Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 127 (2007) 423–430
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Synthesis and two-photon optical characterization of D–π–D type Schiff bases

Lei Tian[a], Zhangjun Hu[a], Pengfei Shi[a], Hongping Zhou[a], Jieying Wu[a], Yupeng Tian[a,b,c,*], Yufang Zhou[b], Xutang Tao[b], Minghua Jiang[b]

[a]*Department of Chemistry, Anhui University, Hefei 230039, PR China*
[b]*State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China*
[c]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China*

Received 7 September 2006; received in revised form 5 February 2007; accepted 6 February 2007
Available online 27 February 2007

Abstract

The title compounds, several Schiff bases with D–π–D type have been successfully synthesized from reaction of 4-(*N*-dialkylamino) benzaldehyde and hydrazine or *p*-phenylenediamine in ethanol. These compounds were characterized by IR, ^{1}H NMR, elemental analysis and electronspray mass spectrometry. One-photon fluorescence and two-photon fluorescence properties have been investigated. The two-photon absorption (TPA) cross section (σ) of these compounds was obtained by using the open-aperture Z-scan technique. Based on theoretical calculations and factual test, the influence that a series of substituted groups and the conjugated frame imposed on TPA cross section were systematically discussed.

Keywords: Schiff bases; Two-photon absorption; Z-scan

1. Introduction

Two-photon excitation (TPE) has become particular practical significance because of the development of highly efficient two-photon absorbing (TPA) materials and their applications [1–5]. Organic materials with striking TPA effect and large TPA cross section have attracted considerable attention for their potential applications such as two-photon up-converted lasing [6–10], three-dimensional fluorescence imaging [11–16], optical data storage [17–22], microfabrication [23–27], optical power limiting [28–31] and so on.

Many complicated factors can affect the TPA properties in organic materials. So it is important to investigate the structure and the TPA effect relationship for organic materials. Marder and Prasad and their co-workers have made excellent work in this field, and they emphasized particularly on the study of two different structural molecules' TPA effect, respectively. Marder et al. have focused on symmetric organic compounds and reported a design strategy for symmetrically substituted conjugated molecules, while Prasad et al. have emphasized the D–π–A-type chromophores. The former emphasized the importance of conjugation length and molecular symmetry, while the latter laid stress on the planarity of π-center and donor–acceptor strength. In 1999, Marder improved further symmetric charge transfer model, first reporting that the symmetrical molecules can be used as two-photon polymerization initator [24], which can be applied as three-dimensional microfabrication and the manufacture of photonic crystal. These practical applications have been receiving increasing attentions.

Recently, scientists try to find novel compounds with excellent TPA effect. However, most of these compounds employed C=C bonds as the conjugation bridge, the compounds with C=N structure such as Schiff bases are

*Corresponding author. Department of Chemistry and Engineering, Anhui University, No. 3, Feixi Road, Hefei 230039, PR China.
Tel.: +86 551 5108151; fax: +86 551 5107342.
E-mail address: yptian@ahu.edu.cn (Y. Tian).

0022-2313/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2007.02.040

less studied to our knowledge. The synthesis of these compounds is very convenient, and the conjugated length in the molecules can also be tuned. Recently, several Schiff base complexes were reported [32,33], in which a very simple strategy to induce exceptionally large σ values on a Schiff base through metal complexation was adopted, and the high thermal stability as well as high-TPA cross section make these complexes potential candidates for NLO applications. Herein, we report the synthesis of two groups of symmetric Schiff bases with D–π–D type, and discuss systematically the influence of a series of push-electron groups and the conjugated frame on TPA properties. Our work deduces that increasing the strength of conjugation length and donor moieties attached to a conjugated linker can result in the enhancement of the TPA cross section.

2. Experimental

2.1. Materials and methods

All chemicals used were of analytical grade. Solvents were purified by conventional methods. IR spectra were recorded with a Nicolet Nexus-870 instrument (KBr discs) in the 4000–400 cm^{-1} region. Element analysis data were recorded with a Pekin-Elmer 240 instrument. UV–Vis spectra were recorded with an UV-265 spectrophotonmeter and corrected by subtracting solvent backgrounds. The single-photon emission fluorescence spectra measurements were performed using Perkin-Elmer LS-55B fluorospectrometer. The two-photon fluorescence spectra were measured using a streak camera (C5680-01, Hamamatsu) and imaging spectrography (C5094, Hamamatsu). The pump laser beam came from a mode-locked Ti:sapphire laser system operating at 780 nm, pulse duration <200 fs and repetition rate 76 MHz (Coherent Mira900-D). The σ values and coefficient β were determined by the Z-scan technique. The excited light source was a Q-switched Nd:YAG laser providing a pulse at the second-harmonic 532 nm. The pulse duration was 20 ns and the repetition frequency was 1 Hz. The pulse energy was recorded on an energy detector (EPM2000, Molectron). To assure thin-sample approximation, a 1.0 mm path length glass cell was used.

2.2. Preparation of two groups of Schiff bases derivation

The synthesis route to the target Schiff bases is described in Scheme 1.

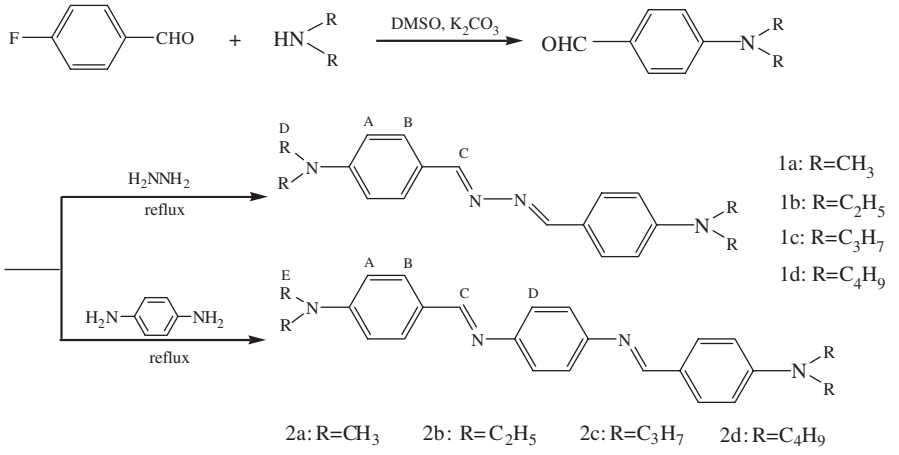
2.2.1. 4-(N-dialkylamino) benzaldehyde [34]

A flask fitted with a magnetic stirrer and condenser was charged with 4-fluorobenzaldehyde (124 g, 1 mol), dialkyl amine (1.5 mol), potassium carbonate (138 g, 1 mol) and aliquat-336 (0.5 cm^3) in dimethyl sulfoxide (400 cm^3). The mixture was heated at 95 °C for 72 h, then cooled to room temperature and poured into ice water, the pH value of the solution was adjusted to 2 by addition of hydrochloric acid. The aqueous layer was separated and neutralized using saturated aqueous NaOH (adjust the pH > 11). Then, the aqueous layer was extracted with CH_2Cl_2, and the organic layer was separated, and dried using anhydrous $MgSO_4$. After CH_2Cl_2 was removed, the yellow precipitate was obtained. Yield: ~80%.

2.2.2. Two groups of Schiff bases derivatives (compounds 1a–d and 2a–d)

Compounds 1a–d and 2a–d were obtained by the similar method as described below:

Compound 1a: An ethanol (20 cm^3) solution of 4-(*N*-dimethylamino) benzaldehyde (1.492 g, 0.01 mol) was added to a solution of hydrazine (1.603 g, 0.05 mol) in ethanol (20 cm^3). After the mixture was refluxed and stirred for 4 h, the solid formed was filtered off, washed with ethanol to give a pale yellow powder of 1a. Yield: 80%. IR date (KBr discs, cm^{-1}): 1602 ($\nu_{C=N}$); 1364 (ν_{C-H} of methyl). Anal. Calcd for 1a ($C_{18}H_{22}N_4$): C, 73.44%; H, 7.53%; N, 19.03%. Found: C, 73.52%; H 7.71%; N, 19.11%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.58 (2H, s, H_C);



Scheme 1. Strategy of synthesis for compounds 1a–d and 2a–d.