



Third-order nonlinear optical properties of cyanine dyes with click chemistry modification



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ABSTRACT

A series of organic NIR third-order NLO cyanine dyes were designed and synthesized using a Sonogashira coupling reaction and the high-yielding [2 + 2] click reaction. The photophysical and the click reactions were characterized by means of UV/Vis absorption spectroscopy. The electrochemical properties were characterized by means of cyclic voltammetry. In addition, the third-order nonlinear properties, including the nonlinear susceptibilities and the nonlinear absorption, were measured by using Z-scan techniques. The novel cyanine dyes show excellent water solubility, and many different properties comparing with our previous work. It was surprisingly found that the new click compounds also retained the properties of the original cyanine dye while extending the absorption wavelength to the near infrared region. The fascinating advantages mentioned above were exactly what we need. Furthermore, these dyes with click chemistry modification exhibited a typical reserve saturable absorption (RSA)-saturable absorption (RA) transition and strong nonlinear refraction. All of the click compounds showed the considerable third-order susceptibility $\chi^{(3)}$ values. The results of these studies can provide new molecular-design strategies for third-order nonlinear optical materials for photoelectric and biological fields.

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1. Introduction

Considerable interest has been generated on organic near-infrared (NIR) absorbing nonlinear optical (NLO) materials in recent years for their promise in the important applications, such as optical power-limiting [1,2], two-photon microscopic imaging [3,4], optical data storage [5,6] and photodynamic therapy [7,8]. Previous works have been focused on oil soluble materials such as porphyrins [9], fullerenes [10] and organometallic compounds [11–13]. However, the low water solubility of these organic nonlinear conjugate materials limits their application in the biological field.

Cyanine dyes, a kind of functional dyes, have gained great interest in terms of their potential advantage such as large microscopic polarizabilities, excellent water solubility, tunable optical properties and high extinction coefficients [14–18]. These dyes are considered promising candidates for various applications such as

biological probe, optical power-limiting and future advanced photonic applications [19–21]. However, there are still some problems with NIR absorbing functional cyanine dyes, such as low productivity, synthetic difficulties and so on. Therefore, how to expand the scope of cyanine dye λ_{\max} and optimize their application performance remains a key direction of research in this field today.

Formal [2 + 2] cycloaddition-cycloreversion (CA-CR) between electron alkynes and electron-deficient alkenes has been developed as a convenient and robust method for preparing nonplanar, π -conjugated, donor-acceptor chromophores that exhibit intense, low-energy, intramolecular charge-transfer (ICT) and high third-order optical nonlinearities [22–25]. Hence features render the 1, 3-butadiene CA-CR products attractive for NLO application and the transformations are generally fast, high-yielding, catalyst-free, 100% atom-economic, and the resulting products can be easily purified by precipitation or washing.

Based on the this information and in extension of our interest on the synthesis and feature of new function dyes, it was worth synthesizing the novel cyanine dyes (Fig. 1) by using sample and high-yielding click chemistry and to test its NLO properties. One obvious

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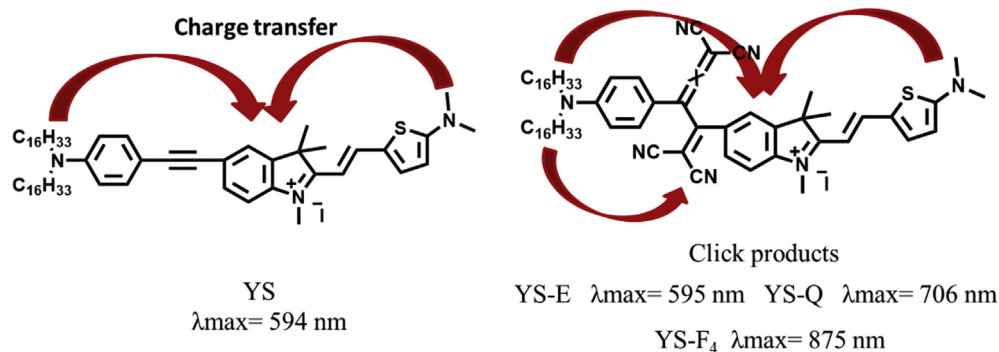


Fig. 1. Structures and properties of cyanine dye **YS** and click products **YS-X**.

feature of the cyanine dyes was the ease in which a broad range of absorptivities could be acquired, and the maximum absorption wavelength reached the near infrared region. Specifically, the large difference in absorption maxima introduced by using click reagents was a useful property of the dye class [26]. Another important consideration was the water solubility of cyanine dyes. Our previous work was explored by oil-soluble materials, which greatly limited its application in biology, so it was important to design synthetic water-soluble dye molecules. The ionized cyanine dye provided the excellent water solubility for biological detection reporters. This allows the dye molecules to be the effective NIR water-soluble nonlinear optical molecules, which are also expected to be used in biological applications in the future.

2. Experimental

2.1. General information

Reagents were purchased from commercial sources and used without further purification. ¹H NMR spectra were measured on a BRAKER AVANCE III HD NMR spectrometer (500 MHz) at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. FT-IR was recorded on a Perkin Elmer LR-64912C Fourier transform infrared spectrometer. Elemental analyses were performed at the Institute of Chemistry Chinese Academy of Sciences, with a Flash EA 1112 instrument. The TGA and DSC were carried out on METTLER TOLEDO TGA/DSC 1/1600HT instrument with a heating rate of 10 °C/min under the protection of nitrogen. UV/Vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using glassy carbon working electrodes, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI 660C instrument in CH₂Cl₂/Bu₄NPF₆ at RT. The NLO properties response by means of the Z-scan technique was measured, employing 21 fs laser pulses at 800 nm delivered by a modelocked Nd:YAG laser. In addition, it has been previously reported that CH₂Cl₂ showed low NLO activity. The NLO property of pure CH₂Cl₂ was also measured at the same conditions to clarify the solvent contribution.

2.2. Synthetic procedures and characterization data for new compounds

2.2.1. N,N-dihexadecyl-4-((2,3,3-trimethyl-3H-indol-5-yl)ethynyl)aniline (**3**)

4-Ethynyl-N,N-dihexadecylaniline (1.8 g, 3.2 mmol) obtained from previous work [27] and 5-bromo-2,3,3-trimethyl-3H-indole

(507.7 mg, 2.1 mmol) prepared by appropriate means [28] were dissolved in 10 mL trimethylamine. After the solution was flushed with bubbling Ar for 40 min, Pd(PPh₃)₂Cl₂ (29.5 mg, 0.042 mmol) and CuI (16.04 mg, 0.084 mmol) were added. The reaction mixture was then stirred at 80 °C for 10 h under an Ar atmosphere. After cooling to room temperature the reaction mixture was diluted with ether (50 mL) and washed with H₂O (2 × 50 mL) and brine (50 mL). The organic phase was dried and evaporated, leaving a red-brown, oily residue. The residue was subjected to rapid silica filtration to give **3** as a yellow oil matter (1.14 g, 75%). R_f (1:8 hexanes: ethyl acetate) = 0.30; ¹H NMR (CDCl₃, 500 MHz): δ = 0.91 (6H, m), 1.29 (58H, m), 1.51 (4H, m), 2.30 (3H, m), 3.29 (4H, m), 6.59 (2H, d, J = 8.5 Hz), 7.38 (2H, d, J = 9.0 Hz), 7.44 (1H, s), 7.48 (2H, d, J = 5.0 Hz) ppm; FT-IR (KBr, cm⁻¹): ν = 3467, 2853, 2199, 1606, 1576, 1519, 1465, 1399, 1369, 1246, 1193, 1152, 1163, 812, 721; MALDI-TOF-MS (dithranol): m/z : calcd for C₅₁H₈₂N₂: 723.23 g mol⁻¹; found: 724.7 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for C₅₁H₈₂N₂ (723.23): C 84.70, H 11.43, N 3.87; found: C 84.71, H 11.43, N 3.85.

2.2.2. 5-((4-(dihexadecylamino)phenyl)ethynyl)-1,2,3,3-tetramethyl-3H-indol-1-ium iodide (**4**)

A black solution of **3** (1.14 g, 1.6 mmol) and CH₃I (1.2 mL, 2.1 mmol) in acetonitrile (5 mL) was heated under reflux for 4.5 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was suspended in ethyl acetate (5 mL) and the solid was collected by vacuum filtration, washed with ethyl acetate and Ether and air dried to give **4** as a dark grey solid (1.09 g, 75%). ¹H NMR (CDCl₃, 500 MHz): δ = 0.92 (9H, m), 1.28 (52H, m), 1.43 (6H, m), 1.56 (4H, m), 3.29 (4H, m), 6.61 (2H, d, J = 8.5 Hz), 7.39 (2H, d, J = 9.0 Hz), 7.43 (1H, s), 7.58 (2H, d, J = 5.0 Hz) ppm; FT-IR (KBr, cm⁻¹): ν = 3468, 2852, 2188, 1615, 1566, 1524, 1464, 1398, 1366, 1246, 1193, 1152, 1163, 812, 721; MALDI-TOF-MS (dithranol): m/z : calcd for C₅₂H₈₄N₂SI: 864.16 g mol⁻¹; found: 865.7 g mol⁻¹ [MH]⁺; elemental analysis calcd (%) for C₅₂H₈₄N₂I (864.16): C 72.27, H 9.80, N 3.24; found: C 72.29, H 9.81, N 3.21.

2.2.3. (E)-5-((4-(dihexadecylamino)phenyl)ethynyl)-2-(2-(5-(dimethylamino)thiophen-2-yl)vinyl)-1,3,3-trimethyl-3H-indol-1-ium iodide (**YS**)

(E)-5-((4-(dihexadecylamino)phenyl)ethynyl)-2-(2-(5-(dimethylamino)thiophen-2-yl)vinyl)-1,3,3-trimethyl-3H-indol-1-ium iodide (**YS**) were synthesized by a condensation reaction of **4** with **5** which was obtained by previous work [29] in the presence of piperidine. After cooling to room temperature, the organic phase was dried and evaporated, leaving a blue solid residue. The residue was subjected to rapid silica filtration to give **YS** as a blue solid (75%). R_f (18:1 CH₂Cl₂: MeOH) = 0.40; ¹H NMR (CDCl₃, 500 MHz):

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