Dyes and Pigments 96 (2013) 189-195

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments



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

Third-order nonlinear optical properties of unsymmetric pentamethine cyanine dyes possessing benzoxazolyl and benzothiazolyl groups

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ARTICLE INFO

Article history: Received 4 April 2012 Received in revised form 10 July 2012 Accepted 10 July 2012 Available online 20 July 2012

Keywords: Cyanine dye Third-order Nonlinear optical material Z-Scan Functional dyes Optical material

1. Introduction

Functional dyes play an important role in material science. Cyanine dyes, which were discovered in the nineteenth century, were used in the field of photography [1]. The developments of cyanine dyes have come into limelight both in experimental and theoretical aspects; they present favorable optical properties and have been explored as important organic functional materials in many fields, such as data storage materials [2], laser disks materials [3], sensitizers in solar cells [4], fluorescence labels in DNA [5–8], protein [9–12] detection and nonlinear optical material [13–16].

It is believed that the existence of intermediate diradical and zwitterionic character in the molecules and the large coupling between these two covalent band resonance forms are responsible for the third-order nonlinear optical (NLO) susceptibilities $\chi^{(3)}$ and the second-order hyperpolarizabilities γ' [17,18] The candidates with intermolecular charge transfer abilities and large polarization were good selections for the third-order NLO materials. The earlier reported research of the third-order NLO properties of cyanine dyes

ABSTRACT

A series of unsymmetric pentamethine cyanine dyes featuring benzoxazolyl and benzothiazolyl groups were synthesized, the structures were characterized by ¹H NMR, UV–vis absorption spectroscopy and mass spectrometry. The dyes with different anions such as chloride, tetraphenylborate and tetra(4-fluorophenyl)borate were also obtained and their solubility can be changed by the choice of the anion part. The third-order nonlinear optical properties were measured by the Z-scan technique with a picosecond laser beam at 532 nm in DMF solution. The third-order nonlinear optical susceptibilities $\chi^{(3)}$ and the second-order hyperpolarizabilities γ' were obtained. The results reveal that these dyes exhibit strong reverse saturable absorption and nonlinear refraction.

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focused on the symmetric cyanine dyes with the four-wave mixing method [19]. Recently, the third-order NLO properties of cyanine dyes were re-investigated and designs were focused on the heteroatom containing symmetric cyanines. The selenium containing symmetric cyanines with different anion parts were looked as potential optical switch materials [20]; and sulfur containing symmetric cyanines with pentamethines were used for the thirdorder NLO research in the solution and the solid state [21]. Although some attention was directed towards the second-order NLO properties for the unsymmetric cyanines [22], little attention has been focused on the unsymmetric heterocyclic cyanine dyes [23,24]. The unsymmetric pentamethine cyanine dyes with either an oxygen or sulfur containing heterocycle were synthesized in this paper, and their third-order NLO properties using the picosecond Zscan technique at 532 nm in N,N-dimethylformamide (DMF) solution are discussed.

2. Experimental section

2.1. General information

All the starting materials were purchased from TCI (Shanghai) Development Co., Ltd. or Sinopharm Chemical Reagent Co., Ltd. All analytic grade solvents (A.R.) were obtained from commercial



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suppliers and used directly. Dyes **3b-f** were synthesized according to the similar procedure of **3a**, dyes **4b-f** were obtained by the similar procedure described for dye **4a**, dyes **5b-f** were prepared by the same procedure as that of **5a**. Melting points were determined on X-4 microscope electron thermal apparatus (Taike, China) without correction. Absorption spectra were taken on U-3900 UV–Vis spectrophotometer. ¹HNMR spectra were recorded on Varian-300 or 400 NMR spectrometer, and TMS or solvent peak were used as an internal standard. Mass spectra were recorded on Finnigan MAT95 mass spectrometer (ESI). IR spectra were recorded on a Ni-colet 5200 FT-IR instrument using solid samples dispersed in KBr pellets. The third-order NLO properties were measured by the Z-scan technique. A Nd:YAG 532 nm laser (EKSPLA) with a pulse width of 21 ps (fwhm) and repetition rate of 10 Hz was used for picosecond Z-scan measurements.

2.2. Synthesis and characterization of compounds 2c-5f

2.2.1. 5-Chloro-3-methyl-2-(4-(N-phenylacetamido)buta-1,3-dien-1-yl)benzothiazol-3-ium iodide (**2c**)

A suspension of **1c** (1.63 g, 5.0 mmol) and 3-(phenylamino)allylidene aniline hydrochloride (1.50 g, 5.0 mmol) in acetic anhydride (7.0 mL) and acetic acid (7.0 mL) was heated under reflux for 2 h. The reaction was cooled to room temperature. After most of the solvent was removed by vacuum distillation, ethyl ether (50.0 mL) was added. The suspension was heated under reflux for 30 min. The solid was collected by filtration and washed with ethyl ether (3×15.0 mL) to afford **2c** as a red solid. Yield 59%, mp 213–214 °C; ¹H NMR (300 MHz, DMSO): δ 8.57 (d, *J* = 13.4 Hz, 1H), 8.34–8.18 (m, 3H), 7.75–7.72 (m, 1H), 7.65–7.54 (m, 3H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 14.7 Hz, 1H), 5.47–5.39 (m, 1H), 3.99 (s, 3H), 1.99 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₀H₁₈ClN₂OS⁺ 369.0828 [M-I⁻]⁺, found 369.0826.

2.2.2. 3-Methyl-2-(5-(3-methylbenzoxazol-2(3H)-ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium chloride (**3a**)

To a mixture of **2a** (0.22 g, 0.50 mmol) and **1b** (0.15 g, 0.50 mmol) in ethanol (12 mL), Et₃N (0.3 mL) was added in portions, and then the mixture was refluxed for 1 h. The reaction was cooled to room temperature, and ethyl ether (20 mL) was added slowly during 0.5 h. The solid was filtrated, washed with ethyl ether (3 \times 10.0 mL) and water (3 \times 10.0 mL) to afford the iodide salt. A solution of the iodide salt in methanol was passed through the anion-exchange resin (Amberlite IRA-400, chloride form), and the resin was washed with methanol. After the concentration of the eluent chloride, the residue was collected to give 3a as dark blue powder. Yield 59%, mp 182-183 °C; IR (KBr, cm⁻¹): 1636, 1577, 1488, 1464, 1357, 1317, 1152, 818. ¹H NMR (300 MHz, DMSO): δ 7.96 (d, J = 6.6 Hz, 2H), 7.71–7.64 (m, 3H), 7.55–7.23 (m, 5H), 6.46 (d, J = 12.2 Hz, 2H), 6.09 (d, J = 12.5 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H). HRMS (ESI⁺): *m*/*z* calcd for C₂₁H₁₉N₂OS⁺ 347.1218 [M-Cl⁻]⁺, found 347.1225.

2.2.3. 5-Chloro-3-methyl-2-(5-(3-methylbenzoxazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium chloride (**3b**)

Dark blue powder, yield 67%, mp 193–194 °C; IR (KBr, cm⁻¹): 1623, 1577, 1500, 1466, 1351, 1303, 1182, 873. ¹H NMR (300 MHz, DMSO): δ 8.05–7.85 (m, 2H), 7.74–7.61 (m, 4H), 7.48–7.40 (m, 2H), 7.33 (d, *J* = 8.3 Hz, 1H), 6.55–6.35 (m, 2H), 6.23 (d, *J* = 13.4 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈ClN₂OS⁺ 381.0828 [M-Cl⁻]⁺, found 381.0821.

2.2.4. 5-Fluoro-3-methyl-2-(5-(3-methylbenzoxazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium chloride (**3c**)

Dark blue powder, yield 45%, mp 197–198 °C; IR (KBr, cm⁻¹): 1623, 1580, 1466, 1351, 1340, 1147, 922. ¹H NMR (300 MHz, DMSO):

δ 8.05–7.91 (m, 2H), 7.74–7.60 (m, 4H), 7.53–7.41 (m, 2H), 7.29–7.16 (m, 1H), 6.56–6.37 (m, 2H), 6.21 (d, J = 13.6 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H). HRMS (ESI⁺): m/z calcd for C₂₁H₁₈FN₂OS⁺ 365.1124 [M-Cl⁻]⁺, found 365.1118.

2.2.5. 5-Chloro-3-methyl-2-(5-(3-methylbenzothiazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium chloride (**3d**)

Dark blue powder, yield 68%, mp 217–218 °C; IR (KBr, cm⁻¹): 1654, 1577, 1498, 1463, 1356, 1323, 1190, 871. ¹H NMR (300 MHz, DMSO): δ 8.05–7.96 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.82–7.53 (m, 5H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 13.4 Hz, 1H), 6.53–6.38 (m, 2H), 3.86, 3.80 (s, 3H), 3.77, 3.71 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈ClN₂S⁺₂ 397.0600 [M-Cl⁻]⁺, found 397.0594.

2.2.6. 5-Fluoro-3-methyl-2-(5-(3-methylbenzothiazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium chloride (**3e**)

Dark blue powder, yield 58%, mp 227–228 °C; IR (KBr, cm⁻¹): 1577, 1495, 1467, 1357, 1318, 1188, 932, 826. ¹H NMR (300 MHz, DMSO): δ 8.06–7.94 (m, 2H), 7.83–7.53 (m, 5H), 7.47–7.37 (m, 1H), 7.31–7.19 (m, 1H), 6.66–6.42 (m, 3H), 3.87, 3.81, 3.78, 3.73 (s, 6H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈FN₂S[±] 381.0895 [M-Cl⁻]⁺, found 381.0900.

2.2.7. 2-(5-(5-Chloro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-5-fluoro-3-methylbenzothiazol-3-ium chloride (**3f**)

Dark blue powder, yield 45%, mp 223–224 °C; IR (KBr, cm⁻¹): 1655, 1578, 1500, 1353, 1219, 1118, 933, 872. ¹H NMR (300 MHz, DMSO): δ 8.04–7.96 (m, 2H), 7.84–7.69 (m, 4H), 7.45–7.34 (d, J = 8.4 Hz, 1H), 7.32–7.21 (s, 1H), 6.57–6.42 (m, 3H), 3.77 (s, 6H). HRMS (ESI⁺): m/z calcd for C₂₁H₁₇ClFN₂S[±] 415.0506 [M-Cl⁻]⁺, found 415.0500.

2.2.8. 3-Methyl-2-(5-(3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)benzoxazol-3-ium tetraphenylborate (4a)

The iodide salt was synthesized in the same way as described in the synthesis of dye **3a**. To a clear solution of the iodide salt (0.060 g, 0.125 mmol) under reflux sodium tetraphenylborate (0.083 g, 0.25 mmol) was added in portions, and then the mixture was heated under reflux for 1 h. The solid was filtrated and washed by ethanol to afford **4a** as dark green powder. Yield 67%, mp 230–231 °C; IR (KBr, cm⁻¹): 2925, 1619, 1579, 1480, 1431, 1357, 1322, 1175, 824. ¹H NMR (300 MHz, DMSO): δ 7.96–7.93 (m, 2H), 7.73–7.64 (m, 4H), 7.52–7.35 (m, 4H), 7.16 (s, 8H), 6.93–6.89 (m, 8H), 6.79–6.75 (m, 4H), 6.54–6.43 (m, 2H), 6.11–6.05 (m, 1H), 3.77 (s, 3H), 3.71 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₉N₂OS⁺ 347.1218 [M-Cl⁻]⁺, found 347.1225; HRMS (ESI⁻): *m/z* calcd for C₂₄H₂₀B⁻ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.9. 2-(5-(5-Chloro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-3-methylbenzoxazol-3-ium tetraphenylborate (**4b**)

Dark green powder, yield 70%, mp > 250 °C; IR (KBr, cm⁻¹): 2926, 1627, 1582, 1479, 1430, 1345, 1182, 1085, 872. ¹H NMR (300 MHz, DMSO): δ 8.04–7.96 (m, 1H), 7.90–7.84 (m, 1H), 7.73–7.61 (m, 4H), 7.51–7.40 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.15 (s, 8H), 6.92–6.87 (m, 8H), 6.78–6.74 (m, 4H), 6.53–6.32 (m, 2H), 6.21 (d, *J* = 13.6 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈ClN₂OS⁺ 381.0828 [M-Cl⁻]⁺, found 381.0821; HRMS (ESI⁻): *m/z* calcd for C₂₄H₂₀B⁻ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.10. 2-(5-(5-Fluoro-3-methylbenzothiazol-2(3H)-ylidene)penta-

1,3-dien-1-yl)-3-methylbenzoxazol-3-ium tetraphenylborate (4c)

Dark green powder, yield 65%, mp > 250 °C; IR (KBr, cm^{-1}): 3047, 1581, 1518, 1471, 1431, 1346, 1175, 930. $^1{\rm H}$ NMR (300 MHz,

DMSO): δ 8.00–7.90 (m, 2H), 7.69 (s, 4H), 7.45 (s, 2H), 7.14 (s, 8H), 6.89 (m, 8H), 6.78–6.75 (m, 4H), 6.53–6.34 (m, 3H), 6.20 (s, 1H), 3.74 (s, 3H), 3.68 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈FN₂OS⁺ 365.1124 [M-Cl⁻]⁺, found 365.1118; HRMS (ESI⁻): *m/z* calcd for C₂₄H₂₀B⁻ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.11. 5-Chloro-3-methyl-2-(5-(3-methylbenzothiazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium tetraphenylborate (**4d**)

Dark green powder, yield 79%, mp > 250 °C; IR (KBr, cm⁻¹): 2925, 1570, 1450, 1342, 1303, 1116, 1032, 863. ¹H NMR (300 MHz, DMSO): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.84 (s, 2H), 7.73 (t, *J* = 12.7 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.16 (s, 8H), 6.91 (s, 8H), 6.77 (s, 4H), 6.53–6.40 (m, 4H), 3.76 (s, 6H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈ClN₂S¹/₂ 397.0600 [M-Cl⁻]⁺, found 397.0594; HRMS (ESI⁻): *m/z* calcd for C₂₄H₂₀B⁻ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.12. 5-Fluoro-3-methyl-2-(5-(3-methylbenzothiazol-2(3H)ylidene)penta-1,3-dien-1-yl)benzothiazol-3-ium tetraphenylborate (**4e**)

Dark green powder, yield 77%, mp $>250\ ^\circ\text{C};$ IR (KBr, cm $^{-1})$: 2924, 1572, 1463, 1352, 1320, 1177, 931. ^1H NMR (300 MHz, DMSO): δ 8.03–7.91 (m, 2H), 7.81–7.54 (m, 5H), 7.44–7.40 (m, 1H), 7.15 (s, 8H), 6.93–6.88 (m, 8H), 6.79–6.75 (m, 4H), 6.63–6.40 (m, 4H), 3.84, 3,79 (s, 3H), 3.76, 3.71 (s, 3H). HRMS (ESI^+): m/z calcd for C_{21}H_{18}FN_2S^{1}_{2} 381.0895 [M-Cl⁻]⁺, found 381.0900; HRMS (ESI⁻): m/z calcd for C_{24}H_{20}B $^-$ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.13. 2-(5-(5-Chloro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-5-fluoro-3-methylbenzothiazol-3-ium tetraphenylborate (**4f**)

Dark green powder, yield 82%, mp > 250 °C; IR (KBr, cm $^{-1}$): 2925, 1572, 1465, 1344, 1254, 1172, 993, 873. ¹H NMR (300 MHz, DMSO): δ 7.98 (s, 2H), 7.82–7.69 (m, 4H), 7.41 (s, 1H), 7.26 (s, 1H), 7.14 (s, 8H), 6.90 (s, 8H), 6.76 (s, 4H), 6.55–6.40 (m, 3H), 3.75 (s, 6H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇ClFN₂S[±] 415.0506 [M-Cl⁻]⁺, found 415.0500; HRMS (ESI⁻): *m/z* calcd for C₂₄H₂₀B⁻ 319.1658 [B(C₆H₅)₄]⁻, found 319.1664.

2.2.14. 3-Methyl-2-(5-(3-methylbenzothiazol-2(3H)-ylidene) penta-1,3-dien-1-yl)benzoxazol-3-ium tetrakis(4-fluorophenyl) borate (5a)

The iodide salt was synthesized in the same way as described in the synthesis of dye **3a**. To the solution of the iodide salt (0.060 g, 0.125 mmol) under reflux sodium tetra(4-fluorophenyl)borate (0.52 g, 0.125 mmol) was added in portions, then mixture was heated under reflux for 1 h. The residue was purified via silica gel chromatography (CH₂Cl₂/CH₃OH = 10/1) to afford **5a** as dark green powder. Yield 29%, mp 231–232 °C; IR (KBr, cm⁻¹): 2927, 1580, 1460, 1357, 1321, 1149, 923, 815. ¹H NMR (300 MHz, DMSO): δ 7.98–7.93 (m, 2H), 7.72–7.63 (m, 4H), 7.54–7.35 (m, 4H), 7.03 (s, 8H), 6.76–6.70 (m, 8H), 6.53–6.42 (m, 2H), 6.09–6.05 (m, 1H), 3.76 (s, 3H), 3.71 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₉N₂OS⁺ 347.1218 [M-Cl⁻]⁺, found 347.1225; HRMS (ESI⁻): *m/z* calcd for C₂₄H₁₆BF₄ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

2.2.15. 2-(5-(5-Chloro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-3-methylbenzoxazol-3-ium tetrakis(4-fluorophenyl) borate (**5b**)

Dark green powder, yield 31%, mp 222–223 °C; IR (KBr, cm⁻¹): 2927, 1580, 1463, 1341, 1216, 1174, 1083, 871. ¹H NMR (300 MHz, DMSO): δ 8.04–7.84 (m, 2H), 7.73–7.61 (m, 4H), 7.51–7.39 (m, 2H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.07–6.99 (m, 8H), 6.75–6.69 (m, 8H), 6.53–6.32 (m, 2H), 6.21 (d, *J* = 13.7 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H). HRMS (ESI⁺): *m*/*z* calcd for C₂₁H₁₈ClN₂OS⁺ 381.0828 [M-Cl⁻]⁺,

found 381.0821; HRMS (ESI⁻): m/z calcd for C₂₄H₁₆BF₄⁻ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

2.2.16. 2-(5-(5-Fluoro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-3-methylbenzoxazol-3-ium tetrakis(4-fluorophenyl) borate (**5c**)

Dark green powder, yield 22%, mp 216–217 °C; IR (KBr, cm⁻¹): 2927, 1578, 1465, 1338, 1209, 1150, 921, 834. ¹H NMR (400 MHz, DMSO): δ 8.02–7.93 (m, 2H), 7.79–7.60 (m, 4H), 7.52–7.42 (m, 2H), 7.29–7.17 (m, 1H), 7.05 (s, 8H), 6.77–6.72 (m, 8H), 6.55–6.37 (m, 2H), 6.20 (d, *J* = 13.0 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈FN₂OS⁺ 365.1124 [M-Cl⁻]⁺, found 365.1118; HRMS (ESI⁻): *m/z* calcd for C₂₄H₁₆BF₄⁻ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

2.2.17. 2-(5-(5-Chloro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-3-methylbenzothiazol-3-ium tetrakis(4-fluorophenyl)borate (**5d**)

Dark green powder, yield 37%, mp 230–231 °C; IR (KBr, cm⁻¹): 2927, 1573, 1463, 1345, 1212, 1122, 983, 870. ¹H NMR (400 MHz, DMSO): δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 2H), 7.77 (t, *J* = 12.7 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.05 (s, 8H), 6.77–6.72 (m, 9H), 6.55–6.47 (m, 3H), 3.78 (s, 6H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈ClN₂S¹₂ 397.0600 [M-Cl⁻]⁺, found 397.0594; HRMS (ESI⁻): *m/z* calcd for C₂₄H₁₆BF⁻₄ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

2.2.18. 2-(5-(5-Fluoro-3-methylbenzothiazol-2(3H)-ylidene)penta-1,3-dien-1-yl)-3-methylbenzothiazol-3-ium tetrakis(4fluorophenyl)borate (**5e**)

Dark blue powder, yield 34%, mp 231–232 °C; IR (KBr, cm⁻¹): 2927, 1577, 1460, 1352, 1207, 1148, 1112, 932, 815. ¹H NMR (400 MHz, DMSO): δ 8.05–7.93 (m, 2H), 7.85–7.57 (m, 5H), 7.46–7.39 (m, 1H), 7.27–7.19 (m, 1H), 7.07–7.06 (s, 8H), 6.78–6.73 (m, 8H), 6.65–6.42 (m, 3H), 3.86, 3.81 (s, 3H), 3.78, 3.73 (s, 3H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₈FN₂S[±]₂ 381.0895 [M-Cl⁻]⁺, found 381.0900; HRMS (ESI⁻): *m/z* calcd for C₂₄H₁₆BF⁻₄ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

2.2.19. 5-Chloro-2-(5-(5-fluoro-3-methylbenzothiazol-2(3H)ylidene)penta-1,3-dien-1-yl)-3-methylbenzothiazol-3-ium tetrakis(4-fluorophenyl)borate (**5f**)

Dark green powder, yield 39%, mp 225–226 °C; IR (KBr, cm⁻¹): 2925, 1577, 1464, 1344, 1211, 1153, 931, 871. ¹H NMR (300 MHz, DMSO): δ 7.97 (s, 2H), 7.80–7.71 (m, 4H), 7.39 (s, 1H), 7.24 (s, 2H), 7.03 (s, 8H), 6.71 (s, 8H), 6.50 (s, 2H), 3.75 (s, 6H). HRMS (ESI⁺): *m/z* calcd for C₂₁H₁₇ClFN₂S⁺₂ 415.0506 [M-Cl⁻]⁺, found 415.0500; HRMS (ESI⁻): *m/z* calcd for C₂₄H₁₆BF⁻₄ 391.1281 [B(C₆H₄F)₄]⁻, found 391.1287.

3. Results and discussion

3.1. Synthesis

The synthesis of dyes **3–5** were represented in Scheme 1, the iodide **1a-d** were synthesized by the reaction of starting materials with methyl iodide in DMF solution for 24 h as reported in our previous work [25]. The intermediates **2a-c** were synthesized from **1a-c** with 3-(phenylamino)allylidene aniline hydrochloride according to the reported references [26] with some modification. The iodide dyes **3a-f** were obtained from the reaction of **2a-c** with **1b-d**, then ion-exchange procedures were taken using IRA-400(Cl), NaB(C₆H₅)₄ and NaB(C₆H₄F)₄ to afford the final products according to references [27,28]. Dyes **4a-f** were obtained by filtration and washed by hot ethanol. Dyes **5a-f** were obtained by silica gel chromatography (CH₂Cl₂/CH₃OH = 10/1) with *R*_f values were nearly



3a: X¹=O, R¹=H, X²=S, R²=H, X=CI **4a**: X¹=O, R¹=H, X²=S, R²=H, X=B(C₆H₅)₄ **5a**: X¹=O, R¹=H, X²=S, R²=H, X=B(C₆H₄F)₄ **3b:** X¹=O, R¹=H,X²=S, R²=CI,X=CI **4b:** X¹=O,R¹=H,X²=S,R²=CI,X=B(C₆H₅)₄ **5b:** X¹=O,R¹=H,X²=S,R²=CI,X=B(C₆H₄F)₄ **3c**: X¹=O, R¹=H,X²=S, R²=F,X=CI **4c**: X¹=O, R¹=H,X²=S, R²=F,X=B(C₆H₅)₄ **5c**: X¹=O, R¹=H,X²=S, R²=F,X=B(C₆H₄F)₄ **3d:** X¹=S, R¹=H,X²=S, R²=CI,X=CI **4d:** X¹=S, R¹=H,X²=S, R²=CI,X=B(C₆H₅)₄ **5d:** X¹=S, R¹=H,X²=S, R²=CI,X=B(C₆H₄F)₄ **3e:** X¹=S, R¹=H,X²=S, R²=F,X=CI **4e:** X¹=S, R¹=H,X²=S, R²=F,X=B(C₆H₅)₄ **5e:** X¹=S, R¹=H,X²=S, R²=F,X=B(C₆H₄F)₄ **3f:** X¹=S. R¹=CI,X²=S. R²=F,X=CI **4f:** X¹=S, R¹=CI,X²=S, R²=F,X=B(C₆H₅)₄ **5f:** X¹=S, R¹=CI,X²=S, R²=F,X=B(C₆H₄F)₄

Scheme 1. The synthesis of dyes 3–5.

at 0.60, while the corresponding iodide salts cannot be washed out. Their structures were characterized by ¹H NMR spectroscopy and mass spectrometry (ESI). The ¹H NMR spectra of dyes **3b**, **4b** and **5b** with different anions are shown in Fig. 1. The numbers of the protons indicated the full changes of the anion parts of **4b** and **5b**.

Dyes **5a-f** with a tetra(4-fluorophenyl)borate anion possess favorable solubility in methanol, ethanol and DMF, while dyes 4a-f featuring a tetraphenylborate anion have poor solubility in the same solvents. Dyes **3a-f** with a chloride counter ion could be dissolved in DMF, but possessed very low solubility in methanol and ethanol.



Fig. 1. The ¹H NMR spectra of dyes 3b, 4b and 5b.

3.2. Absorption spectra

The UV–vis absorption spectra of dyes **3**–**5** were measured in DMF solution at a concentration of 1×10^{-5} mol L⁻¹. The absorption spectra of dyes **4a-f** were presented in Fig. 2; and the absorption spectra of dyes **3a-f** and **5a-f** were presented in Fig. S1 (supplementary data). As shown in Fig. 2 and Fig. S1, the absorption bands and absorption intensities of these dyes were similar. Comparing the influence of different anions, the absorption bands did not show any obvious changes with the variation of anion from Cl⁻ to $[B(C_6H_5)_4]^-$ and $[B(C_6H_4F-p)_4]^-$. Meanwhile, the fluorine (**3c-5c**, **3e-5e** and **3f-5f**) or chlorine (**3b-5b**, **3d-5d** and **3f-5f**) substituents on the benzothiazolyl or benzoxazolyl rings just made a slightly shift. However, the maximum absorption bands were obviously affected by the different heteroatoms, and the maximum absorption bands red-shifted by about 20 nm with the change of oxygen heteroatom to sulfur as expected [32].

3.3. Nonlinear optical (NLO) properties

The measurements of third-order NLO properties were performed on all compounds using the Z-scan technique at 532 nm in DMF solution. In order to get an appropriate transmittance (T_0), Dyes **3d-f**, **4d-f** and **5d-f** were measured at the concentration of 1×10^{-4} mol L⁻¹, dyes **3a-c**, **4a-c** and **5a-c** were measured at the concentration of 5×10^{-5} mol L⁻¹.

The open-aperture Z-scan signals of dyes **3a-f, 4a-f** and **5a-5f** are shown in Fig. 3 and Fig. S2 (supplementary data) respectively. As can be seen from Fig. 3 and Fig. S2, there is a dip in the signal around the sample position of Z = 0 mm, indicative of reduced transmission of 532 nm pulses at the focus, caused by a reverse saturable nonlinear absorption. The light transmittance (*T*) is a function of the sample's *Z* position (against focal point Z = 0). The nonlinear absorption data can be obtained from Eq. (1) [29], where α_0 and α are linear and effective third-order NLO absorptive coefficients. τ is the time, and *L* is the optical path.

$$T(Z) = \frac{\alpha_0}{\sqrt{\pi}\alpha I_i(Z)(1 - e^{-\alpha_0 L})} \int_{-\infty}^{+\infty} \ln\left[1 + \alpha I_i(Z)\frac{1 - e^{-\alpha_0 L}}{\alpha_0}e^{-\tau^2}\right] d\tau$$
(1)



Fig. 2. UV-vis spectra of dyes 4a-f.



Fig. 3. The open-aperture Z-scan signals of dye 3d (Cycles are the test data points and line is the fit curve).

The close-aperture Z-scan signals of dyes **3a-f, 4a-f** and **5a-5f** are shown in Fig. 4 and Fig. S3 (supplementary data) respectively. The strong nonlinear refractions were exhibited for dyes. The valleypeak shape presented a positive nonlinear refraction for the samples, which indicated a self-focusing behavior. The nonlinear refractive data can be obtained from the ratio of the closed aperture transmittance divided the open aperture transmittance. The effective third-order nonlinear refractive index n_2 can be calculated from the equations: $\Delta Z_{V-P} = 1.72\pi\omega_0^2/\lambda$, $n_2^{\text{eff}} = \lambda \alpha_0 \Delta T_{V-P}/[0.812\pi I$ $(1-e^{-\alpha L})]$, where ΔZ_{V-P} is the difference between the normalized transmittance values at the valley and peak positions, *L* is the sample thickness, λ is the wavelength of the laser, *I* is the peak irradiation intensity at focus and α_0 is the linear coefficient [30]. The effective third-order nonlinear optical (NLO) susceptibility values of cyanine dyes **3–5** can be derived from the equations: $\chi_1^{(3)} = 9 \times 10^8 \varepsilon_0 n_0^2 c^2 \beta/$ ($4\omega\pi$), $\chi_R^{(3)} = cn_0^2 n_2/(80\pi)$, $\chi^{(3)} = [(\chi_1^{(3)})^2 + (\chi_R^{(3)})^2]^{1/2}$. The secondorder hyperpolarizabilities γ' of the compounds were obtained by equation: $\gamma' = \chi^{(3)}/[N ((n_0^2+2)/3)^4]$, where *N* is the density of



Fig. 4. The close-aperture Z-scan signals of dye 4d (Cycles are the test data points and line is the fit curve).

Table 1
Key parameters related to NLO properties of dyes 3–5 .

Dyes	$T_0^{\mathbf{b}}$	$n_2^{\rm c}(10^{-18} {\rm m}^2 {\rm W}^{-1})$	$\beta^{d}(10^{-11} \text{ m W}^{-1})$	$\chi_R^{(3)} (10^{-12} \text{ esu})$	$\chi_I^{(3)} (10^{-12} \text{ esu})$	$\chi^{(3)} (10^{-12} \text{ esu})$	γ' (10 ⁻³² esu)	$\chi_{R}^{(3)}/\chi_{I}^{(3)}$
3a ^a	0.82	2.40	0.75	1.86	0.24	1.87	1.88	7.75
3b ^a	0.79	2.80	1.30	2.17	0.42	2.21	2.04	5.17
3c ^a	0.82	2.40	0.82	1.86	0.26	1.88	1.88	7.15
3d ^a	0.75	4.50	5.60	3.48	1.83	3.94	1.98	1.90
3e ^a	0.80	4.50	3.80	3.48	1.24	3.70	1.86	2.80
3f ^a	0.82	3.20	3.60	2.48	1.17	2.74	1.37	2.11
4a ^a	0.78	4.00	1.80	3.09	0.59	3.15	3.16	5.23
4b ^a	0.68	5.50	2.60	4.26	0.85	4.34	4.32	5.11
4c ^a	0.73	3.90	1.50	3.02	0.49	3.06	3.06	6.06
4d ^a	0.81	3.40	4.10	2.63	1.34	2.95	1.47	1.96
4e ^a	0.75	4.90	4.60	3.79	1.50	4.07	2.04	2.52
4f ^a	0.79	3.90	4.60	3.02	1.50	3.38	1.69	2.01
5a ^a	0.76	4.30	2.20	3.33	0.72	3.41	3.42	4.62
5b ^a	0.73	4.40	1.90	3.40	0.62	3.46	3.46	5.48
5c ^a	0.77	3.10	1.30	2.40	0.42	2.44	2.44	5.71
5d ^a	0.80	4.10	5.20	3.17	1.70	3.61	1.81	1.86
5e ^a	0.77	4.90	4.80	3.79	1.57	4.09	2.06	2.41
5f ^a	0.80	3.90	3.80	3.02	1.24	3.27	1.64	2.43

^a With picosecond laser beam at 0.2 μ J.

^b The light transmittance.

^c The third-order nonlinear refractive index.

^d The third-order nonlinear absorptive index.

molecules in the unit of number of molecules per cm³ and n_0 is the linear refractive index of the DMF ($n_0 = 1.4305$). The detailed parameters of nonlinear optical (NLO) properties of these dyes were collected in Table 1.

From Table 1, it is found that the third-order nonlinear optical (NLO) susceptibility $\chi^{(3)}$ and second-order hyperpolarizabilities γ' of dyes **3–5** are up to 10⁻¹² and 10⁻³² esu under picosecond laser bean irradiation at 532 nm, respectively. To dyes **3d-f**, **4d-f** and **5df**, the values of $\chi_R^{(3)}$ were at the level of 10^{-12} esu, with the imaginary parts at the same magnitude. While the $\chi_R^{(3)}$ values of dyes **3ac**, **4a-c** and **5a-c** were at the level of 10^{-12} esu, the imaginary parts were nearly an order of magnitude lower. The $\chi_R^{(3)}/\chi_R^{(3)}$ values of dyes **3a-c**, **4a-c** and **5a-c** were from 4.62 to 7.75, nearly two times more than those of dyes **3d-f**, **4d-f** and **5d-f**, whose $\chi_R^{(3)}/\chi_L^{(3)}$ values were from 1.90 to 2.80. Comparing the influence of different anions from Cl^- to $[B(C_6H_5)_4]^-$ and $[B(C_6H_4F)_4]^-$, the third-order NLO susceptibility $\chi^{(3)}$ and second-order hyperpolarizabilities γ' values do not show any obvious change. When the different substituents Cl and F were taken into consideration, it can be seen that the different substituents have little influence on the third-order NLO properties of these dyes. However, the influence of different heteroatoms could not be neglected, when one oxygen atom was replaced by one sulfur atom, the $\chi^{(3)}$ values decreased, while the $\chi_R^{(3)}/\chi_I^{(3)}$ values increased. The $\chi^{(3)}$ values of cyanine dyes with two sulfur atoms were

The $\chi^{(3)}$ values of cyanine dyes with two sulfur atoms were higher than cyanine dyes with one oxygen atom and one sulfur atom. As many references reported, sulfur atoms possessed stronger electron donation properties (less electronegative) compared with oxygen atoms [31,32]. Therefore, the distribution of the electronic density will be more equally shared between sulfur and carbon than between oxygen and carbon. Consequently, the π orbitals in sulfur-containing aromatic heterocycles are better delocalized than in molecules containing oxygen. The effect of this contribution will also be a reduction in the energy of the π – π * transition, and a higher hyperpolarizability would be consequently obtained. Besides, with ion-exchange procedures, dyes **5a-f** with anion [B(C₆H₄F)₄]⁻ possessed good solubility. This advantage will be helpful in fabrication of nonlinear optical device.

The results of the $\chi_{R}^{(3)}/\chi_{l}^{(3)}$ values do not show the big difference with different anion parts [20], and the third-order NLO properties of the title compounds show moderate abilities comparing with recently reported sulfur containing polymethine dyes [21]. This

indicated that the terminal cation structures would be hopeful candidates for the next stage.

4. Conclusion

A series of novel unsymmetric pentamethine cyanine dyes were synthesized and their UV–vis absorption spectra were reported. Dyes with a tetra(4-fluorophenyl)borate counter anion have favorable solubility in common solvents. The third-order nonlinear optical properties were measured with Z-scan technique at 532 nm in DMF solution. The third-order nonlinear optical susceptibility $\chi^{(3)}$ and the second-order hyperpolarizabilities γ' of these dyes were obtained under picosecond laser bean irradiation with the energy of 0.2 µJ. It was found that these dyes exhibit reverse saturable nonlinear absorption and strong nonlinear refraction. The third-order NLO susceptibility $\chi^{(3)}$ and second-order hyperpolarizabilities γ' were at the level of 10^{-12} and 10^{-32} esu. When one oxygen atom was replaced by one sulfur atom, the values of $\chi_R^{(3)}/\chi_1^{(3)}$ increased, while the $\chi_1^{(3)}$ values decreased.

Acknowledgements

The project is financially supported from National Natural Science Foundation of China (51273136, 20902065, 21071105), the National High Technology Research and Development Program of China (863 Program, SQ2009AA06XK1482331), the Natural Science Fund (BK2009113) in Jiangsu Province and the Project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.dyepig.2012.07.007.

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