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Synthesis and two-photon absorption properties of unsymmetrical metallosalophen complexes

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ABSTRACT

Several new unsymmetrical metallosalphen complexes derived from the condensation of a monoimine and salicylaldehyde in the presence of a transition metal ion as a template have been synthesized and characterized. Their linear and third-order non-linear optical (NLO) properties have been investigated in detail. With different substituted donor or acceptor groups at the 5-position of the salicylidene fragment, these metallosalophen complexes exhibit slightly different two-photon absorption (TPA) cross-section $\sigma^{(2)}$ values. Theoretical calculations based on density functional theory were also carried out to help with the interpretations of the experimental results.

1. Introduction

In the past decade, there has been growing interest in the design and construction of new molecular materials displaying a two-photon absorption (TPA) because of their potential applications in two-photon up-conversion lasing [1], three-dimensional optical data storage [2], photodynamic therapy [3], non-linear photonics [4] and so on. The TPA process is a third-order non-linear optical (NLO) phenomenon, and the efficiency of this process is determined by measuring the values of the TPA cross-section $\sigma^{(2)}$. The most important feature of large TPA molecules is the presence of a long conjugated system consisting of substituents of strong donor and/or acceptor groups, leading to potential intramolecular charge transfer capabilities [5]. Various organic molecules containing π-conjugated electrons with appropriate donor and acceptor groups exhibit moderate to strong TPA properties. In recent years, the development of metal complexes containing TPA chromophores has received a great deal of interest because of their structural diversity and multifunctional nature [5a,6]. Bharadwaj and co-workers observed that bis-cinnamaldiminato Schiff base metal coordination complexes possess very large $\sigma^{(2)}$ values of up to 10,736 GM, as measured by a femtosecond open aperture Z-scan technique [7]. Transition metal N_2O_2 Schiff base complexes, in which the ligands are derived from salicylaldehyde and diamines (generically coined as salen or salophen), have also been studied as a class of efficient chromophores exhibiting potentially large NLO responses [6–9]. They are particularly interesting because of their preparative accessibility and their high thermal stability. In such compounds, metal complexation leads to the formation of geometrically constrained acentric, generally planar structures that always involve an enhancement of optical nonlinearity of the Schiff base complexes compared to that of the related free ligands [7,10]. Furthermore, the electron-donating (D) and -accepting (A) capabilities of organometallic fragments have been successfully applied for the design and development of new highly efficient dipolar chromophores for achieving high second-order NLO responses [9g,10a,11]. To the best of our knowledge, only a few examples of the TPA properties of N_2O_2 Schiff base metal complexes have been reported in the literature, and these are rarely derived from unsymmetric metallosalophens [7,12]. We present here several new metal-containing chromophores based on unsymmetric donor-acceptor Schiff base frameworks. The TPA properties of these unsymmetric metallosalophens were investigated by fluorescence emission spectroscopy as well as by the femtosecond Z-scan technique to obtain their $\sigma^{(2)}$ values. Besides, theoretical

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calculations employing linear and quadratic response functions were carried out at the density functional theory (DFT) level to aid the interpretations of the experimental results.

2. Experimental

2.1. Chemicals and measurements

2.1.1. General

The commercially available chemicals were purchased and used as received. Silica gel 60 (0.04–0.063 mm) for column chromatography was purchased from Merck. NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. Low-resolution FAB mass spectra were obtained with a Finnigan TSQ710 mass spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Bruker Autoflex MALDI-TOF mass spectrometer. All solution spectroscopic measurements were prepared in spectrophotometric grade *N,N′*-dimethylformamide (DMF) (Aldrich) and degassed with freeze-pump-thaw cycles (three times). Electronic absorption spectra in the UV–Vis region were recorded with a Varian Cary 100 UV/Vis spectrophotometer, and elemental analyses were performed on a Carlo Erba 1106 instrument. The IR spectra (KBr pellets) were recorded with a Nicolet Magna 550 FTIR spectrometer. Steady-state visible fluorescence and PL excitation spectra were recorded on a Photon Technology International (PTI) Alphascan spectrofluorimeter and visible decay spectra on a pico-N_2 laser system (PTI Time Master) with $\lambda_{exc} = 337$ nm. Quantum yields of visible emissions were calculated according to the literature method using quinine sulfate in 1.0 N H_2SO_4 as the reference standard ($\Phi_f = 0.55$ in air-equilibrated water) [13,14].

2.1.2. Two-photon induced fluorescence (TPIF) measurements

The 750 nm excitation femto-second laser pulses were generated by a mode-locked Ti:Sapphire laser (Tsunami, Spectra-Physics) and Ti:Sapphire regenerative amplifier (Spitfire, Spectra-Physics) with a pulse energy of 1 mJ per pulse, duration of ~120 fs and a repetition rate of 1 kHz. Two polarizers were used to alter the excitation laser intensity before it reached the sample. The emission from the sample was monitored by a spectrometer system with a monochromator (SpectraPro 2300i, ACTON research corporation) and photomultiplier tube (R636-10, Hamamatsu).

2.1.3. Two-photon absorption measurements

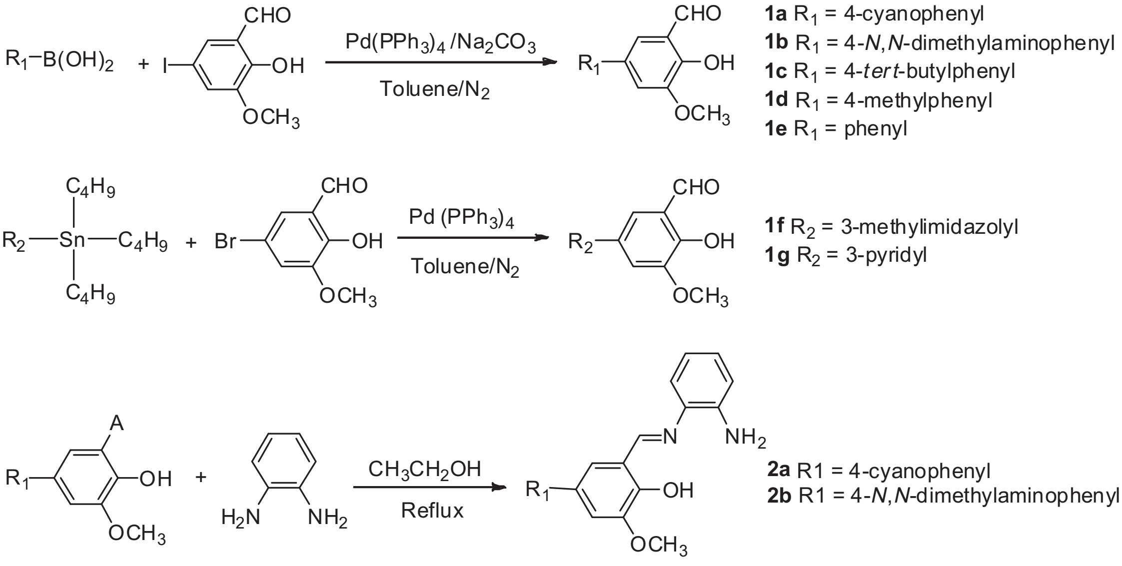
The two-photon-absorption spectra (i.e. Z-scan traces) were measured at 800 nm by the open-aperture Z-scan method using 100 fs laser pulses with a peak power of 276 GW cm^{-2} from an optical parametric amplifier operating at a repetition rate of 1 kHz, generated from a Ti:sapphire regenerative amplifier system [15]. The laser beam was split into two parts by a beam splitter. One was monitored by a photodiode (D1) as the incident intensity reference, I_0, and the other was detected as the transmitted intensity by another photodiode (D2). After passing through a lens with $f = 20$ cm, the laser beam was focused and passed through a quartz cell. The position of the sample cell, z, was moved along the direction of the laser beam (z axis) by a computer-controlled translatable table so that the local power density within the sample cell could be changed under the constant incident intensity laser power level. Finally, the transmitted intensity from the sample cell was detected by the photodiode D2. The photodiode D2 was interfaced to a computer for signal acquisition and averaging. Each transmitted intensity datum represents the average of over 100 measurements. Assuming a Gaussian beam profile, the non-linear absorption coefficient, β, can be obtained by curve-fitting to the observed open-aperture traces, $T(z)$, with Eq. (1) [16], where α_0 is the linear absorption coefficient, l is the sample length (1 mm quartz cell) and z_0 is the diffraction length of the incident beam. After obtaining the non-linear absorption coefficient, β, the TPA cross-section, $\sigma^{(2)}$, of the sample molecule (in units of 1 GM = 10^{-50} cm^4 s $photon^{-1}$) can be determined using Eq. (2), where N_A is Avogadro's constant, d is the concentration of the sample compound in solution, h is Planck's constant and v is the frequency of the incident laser beam.

$$T(z) = 1 - \frac{\beta I_0(1 - e^{-\alpha_0 l})}{2\alpha_0[1 + (z/z_0)]^2} \tag{1}$$

$$\sigma^2 = \frac{1000\beta h\nu}{N_A d} \tag{2}$$

2.2. Preparation of the unsymmetric metallosalophen complexes

The salicylaldehydes **1a** [17], **1b**–**1c**, **1d** [18], **1e** [19], **1f** [20], and **1g** [21] were prepared from the commercially available chemical 2-hydroxy-5-iodo-3-methoxybenzaldehyde in moderate yields



Scheme 1. Synthesis of electron-donating and electron-accepting functionalized salicylaldehydes **1a**–**1g** and monoimines **2a** and **2b**.