Dyes and Pigments 102 (2014) 1–5

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis and photophysical properties of three ladder-type chromophores with large and rigid conjugation structures

Kaichen Zhang [a], Yong Dai [b,]**, Xinfu Zhang [a], Yi Xiao [a,]*

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China
[b] Department of Criminal Science and Technology, Sichuan Police College, Luzhou 646000, China

ARTICLE INFO

Article history:
Received 16 September 2013
Received in revised form
18 October 2013
Accepted 21 October 2013
Available online 28 October 2013

Keywords:
Synthesis
Linear optics properties
Electrochemical
Two-photon absorption
Intramolecular charge transfer
Ladder-conjugated chromophore

ABSTRACT

Three novel ladder-conjugated chromophores indicated as LT1–LT3 were synthesized and characterized. Further studies on linear, nonlinear optics and electrochemical properties demonstrated their photophysical features respectively. Compound LT1 shows good two-photon absorption cross-section (δ) up to ~1200 GM at 810 nm in tetrahydrofuran, which is attributed to intramolecular charge transfer effect, as supported by density functional theory theoretical calculations. Compound LT2 and LT3 show considerable molar extinction coefficients, which are more than 10^5, and higher quantum yields. Structure–function relationship is further discussed, suggesting a rational strategy to develop ladder-conjugated small molecules.

1. Introduction

Two-photon absorption (TPA) has obtained lots of attention since it was first proposed by M. Goppert-Mayer in her doctoral dissertation in 1931 [1]. Due to their potential applications in photonics [2–6], including, three-dimensional optical data storage [7,8], two-photon-excited fluorescence microscopy [9,10], optical power limiting [11,12], and photodynamic therapy [13], etc, intensive efforts are put into the manufacture of new two-photon materials in the recent years. The applications of TPA need dyes having large two-photon absorption cross section [14,15]. Simultaneously, due to the popularity and easy availability of 800 nm laser sources, designing and synthesizing TPA chromophores with the optimal performance at this wavelength is the main goal [4].

In 2012, our group reported one dye, which has excellent two-photon properties, and the maximum of δ is 11,000 GM at 990 nm. This is caused by its large π-conjugated system, completely rigid and coplanar structure, and the intramolecular charge transfer (ICT) effect [16]. For the two-photon absorption in the case of the π-conjugated bonds, principal role begin to play dipole–dipole interactions between the chromophore and the polymer chains [17]. Herein, three novel ladder conjugated chromophores were synthesized by condensation reaction using TABEF (2, 3, 6, 7-tetraamino-9, 9-bis (2-ethylhexyl) fluorene). Quadrupolar molecules are usually considered to be more effectively polarized resulting in larger transition moment and higher TPA cross-section, and chromophores LT1–LT3 had structures of completely rigid planar. And most importantly, they had similar structure and conjugated length. The changes of two sides of them may bring about different optical and physical properties for these materials. To obtain an effective ICT process, a π-conjugated bridge-fluorene was used to facilitate the intramolecular electronic flow. At the same time, it could play as π-donor owing to its higher electron density compared with the electron-deficient parts. Thirdly, to release intermolecular π–π stacking resulting in increasing solubility, two isooctyl groups were introduced to the fluorene moiety.

The synthesis, linear optics, two-photon absorption and the electrochemistry properties of these chromophores were presented in this work. The TPA cross-section was measured in the range from 700 nm to 1040 nm.

2. Experimental

2.1. Materials and instruments

Commercially available reagents were purchased and were used without further purification. All the solvents were of analytic grade.

---

* Corresponding author. Tel.: +86 411 84986251.
** Corresponding author.
E-mail addresses: sdy-0502@163.com (Y. Dai), xiaoyi@dlut.edu.cn (Y. Xiao).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.10.030

NMR spectra in $CDCl_3$ were measured with a 400 MHz Bruker spectrometer using TMS as internal reference for ^1H and ^{13}C NMR. Accurate mass correction was measured with MALDI Tof Mass Spectrometer (MALDI micro MX). Electrochemical studies made use of cyclic voltammetry (CV) with a conventional 3-electrode system using a BAS 100W electrochemical analyzer in deoxygenated and anhydrous CH_2Cl_2 at room temperature. UV–vis absorption spectrums were measured with UV–vis Spectrophotometer (HP 8453). Fluorescence spectra were obtained with a FP-6500 spectrophotometer (Jasco, Japan). Melting points were measured on a Digital Melting Point Apparatus without correction.

Two-photon absorption spectra were measured by using a femtosecond (fs) fluorescence measurement technique as described in the literature [18]. The samples were dissolved in THF at a concentration of $1.0*10^{-5}$ M. Fluorescence emission curve excited by different laser wavelengths, from 700 nm to 1040 nm (10 nm per step) was detected. The TPA cross-section (δ) of chromophores LT1–LT3 in THF ($1.0*10^{-5}$ M) were measured using fluorescein in pH = 11 NaOH aqueous solution as the reference [19]. The δ was calculated according to the following equation [20].

$$\delta_s = \delta_r \times (S_s \times \Phi_r \times \eta_r \times N_r)/(S_r \times \Phi_s \times \eta_s \times N_s) \quad (1)$$

where the subscripts s and r stand for the sample and reference molecule, S is the corrected intensity of two-photon-induced fluorescence, Φ is the fluorescence quantum yield, N is the concentration of the chromophore, and η is the collection efficiency of the experimental setup, δ_r is the TPA cross section of the reference molecule.

2.2. Theoretical calculations

In order to understand the nature of the ground-state and the low-lying excited states, quantum chemical calculations were performed for chromophores LT1–LT3. The structures of them were optimized using density functional theory (DFT) with B3LYP functional and 6-31G basis set. All calculations were performed with Gaussian 09 [21].

2.3. Synthesis

A mixture of 0.133 g 1,8-Naphthalic anhydride (0.67 mmol), 0.2 g TABEF·4HCl [22] (0.335 mmol) and 5 ml glacial acetic acid was heated to reflux for 4 h under argon. After cooling, the reaction product was precipitated by the addition of MeOH (25 ml), collected by vacuum filtration, and dried in air. The crude product was dissolved in dichloromethane, preadsorbed on silica gel, and purified by column chromatography (silica gel, CH_2Cl_2:hexane = 1:1 as eluent, gathering the band (Rf = 0.2)) resulting in an orange solid compound LT1. (118 mg, yield: 45%) Compounds LT2–LT6 were synthesized in the similar procedure.

Compound LT1: orange powder, yield 45%. m.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 9.08 (s, 2H), 8.89–8.88 (d, J = 5.6 Hz, 4H), 8.31–8.29 (d, J = 7.2 Hz, 2H), 8.16–8.14 (d, J = 7.6 Hz, 2H), 7.89–7.82 (m, 6H), 2.20 (s, 4H), 0.91–0.73 (m, 18H), 0.59–0.51 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 161.0, 149.9, 149.7, 144.0, 139.8, 135.5, 132.6, 131.9, 127.7, 127.7, 127.2, 123.7, 121.2, 115.5, 107.5, 54.7, 46.2, 34.8, 33.7, 28.2, 26.8, 22.9, 14.1, 10.3; TOF HRMS ES + calcd for $C_{53}H_{51}N_4O_2$ 775.4012 $[M + H]^+$, found 775.3949.

Compound LT2: yellow powder, yield 72%. m.p. 243.1–245.7 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 9.34–9.19 (m, 4H), 8.70–8.66 (t, J = 6.4 Hz, 2H), 8.46–8.37 (m, 6H), 7.78–7.67 (m, 8H), 2.46–2.45 (d, J = 5.2 Hz, 4H), 1.04–0.73 (m, 18H), 0.59–0.51 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 153.7, 142.9, 142.6, 142.2, 142.2, 142.1, 132.0, 131.8, 130.4, 130.3, 130.1, 127.8, 127.8, 126.3, 126.0, 124.3, 124.2, 124.1, 122.8, 120.7, 54.9, 47.2, 35.2, 33.5, 27.9, 26.9, 22.7, 13.8, 10.2; TOF HRMS ES + calcd for $C_{57}H_{55}N_4$ 795.4427 $[M + H]^+$, found 795.4436.

Compound LT3: light yellow powder, yield 76%. m.p. 225.6–227.3 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 8.67 (s, 2H), 8.44–8.42 (d, J = 6.8 Hz, 4H), 8.31–8.29 (t, J = 4.4 Hz, 2H), 8.09–8.06 (d, J = 8 Hz, 4H), 7.87–7.81 (dd, J = 8 Hz, 15.6 Hz, 4H), 2.38–2.31 (t, J = 14.8 Hz, 4H), 0.95–0.73 (m, 18H), 0.55–0.52 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 154.0, 153.7, 153.2, 142.0, 141.8, 141.5, 136.5, 132.0, 130.0, 129.4, 129.4, 128.8, 128.7, 124.7, 124.6, 124.5, 121.8, 120.8, 55.1, 46.6, 35.1, 33.5, 28.0, 26.8, 22.6, 13.8, 10.2; TOF HRMS ES + calcd for $C_{53}H_{51}N_4$ 743.4114 $[M + H]^+$, found 743.4125.

Compound LT4: green yellow powder, yield 84%. m.p. 160.1–162.3 °C [23].

Compound LT5: milk white floc, yield 79%. m.p. 173.1–174.5 °C [24].

Compound LT6: milk white powder, yield 81%. m.p. 191.1–192.8 °C [25].

3. Results and discussion

3.1. Design and synthesis

Chromophores LT1–LT3 were synthesized by one-step condensation reaction using TABEF·4HCl as the key intermediate, and had the similar structures and π-conjugated length. To obtain the larger two-photon absorption cross section, three quadrupolar chromophores LT1–LT3 with the changes of the substituents at the terminal position were synthesized. In the synthesis of compound LT1, two isomers were found in the product. The symmetric compound LT1 can be separated from them through column chromatography. The other compounds LT2 and LT3 have the certain structures without isomer. All these compounds LT1–LT6 were synthesized as described in Scheme 1. Compounds LT1–LT3 and compounds LT4–LT6 correspondingly have the similar structure.

3.2. Linear photophysical properties

The comprehensive photophysical properties of these compounds in CH_2Cl_2 and THF are listed in Table 1. Linear absorption and single-photon excited fluorescence (SPEF) spectra of chromophores LT1–LT3 in THF are respectively shown in Fig. 1(a) and (b).

Due to the larger π-conjugated system, compounds LT1–LT3 exhibit longer absorption wavelength and larger molar extinction coefficient compared with reference compounds LT4–LT6, respectively. As shown in Table 1, one can see that the absorption peak position and emission peak position of compounds LT1–LT6 all exhibit slight blue shift from CH_2Cl_2 to THF. Due to rigid structure without geometry relaxation upon photoexcitation, compounds LT2 and LT3, exhibit the smaller Stocks Shifts and the higher quantum yields. Remarkably, they exhibit considerable molar extinction coefficients, which are more than 10^5. Caused by the introduction of benzimidazole unit, compounds LT1 and LT4 show smaller molar extinction coefficients, and larger Stocks Shifts of them were caused by the ICT effect. Notably compound LT1 has the lower quantum yield compared with compound LT4 due to introduction of one more benzimidazole unit, and this have been verified by the compounds of perylene diimide class [26].

3.3. Electrochemical properties

In order to investigate the electrochemical behavior of these compounds, CV measurements were performed in CH_2Cl_2 solution