

Synthesis, structure and two-photon absorption properties of a new multi-branched compound, 1,2,4,5-tetrakis(4-pyridylvinyl)benzene

Lei Wang, Xu-Tang Tao*, Jia-Xiang Yang, Wen-Tao Yu, Yan Ren, Qian Xin, Zhi Liu, Min-Hua Jiang

State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Shanda Nan Road, Jinan City, Shandong Province 250100, PR China

Received 8 July 2004; received in revised form 31 August 2004; accepted 31 August 2004

Abstract

A conjugated and symmetric multi-branched compound, 1,2,4,5-tetrakis(4-pyridylvinyl)benzene (TKPVB), has been synthesized and the crystal structures of TKPVB and its intermediate, 1,2,4,5-tetrakis(dimethoxyphosphorylmethyl)benzene, were determined by diffraction method. TKPVB with four units of 4-vinylpyridine moieties attached to the central benzene core presents an A- π -A general framework, where A is a π -deficient pyridine ring. The single-photon and two-photon absorption and fluorescence properties in different solvents of varying polarity have been investigated. It is also found that the one- and two-photon-induced fluorescence spectra are quite similar, which indicate that the one- and two-photon allowed-excited states are the same.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Two-photon absorption; Multi-branched compound; 1,2,4,5-tetrakis(4-pyridylvinyl)benzene; Single-crystal X-ray crystallography

1. Introduction

The first theoretical prediction of simultaneous two-photon absorption was made by Göppert-Mayer in 1931 [1], and experimentally observed in the 1960s [2]. Organic materials with large two-photon absorption cross-sections are currently under considerable investigation for applications such as 3D microfabrication [3], two-photon upconversion lasing [4,5], optical power limiting [6], two-photon fluorescence microscopy [7], and three-dimensional optical data storage [8]. However, the early development of TPA-based application was limited because the available materials had relatively small two-photon cross-section.

To expand the utility of two-photon absorption materials, it is necessary to further increase their two-photon absorption cross section either by increasing the

conjugation length of the molecule, increasing the extent of intramolecular charge transfer or by increasing the chromophore number density without causing aggregation. The research of Chung et al. [9] shows that there is strong cooperative enhancement of two-photon absorption in multi-branched structure. This conclusion was verified by Macak [10] that not only electron coupling between different branches but vibrant contributions play an important role in multi-branched structures. Further research was conducted by Drobizhev et al. [11] and for the first time, they present unambiguous spectroscopic evident of strong cooperative enhancement of two-photon absorption in a series of dendrimers. Our group has also devoted to develop chromophores with multi-branched structures and conjugation patterns [12,13]. Here, we report in detail the synthesis, crystal structure and single- and two-photon-related photophysical properties of a new multi-branched compound and supply the experimental evident for the relationship between the structure and properties.

*Corresponding author. Fax: +86-531-857-4135.
E-mail address: txt@icm.sdu.edu.cn (X.-T. Tao).

2. Experimental section

2.1. Chemicals

1,2,4,5-Tetrakis(bromomethyl)benzene (95%) and 4-pyridinecarboxaldehyde (98%) were products of Acros Organics. Trimethyl phosphite was AR grade. The above chemicals were used without further purification. Potassium *tert*-butoxide, which contained ca. 30% *tert*-butoxide alcohol, was prepared immediately before use.

Photoluminescence and absorption measurements were conducted in various solvents including toluene, chloroform, ethanol and *N,N*-dimethylformamide (DMF). All of the above solvents were anhydrous grade after further purification.

2.2. Instruments

Nuclear magnetic resonance spectra were obtained on Bruker Avance 600 spectrometer. The electrospray mass spectrum (ES-MS) was determined on an ABI 4000 mass spectrograph. The diluted solution was electro-sprayed with a needle voltage of +5.5 kV. The mobile phase was an aqueous solution of methanol (V/V, 1:1). Elemental analysis was performed using Vario.ELIII (German) elemental analyzer. Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer using a liquid-nitrogen-cooled detector. The samples were prepared as KBr pellets. The UV-visible-near-IR absorption spectra of dilute solutions were recorded on a TU-1800 SPC spectrophotometer using a quartz cuvette having 1-cm path length.

The one-photon fluorescence spectra were obtained on an Edinburgh FLS920 spectrofluorimeter equipped with a 450-W Xe lamp and a time-correlated single-photon counting card. The fluorescence lifetime measurement of TKPVB in different solvents was performed on the same spectrofluorimeter with a Hydrogen flash lamp (pulse duration < 1 ns) as the excitation source. Reconvolution fits of the decay profiles were made with F900 analysis software to obtain the lifetime values. The fluorescence quantum yields Φ was determined by the literature method using rhodamine B, which has the same concentration with the other samples as the reference [14].

In our two-photon excited fluorescence experiment, the laser beam from a mode-locked Ti:sapphire laser (Coherent Mira 900 F) is the pump source with a pulse duration of 200 fs, a repetition rate of 76 MHz, and a single-scan streak camera (Hamamatsu Model C5680-01) together with a monochromator as the recorder. The data was recorded in the excitation wavelength range of 710–900 nm with a step size of 5 nm. As shown in Fig. 7, TKPVB with the concentration of 5×10^{-4} M in DMF was excited at 710 nm.

The two-photon absorption cross-section of TKPVB has been measured with the two-photon-induced fluorescence method by using femtosecond Ti:sapphire laser pulses as described before [15]. The sample was dissolved in DMF at a concentration of 5×10^{-4} M and the two-photon-induced fluorescence intensity was measured. Fluorescein in water at pH = 11 was selected as a reference materials [16]. At the excitation wavelength of 720 and 700 nm, the TPA cross-section of fluorescein is 19 GM [16,17]. The TPA cross-section was calculated using Eq. (1) (see Section 3).

2.3. Synthesis

2.3.1. 1,2,4,5-tetrakis(dimethoxyphosphorylmethyl)benzene (tdmpmb)

A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (3.0 g, 6.7 mmol) and $P(OCH_3)_3$ (10 ml) was refluxed for 12 h. The excess $P(OCH_3)_3$ was distilled out. The residual solid was purified by crystallization in dichloromethane to give colorless crystal of TDMPMB (3.45 g, 6.0 mmol, 91%). m.p. (183–185 °C). 1H NMR (600 MHz, $CDCl_3$, TMS): $\delta_H = 3.3$ – 3.4 (*d*, $J = 19.8$ Hz, 8H), 3.65–3.69 (*q*, 24H), 7.18 ppm (*s*, 2H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 134.002, 129.606, 52.298, 29.4685. Element analysis calcd (%) for $C_{18}H_{34}O_{12}P_4$: C 38.17, H 6.05; found: C 37.85; H 5.913.

2.3.2. 1,2,4,5-tetrakis(4-pyridylvinyl)benzene (tkpvb)

1,2,4,5-Tetrakis(dimethyl phosphonate)benzene (2.0 mmol), 4-pyridinecarboxaldehyde (8.0 mmol) and potassium *tert*-butoxide (9.6 mmol) were ground by hand in a dried mortar. The color change and the thermal releasing of the reactants indicate the occurrence of the reaction. The reaction was stopped until the reactant in the mortar became yellow. The solid was purified by crystallization in chloroform and isopropanol to give pale yellow crystals of TKPVB (0.34 g, 34.6%). m.p. (327–330 °C decomposition). ES-MS, *m/z* (%): 491.5 ($[M^+]$, 100), 246.5 (31). 1H NMR (600 MHz, $CDCl_3$, TMS) $\delta_H = 1.21$ – 1.23 (*d*, $J = 6.012$, 6H), 1.63223 (*br*), 4.02–4.05 (*t*, 1H), 7.04–7.08 (*d*, $J = 16.062$ Hz, 4H), 7.42–7.44 (*d*, $J = 4.806$ Hz, 8H), 7.64–7.67 (*d*, $J = 16.08$ Hz, 4H), 7.86 (*s*, 2H), 8.65–8.66 ppm (*d*, $J = 5.004$ Hz, 2H); ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm) 150.488, 144.081, 135.716, 130.160, 129.809, 125.908, 120.980, 64.9, 25.375. IR(KBr): $\bar{\nu} = 3045.101$ (m), 3027.08 (m), 1596.11 (m), 1549.93 (m), 1498.29 (m), 1416.71 (m), 958.46 (s) cm^{-1} . Element analysis calcd (%) for $C_{34}H_{26}N_4 \cdots C_3H_8O \cdots H_2O$: C 78.14, H 6.38, N 9.85; found: C 78.48, H 5.868, N 9.913.

2.4. Structure determination

A colorless prism (0.40 mm \times 0.32 mm \times 0.23 mm) of TDMPMB and a yellow plate (0.31 mm \times

Table 1
Crystal data, diffraction data and refinement data of TDMPMB and TKPVB

Compound	TDMPMB	TKPVB
Formula	C ₁₈ H ₃₄ O ₁₂ P ₄	C ₃₄ H ₂₆ N ₄ · C ₃ H ₈ O
Formula weight	566.33	550.68
Crystal system	Monoclinic (no.14)	Triclinic
Space group	P21/c	P-1
a/Å	12.368(2)	9.555(2)
b/Å	20.224(2)	12.604(3)
c/Å	16.027(3)	14.076(3)
α/°	90	78.851(13)
β/°	95.568	70.786(14)
γ/°	90	77.657(19)
Crystal size (mm)	0.40 × 0.32 × 0.23	0.31 × 0.20 × 0.09
D _c (g cm ⁻³)	1.414	1.180
2θ _{max} (deg)	50	50
Cell volume/Å ³	3989.9(10)	1550.0(6)
Final R indices (I > 2σ(I))	R ^a = 0.0626, wR ^b = 0.1609	R ^a = 0.0967, wR ^b = 0.2139
Z	6	2
Absorption coefficient	0.34 mm ⁻¹	0.072 mm ⁻¹
Measured reflections	8558	6516
Independent reflections	7016	5446
Residual electron density (e Å ⁻³)	0.494; -0.319	0.252; -0.182

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega|F_o|^2]^{1/2}.$$

0.20 mm × 0.09 mm) of TKPVB was mounted on a Bruker P4 four-circle diffractometer with a graphite monochromator using MoK α radiation at 293(2) K, respectively and used for measurements of precise cell constants and intensity data collection (Tables 1–3, Figs. 1–4). The structures were solved by direct methods (SHELXS-97) and completed by full-matrix least-squares techniques on F² (SHELXS-97). A total of 8558 reflections of TDMPMB were collected at room temperature (ω scan method, 2 θ range, 3.88–50°). Of the unique 7016 reflections, only 3682 were observed. For TKPVB, there were 6516 reflections collected (ω scan method, 2 θ range, 2.24–50°). Of the unique 5446 reflections, only 1299 were observed. The absorption corrections by psi scans were applied to the intensity data. Hydrogen atoms were located and refined isotropically.

3. Results and discussion

As outlined in Scheme 1, a new compound 1,2,4,5-tetrakis(4-pyridylvinyl)benzene (TKPVB) was synthesized by the solvent-free Wittig–Horner reaction from phosphonate and 4-pyridinecarboxaldehyde (Scheme 1) exothermally in a dry mortar. The heat generated and the energy supplied by grinding drive the reaction to

Table 2
The selected bond length (Å) and bond angle (°) of TDMPMB and TKPVB

TDMPMB	TKPVB
C1–C7	1.470(8)
C2–C10	1.306(7)
C4–C13	1.439(8)
C5–C16	1.485(10)
C7–P1	1.316(9)
C10–P2	1.497(11)
C13–P3	1.63(3)
C16–P4	1.24(4)
O1–P1	1.49(3)
O2–P1	1.480(9)
O3–P1	1.324(9)
O4–P2	1.461(9)
O5–P2	128.6(7)
O6–P2	126.9(7)
O7–P3	124.7(8)
O8–P3	128.5(9)
O9–P3	127.4(8)
O10–P4	127.7(8)
O11–P4	
O12–P4	
C8–O1	
C9–O2	
C11–O4	
C12–O5	
O11–C17	
O10–C18	
O7–C14	
O8–C15	
C2–C1–C7	
C6–C1–C7	
C1–C7–P1	
C8–O1–P1	
C1–C2–C10	
C3–C2–C10	
C2–C10–P2	
C12–O5–P2	

completion within a few minutes. Compared with liquid-state reaction, the solid-state reaction is facile and has no environmental contamination.

3.1. Structural studies

The crystal structures of 1 and 2 were determined by single crystal X-ray diffraction and are shown in Fig. 1 and Fig. 3, respectively. As shown in Fig. 1, the asymmetric unit contains two independent molecules, which are chemically identical in composition but have a little difference in structure. Each molecule has a benzene ring to which four dimethoxyphosphorylmethyl groups are connected via C–C bonds on 1, 2, 4, 5 position. On 1, 2 positions, the C atoms of dimethoxy are disordered over the two positions with roughly equal populations. While in the other molecule, the O and C

Table 3
Hydrogen-bonding geometry (Å,°)

D–H...A	D–H	H...A	D...A	D–H...A
<i>TDMPMB</i>				
C(3)–H(3A)...O(3)	0.93	2.39	3.2697	157
C(6)–H(6A)...O(18)	0.93	2.52	3.3789	154
C(7)–H(7A)...O(6)	0.97	2.42	3.2446	143
C(7)–H(7B)...O(17)	0.97	2.50	3.2910	139
C(9)–H(9A)...O(5)	0.96	2.59	3.4520	150
C(12)–H(12C)...O(3)	0.96	2.60	3.5447	170
C(13)–H(13B)...O(12)	0.97	2.43	3.2885	147
C(14')–H(14F)...O(8)	0.96	2.52	2.8610	101
C(19)–H(19A)...O(9)	0.93	2.48	3.3428	154
C(22)–H(22A)...O(14)	0.97	2.44	3.2445	140
C(22)–H(22B)...O(1)	0.97	2.50	3.3656	149
<i>TKPVB</i>				
O(1)–H(1F)...N(4)	0.82	2.25	2.9023	137
C(2)–H(2A)...N(2)	0.93	2.61	3.4312	147

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1/2+y, 1/2-z$; (iii) $-x, 1-y, -z$.

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, y, -1+z$.

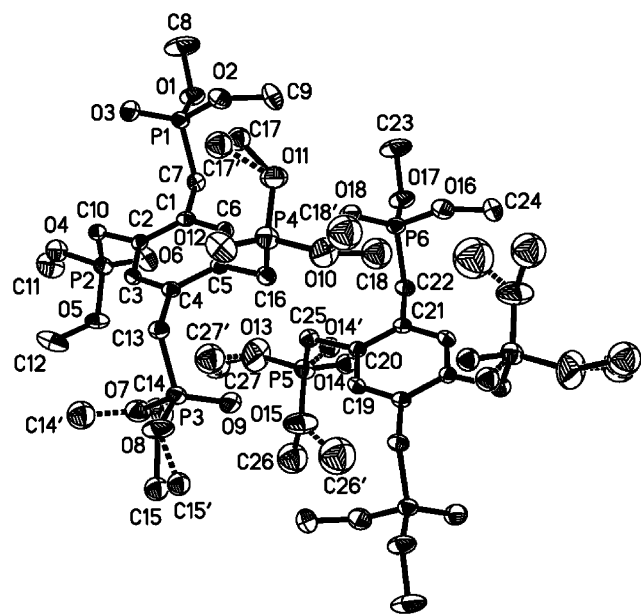


Fig. 1. Molecular structure of TDMPMB. Hydrogen atoms have been omitted for clarity.

atoms of the dimethylphosphite groups are disordered on 2, 5 position.

Except the C atoms of dimethoxy, both benzene ring and C atoms are coplanar (valence angles = 360° , 359.8° , 360° and 360° , respectively) [18]. The PO(OMe)₂ substituents are above and below the benzene plane.

Both angles and distance of the dimethyl phosphite group are typical. The dimethyl phosphite group P(2) has mean P–O distance and P–O–C angles of $1.567(3)$ Å

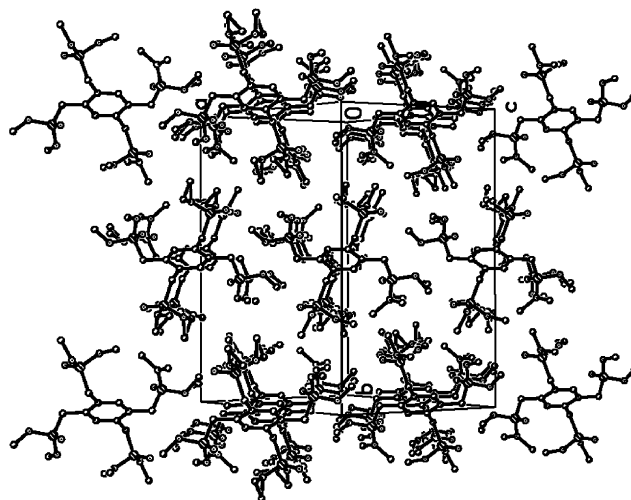


Fig. 2. Stereoscopic packing diagram of TDMPMB. The view is approximately down z . Hydrogen atoms have been omitted for clarity.

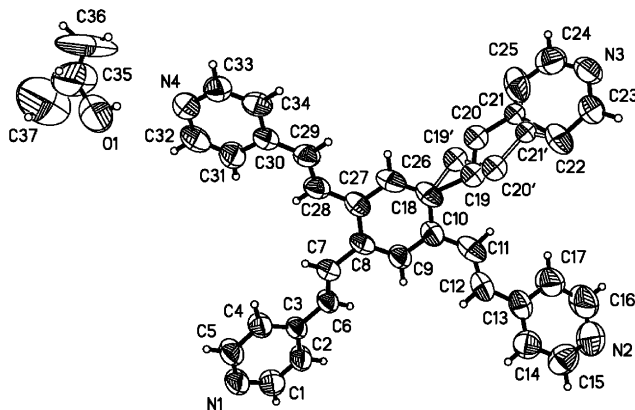


Fig. 3. Molecular structure of TKPVB. Hydrogen atoms have been omitted for clarity.

and $121.15(4)^\circ$, respectively, which is similar to the mean values for the same distance and angles in *p*-MeOC₆H₄TeBr₂ [S₂P(OMe)₂] of $1.567(8)$ Å and $121.2(5)^\circ$, respectively [19]. The short P–O bond length of $1.567(3)$ Å implies a considerable amount of double-bond character. This is probably due to overlap of *p*-orbitals of the oxygen with *d*-orbitals on phosphorous, as proposed by Husebye [20,21]. As expected the P=O distance [$1.451(3)$ Å] is much shorter than the P–O(Me) distance [$1.567(3)$ Å].

The unit cell of 1,2,4,5-tetrakis(dimethoxyphosphorylmethyl)benzene consists of six molecules, as can be seen from Fig. 2. The hydrogen bonding also plays an important role in the crystal packing (Table 3).

From Fig. 3 we can see that there is isopropanol molecule co-crystallized in the crystal of TKPVB. The benzene ring and the pyridine rings in the crystal of TKPVB are all of aromatic character. The dihedral angle between the benzene ring and four adjacent

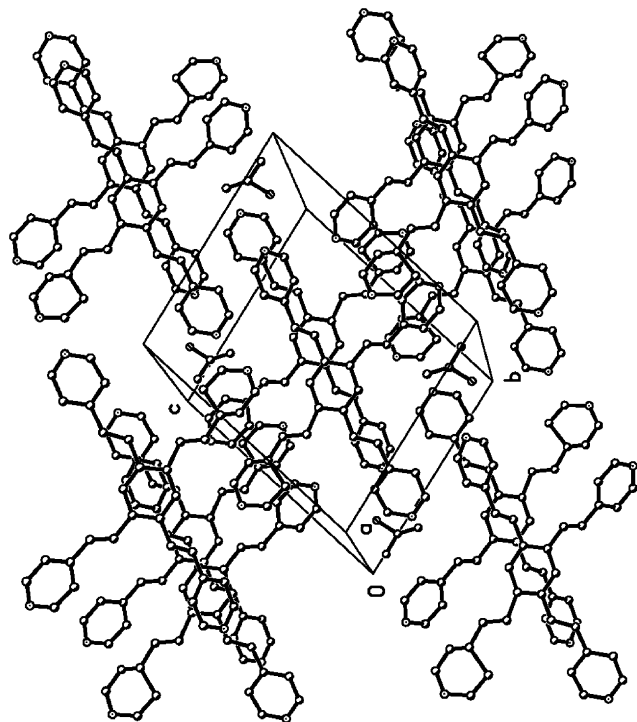
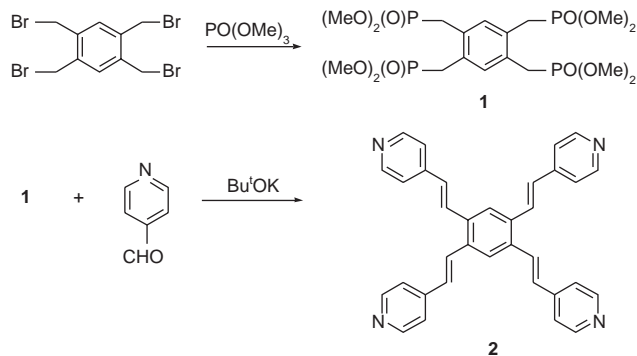


Fig. 4. Packing diagram of TKPVB.



Scheme 1.

pyridine ring is only 23.9° , 24.8° , 31.2° , 38.7° , respectively. One of the bridge bond of C3–C6=C7–C8 between the benzene ring and the pyridine ring are highly conjugated with bond length of $1.439(8)\text{Å}$ (C3–C6), $1.306(7)\text{Å}$ (C6=C7), $1.470(8)\text{Å}$ (C7–C8). These suggest that all nonhydrogen atoms are quite conjugated. At each end of the branch, the pyridine ring and its neighboring carbon atoms are perfectly coplanar with the sum of the three C–C–C angles (360°). In addition, the quasi-planar and conjugated configuration of entire molecule which allows direct interbranch conjugation throughout the molecule reveal that TKPVB has a highly delocalized π -electron system. This structural characteristic is a necessary condition for two-photon absorption. From Fig. 4, we can see that all

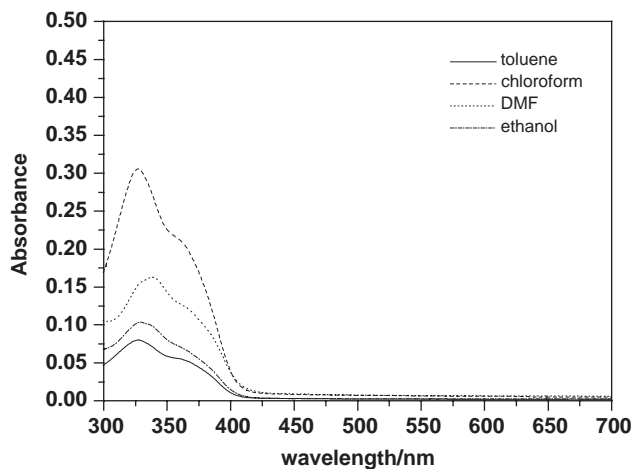
molecules in crystals of TKPVB are packed in a parallel manner. The distance between the different molecules was 3.57 and 4.36Å , respectively, which means there is offset π - π interaction between the quasi-plane of different molecules.

3.2. Spectrum discussion

In the ^1H NMR spectrum of TKPVB, the relative peak heights and splitting patterns are entirely consistent with the stoichiometry of the groups attached to the central benzene ring. The C_6H_2 ring protons are seen as a singlet, corresponding to 2H , centered at 7.858ppm . The double bond protons are seen as a pair of doubles, each of intensity corresponding to 4H , centered at 7.64 – 7.67 and 7.04 – 7.08ppm with $J=16.08$ and 16.062Hz , respectively. The pyridine ring protons are also seen as a pair of doubles, each of intensity corresponding to 8H , centered at 8.65 – 8.66 and 7.42 – 7.44ppm with $J=5.004$ and 4.806Hz , respectively. ^{13}C NMR spectra is corresponding to ^1H NMR. In the ^1H NMR spectrum of TDMPMB, the C_6H_2 ring protons centered at 7.18ppm . We attribute the signals at $\delta = 3.3$ – 3.4ppm ($J = 19.8\text{Hz}$) to the methylene protons. Both the ^1H - and ^{13}C NMR spectra confirm the presence of four distinct $\text{P}(\text{O})(\text{OCH}_3)_2$ groups in the molecule. The IR spectra of TKPVB show $\nu(\text{C}=\text{C})$ absorption at 1596.11cm^{-1} and the absorption of benzene ring and pyridine ring at 3045.10 and 3027.08cm^{-1} .

3.3. Linear absorption

Fig. 5 is the UV-visible absorption spectra of TKPVB in different solutions. It shows that there is one strong absorption band attributed to the solute molecules. In addition, absorption spectra of compound 2 show small

Fig. 5. Linear absorption spectra of compound 2 in different solvents at a concentration of $5 \times 10^{-6}\text{mol L}^{-1}$.

solvatochromism. A slight red shift is observed in low polar solvents ($\lambda_{\max} = 328$ nm in toluene), while the absorption peaks are found to be blue shifted in high polar solvent ($\lambda_{\max} = 327$ nm in ethyl acetate). But the shift of λ_{\max} is very limited.

3.4. Single-photon fluorescence

The single-photon related photophysical properties are summarized in Table 4. The fluorescence spectra of TKPVB in different solvents are displayed in Fig. 6. It is observed that none of these spectra have multiple peaks, which indicates that the fluorescence photon is emitted from the lowest excited state [22]. In contrast to the absorption spectra, the fluorescence spectra exhibit bigger bathochromic shifts with increasing the polarity of solvents. Such behavior which has been noted for other styrylbenzenes [23] is attributed to close interaction of π , π^* and charge transfer excited singlet states. Also, it can be explained by the twisted intramolecular charge transfer process [24]. The energy gap between the ground and excited electronic states is keenly dependent

Table 4
Single photon-related photophysical properties of TKPVB in different solutions

Solvents	λ_{\max}^a	λ_{\max}^b	Φ^c	τ^d
Toluene	328	432	0.11	4.94
Chloroform	327	430	0.07	5.46
Ethanol	330	436	0.29	2.40
DMF	338	446	0.27	4.22

^a λ_{\max} of the one-photon absorption spectra in nm.

^b λ_{\max} of the one-photon emission spectra in nm.

^cFluorescence quantum yield.

^dFluorescence lifetime in ns.

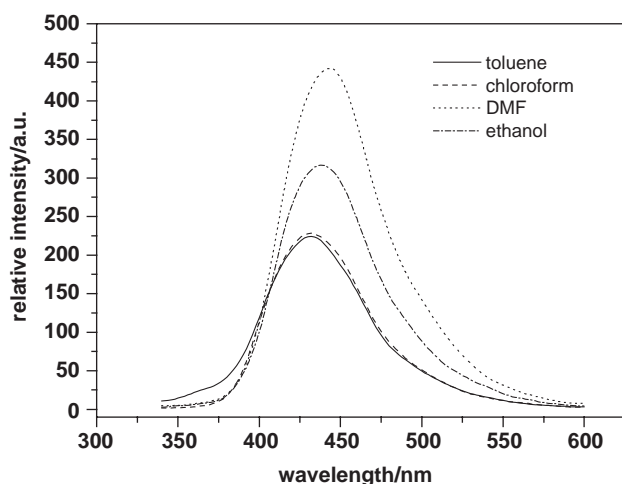


Fig. 6. Single-photon fluorescence spectra of compound 2 in different polarity solvents at a concentration of 5×10^{-6} mol L⁻¹ after one-photon excitation.

on the solvation energy. Increasing the polarity of the solvent will enhance dipole–dipole interactions between the solute and the solvent molecules and significantly decrease the energy level of the excited state.

Fluorescence quantum yield was measured by the literature method using rhodamine B as the reference [25]. The recovered quantum yield of TKPVB in various solvents is presented in Table 4. There is clearly a significant decrease in the quantum yield of TKPVB upon increasing the solvent polarity. The decrease in the quantum yield is primarily due to an increase in the nonradiative decay process [26].

3.5. Two-photon fluorescence spectra and two-photon cross section

Comparing Fig. 6 with Fig. 7, one interesting phenomenon can be observed that the two-photon-induced fluorescence spectra of TKPVB is quite similar to the single-photon-induced fluorescence spectra which indicates that although the electrons can be pumped to the different excited states by linear absorption or two-photon absorption due to the different selection rules, they would finally relax to the same lowest excited state via internal conversion and/or vibrational relaxation. Also, the emission spectra of one- and two-photon-induced fluorescence were observed to be overlapping on each other. This verified that the emission of TKPVB, one- or two-photon-induced, is from the same excited-state. From Fig. 7, we can see the two-photon fluorescence spectra are not centrosymmetric. This is because of the re-absorption of the sample solution due to the higher concentration (5×10^{-4} M).

The intensities of the two-photon induced fluorescence spectra of the reference and sample emitted at the same excitation wavelength were determined. The two-photon cross-section σ_s was calculated by using the

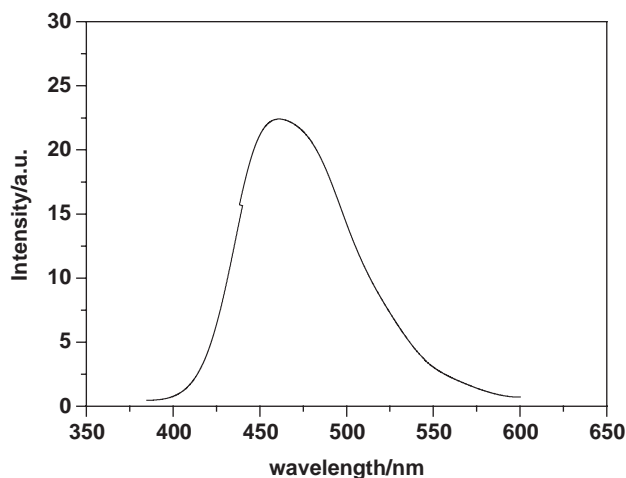


Fig. 7. Two-photon-induced fluorescence excitation spectra of 2 in DMF at a concentration of 5×10^{-4} M.

two-photon-induced fluorescence measurement technique with the following equation [15]:

$$\sigma_s = \sigma_r \frac{\Phi_r c_r n_r F_s}{\Phi c n F_r}, \quad (1)$$

where the subscripts s and r refer to the sample and the reference material, respectively. The terms c and n are the concentration and refractive index of the sample solution, respectively. Φ is the fluorescence quantum yield. F is two-photon excited fluorescence integral intensity. σ_r is the TPA cross-section of the reference molecule, where $\sigma_r = 19 \text{ GM}$. The obtained TPA cross section of TKPVB is 21.58 GM, where 1 GM (Göppert-Mayer) = $1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$.

4. Conclusion

A new multi-branched compound TKPVB was synthesized by solvent-free Wittig–Horner reaction. The method is facile and need not column chromatography. The crystal structures of TKPVB and its intermediate were described. The related single- and two-photon fluorescence properties of TKPVB in different solvents were characterized in detail. The new dye has a moderate two-photon cross-section of 21.58 GM attribute to the multi-branched structure and the conjugation of the whole network. But the relationship between structure and properties is need to make further investigation.

Acknowledgments

The authors gratefully acknowledge the financial support of the state National Natural Science Foundation of China (Grant No. 50323006, 50325311).

References

- [1] M. Göppert-Mayer, *Ann. Phys.* 9 (1931) 273.
- [2] P.M. Rentzepis, Y.H. Pao, *Appl. Phys. Lett.* 5 (1964) 156.
- [3] B. Smith, M. Straub, M. Gu, *Austr. Opt. Soc. News* 15 (2001) 12–13.
- [4] G.S. He, C.F. Zhao, J.D. Bhawalkar, P.N. Prasad, *Appl. Phys. Lett.* 67 (1995) 3703–3705.
- [5] C.F. Zhao, G.S. He, J.D. Bhawalkar, C.K. Park, P.N. Prasad, *Chem. Mater.* 7 (1995) 1979–1983.
- [6] G.S. He, J. Swiatkiewicz, Y. Jiang, P.N. Prasad, B.A. Reinhardt, L.S. Tan, R. Kannan, *J. Phys. Chem. A* 104 (2000) 4805–4810.
- [7] R.H. Köhler, J. Cao, W.R. Zipfel, W.W. Webb, M.R. Hansen, *Science* 276 (1997) 2039–2042.
- [8] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.Y.S. Lee, D. McCord-Maughon, J. Qin, H. Rckel, M. Rumi, X.-L. Wu, S.R. Marder, J.W. Perry, *Nature* 398 (1999) 51–54.
- [9] S.J. Chung, K.S. Kim, T.C. Lin, G.S. He, J. Swiatkiewicz, P.N. Prasad, *J. Phys. Chem. B* 103 (1999) 10741–10745.
- [10] P. Macak, Y. Luo, P. Norman, H. Agren, *J. Chem. Phys.* 113 (2000) 7055–7061.
- [11] M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo, C.W. Spangler, *J. Phys. Chem. B* 107 (2003) 7540–7543.
- [12] Y.X. Yan, X.T. Tao, Y.H. Sun, C.K. Wang, G.B. Xu, J.X. Yang, Y. Ren, X. Zhao, Y.Z. Wu, X.Q. Yu, M.H. Jiang. *J. Mater. Chem.*, in press.
- [13] Y.X. Yan, X.T. Tao, Y.H. Sun, W.T. Yu, C.K. Wang, G.B. Xu, J.X. Yang, Y.Z. Wu, X. Zhao, M.H. Jiang. *J. Mol. Struct.*, in press.
- [14] G.A. Reynolds, K.H. Drexhage, *Opt. Commun.* 13 (1975) 222–225.
- [15] Z.Q. Liu, Q. Fang, D. Wang, D.X. Cao, G. Xue, W.T. Yu, H. Lei, *Chem. Eur. J.* 9 (2003) 5074–5084.
- [16] C. Xu, W.W. Webb, *J. Opt. Soc. Am. B* 13 (1996) 481–491.
- [17] M.A. Albota, C. Xu, W.W. Webb, *Appl. Opt.* 37 (1998) 7352–7356.
- [18] P.K. Baker, G.K. Barker, M. Green, *J. Am. Chem. Soc.* 102 (1980) 7811–7812.
- [19] R.K. Chadha, J.E. Drake, B.A. Mcmanus, B.A. Quinlan, A.B. Sarkar, *Organometallics* 6 (1987) 813–819.
- [20] S. Husebye, *Acta Chem. Scand.* 20 (1966) 24–32.
- [21] S. Husebye, K. Maartmann-Moe, Y. Mikalsen, *Acta Chem. Scand.* 43 (1989) 868–870.
- [22] B.R. Cho, K.H. Son, S.H. Lee, Y.S. Song, Y.K. Lee, S.J. Jeon, J.H. Choi, H. Lee, M. Cho, *J. Am. Chem. Soc.* 123 (2001) 10039–10045.
- [23] S. Bernd, S.M. Ananda, D. Heiner, *Chem. Phys. Chem.* 4 (2003) 249–259.
- [24] N. Sarkar, K. Das, N.D. Nath, K. Bhattacharyya, *Langmuir* 10 (1994) 326–329.
- [25] J.N. Demas, G.A. Crosby, *J. Phys. Chem.* 75 (1971) 991–1024.
- [26] U. Narang, C.F. Zhao, J.D. Bhawalkar, F.V. Bright, P.N. Prasad, *J. Phys. Chem.* 100 (1996) 4521–4525.