Electro-optic Materials

Concise Multigram-Scale Synthesis of Push–Pull Tricyanofuran-Based Hemicyanines with Giant Second-Order Nonlinearity: An Alternative for Electro-optic Materials

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Abstract: Highly stable and highly soluble push–pull heptamethine hemicyanines based on the tricyanofuran electron-accepting group can be prepared on a 15 g scale. The compounds display giant second-order nonlinear figure of merit, $\mu\beta$ of up to 31,000 × 10^{-48} esu, and lead to poled material with a second-order nonlinear response, r_{33} of 90 pm V^{-1} at 1.06 μm

Electro-optic modulators are key devices in telecommunication and information systems that encode signals on the light beams carrying data along optical fibers. The active component is traditionally made of non-centrosymmetric crystals displaying second-order nonlinear optical properties, such as lithium niobate ($LiNbO_3$), and the best modulators based on $LiNbO_3$ operate at 40 Gb s^{-1} with a bandwidth of 30–35 GHz. With a growing need for faster devices that are able to send large amounts of information at high bit rates, this well established technology seems to have reached its limit. The all-organic approach based on polymers containing second-order nonlinear chromophores offers an interesting alternative for high-speed electro-optic (EO) devices requiring higher modulation frequencies.[1] Organic polymers have the potential for exhibiting exceptional device bandwidths (> 100 GHz) and low drive voltage (< 5 V), combined with high versatility in structure, low-cost production on a large scale, high processability, and facile integration with semiconductor electronics. As such, during the last 20 years, considerable research efforts have been devoted to the development of useful and efficient electro-optic poled polymers displaying a large electro-optic response (r_{33}). Modulators based on organic polymers with values of half-wave voltage, V_π, of less than 1 V[2] or operating at frequencies as high as 165 GHz have been demonstrated;[3] however, only prototypes have been described. Current devices on the market work at 40 GHz.[4]

The active component of all-organic electro-optic materials is a chromophore, which are almost exclusively dipolar push–pull molecules, that is, compounds in which a π-conjugated bridge connects an electron donor moiety with an electron-acceptor moiety, displaying high molecular quadratic optical nonlinearities (β or $\mu\beta$). For practical use in devices, the nonlinear optical (NLO) chromophore must not only possess large hyperpolarizability but must also display good processability, good solubility, as well as good thermal and chemical stability.[1a] Consequently, in parallel with the development of electro-optic materials, a great deal of research has focused on the molecular engineering requirements for optimized second-order nonlinearities in push–pull molecules.[1a] Ever-increasing values of figure of merit, $\mu\beta$, have been obtained and a milestone has been reached with the introduction of the tricyanofuran (TCF) acceptor group in highly efficient chromophores such as FTC[5] and CLD (Scheme 1).[6] These chromophores exhibit not only exceptional values of figure of merit but are also quite soluble in spin-casting solvents, processable, and thermally stable up to 275 °C, as proved by thermogravimetric (TGA) and differential scanning calorimetry (DSC). CLD has now become a benchmark compound for values of second-order nonlinear optical figure of merit. CLD-type chromophores have enabled the preparation of a composite material that is 25 wt % in polycarbonate and exhibits an average electro-optic (EO) coefficient of 92 pm V^{-1} at 1.06 μm.[6] Systematic modifications around the CLD structure have been realized to further improve the properties and introduce functional groups for covalent incorporation in polymers, leading to r_{33} values greater than 250 pm V^{-1}.[7] Nevertheless, the synthesis of CLD requires at least six linear steps with an overall yield of less than 6 %, the crucial step being the elongation of an aminophenyldienone intermediate to a more reactive aminophenyltrienal.[6] Although the synthesis has been improved over time, it remains

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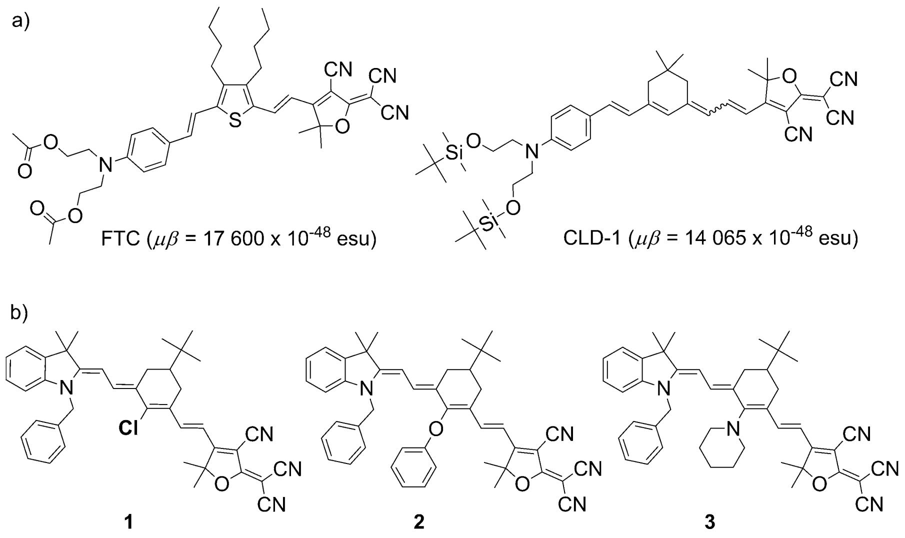
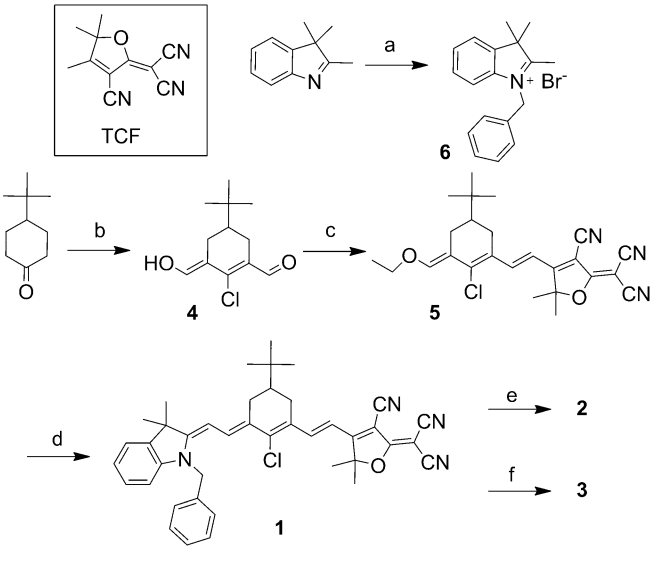


Scheme 1. a) Molecular structures and second-order nonlinearity of FTC and CLD-1. b) Molecular structures of dyes **1**, **2**, and **3**.

complicated and challenging with respect to structural modifications. So despite the push in establishing CLD derivative as the sole compounds for electro-optic organic materials, there is still room for improved molecules, with high electro-optic efficiencies, presenting different structures, and that are much easier to synthesize and functionalize (Scheme 2).

In a recent study, we described a new heptamethine dipolar chromophore displaying third-order nonlinear optical properties and optical limiting in the near infrared.[8] This push–pull molecule (**1**, Scheme 1) is based on the classical TCF electron-accepting group, but the originality of the structure lies in the electron-donating group (a trimethylindolenine moiety) and especially in the conjugated bridge, a heptamethine chain, that is, including an odd number of carbon atoms. The polyenic backbone is locked in a cyclohexyl ring bearing a lateral bulky *tert*-butyl group, affording very good solubility in most organic solvents and relatively high photostability. The X-ray crystal structure reveals a perfectly planar molecule. The backbone, which contains twelve sp^2 carbon atoms, linking the donor to the acceptor groups is arranged in an all *trans* conformation and presents a very regular alternation of single and double bonds, the average lengths of which are 1.425 and 1.364 Å, respectively. These values confirm the strong dipolar character of the molecule with complete delocalization over the extended π-conjugated skeleton, which suggest very good second-order nonlinear properties. Herein, we present an improved synthesis of **1** on a 15 gram scale, functionalization of the chromophore, measurements of the second-order figure of merit values of **1** and derivatives **2** and **3**, and a polymeric guest–host material containing **1** that displays high macroscopic second-order nonlinearity. Notably, during the course of this work, similar chromophores were described and their second-order nonlinear properties reported; however, the different synthetic route involved gave a much lower overall yield and no materials incorporating these compounds were reported.[9]



Scheme 2. Synthesis of dyes **1**–**3**: Reaction conditions: a) benzyl bromide, toluene, reflux, 15 h, 95 %; b) $POCl_3$, DMF, 0 to 80 °C, 3 h, 92 %; c) anhydrous ethanol, reflux, 15 h, 95 %; d) **5**, **6**, pyridine, anhydrous ethanol, reflux, 15 h, 95 %; e) phenol, NaH, DMF, RT, 8 h, 55 %; f) piperidine, DMF, 100 °C, 2 h, 65 %.

Compound **1** was synthesized on a 15 g scale following the reaction sequence described in Scheme 1. This synthesis is an optimization of our previously published method.[8] It involved two successive Knoevenagel condensations on 5-*tert*-butyl-2-chloro-3-hydroxymethylene-cyclohex-1-enecarbaldehyde **4**.[10] The first Knoevenagel reaction of TCF and **4** in refluxing ethanol afforded monoaddition product **5** in excellent yield (96 %) after simple filtration from the reaction mixture. Compound **5** was then reacted with indolenium bromide **6** in a second Knoevenagel condensation in refluxing ethanol by using pyridine as a base. Again, a simple filtration from the cooled mixture afforded the final push–pull compound, **1**, in almost quantitative yield (95 %). The overall yield of the synthesis is 79 %, the most limiting reaction being the formation of the indolenium salt. The chlorine-bearing carbon atom on the central bridge is the most obvious site for a further functionalization. For heptamethinecyanine dyes, the central chlorine atom is known to undergo nucleophilic substitution with various nucleophiles, such as phenolate, thiophenolate, or amine,[11] thus yielding new chromophores having optical properties that are different from the starting material. The reaction of **1** with excess piperidine at 100 °C in *N*,*N*-dimethylformamide (DMF) or with sodium phenolate in DMF at room temperature (Scheme 2) gave functionalized compounds **2** and **3**

(Scheme 1), where the chlorine atom has been replaced, in moderate yields, thus confirming that functionalization on that position was possible. Differential scanning calorimetry (DSC) curves of the different compounds indicate no peak melting temperature up to 250 °C. Thermal gravimetric analysis (TGA) confirms the thermal robustness of all compounds with 10% weight loss at temperatures of around 250 °C (Table 1, see Figures SI3–SI5 in the Supporting Information), a characteristic that is of prime importance for further applications in second-order nonlinear materials. All three compounds, **1**, **2** and **3**, exhibit very good solubility in organic solvents, owing to the presence of the bulky *tert*-butyl fragment in the central part of the molecule, a characteristic that is of prime importance for high-level doping in host polymers.

Table 1. Spectroscopic and thermal data for compounds **1**–**3**.

Compound	λ_{max} [nm]$^{[a]}$	ε [L mol^{-1} cm^{-1}]$^{[a]}$	T_{d10} [°C]$^{[b]}$	$\mu\beta$ [10^{-}48 esu]$^{[c]}$
1	810	91,000	250	31,000
2	801	80,000	258	29,500
3	692	58,000	245	5,700

[a] In CH_2Cl_2 [b] Decomposition temperature with 10% weight loss measured by TGA. [c] Measured by EFISH at 1907 μm in CH_2Cl_2.

The absorption spectra of **1**–**3** were recorded in different solvents (Figure 1). Very similar spectra were obtained for compounds **1** and **2**. In dichloromethane, chloroform, acetonitrile, and dimethylsulfoxide, intense and structured absorption is observed with maxima ranging from 794 nm ($CHCl_3$) to 853 nm (DMSO) for **1** and from 790 nm ($CHCl_3$) to 837 nm (DMSO) for **2** in the same solvents. In the less polar solvent, 1,4-dioxane, the absorption band is broader and considerably blue-shifted with maxima at 696 nm and 693 nm for **1** and **2**, respectively. The absorption of compound **3** on the other hand is only slightly dependent of the solvent polarity and a small negative solvatochromism is observed when going from 1,4-dioxane (707 nm) to DMSO (687 nm) for the broad structureless band. This hypsochromic shift is also accompanied by a strong decrease of molar extinction coefficient (Table 1). The effect upon substitution can be compared to what was observed on cationic cyanines dyes[11d] and may be attributed to a change in the internal charge transfer. The large solvatochromism of **1** and **2** relative to that of **3** is in good agreement with the much better molecular second-order nonlinearity of **1** and **2**. This is confirmed by the very large figure of merit values, $\mu\beta$ (31,000 and 29,000 × 10^{-48} esu for **1** and **2**, respectively), values that were measured by electric-field-induced second-harmonic generation (EFISH) experiments in chloroform at 1.907 μm;[12] a much lower value was obtained for **3** (5,700.10^{-48} esu). Such values compares well with the very best chromophores described to date[13] and are of the same order of magnitude as those of FTC or CLD-1 (Scheme 1), thus making **1** and **2** promising compounds for electro-optical materials.

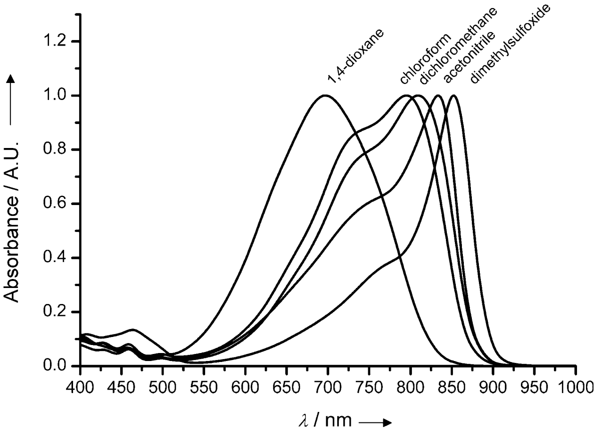


Figure 1. Absorption spectra of compound **1** in different solvents of various polarity.

In order to compare potentialities of this cyanine series to those of FTC or CLD-1, we estimated the nonlinear optical performance of **1** in a thin-film polymer matrix, as performed previously for CLD-1.[6] Poly[bisphenol A carbonate-*co*-4,4′-(3,3,5-trimethylcyclohexylidene) diphenol carbonate] (APC) was chosen as the host polymer. A solid solution obtained by doping **1** in APC at 17% weight chromophore loading was first prepared. This mixture exhibited a glass transition temperature of 155 °C (midpoint) as measured by DSC analysis. The refractive index dispersion of APC-doped **1** (17% weight) was determined by ellipsometry on a 1.7 μm thick film deposited on a silicon wafer. At 1500 nm, the refractive index was found to be as high as 1.626 ± 0.001. A 1.5 μm thick film for electro-optic coefficient measurement was prepared by spin coating a 0.2 μm filtered solution of APC and **1** in 1,1,2-trichoroethane onto an indium tin oxide (ITO) coated glass substrate (with a spin speed of 1000 rpm). Concentrations of APC and **1** were 100 g L^{-1} and 20.5 g L^{-1}, respectively. After deposition, the layer was dried by baking it for 12 h in a vacuum oven at 120 °C. As **1** cannot withstand Corona poling, electrical poling was performed by the contact method, which required the evaporation of a thin gold counter electrode onto the guest–host film. 160 °C was found to be the best poling temperature. The r_{33} component of the electro-optic coefficient was determined by using a setup based on that originally proposed by Teng and Man[14] and assuming weak-field cylindrical symmetry poling conditions ($r_{33}/r_{13} = 3$).[15] With a DC poling field of 100 V μm^{-1}, r_{33} values of 90 pm V^{-1} and 47 pm V^{-1} were obtained at 1.06 μm and 1.32 μm, respectively. These values are the same order of magnitude as the values obtained with the guest–host systems based on CLD-1 and APC, namely 90 pm V^{-1} at 1.06 μm (at 25% weight).[16].

In conclusion, we have described a novel family of push–pull hemicyanines with giant quadratic nonlinear responses. These chromophores fulfill a lot of requirements for the design of efficient electro-optic modulators that are expected to compete with the best reference chromophores in this field. These compounds were intentionally designed to have high thermal and chemical stability ($T_d > 250$ °C), to have high solubility, and to be easily synthesized on a large scale (the sequence being conducted on a 15 g scale herein). Chromophore **1** was dissolved as a guest in an APC polymer matrix at 17% weight and the material was poled by using contact poling. A r_{33} value of 90 pm V^{-1} in APC at 1.06 μm was thus achieved. This value compares well with that obtained for the best benchmark chromophore, CLD-1, in the same polymer host.[6] We have also demonstrated that the central chlorine atom can easily be replaced by a phenoxy group without loss of the second-order nonlinear properties, behavior that is essential for its covalent grafting on polymers to give better materials, as recently shown.[17] We now have in hand a very promising structure that gives new opportunities in the design of highly efficient functionalized second-order nonlinear optical chromophores that can be incorporated into electro-optical devices.

Experimental Section

Synthesis of 1

Under argon, compound **5** (11.04 g, 0.025 mmol, 1 equiv) and 1-benzyl-2,3,3-trimethylindolium bromide **6** (10 g, 0.03 mol, 1.2 equiv) were dissolved in anhydrous ethanol (500 mL). Pyridine (2.6 mL, 0.033 mol, 1.3 equiv) was added and the solution was refluxed overnight. The precipitate was filtered and dried under vacuum to afford **1** as a green solid. Yield: 95%. (15.3 g). ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 8.08$ (d, 1H, $J = 16$ Hz), 7.87 (d, 1H, $J = 13$ Hz), 7.1–7.4 (m, 7H), 7.06 (d, 1H, $J = 8$ Hz), 6.88 (d, 1H, $J = 8$ Hz), 6.35 (d, 1H, $J = 16$ Hz), 5.63 (d, 1H, $J = 13$ Hz), 4.99 (d, 1H, $J = 16$ Hz), 4.93 (d, 2H, $J = 10$ Hz), 2.65 (m, 2H), 2.08 (m, 2H), 1.75 (s, 6H), 1.70 (s, 6H), 1.49 (m, 1H), 0.97 ppm (s, 9H); ^{13}C NMR (50 MHz, CDCl$_3$): $\delta =$ 176.2, 173.2, 164.8, 146.9, 144.4, 142.6, 143.9, 139.6, 135.7, 135.3, 129.2, 128.4, 128.0, 126.7, 126.5, 122.6, 122.2, 113.1, 112.2, 111.6, 111.1, 108.1, 96.9, 96.5, 94.0, 47.4, 47.0, 42.3, 32.3, 28.5, 28.4, 27.6, 27.4, 27.2, 27.5 ppm; IR (KBr): $\nu_{C\equiv N} = 2218$ cm^{-1}; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 810 nm (91,000 L mol^{-1} cm^{-1}); MS (ES): *m/z* (%): 641 [M+H]$^+$ (100); elemental analysis calcd (%) for $C_{41}H_{41}ClN_4O$: C 76.79, H 6.44, N 8.74; found: C 76.61, H 6.53, N 8.45.

Synthesis of 2

Phenol (48 mg, 0.51 mmol, 1.1 equiv) was dissolved in 10 mL of freshly distilled THF under argon. NaH (23 mg, 1.2 equiv) was added. The solution was stirred 30 min after which time, **1** (300 mg, 0.47 mmol, 1 equiv) dissolved in 10 mL of THF was added. The solution was stirred at RT for 2 h. Hydrochloric acid (as a dilute solution in water) was slowly added. The product was extracted with 50 mL of dichloromethane, washed with water (3× 25 mL), dried with Na$_2$SO$_4$, and the solvent was evaporated. Purification by column chromatography on silica gel eluting with dichloromethane, then dissolution in the minimum amount of dichloromethane and precipitation in absolute ethanol afforded a green solid (180 mg, 55%). ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.58$ (d, $J = 15$ Hz, 1H), 7.1–7.5 (m, 7H), 6.95 (m, 4H), 6.80 (d, $J = 8$ Hz, 1H), 6.25 (d, $J = 15$ Hz, 1H), 5.53 (d, $J = 12$ Hz, 1H, C=C-H), 4.94 (d, $J = 16$ Hz, 1H), 4.86 (d, $J = 16$ Hz, 1H), 2.64 (dd, $J = 16$ Hz, $J = 16$ Hz, 2H), 2.12 (dd, $J = 16$ Hz, $J = 16$ Hz, 1H), 1.93 (dd, $J = 16$ Hz, $J = 16$ Hz, 1H), 1.31 (s, 3H), 1.38 (s, 6H), (s, 9H), 1.28 ppm (s, 3H); ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 173.3$, 165.1, 160.4, 159.4, 143.8, 142.0, 139.7, 135.3, 133.8, 132.5, 130.2, 129.2, 128.3, 128.0, 126.5, 125.6, 122.6, 122.5, 122.4, 122.0, 114.6, 113.4, 112.6, 111.7, 110.4, 109.5, 108.1, 96.2, 92.7, 52.8, 47.1, 42.9, 32.5, 28.1, 27.5, 26.9, 26.8, 25.5, 25.1 ppm; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 810 nm (91,000 L mol^{-1} cm^{-1}); MS (ES): *m/z* (%): 721 [M+Na]$^+$ (100); elemental analysis calcd for $C_{47}H_{46}N_4O_2{\cdot}3H_2O$: C 74.97, H 6.96, N 7.44; found: C 74.99, H 6.32, N 7.47.

Synthesis of 3

To a solution of **1** (100 mg, 0.16 mmol, 1 equiv) dissolved in DMF (10 mL), piperidine (0,09 mL, 5 equiv) was added. The solution was stirred at 100 °C for 2 h. After cooling down, dichloromethane (50 mL) was added and the solution was washed with an aqueous solution of NH$_4$Cl and then with water. The solution was dried over Na$_2$SO$_4$ and the solvents were evaporated. The crude material was then dissolved in the minimum amount of dichloromethane and precipitated with pentane to afford a blue solid (70 mg, 65%). ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 8.05$ (d, $J = 14$ Hz, 1H), 6.95–7.40 (m, 8H), 6.85 (d, $J = 8$ Hz, 1H), 5.56 (d, $J = 13$ Hz, 1H), 5.45 (d, $J = 14$ Hz, 1H), 5.01 (d, $J = 16$ Hz, 1H), 4.90 (d, $J = 16$ Hz, 1H), 3.5–3.8 (m, 4H), 2.30–2.50 (m, 2H), 1.20–1.95 (m, 8H), 0.70–1.10 ppm (m, 12H); ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 177.8$, 174.1, 167.5, 165.1, 143.8, 143.4, 139.4, 136.4, 134.9, 129.2, 128.5, 128.0, 126.2, 125.8, 122.7, 122.5, 122.1, 116.7, 116.2, 115.3, 108.1, 101.0, 95.2, 94.2, 56.6, 47.0, 46.9, 44.5, 32.7, 29.0, 28.8, 27.7, 27.4, 27.3, 27.0, 26.5, 26.2, 24.3 ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}(\varepsilon) = 697$ nm (59,000 L mol^{-1} cm^{-1}); MS (ES): *m/z* (%): 690 [M+H]$^+$ (100); HRMS (ESI): *m/z* calcd for $C_{46}H_{51}N_5O$: 689.4094 [M+H]$^+$; found: 690.4214.

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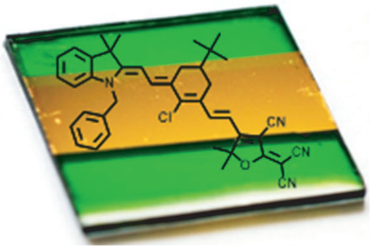
Concise Multigram-Scale Synthesis of Push–Pull Tricyanofuran-Based Hemicyanines with Giant Second-Order Nonlinearity: An Alternative for Electro-optic Materials



Highly stable and highly soluble push–pull heptamethine hemicyanines based on the tricyanofuran electron-accepting group (see figure) can be prepared on a 15 g scale. The compounds display giant second-order nonlinear figure of merit, $\mu\beta$ of up to $31{,}000 \times 10^{-48}$ esu, and lead to poled material with a second-order nonlinear response, r_{33} of 90 pm V^{-1} at 1.06 µm.