# Strong two-photon absorption at telecommunications wavelengths in nickel bis(dithiolene) complexes

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The two-photon absorption spectrum of a nickel bis(dithiolene) complex with extended conjugation and $\pi$-donor substitution is measured by using Z-scan and pump–probe techniques with femtosecond pulses over the spectral range from 1.20 to 1.58 $\mu$m, which includes much of the telecommunications range. The peak two-photon cross section of over 5000 GM (1 GM $=10^{-50}$ cm$^4$ s photon$^{-1}$ molecule$^{-1}$) occurs at $\sim$1.24 $\mu$m, with significant two-photon absorption (>440 GM) throughout the spectral range examined. © 2007 Optical Society of America

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Materials exhibiting strong two-photon absorption (2PA) have recently attracted considerable attention due to their potential application for three-dimensional microfabrication, high-density memory, biological imaging, and photodynamic therapy.[1] However, there have been few studies of two-photon absorption in the telecommunications wavelength range of 1.3–1.55 $\mu$m, where applications potentially include optical pulse suppression,[2] all-optical beam stabilization, dynamic-range compression, and the sensitization of photorefractive composites. A high-peak 2PA cross section, $\delta_{\max}$, of $\sim$1500 GM (1 GM $=10^{-50}$ cm$^4$ s photon$^{-1}$ molecule$^{-1}$) for non-frequency-degenerate 2PA, equivalent to degenerate 2PA of 1.44 $\mu$m photons with $\delta=\sim 900$ GM, has been measured for a dipolar chromophore,[3] and another dipolar chromophore has been used to sensitize photorefractive composites via 2PA at 1.55 $\mu$m.[4,5] More recent work has found $\delta=1600$ and $\delta=800$ GM at 1.3 and 1.5 $\mu$m, respectively, for a quadrupolar squaraine chromophore,[6] $\delta_{\max}=7200$ GM at 1.38 $\mu$m for an azulene-fused porphyrin,[7] and $\delta_{\max}$ $=115{,}000$ GM at 1.33 $\mu$m in a high-molecular-weight double-stranded zinc porphyrin oligomer[8] (8900 GM per repeat unit).

In this Letter we report 2PA spectra for nickel bis-(dithiolene) complexes in the vicinity of the telecommunications wavelength range. Nickel bis(dithiolene)s have delocalized electronic structures in which Ni-, S-, and C-based orbitals all contribute significantly to the orbitals involved in the optical transitions; this is reflected in the possibility of writing reasonable representations of the structure with the oxidation state of Ni varying from 0 to IV, as shown in Fig. 1. Their low-energy one-photon absorption maxima (1PA) indicate the possibility of 2PA-allowed states with sufficiently low-lying energies for 2PA at telecommunications wavelengths. Previous investigations of the nonlinear optical properties of nickel bis(dithiolene)s have focused on third-order susceptibilities at 1.06 $\mu$m and their exploitation in applications such as all-optical signal processing.[9,10] For a few compounds the 2PA at 1.06 $\mu$m has been measured, since nonlinear absorption is detrimental to all-optical signal-processing; low 2PA coefficients were observed.[11,12]

We synthesized samples 1[13] and 2[14,15] according to literature procedures. The new compound 3 was synthesized starting with the Wittig reaction of $Ph_3PMeBr$ and 3,4-bis(dodecyloxy)benzaldehyde in the presence of $K_2CO_3$ in refluxing $p$-dioxane to give 3,4-bis(dodecyloxy)styrene (66%), which was then coupled to 4,4′-dibromobenzil under Heck conditions [$Pd(OAc)_2$ as a catalyst, $K_2CO_3$, $Bu_4NBr$, and LiCl in

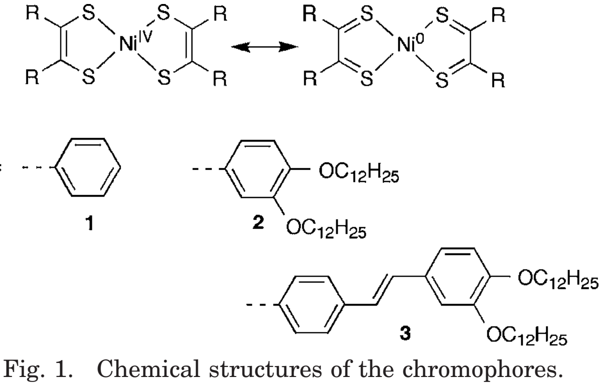


Fig. 1. Chemical structures of the chromophores.

 

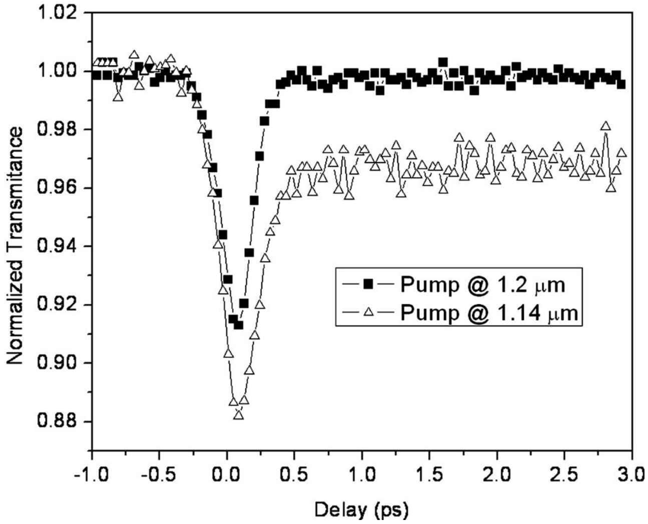


Fig. 2. Pump–probe experiments for sample 3. Data for two different excitation wavelengths are shown; in both cases the probe wavelength is 1.24 $\mu$m. Note that for the shorter pump wavelength there is strong contribution of ESA.

dry $N$,$N$-dimethylformamide at 100 °C] to give the ketone di[3,4-bis(dodecyloxy)styryl]benzil (76%). Finally the diketone was treated with $P_2S_5$ in refluxing $p$-dioxane, followed by $NiCl_2 \cdot 6H_2O$, also in refluxing $p$-dioxane. Sample 3 was obtained as a green solid in 30% yield after purification by column chromatography and was characterized by $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy and by matrix-assisted laser desorption ionization mass spectrometry.

Solution 2PA spectra were measured by using the open-aperture Z-scan technique.[16,17] A Ti:sapphire regenerative amplification system (CPA2010, CLARK-MXR), providing laser pulses at 775 nm with 140 fs duration (FWHM) at a 1 kHz repetition rate, was used to pump an optical parametric amplifier system (TOPAS, Light Conversion), which was used to tune the wavelength with output energies of 10–300 nJ. For regions close to the 1PA resonance (close to the 2PA peak of the present compounds), where linear absorption is important, the open-aperture Z-scan cannot easily separate the 2PA from 1PA followed by excited-state absorption (ESA), since both are two-photon processes. However, while 2PA is an instantaneous process, ESA has a response time (longer than the pulse width of ~140 fs) determined by the excited-state dynamics. Accordingly, we performed time-resolved analysis via femtosecond pump and probe measurements at these wavelengths.[18] This allows us to separate these effects because of the difference in the response time. Figure 2 shows data for sample 3 acquired with a probe wavelength of 1.24 $\mu$m and pump wavelengths of 1.20 and 1.14 $\mu$m. The data for the 1.20 $\mu$m pump show a response that follows the pulse, i.e., instantaneous nonlinearity associated with near-degenerate 2PA. Data for the 1.14 $\mu$m pump show a response that follows the pulse followed by a plateau region, indicative of the creation of excited states that are long-lived compared with the 3 ps delay shown in Fig. 2. These data show that around the wavelength of the pump–probe the average photon energy (1.22 and 1.19 $\mu$m, respectively, for the two traces shown) excited states become important in the frequency-degenerate nonlinear response. However, the data shown in Fig. 2 indicate that 2PA is still dominant at these wavelengths, given the ratio of the change in transmittance from the peak 2PA and the plateau region. At still shorter wavelengths this is no longer true. These pump and probe results ensure that, for the wavelengths reported in Fig. 3, the two-photon cross section is due primarily to pure 2PA, and strong contribution from ESA occurs only at shorter wavelengths.

As is shown in Fig. 3, all three compounds show qualitatively similar visible and near-IR linear absorption spectra; the redshift of the low-energy band of the alkoxy-substituted species 2 and 3, relative to that of 1, is consistent with the previously described effect of $\pi$-donor groups on the spectra of nickel bis(dithiolene) complexes.[19] The most significant difference between the spectra of 2 and 3 is in the much stronger UV absorption of the latter, presumably due to more intense ligand-centered transitions. The 2PA cross sections in the near IR are, however, very different. Species 1 was found to exhibit only moderate 2PA at three near-IR wavelengths. Substitution with alkoxy electron-donor groups in 2 leads to much stronger 2PA, with $\delta_{max}=1400$ GM at ~1.2 $\mu$m (given the error bars in the measurement of $\delta$, we cannot exclude the possibility that the peak occurs at shorter wavelength) and $\delta=570$ GM at 1.3 $\mu$m. The effect of symmetrical donor substitution on $\delta$ is reminiscent of that previously seen with bis(donor)-substitution of stilbene and bis(styryl)benzene chromophores.[20] Extending the conjugation in species 3 leads to an even higher $\delta_{max}=5300$ GM, also at ~1.2 $\mu$m (again, the true peak may lie at shorter wavelength), with $\delta=2500$ GM at 1.3 $\mu$m and in excess of 440 GM throughout the entire telecommunications range. Although the state accessed by the 2PA clearly lies at a very similar energy to the states accessed by the weak 1PA transitions seen in the 550–700 nm range (which have previously been assigned to $d$–$d$

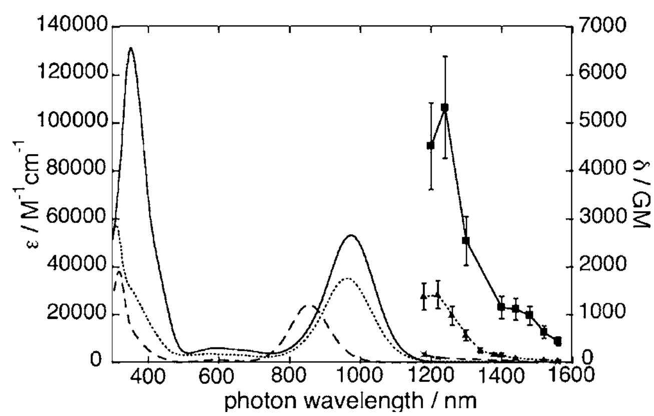


Fig. 3. One-photon and two-photon spectra of sample 1 (dashed curve and dashed curve with crosses marking data points, respectively, data measured in $CH_2Cl_2$), 2 (dotted curve, dotted curve with triangles, $CHCl_3$), and 3 (solid curve, solid curve with squares, THF).

transitions[19]), there is clearly considerable ligand involvement in the 2PA states, since the cross section varies so extensively among 1, 2, and 3. It is clear, however, that the small detuning energy (<0.3 eV for both 2 and 3) between the virtual state associated with the 2PA peak and the strongly one-photon-allowed $\pi-\pi^*$ state, along with the $\pi-\pi^*$ transition dipole moments (6.1, 8.0, and 11.2 Debye for 1, 2, and 3, respectively), are important factors leading to the high $\delta$ through the three-state expression

$$\delta \propto E_{ge'}^2 \frac{\mu_{ge}^2 \mu_{ee'}^2}{[E_{ge} - (E_{ge'}/2)]^2}, \quad (1)$$

where $g$, $e$, and $e'$ subscripts refer to ground, 1PA, and 2PA states, respectively, $E$ denotes transition energy, and $\mu$ denotes transition dipole moment. Other chromophores in which near-double resonance (small detuning energy) leads to high $\delta$ include perylene diimides,[21] porphyrin oligomers,[8,22] and squaraines.[6] Equation (1) also suggests that the differences in $\delta_{\max}$ between species 2 and 3 (for which the detuning energies are approximately the same) are likely to arise from larger $\mu_{ee'}$ in the latter compound, in addition to larger $\mu_{ge}$.

In conclusion, we have reported that nickel bis-(dithiolene) complexes can show strong 2PA in the near IR, with the strength of this 2PA being strongly dependent on the nature of the dithiolene ligand. The tail of the 1PA extends to wavelengths around the 2PA peak, limiting the potential applications at these wavelengths; however, the still sizable cross sections found at longer wavelengths, coupled with the good photostability of these compounds,[19] suggests that carefully chosen members of this class of compounds, especially those that can be readily processed into optical quality films, may be useful for applications at telecommunications wavelengths.

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