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# Synthesis and electro-optic activities of new side-chain polycarbonates containing nonlinear optical chromophores and isolation groups†

Cite this: *RSC Adv.*, 2014, 4, 4395Guowei Deng,<sup>ab</sup> Heyan Huang,<sup>ab</sup> Chengcheng Peng,<sup>ab</sup> Airui Zhang,<sup>ab</sup> Maolin Zhang,<sup>a</sup> Shuhui Bo,<sup>\*a</sup> Xinhou Liu,<sup>a</sup> Zhen Zhen<sup>a</sup> and Ling Qiu<sup>\*a</sup>

Dendritic julolidine-based nonlinear optical (NLO) chromophore (JTCFC) possessing isolation group was designed and synthesized to realize effective isolation of NLO chromophores in the polymer backbone. Electro-optic (EO) polycarbonates (PC-JTCFCs) consisting of the dendritic JTCFC and comonomers were prepared through a facile copolymerization strategy. The sufficiently high polymerizability of the dendritic JTCFC, which could be caused by the well-isolation of chromophores and lack of steric effect, afforded the EO polycarbonates with ultra-high molecular weight ( $M_w$  up to 145 990). The DSC analysis showed that the EO polycarbonates exhibited similar  $T_g$  values (near 150 °C), indicating that the interchromophore interactions are effectively suppressed. The effective isolation of NLO chromophores directly suppressed the dipole–dipole interactions and improved the translation of microscopic hyperpolarizability into macroscopic EO activity. After corona poling, the synthesized EO polycarbonates exhibited a maximum EO coefficient ( $r_{33}$ ) of 55 pm V<sup>−1</sup> at 1310 nm, which was greatly enhanced as compared to the guest–host systems reported previously. Moreover, the prepared EO polycarbonates also possessed good temporal stability, 85% of the initial  $r_{33}$  value of PC-JTCFC-3 could be kept after 500 h at 85 °C.

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## Introduction

Electro-optic (EO) materials are extensively used in the field of telecommunications, optical modulation, THz generators, photonic devices, *etc.*<sup>1–5</sup> Owing to the advantages over traditional inorganic/semi-conductor EO materials, such as potentially higher EO activity, lower dielectric constants and driving voltage, faster response time and higher bandwidth, the organic EO materials attract increasing attention.<sup>1,4,6–9</sup> The device's application demanded organic polymeric EO materials to fulfil several requirements, including larger optical nonlinearity, lower optical loss at operation wavelength, good processability, mechanical strength, thermal stability and long-term alignment stability of nonlinear optical (NLO) chromophores.<sup>10–12</sup> To realize the device application of organic EO materials, much effort has been spent on developing NLO chromophores and polymers.<sup>13</sup> During the past decades, the molecular

hyperpolarizability ( $\beta$ ) values of NLO chromophores have been greatly enhanced through molecular design.<sup>1,7,11,14</sup>

However, the chromophores' larger hyperpolarizability generally leads to a stronger dipole–dipole electrostatic interaction between chromophores, and such interaction could cause the chromophores' aggregation, which make the chromophores not being able to effectively orient to the poling direction and translate the microscopic hyperpolarizability into macroscopic EO activity.<sup>12,15,16</sup> The strong dipole–dipole interaction among the chromophore moieties have become a major obstacle hindering the rapid development of organic EO materials.<sup>17–22</sup> Fortunately, Dalton *et al.* and Li *et al.* proposed the site-isolation principle and the “concept of suitable isolation group” respectively,<sup>23–30</sup> and their work have demonstrated that the dipole–dipole interactions could be effectively suppressed through introduction of isolation groups.

Our previous work indicated that 8-hydroxy-1,1,7,7-tetra-methyl-formyljulolidine as the electron donor for preparation of NLO chromophores could provide excellent hindrance, and the julolidine-based NLO chromophores exhibited better macroscopic EO activity than conventional aniline-based NLO chromophores.<sup>31,32</sup> However, up to now, the covalently attached EO polymers containing julolidine-based NLO chromophores, which offer many advantages over the simple guest–host materials,<sup>33,34</sup> have rarely been reported. Here, we attempted to design and synthesize a new series of EO polycarbonates

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† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR spectra, TGA curves, the modified structure of JTCFC, and <sup>1</sup>H NMR spectra, GPC traces for PC-JTCFC. See DOI: 10.1039/c3ra45514a

containing the julolidine-based NLO chromophore. In order to further weaken the dipole–dipole electrostatic interaction, we designed a dendron as the isolation group and linked to the 8-position of julolidine electron donor, and the dendron also provided dihydroxyl groups that are necessary for the preparation of polycarbonates adopting the copolymerization strategy reported previously.<sup>35,36</sup> We hope that the designed dendron's isolation, electron donor's hindrance and the polymer backbone's isolation could all effectively suppress the dipole–dipole interaction (Scheme 1). The synthesis, characterization and properties of the novel EO polycarbonates are presented in detail. The obtained results indicated that the designed dendron could play an effective role in the translation of microscopic hyperpolarizability into macroscopic EO activity. The new polymers exhibited maximum EO coefficients up to 55 pm V<sup>−1</sup> (PC-JTCFC-3), which was much better than the guest–host system reported previously. The poled films of these EO polycarbonates also showed desirable thermal stability of the dipole alignment, and the EO activity could be kept above 85% for more than 500 h at 85 °C. The research provided promising materials for potential practical application of devices fabrication.

## Experimental

### Materials and instruments

All reagents and solvents were purchased from commercial sources and used without further purification. DMF and 1,2-dichloroethane (DCE) were freshly distilled prior to use. TCF was prepared according to previous literature sources.<sup>37</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined using Advance Bruker (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a Varian 3100 FT-IR spectrometer at a resolution of 2 cm<sup>−1</sup> with a minimum of 64 scans. UV-Vis spectra were obtained using a Hitachi U2001 spectrophotometer. The number-average molecular weight (*M*<sub>n</sub>) and weight-average molecular weight (*M*<sub>w</sub>) values of the obtained polycarbonates

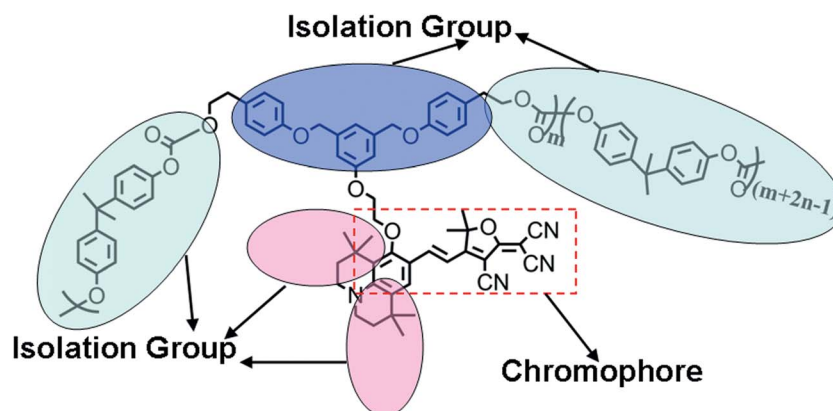
were estimated by gel permeation chromatography (GPC), tetrahydrofuran (THF) was used as the eluent and polystyrene (PS) standards were used for the molecular weight calibration. Thermogravimetric analysis (TGA) was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C min<sup>−1</sup> under the protection of nitrogen. Differential scanning calorimetry (DSC) measurements (*T*<sub>g</sub> and melt points) were performed on a TA5000, 2910MDSC with a heating rate of 10 °C min<sup>−1</sup> under the protection of nitrogen.

### Synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate (1)

A mixture of dimethyl 5-hydroxyisophthalate (4.2 g, 20 mmol), K<sub>2</sub>CO<sub>3</sub> (3.31 g, 2.4 mmol) and dry DMF (30 mL) was stirred for 5 min. Subsequently, 2-bromoethanol (3 g, 24 mmol) was added and the mixture was stirred at 90 °C overnight. After cooling to rt, the mixture was poured into water (200 mL), extracted with ethyl acetate (3 × 50 mL) and dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography using hexane/acetone (5 : 1) as eluent to give the product as white solid (3.6 g, yield 71%). mp: 109–111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.28 (t, *J* = 1.4 Hz, 1H), 7.76 (d, *J* = 1.4 Hz, 2H), 4.17 (t, *J* = 4.3 Hz, 2H), 4.00 (t, *J* = 4.3 Hz, 2H), 3.94 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 166.81, 159.53, 132.64, 124.13, 120.65, 70.64, 62.02, 53.22. EI-MS *m/z* 254.1 (M)<sup>+</sup>. Element analysis (%; found/calcd): C, 56.58/56.69; H, 5.60/5.55.

### Synthesis of 5-(2-hydroxyethoxy)-1,3-bis(hydroxymethyl)benzene (2)

To a solution of LAH (2 g, 52.7 mmol) and anhydrous diethyl ether (40 mL) in a 100 mL round-bottom flask, and compound 1 (3 g, 11.8 mmol) in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the solution dropwise. After that, the reactive mixture was stirred at rt overnight. Ethyl acetate and water were added sequentially to quench the residual LAH. The precipitate was filtered and the filtrate was collected, washed with NaCl solution and dried over MgSO<sub>4</sub>, after removal of the solvent, the pure product 2 was obtained as colorless viscous liquid (2.1 g, yield 90%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 6.82 (s, 1H), 6.73 (s, 2H), 5.12 (s, 2H), 4.82 (s, 1H), 4.44 (s, 4H), 3.94 (t, *J* = 5.1 Hz, 2H), 3.69



Scheme 1 Structure of PC-JTCFCs.

(t,  $J = 5.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 159.87, 145.45, 117.42, 111.92, 70.35, 64.13, 60.86. HR-ESI-MS:  $m/z$  calcd for  $[\text{M} + \text{H}]^+ \text{C}_{10}\text{H}_{15}\text{O}_4$ : 199.09649; found: 199.09606, error: 2.1 ppm.

### Synthesis of 5-(2-chloroethoxy)-1,3-bis(chloromethyl)-benzene (3)

Compound 2 (2.1 g, 10.6 mmol) and dioxane (30 mL) were added into a 50 mL round-bottom flask equipped with a reflux condenser. Thionyl chloride (3.0 mL) was added into the solution slowly, and after that, the reaction mixture was refluxed overnight. Cooled to rt, the solvent was removed by rotary evaporator and the residue was purified by column chromatography using hexane/acetone (20 : 1) to give the product as yellow viscous liquid (1.62 g, yield: 60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.02 (s, 1H), 6.91 (s, 2H), 4.54 (s, 4H), 4.24 (t,  $J = 5.8$  Hz, 2H), 3.81 (t,  $J = 5.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 159.48, 140.32, 122.33, 115.63, 68.97, 46.45, 42.59. HR-ESI-MS:  $m/z$  calcd for  $[\text{M} + \text{H}]^+ \text{C}_{10}\text{H}_{12}\text{Cl}_3\text{O}$ : 252.99482; found: 252.99506, error: 0.9 ppm.

### Synthesis of 5-(2-chloroethoxy)-1,3-bis((4-hydroxyethyl)phenoxy)methylbenzene (4)

A mixture of 4-hydroxyphenethyl alcohol (2.12 g, 15.3 mmol)  $\text{K}_2\text{CO}_3$  (4.4 g, 31.9 mmol) and dry acetone (30 mL) were stirred for 5 min. Subsequently, compound 3 (1.62 g, 6.38 mmol) dissolved in 10 mL acetone was added and the reaction mixture was refluxed overnight. After cooling to rt, the solid was filtered, and the filtrate was collected. After removal of the solvent, the residue was purified by column chromatography using hexane/acetone (3 : 1) as eluent to give the pure product as yellow liquid (2.62 g, yield 90%).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 7.12 (d,  $J = 8.4$  Hz, 5H), 6.98 (s, 2H), 6.91 (d,  $J = 8.5$  Hz, 4H), 5.07 (s, 4H), 4.30–4.22 (m, 2H), 3.97–3.89 (m, 2H), 3.56 (t,  $J = 7.1$  Hz, 4H), 2.65 (t,  $J = 7.1$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 158.12, 156.51, 139.37, 131.69, 129.66, 119.03, 114.69, 112.90, 68.84, 68.47, 62.37, 55.92, 38.13. EI-MS  $m/z$  456.2 ( $\text{M}^+$ ).

### Synthesis of dihydroxyl-modified julolidine electron donor (5)

To a solution of 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine (2.13 g, 7.37 mmol) in anhydrous DMF was added compound 4 (2.8 g, 6.14 mmol) and  $\text{K}_2\text{CO}_3$  (2.54 g, 18.4 mmol). The mixture was stirred at 110 °C for 12 h. After cooling to rt, the mixture was poured into water (200 mL), extracted with ethyl acetate ( $3 \times 50$  mL) and dried over  $\text{MgSO}_4$ , after removal of the solvent, the residue was purified by column chromatography using hexane/acetone (5 : 1) as eluent to give the product as red solid (2.34 g, yield 55%). mp: 88–91 °C.  $^1\text{H}$  NMR (400 MHz, Acetone)  $\delta$  (ppm): 10.02 (s, 1H), 7.58 (s, 1H), 7.16 (dd,  $J = 8.8, 10.2$  Hz, 7H), 6.94 (d,  $J = 8.6$  Hz, 4H), 5.12 (s, 4H), 4.51 (m, 2H), 4.41 (m, 2H), 3.71 (dd,  $J = 12.6, 7.0$  Hz, 4H), 3.60 (t,  $J = 5.4$  Hz, 2H), 3.40–3.29 (m, 4H), 2.75 (t,  $J = 7.0$  Hz, 4H), 1.77–1.69 (m, 4H), 1.47 (s, 6H), 1.28 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz, acetone)  $\delta$  (ppm): 187.42, 161.18, 160.21, 157.92, 148.87, 140.45, 132.77, 130.45, 127.20, 126.80, 124.52, 119.52, 117.87, 115.44, 113.70, 76.43, 70.14, 68.23, 64.08, 47.79, 47.15, 40.10, 39.34, 36.25, 33.20, 32.63, 30.99,

30.42, 26.77. MS (MALDI-TOF):  $m/z$  calcd for  $\text{C}_{54}\text{H}_{58}\text{N}_4\text{O}_7$ : 693.87; found: 693.99. Element analysis (%), found/calcd): C, 74.30/74.43; H, 7.45/7.41; N, 1.95/2.02.

### Synthesis of JTCFC

A mixture of compound 5 (1 g, 1.44 mmol) and TCF (0.3 g, 1.5 mmol) in methanol (20 mL) was refluxed for 4 h. After cooled to rt, the crude product was collected by filtration and washed with methanol. The product was further purified by column chromatography using hexane/acetone (3 : 1) as eluent. Blue solids (0.8 g yield 64%) was obtained as the pure product. mp: 207–210 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.16 (d,  $J = 15.3$  Hz, 1H), 7.72 (s, 1H), 7.11 (s, 5H), 7.01 (s, 2H), 6.91 (d,  $J = 6.7$  Hz, 4H), 6.81 (d,  $J = 15.3$  Hz, 1H), 5.08 (s, 4H), 4.44 (s, 2H), 4.14 (s, 2H), 3.55 (s, 6H), 3.46 (s, 2H), 3.40 (s, 2H), 2.65 (s, 4H), 1.70 (s, 10H), 1.39 (s, 6H), 1.29 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 182.73, 179.65, 164.80, 163.73, 161.73, 154.89, 148.95, 144.48, 136.90, 135.02, 133.87, 127.48, 123.96, 120.30, 119.78, 119.27, 118.57, 118.42, 117.90, 111.87, 102.54, 92.85, 80.24, 74.07, 72.32, 67.63, 54.27, 52.62, 51.97, 43.41, 39.71, 37.32, 37.07, 35.90, 34.63, 33.98, 31.05. MS (MALDI-TOF):  $m/z$  calcd for  $\text{C}_{54}\text{H}_{58}\text{N}_4\text{O}_7$ : 875.06; found: 875.26. Element analysis (%), found/calcd): C, 73.98/74.12; H, 6.66/6.68; N, 6.38/6.40.

### General procedure for the synthesis of polycarbonate

A solution of bisphenol A bis (chloroformate) in DCE was added dropwise into the mixture of bisphenol A, JTCFC and 0.2 mL pyridine dissolved in DCE under general reflux. And then, the reaction mixture was stirred for another 3 h under reflux. The solution was precipitated in MeOH (200 mL) after cooling to room temperature, and the precipitates were collected by filtration. Then the crude precipitates were further purified by re-precipitation in MeOH and extraction in a Soxhlet extractor with ethyl ether. Next, the pure polycarbonates were dried under vacuum.

**PC-JTCFC-1:** bisphenol A (110 mg, 0.482 mmol), JTCFC (100 mg, 0.114 mmol), and bisphenol A bis (chloroformate) (250 mg, 0.708 mmol). PC-JTCFC-1 was obtained as deep purple powder (0.34 g, yield 92%). GPC:  $M_w = 46\,450$ ,  $M_w/M_n = 1.56$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.14 (d, 16.6 Hz, 1H, vinylic), 7.70 (s 1H, aromatic), 7.38–6.89 (m, 92.7H, aromatic), 6.81 (d, 15.3 Hz, 1H, vinylic), 5.08 (s, 4H, Ph- $\text{OCH}_2\text{O}$ Ph), 4.42 (s, 2H, Ph- $\text{OCH}_2\text{CH}_2\text{O}$ -julolidine), 4.33 (s, 4H, Ph- $\text{CH}_2\text{CH}_2\text{OCO}$ -), 4.12 (s, 2H, Ph- $\text{OCH}_2\text{CH}_2\text{O}$ -julolidine), 3.42 (s, 2H,  $-\text{NCH}_2\text{CH}_2-$ ), 3.35 (s, 2H,  $-\text{NCH}_2\text{CH}_2-$ ), 2.89 (s, 4H, Ph- $\text{CH}_2\text{CH}_2\text{OCO}$ -), 1.76–1.55 (m, 71.2H,  $-\text{CH}_3$  of TCF and  $-\text{NCH}_2\text{CH}_2-$ ), 1.39 (s, 6H,  $-\text{CH}_3$  of julolidine), 1.29 (s, 6H,  $-\text{CH}_3$  of julolidine). IR (KBr pellet,  $\text{cm}^{-1}$ ): 2968 and 2870 ( $-\text{CH}_3$  and  $-\text{CH}_2-$ ), 2224 ( $-\text{CN}$ ), 1774 ( $\text{C}=\text{O}$ ), 1506 (aromatic C-C), 1228 (C-O), UV-Vis (THF):  $\lambda_{\text{max}}$  (nm) = 613.

**PC-JTCFC-2:** bisphenol A (83 mg, 0.364 mmol), JTCFC (200 mg, 0.229 mmol), and bisphenol A bis (chloroformate) (250 mg, 0.708 mmol). PC-JTCFC-2 was obtained as deep purple powder (0.4 g, yield 90%). GPC:  $M_w = 73\,710$ ,  $M_w/M_n = 1.56$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.14 (d, 16.6 Hz, 1H, vinylic), 7.70

(s 1H, aromatic), 7.38–6.89 (m, 48.7H, aromatic), 6.81 (d, 15.3 Hz, 1H, vinylic), 5.08 (s, 4H, Ph–OCH<sub>2</sub>OPh), 4.42 (s, 2H, Ph–OCH<sub>2</sub>CH<sub>2</sub>–O–julolidine), 4.33 (s, 4H, Ph–CH<sub>2</sub>–CH<sub>2</sub>OCO–), 4.12 (s, 2H, Ph–OCH<sub>2</sub>CH<sub>2</sub>–O–Julolidine), 3.42 (s, 2H, –NCH<sub>2</sub>–CH<sub>2</sub>–), 3.35 (s, 2H, –NCH<sub>2</sub>–CH<sub>2</sub>–), 2.89 (s, 4H, Ph–CH<sub>2</sub>–CH<sub>2</sub>OCO–), 1.76–1.55 (m, 38.3H, –CH<sub>3</sub> of TCF and –NCH<sub>2</sub>–CH<sub>2</sub>–), 1.39 (s, 6H, –CH<sub>3</sub> of julolidine), 1.29 (s, 6H, –CH<sub>3</sub> of julolidine). IR (KBr pellet, cm<sup>–1</sup>): 2968 and 2870 (–CH<sub>3</sub> and –CH<sub>2</sub>–), 2224 (–CN), 1772 (C=O), 1506 (aromatic C–C), 1228 (C–O), UV–Vis (THF):  $\lambda_{\text{max}}$  (nm) = 613.

**PC-JTCFC-3:** bisphenol A (56 mg, 0.246 mmol), JTCFC (300 mg, 0.343 mmol), and bisphenol A bis (chloroformate) (250 mg, 0.708 mmol). PC-JTCFC-3 was obtained as deep purple powder (0.48 g, yield 92%). GPC:  $M_w = 145\,990$ ,  $M_w/M_n = 1.57$ . <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 8.14 (d, 16.6 Hz, 1H, vinylic), 7.70 (s 1H, aromatic), 7.38–6.89 (m, 35.8H, aromatic), 6.81 (d, 15.3 Hz, 1H, vinylic), 5.08 (s, 4H, Ph–OCH<sub>2</sub>OPh), 4.42 (s, 2H, Ph–OCH<sub>2</sub>CH<sub>2</sub>–O–julolidine), 4.33 (s, 4H, Ph–CH<sub>2</sub>–CH<sub>2</sub>OCO–), 4.12 (s, 2H, Ph–OCH<sub>2</sub>CH<sub>2</sub>–O–julolidine), 3.42 (s, 2H, –NCH<sub>2</sub>–CH<sub>2</sub>–), 3.35 (s, 2H, –NCH<sub>2</sub>–CH<sub>2</sub>–), 2.89 (s, 4H, Ph–CH<sub>2</sub>–CH<sub>2</sub>OCO–), 1.76–1.55 (m, 28.5H, –CH<sub>3</sub> of TCF and –NCH<sub>2</sub>–CH<sub>2</sub>–), 1.39 (s, 6H, –CH<sub>3</sub> of julolidine), 1.29 (s, 6H, –CH<sub>3</sub> of julolidine). IR (KBr pellet, cm<sup>–1</sup>): 2968 and 2870 (–CH<sub>3</sub> and –CH<sub>2</sub>–), 2224 (–CN), 1765 (C=O), 1506 (aromatic C–C), 1228 (C–O), UV–Vis (THF):  $\lambda_{\text{max}}$  (nm) = 612.

### Preparation of the polymer films

The synthesized PC-JTCFCs were dissolved in cyclopentanone to form the 15 wt% solution. After filtering with a 0.2  $\mu\text{m}$  syringe filter to remove large particulates, the obtained polymer solutions were spin-coated on indium-tin oxide (ITO) glass substrates. To remove the residual solvent, the films were dried *in vacuo* for 12 h.

## Results and discussion

### Chromophore and polymer synthesis

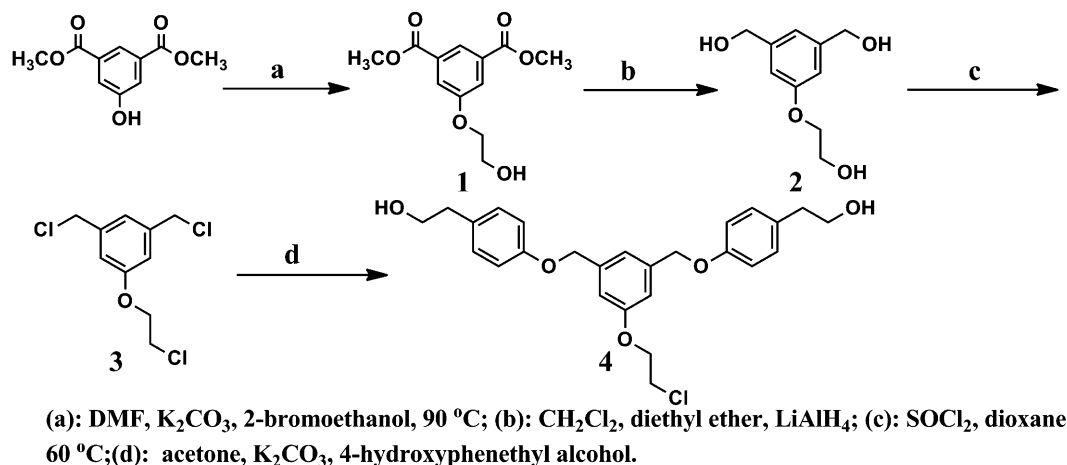
As previously reported,<sup>35,36</sup> the synthesis of EO polycarbonates adopting the copolymerization strategy required the NLO chromophores possess two hydroxyl groups. However, the

julolidine electron donor reported in the previous work only has one phenolic hydroxyl group. In order to synthesis the diol-functionalized dendritic NLO chromophore, a dendron with two hydroxyl groups was designed and synthesized starting from the commercially available 5-hydroxyisophthalate firstly (Scheme 2). Treatment of 5-hydroxyisophthalate with 2-bromoethanol in the presence of K<sub>2</sub>CO<sub>3</sub> afforded compound **1**, followed by the LAH reduction yielded the triol compound **2**. Chlorination of compound **2** with thionyl chloride provided the corresponding trichloro substituted compound **3** in a good yield. Owing to the different reactivity of phenyl chloride and alkyl chloride, treating compound **3** with 4-hydroxyphenethyl alcohol selectively afforded the diol-functionalized dendron compound **4**. Through a S<sub>N</sub>2 reaction with 8-hydroxy-1,1,7,7-tetramethyl-formyljulolidine in anhydrous DMF, the dihydroxyl-modified dendritic julolidine electron donor **5** was synthesized. Finally, the diol functionalized dendritic chromophore JTCFC was prepared through the Knoevenagel reaction with TCF electron acceptor in methanol (Scheme 3). The dendritic chromophore and all intermediates are isolated and characterized by MS, <sup>1</sup>H NMR and <sup>13</sup>C NMR, which demonstrated successful preparation of the designed chromophore.

Scheme 4 features the copolymerization of synthesized JTCFC with bisphenol A bis (chloroformate) to EO polycarbonates using the method proposed previously.<sup>35</sup> Polycondensation of the JTCFC and bisphenol A with bisphenol A bis(chloroformate) in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> solution using pyridine as acid scavenger afforded the polycarbonates PC-JTCFCs with a yield of 90–92%, where bisphenol A was used to adjust the chromophore content. The resultant polycarbonates were soluble in common polar organic solvents such as DMSO, DMF, THF, halogenated solvents and cyclopentanone. These polymers also exhibited good film forming property. Homogeneous, smooth, and high-quality films were obtained through spin-coating from the corresponding polymers solution.

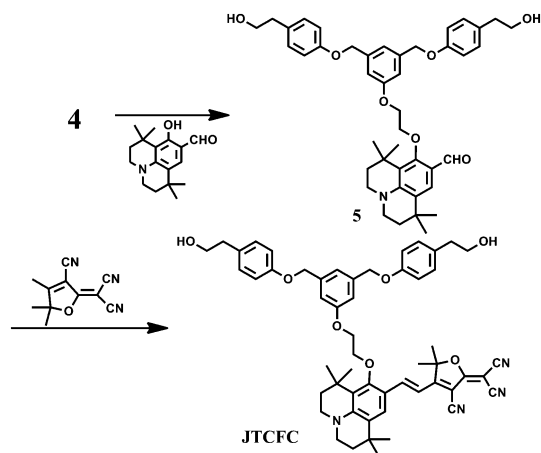
### Structure characterization

To demonstrate the successful preparation of the designed EO polycarbonates, FT-IR and <sup>1</sup>H NMR spectra are used to



Scheme 2 Structure and synthesis of the designed dendron.





Scheme 3 The synthesis of dendritic JTCFC.

determine the structure of obtained polymers. Fig. 1 shows the FT-IR spectra of PC-JTCFCs. The absorption band near 1779 and 1230  $\text{cm}^{-1}$  are the characteristic absorption band of carbonate's carbonyl group and  $-\text{C}-\text{O}-$  group, indicating the formation of carbonate group. There was an absorption band derived from the  $-\text{CN}$  at 2224  $\text{cm}^{-1}$  in the FT-IR spectra, which indicated that the JTCFC moieties were stable during polymerization. Fig. S1 and S3<sup>†</sup> show the  $^1\text{H}$  NMR of JTCFC and the obtained polymers respectively. In Fig. S3<sup>†</sup>, the signals of JTCFC could be easily found in the  $^1\text{H}$ -NMR spectra of polymers. The feature signal of double bond proton in PC-JTCFCs was appeared at 8.14 ppm, which is more or less the same as JTCFC, and this further indicated that the D- $\pi$ -A structure hadn't been destroyed during the polymerization process and the chromophore could tolerate the polymerization condition even if the polymerization was carried out at a higher temperature for a long time. In  $^1\text{H}$  NMR spectra of JTCFC, the signal of  $\text{CH}_2$  in  $\text{HO}-\text{CH}_2\text{CH}_2-\text{Ph}$  appeared at 3.55 ppm, and it moved to 4.33 ppm after

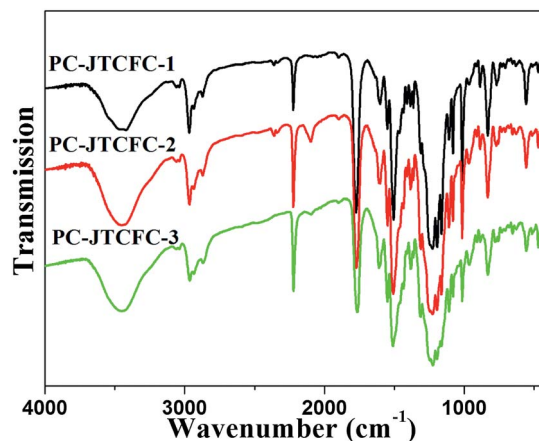
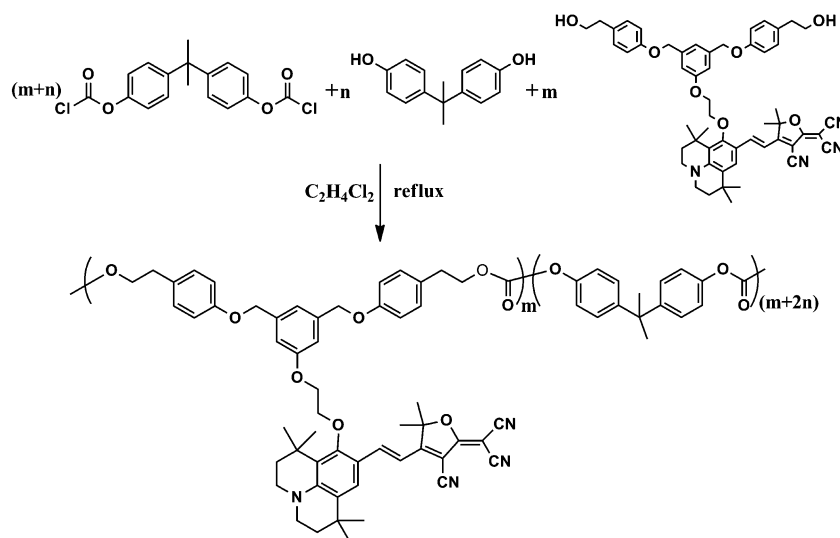


Fig. 1 FT-IR spectra of PC-JTCFCs.

polymerization. The signals of aromatic protons and methyl proton in bisphenol A appeared at 7.25 and 1.60, and these two signals were overlapped by the corresponding singlets of JTCFC. Except these signals, the other signals of PC-JTCFCs are consistent with the JTCFC, indicating the designed polymers were successfully prepared.

The molar ratio of JTCFC and bisphenol A in the synthesized polycarbonates could be calculated from the integration ratios of double bond's proton and aromatic proton (or methyl proton). The measured ratio of PC-JTCFC-1, PC-JTCFC-2 and PC-JTCFC-3 are 1 : 10.2, 1 : 4.7 and 1 : 3.1, respectively, which were very close to the feed ratio (details of feed ratio and measured ration are listed in Table 1). These results indicated that the chromophore content in the polycarbonates could be well-controlled by controlling the feed ratio, which directly guaranteed the reproducibility of the polymers' properties.

The molecular weight and molecular distribution were estimated by GPC on the basis of PS standards (see Fig. S4<sup>†</sup> and the related results are listed in Table 1). The obtained



Scheme 4 General strategy for the synthesis of PC-JTCFCs.

Table 1 Characterization and properties of EO polycarbonates

Product	Feed ratio <sup>a</sup>	Measured ratio <sup>b</sup>	Content <sup>c</sup> (wt%)	Yield (%)	$M_w^d$	$M_w/M_n^d$	$T_g^e$ (°C)	$\lambda_{\max}$ (THF) (nm)	$n_{(1310\text{ nm})}$	$r_{33}^f$ (pm V <sup>-1</sup> )
PC-JLTCFC-1	1 : 9.4	1 : 10.2	13%	92	46 450	1.56	150	613	1.590	30
PC-JLTCFC-2	1 : 4.2	1 : 4.7	22%	90	73 710	1.56	149	613	1.613	53
PC-JLTCFC-3	1 : 2.4	1 : 3.1	26%	92	145 990	1.57	151	612	1.629	55

<sup>a</sup> The ratio of JTCFC: the sum of bisphenol A and bisphenol A bis (chloroformate). <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Core of chromophore, not include the isolation group. <sup>d</sup> Determined by GPC in THF on the basis of a polystyrene calibration. <sup>e</sup> Performed at a heating rate of 10 °C.min<sup>-1</sup> under nitrogen atmosphere by DSC. <sup>f</sup> Measured by simple reflection technique at 1310 nm.

polycarbonates possess higher molecular weight in the range of 46 450–145 990, and molecular weight distributions near 1.56. Not like the EO polycarbonates reported previously, where the molecular weight decreased as the increase of the chromophores content owing to the steric effect, the molecular weight of PC-JTCFCs increased as the increase of the chromophores content in the polymer backbone. This may be caused by increase of the content of high molecular weight monomer, at the same time, the molecular modification weakens the steric effect, which makes the obtained polymers maintain a higher polymerization degree. To further understand this and study the influence of the dendron on chromophore's configuration, JTCFC's structure optimization using Gaussian03 was carried out at hybrid B3LYP level by employing the split valence 6–31 g(d) basis set as shown in Fig. S5.†, <sup>38</sup> It could be easily found that the dendron was perpendicular to the chromophore's D- $\pi$ -A conjugated plane of chromophore after linking to the 8-position of electron donor. The two hydroxyl groups stayed far away from the conjugated plane, so chromophore's steric effect was greatly weakened when polymerization compared to the conventional dihydroxyl aniline-based chromophores, and this is consistent with the explanation of molecular weight results. According to this analysis, it could also be deduced that the chromophores in the polymer backbones could be well isolated and stay far away from each other, and the dipole–dipole interaction were effectively suppressed.

### Thermal properties of polymers

The thermal behavior of prepared polycarbonates is studied through investigating the TGA and DSC. TGA thermograms of

PC-JTCFCs are shown in Fig. 2. Similar to the decomposition behavior of JTCFC (Fig. S6†), PC-JTCFCs began to decompose at 240 °C, which indicated that decomposition at lower temperature was mainly induced by the NLO chromophore segment. These thermal stabilities are good enough for the EO materials' application, because the real use generally carried out under 200 °C. Fig. 3 shows the DSC curves of PC-JTCFCs, with the results summarized in Table 1. All the  $T_g$ s appear at nearly 150 °C. Unlike the EO polycarbonates reported previously,<sup>35,36</sup> the  $T_g$  values of PC-JTCFCs changed slightly with the variation of chromophores content. Such phenomenon could be explained by the  $T_g$  drop caused by the introduction of bulk group being offset by the increase of molecular weight. Previous work indicated that the  $T_g$  values will increase with the increase of chromophore content due to the stronger interchromophore interactions,<sup>35</sup> and such phenomenon didn't appear here, indicating that the interchromophore interactions play an unimportant role in PC-JTCFCs. To some extent, the  $T_g$  results showed that the molecular modification effectively suppressed the interchromophore interaction.

### EO properties of polymers

In order to evaluate the EO activities of synthetic polycarbonates, the asymmetric alignment of the NLO chromophores was realized adopting the corona poling method. PC-JTCFCs films were baked to the poling temperature (near  $T_g$ ),

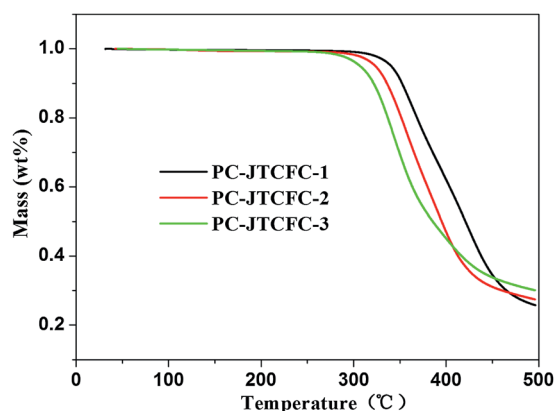


Fig. 2 TGA curves of PC-JTCFCs.

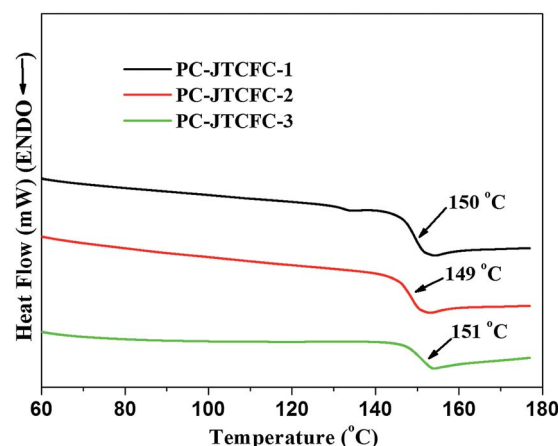


Fig. 3 DSC curves of PC-JTCFCs.

then the poling voltage was applied and kept for 10 min. After the samples cooled to room temperature, the poling voltage was removed.

The EO coefficients of the poled films were determined by the simple reflection technique initially proposed by Teng and Man.<sup>39</sup> The  $r_{33}$  values were calculated by the following equation:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{3/2}}{(n^2 - 2 \sin^2 \theta)} \frac{1}{\sin^2 \theta} \quad (1)$$

where  $r_{33}$  is the EO coefficient of the poled polymer;  $V_m$  is the modulating voltage;  $\theta$  is the incidence angle;  $I_c$  is the output beam intensity;  $I_m$  is the amplitude of the modulation;  $n$  is the refractive indices of the polymer films;  $\lambda$  is the optical wavelength.

Table 1 lists the obtained  $r_{33}$  values measured under optimum poling conditions. PC-JTCFC-1 (13 wt%) obtained the desirable  $r_{33}$  value of 30 pm V<sup>-1</sup>. When the chromophore content increased to 22 wt%, the  $r_{33}$  values reached 53 pm V<sup>-1</sup>. However, when concentration was increased to 26 wt%, the  $r_{33}$  values only changed slightly and reached the saturated value. The maximum value of PC-JTCFCs was obtained as 55 pm V<sup>-1</sup> at 26 wt% (PC-JTCFC-3), and this result is much better than the doped guest–host systems we reported previously where the analogue julolidine-based chromophores doped into APC could only obtain the maximum value of 36 pm V<sup>-1</sup> at 40 wt%.<sup>32</sup> The enhanced EO activity indicated that the chromophores in PC-JTCFCs could be effectively oriented, which was probably attributed to the fact that the chromophores in PC-JTCFCs are well-isolated and the inter-chromophore dipole–dipole interaction are effectively suppressed below the saturated loading density. The results also proved that the designed dendron really plays an important role in the translation of microscopic molecular hyperpolarizability into macroscopic EO activity, which is consistent with our original design. In comparison of PC-JTCFCs and guest–host system, we could find that the PC-JTCFCs' saturated loading density is lower than the doped system, and this indicated that there could exist inevitable aggregation of dipolar chromophores in an antiparallel manner which could be difficult to dissociate during the poling process in the doped system even below the saturated loading density, and the effective concentration (the non-aggregated chromophores) is lower than the doped concentration. The lower saturated loading density further proved the effective suppression of chromophore aggregation.

The long-term alignment stability of the poled films was evaluated by heating the poled samples at 85 °C and monitoring the  $r_{33}$  changes as shown in Fig. 4. After fast decay during the first 24 h because of the recovery of the bond angle and bond length of the oriented chromophores,<sup>40</sup> PC-JTCFC-3 retained 85% of the initial  $r_{33}$  value and stayed almost unchanged for more than 500 h. The desired temporal stability was attributed, first to the higher  $T_g$  of the polycarbonate which made the polymer backbone need more energy to move,<sup>41</sup> and second, to the advantage of the covalent attachment strategy where chromophores were covalently tethered to the polymer backbone.

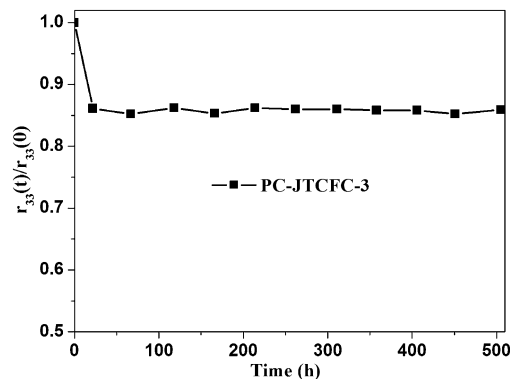


Fig. 4 Temporal stability of poled PC-JTCFC-3 film at 85 °C for 500 h.

## Conclusions

Adopting a simple copolymerization strategy, we successfully prepared a series of novel EO polycarbonates incorporating julolidine-based NLO chromophores and isolation groups. Owing to the synergistic effect of julolidine electron donor's hindrance, dendron and polymer backbone's isolation, the NLO chromophores in the polycarbonates backbone were well-isolated and the interchromophore interactions were effectively suppressed which was demonstrated by the polymers' molecular weight and  $T_g$  values. Such strategy effectively translates the hyperpolarizability into macroscopic EO activity, and the poled films of PC-JTCFC-3 revealed a maximum  $r_{33}$  value of 55 pm V<sup>-1</sup> which was greatly enhanced as compared to the guest–host system. The poled film also exhibited a desirable temporal stability at 85 °C for more than 500 h. These results indicated that the proposed design strategy for NLO chromophores and EO polymers provides an effective method for the preparation of excellent EO materials, which are expected to be used in device fabrication.

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## References

- 1 L. R. Dalton, P. A. Sullivan and D. H. Bale, *Chem. Rev.*, 2010, **110**, 25–55.
- 2 P. A. Sullivan and L. R. Dalton, *Acc. Chem. Res.*, 2010, **43**, 10–18.
- 3 J. Luo, X.-H. Zhou and A. K. Y. Jen, *J. Mater. Chem.*, 2009, **19**, 7410–7424.
- 4 M. J. Cho, D. H. Choi, P. A. Sullivan, A. J. P. Akelaitis and L. R. Dalton, *Prog. Polym. Sci.*, 2008, **33**, 1013–1058.
- 5 H.-L. Lin, T.-Y. Juang, L.-H. Chan, R.-H. Lee, S. A. Dai, Y.-L. Liu, W.-C. Su and R.-J. Jeng, *Polym. Chem.*, 2011, **2**, 685–693.



- 6 X. Piao, X. Zhang, Y. Mori, M. Koishi, A. Nakaya, S. Inoue, I. Aoki, A. Otomo and S. Yokoyama, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 47–54.
- 7 Z. Li, Q. Li and J. Qin, *Polym. Chem.*, 2011, **2**, 2723–2740.
- 8 A. Scarpaci, C. Cabanetos, E. Blart, Y. Pellegrin, V. Montembault, L. Fontaine, V. Rodriguez and F. Odobel, *Polym. Chem.*, 2011, **2**, 157–167.
- 9 C. Peng, J. Wu, J. Liu, L. Qiu, X. Liu, S. Bo and Z. Zhen, *Polym. Chem.*, 2013, **4**, 2703–2708.
- 10 G. Deng, S. Bo, T. Zhou, R. Zhang, J. Liu, X. Liu, Z. Zhen and L. Qiu, *Sci. China: Chem.*, 2013, **56**, 169–173.
- 11 T. D. Kim, J. D. Luo, Y. J. Cheng, Z. W. Shi, S. Hau, S. H. Jang, X. H. Zhou, Y. Tian, B. Polishak, S. Huang, H. Ma, L. R. Dalton and A. K. Y. Jen, *J. Phys. Chem. C*, 2008, **112**, 8091–8098.
- 12 W. Wu, S. Xin, Z. Xu, C. Ye, J. Qin and Z. Li, *Polym. Chem.*, 2013, **4**, 3196–3203.
- 13 Y. Mori, K. Nakaya, X. Piao, K. Yamamoto, A. Otomo and S. Yokoyama, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 1254–1260.
- 14 W. Wu, C. Wang, C. Zhong, C. Ye, G. Qiu, J. Qin and Z. Li, *Polym. Chem.*, 2013, **4**, 378–386.
- 15 T. Zhou, J. Liu, G. Deng, J. Wu, S. Bo, L. Qiu, X. Liu and Z. Zhen, *Mater. Lett.*, 2013, **97**, 117–120.
- 16 J. Luo, H. Ma, M. Haller, A. K. Y. Jen and R. R. Barto, *Chem. Commun.*, 2002, 888–889.
- 17 W. Wu, Q. Huang, G. Qiu, C. Ye, J. Qin and Z. Li, *J. Mater. Chem.*, 2012, **22**, 18486–18495.
- 18 W. Wu, Z. Zhu, G. Qiu, C. Ye, J. Qin and Z. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 5124–5133.
- 19 W. Wu, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin and Z. Li, *Chem.–Eur. J.*, 2012, **18**, 11019–11028.
- 20 W. Wu, L. Huang, L. Xiao, Q. Huang, R. Tang, C. Ye, J. Qin and Z. Li, *RSC Adv.*, 2012, **2**, 6520–6526.
- 21 W. Wu, G. Yu, Y. Liu, C. Ye, J. Qin and Z. Li, *Chem.–Eur. J.*, 2013, **19**, 630–641.
- 22 Z. Li, W. Wu, C. Ye, J. Qin and Z. Li, *Polym. Chem.*, 2010, **1**, 78–81.
- 23 J. Luo, S. Liu, M. Haller, L. Liu, H. Ma and A. K. Y. Jen, *Adv. Mater.*, 2002, **14**, 1763–1768.
- 24 H. Ma, B. Chen, T. Sassa, L. R. Dalton and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2001, **123**, 986–987.
- 25 P. A. Sullivan, H. Rommel, Y. Liao, B. C. Olbricht, A. J. P. Akelaitis, K. A. Firestone, J.-W. Kang, J. Luo, J. A. Davies, D. H. Choi, B. E. Eichinger, P. J. Reid, A. Chen, A. K. Y. Jen, B. H. Robinson and L. R. Dalton, *J. Am. Chem. Soc.*, 2007, **129**, 7523–7530.
- 26 Z. Li, Z. Li, C. a. Di, Z. Zhu, Q. Li, Q. Zeng, K. Zhang, Y. Liu, C. Ye and J. Qin, *Macromolecules*, 2006, **39**, 6951–6961.
- 27 Z. Li, W. Wu, Q. Li, G. Yu, L. Xiao, Y. Liu, C. Ye, J. Qin and Z. Li, *Angew. Chem., Int. Ed.*, 2010, **49**, 2763–2767.
- 28 W. Wu, L. Huang, C. Song, G. Yu, C. Ye, Y. Liu, J. Qin, Q. Li and Z. Li, *Chem. Sci.*, 2012, **3**, 1256–1261.
- 29 Q. Zeng, Z. a. Li, Z. Li, C. Ye, J. Qin and B. Z. Tang, *Macromolecules*, 2007, **40**, 5634–5637.
- 30 W. Wu, C. Ye, J. Qin and Z. Li, *Polym. Chem.*, 2013, **4**, 2361–2370.
- 31 J. Wu, S. Bo, J. Liu, T. Zhou, H. Xiao, L. Qiu, Z. Zhen and X. Liu, *Chem. Commun.*, 2012, **48**, 9637–9639.
- 32 J. Wu, J. Liu, T. Zhou, S. Bo, L. Qiu, Z. Zhen and X. Liu, *RSC Adv.*, 2012, **2**, 1416–1423.
- 33 F. Kajzar, K. S. Lee and A. K. Y. Jen, in *Polymers for Photonics Applications II: Nonlinear Optical, Photorefractive and Two-Photon Absorption Polymers*, ed. K. S. Lee, Springer, New York, 2003, vol. 161, ch. 1, pp. 1–85.
- 34 T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays and A. Persoons, *J. Mater. Chem.*, 1997, **7**, 2175–2189.
- 35 G. Deng, S. Bo, T. Zhou, H. Huang, J. Wu, J. Liu, X. Liu, Z. Zhen and L. Qiu, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 2841–2849.
- 36 G. Deng, H. Huang, P. Si, H. Xu, J. Liu, S. Bo, X. Liu, Z. Zhen and L. Qiu, *Polymer*, 2013, **54**, 6349–6356.
- 37 S. Liu, M. A. Haller, H. Ma, L. R. Dalton, S. H. Jang and A. K. Y. Jen, *Adv. Mater.*, 2003, **15**, 603–607.
- 38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheseman, J. A. Montgomery Jr, T. K. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. D. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh, PA, 2003.
- 39 C. C. Teng and H. T. Man, *Appl. Phys. Lett.*, 1990, **56**, 1734–1736.
- 40 R. Zhang, J. Liu, S. Bo, G. Deng, C. Peng, X. Liu and Z. Zhen, *Colloid Polym. Sci.*, 2012, **290**, 1819–1823.
- 41 M. Faccini, M. Balakrishnan, M. B. J. Diemeer, R. Torosantucci, A. Driessen, D. N. Reinhoudt and W. Verboom, *J. Mater. Chem.*, 2008, **18**, 5293–5300.