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ARTICLE

## Two Photon Absorption Properties of Four Coordinated Transition Metal Complexes of Tetraaryl-Azadipyrromethene Compounds

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New tetraarylazadipyrromethene metal complexes with four coordinate metals (cobalt(II), nickel(II), copper(II) and zinc(II)) and with three moieties (4-methylphenyl, 4-methoxyphenyl and 1-naphthyl) were designed and synthesized targeting applications utilizing two photon absorption. The effects of metals with filled or unfilled *d* orbitals and substitutions with various electron donor properties on charge transfer mechanism and two photon absorption properties of tetraarylazadipyrromethene compounds were investigated by ultrafast pump-probe spectroscopy and open aperture Z-scan experiments as well as Density Functional Theory (DFT) calculations. Ultrafast transient absorption spectra provide evidence of an efficient photoinduced intramolecular charge transfer between ligand and metals which is independent of filled or unfilled *d* orbital of metals. Although zinc have filled *d* orbitals, its complexes possess absorption maximum including the shoulder which is dedicated to partial ligand to metal  $L(\pi) \rightarrow M(d^*)$  charge transfer character (LMCT). Due to charge transfer mechanism, metal complexes of tetraarylazadipyrromethene compounds exhibited two photon absorption properties in the femtosecond regime at 800 nm wavelength. The greatest two photon absorption cross section value was measured as 2690 GM for  $Zn(L^2)_2$  and 2374 GM for  $Co(L^2)_2$  complex.

### Introduction

Materials with large two photon absorption (TPA) properties have attracted attention due to their wide range of potential applications including optical power limiting,<sup>1,2</sup> TPA imaging microscopy,<sup>3</sup> three-dimensional micro fabrication,<sup>4,5</sup> optical data storage,<sup>6,7</sup> photodynamic therapy,<sup>8</sup> multi photon fluorescence sensing,<sup>9</sup> and TPA up conversion lasing.<sup>10</sup>

Wide varieties of organic and inorganic materials with large TPA properties have been studied. Materials with donor (D) and/or acceptor (A) substituents linked by a conjugated  $\pi$  bridge are very efficient<sup>11</sup> due to delocalization of electrons and therefore enhancement of polarization of molecules. TPA properties of trans-stilbene,<sup>12,13</sup> fluorene,<sup>14</sup>

dithienothiophene,<sup>15,16</sup> butadiyne,<sup>17</sup> triphenyl-amine,<sup>18</sup> [2.2]paracyclophanes,<sup>19</sup> and porphyrin<sup>20,21</sup> have been studied extensively. On the other hand, there are a few reports in the literature about TPA properties of metal-organic compounds.<sup>22</sup> Exceptionally, large TPA cross-section (TPCS) value (10736 GM) was obtained from a Schiff base through Zn(II) metal complexation.<sup>23</sup> Previously, we studied the influence of the central metal ion on TPA properties and the excited-states dynamics of tetraaryl porphyrins with different central metal ions.<sup>22</sup> We found that TPA properties depend on the central metal ions for porphyrin molecules. In another recent work, it was found that charge transfer in transition metal porphyrins enhanced TPA properties.<sup>24</sup> Additionally, it was shown that TPA properties of phenanthroline-based  $\pi$  conjugated chromophores increased from 165 GM to 578 GM upon binding Ni(II) ion.<sup>25</sup>

On the other hand, it is known that in addition to the enhancement of polarization of molecules, relaxation dynamics of excited states also play important role in the nonlinear optical response of the organic conjugated materials.<sup>26</sup> Ultrafast dynamics of organic conjugated systems with intense TPA response has been a popular research field.<sup>27,28</sup> Therefore, studies linking ultrafast relaxation dynamics and TPA properties of newly designed and synthesized molecules directly impact the application of these materials.

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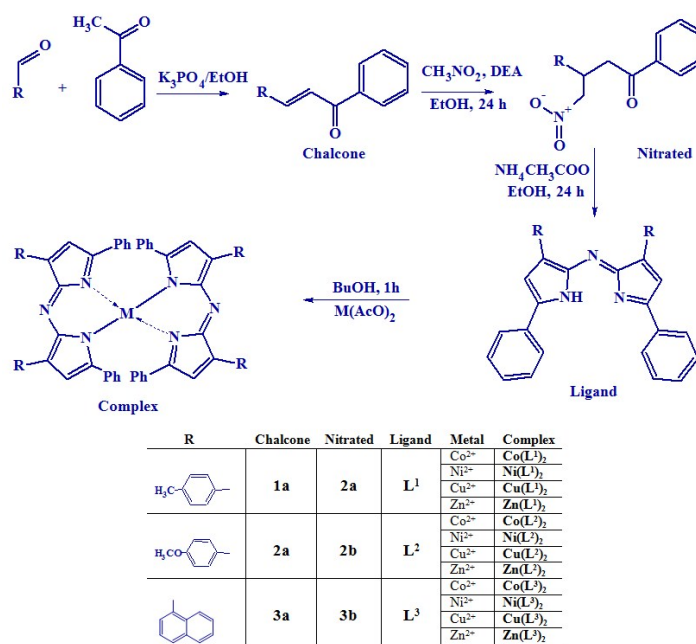
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Scheme 1. Synthetic routes to the tetraphenylazadiopyrromethene free ligands and their metal complexes.

The synthesis and photophysical properties of BF<sub>2</sub> chelated tetraarylazadiopyrromethene have been studied in literature.<sup>29,30</sup> TPA properties of these compounds were investigated in our previous works.<sup>31-33</sup> The results of our previous works show that TPA properties of BODIPY and aza-BODIPY compounds increase with increasing charge transfer. On the other hand, there are a few studies in literature about photophysical properties of metal complexes of tetraarylazadiopyrromethene compounds.<sup>34-36</sup>

Especially, charge transfer properties of metal complexes of tetraarylazadiopyrromethene compounds were not investigated by ultrafast absorption spectroscopy and therefore, the effects of metals to the TPA properties were not studied before.

In an attempt to fill the gap in the literature, we designed and synthesized a group of metal complexes of

tetraarylazadiopyrromethene compounds by altering metal atoms with filled and unfilled *d* orbitals and electron donating substituents with various donor/acceptor properties (Scheme 1). The synthesis method is given in supporting information. We investigated the electron transfer mechanisms affected by metal atoms/substituents and its contribution to the TPA properties of tetraarylazadiopyrromethene metal complexes by using ultrafast time resolved spectroscopy and open aperture Z-scan experimental techniques.

## Result and Discussion

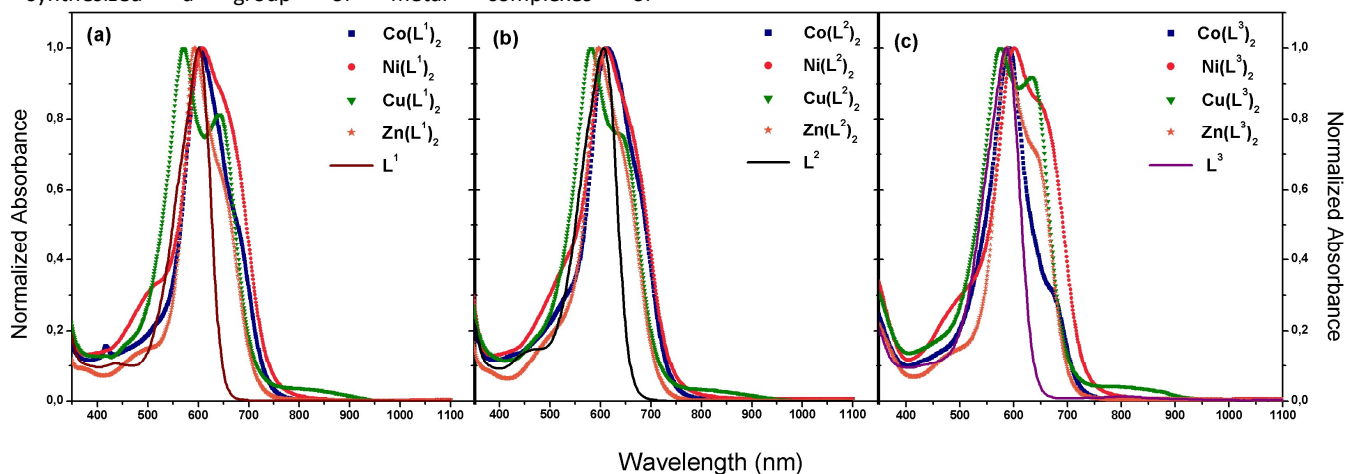


Fig. 1 Absorption spectra of ligand and metal complexes with (a) 4-methylphenyl (b) 4-methoxyphenyl and (c) 1-naphthyl groups in THF

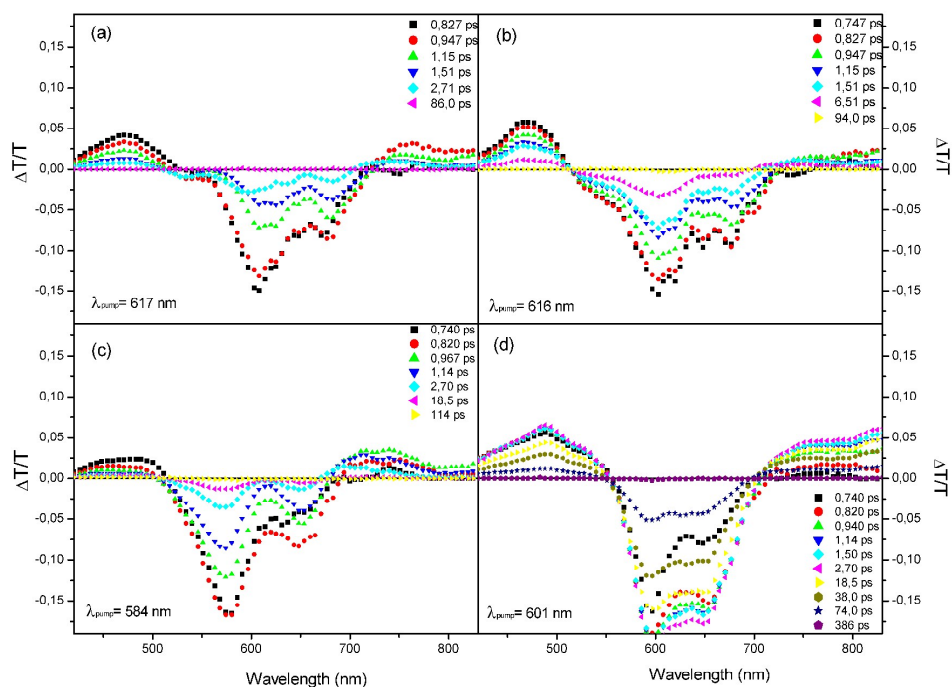


Fig. 2 Transient absorption spectra of  $M(L^2)_2$  compounds (a)  $Co(L^2)_2$  compound (b)  $Ni(L^2)_2$  compound (c)  $Cu(L^2)_2$  compound (d)  $Zn(L^2)_2$  compound at different time intervals

### Steady State Absorption Measurement

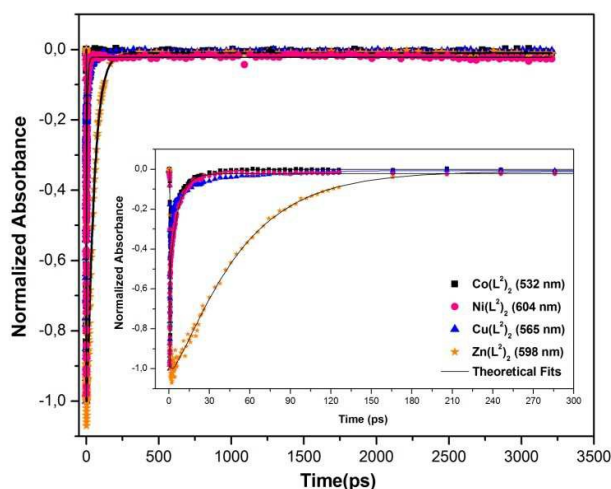
Fig. 1a-c show absorption spectra of ligand and metal complexes ( $Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$ ) of tetraarylazadipyrromethene for 4-methylphenyl( $L^1$ ), 4-methoxyphenyl( $L^2$ ) and 1-naphthyl ( $L^3$ ) substituents, respectively. The linear spectroscopic data of  $L^{1-3}$  and  $M(L^{1-3})_2$  are summarized in Table 1.

Table 1. Optical properties of studied compounds

Substituent	Compounds	$\lambda_{max}^a$ (nm)	$\sigma_2^c$ (GM)
4-methylphenyl	$L^1$	601	-
	$Co(L^1)_2$	610	2192
	$Ni(L^1)_2$	615	-
	$Cu(L^1)_2$	575	-
	$Zn(L^1)_2$	600	1631
4-methoxyphenyl	$L^2$	607	-
	$Co(L^2)_2$	617	2036
	$Ni(L^2)_2$	616	-
	$Cu(L^2)_2$	584	-
	$Zn(L^2)_2$	601	2690
1-naphthyl	$L^3$	585	-
	$Co(L^3)_2$	595	2374
	$Ni(L^3)_2$	605	-
	$Cu(L^3)_2$	573	-
	$Zn(L^3)_2$	592	1565

The ligands  $L^{1-3}$  exhibit a broad absorption band with  $\lambda_{max}$  at 600 nm which is a combination of  $\pi-\pi^*$  and Intra-Ligand Charge Transfer (ILCT) transitions. This band is significantly red-shifted upon complexation with metal ions. This is attributed to the change in the electronic properties of  $L^{1-3}$  into a more strongly polarized D- $\pi$ -A- $\pi$ -D unit. In a recent work, it was shown that the copper complex of tetraarylazadipyrromethene showed a clear splitting of the longest wavelength band, which may be indicative of the strain within the ligand while the other complexes ( $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ) exhibited distinct red-shifted shoulders of the main absorption band.<sup>36</sup> Similarly, the longest wavelength band in our samples split for the  $Cu(II)$  complexes i.e. 4-methylphenyl ( $Cu(L^1)_2$ ), 4-methoxyphenyl ( $Cu(L^2)_2$ ) and 1-naphthyl ( $Cu(L^3)_2$ ) complexes, while  $Co(II)$ ,  $Ni(II)$  and  $Zn(II)$  complexes show significant red-shifted shoulders of the main absorption band (Fig. 1a-c).<sup>36</sup> The red shifted shoulders correspond to charge transfer between ligand and  $d$  orbitals of metals. Although zinc has filled  $d$  orbitals, its complexes possess absorption maximum including the shoulder which is dedicated to partial ligand to metal  $L(\pi) \rightarrow M(d^*)$  charge transfer character (LMCT).<sup>35</sup>

When the electron-donating group is at the para position of the phenyl rings ( $\alpha$ ) attached to pyrrole in azadipyrromethene ligands, slightly bathochromic shift is observed in the absorption spectra as observed previously.<sup>37</sup> The naphthyl group has more acceptor nature and longer conjugation than that of methyl and methoxy groups. Therefore, absorption spectra are hypsochromic shifted by the naphthyl groups



**Fig. 3** Effects of unfilled and filled  $d$  orbitals on decay profile for bleaching signal of  $M(L^2)_2$  compounds

binding to the azadipyrromethene core as seen in Fig. 1 and Table 1.

All metal complexes with three different substituents are non-emissive and show no fluorescence due to charge transfer from ligand to transition metals (Co(II), Ni(II), Cu(II) and Zn(II)).

We investigated the electron transfer mechanisms affected by metal atoms/ substituents of tetraarylazadipyrromethene metal complexes by using ultrafast time resolved spectroscopy experimental technique.

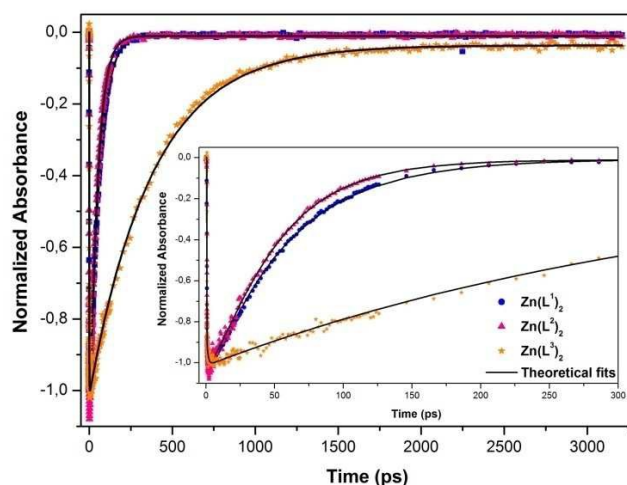
#### Ultrafast Pump-Probe Spectroscopy Experiments

Ultrafast pump-probe spectroscopy experiment with white light continuum was used to investigate the optical dynamics and decay processes of excited states of all metal complexes. Pump wavelengths for the experiments were chosen according to maximum absorption wavelengths of investigated compounds as given in Table 1.

Transient absorption spectra of metal free azadipyrromethene ligands were measured as control experiments. They show an

**Table 2.** Excited state lifetimes of metal complexes

Substituent	Complexes	$\tau_1$ (ps)	$\tau_2$ (ps)
4-methylphenyl	$Co(L^1)_2$	0,15	12
	$Ni(L^1)_2$	0,16	7
	$Cu(L^1)_2$	0,32	36
	$Zn(L^1)_2$	0,82	58
4-methoxyphenyl	$Co(L^2)_2$	0,15	10
	$Ni(L^2)_2$	0,16	7
	$Cu(L^2)_2$	0,28	25
	$Zn(L^2)_2$	0,76	44
1-naphthyl	$Co(L^3)_2$	0,16	15
	$Ni(L^3)_2$	0,17	9
	$Cu(L^3)_2$	0,35	55
	$Zn(L^3)_2$	0,95	380



**Fig. 4** Effects of moieties with different electron donor properties orbitals on decay profile for bleaching signal of  $Zn(L^{1-3})_2$  compounds

intense single bleach signal at the peak of their linear absorption bands (around 600 nm). As an example, the result of  $L^2$  is given in supporting information document (Fig. S16).

Transient absorption spectra of metal complexes containing 4-methoxyphenyl ( $M(L^2)_2$ ), 4-methylphenyl ( $M(L^1)_2$ ) and 1-Naphthyl ( $M(L^3)_2$ ) compounds were given in Fig. 2, Fig.S17 and Fig. S18, respectively. These results clearly show that bleach signal in the transient absorption spectra at 600 nm splits into two spectral components upon binding metal atoms to the ligands, which is in line with steady state absorption spectra of these compounds.

The second bleach signals, which are located around 650 nm are attributed to charge transfers from  $\pi$  orbital of ligand to  $d$  orbitals of transition metals.<sup>38</sup> Fig. 2 also shows two positive signals, which are located below 450 nm and above 750 nm for  $M(L^2)_2$  compounds. These positive signals correspond to excited state absorption. The transient absorption spectra of metal complexes containing 4-methylphenyl and 1-naphthyl groups have similar optical characteristic behaviors with slightly hypsochromic shifting of transient absorption spectra depending on moieties as shown in Fig. S17 and Fig. S18.

The effects of charge transfers (from ligand to  $d$  orbitals) on excited state lifetimes (i.e. the decays of the bleach signals) were shown in Fig. 3 for compounds containing 4-methoxyphenyl moieties. Excited state lifetimes of metal complexes of azadipyrromethene compounds (Table 2) indicate different characteristics depending on the filled or unfilled  $d$  orbitals of transition metals.

Complexes containing metals with unfilled  $d$  orbitals (i.e. Co(II), Ni(II) and Cu(II)) show shorter excited state lifetimes than that of complexes with filled  $d$  orbitals (Zn(II)), due to faster charge transfer to unfilled  $d$  orbitals.

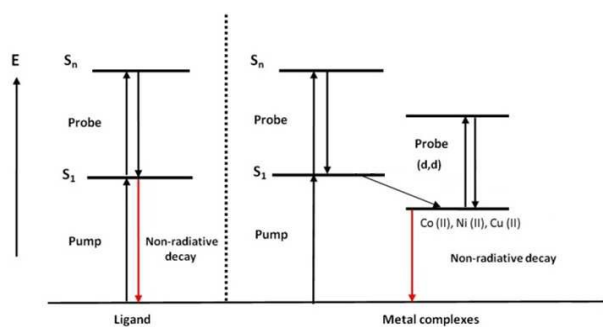


**Table 3.** Selected parameters for the vertical excitation (UV-Vis absorption) of the compounds. Electronic excitation energies (eV) and oscillator strengths ( $f$ ), configurations of the low-lying excited states of  $\text{Co}(\text{L}^2)_2$  and  $\text{Zn}(\text{L}^2)_2$ . Calculated by TDDFT/UB3LYP/GENECP, based on the optimized ground state geometries.

Electronic transition <sup>a</sup>	TDDFT/ UB3LYP/GENECP				
	Excitation energy	$f^b$	Composition <sup>c</sup>	CI <sup>d</sup>	
$\text{Co}(\text{L}^2)_2$	$S_0 \rightarrow S_{17}$	1.85eV (670nm )	0.2635	H-3(B) $\rightarrow$ L(B)	0.3969
				H(A) $\rightarrow$ L + 1(A)	0.3654
	$S_0 \rightarrow S_{21}$	1.92eV (645nm )	0.1690	H-3(B) $\rightarrow$ L(B)	0.5346
				H-3(A) $\rightarrow$ L + 1(A)	0.3599
	$S_0 \rightarrow S_{23}$	2.08eV( 595 nm )	0.2292	H-3(B) $\rightarrow$ L(B)	0.4468
			H-3(A) $\rightarrow$ L + 1(A)	0.3859	
			H-4(A) $\rightarrow$ L(A)	0.3177	
$\text{Zn}(\text{L}^2)_2$	$S_0 \rightarrow S_1$	1.80eV (688nm )	0.0190	H $\rightarrow$ L	0.5854
				H - 1 $\rightarrow$ L + 1	0.3908
	$S_0 \rightarrow S_3$	2.06eV (603nm )	0.5352	H - 1 $\rightarrow$ L + 1	0.5823
				H $\rightarrow$ L	0.3819
	$S_0 \rightarrow S_4$	2.08eV (597nm )	0.7657	H $\rightarrow$ L + 1	0.5623
			H- 1 $\rightarrow$ L	0.3876	
	$S_0 \rightarrow S_5$	2.37eV( 522 nm )	0.5960	H- 2 $\rightarrow$ L	0.6567
			H- 3 $\rightarrow$ L + 1	0.2526	

<sup>a</sup>Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. <sup>b</sup>Oscillator strength. <sup>c</sup>H stands for HOMO and L stands for LUMO. Only the main configurations are presented. <sup>d</sup>Coefficient of the wavefunction for each excitations. The CI coefficients are in absolute values. <sup>e</sup>Based on the optimized  $S_1$  state geometry.

Besides, excited state lifetimes of unfilled  $d$  orbitals are short for all moieties of studied compounds (4-methylphenyl, 4-methoxyphenyl and 1-naphthyl). On the other hand, different electron donating properties of moieties effect excited state lifetime as well. We observed that complexes including 1-naphthyl moiety has longer excited state lifetime due to their relatively stronger electron acceptor nature<sup>39</sup> and possession of long of long conjugation length especially in Zn(II) metal complexes as seen in Fig. 4. Based on the transient absorption results, the photophysical processes involved in the charge transfer between  $\pi$  orbital of ligand and  $d$  orbitals of metal upon photo excitation of singlet state of ligand are depicted in the energy level diagrams in Fig. 5.



**Fig. 5** Energy level diagram of ligand and metal complexes

### DFT calculations on the photophysical properties of the $\text{Co}(\text{L}^2)_2$ and $\text{Zn}(\text{L}^2)_2$ complexes

In order to reveal the charge transfer characteristics of filled and unfilled  $d$  orbitals of the metal complexes,  $\text{Co}(\text{L}^2)_2$  and  $\text{Zn}(\text{L}^2)_2$  complexes were chosen as representative coordination compounds to optimize the ground state geometries with the DFT theory. The calculated excitation energy, oscillator strength ( $f$ ), main compositions and coefficient of the wavefunction for each excitations for the  $\text{Co}(\text{L}^2)_2$  and  $\text{Zn}(\text{L}^2)_2$  complexes are presented in Table 3. The molecular orbitals of metal complexes  $\text{Co}(\text{L}^2)_2$  and  $\text{Zn}(\text{L}^2)_2$  involved in the dominant electronic transitions are given in Fig.6. In order to describe different charge transition characteristics of Co(II) and Zn(II) complexes, electron density difference between the ground state and the dominant excited state were calculated as seen in Fig. 7 and Fig. 8. It can be seen from these figures that, the increasing electron density in  $\text{Co}(\text{L}^2)_2$  complex localizes on Co(II) and no localization was observed on Zn(II) due to its filled  $d$  orbitals. These findings indicate that LMCT is dominant on  $\text{Co}(\text{L}^2)_2$  complex, which is convenient with the results and discussion of ultrafast spectroscopy experiments given in Fig. 3-5.

### Two Photon Absorption Properties

It is known that TPA properties are enhanced by increasing charge transfer in organic molecules.<sup>31-33</sup> Metal complexes of tetraarylazadipyrromethene compounds also show charge

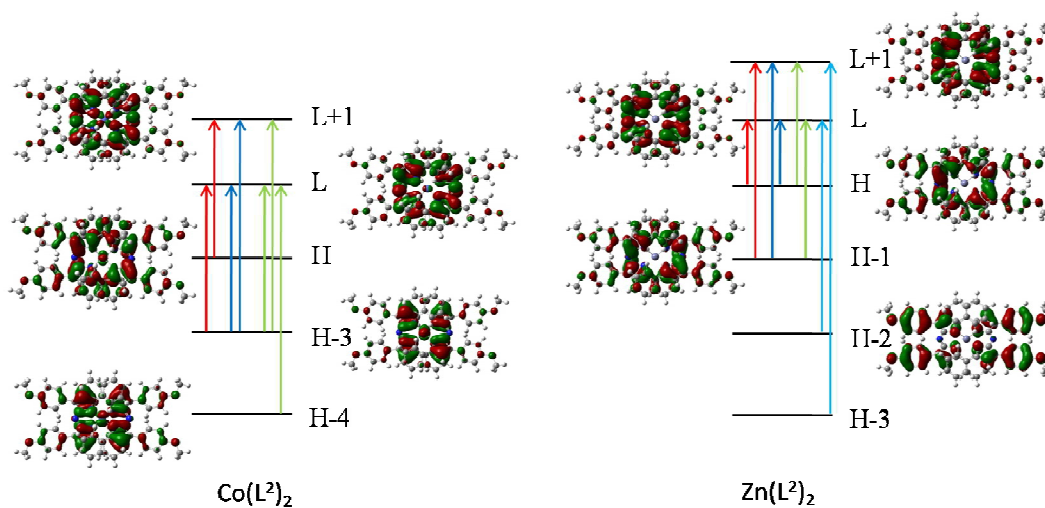


Fig. 6 The molecular orbitals of metal complexes  $\text{Co}(\text{L}^2)_2$  and  $\text{Zn}(\text{L}^2)_2$  involved in the dominant electronic transitions.

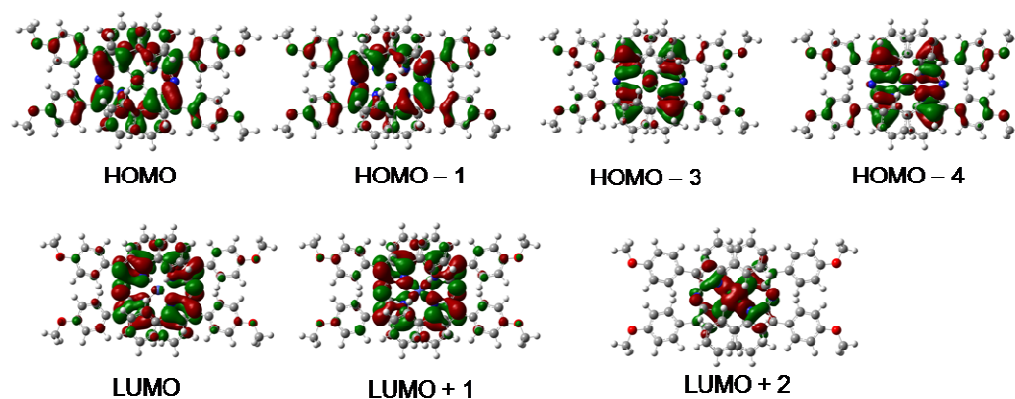


Fig. 7 Selected frontier molecular orbitals involved in the excitation of  $\text{Co}(\text{L}^2)_2$ . The calculations are at the TDDFT/UB3LYP/GENECP level using Gaussian 09W.

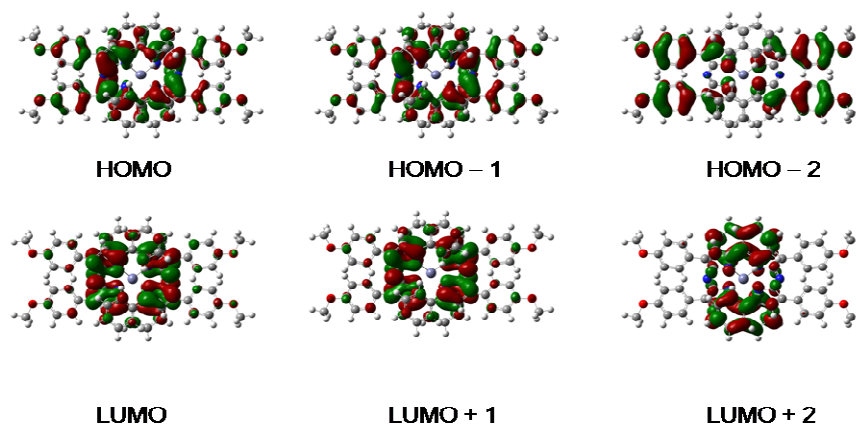


Fig. 8 Selected frontier molecular orbitals involved in the excitation of  $\text{Zn}(\text{L}^2)_2$ . The calculations are at the TDDFT/UB3LYP/GENECP level using Gaussian 09W.

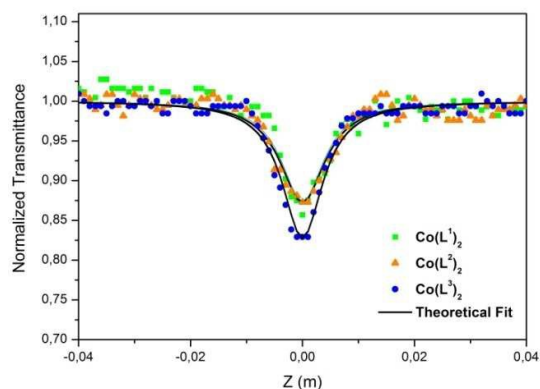


Fig. 9 Experimental results and theoretical fits of open aperture Z-scan experiments for  $\text{Co}(\text{L}^{1-3})_2$  complexes with different substituents in THF

transfer mechanism. In an attempt to show the effect of charge transfer and the effect of heavy metal on the TPA properties, open aperture (OA) Z-scan experiments<sup>40,41</sup> were conducted by using a mode-locked Ti: Sapphire laser amplifier system with 1 ps pulse duration, 1 kHz repetition rate and 800 nm wavelength.

The OA Z-scan experiment could not be performed for Ni(II) and Cu(II) complexes due to presence of linear absorption at 800 nm. The OA Z-scan experiments were performed for free ligands ( $\text{L}^{1-3}$ ) and TPA properties could not observe. The Schiff base ligand (L) belongs to the D- $\pi$ -A- $\pi$ -D analogue since the central diimine part possesses very weak electron-withdrawing character. Complexation with Zn(II) or Co(II) enhances the electron-acceptor character of the central diimine moiety, converting L to a more strongly polarized D- $\pi$ -A- $\pi$ -D unit that makes these complexes potential candidates for third-order nonlinear responses.<sup>22</sup>

OA Z-scan experimental results of Co(II) metal complexes with three different substituents (4-methylphenyl, 4-methoxyphenyl and 1-naphthyl) are shown in Fig. 9.

TPA coefficient ( $\beta$ ) was calculated from these experimental results by using the following equation.<sup>42</sup>

$$T(I_0) = \frac{1}{1 + I_0 \beta l} \quad (1)$$

Nonlinear transmittance T is given in terms of laser intensity and the optical path length. The TPCS value ( $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ ) was calculated from the following equation,

$$\sigma_2 = \frac{h\nu\beta}{N_A d_0 \times 10^{-3}} \quad (2)$$

where,  $N_A$  is the Avogadro number and  $d_0$  is the molar concentration of the solution.

Obtained TPCS values are given in Table 1. TPCS value for Zn(II) metal complex with 4-methoxyphenyl substituent (2690 GM) is bigger than that for Co(II) metal (2036 GM). It is known that methoxy group has electron donating property (D) and therefore metal complexes with 4-methoxyphenyl substituent are in the form of D- $\pi$ -A- $\pi$ -D structure.<sup>22</sup> Metal atom with stronger electron accepting properties (A) is expected to show bigger TPCS in D- $\pi$ -A- $\pi$ -D structure due to efficient charge transfer mechanism. The effect of the structure of the whole complex is more dominant than the effect of the metal alone. Therefore, we need to consider not only the electron accepting property of metal atoms but also electron accepting/donating properties of substituents on the ligands: Since Zn(II) is stronger electron acceptor than Co(II), Zn(II) metal complex with 4-methoxyphenyl substituent has greater TPCS values than that of Co(II) complex. On the other hand, 1-naphthyl substituent has electron acceptor property (A). Therefore, metal complexes with 1-naphthyl substituent are in the form of A- $\pi$ -D- $\pi$ -A structure. Metal complexes with stronger donating properties are expected to exhibit greater TPCS value with 1-naphthyl substituent. TPCS value of  $\text{Co}(\text{L}^3)_2$  (2374 GM) is greater than  $\text{Zn}(\text{L}^3)_2$  (1565 GM) due to stronger electron donating property of Co(II). Among the studied compound, the biggest TPCS value (2690 GM) is measured for  $\text{Zn}(\text{L}^2)_2$ . This result may indicate that D- $\pi$ -A- $\pi$ -D structure is more efficient than A- $\pi$ -D- $\pi$ -A structure for TPA property. Since TPA properties of tetraarylazadipyrromethene metal complexes has not been studied before we could only compare our result with tetraarylazadipyrromethene  $\text{BF}_2$  (Aza-BODIPY) complexes, which has highest TPCS value as 610 GM in 800 nm wavelength ranges.<sup>43</sup>

## Experimental Section

### Synthesis

All solvents and reagents were purchased from Sigma-Aldrich Chemical Company and used as received without further purification. Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets (Merck 60 PF-254). Compounds,  $\text{L}^1$ ,  $\text{L}^3$ ,  $\text{Co}(\text{L}^1)_2$ ,  $\text{Ni}(\text{L}^1)_2$ ,  $\text{Cu}(\text{L}^1)_2$ ,  $\text{Zn}(\text{L}^1)_2$ ,  $\text{Co}(\text{L}^2)_2$ ,  $\text{Ni}(\text{L}^2)_2$ ,  $\text{Cu}(\text{L}^2)_2$ ,  $\text{Zn}(\text{L}^2)_2$ ,  $\text{Co}(\text{L}^3)_2$ ,  $\text{Ni}(\text{L}^3)_2$ ,  $\text{Cu}(\text{L}^3)_2$ ,  $\text{Zn}(\text{L}^3)_2$ , were prepared according to procedure.<sup>36,44</sup>

### Characterization

Melting points were determined on a Gallenkamp melting point apparatus. Flash column chromatography was carried out using silica columns on Combi Flash Rf 200 (Teledyne-Isco, Lincoln, NE) instruments unless otherwise mentioned. The IR spectra were determined on a Perkin Elmer 100 FT-IR spectrophotometer by dispersing samples in KBr disks. UV-Visible spectra were recorded on a SHIMADZU UV-1800 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a



Perkin Elmer LS55 Fluorescence Spectrometer. Microanalyses were performed on a LECO CHNS-932 Elemental Analyzer. Mass spectral analyses were performed on a Waters 2695 Alliance Micromass ZQ LC/MS spectrometer and High Resolution Mass Spectrometer Agilent 6224 TOF LC/MS.

$^1\text{H}$  NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer.  $^1\text{H}$  NMR chemical shifts ( $\delta$ ) are given in ppm downfield from  $\text{Me}_4\text{Si}$ , determined by chloroform ( $\delta = 7.26$  p.m.).  $^{13}\text{C}$  NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer.  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) were reported in ppm with the internal  $\text{CDCl}_3$   $\delta$  77.0 ppm as standard.

Wavelength dependent ultrafast pump probe spectroscopy measurements were performed using Ti:Sapphire laser amplifier-optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) with a commercial experimental setup (Spectra Physics, Helios). Pulse duration was measured as 100 fs.

Nonlinear optical absorption properties of tetraarylazadipyrromethene metal complexes were investigated by using open aperture (OA) Z-scantechinque. Laser source is mode-locked Ti:Sapphire laser amplifier system with 800 nm wavelength, 1 ps pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS). Laser beam was focused on solution in 1 mm thick cell by a lens with 20 cm focal length. Concentrations of the solutions for two photon absorption measurements were 0.001 M.

## Conclusions

We designed and synthesized a group of metal complexes of tetraarylazadipyrromethene compounds with four metal atoms, which have filled and unfilled  $d$  orbitals and three substituents, which have electron donor/acceptor properties. The intermolecular charge transfer from ligand to metal (LMCT) was observed by using the ultrafast pump-probe spectroscopy experiments. Experimental findings were also supported by Density Functional Theory (DFT) calculations. Two photon absorption properties were investigated by using open aperture Z-scan experiment at 800 nm. The results indicate that, the two photon absorption properties of compounds depend on electron acceptor/donor properties of the substituents and coordinating metal ion located in centre of the compound. Metal complexes with substituents having strong electron accepting or donating properties form A- $\pi$ -D- $\pi$ -A or D- $\pi$ -A- $\pi$ -D structure, respectively. Electron accepting property of the central metal ion increases ligand to metal charge transfer and therefore enhances two photon absorption property for D- $\pi$ -A- $\pi$ -D structure. On the other hand, for A- $\pi$ -D- $\pi$ -A structure electron donating property of central metal atom enhances two photon absorption properties. The two photon absorption cross section (TPCS) values measured at 800 nm wavelength were found as 2690 GM and 2374 GM for  $\text{Zn}(\text{L}^2)_2$  (D- $\pi$ -A- $\pi$ -D) and  $\text{Co}(\text{L}^3)_2$  (A- $\pi$ -D- $\pi$ -A) complexes, respectively. This result may indicate that D- $\pi$ -A-

$\pi$ -D structure is more efficient than A- $\pi$ -D- $\pi$ -A structure for TPA property.

To the best of our knowledge, this study is the first research about the nonlinear optical properties of metal complexes of tetraarylazadipyrromethene compounds. Therefore, this paper will open a pathway to the synthesis of new metal complexes of tetraarylazadipyrromethene compounds with stronger two photon absorption properties for the wide range potential application in these fields.

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