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The preparation of two-dimensional spindle-type chromophores for second-order nonlinear optical materials

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A series of two-dimensional spindle-type chromophores has been synthesized. The detailed synthetic procedure was reported. The factors that influence the nonlinear optical properties such as the donors and acceptor character have been investigated. The chemical structures of the target products have been confirmed by IR, UV–Vis and NMR spectroscopy, elemental and thermal analysis. The spindle-type chromophores have been used to prepare host-guest doped films which exhibited very good thermal and temporal stability. The nonlinear electro-optical coefficients of the host-guest doped films were measured by the Teng-Man technique and gave values in the range from 21 to 29 pm/V.

1. Introduction

Electro-optical (EO) materials with potential applications in photonic devices for telecommunications and optical information processing usually involve a host polymeric matrix containing second-order nonlinear optical (NLO) chromophores either as guest molecules or covalently attached to the polymer backbone [1–3]. The structural noncentrosymmetry of the material, a necessary condition for second-order NLO activity, is generally achieved by electric field orientation of the chromophore at the temperature close to the glass transition temperature (T_g) of the polymer. Designing organic molecules with large molecular nonlinearity continues to be a challenging subject for materials application in optoelectronic fields [4]. Besides a high molecular nonlinear optical (NLO) response, many optical applications also require materials to possess good thermal stability and transparency in the fundamental region of emission [5–7].

Molecular NLO-phores are traditionally constituted by electron donor and acceptor moieties covalently connected through a conjugated bridge, and a wide variety of π-conjugated and heterobridges have been investigated. Experimental and theoretical studies have demonstrated that replacing the benzene ring of a chromophore bridge with easily delocalizable heteroaromatic rings [8–11], such as thiophene, pyrrole, thiazole and benzimidazole, results in an enhanced molecular hyperpolarizability of donor-acceptor compounds [9,12–20]. These chromophores exhibit large first-order hypersusceptibility. However, the one-dimensional compounds provide less phase-matching behavior owing to their small off-diagonal component [21]. Experiments have shown that two-dimensional (2-D) chromophores possess better phase-matching than one-dimensional chromophores because of their larger off-diagonal components [22]. Such chromophores provide not only a better phase-matching capacity but also an asymmetric arrangement [23].

Here, we present the synthesis, characterization of two-dimensional spindle-type chromophores STC-1-4. The chromophores and Poly(GMA-co-MMA) were used to prepare host-guest doped second-order nonlinear optical films. The nonlinear property of the films was investigated. To our best knowledge, no similar chromophores containing a terphenyl structure conjugated bridge linked to donor and acceptor groups have been reported in the literature. Thermogravimetric analysis showed that these two-dimensional spindle-type chromophores have good thermal stability ($T_d > 200$ °C) in nitrogen.

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2. Experimental method

2.1. Materials

Tetrahydrofuran (THF) and toluene were purified by fractional distillation over sodium. Potassium tert-butoxide was purchased from Acros Organics and piperidine was purchased from Aldrich and purified by distillation under reduced pressure before use. 1,3,3-Trimethyl-5-dicyanovinyl-1-cyclohexene (TDC) and tricyanovinyldihydrofuran (TCF) were prepared according to previous literatures [24,25]. Poly(MMA-co-GMA) was synthesized according to the literature [26]. All the other solvents and chemical reagents were used as received, without further purification.

2.2. Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE NMR spectrometer at a resonance frequency of 500 MHz in $CDCl_3$, and tetramethyl chlorosilane (TMS) was used as internal standard. IR spectra were taken on an AVATAR 360 FTIR spectrometer. Elemental analysis was carried out with a vario MICRO elemental analyzer. The melting point data of all solid compounds were measured on X-4 Melting point apparatus with microscope. The decomposition temperatures of the chromophore molecules were analyzed by using Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min in nitrogen. Thermal degradation temperatures were measured in the range 50 °C–750 °C. Ultraviolet–visible (UV–vis) absorption spectra were measured on an SHIMADZUUV-3100 spectrophotometer.

2.3. Synthesis

2.3.1. 4-(Hydroxymethyl)phenylboronic acid (*1*)

This compound was synthesized according to the literature [27], and a white solid was obtained. Mp = 265 °C ν_{max} (KBr)/cm^{-1} 3434(–OH). ^{1}H NMR (500 MHz; D_2O) δ (ppm) 1.94 (2H, s, $-B(OH)_2$), 4.54 (2H, s, $-CH_2-$), 7.30–7.32 (2H, d, Ar) and 7.65–7.66(2H, d, Ar). Anal. calcd for $C_7H_9BO_3$: C, 55.33; H, 5.97. Found: C, 55.50; H, 5.86.

2.3.2. 2,5-(4-Hydroxymethylphenyl)benzene-1,4-dicarbaldehyde (*2*)

2,5-Dibromobenzene-1,4-dicarbaldehyde (1.0 g, 3.43 mmol), 4-(hydroxymethyl)phenylboronic acid (1.04 g, 6.85 mmol, 2 equiv) were dissolved in THF (60 mL) under a nitrogen purge. The solution was treated with palladium acetate (9.3 mg, 0.041 mmol, 0.006 equiv), triphenylphosphine (32.3 mg, 0.124 mmol, 0.018 equiv), 25.2 mL of 2 M sodium carbonate (Na_2CO_3) (0.321 mol, 1.2 equiv), deionized water (13.2 mL) and heated under reflux under a nitrogen atmosphere. The resulting solution was stirred under reflux at 90 °C for 6 h. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel eluting with dichloromethane-methanol (50:1) to give yellow solid 0.9 g (83%). Mp = 179 °C ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) 10.00(s, 2H, –C**H**O), 7.96(s, 2H, Ar–Ar–Ar), 7.65–7.67(m, 4H, $HOCH_2$–**Ar**), 7.58–7.60(m, 4H, $HOCH_2$–**Ar**), 5.38(s, 2H, –O**H**), 4.61(s, 4H, –C**H$_2$**–OH). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 65.2, 127.6, 130.6, 134.6, 136.1, 138.4, 144.6, 192.87. ν_{max} (KBr)/cm^{-1} 3440(–OH), 1652(–CHO). Anal. calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24; N, 18.48. Found: C, 75.96; H, 5.41; N, 18.25.

2.3.3. 2,5-(4-Hydroxymethylphenyl)-4-(4-(dimethylamino)styryl) benzaldehyde (*3*)

Compound 2 (0.75 g, 2.17 mmol) was dissolved in THF 30 mL, (4-dimethylaminobenzyl)triphenylphosphonium iodide (1.136 g, 2.17 mmol) and t-BuOK (0.37 g, 3.26 mmol) were added, and the mixture stirred at room temperature for 2 h. A yellow solution was obtained. Solvents were removed under reduced pressure, and then column chromatography, eluting with petroleum–ethyl acetate (1:1) gave the title compound 0.81 g (80%) as a yellow solid. Mp = 101 °C ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) trans:-cis = 2:3; trans 2.05(s, 2H, –O**H**), 2.98(s, 6H, –C**H$_3$**), 4.75–4.77(d, 4H, –C**H$_2$**–), 7.28–7.30(d, 2H, N–**Ar**), 6.54–6.57(d, 1H, C**H**=CH), 7.14–7.17(d, 1H, CH=C**H**), 7.66–7.68(d, 2H, N–**Ar**), 7.65–7.67(d, 2H, $HOCH_2$–**Ar**), 7.51–7.53(d, 4H, $HOCH_2$–**Ar**), 7.69(s, 1H, Ar–Ar–Ar), 8.03(s, 1H, Ar–Ar–Ar), 9.99(s, 2H, –C**H**O). cis: 2.05(s, 2H, –O**H**), 2.97(s, 6H, –C**H$_3$**), 4.81–4.83(d, 4H, –C**H$_2$**–), 7.22–7.24(d, 2H, N–**Ar**), 6.95–6.97(d, 1H, C**H**=CH), 7.00–7.02(d, 1H, CH=C**H**), 7.64–7.66(d, 2H, N–**Ar**), 7.38–7.40(d, 4H, $HOCH_2$–**Ar**), 7.46–7.48(d, 4H, $HOCH_2$–**Ar**), 7.97(s, 1H, Ar–Ar–Ar), 7.77(s, 1H, Ar–Ar–Ar), 9.99(s, 2H, –C**H**O). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 40.3, 65.15, 112.3, 121.7, 122.2, 125.5, 126.9, 130.2, 132.5, 133.0, 136.8, 140.32, 144.5, 150.6, 191.9. ν_{max} (KBr)/cm^{-1}: 3385(–OH), 2855(–CH_3), 1681(–CHO), 1606(Ar). Anal. calcd for $C_{31}H_{29}NO_3$: C, 80.32; H, 6.31; N, 3.02. Found: C, 80.46; H, 6.34; N, 3.15.

2.3.4. 2,5-(4-Hydroxymethylphenyl)-4-(4-(diphenylamino)styryl) benzaldehyde (*4*)

A similar procedure was followed for compound 3 and for compound 2 (0.93 g, 2.69 mmol) (4-diphenylaminobenzyl)triphenylphosphonium bromide (1.62 g, 2.69 mmol) and t-BuOK (0.493 g, 4.03 mmol) were dissolved in THF (10 mL). The product was purified by column chromatography, eluting with petroleum–ethyl acetate (2:1) gave the title compound (0.9 g, 53%) as a dark yellow solid. Mp = 135 °C ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) trans:cis = 1:1; trans 9.96(s, 1H, C**H**O), 7.99(s, 1H, C**H**O–Ar), 7.77(s, 1H, CHO–**Ar**), 7.45–7.47(m, 4H, $HOCH_2$–**Ar**), 7.42–7.44(m, 4H, $HOCH_2$–Ar), 7.59–7.61(d, 2H, N–**Ar**), 7.10–7.11(m, 6H, N–**Ar**), 7.08–7.09(m, 4H, N–**Ar**), 6.97–6.99(d, 2H, N–**Ar**), 7.18–7.21(d, 1H, C**H**=CH), 7.13–7.16(d, 1H, CH=C**H**), 4.79–4.82(d, 4H, –C**H$_2$**–); cis: 10.00(s, 1H, C**H**O), 8.01(s, 1H, CHO–**Ar**), 7.54(s, 1H, CHO–**Ar**), 7.50–7.52(m, 4H, $HOCH_2$–**Ar**), 7.49–7.51(m, 4H, $HOCH_2$–Ar), 7.27–7.28(d, 2H, N–**Ar**), 7.23–7.24(m, 6H, N–**Ar**), 7.24–7.25(m, 4H, N–**Ar**), 6.94–6.96(d, 2H, N–**Ar**), 6.58–6.60(d, 1H, C**H**]CH), 6.34–7.36(d, 1H, CH=C**H**), 4.75–4.77(d, 4H, –C**H$_2$**–). ν_{max} (KBr)/cm^{-1}: 3390(–OH), 2921, 2856(–CH_3 , –CH_2–), 1681(–CHO), 1586(Ar). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 65.6, 123.5, 123.7, 124.9, 127.2, 127.4, 127.8, 129.4, 129.7, 130.1, 130.4, 130.6, 132.0, 134.9, 139.6, 140.2, 140.4, 140.5, 147.7, 147.9, 168.1. Anal. calcd for $C_{41}H_{33}NO_3$: C, 83.79; H, 5.66; N, 2.38. Found: C, 83.53; H, 5.74; N, 2.45.

2.3.5. 2-(3-(2,5-(4-Hydroxymethylphenyl)-4-(4-(dimethylamino) styryl)styryl)-5, 5-dimethylcyclohex-2-enylidene)malononitrile (STC-1)

Compound 3 (0.253 g, 0.55 mmol) was dissolved in THF 10 mL, TDC (0.102 g, 0.55 mmol) and piperidine (0.05 mL) were added, and the stirred mixture was then heated to reflux for 6 h. A dark solution was obtained. The product was purified by column chromatography on silica gel eluting with dichloromethane–methanol (50:1) to give a red powder (0.26 g, 79%). Mp = 113 °C.^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) 7.72(s, 1H, Ar–Ar–Ar), 7.66(s, 1H, Ar–Ar–Ar), 7.50–7.52(d, 4H, $HOCH_2$–**Ar**), 7.46–7.48(d, 2H, N–**Ar**), 7.43–7.45(d, 4H, $HOCH_2$–**Ar**), 7.27–7.30(d, 1H, N–Ar–CH=C**H**), 7.11–7.14(d, 1H, C**H**=CH-TDC), 7.06–7.09(d, 1H, N–Ar–C**H**=CH), 7.00–7.02 (d, 2H, N–**Ar**), 6.90–6.93(d, 1H, CH=C**H**-TDC), 6.77(s, 1H, C**H**) , 4.81(s, 4H, HO–C**H$_2$**), 2.98(s, 6H, C**H$_3$**–N), 2.55(s, 2H, -C**H$_2$**-), 2.24(s, 2H, –C**H$_2$**–), 1.01(s, 6H, C**H$_3$**–C). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ (ppm) 28.3, 30.1, 32.4, 40.9, 43.3, 65.7, 78.0, 112.7, 112.9, 122.2, 124.2, 127.3, 128.0, 128.3, 128.7, 130.6, 131.4, 131.8, 132.3, 136.0, 136.9, 137.9, 140.3, 140.8, 150.4, 169.6. ν_{max} (KBr)/cm^{-1}: 3405(−OH), 2923, 2852(−CH$_3$, −CH$_2$−), 2219(CN), 1605(Ar). Anal. calcd for $C_{43}H_{41}N_3O_2$: C, 81.74; H, 6.54; N, 6.65. Found: C, 81.62; H, 6.63; N, 6.59.

2.3.6. 2-(3-(2,5-(4-Hydroxymethylphenyl)-4-(4-(diphenylamino) styryl)styryl)-5, 5-dimethylcyclohex-2-enylidene)malononitrile (STC-2)

A similar procedure was followed to that for STC-1, compound 4 (0.3 g, 0.511 mmol), TDC (0.095 g, 0.55 mmol) and piperidine (0.04 mL) were dissolved in THF (10 mL). The product was purified by column chromatography on silica gel eluting with dichloromethane−methanol (50:1) to give a red powder(0.26 g, 79%). Mp = 126 °C ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 7.78(s, 1H, Ar−Ar−Ar), 7.70(s, 1H, Ar−Ar−Ar), 7.50−7.52 (d, 4H, HOCH$_2$−**Ar**), 7.44−7.46(d, 4H, HOCH$_2$−**Ar**), 7.24−7.25(d, 2H, N−Ar−CH=CH), 7.21−7.23(m, 4H, N−**Ar**), 7.18−7.20(d, 1H, N−Ar−CH=C**H**), 7.11−7.14(d, 1H, C**H**=CH-TDF), 7.08−7.11(m, 6H, N−**Ar**), 7.02−7.04(m, 2H, N−**Ar**), 6.97−6.99(d, 1H, N−Ar−C**H**=CH), 6.91−6.94(d, 1H, CH=C**H**-TDF) , 6.78(s, 1H, −**CH**−), 4.79−4.80(d, 4H, HO−C**H$_2$**), 2.55(s, 2H, −**CH$_2$**−), 2.24(s, 2H, −C**H$_2$**−), 1.01(s, 6H, **CH$_3$**−C). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 27.9, 29.6, 40.8, 42.9, 65.1, 80.1, 112.3, 121.6, 122.5, 122.5, 123.0, 123.2, 123.4, 123.9, 124.5, 124.7, 124.8, 126.8, 126.9, 127.3, 127.4, 127.7, 127.5, 129.0, 129.1, 129.3, 129.9, 130.0, 130.1, 181.2. ν_{max} (KBr)/cm^{-1}: 3347(−OH), 2926, 2860(−CH$_3$, −CH$_2$−), 2219(CN), 1590(Ar). Anal. calcd for $C_{53}H_{45}N_3O_2$: C, 84.21; H, 6.00; N, 5.56. Found: C, 84.31; H, 6.07; N, 5.59.

2.3.7. 2-(3-Cyano-4(2,5-(4-hydroxymethylphenyl)-4-(4-(dimethylamino)styryl)styryl)-5, 5-dimethyl-5H-furan-2-ylidene)-malononitrile (STC-3)

A similar procedure was followed for the STC-1, compound 3 (0.32 g, 0.7 mmol), TCF (0.14 g, 0.7 mmol) and piperidine (0.05 mL) were dissolved in THF (10 mL). The product was purified by column chromatography on silica gel eluting with petroleum−ethyl acetate (1:1) to give a red powder (0.28 g, 63%). Mp = 109 °C ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 7.78(s, 1H, Ar−Ar−Ar), 7.69(s, 1H, Ar−Ar−Ar), 7.66−7.68 (d, 4H, HOCH$_2$−**Ar**), 7.64−7.66(d, 4H, HOCH$_2$−**Ar**), 7.38−7.40(d, 2H, N−**Ar**), 7.11−7.14(d, 1H, C**H**=CH-TCF), 7.18−7.21(d, 1H, N−Ar−CH=C**H**), 6.91−6.94(d, 1H, CH=C**H**-TCF), 6.81−6.84(d, 1H, N−Ar−C**H**=CH) , 6.65−6.67(d, 2H, N−**Ar**), 4.80−4.82(d, 4H, HO−C**H$_2$**), 2.97(s, 6H, C**H$_3$**−N), 1.49(s, 6H, C**H$_3$**−C). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 27.9, 29.6, 44.4, 46.0, 65.0, 99.8, 100.1, 111.5, 112.5, 114.5, 120.1, 127.0, 127.1, 127.3, 127.4, 128.1, 128.3, 128.5, 128.6, 129.7, 129.9, 131.8, 131.8, 132.0, 132.1, 132.3, 153.5, 160.6, 184.7. ν_{max} (KBr)/cm^{-1}: 3383(−OH), 2928, 2856(−CH$_3$, −CH$_2$-), 2226(CN), 1608(Ar). Anal. calcd for $C_{42}H_{36}N_4O_3$: C, 78.24; H, 5.63; N, 8.69. Found: C, 78.43; H, 6.01; N, 8.82.

2.3.8. 2-(3-Cyano-4-(2,5-(4-hydroxymethylphenyl)-4-(4-(diphenylamino)styryl)styryl)-5, 5-dimethyl-5H-furan-2-ylidene)-malononitrile (STC-4)

A similar procedure was followed for the STC-1, compound 4 (0.16 g, 0.273 mmol), TCF (0.055 g, 0.273 mmol) and piperidine 0.03 mL were dissolved in THF 10 mL. The product was purified by column chromatography on silica gel eluting with petroleum−ethyl acetate (1:1) to give a red powder(0.117 g, 56%). Mp = 123 °C ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ (ppm) 7.78(s, 1H, Ar−Ar−Ar), 7.70(s, 1H, Ar−Ar−Ar), 7.50−7.52 (d, 4H, HOCH$_2$−**Ar**), 7.44−7.46(d, 4H, HOCH$_2$−**Ar**),7.38−7.40(d, 2H, N−Ar−CH=CH), 7.22−7.25(m, 4H, N−**Ar**), 7.07−7.09(m, 6H, N−**Ar**), 7.03−7.05(m, 2H, N−**Ar**), 7.14−7.17(d, 1H, C**H**=CH-TCF), 7.17−7.20(d, 1H, N−Ar−CH=C**H**), 6.82−6.85(d, 1H, CH=C**H**-TCF), 6.93−6.96(d, 1H, N−Ar−C**H**=CH) , 4.80−4.81(d, 4H, HO−C**H$_2$**), 1.49 (s, 6H, C**H$_3$**−C). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ (ppm) 26.3, 30.1, 37.8, 65.4, 87.1, 112.0, 115.5, 121.2, 123.2, 123.8, 124.4, 125.2, 127.5, 127.7, 127.8, 128.1, 129.0, 129.7, 130.1, 130.3, 130.6, 130.9, 131.1, 131.9, 138.9, 139.3, 140.9, 141.6, 144.4, 143.5, 148.5, 176.7. ν_{max} (KBr)/cm^{-1}: 3347(−OH), 2924, 2856(−CH$_3$, −CH$_2$−), 2226(CN), 1580(Ar). Anal. calcd for $C_{52}H_{40}N_4O_3$: C, 81.23; H, 5.24; N, 7.29. Found: C, 80.98; H, 5.45; N, 7.42.

2.4. Preparation of guest-host doped thin films

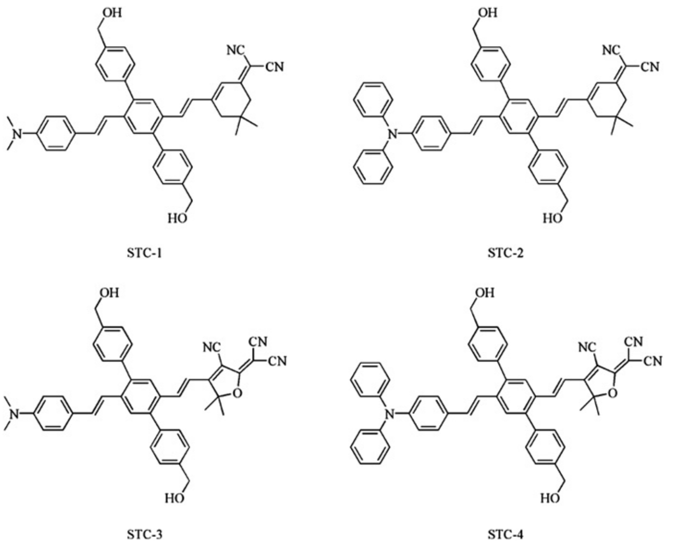
To prepare the doped films, the chromophores STC-1-4 and the Poly(MMA-co-GMA) containing 0.5wt% 2-methylimidazole were dissolved in butyl acetate with a weight concentration of 0.01 g/mL and 0.1 g/mL, respectively. The solutions were filtered through a syringe fitted with a 0.22 μm pore size filter, and spin-coated on indium-tin-oxide (ITO)-coated glass substrates, which had been previously cleaned by *N,N*-dimethylformide (DMF), acetone, THF and distilled water sequentially in an ultrasonic bath. The films were baked in air for 1 h to remove the majority of any volatiles. The residual solvent was removed by heating the films in a vacuum oven at 40 °C for 10 h.

3. Results and discussion

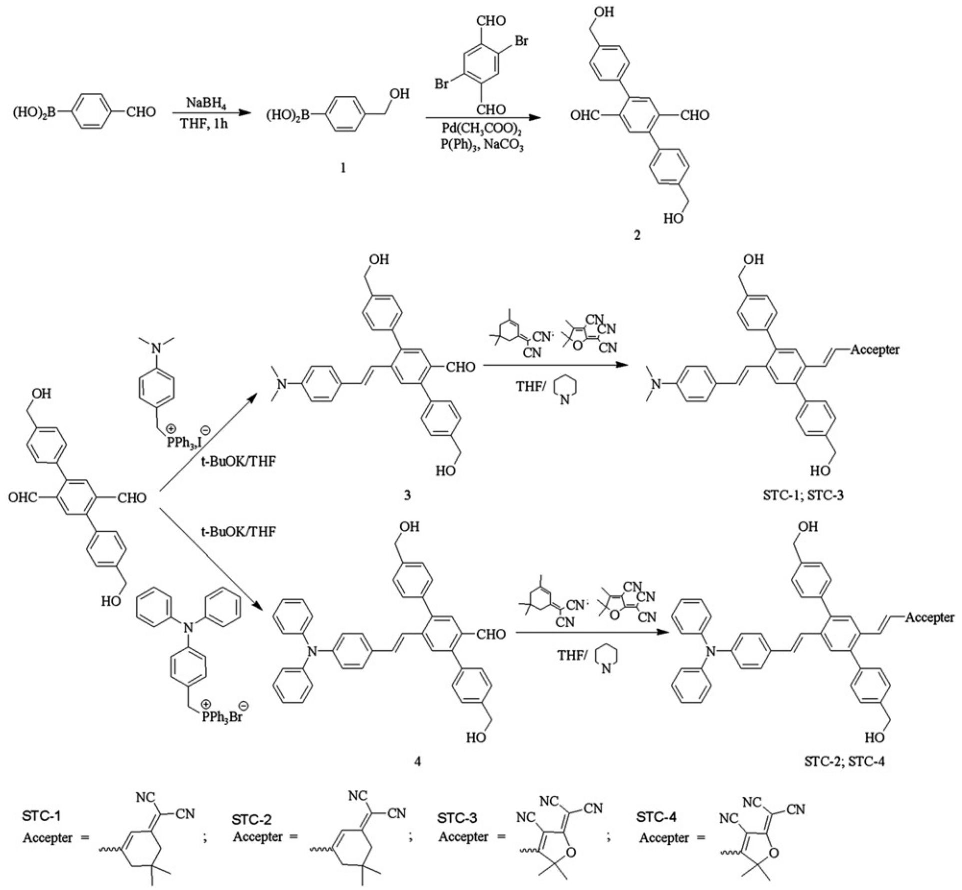
3.1. Synthesis

The preparation of the chromophores was accomplished by three different strategies in Scheme 2. Compound **2** was obtained via Suzuki cross-coupling reaction. The compound **3** and compound 4 were synthesized using Wittig reaction. The chromophores STC-1-4 were obtained via Knoevenagel condensation reaction.

The synthesis of the target chromophores were outlined in Scheme 1. Compound **1** was achieved by a one-step synthesis in a reasonable yield by reduction of the 4-formylphenylboronic acid with NaBH$_4$ (4-Diphenylaminobenzyl) triphenylphosphonium bromide and (4-dimethylaminobenzyl) triphenylphosphonium iodide were easily obtained under routine conditions [28]. 2,5-Dibromobenzene-1,4-dicarbaldehyde with excess compound **1** under Suzuki cross-coupling conditions in the presence of palladium acetate as a catalyst and aqueous solution of 2 M Na$_2$CO$_3$ as



Scheme 1. The structure of the chromophores.



Scheme 2. Synthetic route of the chromophores.

base in THF at reflux afforded the desired compound 3 in 80% yield as a mixture of isomers (trans:cis = 2:3). Compound **4** was prepared as a mixture of isomers (trans:cis = 1:1) by NMR spectroscopy from a Wittig reaction between phosphonium salt and compound **2**. The final compounds STC-1 − 4 were obtained by a Knoevenagel condensation with the acceptor TDC and TCF to afford chromophores containing 4-(hydroxymethyl) phenyl as side group and divinyl phenyl as the conjugating bridge conveniently.

3.2. *Structural characterization*

All of the compounds were characterized by spectroscopic methods and gave satisfactory spectral data (see Fig. 1 for detailed analysis data). The ^{1}H NMR spectrum of chromophores shows a singlet for the equivalent methyl groups at 1.01 ppm assigned to the TDF units for STC-1 and STC-2, and a single signal at 1.50 ppm was assigned to the equivalent methyl groups of the TCF units for STC-3 and STC-4. Fig. 1 shows the IR spectra of the chromophores. The strong band around 3340 cm^{-1}-3410 cm^{-1} was attributed to the O–H stretching. The O–H stretching was broad, and this suggested that the triphenyl structure was formed under Suzuki cross-coupling condition. A strong absorption peak appeared at about 2220 cm^{-1}, which was attributed to the vibration of the cyano group.

3.3. *Thermal properties of the chromophores*

The thermal property of chromophores was investigated by TGA under a nitrogen atmosphere. In Fig. 2, all of the chromophores displayed high thermal stability with 5% weight loss temperature (T$_d$) higher than 200 °C. STC-4 had the highest T$_d$ about 254 °C. This result indicated that the different donors and accepters had a significant impact on the overall thermal stability of the chromophores.

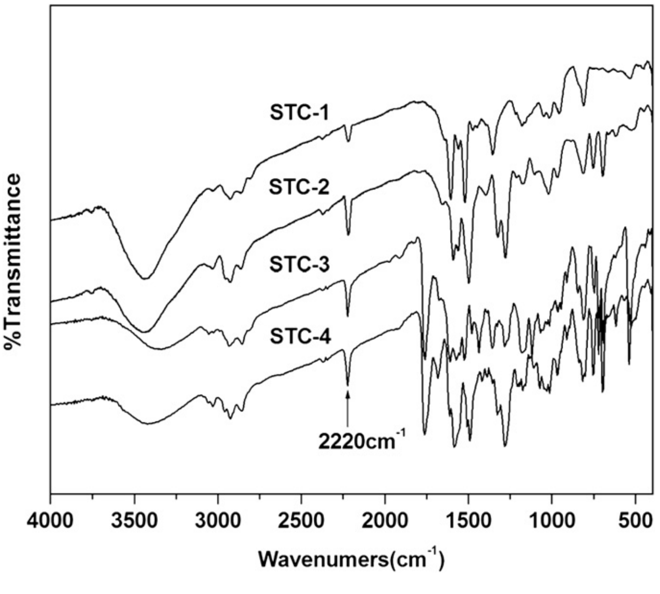


Fig. 1. IR spectrum of the chromophores.

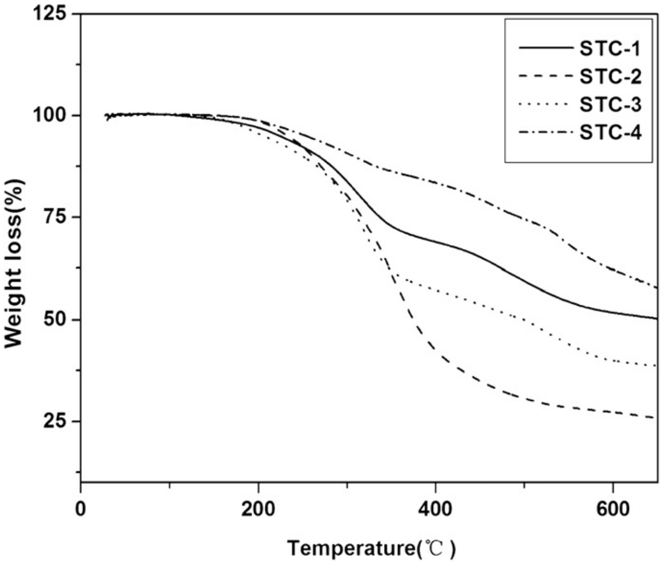


Fig. 2. TGA thermograms of the chromophores in nitrogen atmosphere at a heating rate of 10 °C/min.

3.4. UV–Vis spectra

The UV–vis absorption spectra of chromophore STC-1 in different solvents is presented in Fig. 3. The charge transfer band shows a bathochromic shift with the increase of the solvent polarity from dioxane to NMP. This positive solvatochromism has been commonly regarded as an indication of molecular nonlinearity ($\mu\beta$) of NLO-phores [29,30]. The absorption wavelength (λ_{max}) of the four chromophores was different in the same solvent in Fig. 4. In the UV–Vis spectra the absorption coefficients were 6.9 M^{-1} cm^{-1}, 2.4 M^{-1} cm^{-1}, 1.2 M^{-1} cm^{-1} and 1.7 M^{-1} cm^{-1} for STC-1 – STC-4 in dichloromethane. All of the absorption wavelengths (λ_{max}) of chromophores were less than 480 nm, which indicated that the chromophores possessed good transparency in the longer wavelength visible region of the spectrum.

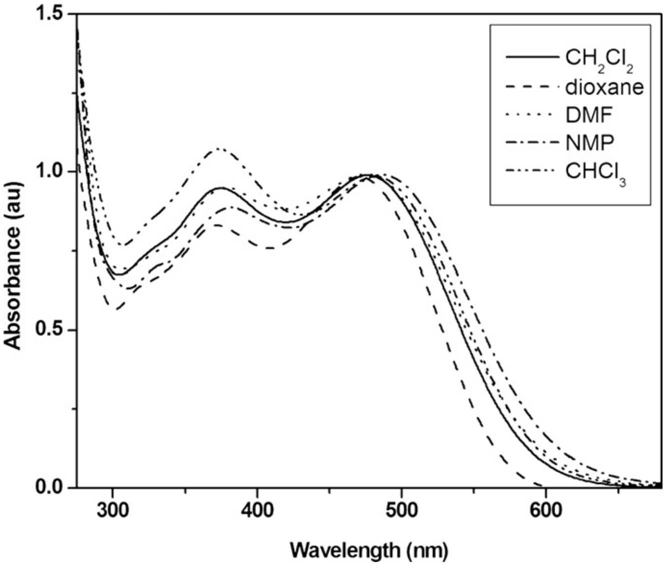


Fig. 3. UV–vis absorption spectra of chromophore STC-1 in different solvents.

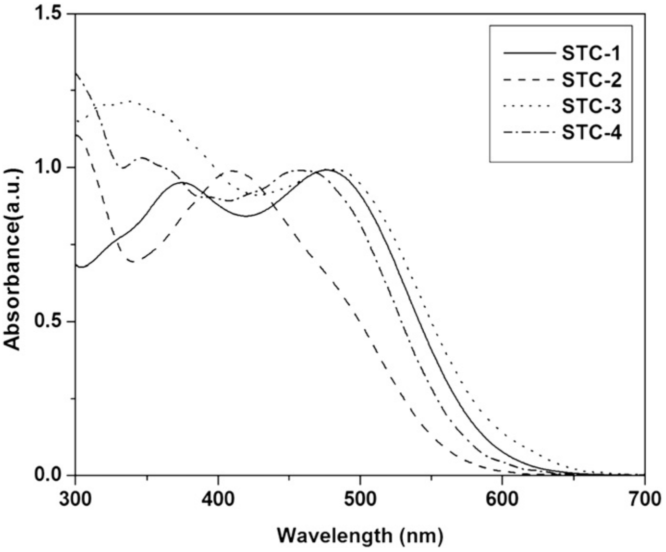


Fig. 4. UV–vis absorption spectra of the chromophores in THF.

3.5. Nonlinear optical properties

The films were prepared using Poly(GMA-co-MMA) and evidence of cross-linking was determined by FTIR spectroscopy through monitoring the C–O–C stretching band ar ca. 910 cm^{-1}. Dynamic DSC analysis at 150–190 °C was also used to confirm that the polymer was fully cross-linked. To exhibit an EO effect the chromophores in the films must be noncentrosymmetric. High electric field poling was utilized to orient the chromophores along the applied electric field and thus produce a noncentrosymmetric arrangement. Poling conditions were as follows: at a temperature about 110 °C and applying a high dc voltage 5.0 kV at the tungsten wire across the films for about 1 h at the gap distance 1.0 cm. The temperature was then increased to 130 °C for about 30 min to ensure the epoxy groups were fully cross-linked. Finally, the temperature was decreased to room temperature with the electric field still applied.

The EO coefficients of the guest-host doped films were measured with the Teng-Man setup at 1310 nm [31]. All of the films had the same composition and amount of chromophore and their EO coefficients were determined to be 25, 26, 21 and 29 pm/V for STC-1-4, respectively. Chromophore STC-4 with stronger donor and acceptor groups displayed the largest EO coefficient [32].

The long-term stability of the films at elevated temperature is very important for the practical use of NLO materials. To investigate the long-term NLO stability of the guest-host doped films, dipole reorientation of chromophores was observed by measuring the EO coefficient ($r_{33}(t)/r_{33}(t_0)$) as a function of time at 80 °C. Fig. 5 shows the temporal stability of the EO coefficient for the host-guest doped films at 80 °C. The temporal stability of the EO response was found to be good, as the r_{33} value of the films maintained more than 85% of their original value after holding at 80 °C in air over 100 h. There are two reasons for obtaining these results. The former is that the structural architecture of the chromophore has a large effect on the temporal stability. A two-dimensional chromophore requires a larger rotational sphere volume than one-dimensional one [23]. Short-range relaxation such as crankshaft motion cannot provide enough local free volume to randomize the oriented dipoles. The local free volume can be increased by increasing the temperature which provides sufficient free volume for reorientation of the chromophores. The second reason is that the increased temperature in the poling process ensures that all of the epoxy groups

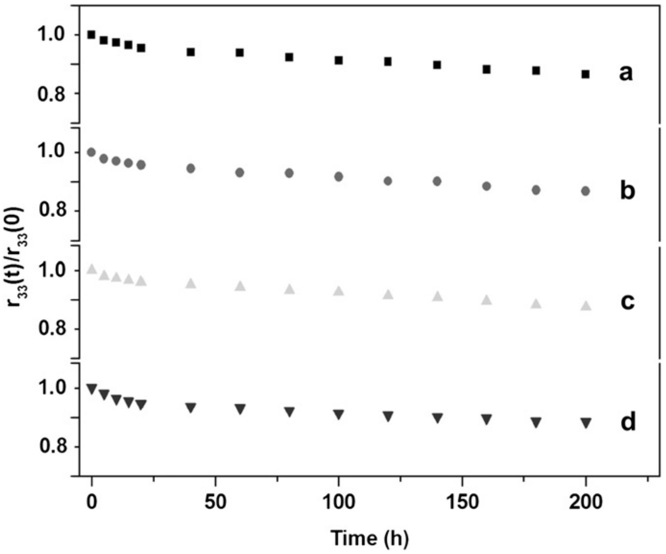


Fig. 5. Temporal stability of the EO coefficient for the host-guest doped films of STC-1 (a), STC-2 (b), STC-3 (c) and STC-4 (d) with Poly(GMA-co-MMA) at 80 °C, respectively.

cross-link and form network structure in poling process. The local free volume surrounding each chromophore is thus further decreased. The decrease of local free volume restricted the dipole reorientation of the chromophores. As a result, the effective EO coefficient only decayed slightly at 80 °C [33,34].

4. Conclusion

A new series of two-dimensional spindle-type chromophores bearing diphenylamino/dimethylamino as a donor connected to divinylbenzene and TDF/TCF as an acceptor have been synthesized. In agreement with their nature, the chromophores STC-1-4 showed large second-order NLO responses. The results indicate that the structural architecture of chromophores and the cross-linked network structure have a good nonlinear stability at elevated temperatures. Therefore, two-dimensional spindle-type chromophores are interesting NLO-phores which exhibit large r_{33} values and thermal stabilities, and may have great potential applications for EO devices.

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