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Synthesis and two-photon absorption properties of a red-emitting poly (2,6-anthracenevinylene) derivative with donor–acceptor–donor motif

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ABSTRACT

A novel poly(2,6-anthracenevinylene) derivative (Pr) with donor–acceptor–donor motif was synthesized by Witting reaction of 9,10-dicyano-2,6-bis(diethylphosphoryl-methyl)anthracene and 4,6-bis(bis(2-ethylhexyl)amino)isophthalaldehyde, and its one- and two-photon properties were investigated. Pr showed a number-average molecular weight of 11,360 by end-group analysis and 15,300 by GPC, respectively. The Pr solution in toluene exhibited a maximal absorption wavelength peaked at 591 nm with the onset wavelength of 690 nm and emitted a red fluorescence centered at 665 nm with a fluorescence quantum yield of 0.10. Pr exhibited the maximum two-photon absorption cross-section of 1430 g per repeating unit at 920 nm measured by two-photon-induced fluorescence method. The results indicate the polymers with large TPA cross sections can be obtained by employing effective TPA chromophores as the building blocks, and the wavelength of the maximal TPA for 2,6-anthracenevinylene-based polymers could be tuned by attaching appropriate donor and/or acceptor substituents.

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1. Introduction

Two-photon absorption (TPA) is an important non-linear optical phenomenon, which involves the simultaneous interaction of two photons. The simultaneous absorption of two photons by the same molecule was first analyzed theoretically in 1931 by Göppert-Mayer [1], and was first demonstrated experimentally for organic dyes in 1963 by Rieckhoff and coworkers [2], but it was only in the late 1990 s that structure–property relationships emerged for the rational design of two-photon dyes [3]. Overall, the TPA cross-section (δ) increases with the donor/acceptor strength, conjugation length, molecular dimensionality and planarity of the π-center. Up to now, a variety of compounds exhibiting TPA properties, including donor–acceptor–donor (D–A–D) type molecules, donor–π-bridge–acceptor (D–π–A) type molecules, donor–π-bridge–donor (D–π–D) type molecules, macrocycles, dendrimers, polymers, and multibranched compounds have been synthesized, and the potential applications of organic molecules exhibiting large δ have been demonstrated in three-dimensional (3-D) fluorescence imaging, optical power limitation, lasing up-conversion, 3-D optical data storage, 3-D microfabrication, and the photo-dynamic therapy [4]. In the past decade, small conjugated organic molecules have been the mainstay of TPA materials, and conjugated polymers did not start to draw serious research attention [4]. Since polymeric materials might provide higher local concentration of the absorptive and fluorescent centers without aggregation, improved optochemical and optophysical stability upon heat or intense radiation, and ease of processing and selective thermal cross-linkable to produce glassy and/or gel-type polymeric framework structures [4d], it is interesting to investigate the TPA properties of the polymers. However, the real δ values of typical conjugated polymers, such as ladder-type poly(*p*-phenylene) [5], poly(phenylenevinylene)s [6], polyfluorence [7], poly(*p*-phenyleneethynylene) [8], et al. were rather low. Therefore, there remains a need for polymeric chromophores exhibiting large TPA cross sections.

We consider that polymers with large TPA cross sections can be obtained by employing effective TPA chromophores as the building blocks. In previous works, we have reported the synthesis, one- and two-photon absorption and emission properties of several anthracene-centered polymers with D–π–D motif [9], and they emitted green fluorescence and showed peak δ at 800 nm. In the current paper, we report the synthesis, one- and two-photon absorption, and one- and two-photon emission properties of a novel donor–acceptor–donor-type poly(2,6-anthracenevinylene) derivative (Pr). The D–A–D structure of Pr makes it emit red two-photon excited fluorescence and show the wavelength of the peak δ at a long wavelength region (920 nm). For the sake of comparison, it model compound, 9,10-dicyano-2,6-bis(dihexylaminostyryl)anthracene (M), was again synthesized and measured.

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2. Experimental

2.1. Materials

9,10-Dicyano-2,6-bis(diethylphosphorylmethyl)anthracene and 9,10-Dicyano-2,6-bis(dihexylaminostyryl)anthracene (M) were synthesized according to previous works [10]. All the chemicals were purchased from Aldrich Chemical Co. Other solvents and reagents were analytical grade and used as received. Toluene and tetrahydrofuran were distillated over metallic sodium respectively before use.

2.2. Synthesis

N,N,N′,N′-Tetraoctyl-benzene-1,3-diamine (A): A mixture of benzene-1,3-diamine (1.21 g, 11.2 mmol), K_2CO_3 (13.3 g, 96.4 mmol) and 2-ethylhexyl bromide (10.8 g, 55.9 mmol) in DMF (50 mL) was stirred at 120 °C for 36 h. The mixture was poured into water and extracted with ether, and the resulting organic phase was washed with water three times and then dried over $MgSO_4$. The solvent was evaporated off and the crude product was purified by column chromatography on silica gel using light petroleum ether as the eluent to afford a colorless liquid (4.75 g, 76% yield). ^1H NMR(300 MHz,$CDCl_3$,ppm): δ 7.01(b, 1H), 6.02 (d, 2H, $J=9.0$ Hz), 6.01 (s, 1H), 3.15 (d, 8 H, $J=7.5$ Hz), 1.82 (b, 4H), 1.29 (m, 32H), 0.89 (m, 24H). Anal. Calcd. for $C_{38}H_{72}N_2$: C 81.94; H 13.03; N 5.03. Found: C, 81.90; H, 12.99; N, 5.08.

4,6-Bis(bis(2-ethylhexyl)amino)-benzene-1,3-dialdehyde (B) and *2,4-Bis-di(2-ethyl-hexylamino)-benzaldehyde* (C): N,N,N′,N′-Tetraoctyl-benzene-1,3-diamine (4.2 g, 7.54 mmol) in DMF (10 mL) was added to the mixture of DMF (20 mL) and $POCl_3$ (2.3 g, 15 mmol), and the resulting mixture was stirred at 60 °C for 2 h. The mixture was poured into smashed ice to quench the reaction and then extracted with ether, and the resulting organic phase was washed with water three times and dried over $MgSO_4$. The solvent was evaporated off and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5/1) as the eluent to afford two fractions. First one is 2,4-bis-di(2-ethylhexylamino)-benzaldehyde (**C**) (0.35 g). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 10.00 (s, 1H), 7.65 (d, 1H, $J=9.0$ Hz), 6.31 (d, 1H, $J=9.0$ Hz), 6.20 (d, 1H, $J=3.0$ Hz), 3.26 (d, 4H, $J=6.0$ Hz), 3.06 (d, 4H, $J=6.0$ Hz), 1.79 (m, 2H), 1.64 (m, 2H), 1.17–1.32 (m, 32H), 0.84 (m, 24H). Anal. Calcd. For C39H72N2O: C 80.07; H 12.41; N 4.79. Found: C, 80.03; H, 12.48; N, 4.83. Second one is 4,6-Bis(bis(2-ethylhexyl)amino)-benzene-1,3-dialdehyde (B) (2.1 g). 1H NMR (300 MHz, CDCl3, ppm): δ 9.80 (s, 2H), 8.11 (s, 1H), 6.28 (s, 1H), 3.21 (d, 8H, J=6.0 Hz), 1.72 (b, 4H), 1.23 (m, 32H), 0.82 (m, 24H). Anal. Calcd. for $C_{40}H_{72}N_2O_2$: C 78.37; H 11.84; N 4.57. Found: C, 78.33; H, 12.02; N, 4.60.

2.3. Polymerization

Poly(9,10-dicyano-2,6-anthracenevinylene)-alt-(4,6-bis-dihexylamino-benzene-1,3-diyl) (Pr): *t*-BuOK (0.34 g, 0.31 mmol) was added at once to a degassed solution of 9,10-dicyano-2,6-bis(-diethoxyphosphorylmethyl)anthracene (0.2642 g, 0.500 mmol) and 4,6-bis(bis(2-ethylhexyl)amino)benzene-1,3-dialdehyde (0.3066 g, 0.500 mmol) in anhydrous tetrahydrofuran (10 mL) at room temperature under nitrogen atmosphere. After the resulting mixture was stirred for 5 h, 2,4-bis-di(2-ethylhexylamino)-benzaldehyde (0.102 g, 0.17 mmol) was added under nitrogen atmosphere and stirred for additional 4 h. This mixture was poured into 30 mL of methanol to precipitate the polymer. The collected solid was dissolved into chloroform and filtered through a short pad of silica gel column. The filtrate was concentrated to ~20 mL and precipitated into stirred ethanol (50 mL). The formed precipitate was collected and dried under vacuum to afford Pr as a brown solid. Yield: 0.31 g (74%). ^1H NMR (300 MHz, CDCl3, ppm): δ 10.1 (s, 0.07H, formyl group), 8.46 (b, 4H), 8.16 (d, 2H, $J=9.0$ Hz), 8.04 (s, 1H), 7.90 (d, 2H, $J=15.0$ Hz), 7.40 (d, 2H, $J=15.0$ Hz), 6.98 (s, 1H), 3.01 (m, 8H), 1.26 (m, 32H), 0.86 (m, 24H). Elemental analysis: Anal. Calcd. (%) for $[C_{58}H_{78}N_4]_n$: C, 83.32; H, 9.74; N, 6.94. Found: C, 83.19; H, 9.87; N, 7.16.

2.4. Measurements

^1H NMR spectra were recorded on a JEOL JNM-LA-300 (500 MHz) spectrometer in $CDCl_3$ solutions with tetramethylsilane (TMS) as an internal standard. Molecular weights and polydispersity index were determined using gel permeation chromatography (GPC, Waters 1515 HPLC) equipped with Styrgel columns and using THF as an eluent. The calibration was made with a series of mono-dispersed polystyrene standards. The elemental analysis was performed on Perkin–Elmer 2400. The fluorescence quantum yield Φ_f was determined in THF at room temperature by the literature method using rhodamine B in methanol as the reference [11]. UV–vis absorption spectra were obtained on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried out on a Hitachi F-4600 luminescence spectrophotometer, and the absorption maximum of the chromophore was used as the excitation wavelength.

The two-photon absorption cross-sections of the polymer and its model compound were measured with the two-photon-induced fluorescence method by using the femto-second (fs) laser pulses as described previously [10]. The pulse width and repetition rate of the laser are 60 fs and 1 kHz, respectively. Samples were dissolved in THF at repeat unit concentrations of 1.0×10^{-5} M and the two-photon induced fluorescence intensity was measured at 720–900 nm by using rhodamine B (1.0×10^{-5} M in methanol) as the reference, whose two-photon properties have been well characterized in the literature [12]. The intensities of the two-photon induced fluorescence spectra of the reference and sample under the same measurement conditions were determined and compared. The TPA cross section of sample δ_s, measured by using the two-photon-induced fluorescence measurement technique, can be calculated by using the equation: $\delta_s=[(S_s\Phi_r c_r)/(S_r\Phi_s c_s)]\delta_r$ [13], where the subscripts s and r stand for the sample and reference molecules respectively. S is the integral area of the two-photon fluorescence; Φ is the fluorescence quantum yield and c is the number density of the molecules in solution. δ_r is the TPA cross section of the reference molecule. The errors in the determination of the TPA cross-sections are about 15%.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis and chemical structure of Pr are shown in Scheme 1. For the sake of comparison, 9,10-dicyano-2,6-bis-(*p*-dihexylaminostyryl)-anthracene (M, as listed in Scheme 1) [10] was used as the model compound of the structural unit of Pr. 9,10-dicyano-2,6-bis(diethylphosphorylmethyl)anthracene and M was available from previous study. The alkylation of 1,3-diaminobenzene with 2-ethylhexyl bromide afforded N,N,N′,N′-tetraoctyl-benzene-1,3-diamine (**A**). The formylation of **A** with $POCl_3$/DMF gave a mixture of 4,6-bis(bis(2-ethylhexyl)amino)-benzene-1,3-dialdehyde (**B**) and 2,4-bis(dioctylamino)benzaldehyde (**C**), which were separable by column chromatography on silica gel. To synthesize polymer Pr, the Wittig reaction between 9,10-dicyano-2,6-bis(diethylphosphorylmethyl)anthracene and **B**

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