

New “Y” type nonlinear optical chromophores with good transparency and enhanced nonlinear optical effects

Wei Gong^a, Qianqian Li^a, Suyue Li^a, Changgui Lu^b, Zhen Li^{a,*}, Jing Zhu^b, Zhichao Zhu^a,
Zhong'an Li^a, Qingrong Wang^a, Yiping Cui^{b,*}, Jingui Qin^{a,*}

^a Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, China

^b Advanced Photonics Center, Department of Electronic Engineering, Southeast University, Nanjing 210096, China

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Abstract

Two new “Y” type triaryl amino chromophores with tricyanovinylidihydrofuran groups as electronic acceptor are synthesized and found to exhibit blue-shifted absorption in comparison with the corresponding D– π –A analogues while demonstrating significantly enhanced optical nonlinearity, as well as good thermal stability.

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1. Introduction

Considerable attention has been attracted in the organic electro-optic (EO) materials due to their potential applications in photonics [1]. As one of the key points of second-order nonlinear optical (NLO) materials, organic chromophores, which exhibit good properties such as high thermal and chemical stability, large nonlinearity, and transparency are currently being pursued for the next generation of high-performance photonics devices [2]. However, it is difficult to simultaneously achieve the three criteria required for usefulness, and there are experimentally observed tradeoffs, such as the nonlinearity–thermal stability tradeoff, and the nonlinearity–transparency tradeoff. Here, we report the synthesis, optical, and thermal properties of a series of new triaryl amino chromophore with tricyanovinylidihydrofuran (TCF) groups as the electron acceptor (Scheme 1), which demonstrate good thermal stability, relatively better transparency and large nonlinearity.

In general, the additional thermal stability can be added to a nonlinear chromophore by substitution of aromatic moieties for aliphatic ones along the delocalized path, and triphenylamino group is often used as the donor part to provide better optimization of the nonlinearity–thermal stability tradeoff [3]. However, some triaryl

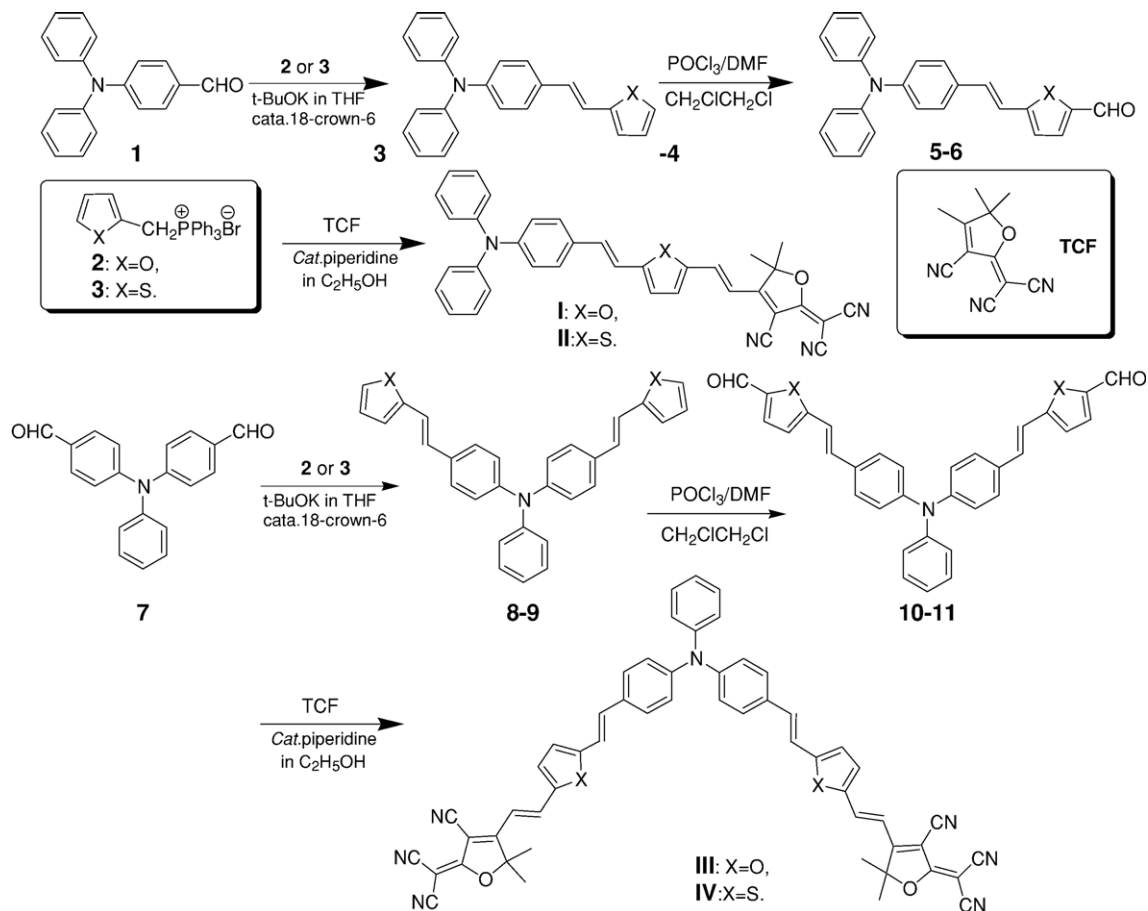
amino chromophores have shown increased thermal stability, but decreased molecular hyperpolarizability [4]. By using one of the strongest known acceptors, TCF, there was report of triaryl amino chromophores showing large nonlinearity and good thermal stability [5]. The preparation of “Y” type chromophore coupling triphenyl amine donor with strong acceptor, however, has not been reported, though other “Y” type chromophores have proved to show good comprehensive properties [6]. In this study, triphenyl amine donors are for the first time used in the “Y” type chromophores, bridged to TCF via vinyl thiophene or furan linkages, which demonstrate a combination of relatively good transparency, high thermal stability, and large nonlinearity.

2. Results and discussion

The syntheses of chromophores I–IV are shown in Scheme 1. A Vilsmeier reaction of triphenyl amine yielded aldehyde 1 according to the previous literature [7], which condensed with furan or thiophene methyl triphenylphosphonium bromide [8] gave the intermediate 3 or 4 in the yields of 84 and 64% for furan and thiophene moieties respectively. Also by the Vilsmeier reactions, the aldehydes 5 and 6 were obtained in the yields of 80 and 60% respectively. Finally, chromophores I and II were synthesized by condensation of the aldehydes 5 and 6 with TCF [9] in 46 and 61% yields, respectively. And those of chromophores III and IV were prepared by similar procedures with dialdehyde [10] used instead of aldehyde 1. All the intermediates and chromophores were isolated as pure compounds by chromatography on silica gel followed by recrystallization from organic solvents, and gave satisfied spectroscopic data [11]. The chromophores are soluble in common organic solvents, such as chloroform, THF, DMF, etc.

* Corresponding authors. Tel.: +86 27 62254108; fax: +86 27 68756757.

E-mail addresses: lizhen@whu.edu.cn (Z. Li), cyp@seu.edu.cn (Y. Cui), jgqin@whu.edu.cn (J. Qin).



Scheme 1.

The β values of the chromophores **I–IV** were measured by Hyper-Rayleigh Scattering (HRS) technique [12] in chloroform using the fundamental excitation wavelength of 1064 nm, and the known β value of *p*-nitroaniline was used as an external reference. The measured hyperpolarizabilities β and the static β_0 obtained from the two-level modulation of these chromophores, the UV–visible absorption maxima, λ_{\max} , and thermal decomposition temperature (T_d) of the chromophores were summarized in Table 1.

The prediction by the theoretical calculation and earlier results demonstrated that for a given acceptor and donor, the β_0 values are larger for the chromophores with thiophene as conjugation than those for the chromophores containing the bridge of furan [13]. However, there were reported results in contrast to the above idea [14,15]. In our case, the β_0 values of **I** and **III** are a little smaller than those of **II** and **IV** respectively. However, considering the possible deviation of the testing setup, the results might only indicate that the furan moieties are as good as the conjugation bridges of thiophene groups for this system.

The β_0 values of the “Y” type chromophores **III** and **IV** are enhanced at a large degree, in comparison with those of chromophores **I** and **II**, with the improvement of 47% and 46% from **I** to **III** and **II** to **IV**, respectively. This is very exciting but understandable. In the “Y” type chromophores **III** and **IV**, there are two acceptors and one donor, the ground state can be described as DA_1A_2 , and it would be difficult for the two acceptor groups to interact with each other because of their rigid structure. Then, there will be two degenerated excited states: $D^+A_1^-A_2$ and $D^+A_1A_2^-$, similar as in the case of symmetric (dicyanomethylene)pyran (DCM) derivatives [6], which possess two donors and one acceptor. And just like in the DCM series, the two low-lying electronic excited states in chromophores **III** and **IV** should also

contribute to the molecular hyperpolarizability β in an additive manner, making these two chromophores enhanced NLO properties, compared to their corresponding D– π –A analogues, chromophores **I** and **II**. Even so, the improvement was very large, showing the advantages of the “Y” type NLO chromophores, and providing a new route to enhance the molecular hyperpolarizabilities of chromophores with triphenyl amino groups as the electronic donor moieties. It is also interesting to note that the improvement degree from chromophore **I** to **III** is nearly the same to that from chromophore **II** to **IV**, possibly indicating that the electronic properties of the furan moieties are similar to those of the thiophene groups.

It is interesting that chromophores **III** and **IV** show similar absorption wavelengths when compared with their corresponding D– π –A

Table 1

Cpd	$\lambda_{\max}/\text{nm}^a$	β_{HRS}^b	β_0^c	T_d^d
I	628	648	166	310
II	620	728	172	298
III	621	1023	244	
IV	618	1091	252	283

^a Tested in chloroform.

^b β values (in unit of 10^{-30} esu) measured by Hyper-Rayleigh Scattering (HRS) technique in chloroform using the fundamental excitation wavelength of 1064 nm, with *p*-nitroaniline (*p*-NA) in the same solvent used as the external reference ($\beta=23 \times 10^{-30}$ esu).

^c Dispersion-corrected β values calculated by using an approximate two-level model.

^d T_d = TGA onset in nitrogen at a heating rate of 10 °C/min.

analogues. To check the reproducibility, we repeated the measurements several times and got the same results. Then, it is for sure that chromophores **III** and **IV** exhibit similar UV–visible absorption maxima (λ_{\max}) instead of red-shifted absorption, although their molecular hyperpolarizabilities were enhanced at a large degree. This might be due to the presence of the two charge-transporting levels in the chromophores as other “ Λ ” type chromophores reported previously [16]. Thus, our examples provide a new opportunity for defeating nonlinearity–transparency tradeoff in designing second-order nonlinear optical chromophores by using triphenyl amino groups as the donor part.

The decomposition temperature T_d of the chromophores was measured by thermal gravimetric analysis (TGA) in nitrogen, with a heating rate of 10 °C/min. The T_d of the chromophores was in the range of 283–310 °C, with chromophore **I** showing the highest thermal decomposition at 310 °C.

3. Conclusions

In summary, we have synthesized two new “Y” type chromophores with triphenyl amino groups as the donor, bridged to one of the strongest known acceptors, TCF, via vinyl furan or thiophene linkages. The two chromophores demonstrated enhanced nonlinear response without sacrifice in their transparency but with a similar absorption in comparison with their corresponding D– π –A analogues, also they are thermally stable up to 280 °C. Thus, the two chromophores may be used as NLO active moieties in the practical EO applications.

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- [11] The yield (%), melting point (°C), NMR (300M), IR (neat) and MS data for the four chromophores. **I**: yield 46; mp 286–287; NMR (DMSO- d_6) δ (ppm): 7.75 ($d, J=15.3$ Hz, 1H), 7.56 ($d, J=8.7$ Hz, 2H), 7.33–7.41 (m, 6H), 7.07–7.09 (m, 7H), 6.82–6.93 (m, 4H), 1.77 (s, 6H); IR: 2225 cm^{-1} (C \equiv N); ESI-MS m/z (%) 546.2 (M^+); HRMS calcd for $C_{36}H_{26}N_4O_2$: 546.2058, Found: 546.2050. **II**: yield 61; mp 247–249; NMR (DMSO- d_6) δ (ppm): 8.11 ($d, J=15.6$ Hz, 1H), 7.75 ($d, J=3.6$ Hz, 1H), 7.53 ($d, J=8.1$ Hz, 2H), 7.32–7.37 (m, 6H), 7.05–7.13 (m, 6H), 6.91 ($d, J=7.8$ Hz, 3H), 6.71 ($d, J=16.2$ Hz, 1H), 1.79 (s, 6H); IR: 2225 cm^{-1} (C \equiv N); ESI-MS m/z (%) 585.2 ($M+Na^+$); HRMS calcd for $C_{36}H_{26}N_4OSNa$: 585.1735, Found: 585.1720. **III**: yield 36; mp 210–212; NMR (CDCl $_3$) δ (ppm): 7.80 ($d, J=16.2$ Hz, 2H), 7.60 ($d, J=8.4$ Hz, 4H), 7.47–7.37 (m, 6H), 7.32 ($d, J=3.6$ Hz, 2H), 7.19–7.17 (m, 5H), 7.11–7.02 (m, 4H), 6.86 ($d, J=3.6$ Hz, 2H), 1.76 (s, 12H); IR: 2226 cm^{-1} (C \equiv N); ESI-MS m/z (%) 870.3 ($M+Na^+$); HRMS calcd for $C_{54}H_{37}N_7O_4Na$: 870.2803, Found: 870.2799. **IV**: yield 46; mp 200–202; NMR (DMSO- d_6) δ (ppm): 8.11 ($d, J=16.2$ Hz, 2H), 7.75–7.76 (m, 2H), 7.58 ($d, J=9$ Hz, 4H), 7.33–7.46 (m, 6H), 7.09–7.27 (m, 5H), 7.00 ($d, J=8.1$ Hz, 4H), 6.71 ($d, J=15.9$ Hz, 2H), 1.79 (s, 12H); IR: 2226 cm^{-1} (C \equiv N); ESI-MS m/z (%) 902.2 ($M+Na^+$); HRMS calcd for $C_{54}H_{37}N_7O_2S_2Na$: 902.2352, Found: 902.2342.
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