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Preparation and nonlinear optical properties of hybrid films containing dicyanomethylenepyran-based chromophores

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ABSTRACT

A new nonlinear optical (NLO) chromophore 4-dicyanomethylene-2-methyl-6- {4-[4-(*N*-ethyl-*N*-hydroxyethylamino)phenylazo]}styryl-4*H*-pyran (AZP), which features extended conjugated chain based on DCM laser dye, was synthesized and functionalized with alkoxysilane for materials processing. Hybrid films containing chromophore AZP and DCM were prepared via a sol–gel processing. The d_{33} values of films containing AZP are 39-48 pm/V varying with concentration of chromophores, which is similar to that containing DCM. By tuning the organic content, the thermal stability of d_{33} values can be significantly improved by about 30 °C, about 15 °C higher than those containing DCM. The residual rotational stress, along with cavity between chromophores and matrix, is proposed to contribute to the stability of NLO activity of hybrid films.

1. Introduction

DCM-type dyes have been extensively researched as red-fluorescent dopants for efficient organic electroluminescent devices [1–3]. Probably stimulated by the merits of multi-functionality in optical devices application, DCM-type chromophores have been also successfully introduced to nonlinear optical (NLO) materials [4–6], which are increasingly demanded for the future applications in ultrafast information technology [7,8].

As ultralarge NLO coefficients have been achieved [9,10], an increasing focus on improvement of stability of materials will lead to practical application. To improve the stability of polar orientation, the "lattice hardening" approach, which promotes the rigidness of matrix, is dominated in a previous study [11,12]. The knowledge of mechanics about the motion of a rigid body that the angular accelerating velocity is inversely proportional to rotational inertia under a constant angular moment [13] provides an alternative to retard the random rotation of chromophores, although chromophores are relatively flexible and the angular moments of chromophores come from thermal fluctuation. Extending π-conjugated chains of chromophores, therefore, is a general approach to increase the rotational inertia and reduce the random rotation, consequently improving the stability of NLO activity in operation.

To achieve high stability of polar orientation by extending molecular length, we designed and synthesized a new NLO chromophore AZP with extended conjugated chain and dicyanomethylenepyran acceptor (see Scheme 1). The hybrid films were prepared though the hydrolysis and condensation of alkoxysilane-functionalized dye via a sol–gel process. The NLO properties of hybrid films containing AZP were studied in comparison with the films derived from DCM dye of short chain.

2. Experimental

2.1. Materials and measurements

2-[(*N*-ethyl-*N*-phenyl)amino]ethanol (TCI), (3-isocyanatopropyl) triethoxysilane (ICPTES, TCI), tin(II) 2-ethylhexanoate (Aldrich), 4-aminobenzaldehyde and dehydroacetic acid were used as received. Tetrahydrofuran (THF) was dried over molecular sieves (3A).

^{1}H NMR spectra of compounds were recorded on an Advance DMX500 spectrometer (Bruker, 500 MHz). A Vector 22 Fourier transform infrared spectrometer (Bruker) was used for IR data collection in KBr disks. Elemental analysis was taken on Carlo Erba EA1110 elemental analyzer. The UV–vis absorption spectroscopic study was performed with a Hitachi U-4100 spectrometer. The thickness of hybrid films was measured on a Tencor alpha-step 200 surface profiler. The thermal stability was studied via thermogravimetric analysis (TGA) on a TA SDT Q600 thermal analysis system. *In situ* second harmonic generation (SHG) measurements were taken to evaluate the NLO performances of hybrid materials according to the previous literature [14].

2.2. Synthesis

2, 6-Dimethyl-4-pyrone, acceptor 4-dicyanomethylene-2, 6-dimethyl-4*H*-pyran (**5**), DCM dye and its alkoxysilane dye DCMASD were synthesized according to Refs. [15,16].

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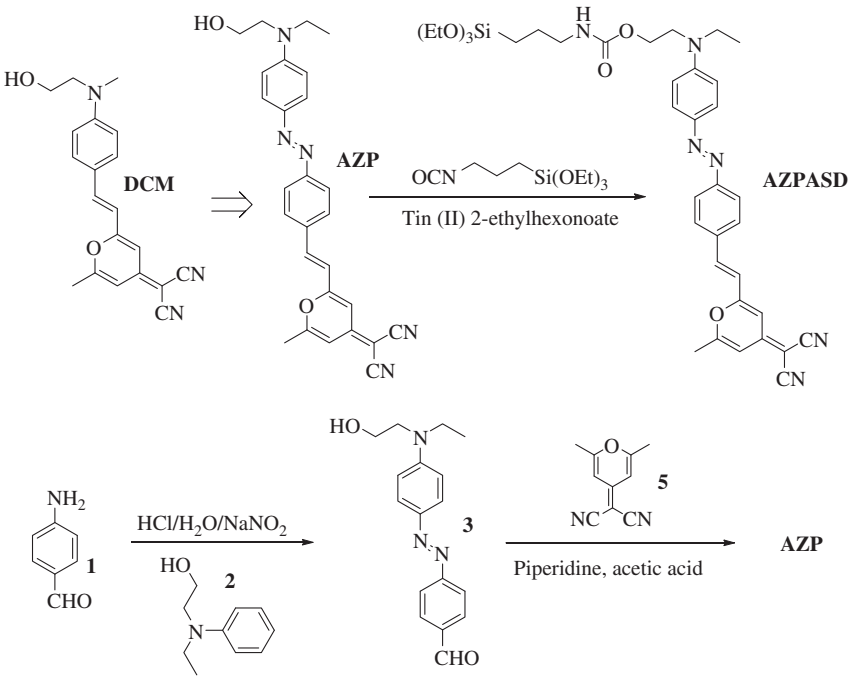

Scheme 1. Structures of NLO chromophore DCM, and extended analogue AZP, and synthetic routes to chromophore AZP and alkoxysilane dye AZPASD.

*2.2.1. Synthesis of 4-[4-(N-hydroxyethyl-N-ethyl)aminophenylazo] benzaldehyde (**3**)*

Fine-milled 4-aminobenzaldehyde (12.10 g, 100 mmol) and $NaNO_2$ (100 mmol, 6.90 g) were mixed in 50 mL of ice paste thoroughly. The resulting mixture was poured into cold hydrochloric acid (100 mL, 4 M) slowly. After removing indissolvable solid by filtration, the orange solution of diazonium salt was kept in ice-water bath, and an ethanol solution of 2-(*N*-ethylanilino)ethanol (8.26 g, 50 mmol) was dropwise added. The red solution was neutralized with potassium carbonate, and the precipitate of azo compound formed. This compound was collected by filtration, followed by recrystallization from ethanol/acetone/water to give flake red crystalline solid (9.81 g, 67%). Mp: 117 °C. ^{1}H NMR(DMSO-d_6): δ (ppm) 10.06 (s, 1H, CHO), 8.04 (d, J = 8.4 Hz, 2H, ArH), 7.91 (d, J = 8.3 Hz, 2H, ArH), 7.82 (d, J = 9.2 Hz, 2H, ArH), 6.87 (d, J = 9.3 Hz, 2H, ArH), 4.84 (s, 1H, OH), 3.62 (s, 2H, CH_2**H**$_2$OH), 3.52 (m, 4H, **H**$_2$$CH_3$ and **H**$_2$$CH_2$OH), 1.16 (t, J = 7 Hz, 3H, CH_2**H**$_3$).

2.2.2. Synthesis of 4-dicyanomethylene-2-methyl-6-{4-[4-(N-ethyl-N-hydroxyethylamino)phenylazo]}styryl-4H-pyran (AZP)

To a solution of aldehyde **3** (5.94 g, 20 mmol) and **5** (3.75 g, 22 mmol) in n-butanol (40 mL), were added piperidine (0.80 mL) and acetic acid (0.40 mL) as catalysts. This solution was refluxed for 2 days, and poured into petroleum ether. The oil-like compound gradually solidified, and the solid mixture was purified by column chromatography using ethyl acetate and petroleum ether (V/V = 1/1) as eluents to give 1.28 g (14%) of red solid, melted with decomposition at 233 °C. ^{1}H NMR (DMSO-d_6): δ (ppm) 7.84 (q, 4H, ArH), 7.79 (d, J = 8.4 Hz, 2H, ArH), 7.61 (d, J = 16 Hz, 1H, CH = C**H**), 7.46 (d, J = 16 Hz, 1H, CH = C**H**), 6.96 (s, 1H, ArH), 6.84 (d, J = 9.3 Hz, 2H, ArH), 6.72 (s, 1H, ArH), 4.85 (t, J = 5.5 Hz, 1H, OH), 3.60 (q, 2H, CH_2**H**$_2$OH), 3.50 (m, 4H, **H**$_2$$CH_2$OH and **H**$_2$$CH_3$), 2.48 (s, 3H, CH_3-pyran), 1.15 (t, J = 7 Hz, 3H, CH_2**H**$_3$). Anal. calcd. for $C_{27}H_{25}N_5O_2$ (451.52): C, 71.82; H, 5.58; N, 15.51. Found: C, 71.83; H, 5.65; N, 15.26.

2.2.3. Synthesis of AZPASD

To a solution of AZP (0.82 g, 1.8 mmol) in dry tetrahydrofuran (10 mL) was added four drops of tin(II) 2-ethylhexanoate, and ICPTES (0.67 g, 2.4 mmol) was added into the solution slowly when it was heated up to 50 °C. The solution was refluxed for 1 h and cooled, the solution was slowly added into petroleum ether with stirring and a lot of the precipitates occurred. The precipitation was collected by filtration, and then was purified by flash column chromatography using the petroleum ether and ethyl acetate (V/V = 1/1) as eluents to give 0.72 g (57%) of red solid. M.p. 155 °C. ^{1}H NMR (DMSO-d_6): δ (ppm) 7.83 (q, 4H, ArH), 7.79 (d, J = 9 Hz, 2H, ArH), 7.59 (d, J = 16.2 Hz, 1H, CH=C**H**), 7.45 (d, J = 16.2 Hz, 1H, CH=C**H**), 7.22 (t, 5.7 Hz, 1H, NH), 6.95 (s, 1H, ArH), 6.87 (d, J = 8.1 Hz, 2H, ArH), 6.71 (s, 1H, ArH), 4.14 (t, J = 5.8 Hz, 2H, CH_2**H**$_2$OC=ONH), 3.73 (q, 6H, Si(O**H**$_2$$CH_3$)$_3$), 3.63 (t, J = 5.6 Hz, 2H, N**H**$_2$$CH_2$O), 3.51 (q, 2H, N**H**$_2$$CH_3$), 2.95 (q, 2H, NH**H**$_2$), 2.47 (s, 3H, CH_3-pyran), 1.44 (m, 2H, NHCH$_2$C**H**$_2$), 1.08–1.23 (m, 12H, Si(OCH$_2$C**H**$_3$)$_3$ and NCH$_2$C**H**$_3$), 0.515 (t, J = 8.4 Hz, 2H, C**H**$_2$Si(OEt)$_3$). Anal. calcd. for $C_{37}H_{46}N_6O_6Si$ (698.88): C, 63.59; H, 6.63; N, 12.02. Found: C, 63.60; H, 6.63; N, 12.14.

2.3. Sol–gel processing for hybrid films

The functionalized alkoxysilane dye AZPASD was employed to silica to form hybrid films via sol–gel methods. Tetraethyl orthosilicate (TEOS, 2.24 ml, 10 mmol) and dilute hydrochloric acid (pH = 1, 0.72 mL, containing 40 mmol of water) was diluted with THF to 10 mL. The required quantity of above solution for the samples of different chromophores content (see Table 1) was dropwise added into a solution of AZPASD (0.14 g, 0.20 mmol) in dry THF (5 mL) whilst vigorously stirring. The solutions were allowed to stir for 12 h, aged for another 60 h, and spin-coated on clean indium tin oxide (ITO) glass substrates. The resultant films were kept at 120 °C for 6 h to remove the residual solvents before poling and SHG measurements. For comparison, NLO films containing chromophore DCM were also prepared in a similar way.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes to chromophore AZP and the alkoxysilane dye AZPASD are shown in Scheme 1. Diazenylbenzaldehyde derivative **3**, which is synthesized from the diazo coupling reaction, was reacted