

Highly efficient, thermally and chemically stable nonlinear optical chromophores based on the α -perfluoroaryldicyanovinyl electron acceptors

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Received (in Cambridge, UK) 5th October 1999, Accepted 20th October 1999

A series of highly efficient, chemically and thermally stable (> 310 °C) nonlinear optical chromophores were prepared through the replacement of the most reactive CN group in tricyanovinylthiophene derivatives with perfluoroaryl units.

In practice, polymer based electro-optic (E-O) devices require that nonlinear optical (NLO) polymers possess excellent E-O properties. The large E-O coefficient (r_{33}) of a polymer is generally realized by aligning the dipole moment (μ) of efficient NLO chromophores with a high external electric field at a temperature above the glass-transition temperature (T_g) of the polymer.¹ Therefore, chromophores with large molecular nonlinearity (β) are crucial to the advancement of NLO polymers, and have drawn interest in their theory-guided design and state-of-the-art synthesis.² Among them, a series of highly polarizable chromophores based on tricyanovinyl-substituted heteroaromatic chromophores have demonstrated very large β values.³ Although poled E-O polymers with these chromophores incorporated either as a guest in a host polymer or as a side-chain polymer have exhibited large electro-optic coefficients (r_{33}), there are several deficiencies associated with these materials [Fig. 1(a)]. For instance, the α -position of the

tricyanovinyl acceptor is very susceptible to attack from nucleophiles, which may easily diminish the nonlinearity of the chromophores.⁴ On the other hand, the flat structures of these charge-transfer chromophores have a strong tendency to form aggregates in a polymer matrix due to intermolecular electrostatic interactions.⁵ This results in lower poling efficiency and a higher light-scattering optical loss. To overcome these problems, a strategy was designed to replace the α -CN with a bulky and electron-deficient moiety which is also inherently not a good leaving group. Here, the tetrafluoropyridyldicyanovinyl (TFPD) and the heptafluorotolyldicyanovinyl (HFTD) acceptors were adapted to improve the efficiency and chemical and thermal stability of NLO chromophores. As shown in the Fig. 1(b), the perfluoroaryl group blocks the α -position, prevents attack from amine nucleophiles⁴ and greatly improves the chemical stability of the derived chromophores. In addition, due to their electron-deficient characteristics, these perfluoroaryl groups will enhance the strength of the dicyanovinyl acceptor, and subsequently increase the β of the chromophores.^{6a} Furthermore, from simple MOPAC molecular modeling, the perfluoroaryl group is twisted out of the main conjugation plane due to steric hindrance. The 3-D structure may help to prevent intermolecular electrostatic interactions among the chromophores, which in turn may enhance the poling efficiency and decrease the scattering-induced optical loss.⁶

The general synthetic route for the α -perfluoroaryldicyanovinyl-containing chromophores is shown in Scheme 1. Tetrafluoropyridyllithium was prepared by the lithiation of tetrafluoropyridine with BuLi at -70 °C. Heptafluorotolylithium was generated by the lithium-halogen exchange reaction of the heptafluoro-*p*-tolyl bromide with 2 equiv. of BuLi at -78 °C. To the prepared perfluoroaryllithium solutions in THF at -70 °C, tricyanovinyl chromophores were added neat in one portion and the reaction mixtures were stirred at -70 °C for 1 h then warmed slowly to room temperature to give compounds **1a–3a** and **1b–3b** after purification by silica gel chromatography. All of the compounds were fully characterized by ¹H NMR and elemental analysis.

The chemical stability of the chromophores to a nucleophile was tested in a CHCl₃ solution that was saturated with a large excess of Et₂NH. The UV-VIS absorption spectra of these perfluoroaryldicyanovinyl containing chromophores showed excellent chemical stability in a nucleophilic environment (Fig. 2), unlike their tricyanovinyl analog which was almost instantaneously decolorized.

The charge-transfer (CT) properties, electrochemical properties and intrinsic thermal stabilities of these chromophores are shown in Table 1. These perfluoroaryldicyanovinyl-containing chromophores have a blue-shifted CT band when compared to their corresponding tricyanovinyl counterparts. For instance, the λ_{\max} values of **1a** and **1b** in dioxane are located at 595 and 590 nm, respectively, while **1** is at 640 nm. The further deviation of the absorption band from the operating wavelengths of the lasers for telecommunication may help to decrease the absorption optical loss. However, the blue-shifted λ_{\max} values of both chromophores also indicated a decrease in strength of the new electron acceptors. This notion was supported by electrochemical measurements using cyclic voltammetry (CV).⁷ The new chromophores **1a** and **1b** both

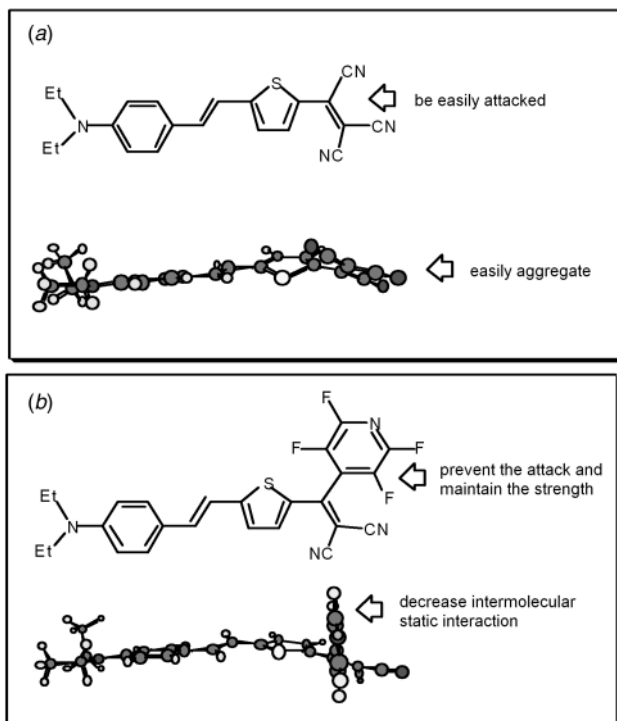


Fig. 1 Simple MOPAC modeling: (a) tricyanovinyl chromophore **1**; (b) α -perfluoropyridyldicyanovinyl chromophore **1a**.

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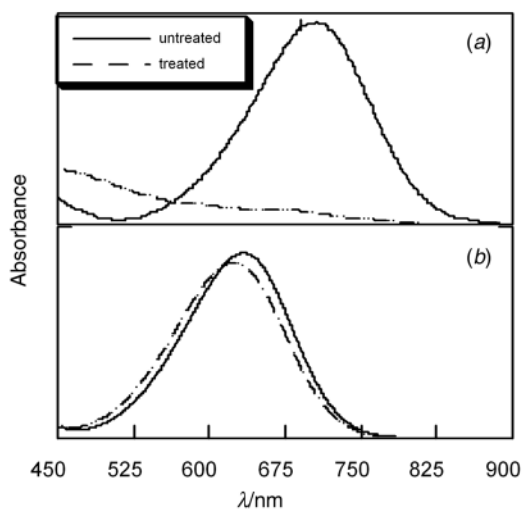
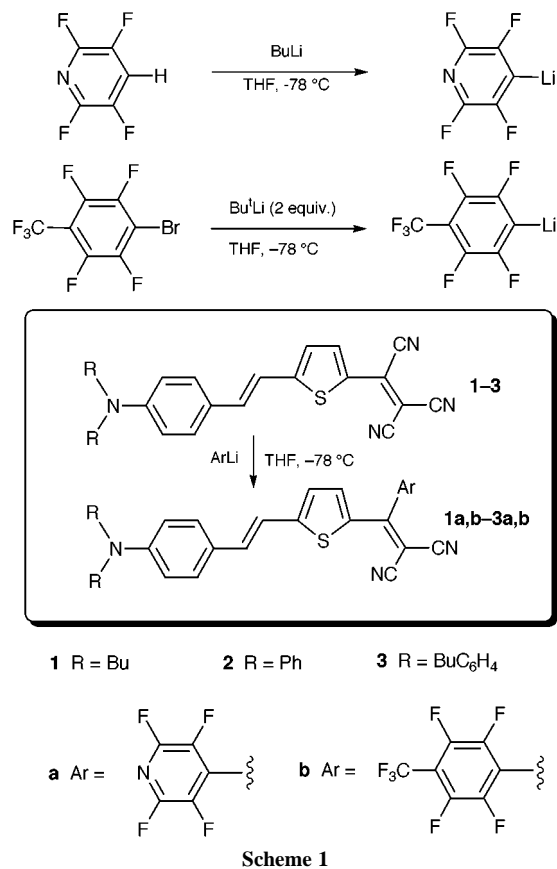


Fig. 2 Testing of the chemical stability of chromophores: a dilute solution of chromophore in CHCl_3 was treated with Et_2NH : (a) tricyanovinyl chromophore **1**; (b) α -perfluoropyridyldicyanovinyl chromophore **1a**.

possess higher reduction potentials, at -1.02 and -1.04 V, respectively, when compared to -0.80 V for the parent compound **1**.

Thermal stability measurements using sealed pan differential scanning calorimetry (DSC) revealed that these chromophores possess excellent thermal stabilities (310 – 390 °C) which are much higher than that of **1** (240 °C).

Optical and E-O studies were performed on the polymers (guest–host) in which chromophores **1a** and **1b** (25 wt%) were formulated into polyquinoline (PQ-100). Optical quality thin films were spin-coated onto glass slides and indium-tin-oxide (ITO) glass substrates using a 12% w/w solution of the resin in

Table 1 Properties of chromophores

	$\lambda_{\text{max}}/\text{nm}^a$	$E_{\text{Red}}^0/\text{V}^b$	$E_{\text{Ox}}^0/\text{V}^b$	$T_d/\text{°C}^c$
1	640	-0.80	0.56	240
2	601	N/A	N/A	315
3	625	N/A	N/A	315
1a	595	-1.02	0.52	320
2a	554	-0.98	0.73	390
3a	577	-1.01	0.61	360
1b	591	-1.04	0.56	310
2b	553	-1.03	0.72	340
3b	573	-1.04	0.61	370

^a In a dilute dioxane solution. ^b In a $\text{ClCH}_2\text{CH}_2\text{Cl}$ solution of Bu_3NPF_6 (0.1 M), vs. Ag^+/Ag . ^c Sealed-pan DSC measurement in N_2 , 20 °C min^{-1} .

cyclopentanone. These films were heated at 85 °C *in vacuo* for 24 h and then briefly baked on a hot stage (160 °C) under nitrogen for 20 min to remove the residual solvent. The dipole alignment of the chromophores was achieved by poling with a high electric field of 1.0 MV cm^{-1} at 200 °C. The r_{33} values of NLO polyquinoline films of **1a** and **1b** were 16 and 14 pm V^{-1} at 1.3 μm . The slight decrease in the E-O coefficients when compared to **1** may be attributed to several factors, such as the lower number density of **1a** and **1b** because of the higher molecular weights of these compounds, and the weaker electron-withdrawing ability of perfluoroaryldicyanovinyl.

The optical loss of the NLO polymer films (< 2 dB cm^{-1} measured at 1.3 μm) is much less than 6.0 dB cm^{-1} for a similar film containing a tricyanovinyl-substituted chromophore.⁸ This supports our hypothesis that the 3-D structure of these perfluoroaryldicyanovinyl groups will prevent chromophores from forming aggregates.

In summary, a series of highly efficient, chemically and thermally stable (> 310 °C) nonlinear optical chromophores were prepared through the replacement of the most reactive CN group in tricyanovinylthiophene derivatives with perfluoroaryl units. The incorporation of these chromophores into high temperature polyquinoline demonstrated both high E-O properties and low optical loss.

We acknowledge the financial support from the Air Force Office of Scientific Research (AFOSR) under grant F49620-97-1-0240 and the Office of Naval Research (ONR) through MURI Center CAMP.

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- The CV measurements were carried out in a chromophore solution (1.0 mg in 10 ml of $\text{CH}_2\text{ClCH}_2\text{Cl}$) in the presence of Bu_3NPF_6 (0.1 M) at room temperature. Platinum, platinum gauze, and Ag/Ag^+ were used as the working electrode, counter electrode, and reference electrode respectively in a conventional three-electrode cell.
- The optical loss was determined by the prism-coupled streak method on a slab waveguide.

Communication 9/08007D