Highly stable binary cross-linkable organic nonlinear optical materials using different acceptors based on Huisgen cycloaddition reaction

Yu Zhang[1], Weijun Zhang[1], Shuhui Bo[2], Wenlong He[1], Chuying Liu[1], Jiahai Wang[1], and Fenggang Liu[3]

[1]guangzhou daxue
[2]Minzu University of China
[3]Guangzhou University

July 16, 2024

Abstract

How to obtain organic electro-optic materials with large electro-optic coefficients, high glass transition temperature, and good optical transparency remains a challenge in this field. To solve this problem, we introduce groups that can undergo Huisgen cycloaddition reactions into the donor and electron bridge of chromophores with large hyperpolarizability using tetrahydroquinoline as the donor. Binary cross-linkable chromophores TLD1-2 with CF3-TCF as the acceptor and chromophores TLD3-4 with 5Fph-TCF as the acceptor were synthesized. After poling and crosslinking, the Tg of TLD1/TLD2 and TLD3/TLD4 were raised to 152 and 174 °C, respectively. The electro-optical coefficients of chromophores TLD1/TLD2 and TLD3/TLD4 were as high as 312 pm/V and 287 pm/V, respectively. The long-term alignment stability test showed that after being left at 85 °C for 500 hours, the cross-linked film TLD3/TLD4 can still maintain more than 98% of the original electro-optical coefficient value, which is higher than that of TLD1/TLD2 (93%). The chromophore TLD3-4 exhibited much blue-shifted maximum absorption wavelengths (˜40nm) compared to TLD1-2 which was beneficial for reducing optical loss in the device. The combination of high electro-optic coefficient, strong stability, and excellent optical transparency makes the TLD series of binary cross-linked materials very promising for practical high-performance electro-optic devices.

Dear Editor and Referee,

We would like to submit the enclosed manuscript entitled "**Highly stable binary cross-linkable organic nonlinear optical materials using different acceptors based on Huisgen cycloaddition reaction** " which we wish to be considered for publication in *Chinese Journal of Chemistry***.** The work described has not been submitted elsewhere for publication, in whole or in part, and all the authors listed have approved the manuscript that is enclosed.

Driven by emerging technologies such as 5G wireless communication, big data, artificial intelligence/machine learning (AI/ML), cloud services, telemedicine and autonomous vehicle, and the demand for telework caused by the COVID-19, the world has experienced an explosive growth in Internet data traffic. Information processing and transmission materials based on photons have shown broad application prospects. At present, lithium niobate ($LiNbO_3$) is the commercialized electro-optic material in electro-optic modulator. However, this kind of material has some disadvantages, such as low electro-optic coefficient (<30 pm/V) and large device size. With the development of organic materials, many organic chromophore materials with super large electro-optic coefficients (>1000pm/V) have been developed.

However, the application of organic nonlinear optical materials to commercial electro-optic modulators and other fields also faces technical bottlenecks (difficult to meet the Telecommunications GR-468-CORE standards). How to obtain organic electro-optic chromophores with both large electro-optic coefficients (r_{33} values), photothermal stability, and polarization orientation stability is still a challenge for the industry. In order to solve the above problem, Crosslinked materials are the most promising solution to the stability of organic electro-optical materials. However, there were few reports on cross-linked electro-optic materials. Traditional high T_g polymeric cross-linked OEO systems have chromophore number density ρ_N usually less than 2.7×10^{20} molecules/cm^3 and r_{33} value usually less than 150 pm/V. We have developed binary cross-linkable chromophores HLD1/HLD2 (Chem. Mater. 2020, 32, 1408-1421) and QLD1/QLD2 (Chem. Sci., 2022, 13, 13393–13402) with 100 wt% chromophores for the first time, resulting in significant increase in the electro-optic coefficient to 290-327pm/V and glass transition temperature as high as 174-185 .HLD1/HLD2 has been successfully applied to many advanced optoelectronic devices (Nature Electronics 2020, 3, (6), 338-345, Nano Lett. 2021, 21, 4539-4545 and so on). In addition, the United States and Europe have also set up corresponding companies to produce HLD1/HLD2 and related optoelectronic devices.

However, the crosslinking method of HLD1-2 and QLD1-2 is limited to the Diels-Alder reaction of anthracene and acrylate. This reaction requires 60 minutes of reaction at 160 degrees celsius to complete crosslinking. Excessive temperature and longer reaction time may cause the decomposition of chromophores and the waste of energy. So it is very important to develop new cross-linkable groups suitable for binary cross-linked chromophores. And there is still a lack of systematic research on pure chromophore crosslinking systems: For this reason, we proposed a systematic research idea of binary cross-linked chromophores:

Azide and alkyne were introduced into the donor and bridge parts of tetrahydroquinoline derivatived chromophores **TLD1 and TLD2** . After the chromophore molecules undergo poling orientation, the temperature continues to rise, and the molecules undergo Huisgen cycloaddition at 150 to form a polymer network, greatly improving the long-term alignment stability of the materials.Electro-optic coefficient up to 312 pm/V and glass transition temperature as high as 152 was achieved in these cross-linked film due to high chromophore density (5.58x 10^{20} molecules/cm^3) and large hyperpolarizability.

In order to further improve the glass transition temperature and optical transparency of the material. We introduced the 5Fph-TCF acceptor into the binary crosslinking system for the first time. The chromophores TLD3 and TLD4 using 5Fph-TCF as acceptor exhibit higher glass transition temperatures and better optical transparency

The glass transition temperatures of chromophores TLD3-4 was 104 and 118, respectively, which was much higher than the 85 and 57 of chromophore TLD1-2, respectively. The glass transition temperature of cross-linked TLD3/TLD4 was as high as 174 , which was also 22 higher than that of cross-linked TLD1-2. In addition, compared to chromophore TLD1-2, the UV absorption wavelength of chromophore TLD3-4 has blue shifted by ˜40 nm, demonstrating better optical transparency. The electro-optic coefficients of crosslinked TLD3/TLD4 was as high as pm/V, respectively, which is also one of the highest electro-optic coefficients of cross-linked materials. The long-term alignment stability test showed that after being left at 85 for 500 hours, the cross-linked chromophores TLD3/TLD4 can still maintain more than 98% of the original electro-optical coefficient value, which is higher than that of TLD1/TLD2 (93%).

The cross-linked chromophores TLD3-4 with 5FPh-TCF as the acceptor has a higher glass transition temperature, better transparency, and leading electro-optic coefficient, all of which are major breakthroughs in the design of binary cross-linked electro-optic materials

Thank you very much for your considering our manuscript for potential publication. I'm looking forward to hearing from you soon.

Best regards

Fenggang Liu

School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China. E-mail address:liufg6@gzhu.edu.cn