Materials Letters 226 (2018) 38–42

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Greatly improved performance for NLO chromophore with 4,4′-bis (diethylamino)benzophenone as donor by introducing stronger acceptor

Ping Wang [a,b], Hua Zhang [a,b], Guilan Zhang [a], Yong Huang [a], Jialei Liu [a,*], Shuhui Bo [a,*]

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China*
[b] *University of Chinese Academy of Sciences, Beijing 100043, PR China*

A R T I C L E   I N F O

Article history:
Received 23 April 2018
Received in revised form 3 May 2018
Accepted 4 May 2018
Available online 4 May 2018

Keywords:
Nonlinear optical materials
Chromophore
Electro-optic
Donor
Acceptor

A B S T R A C T

One novel chromophore C based on 4,4′-bis(diethylamino) benzophenone donor and CF_3-Ph-TCF acceptor was synthesized. Alkoxy isolation group was introduced also. Cyclic voltammetry measurements showed that the new chromophore C had a much smaller energy gap ($\Delta E = 1.25$ eV) than chromophore A and B. UV–Vis absorption indicated that obvious red shift (more than 100 nm) obtained for chromophore C. The doped film C containing CF_3-Ph-TCF chromophore showed a r_{33} value of 235 pm/V at the concentration of 25 wt% which is much higher than that of the TCF based chromophore A (149 pm/V) and B (163 pm/V). The thermal stability were high enough (>200 °C) to be further fabricated in devices and good EO property make application possible.

1. Introduction

The research on highly efficient organic electro-optic (EO) materials has been the focus in recent years for many organic materials groups because of their attractive potential in such applications as optical data transmission and optical information processing [1,2]. The organic and polymeric nonlinear optical (NLO) materials have many advantages over traditional inorganic and semiconductor materials such as large nonlinear optical coefficients, easy syntheses and low cost [3–6].

Second-order NLO chromophore which is consisted of an electron-donating group and an electron-withdrawing group linked via a π-conjugated bridge (D-π-A system) is the core component of NLO materials [1]. Recent studies about NLO materials have mainly focused on the design of electron donor and polymer system [7–9]. Furthermore, the introduction of some isolation groups (IG) into chromophores proved to be efficient to decrease interactions between molecule thus enhances the poling efficiency and EO performance [10–12]. In the previous study, the Y type chromophore was confirmed to own good EO property and additional donor play an important role [13,14], but there are still room for improvement as the electron acceptor could be strengthen and bridge could be modified further [15,16]. In this regard, we have designed and synthesized one new chromophore C which used Y type 4,4′-bis(diethylamino) benzophenone as donor and CF_3-Ph-TCF as acceptor, coupled by alkoxy group modified thiophene bridge. The thermal stability, optical, redox property, and EO activity of the chromophores were systematically studied to explore its potential use in the devices.

2. Experimental section

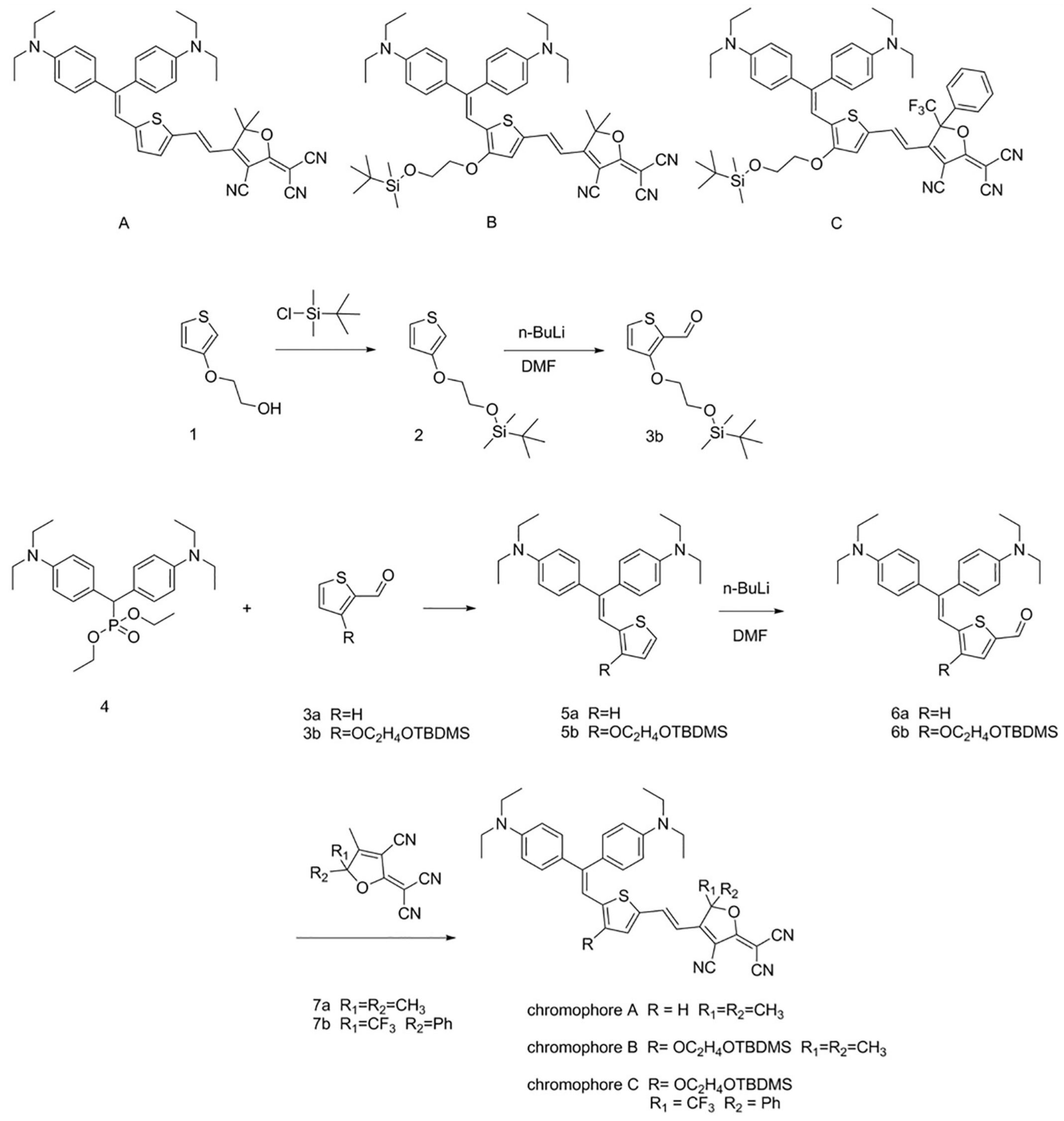
2.1. Materials and instruments

All chemicals are commercially available and are used without further purification unless otherwise stated. N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were 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 (CF_3-Ph-TCF) were prepared according to the literature [17]. TLC analyses were carried out on 0.25 mm thick precoated silica plates and spots were visualized under UV light. Chromatography on silica gel was carried out on Kieselgel (200–300 mesh). ^{1}H NMR spectra were determined on an Advance Bruker 400 M (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.,) spectrometer. UV–Vis spectra were performed on Cary 5000 photo spectrometer. TGA and DSC were determined by TA-instrument Q50 and Q10 with a

---

[*] Corresponding authors.
E-mail addresses: liujialei@mail.ipc.ac.cn (J. Liu), boshuhui@mail.ipc.ac.cn (S. Bo).

https://doi.org/10.1016/j.matlet.2018.05.025
0167-577X/



Scheme 1. The chemical structure and syntheses route of chromophore A–C.

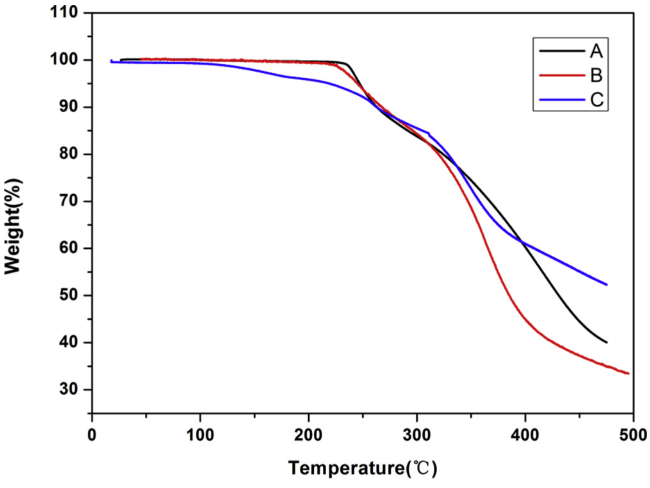


Fig. 1. The TGA curves of chromophore A–C with a heating rate of 10 °C/min under N_2.

heating rate of 10 °C min^{-1} under N_2 respectively. Cyclicvoltammetric data were measured on a Princeton Applied Research Model 283 Potentiostat/Galvanostat.

2.2. Synthesis

2.2.1. Synthesis of chromophore A–B

Compound 6b and chromophore A–B were synthesized according to the literature [14,18] here we no longer give statement.

2.2.2. Synthesis of chromophore C

A mixture of compound 6b (0.3 g, 0.5 mmol) and 7b (0.12 g, 0.4 mmol) in absolute ethanol (10 mL) was stirred at 75 °C for 0.5 h. After removal of the solvent, the residue was purified by column chromatography on a silica gel (hexane-ethyl acetate, v/v, 4: 1). A dark solid was obtained (0.3 g, 0.33 mmol, 83%).

MS: m/z calcd for $C_{51}H_{56}F_3N_5O_3SSi$: 903.38 $[M]^+$; found: 903.26. ^1H NMR (400 MHz, Acetone) δ 7.91–7.85 (m, 5H), 7.65–7.56 (m, 4H), 7.26 (d, J = 8.4 Hz, 2H), 7.20–7.09 (m, 4H), 7.00 (s, 1H), 6.98 (s, 1H), 4.54 (s, 2H), 4.21 (s, 2H), 3.76 (dd, J = 10.9, 7.0 Hz, 8H), 1.50–1.42 (m, 12H), 1.14 (s, 9H), 0.32 (d, J = 4.7 Hz, 6H).