



Short-conjugated zwitterionic cyanopyridinium chromophores: Synthesis, crystal structure, and linear/nonlinear optical properties



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ABSTRACT

A new class of short-conjugated zwitterionic cyanopyridinium chromophores with the absorption maxima less than 550 nm were designed and synthesized. These chromophores display a good solubility in organic solvents and exist in a charge-separated ground state, as confirmed by IR, X-ray crystallography, negative solvatochromism and fluorescence studies. They can be doped up to 10% by weight into poly(ether sulfone) and attached onto a methacrylate polymer by grafting. Without optimization of the poling conditions, a high electro-optic coefficient can be readily achieved using the chromophore-grafted nonlinear optical polymers.

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1. Introduction

Cyanopyridinium-based zwitterionic chromophores are an important type of the intramolecular charge-transfer (ICT) molecules, in which negatively charged cyano-moiety and pyridium cation are separated by a π -conjugated system. Many interesting characteristics, such as highly charge-separated ground state ($D^{\delta+}-\pi-A^{\delta-}$; D: donor; A: acceptor; δ : degree of CT), large molar extinction coefficient, large negative solvatochromism, large dipole moment (μ), and large negative first molecular hyperpolarizability (β), arise from this peculiar structure, which leads to a wide variety of applications including functional dyes [1], nonlinear optical chromophores [2,3], photochromic materials [4] and chemosensors [5]. Based on the high absorptive feature, various forms of deep-colored solutions, as well as films containing zwitterionic cyanopyridinium chromophore can be obtained [6]. Recently, the cyano moiety of the zwitterionic chromophores was found to be capable of selectively and reversibly coordinating with certain metal ions, resulting in distinct color change due to the switch on/off of CT band [5].

Of course, the most widely studied properties are their large negative first molecular hyperpolarizability (β) and the corresponding figure of merit ($\mu\beta$), which is used to characterize their microscopic nonlinear optical (NLO) efficiencies. Zwitterionic cyanopyridinium chromophores have been demonstrated to be one of the promising classes of second-order NLO materials for electro-optic (EO) applications [7,8]. To fabricate EO devices, NLO chromophores are usually doped into or covalently bonded onto polymers, followed by poling films under an externally applied electric field at the glass transition temperature (T_g) in order to achieve a noncentrosymmetric arrangement with a large macroscopic EO coefficient [9–15]. More recently, a novel approach has been explored in which zwitterionic chromophores with negative β were linked to the neutral-ground-state NLO chromophores with positive β [16–18] and showed the interesting application of zwitterionic chromophores in EO devices.

The previously studied zwitterionic cyanopyridinium chromophores are typically synthesized through the addition between tertiary amines and 7,7,8,8-tetracyanoquino-dimethane (TCNQ), such as DEMI [19], PQDM [20–22] and PeQDM [23] (Fig. 1). Besides complicated procedures and low yield, the chromophores obtained by this method have their absorption maxima limited in the red region of the visible spectrum, usually 600 nm–750 nm.

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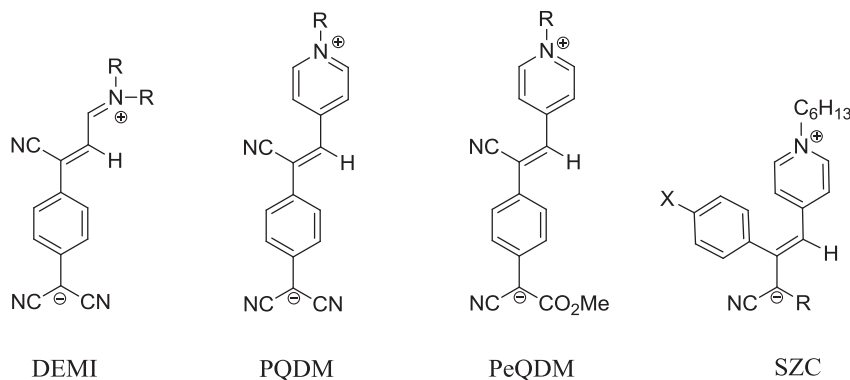


Fig. 1. Chemical structures of zwitterionic chromophores of DEMI, PQDM, PeQDM and SZC.

As functional dyes and chromic materials, zwitterionic cyanopyridinium chromophores with a wide absorptive band are desirable (e.g. 400–600 nm). In addition, as a material for NLO application, in order to minimize the optical loss and light damage, the chromophores should ideally be transparent at the communication wavelengths (1310–1550 nm) and have low absorption at visible region, especially near the double frequency wavelengths (650–750 nm). The basic requirement in zwitterionic cyanopyridinium chromophore design calls for the maximal absorption peak to be significantly blue shifted or ideally less than 600 nm [24,25].

Furthermore, zwitterionic chromophores often display poor solubility in normal organic solvents and low compatibility with a polymer matrix. The large dipole moment and planar structure cause the chromophores to aggregate aggressively in the matrix, thereby limiting their loading level in the guest–host polymer systems. The highly polar zwitterionic nature of the chromophores also leads to an anti-parallel dipole arrangement, which could further diminish or even eliminate the macroscopic nonlinearity in bulk and hamper their EO application [19–23].

Therefore, it is desirable to develop a simple versatile method for the synthesis of processable dipolar zwitterionic chromophores with a short transparency cut-off wavelength. To achieve the blue-shifted zwitterionic chromophores, adjusting the conjugation length of the π -electron bridge is important; meanwhile, due to the fact that zwitterionic chromophores often exist as the combination of two limiting resonance forms (zwitterionic and neutral forms), maintaining the zwitterionic structure as the predominant ground state is critical in order to obtain large $\mu\beta$ values [26,27].

Here we report the highly efficient and facile synthesis of a new class of cyanopyridinium chromophores, composed of a pyridium donor and cyano-moiety acceptor (SZC, in Fig. 1) and corresponding polymers. These chromophores are purposely designed to have a short conjugation length in order to achieve a blue-shift in absorption. They also have various bulky substituents in order to minimize chromophore dipole–dipole interactions and to improve solubility and compatibility with polymer matrix. The new class of zwitterionic chromophores and polymers are fully characterized by spectroscopic methods, X-ray crystallographic analysis, thermal analysis and nonlinear optical measurement.

2. Experimental section

2.1. Materials

4-Bromophenyl acetonitrile, 4-pyridinecarboxaldehyde, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-bromohexane, malononitrile, fluorophenyl acetonitrile, methyl cyanoacetate, cyanoacetic

acid, hydroxyethyl cyanoacetate and poly(methyl methacrylate) (PMMA) were purchased from Aldrich Chemicals. Azobisisobutyronitrile (AIBN) was purchased from Aldrich Chemicals and recrystallized from methanol. DMF and DMAc were dried over CaH_2 and distilled under vacuum. Poly(ether sulfone) (PES, commercial trade name: Ultrason E, $T_g = 225^\circ\text{C}$) was obtained from BASF. The LiNbO_3 wafer was purchased from Thorlabs Inc. (New Jersey, USA) and used for calibration of electro-optic measurement.

2.2. Instruments

^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz (300 and 75 MHz for ^1H and ^{13}C NMR, respectively) or a Bruker AMX 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer 1600 or a Bomen Michelson 120 FTIR spectrometer in the regions of 4000–400 cm^{-1} . Mass spectra were measured with a Micromass Quattro LC ESI mass spectrometer (EI and TOF-ESI). The melting points were determined using a Fisher–Johns melting point apparatus. Differential scanning calorimetric analysis was carried out in nitrogen on a TA DSC Q100 with a heating rate of 10 $^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on a Hi-Res TGA 2950 thermogravimetric analyzer with a heating rate of 10 $^\circ\text{C}/\text{min}$. The decomposition temperatures (T_d) were determined by 5% weight loss from TGA under nitrogen atmosphere. The UV–Vis–NIR spectra were recorded on a Perkin–Elmer Lambda 900 UV–Vis–NIR spectrometer at room temperature. Fluorescence emission spectra were measured on a PTI fluorescence system. The absorption and fluorescence emission spectra of all the samples were taken in a quartz cuvette with a path length of 10.0 mm. Refractive indices were measured using a Metricon 2010 prism coupler. An alpha-step 200 surface profiler was used for measuring the thin film thickness. The M_w and M_n of the polymers were evaluated in DMF with a Waters GPC system (2414 Refractive Index Detector) with Styragel HR4E and HR5E columns using polystyrene standards.

2.3. Synthesis

2.3.1. Synthesis of 2-(4-bromophenyl)-3-pyridine-4-yl-acrylonitrile (**1**)

Under anhydrous and oxygen-free conditions, to a 250-mL round-bottomed flask, 4-bromophenyl acetonitrile (5.90 g, 30.0 mmol), 4-pyridinecarboxaldehyde (3.0 mL, 30.0 mmol), dry THF (80 mL) and DBU (1 mL) were added. The mixture was heated under reflux for 18 h and then cooled to room temperature. The solvent was removed under reduced pressure; the red residue was

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