Influence of the position of the connecting spacer of the chromophore on the nonlinear optical response

David Briers,¹ Lieven De Cremer,¹ Guy Koeckelberghs,¹ Stijn Foerier,² Thierry Verbiest,²
Celest Samyn^{* 1}

Laboratory of Macromolecular and Physical Organic Chemistry, Katholieke Universiteit
Leuven, Celestijnenlaan ¹200 F, ²200 D, 3001 Heverlee, Belgium

Fax: +32(0)16327990

Tel: +32(0)16327425

E-mail: celest.samyn@chem.kuleuven.be

Keywords: fluorinated vinyl copolymers, functionalization of polymers, nonlinear polymers, second-harmonic generation, nonlinear optics

Summary

A new chromophore, **C1**, based on a similar D π A-structure of the **FTC**-chromophore but with a hydroxyalkyl spacer perpendicular to the direction of the dipole moment was synthesized. Both chromophores and the **CLD**-chromophore were used to prepare high T_g nonlinear optical vinyl polymers. The influence of the position of the spacer on the D π A-system on the nonlinear optical response of the resulting polymers was investigated.

Introduction

For nearly two decades, much research has been focussed on the development of polymeric second-order nonlinear optical (NLO) materials due to their great potential to be used to fabricate electro-optic devices.^[1-3] A prerequisite for the design of a NLO polymer is the synthesis of a good NLO chromophore: a strong donor- and acceptor-group connected by a highly polarizable, chemically and thermally stable conjugated π -system. Strong chromophores, such as the **FTC**- and **CLD**-chromophore (Figure 1^[3]), are characterized by a large dipole moment (μ) and a large first order hyperpolarizability (β), but unfortunately tend

to lower the NLO response at higher chromophore loading levels due to aggregation effects. Therefore, it is preferable to introduce side-groups covalently attached to the conjugated π -system in order to make interchromophore electrostatic interactions less favorable, as reported by Dalton et al.^[3-6] Such side-groups also often result in a higher solubility and chemical stability. There is however another point that comes forth regarding the poling-induced alignment of the chromophores that, to our knowledge, has not yet been examined. When one chooses to covalently attach a chromophore to a polymer backbone, the position of the connecting alkyl spacer may be perpendicular to or parallel with the direction of the dipole moment of the chromophore. Since the latter is nearly always the case and one cannot a priori point out the better choice, we report here the synthesis of a new chromophore, **C1** (Figure 1), based on a similar D π A-structure as the **FTC**-chromophore, but in which the spacer is incorporated perpendicular to the direction of the dipole moment. As a consequence, the **FTC**- and **C1**-chromophore have a comparable $\mu\beta$ -value, but differ in the position of the spacer on the D π A-system, allowing us to investigate the influence of the spacer-position on the poling-induced alignment of the chromophores. We also report the synthesis of two easily accessible precursor polymers, poly(adamantyl methacrylate-methacrylic acid) and poly(adamantyl methacrylate-(2-trifluoromethyl)acrylic acid), which can be readily functionalized with hydroxyalkyl chromophores under mild reaction conditions (Mitsunobu reaction).

Experimental part

Materials

All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received, unless otherwise stated. Tetrahydrofuran (THF), dioxane and diethylether were dried over a Na/K alloy. *N,N*-dimethylformamide (DMF) was distilled over P₂O₅ and further dried on molecular sieve (4Å). *N*-methylpyrrolidinone (NMP) was distilled over

calciumhydride. Cyclohexanone was distilled prior to use. Adamantyl methacrylate and the **FTC**- and **CLD**-chromophores were synthesized as reported elsewhere.^[7,8]

Synthesis of chromophore C1

4-Piperidinobenzaldehyde **1**

A mixture of 4-fluorobenzaldehyde (67.7 mL, 63.0 mmol), piperidine (49.3 mL, 50.0 mmol), dry K₂CO₃ (86.9 g, 0.63 mol), DMSO (500 mL) and aliquat (1 mL) was stirred for three days at 95 °C. After cooling to ambient temperature, the mixture was poured into iced water (3 L). The precipitate was filtered off, dissolved in CH₂Cl₂ and dried over MgSO₄. Pure **1** could be obtained after recrystallization from toluene. Yield = 60.7 g (64 %), m.p. = 57.7-62 °C.

¹H-NMR (CDCl₃): δ = 1.68 (m, 6H), 3.40 (m, 4H), 6.89 (d, 2H), 7.72 (d, 2H), 9.75 (s, 1H)

4-Bromo-2-thiophenemethanol **2**

Pure **2** was obtained as an oil in 96 % yield following the usual procedure for reduction, using one equivalent of NaBH₄ and ethanol as a solvent. Hydrolysis was carried out using a saturated NH₄Cl-solution.

¹H-NMR (CDCl₃): δ = 4.75 (s, 2H), 6.90 (s, 1H), 7.15 (s, 1H)

4-Bromo-2-thienylmethylenetriphenylphosphoniumbromide **3**

A mixture of **2** (24.3 g, 126.0 mmol) and triphenylphosphoniumbromide (52.7 g, 126.0 mmol) in acetonitrile (250 mL) was allowed to reflux for 4 hours under argon atmosphere. After cooling to ambient temperature, the precipitate was filtered off and dried under reduced pressure yielding 46.3 g (71 %) of pure **3**, m.p. = 297.8-299.0 °C

¹H-NMR (DMSO-d₆): δ = 5.53 (d, 2H, J = 14.6 Hz), 6.68 (dd, 1H, J = 2.8 Hz, J = 1.1 Hz), 7.62 (dd, 1H, J = 2.8 Hz, J = 1.5 Hz), 7.74 (m, 12H), 7.93 (m, 3H)

N-[4-[2-(4-bromo-2-thienyl)ethenyl]phenyl]piperidine **4**

A mixture of **3** (15.0 g, 29.0 mmol) and **1** (5.50 g, 29.0 mmol) in absolute ethanol (60 mL) was treated with sodium ethanolate [prepared from sodium (1.0 g, 43.5 mmol) and ethanol (35

mL)], followed by heating for 5 hours at 90 °C. When cooled, the precipitate was filtered off, dissolved in CH₂Cl₂, washed with water and dried over MgSO₄. The product was purified by column chromatography (silicagel; eluent: CH₂Cl₂/*n*-hexane (9/1 v/v)) and finally recrystallized from ethylacetate yielding 5.40 g (54 %) of **4**, as a mixture of *cis*/*trans* (40/60), m.p. = 93.0-96.0 °C and 136.0-137.0 °C.

¹H-NMR (CDCl₃): *trans* δ = 1.61 (m, 2H), 1.71 (m, 4H), 3.21 (m, 4H), 6.84 (d, 1H, J = 15.7 Hz), 6.89 (m, 1H), 6.90 (m, 1H), 6.96 (d, 1H, J = 15.7 Hz), 6.99 (d, 2H), 7.35 (d, 2H); *cis* δ = 1.61 (m, 2H), 1.71 (m, 4H), 3.21 (m, 4H), 6.44 (d, 1H, J = 11.7 Hz), 6.53 (d, 1H, J = 11.7 Hz), 6.86 (m, 1H), 6.87 (m, 1H), 6.99 (d, 2H), 7.23 (d, 2H)

N-[4-[2-[4-[(*t*-butyldimethyl)silyloxy]butyl]thien-2-yl-ethenyl]phenyl]piperidine **6**

A freshly prepared Grignard-reagent of **5** [obtained by adding a solution of **5** (4.00 g, 18.0 mmol) in dry diethylether (5 mL) to a suspension of Mg (0.432 g, 18.0 mmol) in dry diethylether (15 mL)] was added *via cannula* to a cooled (0 °C) mixture of **4** (5.35 g, 15.4 mmol) and Ni(dppp)Cl₂ (83.5 mg, 0.154 mmol) in dry THF (20 mL) under argon atmosphere. The resulting mixture was allowed to stir for 24 hours at room temperature and then treated with slightly acidified water followed by the usual work-up (extraction with water and a NaCl-solution followed by drying over MgSO₄). The product was purified by column chromatography (silicagel; eluent: CH₂Cl₂/*n*-hexane (8/2 v/v)), yielding 3.20 g (46 %) of **6** as a mixture of *cis*/*trans* (35/65), m.p. = 44.5-45.5 °C and 77.0-79.0 °C.

¹H-NMR (CDCl₃): *trans* δ = 0.06 (s, 6H), 0.91 (s, 9H), 1.60 (m, 4H), 1.72 (m, 6H), 2.58 (m, 2H), 3.21 (m, 4H), 3.64 (t, 2H), 6.74 (s, 1H), 6.85 (m, 1H), 6.88 (d, 1H, J = 16.1 Hz), 6.89 (m, 2H), 7.03 (d, 1H, J = 16.1 Hz), 7.36 (d, 2H); *cis* δ = 0.06 (s, 6H), 0.91 (s, 9H), 1.60 (m, 4H), 1.72 (m, 6H), 2.58 (m, 2H), 3.21 (m, 4H), 3.64 (t, 2H), 6.45 (d, 1H, J = 12.0 Hz), 6.52 (d, 1H, J = 12.0 Hz), 6.70 (s, 1H), 6.81 (s, 1H), 6.89 (m, 2H), 7.29 (d, 2H)

3-(4-hydroxybutyl)-5-[2-[4-[*N*-piperidinyl]phenyl]ethenyl]thien-2-yl **7**

Under argon atmosphere, *n*-butyllithium (4.36 mL, 10.2 mmol; 2.50 M solution in hexane) was added to a cooled (-78 °C) solution of **6** (3.10 g, 6.80 mmol) in dry THF (20 mL) followed by dry DMF (4.2 mL). A 2 M HCl-solution was added (pH 2~3 after addition) at room temperature. After stirring overnight at 50 °C, the solution was neutralized using a 25 % NH₃-solution followed by the usual work-up. The product was purified by column chromatography (silicagel; eluent: CH₂Cl₂/EtOAc (8/2 v/v)), yielding 2.0 g (80 %) of **7** as a mixture of *cis*/*trans* (5/95), m.p. = 112.0-122.0 °C.

¹H-NMR (CDCl₃): *trans* δ = 1.40 (t, 1H), 1.70 (m, 10 H), 2.98 (t, 2H), 3.27 (t, 4H), 3.71 (t, 2H), 6.90 (d, 2H), 6.93 (s, 1H), 6.98 (d, 1H, J = 16.1 Hz), 7.08 (d, 1H, J = 16.1 Hz), 7.39 (d, 2H), 9.97 (s, 1H); *cis* δ = 1.40 (t, 1H), 1.70 (m, 10H), 2.98 (t, 2H), 3.27 (t, 4H), 3.71 (t, 2H), 6.48 (d, 1H, J = 12.0 Hz), 6.69 (d, 1H, J = 12.0 Hz), 6.90 (d, 2H), 6.93 (s, 1H), 7.26 (d, 2H), 9.91 (s, 1H)

Chromophore **C1**

A mixture of **7** (1.48 g, 4.01 mmol), **TCF**-acceptor (0.960 g, 4.82 mmol) and triethylamine (0.5 mL) in chloroform (90 mL) was allowed to reflux under argon atmosphere using a Soxhlet-apparatus filled with molecular sieve (4Å). Pure *trans* isomer could be isolated after purification by column chromatography (silicagel; eluents: CH₂Cl₂/EtOAc (8/2 v/v)). Yield = 0.73 g (33 %), m.p. = 188.0-190.0 °C

UV (THF): λ_{max} (ε) = 610 nm (43725 L·mol⁻¹·cm⁻¹)

¹H-NMR (CDCl₃): δ = 1.68 (m, 16H), 2.39 (s, 1H), 2.80 (t, 2H), 3.31 (m, 4H), 3.72 (m, 2H), 6.37 (d, 1H, J = 15.4 Hz), 6.89 (d, 2H), 6.96 (s, 1H), 7.02 (d, 1H, J = 16.1 Hz), 7.10 (d, 1H, J = 16.1 Hz), 7.41 (d, 2H), 8.23 (d, 1H, J = 15.4 Hz)

¹³C-NMR (CDCl₃): δ = 22.3, 24.7, 25.9, 26.7, 28.0, 29.3, 32.4, 49.6, 62.5, 70.5, 94.0, 97.4, 110.6, 112.1, 112.5, 112.9, 115.6, 117.1, 125.8, 129.1, 133.4, 135.2, 138.3, 152.7, 153.4, 155.0, 173.8, 176.6

*Synthesis of precursor polymers **P1** and **P2***

A general procedure for the preparation of poly(adamantyl methacrylate-methacrylic acid) **P1** and poly(adamantyl methacrylate-(2-trifluoromethyl)acrylic acid) **P2** is as follows: A mixture of monomers (adamantyl methacrylate/methacrylic acid and adamantyl methacrylate/2-(trifluoromethyl)acrylic acid for respectively **P1** and **P2**) and 2,2'-azobisisobutyronitrile (0.75 weight percent (wt.-%)) in dry dioxane (1.5 mL/mmol monomers) was stirred for 24 hours at 65 °C under argon atmosphere. After cooling and dilution with dioxane, the respective polymers were precipitated in methanol, filtered off and dried under reduced pressure. Yields up to 82 % were obtained.

Functionalization

A general procedure is as follows: Prior to use, chromophore, triphenylphosphine, precursor polymer and solvent were thoroughly dried. The precursor polymer, chromophore and triphenylphosphine (1.6 mol/mol chromophore) were dissolved in THF [10 mL (20 mL for **P2-CLD**)] in a sealed reaction vessel (if necessary a small amount of NMP was added). The cooled (0 °C) mixture was purged with argon, followed by the addition of diisopropyl azodicarboxylate (1.0 mol/mol triphenylphosphine). After 48 hours of stirring at ambient temperature, dry methanol (20 µL) was added and stirring was continued for 48 hours. The polymer was precipitated in methanol, filtered and dried under reduced pressure. This procedure was repeated until the filtrate was colorless.

Measurements

¹H- and ¹³C-NMR measurements were carried out on a Bruker Avance 300 MHz. The number average molecular weights ($\overline{M}_n$) and polydispersities ($\overline{M}_w/\overline{M}_n$) were measured by gel permeation chromatography (GPC) with a Waters HP-GPC with a tunable absorbency detector and a differential refractometer, using THF as eluent towards polystyrene standards. The UV-VIS spectra were recorded on a Varian Cary 400. Glass transition temperatures

(T_g's) of the polymers were determined by differential scanning calorimetry (DSC) on a DSC 7 from Perkin Elmer with a heating rate of 20 °C/min.

Spincoated thin films from a cyclohexanone solution onto ITO glass substrates, were corona-poled (6 ~ 8 kV applied voltage, for two hours at 40 °C below T_g) and measured for their second-harmonic generation coefficient d₃₃ at 1064 nm of induced light using a quartz crystal as reference (d₁₁ = 0.3 pm/V).

Results and discussion

Chromophore **C1** was synthesized consecutively, starting from piperidinylaminobenzaldehyde **1** (Scheme 1). In order to be able to incorporate a hydroxyalkyl spacer perpendicular to the direction of the dipole moment of the chromophore, a 4-bromo functionalized thiophene molecule was built in as the central part of the D π A-structure. This was achieved by means of a Wittig-reaction between donor aldehyde **1** and phosphonium salt **3**, readily obtained by treatment of 4-bromo-2-thiophenemethanol **2** with triphenylphosphonium bromide. Subsequently, a Kumada-reaction between the Grignard-reagent of *t*-butyldimethylsilyl protected 4-chloro-butanol **5** and the 4-bromo-thiophene moiety **4**, resulted in the formation of compound **6**. The latter was then treated with *n*-butyllithium, quenched with DMF which resulted, after hydrolysis, in hydroxyalkyl functionalized aldehyde **7**. Finally, chromophore **C1** could be isolated as *all*-trans isomer after a Knoevenagel-reaction between TCF-acceptor and aldehyde **7**.

Second, two easily accessible precursor polymers were prepared and functionalized with mono-hydroxyalkyl chromophores **FTC**, **CLD** and **C1** (Scheme 2). Both precursor polymers are built up of adamantyl methacrylate which was copolymerized with methacrylic acid or 2-(trifluoromethyl)acrylic acid resulting in respectively **P1** and **P2**. The composition of the methyl esterified copolymers, obtained after treatment of the precursor polymers with diazomethane, was measured by ¹H-NMR. Several copolymerizations were carried out of

which 20 mol percent (mol-%) methacrylic acid resulted in precursor polymer **P1** [19.6 mol-% COOH built in, $\overline{M}_n = 49030$, $\overline{M}_w/\overline{M}_n = 2.2$] and 40 mol-% (trifluoromethyl)acrylic acid resulted in precursor polymer **P2** (15.4 mol-% COOH built in, $\overline{M}_n = 36500$, $\overline{M}_w/\overline{M}_n = 2.2$). No Tg was detected by DSC.

Both precursor polymers were functionalized under Mitsunobu's conditions with chromophores **FTC** and **C1**. Also, the powerful **CLD**-chromophore was used to functionalize precursor polymer **P2**. During each functionalization, methanol was added in a second step to transform the remaining COOH-groups into a methylester. The structure of these terpolymers is given in Scheme 2. The wt.-% of NLO dye in the copolymers, $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$ and Tg's are presented in Table 1.

The NLO polymers show Tg's which are extremely high for vinyl copolymers and which are comparable with other high Tg polymers such as poly(maleimide-methyl-vinylurethane)s,^[9-11] copolymers of adamantyl methacrylate and chromophore functionalized methacrylates^[10] and other maleimide copolymers.^[12] It is also worthy to note that the longer alkyl spacer of chromophore **C1** does not result in much lower Tg's than the **FTC**-chromophore functionalized copolymers with comparable chromophore concentration.

The SHG results from the corona-poled films are summarized in Table 1. The polymers show $d_{33}(2\omega)$ values between 9.2-66.1 pm/V (measured at 1064 nm), depending on the chromophore concentration. These values are resonantly enhanced and were corrected using the two-level model.^[13] In that way, $d_{33}(0)$ values of 2.2-16.6 pm/V were obtained. The highest off-resonant value is obtained when **CLD**-chromophore is incorporated as NLO dye. As already mentioned, an important point we wish to emphasize in this communication is the influence of the position of the alkyl spacer on the poling-induced alignment of the chromophores. In general, the nonresonant susceptibility $\chi^{(2)}(0)$ [= $2d_{33}(0)$] depends on the hyperpolarizability β , the dipole moment μ and the number of chromophores incorporated and

on how effective the chromophores are parallel aligned. As shown in Table 1 (entries 1 and 2), the NLO response of polymer **P1** decreases by a factor 4 when chromophore **C1** is incorporated instead of the **FTC**-chromophore. For polymer **P2**, a decrease in NLO response by a factor 2.1 is observed (entries 3 and 4). Since the chromophore density of polymers **P1-FTC(11)** and **P1-C1(11.6)** as well as **P2-FTC(9.9)** and **P2-C1(9.8)** is (approximately) the same and β of **C1** can be expected to be similar or even higher than β of **FTC** (since a more powerful donor is employed), the observed difference of $\chi^{(2)}(0)$ must be due to a better alignment of the **FTC** chromophore compared with **C1**. The polar ordering was in all cases accomplished by corona poling. The poling process is essentially the alignment of the chromophores in the presence of an electric field in a polymer matrix near T_g . Therefore, the polar ordering depends on the strength of the electric field applied, the dipole moment of the chromophore, the local field factors, which take the difference of the external and local field into account and depend on the nature of the material and finally the poling conditions. The poling conditions (40 °C below T_g , two hours), applied electric field and local field factors (same polymer matrix and similar $D\pi A$ -structure) are the same in all cases. Also, since the **FTC**- and **C1**-chromophore have the same molecular $D\pi A$ -structure, a similar dipole moment can be expected. Hence, we must conclude that the observed, drastic difference in $\chi^{(2)}(0)$ -value between the polymers functionalized with the **FTC**- and **C1**-chromophore must be due to a better alignment of the $D\pi A$ -system if the spacer is parallel with the direction of the dipole moment than in the case when the spacer is perpendicular to it. These results are consistent with the fact that the photo-induced reorientation of azo-containing dyes proved to be highly dependent on the position of the alkyl spacer on the chromophore.^[14]

In summary, we have reported the synthesis of easily accessible precursor polymers which can be readily functionalized with mono-hydroxyalkyl chromophores under Mitsunobu's conditions, resulting in high T_g NLO polymers showing fairly high off-resonant

susceptibilities. Furthermore, SHG measurements of the reported NLO polymers clearly show that the position of the alkyl spacer should be parallel with the direction of the dipole moment of the D π A-structure when one wishes to covalently attach a NLO dye to a polymer with the purpose of inducing a parallel alignment of the chromophores by corona poling.

The results presented in this communication are a part of ongoing research involving the synthesis and characterization of chromophore functionalised side-chain polymers with a high and stable second-order nonlinear optical effect. Further work is in progress.

Acknowledgements

The authors thank the Fund for Scientific Research-Flanders (FWO-Vlaanderen) and the Katholieke Universiteit Leuven (GOA) for financial support. G. K. is a postdoctoral fellow of the Fund for Scientific Research-Flanders. S. Fourier is a research fellow of the IWT.

References

- [1] P. Prasad, D. Williams, "Introduction to nonlinear optical effects in molecules and polymers", Wiley, New York **1991**
- [2] D. M. Burland, R. D. Miller, C. A. Walsh, *Chem. Rev.* **1994**, 94, 31-75
- [3] L. R. Dalton, *Advances in Polymer Science* **2002**, 158
- [4] B.H. Robinson, L. R. Dalton, A. W. Harper, A. Ren, F. Wang, C. Zhang, G. Todorova, M. Lee, R. Aniszfeld, S. Garner, A. Chen, W. H. Steier, S. Houbrecht, A. Persoons, I. Ledoux, J. Zyss, A. K. Y. Jen, *Chemical Physics* **1999**, 245, 35
- [5] Y. Shi, C. Zhang, H. Zhang, J. H. Bechtel, L. R. Dalton, B. H. Robinson, W. H. Steier, *Science* **2000**, 288, 119
- [6] L. R. Dalton, A. Harper, A. Ren, F. Wang, G. Todorova, J. Chen, C. Zhang, M. Lee, *Ind. Eng. Chem. Res.* **1999**, 38, 8
- [7] D. Briers, I. Picard, T. Verbiest, A. Persoons, C. Samyn, *Polymer* **2004**, 45, 19

- [8] D. Briers, G. Koeckelberghs, I. Picard, T. Verbiest, A. Persoons, C. Samyn, *Macromol. Rapid Commun.* **2003**, *24*, 841
- [9] M. Dörr, R. Zentel, R. Dietrich, K. Meerholz, C. Bräuchle, J. Wichern, S. Zippel, P. Boldt, *Macromolecules* **1998**, *31*, 1454
- [10] [10a] M. Eich, H. Beisinghoff, B. Knödler, M. Ohl, M. Sprave, J. Vydra, M. Eckl, P. Strohmriegl, M. Dörr, R. Zentel, M. Ahlheim, M. Stähelin, B. Zysset, J. Liang, R. Levenson, J. Zyss, *SPIE* **1994**, 2285, 104; [10b] M. Eckl, H. Müller, P. Strohmriegl, M. Eich, M. Sprave, J. Vydra, *SPIE* **1995**, 2527, 92; [10c] M. Eckl, H. Müller, P. Strohmriegl, S. Beckmann, K.-H. Etzbach, M. Eich, J. Vydra, *Macromol. Chem. Phys.* **1995**, *196*, 315
- [11] M. Dörr, R. Zentel, *Macromol. Rapid Commun.* **1994**, *15*, 935
- [12] W. Ballet, T. Verbiest, M. Van Beylen, A. Persoons, C. Samyn, *Eur. Pol. J.* **2001**, *37*, 2419
- [13] J. L. Oudar, D. S. Chemla, *J. Chem. Phys.* **1977**, *66*, 2664
- [14] [14a] S. W. Cha, D. H. Choi, J.-I. Jin, *Adv. Funct. Mater.* **2001**, *11*, 355; [14b] S. W. Cha, D. H. Choi, D. K. Oh, D. Y. Han, C. E. Lee, J.-I. Jin, *Adv. Funct. Mater.* **2002**, *12*, 670.

Captions to figures and schemes

Figure 1: Molecular structure and properties of the **FTC**-, **CLD**- and **C1**-chromophores

Scheme 1: Synthesis of chromophore **C1**

Scheme 2: Synthesis of precursor polymers **P1** and **P2** and functionalization with **FTC**-, **CLD**- and **C1**-chromophore

Table 1. Functionalization of precursor polymers **P1** and **P2** and properties

Polymer	$\frac{\overline{M}_n^{a)}}{10^3 \cdot g \cdot mol^{-1}}$	$\frac{\overline{M}_w}{\overline{M}_n}$	$\frac{T_g^{b)}}{^\circ C}$	$\frac{wt. - \%^{c)}}{\%}$	$\frac{\lambda_{max}^{d)}}{nm}$	$\frac{d_{33}(2\omega)^{e)}}{pm \cdot V^{-1}}$	$\frac{d_{33}(0)^{f)}}{pm \cdot V^{-1}}$	$\frac{d_{33}(0)^{g)}}{pm \cdot V^{-1}}$
P1-FTC(11)	25.2	2.2	248	11.0	620	36.8	8.70	5.80 (67)
P1-C1(11.6)	21.4	2.9	246	11.6	621	9.20	2.20	1.80 (82)
P2-FTC(9.9)	22.6	2.5	240	9.90	622	21.5	5.20	3.90 (75)
P2-C1(9.8)	22.3	2.3	232	9.80	624	10.1	2.50	/
P2-FTC(24)	22.3	4.9	226	24.0	618	66.1	15.3	9.60 (63)
P2-CLD(27.5)	21.8	3.1	199	27.5	647	55.0	16.6	12.6 (76)

^{a)} Measured by GPC in THF, towards polystyrene standards

^{b)} Glass transition temperature, measured by DSC

^{c)} Weight percent NLO dye in polymer, measured by UV-VIS spectroscopy in THF

^{d)} λ_{max} of spincoated films

^{e)} Measured at 1064 nm

^{f)} Extrapolated to zero frequency using the two-level model^[13]

^{g)} Off-resonant value after ten days at room temperature (remaining %)

Figure 1

Scheme 1

Scheme 2

Text for table of contents

Two easily accessible copolymers were synthesized and functionalized with a newly synthesized chromophore **C1** and **FTC**- as well as **CLD**-chromophore resulting in high T_g NLO polymers. After corona-poling of spincoated films, fairly high NLO responses were measured. Furthermore, evaluation of the SHG measurements showed that the NLO response significantly depends on the position of the connecting alkyl spacer towards the direction of the dipole moment of the D π A-molecule.