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

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ABSTRACT

A series of unsymmetric pentamethine cyanine dyes featuring benzoxazolyl and benzothiazolyl groups were synthesized, the structures were characterized by ^{1}H 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.

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 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 third-order 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 Z-scan 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. ^{1}HNMR 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; ^{1}H 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 $C_{20}H_{18}ClN_2OS^+$ 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), Et_3N (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 × 10.0 mL) and water (3 × 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. ^{1}H 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 $C_{21}H_{19}N_2OS^+$ 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. ^{1}H 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 $C_{21}H_{18}ClN_2OS^+$ 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. ^{1}H 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 $C_{21}H_{18}FN_2OS^+$ 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. ^{1}H 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 $C_{21}H_{18}ClN_2S_2^+$ 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. ^{1}H 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 $C_{21}H_{18}FN_2S_2^+$ 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. ^{1}H 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 $C_{21}H_{17}ClFN_2S_2^+$ 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. ^{1}H 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 $C_{21}H_{19}N_2OS^+$ 347.1218 [M-Cl$^-$]$^+$, found 347.1225; HRMS (ESI$^-$): *m*/*z* calcd for $C_{24}H_{20}B^-$ 319.1658 [B(C_6H_5)$_4$]$^-$, 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. ^{1}H 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 $C_{21}H_{18}ClN_2OS^+$ 381.0828 [M-Cl$^-$]$^+$, found 381.0821; HRMS (ESI$^-$): *m*/*z* calcd for $C_{24}H_{20}B^-$ 319.1658 [B(C_6H_5)$_4$]$^-$, 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}H NMR (300 MHz,