

Synthesis of a Series of Novel Organic Compounds with Two-photon Absorption and Two-photon pumped Lasing

Xiao Mei WANG, Qi FANG, Chun WANG, Guang Yong ZHOU,
Yan REN, Min Hua JIANG*

State key laboratory of Crystal Materials, Shandong University, Jinan 250100

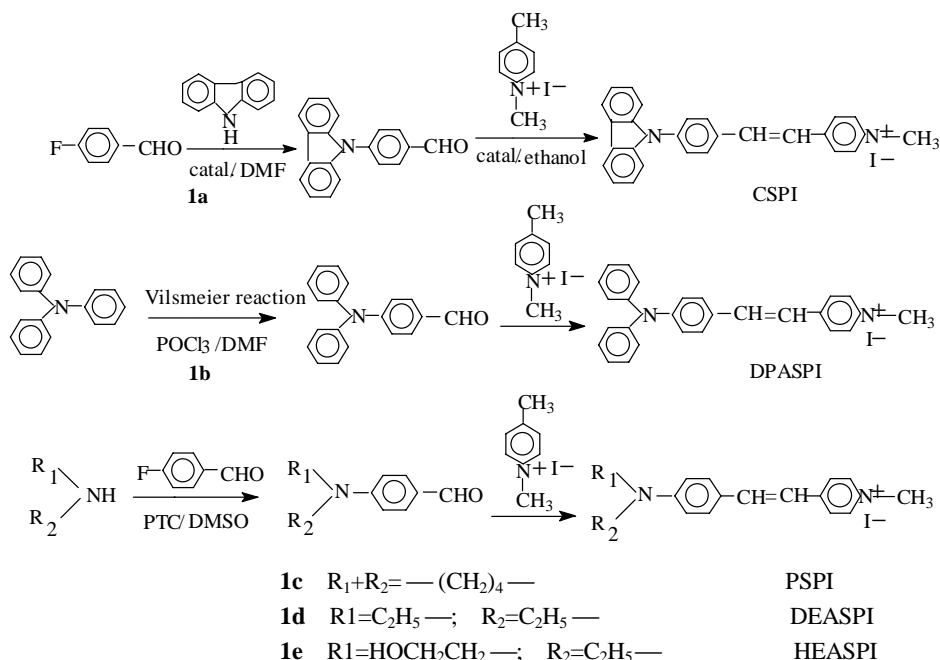
Abstract: A series of novel organic compounds named as CSPI, DPASPI, PSPI DEASPI and HEASPI respectively, with large two-photon absorption has been synthesized and their structures have been determined by ^1H NMR and elemental analysis. The highest two-photon pumped (TPP) output /input efficiency is as high as 13.4% for PSPI in DMF with $d_0 = 0.03 \text{ mol/L}$ and the effective two-photon absorption cross section is $8.8 \times 10^{-48} \text{ cm}^4 \cdot \text{s}/\text{photon}$ for DPASPI in DMF with $d_0 = 0.05 \text{ mol/L}$.

Keywords: Substituted styryl pyridinium derivatives, two-photon absorption cross section, two-photon up-conversion lasing.

Two-photon absorption (TPA) occurs through the simultaneous absorption of two photons *via* virtual states in a medium. Materials with large TPA cross section are gaining increasing attention recently due to their potential applications in optical data storage, two-photon up-converted lasing, two-photon-laser scanning fluorescence microscopy, optical power limiting and photodynamic therapy¹⁻³. Numerous organic compounds have been investigated both experimentally and theoretically in order to understand the structure-property relationship of materials with large two-photon absorption (TPA) cross section⁴⁻⁵. In the course of exploring strong two-photon absorption compounds, π - donor-acceptor compounds attracted attention due to their potentially large TPA cross section. Recently, we synthesized a series of substituted stilbene backbone end-capped with different donors but same acceptor, and measured their TPA cross section values and two-photon pumped (TPP) up-conversion lasing efficiencies for the fundamental wavelength at 1064 nm. The experimental results indicate these chromophores are promising candidates for up-conversion lasing or optical power limiting materials.

Synthesis and characterization

Nuclear magnetic resonance spectra were determined on FX-90Q NMR spectrometer. Elemental analysis were performed on Perkin 2400 (II). The decomposition temperatures were measured on Perkin Elmer TGS-2 thermo-gravimetric analyzer at rate of $20 \text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The diagram of synthesis of synthesis is as follows:



4-carbazyl-benzaldehyde **1a** : A flask fitted with magnetic stirrer and condenser was charged with 8.4g (0.05mol) of carbazole, 6g (0.05mol) 4-fluorobenzaldehyde, 5.5g (0.05mol) potassium tert-butoxide in 200mL of anhydrous DMF. The mixture was heated at 110 °C for 36h, then cooled to room temperature, and poured into ice water. Extracted with dichloromethane, removed the solvent by evaporation, then purified through chromatographic column. The pale yellow crystals were obtained, yield 52% and mp 163 °C.

4-(N,N-dibenzolamino) benzaldehyde⁶ **1b** : 4.9g (0.005mol) of triphenylamine, 3.0g (0.05mol) of dimethyl formamide and 30g (0.2mol) of phosphorus oxychloride were mixed in the vessel under an ice bath. Then refluxing the mixture for about one hour, poured into ice water; neutralized, filtered off and purified through chromatographic column on silica gel. Bright yellow crystals with yield 85% and m.p. 120°C were obtained.

4-pyrrolidinyl benzaldehyde **1c**, 4-(N,N-diethylamino) benzaldehyde **1d**, and 4-(N-hydroxyethyl-N-ethyl amino) benzaldehyde **1e** were synthesized following ref 7.

All chromophores were synthesized by condensation reaction of the appropriate substituted benzaldehyde **1a-1e** and 4-methyl-N-methylpyridinium iodide with a catalytic amount of piperidine.

Trans-4-p-(N-carbazolyl styryl)-N-methyl pyridinium iodide (CSPI): yield (80%) and Td 258.3 °C. ¹HNMR δ : 8.93 (2H, d, J 6.84Hz); 8.28 (4H, d, J 5.86Hz); 8.25~7.71, (4H,q); 7.51~7.15 (8H,q), 4.32 (3H, s) Element analysis: Calcd for C, 64.0; H, 4.33; N, 5.74. Found: C, 64.84; H, 4.45; N, 5.34.

Trans-4-[p-(N,N-diphenylamino) styryl]-N-methyl pyridinium iodide (DPASPI):

yield (82%) and Td 260.2 °C. ¹HNMR (DMSO-d₆) δ: 8.78 (2H, d, J 6.84Hz); 8.14(2H, d, J 5.86Hz); 7.95(1H, d, J 13.9Hz); 7.63 (2H, d, J 8.79); 7.17 (1H, d, 13.9Hz); 6.94 (2H, d, J 8.79Hz); 7.06~7.39 (10H,q); 4.22(3H,s). Element analysis: Calcd for C, 63.68; H, 4.73 ; N,5.71 . Found: C, 63.63; H, 4.85; N, 5.67.

Trans-4-(p-pyrrolidinyl styryl)-N-methyl pyridinium iodide (PSPI): yield 82% and Td 260.6 °C. ¹HNMR (DMSO-d₆) δ: 8.68 (2H, d, J 6.84Hz); 8.04 (2H, d, J 6.84Hz); 7.92 (1H, d, J 15.64Hz), 7.61 (2H, d, J 7.82Hz); 7.14 (1H, d, J 15.63Hz); 6.62 (2H, d, J 8.79Hz); 4.19 (3H,s); 3.32(4H,t); 1.97 (4H, t). Element analysis: Calcd for C, 55.11; H, 5.35; N, 7.14. Found: C, 55.0; H, 4.84; N, 7.59.

Trans-4-[p-(N,N-diethylamino) styryl]-N-methyl pyridinium iodide (DEASPI): yield (82%), and Td 260.2 °C. ¹HNMR (DMSO-d₆) δ: 8.67 (2H, d, J 6.84Hz); 8.04 (2H, d, J 6.84Hz); 7.91 (1H, d, J 15.61Hz), 7.58 (2H, d, J 8.79Hz); 7.12 (1H, d, J 15.63Hz); 6.75 (2H, d, J 8.80Hz); 4.18 (3H,s); 3.43 (4H, q, 6.84); 1.13 (6H, 6.84). Element analysis: Calcd for C, 54.84; H, 5.88; N, 7.10. Found: C, 54.34; H, 5.46; N, 6.98.

Trans-4-[p-(N-hydroxyethyl-N-ethyl)amino]styryl]-N-methyl pyridinium iodide (HEASPI): yield (85%) and Td 286.7. ¹HNMR (DMSO-d₆) δ: 8.69 (2H, d, J 6.84Hz); 8.06 (2H, d, J 6.84Hz); 7.93 (1H, d, J 15.63Hz), 7.60 (2H, d, J 8.8Hz); 7.16 (1H, d, J 15.63Hz); 6.79 (2H, d, J 8.79Hz); 4.60 (1H, s); 4.20 (3H,s); 3.55(6H,q); 1.13 (3H, s). Element analysis: Calcd for C, 52.69; H, 5.69; N, 6.83. Found: C, 52.43; H, 5.21; N, 6.45.

Nonlinear optical properties

Two-photon pumped lasing were measured by two-channel energy-meter with a mode-locked Nd:YAG laser as a pumping source. The conversion efficiency values (η) of two-photon-pumped in **Table 1** are calculated by $\eta = (E_{up} / E_{in}) \cdot 100\%$, in which E_{up} is the energy of upconverted emission in red wavelength, and E_{in} is the energy of the pump laser rather than the absorbed energy.

Two-photon absorption cross sections (δ) were determined using the open aperture Z-scan technique. Details of this experiment are described in the literature 8. The cuvette of 2 mm thick filled with samples and mode-locked Nd: YAG laser with 35 ps duration were used. The experimental data are collected in Table 1.

Table 1 TPA cross sections (δ) and TPP up-conversion lasing efficiencies

Compound	CSPI	DPASPI	PSPI	DEASPI	HEASPI
δ, cm ⁴ ·s /photon (0.05M)	weak	8.8×10 ⁻⁴⁸	5.7×10 ⁻⁴⁸	6.7×10 ⁻⁴⁸	7.0×10 ⁻⁴⁸
η (%)	weak	12.4	13.5	12.01	12.4
	(0.05M)	(0.07M)	(0.03M)	(0.04M)	(0.07M)

Strong TPP up-conversion lasing around 625~630 nm with a width at half maximum of ~ 25 nm for PSPI, DEASPI and HEASPI were observed in DMF solution with the optimum concentration. The largest up-conversion efficiency is as high as 13.5 (%) at 2.12 mJ input energy. To our knowledge, DEASPI, PSPI and HEASPI are among these few laser dyes with the highest up-conversion efficiency. Among six chromophores, DPASPI exhibits largest δ value, as high as 8.8 ×10⁻⁴⁸ cm⁴·s /photon at I₀

= 1.78Gw/cm². Considering that these compounds have a limited conjugation length, the δ value of 8.8×10^{-48} cm⁴·s /photon for DPASPI is remarkable.

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References

1. D.A. Parthenopoulos, P.M. Rentzepis, *J. Appl. Phys.* **1990**, 68, 5814.
2. D.A. Parthenopoulos, P.M. Rentzepis. *Science*. **1989**, 245, 843.
3. J. D. Bhawalkar, G. S. He, P. N. Prasad, *Rep. Prog. Phys.* **1996**, 59, 1052.
4. F. Meyers, S. R. Marder, B. M. Pierce *et al*, *J. Am. Chem. Soc.* **1994**, 116, 10703.
5. T.Kogej, D.Beljonne, F.Meyers *et al*, *Chem. Phys. Lett.* **1998**, 298, 1.
6. C. D. Wilson, N. J Wilmington, US patent, **1951**, 2558285
7. C. F. Zhao, C. K. Park, P. N. Prasad *et al*, *Chem. Mater.* **1995**, 7, 1237.
8. S.B. Mansoor, Ali A. Said, T.H. Wei *et al IEEE Journal of Quantum Electronics*, **1990** 26, 760.

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