



Novel nonlinear optical push–pull fluorene dyes chromophore as promising materials for telecommunications

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Abstract

Two principally novel chromophores A, B based on fluorene electron donor were synthesized and explored by ¹H NMR, ¹³C NMR, and MS spectra. The delocalized energy levels have been estimated by UV–Vis absorption spectra. The principal innovation consists in modification by addition of amino group. The titled materials have demonstrated a high solubility in common organic solvents, good compatibility with polymers. The maximally achieved electro-optic efficiency of the poled film possessing 25 wt% of A doped in PMMA (25 wt% A/PMMA) achieved a value of 18 pm/V at wavelength 1310 nm, and 25 wt% B/PMMA possessed an electrooptical coefficient equal to 43 pm/V. This one open a perspective of their direct application in optoelectronic telecommunication devices for laser light modulation.

1 Introduction

The design and search of novel promising chromophores materials for the optoelectronic applications is very important for modern organic materials science engineering due to their promising parameters with respect to high-speed and broadband telecommunication technology [1–6]. For today different materials are just used for the nonlinear optical and electrooptical laser modulators [7–13].

However, for wide applications, one of the restraining factor consists in reliable production of excellent organic electro-optic (EO) modulator materials to develop NLO chromophores with relatively high first-order hyperpolarizability (β)

[14–16], good thermal, photochemical stabilities as well as good solubility and compatibility with the polymer matrix.

To obtain sufficiently high EO activity and suppress the undesirable dipole–dipole interactions among the chromophores, an appropriate molecular design has been made using the conjugated push–pull molecules. Many efforts have been made here to design and synthesize novel NLO chromophores, searching the NLO molecules with higher electrooptical coefficients (r_{33}) [15–17]. The previous efforts for the NLO chromophores were mainly focused on the construction of the extended charge transfer pi-electron bridges and electron acceptors [16–19]. However, the electron donors, playing crucial role for NLO chromophores, are still less explored and very promising may be traditional alkyl and aryl anilines which are suitable electron donors and for these goals they are just widely studied [20, 21]. Following the mentioned above one can conclude that design and fabrication of novel conjugated groups with stronger electron-donating ability is still extremely desirable.

In this report, fluorene with embedded amino groups have been utilized as electron donor. Two chromophores with these donors were fabricated. Additionally extended and larger peripheral modified groups were added to chromophores to enhance their EO efficiencies. These material demonstrate high solubility in traditional organic solvents, sufficiently good compatibility with polymers, and high EO tensor coefficients for the poled films. ¹H-NMR and ¹³C-NMR analyses were carried out to demonstrate the potential of these chromophores. Thermal stability, photophysical

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features, DFT calculations and EO activities of these chromophores have been complexly explored.

2 Experimental

2.1 Materials and instruments

All the chemicals are commercially available and have been used without additional purification. *N,N*-dimethylformamide (DMF) was distilled over calcium hydride and stored over molecular sieves (pore size 3 Å).

2-Dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran (TCF) and 2-(3-cyano-4-methyl-5-phenyl-5-(trifluoromethyl)furan-2(5H)-ylidene)malononitrile (CF₃-Ph-TCF) were synthesized similarly to the described in the to the references [22, 23]. TLC analyses were performed for 0.25 mm thick pre-coated silica plates and they have been visualized using UV light. Chromatography of silica gel was done on Kieselgel (200–300 mesh), and ¹H NMR spectra were measured by Advance Bruker 400 M (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). UV–Vis spectra were done using Cary 5000 photo spectrometer. TGA and DSC were monitored by TA-instrument Q50 and Q10 with a heating rate of 10 K min⁻¹ under N₂, respectively.

2.2 Synthesis procedure

2.2.1 Compound 2

A mixture of 1 (4.22 g, 20.0 mmol), iron powder (3.35 g, 60.0 mmol, 3.0 equiv.) and ammonia chloride (2.14 g, 40.0 mmol, 2.0 equiv.) in aqueous ethanol (140 mL of alcohol and 40 mL of water) was refluxed in argon atmosphere. After complete transformation of the initial compound (about 5 h) upon inspection by TLC, the reaction mixture was treated with 70 mL of aqueous saturated sodium bicarbonate and filtered. After removing the ethanol from the filtrate obtained under reduced pressure, the resultant mixture was filtered. The solid obtained was then washed with water (3 × 30 mL) and dried in vacuum atmosphere at 50 °C. The crude product was used without further purification for the next step. A solution of the crude product, bromobutane (13.7 g, 100 mmol) and sodium tert-butoxide (9.6 g 100 mmol) in DMF (50 ml) for 8 h, and then poured into distilled water (250 mL). ethyl acetate (3 × 50 mL) was used to extract the product. The extracts were combined, washed with saturated NaCl solution, dried over anhydrous magnesium sulfate. After removal of the solvents, the product was purified by column chromatography and obtained as a syrup (6.01 g, yield: 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 7.9, 3.0 Hz, 2H), 7.55 (dd, *J* = 17.7, 7.4 Hz, 2H),

7.43 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 11.9 Hz, 2H), 3.69–3.59 (m, 4H), 2.34–2.19 (m, 4H), 1.99–1.87 (m, 4H), 1.68 (dd, *J* = 14.9, 7.4 Hz, 4H), 1.43 (dd, *J* = 14.7, 7.3 Hz, 4H), 1.27 (t, *J* = 7.4 Hz, 6H), 1.03 (dd, *J* = 16.6, 9.1 Hz, 10H). ¹³C NMR (101 MHz, CDCl₃) δ 152.41, 149.93, 148.42, 142.33, 129.80, 126.85, 124.96, 122.66, 120.66, 118.29, 111.29, 106.92, 54.92, 51.55, 40.89, 29.91, 26.28, 23.47, 20.74, 14.34, 14.12. ESI–MS (C₂₉H₄₃N): calcd: 405.34; found: [M + 1]⁺, 406.34.

2.2.2 Compound 3

To a solution of compound 2 (5.0 g, 12.3 mmol) in anhydrous chloroform (50 mL) at ambient temperature was successively added anhydrous DMF (1.0 mL, 12.3 mmol) and POCl₃ (1.7 mL, 18.5 mmol), and the mixture was refluxed during one night. After hydrolysis for 2 h under vigorous stirring at ambient temperature using an aqueous solution of sodium acetate 2 M (400 mL), the product has been extracted using CH₂Cl₂. When the solvent was removed, the crude product has been purified by chromatography to receive a yellow oil (3.3, 62.1% yield).

¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.51–7.45 (m, 2H), 6.54 (d, *J* = 8.6 Hz, 1H), 6.49 (s, 1H), 3.30–3.22 (m, 4H), 1.93–1.78 (m, 4H), 1.57–1.49 (m, 4H), 1.29 (dd, *J* = 14.9, 7.4 Hz, 4H), 0.99 (dd, *J* = 14.6, 7.3 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H), 0.62–0.54 (m, 10H). ¹³C NMR (101 MHz, CDCl₃) δ 192.10, 154.28, 150.39, 149.42, 148.96, 133.28, 131.25, 127.32, 122.43, 122.03, 117.78, 111.05, 105.81, 54.73, 51.11, 40.30, 29.54, 25.94, 23.05, 20.40, 14.05, 13.81. ESI–MS (C₃₀H₄₃NO): calcd: 433.33; found: [M + 1]⁺, 434.34, [M + 23]⁺, 456.32.

2.2.3 Compound A

A solution of compound 3 (1.0 g, 2.3 mmol) and TCF acceptor (0.75 g, 3.7 mmol) in ethanol (20 mL) allows to stir at 70 °C during 3 h and after removal of the solvent under reduced pressure, the crude product has been additionally purified by silica chromatography to obtain A as a purple solid in 56.9% yield (0.86 g, 1.4 mmol) ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 6.5 Hz, 3H), 7.49 (s, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.57 (d, *J* = 9.4 Hz, 1H), 3.41–3.34 (m, 4H), 2.02–1.90 (m, 4H), 1.83 (s, 6H), 1.63 (dt, *J* = 15.0, 7.6 Hz, 4H), 1.40 (dd, *J* = 15.0, 7.5 Hz, 4H), 1.12 (dd, *J* = 13.9, 6.6 Hz, 4H), 0.99 (t, *J* = 7.3 Hz, 6H), 0.71 (t, *J* = 7.3 Hz, 6H), 0.67–0.59 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 175.98, 174.25, 154.62, 151.30, 149.90, 149.12, 148.77, 131.01, 130.48, 130.26, 128.95, 127.41, 122.81, 122.37, 118.73, 112.34, 111.94, 111.35, 105.71, 97.39, 97.00, 54.96, 51.23, 40.39, 29.63, 26.88, 26.02, 23.10, 20.47, 14.13, 13.93. ESI–MS

(C₄₁H₅₀N₄O): calcd: 614.40; found: [M + 1]⁺, 615.40, [M + 23]⁺, 637.38.

2.2.4 Compound B

A solution of compound 3 (0.5 g, 1.1 mmol) and CF₃-Ph-TCF acceptor (0.38 g, 1.1 mmol) in ethanol (20 mL) was stirred at 70 °C for 3 h, then after removal of the solvent under reduced pressure, the crude product was purified by silica chromatography to receive B as a green solid in 78% yield (0.65 g, 0.9 mmol)

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 15.8 Hz, 1H), 7.48 (s, 6H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.31 (s, 2H), 6.94 (d, *J* = 15.8 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.46 (s, 1H), 3.30 (t, *J* = 7.1 Hz, 4H), 1.85 (d, *J* = 8.5 Hz, 4H), 1.60–1.50 (m, 4H), 1.32 (dd, *J* = 14.6, 7.2 Hz, 4H), 1.03 (d, *J* = 6.5 Hz, 4H), 0.91 (t, *J* = 7.2 Hz, 6H), 0.62 (t, *J* = 7.1 Hz, 6H), 0.54 (d, *J* = 6.3 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 175.47, 163.52, 155.28, 152.17, 151.39, 150.29, 149.93, 131.73, 131.29, 130.50, 129.95, 129.78, 127.33, 127.05, 123.60, 122.82, 118.79, 111.87, 111.53, 111.02, 110.87, 110.60, 105.63, 98.10, 96.96, 96.64, 54.93, 51.26, 40.24, 29.66, 26.01, 23.06, 20.47, 14.12, 13.90. ESI-MS (C₄₆H₄₉F₃N₄O): calcd: 730.39; found: [M + 1]⁺, 731.39, [M + 23]⁺, 785.40.

3 Results and discussion

3.1 Characterization of chromophore

The synthetic route of the chromophore preparation was sketched in scheme 1. 2-Nitrofluorene reduced with iron powder and then reacted with 1-bromobutane to produce compound 2. Then the door was subjected to Vilsmeier

reactions in the presence of POCl₃ and DMF, affording the aldehyde compound 3. The target chromophore A and B were obtained by condensing aldehyde 3 with TCF and CF₃-Ph-TCF in refluxed ethanol, respectively.

3.2 Thermal properties

The thermal stability of chromophore A and B were explored using TGA. The decomposition temperature (*T*_d, temperature at which 5% weight loss is occurred during heating), is presented in Fig. 1 and Table 1. Chromophores A and B displayed sufficiently good thermal stability with *T*_d equal to about 140 °C, which is quite sufficient for the process of EO device preparation with higher temperatures (> 100 °C) during electric field poling.

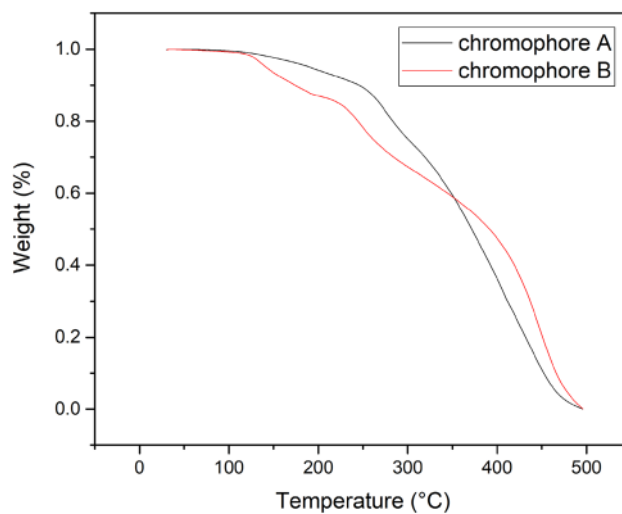


Fig. 1 TGA curves for A and B

Scheme 1 Chemical structures and synthetic scheme for chromophores A and B

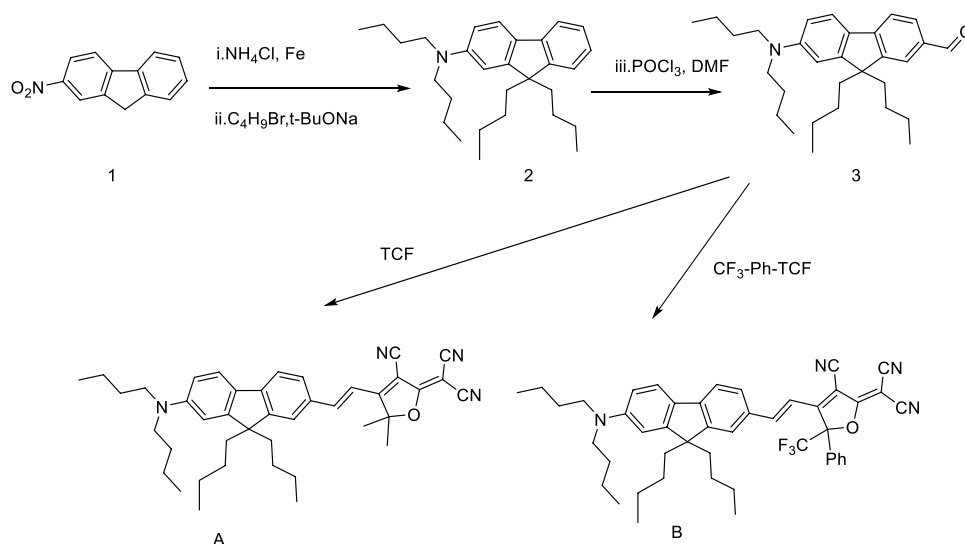


Table 1 The used DFT approach is used for evaluation of the space charge density acentricity which is directly related to the second order non-linear optical susceptibility

compd	λ_{\max}^a (nm)	λ_{\max}^b (nm)	$\Delta\lambda^c$ (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	$\beta^d/(10^{-30}\text{esu})$	r_{33} (pm/V)	T_d^e (°C)
A	575	639	64	-5.28	-3.03	2.25	616	18	145
B	645	720	75	-5.30	-3.16	2.14	701	43	183

^a λ_{\max}^a was measured in dioxane

^b λ_{\max}^b was measured in chloroform

^c $\Delta\lambda = \lambda_{\max}^b - \lambda_{\max}^a$

^d β was calculated based on DFT quantum mechanical methods

^e T_d was determined by an onset point and measured by TGA under nitrogen at a heating rate of 10 °C min⁻¹

3.3 Optical properties

UV–Vis absorption spectra for two chromophores performed on a Cary 5000 photo spectrometer were measured for six organic solvents (see Fig. 2) with spectral resolution 1 nm. The spectral data are summarized in Table 1. The λ_{\max} of the chromophores A and B are equal to 639 nm and 720 nm in chloroform, respectively. Moreover, it should be emphasized that A and B possess a bathochromic spectral shift equal to 64 nm and 75 nm from dioxane to chloroform, respectively. Those results clearly showed that fluorene electron donor modified by amino group play a positive effect on improving the strength of donor and shifting the ICT absorption band of chromophores to lower energy.

3.4 Theoretical simulations

To evaluate the microscopic NLO properties of the designed chromophores, DFT calculations were carried out to explore the frontier molecular orbitals and β value of A and B. The

geometries of chromophores were optimized within a framework of B3LYP/6-31G* level. First hyperpolarizabilities (β) were estimated within the CAM-B3LYP/6-31G* approach. All the calculations were carried out using Gaussian 09 quantum chemical package. The used DFT approach is used for evaluation of the space charge density acentricity which is directly related to the second order nonlinear optical susceptibility.

The calculations performed by the DFT calculations, are summarized in Table 1. The obtained energy gap (ΔE) values of chromophores A and B are equal to 2.25 eV and 2.14 eV, respectively. At the same time the second order hyperpolarizabilities for β of A and B are equal to 616×10^{-30} esu and 701×10^{-30} esu, respectively. The general space distribution of the HOMO and LUMO orbitals are presented in the Fig. 3 for A and B, respectively. These one confirm a fact that fluorene electron dominating donor origin of chromophores A and B which is beneficial for largely improvement of the donor ability due to enhancement of the space acentricity.

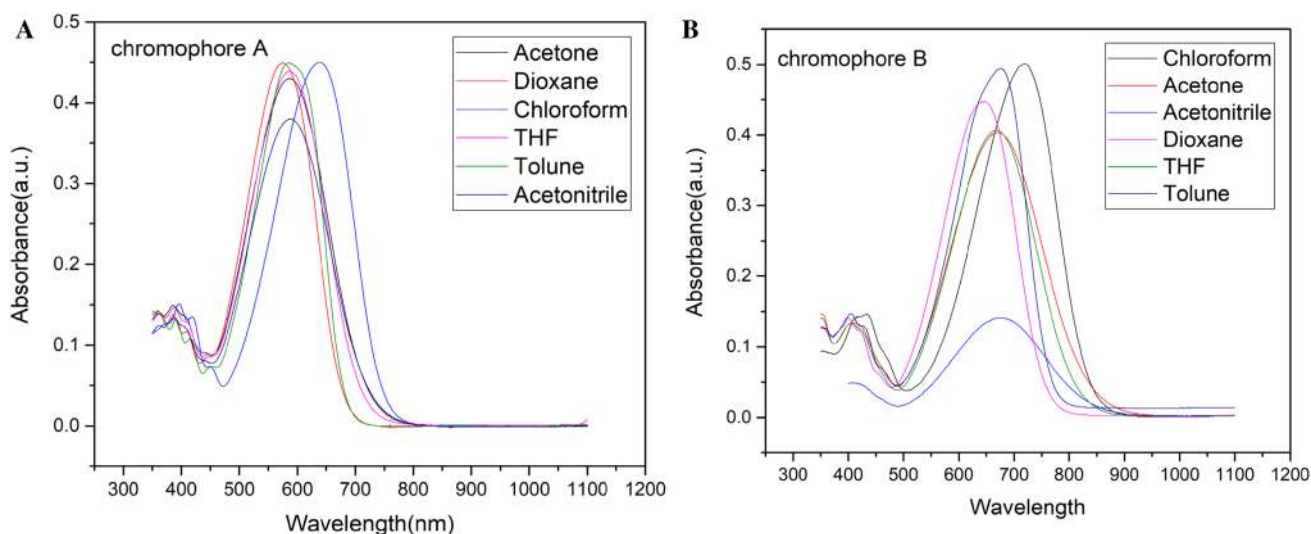
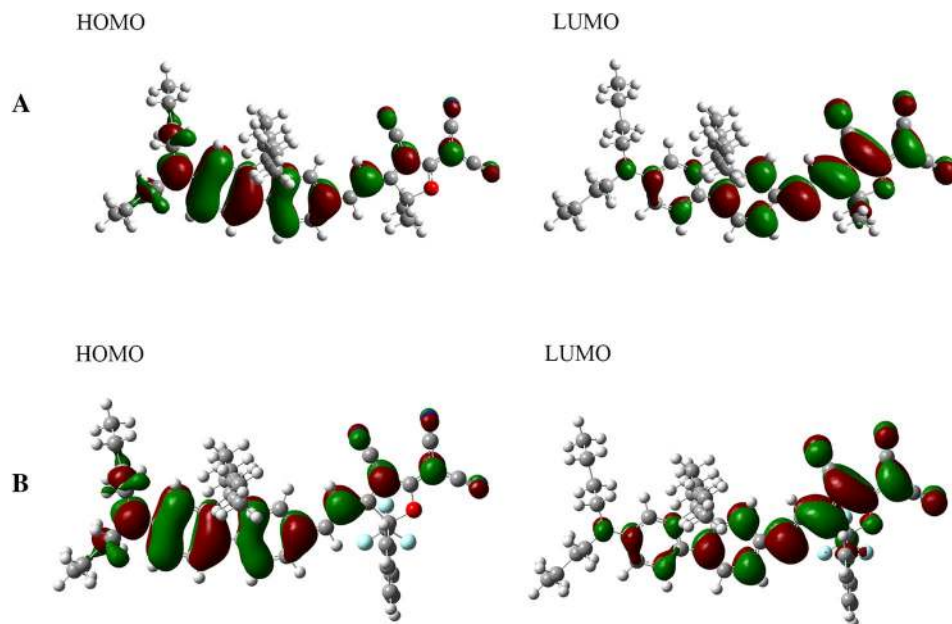


Fig. 2 UV–Vis absorption spectra for chromophores A and B in six solvents

Fig. 3 HOMO and LUMO orbital's space distribution for chromophores A and B



3.5 Electro-optic parameters

To evaluate EO property of guest–host chromophore films A and B were prepared by doping of 25 wt% chromophores in PMMA. Corona poling was applied to induce the acentric long-range ordering of chromophores and EO coefficients were measured at wavelength 1310 nm. Film A and B afforded r_{33} values equal to 18 pm/V and 43 pm/V, respectively. The principal parameters are comparable with other material [24–30]. Following the Table 1 it is necessary to emphasize that the agreement between the calculations and the experiment is very good which confirm that the role of the phonon subsystem is not so important here.

4 Conclusions

Fluorene modified by amino groups have been synthesized as a principally novel electron donor group. These groups possess simpler synthetic route and stronger electron donating ability with respect to the known. The results demonstrate a good performance of chromophores A and B. The EO coefficients of poled 25 wt% A/PMMA and 25 wt% B/PMMA films afford second order optical susceptibilities equal to 18 pm/V and 43 pm/V at wavelength 1310 nm, respectively. In addition, chromophores A and B demonstrate a good solubility and compatibility with traditional polymer matrices. It is demonstrated a good agreement of the experimental magnitudes with the performed quantum chemical simulations which confirm principal role of the electron subsystem and low contribution of the quasi-phonon subsystem. These results indicated that modification in

fluorene may be a promising way to design and preparation of electron donor NLO chromophore.

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