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Two-photon absorption property and excellent optical limiting response of three Schiff base derivatives with large conjugated system

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ABSTRACT

In this work, three Schiff base derivatives with large conjugated system have been elaborately designed and synthesized, in which bithienyl (**1**), pyrenyl (**2**) and anthryl (**3**) connect an azo moiety (N = N) monomer through conjugation linkage (C = N), respectively. Their third-order nonlinear optical (NLO) properties are systematically investigated by performing the picosecond-pulsed Z-scan measurements at the wavelength of 532 nm and femtosecond-pulsed Z-scan measurements at the wavelength of 600 nm. The pump-probe measurements and the linear dependence between the amplitude of transmittance change and different laser energy indicate that the nonlinearity is originated from pure two-photon absorption (2PA) behavior. Among them, compound **1** with the bithiophene group has a larger two-photon absorption cross section up to 8.90×10^4 GM (ps). The reason may be that the electron-rich bithiophene group with lower delocalization energy improves electron transition. In addition, excellent optical limiting (OL) behaviors of the three Schiff base derivatives are observed under ps laser excitations at 532 nm wavelength, which resulted from 2PA induced reverse saturation absorption (RSA). All the experimental results manifest that these compounds could be used as potential NLO materials.

1. Introduction

Organic materials with large third-order NLO properties have been attracted considerable attention due to various applications in optoelectronic devices [1–6], and another important factor is that the photophysical properties of organic materials can be easily tuned and tailored by structural modification [7–14]. Especially, third-order NLO behavior involving a 2PA process is in great demand because of their potential applications in fluorescence microscopy, 3D data storage, optical power limiting and two-photon photodynamic therapy [15–21]. It is known that the nonlinearity in organic materials originates from a strong delocalization of π-electrons along the length of the molecules [22–25]. For the past many years, many efforts have been devoted to develop π-conjugated organic compounds [26–29]. Among a variety of π-conjugated organic compounds, Schiff base derivatives have emerged as promising candidates for nonlinear optical materials on account of the π-electron bridge from carbon-nitrogen double bonds (C = N) [30,31]. The type of linkages in the molecules plays a critical role in enhancing the molecular NLO response [32,33]. For another, it is widely accepted that the third-order NLO susceptibility increases with the length of conjugation within a molecule. According to previous reports, we have learned azo-containing compounds and large π-conjugated molecules are promising third-order nonlinear materials [34–38], because they can provide convenient electronic transfer channel and the delocalization π-electron throughout entire molecular system.

It may be an effective approach that using a Schiff base moiety (C = N) as the conjugation linkage unify an azo (N = N) monomer and an extended polarizable π-core into a molecular system to obtain large third-order materials. As far as we know, bithienyl, pyrenyl and anthryl with large conjugate system are considered as effective nonlinear building blocks. The azobenzene units have good co-planar performance and provide good electronic channels. So, if the two features are connected through π-electron bridge (C = N), then the compounds may be ideal candidates for large and fast optical nonlinearities materials. These compounds possess the extended mobile π-electron clouds over large molecular distances and are easily polarized [39]. Inspired by these ideas, three Schiff base derivatives were successfully synthesized, and their third-order NLO properties have been comparatively investigated. The Z-scan measurements in compounds **1**, **2**, and **3** demonstrate RSA capability. The pump-probe measurements and the

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linear dependence between the amplitude of transmittance change and different laser energy indicate that nonlinearity is originated from pure 2PA behavior. In ps conditions, these compounds exhibit large 2PA cross-sections up to 8.90×10^4 GM (**1**), 3.97×10^4 GM (**2**), 3.41×10^4 GM (**3**). Besides, the time-dependent density functional theoretical (TD-DFT) calculations are performed to insight electronic structure and the photo-physical properties of these compounds. The OL properties of these compounds were also studied, and the optical limiting threshold (LT) value of **1** is lower than **2** and **3**, which is consistent with the results of the 2PA cross section.

2. Experimental section

2.1. Materials and measurements

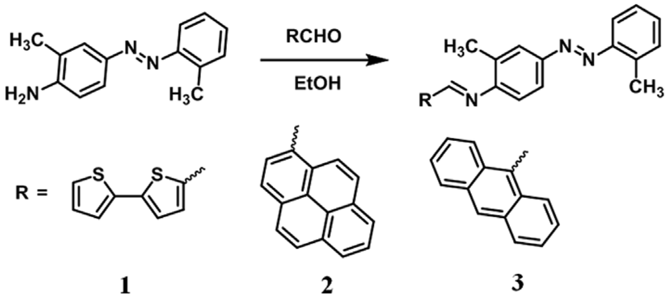
All materials were commercially purchased and used without any further purification. 4-amino-2′,3-dimethylazobenzene hydrochloride (**DI-AZO**), 2,2′-bithiophene-5-carboxaldehyde, 1-pyrenecarboxaldehyde, 9-anthraldehyde were purchased from J&K Chemical Co., Beijing, China. The other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. The precise structures of compounds **1**-**3** have been determined by the following characterization methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 Avance NMR spectrometer operated at 400 MHz. ESI-MS spectra were obtained on Agilent Technologies 6420 triple quadrupole LC/MS without using the LC part. C, H and N analyses were carried out with a USA Thermoscientific FLASHSMART elemental analyzer. UV-vis absorption spectra were recorded on a JASCOV-750 spectrophotometer using 3 mL quartz cuvettes (10 × 10 mm) cells at 25 °C. In addition, the ground-state and excited-state geometries optimizations and the electronic absorption spectra of compounds **1**, **2** and **3** were performed by using TD-DFT method at the level of TD-B3LYP/6-311G + +(2d, 2p). All the calculations were performed using the Gaussian 09 quantum software.

2.2. Synthesis

Compounds **1**-**3** were synthesized according to the synthetic routes shown in Scheme 1. The new compounds were characterized by NMR spectra and ESI-MS spectra. Detailed characterization data are shown in Supplementary Information.

2.2.1. Compound 1

(E)-1-([2,2′-bithiophen]-5-yl*)-N-(2-methyl-4-((E)-o-tolyldiazenyl) phenyl)methanim-ine (1)* 4-amino-2,3-dimethylazobenzene hydrochloride (0.18 g, 0.7 mmol) dissolved in methanol (20 mL) was introduced and heated to reflux in a 50 mL flask, then the methanol solution of 2, 2′-bithiophene-5-carboxaldehyde (0.1 g, 0.5 mmol) was added dropwise. The stirred mixture was heated to reflux for 4 h. After that, the solvent was concentrated under reduced pressure and the crude product was further purified by recrystallization from dichloromethane and methanol (1:4, *v:v*). Compound **1** (0.15 g, 0.37 mmol) was obtained as golden precipitates with a yield of 75%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.74 (s, 1H), 7.84–7.77 (m, 2H), 7.70 (d, 1H), 7.65 (d, 1H), 7.56 (dd, 2H), 7.44 (d, 3H), 7.30 (d, 2H), 7.17 (d, 1H), 2.69 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 152.59, 152.20, 150.98, 142.61, 141.45, 137.93, 136.95, 133.33, 131.25, 130.64, 128.22, 126.45, 125.91, 125.13, 124.79, 124.06, 122.22, 118.35, 115.46, 77.41, 76.77, 18.15, 17.64. ESI-MS spectrometry: *m/z* calculated for $C_{23}H_{19}N_3S_2$ $[M + H]^+$: 402.1; found: 402.0. Anal. Calcd for $C_{23}H_{19}N_3S_2$: C, 68.80; H, 4.77; N, 10.46; S, 15.97. Found: C, 68.03; H, 4.74; N, 10.43; S, 15.86.



Scheme 1. General procedure for synthesis of three Schiff base derivatives.

2.2.2. Compound 2

(E)-N-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)-1-(pyren-1-yl*)methanimine (2)* Compound **2** was prepared with a method similar to **1** and obtained as red precipitates with a yield of 65%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.63 (s, 1H), 9.38 (d, 1H), 8.86 (d, 1H), 8.44 (t, 4H), 8.36 (d, 1H), 8.30 (d, 1H), 8.18 (d, 1H), 7.90 (d, 2H), 7.62 (d, 1H), 7.55 (d, 1H), 7.46 (d, 2H), 7.36 (d, 1H), 2.73 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm): 160.09, 154.04, 150.79, 150.58, 137.94, 133.56, 131.92, 131.57, 131.25, 130.63, 129.70, 128.70, 127.88, 127.15, 126.67, 125.62, 124.61, 124.13, 123.58, 122.61, 119.70, 115.53, 40.53, 40.33, 40.20, 39.89, 39.78, 39.57, 39.36, 18.52, 17.67. ESI-MS spectrometry: *m/z* calculated for $C_{31}H_{23}N_3$ $[M + H]^+$: 438.2; found: 438.1. Anal. Calcd for $C_{31}H_{23}N_3$: C, 85.10; H, 5.03; N, 9.06. Found: C, 84.83; H, 5.19; N, 9.23.

2.2.3. Compound 3

(E)-1-(anthracen-9-yl*)-N-(2-methyl-4-((E)-o-tolyldiazenyl)phenyl)methanimine (3)* Compound **3** was prepared with a method similar to **1** and obtained as orange precipitates with a yield of 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.82 (s, 1H), 8.97 (d, 2H), 8.87 (s, 1H), 8.23 (d, 2H), 7.92 (s, 2H), 7.72–7.68 (m, 2H), 7.63 (dd, 3H), 7.58 (d, 1H), 7.47 (d, 2H), 7.36 (dd, 1H), 2.73 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm): 160.97, 154.39, 150.91, 150.54, 137.98, 133.07, 131.93, 131.63, 131.33, 130.70, 129.56, 128.14, 127.09, 127.05, 126.15, 125.30, 124.59, 122.83, 119.87, 115.53, 40.61, 40.40, 40.10, 39.90, 39.78, 39.57, 39.36, 18.77, 17.66. ESI-MS spectrometry: *m/z* calculated for $C_{29}H_{23}N_3$ $[M + H]^+$: 414.2; found: 414.0. Anal. Calcd for $C_{29}H_{23}N_3$: C, 84.23; H, 5.61; N, 10.16. Found: C, 84.26; H, 5.59; N, 9.80.

2.3. Z-scan technique and optical limiting measurements

The third-order NLO properties of all the compounds were measured by the standard Z-scan technique in the open aperture (OA) mode. This technique provided direct measurement of nonlinear absorption and refraction properties. The fs top-hat Z-scan measurement were performed by utilizing a linearly-polarized pulse laser (repetition frequency at 20 Hz, pulse width of 190 ns, wavelength at 600 nm) and generated from PHAROS High-Power Femtosecond lasers sp. The Gaussian Z-scan experiments (ps) and time-resolved pump-probe experiments (ps) were performed on TNLO-TR transient nonlinear refractometer (Suzhou micronano laser photon technology Co., Ltd.) with a Q-switched Nd:YAG 532 nm laser (GKPPL-1064-1-10, Beijing GK Laser technology Co., Ltd.) as the light source, which provided linearly polarized 21 ps pulses with a repetition rate of 10 Hz at 532 nm, where the sample solution was in 2 mm quartz cell. And the experimental apparatus were similar to that in Ref. [40]. The beam waist (ω_0) of laser pulses is 36 μm, the Rayleigh range ($z_0 = \pi\omega_0^2/\lambda$) is 7.65mm and the input intensity per laser pulse (I_0) is 1.06 GW/cm^2. Compounds **1**-**3** are dissolved in DMF and the concentrations of the solutions are 3×10^{-3} mol/L, 5×10^{-3} mol/L and 4×10^{-3} mol/L, respectively. To carry out Z-scan measurements, the sample was scanned across the focus along the optical axis using a computer-controlled stage, while the transmitted pulse energies were probed by a detector, producing the open-aperture Z-scan trace. The laser source used for ps-pulsed optical