensors for use in two-photon laser scanning applications.

SVPBs **2** and **3** were synthesized through a Horner–Emmons–Wittig (HEW) coupling reaction of [6-formyl(2-pyridylmethyl)amine]bis(2-pyridylmethyl)amine **6**[37] with a suitably-functionalized diethylphosphonate **4** or **5** (Scheme 1) in 19 and 20% yield, respectively. The modest yields refer to isolated compounds after column chromatography that revealed to be a rather difficult task since the highly polar compounds **2** and **3** tend to irreversibly bind onto the stationary phase (either silica gel or alumina), although a steric hindrance to the HEW coupling by the oxyethylene chains cannot be ruled out. HPLC analysis was employed to assess the purity of derivatives **2** and **3** whereas NMR spectroscopy (Fig. S1–S4) and exact mass determination to validate their proposed molecular structure. The *trans–trans* configuration of the double bonds in **2** and **3** was established *via* NMR, through the measurement of the $^{3}J_{HH}$ of the olefin protons which was found to be around 16 Hz, as reported in the literature.[38]



Scheme 1 Reagents and conditions: NaH, THF, 0 °C, 12 h (**2**, 19%; **3**, 20%).



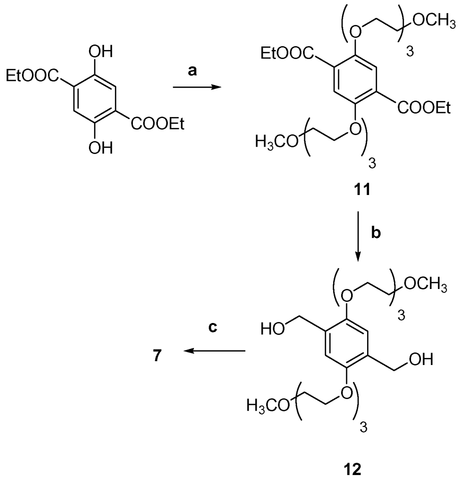
Scheme 2 Reagents and conditions: (a) NaH, THF, 0 °C, 3 h, 74%; (b) PBr_3, THF, 0 °C, 1 h, 84%; (c) $P(OEt)_3$, Δ, 3 h, 87%.

Phosphonates **4** and **5** were prepared by two different routes. Derivative **4** was obtained by a three-step procedure, starting from aldehyde–alcohol **7** (Scheme 2). A HEW coupling of **7** with 4-cyanobenzyl-diethylphosphonate **8** gave *trans*-stilbene **9** in 74% yield. Subsequent bromination with phosphorus tribromide gave bromobenzyl derivative **10** in 84% yield. Phosphonate **4** was obtained from **10** and triethyl phosphite by a Michaelis–Arbuzov reaction in 87% yield.

Aldehyde–alcohol **7** was prepared from bis-alcohol **12** in 90% yield by selective oxydation of one hydroxyl group with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[39] Bis-alcohol **12**, in turn, was obtained in 89% overall isolated yield through nucleophilic displacement of 2-(2-(2-methoxy) ethoxy)ethyl-*p*-toluensulfonate and commercial ethyl 1,4-dihydroxy-2,5-terephthalate, followed by $LiAlH_4$ reduction of the ester functions (Scheme 3).

Although the route illustrated in Scheme 2 afforded phosphonate **4** in good yields, it was not suitable for the production of the corresponding *N*,*N*-dimethylamino derivative **5** because the bromination steps gave mainly an intractable solid, probably produced by an intermolecular reaction of the amine with the reactive bromobenzyl function. Phosphonate **5** was therefore obtained by an alternate route, in 24% yield, through the monofunctionalization of bis-phosphonate **14** with 4-(*N*,*N*-dimethylamino)benzaldehyde (Scheme 4). Compound **14** was synthesized from dibromobenzyl derivative **13** that, in turn, was prepared from bis-alcohol **12** and PBr_3 in 71% yield, followed by a Michaelis–Arbuzov reaction with triethyl phosphite in 84% yield.

The formation of a complex between **2** or **3** and the Zn^{2+} cation (**2-Zn^{2+}** and **3-Zn^{2+}**) was clearly evidenced by mass spectroscopic analysis of a 1 : 1 host/guest mixture in a MeOH solution, showing the peak for the doubly-charged 1 : 1 adduct at *m*/*z* 453.7 (**2-Zn^{2+}**, Fig. S9) and *m*/*z* 462.3 (**3-Zn^{2+}**, Fig. S10). The binding ability of **2** and **3** toward Zn^{2+} was investigated by means of fluorescence titration experiments through the addition of increasing amounts of $Zn(ClO_4)_2$ hexahydrate to a 0.099 μM solution of **2** (or to a 0.104 μM solution of **3**) in CH_3CN. Fluorescence changes as a function of $[Zn^{2+}]$ showed a complete formation of the complex up to one equivalent of Zn^{2+}. This prevented a precise evaluation of the binding constant that, nevertheless, could be



Scheme 3 Reagents and conditions: (a) 2-(2-(2-methoxy)ethoxy) ethyl-*p*-toluensulfonate, K_2CO_3, DMF, 60 °C, 48 h, 96%; (b) $LiAlH_4$, THF, 0 °C-reflux temperature, 0.5 h, 93%; (c) DDQ, CH_2Cl_2, 0–5 °C, 90%.

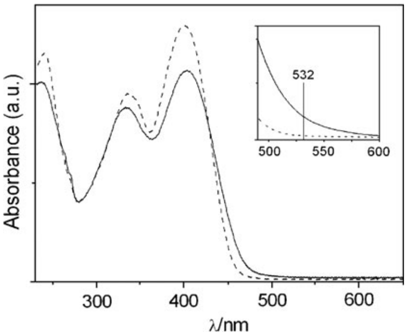


Fig. 1 Absorption spectra of **2** (dashed line) and **2-Zn^{2+}** (solid line) 1.21 × 10^{-3} M in CH_3CN. Inset shows an expanded part of the spectrum around 532 nm.

estimated as $>10^7$.[26] (for stoichiometry and binding constant determination see Fig. S11).

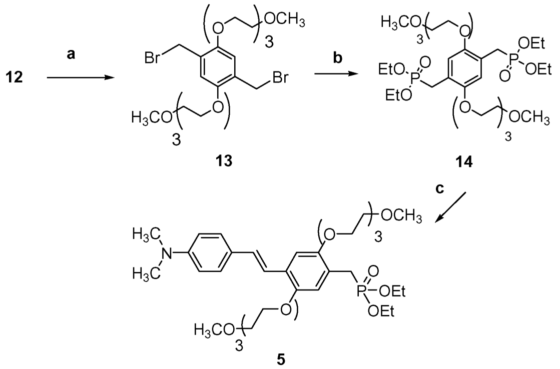
Linear and nonlinear optical measurements

Solutions of metal complexes **2-Zn^{2+}** and **3-Zn^{2+}** for spectrophotometric measurements were prepared in CH_3CN by mixing SVBP **2** or **3** with 2 equiv. of $Zn(ClO_4)_2$ hexahydrate at room temperature. The absorption spectra of CH_3CN solutions of **2** and of **2-Zn^{2+}** are reported in Fig. 1. The corresponding spectra of **3** and **3-Zn^{2+}** are shown in Fig. 2.

The spectra of **2** and **3** show that a variation of the linear absorption follows the formation of the Zn^{2+} complex, as it is clear in the low energy part of the spectrum around 400 nm, where **2-Zn^{2+}** and **3-Zn^{2+}** have a weaker absorption than their uncomplexed counterpart. This can be ascribed to a reduced number of backbone π electrons as a consequence of the participation of the SVPB pyridyl ring to Zn^{2+} complexation. A similar effect was also observed earlier for a DSB-based receptor for Mg^{2+}.[23] However, it is interesting to note that a stronger absorption of the Zn^{2+} complexes is present in the wing of the 400 nm band toward longer wavelengths and that, therefore, at 532 nm **2-Zn^{2+}** and **3-Zn^{2+}** absorb slightly more than **2** and **3**. This condition is fundamental for obtaining a variation of sequential multiphoton absorption[13] because a stronger linear absorption makes it possible to populate the first excited state easier, from which further absorptions may occur.

NL absorption measurements at 532 nm of **2**, **3**, **2-Zn^{2+}** and **3-Zn^{2+}** are shown in Fig. 3a and 4a, respectively, where a lower output intensity is determined by an intensity dependent absorption. One finds that the NL absorption is very important only for **2-Zn^{2+}** and **3-Zn^{2+}**, whereas the almost linear behaviour of **2** and **3** confirms their poor NL activity. This shows that an enhancement of the NL absorption can be obtained upon complexation. Fig. 3b and 4b report the same experimental data of Fig. 3a and 4a, respectively, but directly showing the absorption as a function of input intensities in a logarithmic scale. These plots allow a better inspection of the low intensity part of the data and are useful for controlling the model fitting at these intensities as well. One also finds that **3-Zn^{2+}** displays a larger non-linearity than **2-Zn^{2+}**, pointing out the important role of the functional groups in the SVPB structure.

Explanation of the observed results could be provided by considering the excited state population dynamics of the molecules. In fact, the interaction between light and matter can be described within a density matrix approach, and when



Scheme 4 Reagents and conditions: (a) PBr_3, THF, 0 °C-reflux temperature, 5 h, 71%; (b) $P(OEt)_3$, Δ, 3 h, 84%; (c) 4-(*N*,*N*-dimethylamino)benzaldehyde, tBuOK, DMF, 0 °C, 12 h, 24%.

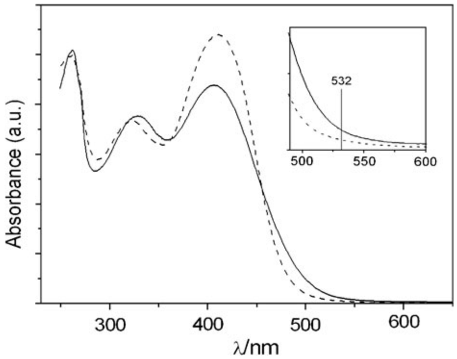


Fig. 2 Absorption spectra of **3** (dashed line) and **3-Zn^{2+}** (solid line) 1.26 × 10^{-3} M in CH_3CN. Inset shows an expanded part of the spectrum around 532 nm.

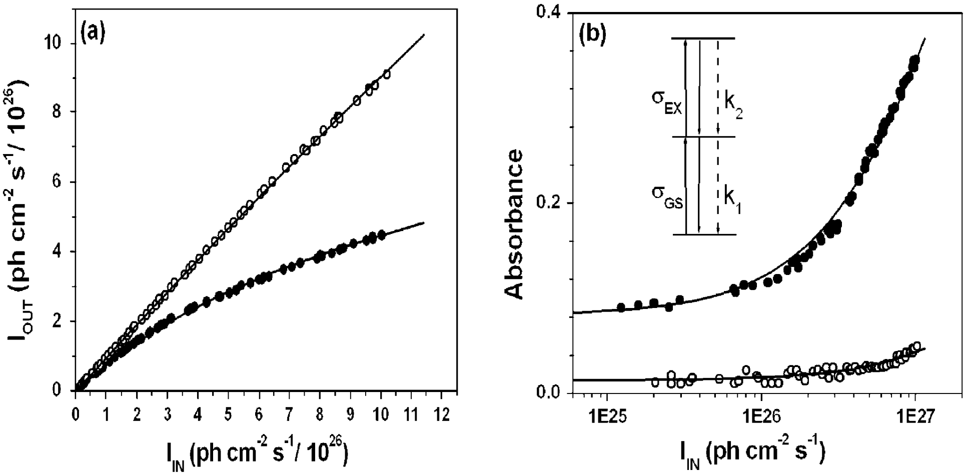


Fig. 3 NL absorption at 532 nm of **2** (○) and of **2-Zn^{2+}** (●) 1.21 × 10^{-3} M in CH$_3$CN. Solid lines are the results of model calculations (see text) whereas the inset shows the model parameters (absorption cross sections σ_{GS} and σ_{EX} and decay rates k_1 and k_2), whose values are reported in Table 1. (a) Recorded output intensities *versus* input intensities; (b) same data as in (a) but plotting the NL absorption as a function of input intensities in a logarithmic scale.

the laser pulse duration is longer than the relaxation processes, as in the present case (see below), one can use the diagonal part of the density matrix, which corresponds to the populations of the states of the system.[40] Solutions of the rate equation for the dynamics of these populations can be obtained according to Ehlert *et al.*[41] The model that has been used for the experimental data description is reported in the inset of Fig. 3b. The first excitation to be considered is in fact related to the linear absorption, with an absorption cross section σ_{GS}, which depends on the linear optical susceptibility, usually larger than higher-order susceptibilities. After the first one-photon excitation, a one- or two-photon absorption from the excited state can occur.[42] We have found that a one-photon absorption, with an absorption cross section σ_{EX}, is sufficient for fitting the experimental data. Four parameters (see inset of Fig. 3b and Table 1) are needed for the fitting. Among them, σ_{GS} is determined from the experimental linear absorption spectrum, whereas the decay time for the second excited state ($\tau_2 = k_2^{-1}$) can be considered very fast (of the order of ps) as it is usually observed for organic molecules.[43] These values and those of the other two parameters (σ_{EX} and the decay rate for the first excited state k_1) that are obtained from the fitting of the experimental data, are reported in Table 1.

It is worth noting that fitting of the data strongly depends on the variation of the cross section for the one-photon excitation from the ground state, which is experimentally evaluated from the UV-Vis spectra. This shows the importance of the population of the first excited state from which the second one-photon absorption starts. Good fittings have been obtained both in the high (Fig. 3a and 4a) and in the low (Fig. 3b and 4b) intensity regions, indicating that the S-2PA model gives a good description of the excited states dynamics that contribute to the NLO properties of the investigated molecules.

Conclusion

Two DSB analogs (SVPB derivatives **2** and **3**) bearing at one terminus the metal ion receptor tris(2-pyridylmethyl)amine,

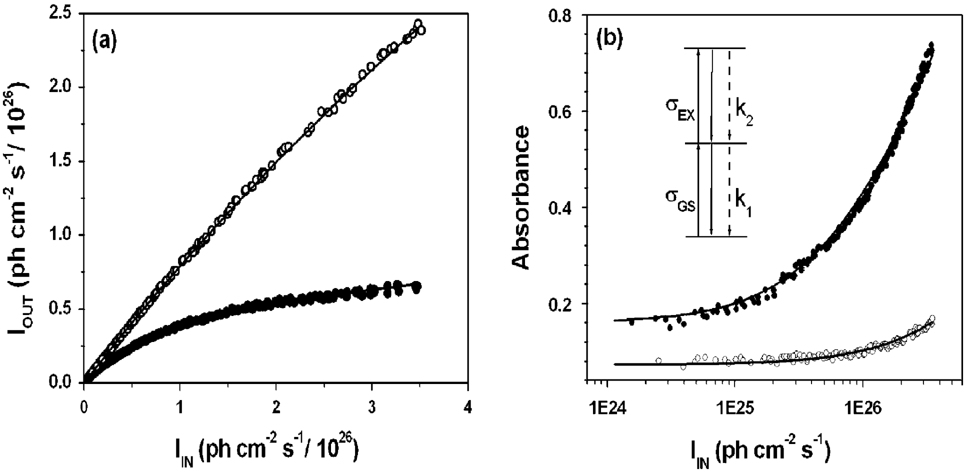


Fig. 4 Corresponding data of Fig. 3 but for **3** (○) and **3-Zn^{2+}** (●) with a concentration of 1.23 × 10^{-3} M in CH$_3$CN.

Table 1 Parameters for the model of the excited states dynamics

	σ_{GS}/cm^2	σ_{EX}/cm^2	k_1/s^{-1}	k_2/s^{-1}
2	2.2×10^{-19}	1.6×10^{-16}	5.0×10^{10}	1.0×10^{13}
2-Zn^{2+}	1.3×10^{-18}	4.0×10^{-16}	5.0×10^{10}	1.0×10^{13}
3	1.1×10^{-18}	5.5×10^{-17}	8.0×10^{9}	1.0×10^{12}
3-Zn^{2+}	2.4×10^{-18}	3.7×10^{-16}	8.0×10^{9}	1.0×10^{12}

have been synthesized and characterized. It has been found that a low absorption of nanosecond pulses at 532 nm is enhanced upon complexation in the **2-Zn^{2+}** and **3-Zn^{2+}** form. A model interpretation of the experimental data shows that this NL behaviour can be described with a sequential two-photon absorption (S-2PA). This mechanism allowed us to observe the NL behaviour at low laser intensities, because of the large polarizability of the first excited state from which the absorption of the second photon occurs. The results presented in this paper complement our previously reported study[13] on a DSB-based Zn^{2+} ligand that showed an opposite behavior, namely a larger NL activity for the uncomplexed molecule. In the present case, it has also been found that **3-Zn^{2+}** displays a larger nonlinearity than **2-Zn^{2+}**, pointing out the important role of the substituent (acceptor or donor) at the side benzene ring of the SVPB structure. The observation of S-2PA phenomena can be predicted also in spectral regions different from that explored in the present work, provided that molecular structures with appropriate variation of their linear absorption, upon complexation, are synthesized. To this end, the coordination of metal cations different from Zn^{2+}, such as Cu^{2+} or lanthanide ions, could enhance the control of excited state absorption thus offering further prospects for switching and sensing.

Experimental

Materials

All reagents, including dry solvents, were purchased from Aldrich and used without further purification. [6-Formyl(2-pyridylmethyl)amine]bis(2-pyridylmethyl)amine **6** was prepared as reported in the literature.[37] 4-Cyanobenzyl-diethylphosphonate **8** was prepared in 95% yield from 4-cyanobenzyl bromide and triethylphosphite, following the standard Michaelis–Arbuzov procedure. 2-(2-(2-Methoxy)ethoxy)ethyl-*p*-toluenesulfonate was synthesized in 96% yield from triethyleneglycol monomethylether and tosyl chloride in the presence of NaOH.

Instrumentation

Melting points were measured on a Leitz Laborlux 12 melting point apparatus and are uncorrected. Thin layer (TLC) and column chromatography were performed using a Polygram SilG/UV$_{254}$ (TLC plates) and silica gel MN 60 (70–230 Mesh) by Macherey-Nagel. ^{1}H (250.1 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded on a Bruker AC-F 250 spectrometer. The ESI-MS spectra were taken on a Thermo Finnigan AQA LC/MS: −4 kV spray voltage; −10 V capillary voltage; 180 °C capillary temperature; nitrogen as nebulizing gas. The samples were dissolved in methanol containing 1% trifluoroacetic acid. The exact mass determination was provided by the University of Calabria, Arcavacata di Rende Mass Spectrometry Resource. Compounds **2** and **3**, dissolved in MeOH and diluted to obtain non-saturating ion in the molecular ion region, were added to an α-cyano-4-hydroxycinnamic acid matrix. The mass spectra were taken on a MALDI-TOF/TOF, 4700 proteomic analyzer from Applied Biosystem equipped with a Nd:YAG pulsed laser at 355 nm. IR spectra were recorded on a Perkin-Elmer FT-IR model 1720X. HPLC analyses of **2** and **3** were carried out on a Shimadzu LC-8A instruments, equipped with a Shimadzu SPD-6A UV/Vis detector, working at 254 nm, using a Phenomenex Synergi Polar-RP column (150 × 4.6 mm, 4 μm, eluent: H_2O/CH_3CN, 0.1% trifluoroacetic acid, flow rate: 2 ml min^{-1}; linear gradient from 10 to 90% H_2O in 20 min): SVPB **2** (R_f = 16 min), SVPB **3** (R_f = 11 min).

NLO measurements

Multiphoton absorption properties of **2**, **3** and of **2-Zn^{2+}** and **3-Zn^{2+}** were obtained by NL transmission measurements using 9 ns pulses of a Nd:YAG laser (Quantel 982E) at 532 nm with solutions in 2 mm glass cells. The pulse energy was controlled with a polarizing cube beamsplitter and a $\lambda\backslash2$ wave plate, and measured with a pyroelectric detector (Scientech SPHD25). An open aperture configuration (solid angle 0.1 sterad) was used to avoid NL scattering or refraction effects. A calibrated photodiode was also employed to monitor pulse-to-pulse energy variations. Control of the pulse energies and recording of the detector signals were obtained with a home made program based on Labview®.

Syntheses and selected analytical data for derivatives 2 and 3

SVPB 2. To a solution of phosphonate **4** (212 mg, 0.31 mmol) in dry THF (20 ml) at 0 °C, NaH (15 mg, 0.37 mmol) was added under a nitrogen atmosphere, and the resulting solution was stirred for 20 min. Then, a solution of aldehyde **6** (100 mg, 0.31 mmol) in dry THF (10 ml) was added dropwise over a period of 10 min. When the addition was complete, the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the crude product purified by flash column chromatography (SiO_2, eluent: ethyl acetate/ethanol 8 : 2, then ethyl acetate/petroleum ether/isopropanol/aqueous ammonia 6 : 3 : 1 : 0.1). 50 mg (19%) of **2** were isolated as a fluorescent yellow-greenish oil. ^{1}H-NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ 8.51–8.49 (m, 2H), 7.94–7.88 (d, 1H, ^3J(H,H) = 16.0 Hz), 7.71–7.62 (m, 10H), 7.65–7.58 (d, 1H, ^3J(H,H) = 16.0 Hz), 7.47–7.44 (m, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 7.21–7.15 (d, 1H, ^3J(H,H) = 16.0 Hz), 7.18–7.12 (m, 3H), 4.26–4.22 (t, 4H, J = 4.0 Hz), 3.92–3.88 (t, 4H, J = 4.0 Hz), 3.88 (s, 4H), 3.87 (s, 2H), 3.73–3.70 (m, 4H), 3.65–3.54 (m, 8H), 3.48–3.44 (m, 4H), 3.29 (s, 3H), 3.28 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ 155.42, 151.41, 148.95, 137.93, 137.25, 137.10, 136.80, 132.41, 129.68, 127.57, 127.36, 127.97, 126.89, 126.17, 124.10, 123.16, 122.27, 121.92, 121.19, 119.09, 111.78, 111.59, 110.25, 71.85, 71.82, 70.79, 70.77, 70.63, 70.62, 70.53, 70.47, 69.79, 69.16, 69.02; IR (KBr) $\tilde{\upsilon}$ 2917, 2222, 1591, 1102, 1046 cm^{-1}; ESI-MS: m/z 844 $[M + H]^+$. HR-MS: 844.4359, $\Delta = -8.72$ ppm.

SVPB 3. To a solution of phosphonate derivative **5** (130 mg, 0.18 mmol) in dry THF (20 ml) at 0 °C, NaH (9 mg, 0.22 mmol) was added under a nitrogen atmosphere, and the resulting solution was stirred for 20 min. Then, a solution of tris(pyridyl)amino aldehyde **6** (59 mg, 0.18 mmol) in dry THF (10 ml) was added dropwise over a period of 10 min. When the addition was complete, the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the crude product purified by flash column chromatography (SiO_2, eluent: ethyl acetate/ethanol 8 : 2, then ethyl acetate/petroleum ether/isopropanol/aqueous ammonia 6 : 3 : 1 : 0.1). 31 mg (20%) of **3** were isolated as a fluorescent yellow-greenish oil. ^{1}H-NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ 8.55–8.54 (m, 2H), 7.92–7.86 (d, 1H, ^3J(H,H) = 16.5 Hz), 7.68–7.60 (m, 6H), 7.45–7.36 (m, 4H), 7.32–7.25 (d, 1H, ^3J(H,H) = 16.5 Hz), 7.18–7.16 (m, 4H), 7.09–7.03 (d, 1H, ^3J(H,H) = 16.5 Hz), 6.74–6.70 (d, 2H, J = 8.7 Hz), 4.26–4.18 (m, 4H), 4.05 (s, 4H), 4.02 (s, 2H), 3.93–3.91 (m, 4H), 3.88–3.64 (m, 12H), 3.54–3.50 (m, 4H), 3.35 (s, 3H), 3.33 (s, 3H), 2.99 (s, 6H); ^{13}C-NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ 155.76, 151.55, 150.56, 150.09, 149.44, 149.09, 148.90, 137.76, 137.07, 136.71, 129.70, 129.17, 127.72, 126.16, 125.28, 123.47, 123.20, 122.47, 122.26, 120.88, 119.76, 118.59, 112.40, 111.79, 110.57, 71.87, 71.84, 70.88, 70.79, 70.64, 70.63, 70.52, 70.49, 69.88, 69.85, 69.23, 69.07, 59.90, 58.98, 40.44; IR (KBr) $\tilde{\nu}$ 2921, 1588, 1432, 1109, 1060 cm^{-1}. ESI-MS: m/z 862 $[M + H]^+$. HR-MS: 862.4733, $\Delta = 2.54$ ppm.

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