



Synthesis and two-photon absorption property of novel salen complexes incorporated with two pendant azo dyes

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ABSTRACT

New salen compounds have been developed to possess two pendant azo dye chromophores. The two-photon absorption properties have been observed which result from the chromophores. The additive property has been found to exist as a result of no detrimental dipole–dipole interaction between chromophores.

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Applications of two-photon absorption (2PA) technology have been manifested in many important areas such as optical power limiting, up-converted lasing, photodynamic therapy and generation of singlet oxygen, three-dimensional microfabrication and data storage, and three-dimensional fluorescence microscopy,^{1–6} Requiring molecules with desirable two-photon absorption properties have led to the development of several design strategies. Molecules with various geometries (linear, branched, and dendritic) coupled with D– π –D, D– π –A– π –D, and A– π –D– π –A structural features have been found to enhance the two-photon absorptivity.^{7–12} Recently, the development of metal-containing two-photon absorbing chromophores has received a great interest due to the potential applications from multi-functional systems. Maggini and Meneghetti showed Zn-induced on-off switching of nonlinear transmittance through coordination to donating atoms.¹³ Humphrey and co-workers observed reversible electrochemical switching of nonlinear absorption in ruthenium complexes, where metal centers are directly embedded in the conjugated systems.¹⁴ Perry and co-workers have demonstrated the ultrabright beacon effect with 2PA molecules-coated nanoparticles where 2PA molecules are tethered to nanoparticles via long alkyl chains.¹⁵ We disclose here the synthesis and 2PA properties of new salen metal complexes incorporated with azo dyes.

The synthetic approach to salen-azo dye **4** started with 2,3-dihydroxybenzaldehyde. The hydroxyl group at the 2-position

was selectively masked to give **1**.¹⁶ The hydroxyl at the 3-position of **1** coupled with azo dye **2** under Mitsunobu condition led to the formation of **3**. The release of hydroxyl group at the 2-position was achieved by the deprotection of **3** using Pd–C in the presence of HClO₄. Azo dyes-containing salen ligand **4** was obtained by condensation of **3** with ethylenediamine. Reactions of **4** with Cu(OAc)₂ and VO(acac)₂ gave desirable complexes **5** and **6**,¹⁷ respectively (Scheme 1).

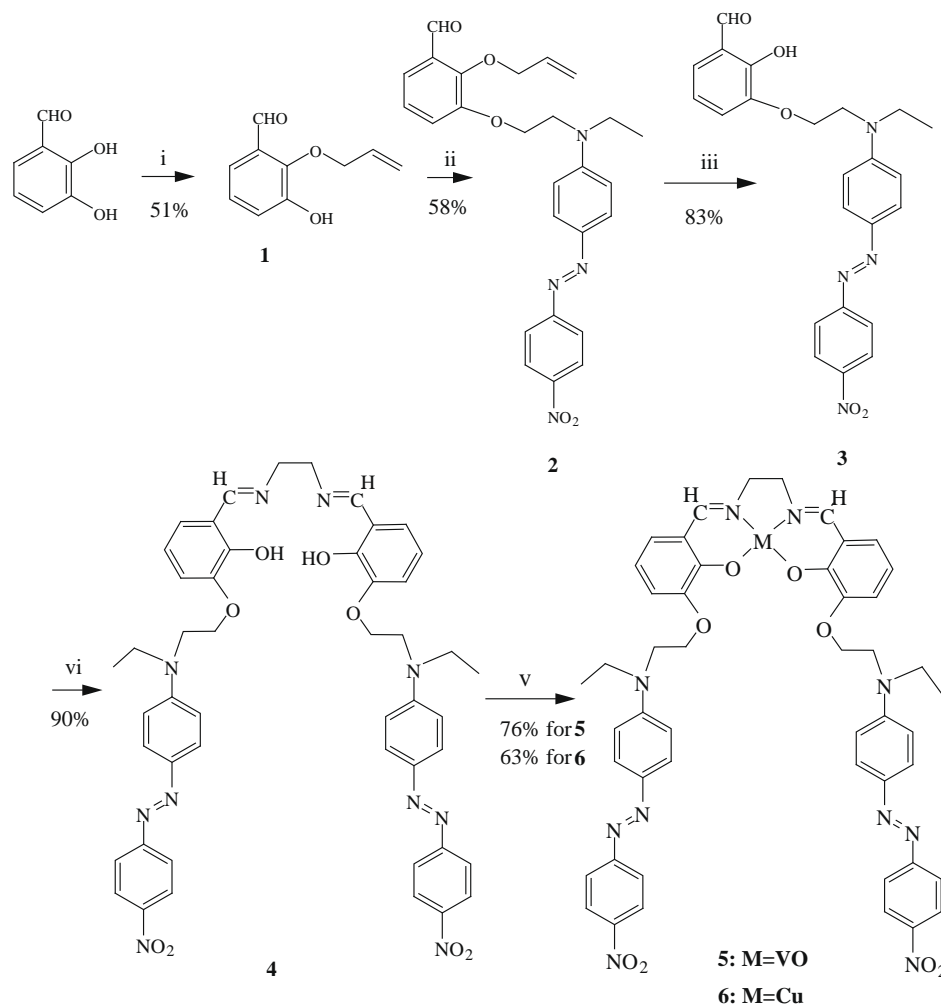
Ligand **4** and complexes **5–6** are found to be dominated with one $\pi \rightarrow \pi^*$ absorption band in the visible region (at ca. 500 nm, NMP solution). The d–d transitions from the metal complexes are masked by the strong $\pi \rightarrow \pi^*$ band in the same region. It is completely transparent beyond 640 nm. The linear absorption was measured with a concentration in the order of 2.5×10^6 molecules/cm³ (left side, solid line, Fig. 1).

The 2PA spectrum of the vanadyl complex is shown in Figure 1 (right side, middle, solid dots). A 2PA band was found to be at ca. 1000 nm, which is twice the one-photon absorption wavelength. The 2PA cross-section was found to be monotonically increasing below 800 nm, which is due to the resonance enhancement as one-photon transition is approached. The copper complex showed the same 2PA properties (Fig. 1, bottom, solid dots). These results indicate that azo-dye components uniquely dominate the 2PA process. This is further manifested by the fact that the ligand **4** also shows the identical 2PA properties.

The current ligand and complex systems were also found to possess additive 2PA properties. This conclusion was made by comparison with DR1 dye (see the structure in Scheme 1), the azo chromophore used in the salen ligand **4** and complexes

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Scheme 1. Reagent and conditions: (i) allyl bromide/NaH; (ii) *p*-[HOCH₂CH₂N(C₂H₅)₂]₂C₆H₄N₂C₆H₄-(*p*-NO₂), **DR1**, DEAD/PPh₃; (iii) DMF–H₂O/Pd–C; (iv) H₂NCH₂CH₂NH₂; (v) Cu(OAc)₂ or VO(acac)₂/EtOH.

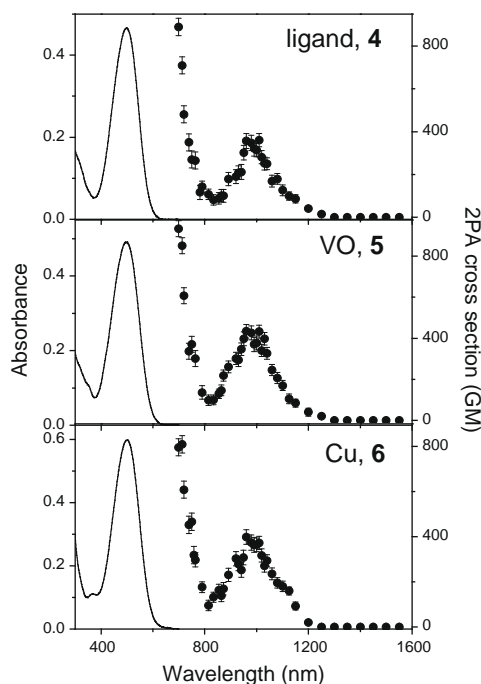


Figure 1. One-photon (left, solid line) and two-photon (right, solid dot) absorption spectra.

5–6. The ligand **4** showed that its 2PA cross-section magnitude is twice that of DR1,¹⁸ when concentrations of **4** and DR1 are normalized to be the same. Both copper and vanadyl complexes also showed the same increase. The 2PA properties being the sum of two discrete azo dye chromophores indicate that there is no detrimental dipole–dipole interaction between them.¹⁹ The molecular modeling suggests that two azo dye chromophores units are pointed away from each other, and the coordination core essentially acts as a scaffold to distance the two chromophores. Each unit exhibits an inherent 2PA property on its own so that it is possible for the current salen system with high chromophore density to exhibit corresponding additive 2PA properties.

In summary, we have developed a new class of salen complexes that possess two discrete azo dye chromophores with the coordination core serving as a scaffold to separate the two units. The 2PA cross-section peak is found to be ca. 1000 nm. The additive 2PA properties have been found to be the sum of the two chromophore units.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2008.12.112](https://doi.org/10.1016/j.tetlet.2008.12.112).

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