

The Synthesis of Third-order Optical Nonlinear Organic Polyheterocyclic Materials

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Abstract: Synthesis of the third-order nonlinear materials: bis (1,4-dihydroxynaphthalene) tetrathiafulvalene and bis (1,4-dialkoxylnaphthalene) tetrathiafulvalene has been achieved in four steps, starting from 2,3-dichloro-1,4-naphthaquinone. The materials exhibit larger third-order nonlinear optical susceptibilities $\chi^{(3)}$.

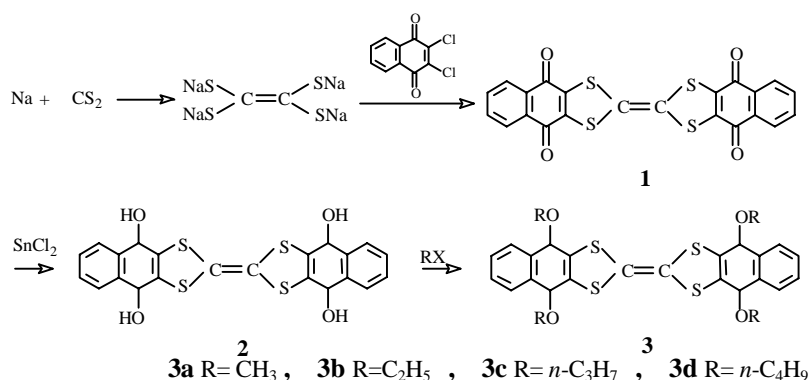
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The drive toward miniaturization of electronic devices has renewed interest in the feasibility and applications of molecular electronics. In the rapidly growing field the third-order nonlinear optical (NLO) organic materials are at the forefront of the research¹⁻³. Polycyclic and polyheterocyclic conjugated molecules with electron-donating and electron-accepting substituents have a large nonlinear electronic polarizability caused by the large dipole moment charge in the process from the ground state to the excited state by optical radiation^{4,5}. We have studied the third-order nonlinear optical properties of bis(1,4-dihydroxynaphthalene) tetrathiafulvalene, bis (1,4-dialkoxylnaphthalene)tetrathiafulvalene and some other kind of polyheterocyclic material⁶⁻⁸. Bis (1,4-naphthaquinone) tetrathiafulvalene **1**, bis (1,4-dihydroxynaphthalene)tetrathiafulvalene **2** and bis (1,4 -dial-koxynaphthalene)tetrathiafulvalene **3a-d** are the new materials with symmetrically poly-heterocyclic structure and different substituents. They were synthesized in four steps (shown in **Scheme 1**).

Tetrathiafulvalene (TTF) and their CT complexes have been synthesized as synthetic materials and organic superconductors⁹. Bis (1,4-naphthaquinone)tetrathiafulvalene **1** was synthesized by the condensation of carbon disulfide, soduim and 2, 3-dichloro-1, 4-naphthaquinone in DMF. After reduction it was reacted with different alkylating agents to yield bis (1,4-dihydroxynaphthalene)tetrathiafulvalene **2** and bis (1,4-dialkoxylnaphthalene)tetrathiafulvalene **3a-d**.

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Scheme 1



Experimental

The melting points were measured on the WRS-T digital melting apparatus. The $^1\text{H-NMR}$ were obtained on JEOL FX-90Q spectrometers using DMSO as solvent. IR, MS were recorded on Hitachi 260-511 and Finnigan MAT 200GS-MS spectrometers respectively. Microanalysis was carried out on PE-2400 instrument.

Procedure for bis(1,4-naphthaquinone) tetrathiafulvalene 1

Sodium 4.2 g (0.18 mol) was suspended in DMF 40 mL and carbon disulfide 23g (0.30 mol) was added at $0\sim 5^\circ\text{C}$. The mixture was stirred for 2~3 hr and 2,3-dichloro-1,4-naphthaquinone 20 g (0.088 mol) was added. The mixture was stirred for 15~20 hr. The resulting precipitate was filtered, washed with methanol and DMF to give a pale green powder, yield 85%, mp $314\sim 315^\circ\text{C}$. Anal. calcd. for $\text{C}_{22}\text{H}_8\text{O}_4\text{S}_4$: C, 56.90, H, 1.73. Found: C, 57.12, H, 1.51.

Procedure for bis(1,4-dihydroxynaphthalene) tetrathiafulvalene 2

Bis(1,4-naphthaquinone)tetrathiafulvalene 10 g (0.021 mol) was suspended in methanol 100 mL and tin dichloride 70 g, 32% hydrochloride acid 10 mL were added. The mixture was refluxed for 15~20 hr. The reaction mixture was poured into water (200 mL) and the precipitate was collected by filtration, washed with methanol to give the product, yield 70%, mp $215\sim 216^\circ\text{C}$, Ms: (m/z) 468 (M^+ , 100%). The compound was easily oxidized by air. Anal. calcd. for $\text{C}_{22}\text{H}_{12}\text{O}_4\text{S}_4$: C, 56.41, H, 2.56. Found: C, 56.53, H, 2.42.

General procedure for bis(1,4-dialkoxynaphthalene) tetrathiafulvalene 3

Bis(1,4-dihydroxynaphthalene)tetrathiafulvalene 0.016 mol was suspended in propanone 50 mL and potassium carbonate 10 g and alkyl halide 0.069 mol were added. The

mixture was refluxed for 10~12 hr. After cooling the reaction mixture was poured into water (200 mL) and the precipitate was collected by filtration, recrystallized from DMF.

Bis (1,4-dimethoxynaphthalene) tetrathiafulvalene 3a

Pale yellow powder, yield 67%, mp 207~208°C, Ms: (*m/z*) 524 (M+, 100%). IR (KBr cm^{-1}): $\nu = 2934, 2841, 1358, 1081$. $^1\text{H-NMR}$ (in DMSO) δ ppm: 7.98-8.10 (m, 4H), 7.44-7.56 (m, 4H), 4.06-4.13 (s, 12H). Anal. calcd. for $\text{C}_{26}\text{H}_{20}\text{O}_4\text{S}_4$: C, 59.54, H, 3.82. Found: C, 59.72, H, 3.67

Bis (1,4-diethoxynaphthalene) tetrathiafulvalene 3b

Pale yellow powder, yield 64%, mp 193~195°C, Ms: (*m/z*) 580 (M+, 100%). IR (KBr cm^{-1}): $\nu = 2976, 2929, 2883, 1346, 1070$. $^1\text{H-NMR}$ (in DMSO) δ ppm: 7.80-8.01 (m, 4H), 7.39-7.51 (m, 4H), 4.07-4.36 (q, 8H), 1.46-1.71 (t, 12H, $J=10.2$ Hz). Anal. calcd. for $\text{C}_{30}\text{H}_{28}\text{O}_4\text{S}_4$: C, 62.07, H, 4.83. Found: C, 62.30, H, 4.81

Bis (1,4-dipropoxynaphthalene) tetrathiafulvalene 3c

Pale yellow powder, yield 63%, mp 187~189°C, Ms: (*m/z*) 636 (M+, 100%). IR (KBr cm^{-1}): $\nu = 2962, 2933, 1874, 1337, 1079$. $^1\text{H-NMR}$ (in DMSO) δ ppm: 7.90-8.03 (m, 4H), 7.32-7.52 (m, 4H), 4.01-4.20 (q, 8H), 1.86-2.10 (q, 8H), 1.08-1.32 (t, 12H, $J=9.0$, Hz). Anal. calcd. for $\text{C}_{34}\text{H}_{36}\text{O}_4\text{S}_4$: C, 64.15, H, 5.66. Found: C, 64.39, H, 5.44

Bis (1,4-dibutoxynaphthalene) tetrathiafulvalene 3d

Pale yellow powder, yield 61%, mp 166~168°C, Ms: (*m/z*) 692 (M+, 100%). IR (KBr cm^{-1}): $\nu = 2954, 2931, 2870, 1377, 1020$. $^1\text{H-NMR}$ (in DMSO) δ ppm: 7.88-8.04 (m, 4H), 7.37-7.47 (m, 4H), 3.97-4.07 (q, 8H), 1.43-1.97 (m, 16H), 0.95-1.12 (t, 12H, $J=6.4$ Hz). Anal. calcd. for $\text{C}_{38}\text{H}_{44}\text{O}_4\text{S}_4$: C, 65.90, H, 6.65. Found: C, 66.08, H, 6.37.

The third-order nonlinear optical properties of materials

The phase-matched three-dimensional degenerate four-wave mixing (3D DFWM) was used as the nonlinear technique, which provided information about the size of susceptibilities $\chi^{(3)}$. It was performed with a Q-switched frequency-double YAG laser with a wavelength of 1064 nm⁸. In our experiment the medium with known $\chi^{(3)}$ is DMF solution containing 2.5×10^{-4} mol L⁻¹ of material. The $\chi^{(3)}$ value of the samples at 1064 nm deduced and calculated from the experimental results are listed in **Table 1** and that is considerable large for such small organic molecules in solution.

Table 1 The $\chi^{(3)}$ of materials

Material	R	UV/ λ max	n	I ₄ /I _{4S}	$\chi^{(3)}$ (/10 ⁻¹³ esu)
2	H	< 400	1.4305	2.25	5.94
3a	CH ₃	350	1.4372	1.75	5.29
3b	C ₂ H ₅	375	1.4369	1.60	5.05
3c	n - C ₃ H ₇	374	1.4389	1.20	4.37
3d	n - C ₄ H ₉	372	1.4363	1.25	4.48

In summary the simple method for the preparation of bis (1,4-dialkoxylnaphthalene) tetrathiafulvalene was provided in good yields. Bis (1,4-dialkoxylnaphthalene) tetrathiafulvalene consisted of two parts of structure, namely polycycle (dialkoxylnaphthalene) and heterocycle (TTF). The special structure makes the molecules have stronger intramolecular charge-transfer, intermolecular π - π interaction and larger transition moments μ_{xnm} at lower excitation energy E_{gm} . As a result the materials exhibit larger third-order nonlinear optical susceptibilities $\chi^{(3)}$.

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