ARTICLES

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Crystal structures, two-photon absorption and theoretical calculation of a series of bis-vinylpyridine compounds synthesized by one-step solid state reaction

LI DongMei¹, ZHANG Qiong¹, A. M. Showkot HOSSAIN¹, SUN Mei¹, WU JieYing¹, YANG JiaXiang¹, ZHOU HongPing^{1*}, TAO LiMin², WANG ChuanKui² & TIAN YuPeng^{1,3,4*}

¹Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province; Department of Chemistry, Anhui University, Hefei 230039, China
²Department of Physics, Shandong Normal University, Jinan 250014, China

³State Key Laboratory of Crystal Materials; Shandong University, Jinan 250100, China ⁴State Key Laboratory of Coordination Chemistry; Nanjing University, Nanjing 210093, China

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Three bis-vinylpyridine compounds $(4,4'-bis(2-vinylpyridine)biphenyl L_1, 4,4'-bis(3-vinylpyridine) biphenyl L_2, and 4,4'-bis (4-vinylpyridine)biphenyl L_3) were synthesized by one-step solid-state reactions at room temperature, giving nearly quantitative yields. The compounds obtained were fully characterized by IR, MS and NMR spectroscopies. The structures of L₂ and L₃ were determined by single crystal X-ray diffraction analysis. No noticeable solvatochromism was observed in either one-photon absorption or one-photon excited fluorescence spectra. All of the compounds have high fluorescence quantum yields and long fluorescence lifetime. The linear and nonlinear optical properties of the compounds were investigated both experimentally and theoretically. Interestingly, the position of the nitrogen atom from pyridine influences their two-photon absorption across-sections.$

two-photon absorption, one-step solid-state reaction, high quantum yield, pyridine derivatives

1 Introduction

Two-photon absorption (TPA) has many applications *over recent years*, including 3D fluorescence microscopy, optical limiting, 3D optical data storage and 3D microfabrication [1–5]. Up to now, many efforts have been *paid* to develop efficient two-photon chromophores. A large number of researches on synthesis, structures and theory have revealed the importance of certain basic structural motifs for TPA-active organic materials [6, 7] which typically are characterized in the following classes: dipoles [8], quadrupoles [9–11], multibranched molecules [12–15], and dendrimers

[16]. In particular, a framework for mobile π -electrons with electron donor/acceptor groups at the terminal sites with or without donors/acceptors in the middle of the conjugated framework provides the potential application for symmetric charge displacement upon *excitation and enhancing TPA*.

With the above consideration, although some of these materials exhibited large TPA cross-sections and good TPA properties, most of them were obtained through complicated routes, including our recent work [17]. Investigating simple and efficient synthesis of TPA chromophores would be beneficial to the development of TPA materials. In this paper, we present a series of novel TPA chromophores based on pyridine as a terminal group, L_1 , L_2 , and L_3 (Figure 1), which were prepared through one-step solid-state reactions and gave quantitative yields. It is noteworthy here that the

^{*}Corresponding author (email: zhpzhp@263.net; yptian@ahu.edu.cn)

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Figure 1 ORTEP diagram with the atomic numbering scheme of L_2 . Thermal ellipsoids are shown at the 50% probability level.

novel chromophores possess potential application perspective due to their simple preparation, TPA activity and coordinating ability [18, 4, 19]. Furthermore, the structureproperty relationship of the chromophores has been systematically investigated.

2 Experimental

2.1 Materials and apparatus

All chemicals and solvents were dried and purified by usual methods. Elemental analysis was performed with a Perkin-Elmer 240 analyzer. IR spectra (4000–400 cm⁻¹), as KBr pellets, were recorded on a Nicolet FT-IR 170 SX spectrophotometer. The mass spectra were obtained on a Micromass GCT-MS Spectrometer (EI source). Proton nuclear magnetic resonance (¹H NMR) was performed on a Bruker 500 spectrometer with TMS as internal standard.

2.2 Optical measurements

All the solvents used for absorption and fluorescence measurements were HPLC grade. For diluted solutions of c = 4.0 $\times 10^{-5}$ M, in quartz cuvettes of 1 cm path length, one-photon absorption (OPA) spectra were recorded on a UV-265 spectrometer. One-photon excited fluorescence (OPEF) spectra were recorded on a PerkinElmer LS55 fluorescence spectrometer equipped with a 450 W Xe lamp. The concentrations are 1.0×10^{-6} mol/L. The fluorescence lifetime measurements of the compounds in DMF were performed on the Edinburgh FLS920 spectrofluorometer with a Hydrogen flash lamp (pulse duration < 1 ns) as the excitation source. Two-photon emission fluorescence (TPEF) spectra were measured using a streak camera (C5680-01, Hamamatsu) and imaging spectrograph (C5094, Hamamatsu). The pump laser beam came from a mode-locked Ti: sapphire laser system operating from 710 to 790 nm, pulse duration 200 fs, repetition rate of 76 MHz (Coherent Mira900-D).

2.3 X-ray crystallography

In the determination of the structure of the single crystal, X-ray intensities were recorded by a Bruker SMART CCD area detector diffractometer equipped with MoK α radiation using φ - ω scan mode. The structure was solved by direct methods with SHELXS-97 and refined with SHEXLX-97²⁰. All the non-hydrogen atoms were refined by full-matrix techniques with anisotropic displacement parameters. The hydrogen atoms were geometrically fixed at calculated positions attached to their parent atoms, and treated as riding atoms. Additional crystallographic details and complete listings of the compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications with reference number 227584 for L₂ and 227582 for L₃.

2.4 Preparations and characterization

In this research, all the bis-vinylpyridine compounds were synthesized by one-step solid-state reactions (see Scheme 1). The mixture of biphenyl bisphosphonates (1 mmol, 0.364 g), pyridine carboxaldehyde (3 mmol, 0.32 g) and excess potassium *t*-butoxide were manually milled for 10 min at room temperature. The reaction mixture was poured into water and filtered. The precipitates were washed with water to give the yellow product in a quantitative yield. Through the one-step solid-state reactions, the target compounds were isolated as pure with trans-configuration.

Compound L_1

Yield: 90%. Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.58; H, 5.53; N, 7.89. IR (KBr, cm⁻¹) selected bands: 3049 (m), 1435 (m). ¹H NMR (CDCl₃), δ (ppm): 8.59 (d, *J*=4.25 Hz, 2H), 7.77–7.82 (m, 10H), 7.73 (d, *J*=16.10 Hz, 2H), 7.58 (d, *J*=7.78 Hz, 2H), 7.39 (d, *J* = 16.07 Hz, 2H), 7.26–7.28 (m, 2H). ESIMS, *m/z* (%): 361.3 ([M+H]⁺, 100). mp 298.8 °C.

Compound L_2

Yield: 92%. Anal. Calcd. for C₂₆H₂₀N₂: C, 86.64; H, 5.59; N,



Scheme 1 The synthesis of the three TPA chromophores.

7.77. Found: C, 86.71; H, 5.50; N, 7.79. IR (KBr, cm⁻¹) selected bands: 3014 (m), 1566 (m). ¹H NMR (CDCl₃), δ (ppm): 8.81 (s, 2H), 8.46 (d, *J*=4.4 Hz, 2H), 8.10 (d, *J*=7.9 Hz, 2H), 7.79 (d, *J*=8.2 Hz, 4H), 7.73 (d, *J*=8.3 Hz, 4H), 7.47 (d, *J*=16.5 Hz, 2 H), 7.41–7.43 (m, 2 H), 7.36 (d, *J*= 16.6 Hz, 2 H). ESIMS, *m/z* (%): 361.3 ([M+H]⁺, 100). mp 305.8 °C.

Compound L₃

Yield: 92%. Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.55; H, 5.63; N, 7.82. IR (KBr, cm⁻¹) selected bands: 3023 (m), 1506 (m). ¹H NMR (CDCl₃), δ (ppm): 8.57 (d, J = 4.7 Hz, 4H), 7.59–7.83 (m, 12H) 7.23–7.36 (m, 4H). ESIMS, m/z (%): 361.3 ([M+H]⁺, 100). mp 312.5 °C.

3 Results and discussion

3.1 Synthesis

 L_1 has been synthesized using diazonium and 2-vinylpyridine by Ganushchak *et al.* [21]. The process is much more complicated and the yield is not high (33%–70%) while L_3 was obtained through Heck reaction with diiodobiphenyl and vinylpyridine which gave the product by 30% yield [22–24]. However, the compounds were synthesized through onestep solid-state reactions and gave quantitative yields.

3.2 Crystallographic studies

The crystal structures of L_2 and L_3 are shown in Figures 1

Table 1Crystallographic data for L_2 and L_3

and 2, respectively. The crystallography data were listed in Tables 1 and S1, respectively. From the figures, it can be seen that the two molecules adopted the same arrangements to form the central symmetrical species. In each molecule, the central benzene ring and the terminal pyridinium are nearly coplanar with the dihedral angle of 7.8°. The bond lengths of the benzene and pyridinium rings are all of aromatic character. The linkage bond lengths between the benzene rings and the pyridinium units are quite conjugated, for example, C2–C6 (1.464 Å), C6=C7 (1.316 Å) and C7–C8 (1.465 Å). The structural features suggest that all nonhydrogen atoms are highly conjugated and nearly coplanar, which will favour the electronic delocalization in the molecules.

3.3 One-photon absorption (OPA) and one-photon excited fluorescence (OPEF)

One-photon absorption and emission parameters, fluorescence lifetimes for all the compounds have been summarized in Table 2. It can be seen that the linear spectra confirm that all the compounds are only marginally solvatochromic, both in absorption and emission (5 nm excursions in a wide



Figure 2 ORTEP diagram with the atomic numbering scheme of L_3 . Thermal ellipsoids are shown at the 50% probability level.

Formula	$C_{26}H_{20}N_2$	$C_{26}H_{20}N_2$	
Formula weight	360.44	360.44	
Crystal system	monoclinic	monoclinic	
Space group	$P2_{1}/c$	$P2_{1}/c$	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.11(22), 5.562(9), 12.92(2)	12.898(6), 5.714(3), 12.723(6)	
<i>a</i> , <i>β</i> , γ (°)	90.00, 93.25(3), 90.00	90.00, 92.486(8), 90.00	
V [Å ³]	940(3)	936.8(7)	
Ζ	2	2	
D (calc) (g/cm ³)	1.273	1.278	
F(000)	380	380	
Crystal size (mm)	$0.32 \times 0.17 \times 0.13$	$0.43 \times 0.31 \times 0.07$	
Temperature (K)	293(2)	293(2)	
Radiation (Å) MoK α	0.71073	0.71073	
$\theta_{\min-\max}(^{\mathrm{o}})$	2.0, 28.57	1.58, 25.02	
Data set	-19: 20; -18: 20; -21: 20	-15: 12; -6: 6; -15: 15	
Observed data [$I > 2.0 \sigma(I)$]	1652	1661	
$N_{ m ref},N_{ m par}$	3694, 543	4679, 673	
R, wR_2, S	0.0510, 0.0889, 0.716	0.0580, 0.1419, 0.857	

Compound	Solvent	$\lambda_{\max} (nm)^{a)}$	$\lambda_{\max} (nm)^{b)}$	$\lambda_{\max} (nm)^{c}$	$arPsi^{ m d)}$	τ (ns) ^{e)}
L_1	CHCl ₃	347	404, 424			
	CH ₃ CN	348	401, 419			
	Ethanol	347	423			
	DMF	354	423	442, 487	0.90	0.84
L_2	CHCl ₃	348	404, 423			
	CH ₃ CN	349	420			
	ethanol	347	427			
	DMF	353	426	434, 483	0.94	0.86
L_3	CHCl ₃	354	399, 420			
	CH ₃ CN	351	395, 415			
	ethanol	352	399, 418			
	DMF	357	421	440, 488	0.95	0.81

Table 2 One-photon absorption and emission parameters, fluorescence lifetimes for L_1-L_3

a) Absorption peak position in nm $(1 \times 10^{-5} \text{ mol/L})$; b) OPEF peak position in nm; c) TPEF peak position in nm; d) quantum yields determined by using naphthalene as the standard; e) OPEF lifetime.

range of solvents polarities). For the chromophores are centrosymmetry, only weak solvatochromism is to be expected. The optical properties of the three compounds are very similar. The quantum yields (ϕ) (see in supporting information) of L_1 to L_3 in different solvents were determined by using naphthalene as standard. From Table 2, the chromophores obtained possess high quantum yields, and long fluorescence life time with the sequence of $L_2 > L_1 > L_3$, the lifetimes of which in DMF were longer than previous work [25]. Meanwhile, they also had similar trend by comparison with previous pyridine derivatives [26]. One-photon absorption spectra of L_2 in four solvents with different polarity are shown in Figure S4. It can be seen that the absorption maxima show little differences with the increasing solvent polarity. In Figure 3 (left), the three curves show that the absorption maxima at 347 nm for L_1 (with the corresponding mole absorption coefficient $\varepsilon = 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 348 nm for L_2 (ε = 3.0 × 10⁴ M⁻¹ cm⁻¹), and 354 nm for L_3 (ε = 5.3×10^4 M⁻¹ cm⁻¹) are assigned as the π - π * transition of



Figure 3 Linear absorption and one-photon fluorescence spectra of $L_1\text{--}L_3$ in CHCl_3.

the whole molecule. The OPA peak position of L_3 show ca. 5-nm red shift compared to those of L_1 and L_2 in all the solvents, resulting from the higher electron-accepting ability of the 4-pyridyl moiety.

The one-photon fluorescence spectra of L_1 in four organic solvents are shown in Figure S5. As shown in Figure S5 (or see the emission maxima in Table 2), two bands were clearly seen when the three compounds were in the solvents with low polarity. But with the increasing of the solvent polarity, each L tends to show one emission peak. In fact, there exists a single emission of each compound, whereas the vibronic structure changes somewhat from solvent to solvent. The emission spectra of all the compounds in chloroform were also given in Figure 3 (right). In accordance with OPA, the OPEF intensities of the three compounds also exhibit the sequence of $L_3 > L_1 > L_2$.

3.4 Two-photon excited fluorescence (TPEF) and TPA cross-section

The two-photon fluorescence spectra of compounds in DMF with $c = 1.0 \times 10^{-3}$ mol/L are shown in Figure 4. As mentioned above, no linear absorption occurs in the spectral range from 450 to 1000 nm, and the emission exited by 710 nm laser wavelength can be attributed to the TPEF mechanism. By tuning the pump wavelengths incrementally from 710 to 790 nm, keeping the input power fixed, and then recording the TPEF intensity, the two-photon emission spectra of L₁–L₃ were shown in Figure 4 (the excitation wavelength is 710 nm). The spectra of the TPA cross-sections of L₁–L₃ were obtained with the excitation wavelength ranging from 710 to 790 nm, as shown in Figure 5.

The TPA cross-section σ was obtained by comparing the TPEF intensity of the sample with that of the reference compound by the following equation [27],



Figure 4 The two-photon emission fluorescence spectra of L_1-L_3 in DMF ($c = 1.0 \times 10^{-3}$ M, the excitation wavelength is at 720 nm).



Figure 5 The spectra of the two-photon absorption cross-sections of L_1-L_3 (from a 200 fs, 76 MHz Ti:sapphire laser) in DMF vs. excitation wavelengths ranging from 710 to 790 nm.

$$\sigma = \sigma_r F \Phi_r c_r n_r / F_r \Phi c n \tag{1}$$

where the subscript r denotes the reference compound and Fstands for the integral intensity of TPEF peak, Φ is the OPEF quantum yield, *n* is the refractive index of solution, and c is the concentration of solution in mol/L. The experimental errors are estimated to be $\pm 15\%$ from the variations of laser energies and sample concentrations. From Figures 4, 5 and Table 2, it can be seen that the curves of two-photon emission fluorescence (in DMF) and OPEF (in solvent with low polarity) are similar. They both exhibit two peaks and the intensities also follow the sequence of $L_3 > L_1 > L_2$. The TPEF maxima of L_3 and L_1 are red-shifted relative to that of L₂, caused by the weeker electron-accepting ability of 3-pyridyl group. The peak positions around 430 and 480 nm for the three compounds show a 30-nm red shift compared to the OPEF maxima in the same solvent, which can be explained by the effect of re-absorption [28, 29]. As shown in Figure 5, the peak at 730 nm in each spectrum did not correspond to the maxima of the TPA band. It is just a shoulder of a much more intense TP transition placed below 710 nm that, quite unfortunately, is not accessible with our experimental set up. At the excitation wavelength of 710 nm, the σ_{max} values are 106, 98 and 55 GM for L₃, L₁ and L₂, which are smaller than those of other A- π -A chromophores with similar structures [28]. But in this case, these chromophores are much easily prepared in high yield. The intensities of the TPEF spectra and the σ_{max} values show obvious tendency of L₃ > L₁ > L₂, which corresponds to the order in the electron-accepting ability of the terminal groups (— $\langle - \rangle$ >

3.5 Theoretical calculation

In terms of sum-over-state formula, the two-photon matrix element for the two-photon resonant absorption of identical energy is written as [29]

$$S_{\alpha\beta} = \sum_{j} \left[\frac{\langle 0 | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | f \rangle}{\omega_{j} - \omega_{f} / 2} + \frac{\langle 0 | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | f \rangle}{\omega_{j} - \omega_{f} / 2} \right] \quad (2)$$

where $|0\rangle$ and $|f\rangle$ denote the ground state and the final state, respectively. $|j\rangle$ means all the intermediate states, including the ground state. ω_j is the excitation energy of the excited states and μ is the electronic dipole moment. In general, the total TPA probability requires the information of all the excited states that is uneasy to be obtained clearly. On the other hand, a few-state model can often provide satisfying results for TPA cross-section in a visible region [9, 30–32]. The TPA cross-section is given by orientational averaging over the two-photon absorption probability [27].

$$\delta_{lpa} = \sum_{\alpha\beta} \left[F \times S_{\alpha\alpha} S_{\beta\beta}^* + G \times S_{\alpha\beta} S_{\alpha\beta}^* + H \times S_{\alpha\beta} S_{\beta\alpha}^* \right]$$
(3)

where the coefficients *F*, *G* and *H* are related to the incident radiation. For the linearly polarized light, *F*, *G* and *H* are 2, 2 and 2, but for the circular case, they are -2, 3 and 3, respectively. In the present work, we only consider the results with the linearly polarized laser beam. The summation goes over the molecular axe α , $\beta = \{x, y, z\}$.

The TPA cross-section directly comparable with experimental measurements is defined as [28]

$$\sigma_{ip} = \frac{4\pi^2 a_0^5 \alpha}{15c_0} \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{ip}$$
(4)

Here a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, ω is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile, here it is assumed to be a δ -function. Γ_f is the lifetime broadening of the final state, which is assumed to be 0.1 eV.

We utilized the Gaussian-98 program package to optimize the molecular geometrical structure with the hybrid density functional theory (DFT/B3LYP) and a basis set 6-31G. The few-state model is used to study the TPA cross-section of the molecules [17, 29]. The calculated largest TPA cross-sections of the three molecules are 17.3, 6.9 and 32 GM, respectively. All the calculated σ_{max} values are much smaller than the experimental ones. The reason is that here we only consider the electronic contribution to the TPA process. The vibronic contributions also can play an important role. Obviously, the calculations follow the sequence of $L_3 > L_1 > L_2$, which corresponds to the order in the experimental results, caused by the different electron-accepting abilities of the terminal groups ($-\sqrt{N} > -\sqrt{N}$). So it was concluded from these data that the compounds L_1 - L_3 indeed combine moderate TPA cross-sections and high fluorescence quantum yields.

4 Conclusions and outlooks

In summary, three compounds with two-photon absorption activity were synthesized by the one-step solid-state reactions with facile operations in quantitative yields. Their photophysical properties were systematically studied both experimentally and theoretically. Indeed, no noticeable solvatochromism was observed for all the compounds in either OPA or OPEF spectra. Interestingly, the position of the nitrogen atom from pyridine has influence on the molecular two-photon absorption across-sections action. The three compounds were proven to achieve moderate TPA and high fluorescence quantum yields. These results can facilitate the work on facile synthesis for functional compounds, and design of more quadrupolar chromophores for that solvatochromism is not desirable. Furthermore, this kind of chromophores were proven to be potential compounds through pyridyl groups coordinating to metal ions for constructing metal complexes with TPA activity [22].

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