



First hyperpolarizability orientation in asymmetric pyrrole-based polyene chromophores

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ABSTRACT

Novel, asymmetrically shaped, pyrrole-based polyene chromophores were designed to obtain a large angle $\theta(\mu, \beta_{\max})$ between the directions of the maximum first hyperpolarizability β_{\max} and the dipole moment μ , by introducing an asymmetric core pyrrole into the π -conjugated polyene bridge of the chromophore. Asymmetric *N*-substituted pyrrolic nonlinear optical chromophores based on configurationally locked polyene (CLP) were synthesized and their first hyperpolarizabilities were theoretically determined using density functional theory (DFT). High asymmetry with an angle $\theta(\mu, \beta_{\max})$ between the dipole moment μ and the main direction of the charge-transfer transition β_{\max} of up to 48° was achieved.

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1. Introduction

Organic materials exhibiting second-order optical nonlinearity have been considered very attractive for numerous applications during the last 20 years, such as high-speed electro-optic modulation, field detection, frequency conversion [1–8] and terahertz (THz) wave generation and detection [9–12]. Conventional organic nonlinear optical chromophores are based on a long π -conjugated bridge that connects electron donor and electron acceptor groups and which, therefore, display a large dipole moment [1,2]. To achieve a macroscopic second-order nonlinearity, the polar chromophores are aligned by additional external electric-field poling in polymers and by self-assembly based on specific intermolecular interactions in crystals. However, the tendency for highly polar chromophores towards antiparallel dipole–dipole aggregation often leads to reduced poling efficiency in a polymer system [13] and to centrosymmetric arrangement of molecules in the crystalline state [14,15]. Whilst many experimental and theoretical studies have been devoted to the enhancement of molecular nonlinearity

[3,4,16–20], achieving optimal acentric molecular ordering in both polymer and crystal systems remains a challenge.

Various strategies have been suggested to reduce the tendency towards antiparallel alignment of the first hyperpolarizabilities β in bulk materials: for example, by using spherically shaped chromophores and dendritic chromophores with different shape and size of substituents [21,22], or by antiparallel dipole–dipole aggregation of two chromophores bearing opposite sign of the first hyperpolarizability for polymers [23] and crystals [24], as well as by using non-polar octupolar molecules [25–27].

Another interesting approach for achieving acentric alignment of the first hyperpolarizabilities β is to use polar chromophores having a large angle $\theta(\mu, \beta_{\max})$ between the direction of the dipole moment μ and the main direction of the first hyperpolarizability β_{\max} [28]. For example, 2-(5-methyl-3-(4-(pyrrolidin-1-yl)styryl)cyclohex-2-enylidene)malononitrile (MH2) chromophore based on configurationally locked polyene (CLP) [29,30] exhibits a relatively large angle $\theta(\mu, \beta_{\max})$ of about 22° [28]. The dipole moments μ of the molecular pair in the crystalline state are almost antiparallel and therefore the crystal almost non-polar. However, due to the large angle $\theta(\mu, \beta_{\max})$, the first hyperpolarizabilities β still add constructively and MH2 crystals exhibit a large macroscopic second-order nonlinearity [28].

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In this work, we investigate new chromophores that are designed to have a large angle $\theta(\mu, \beta_{\max})$ between the dipole moment μ and the main direction of the charge-transfer transition β_{\max} . In order to achieve this, 2-dimensional chromophores with a strongly asymmetric shape are considered, in contrast to the commonly studied 1-dimensional chromophores and 2-dimensional chromophores with Δ - or X-shape that are in general symmetric [25–27,31–33] and show a high tendency of antiparallel aggregation of the chromophores. To design asymmetric-shaped chromophores having a large angle $\theta(\mu, \beta_{\max})$, we here introduce an asymmetric core pyrrole into the π -conjugated bridge of chromophores. We have designed and synthesized new asymmetric-shaped *N*-substituted pyrrolic chromophores based on configurationally locked polyene (CLP) bridge (see Fig. 1) and investigated the first hyperpolarizabilities theoretically using quantum chemical calculations with density functional theory (DFT). High asymmetry with the angle $\theta(\mu, \beta_{\max})$ between the dipole moment μ and the main direction of the charge-transfer transition β_{\max} of up to 48° has been achieved.

2. Experimental

2.1. Synthesis and characterization

All chemicals were obtained from commercial suppliers (mainly from Aldrich) and used without further purification. ^1H NMR spectra were recorded on a Varian 400 MHz. The chemical shifts are reported in ppm (δ) relative to $(\text{CH}_3)_4\text{Si}$. UV/vis. absorption spectra were recorded by a Jasco V-570 spectrometer. Elemental analysis was performed by LECO CHN-900 for determination of elements C, H, N and LECO RO-478 for determination of element O. The chromophores were prepared by the following synthetic routes as shown in Fig. 1.

2.1.1. 1-(4-Nitrophenyl)-1H-pyrrole-2-carbaldehyde

Pyrrole-2-carbaldehyde (52.6 mmol, 5 g) and 4-fluoronitrobenzene (52.6 mmol, 7.42 g) were dissolved in dry DMF (30 mL). K_2CO_3 (78.9 mmol, 10.9 g) was added to this solution and the mixture was stirred for 5 days at 90 °C. The resulting mixture was cooled to room temperature. The crystalline solid and K_2CO_3 were filtered and then washed with water to remove K_2CO_3 . The crystalline solid was purified by recrystallization in methanol/methylene chloride solution. ^1H NMR (CDCl_3 , δ): 6.49 (1H, m, Py-H), 7.12 (1H, m, Py-H), 7.20 (1H, m, Py-H), 7.51–7.53 (2H, d, $J = 9.2$ Hz, Ar-H), 8.31–8.33 (2H, d, $J = 9.2$ Hz, Ar-H), 9.61 (1H, s, –CHO). Elemental analysis for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_3$: (%) Calcd. C 61.11, H 3.73, N 12.96, O 22.20; Found C 61.10, H 3.70, N 12.85.

2.1.2. Synthesis of pyrrolic CLP chromophores

The equimolar amounts of corresponding aldehyde and 2-(3,5-dimethylcyclohex-2-enylidene)malononitrile were mixed with the catalyst piperidine, and was stirred for 24 h at room temperature [28]. A crystalline solid was obtained by filtration. The materials were purified by recrystallization in methylene chloride/methanol and by column chromatography (methylene chloride:methanol=300:1) (yield >19%).

2.1.3. 2-(3-(2-(1H-Pyrrol-2-yl)vinyl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (HP)

^1H NMR (CDCl_3 , δ): 1.07 (6H, s, – CH_3), 2.42 (2H, s, – CH_2 –), 2.58 (2H, s, – CH_2 –), 6.32 (1H, m, – $\text{C}=\text{CH}$ –), 6.52 (1H, m, Py-H), 6.73 (1H, m, Py-H), 6.96 (1H, m, Py-H), 6.52–6.56 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –), 6.92–6.96 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –), 8.5 (1H, s, NH). Elemental analysis for $\text{C}_{17}\text{H}_{17}\text{N}_3$: (%) Calcd. C 77.54, H 6.51, N 15.96; Found C 77.42, H 6.61, N 15.85.

2.1.4. 2-(5,5-Dimethyl-3-(2-(1-methyl-1H-pyrrol-2-yl)vinyl)cyclohex-2-enylidene)malononitrile (MP)

^1H NMR (CDCl_3 , δ): 1.08 (6H, s, – CH_3), 2.42 (2H, s, – CH_2 –), 2.58 (2H, s, – CH_2 –), 3.72 (3H, s, – NCH_3), 6.21 (1H, m, – $\text{C}=\text{CH}$ –), 6.66–6.78 (3H, m, Py-H), 6.72–6.76 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –), 6.90–6.94 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –). Elemental analysis for $\text{C}_{18}\text{H}_{19}\text{N}_3$: (%) Calcd. C 77.95, H 6.90, N 15.15; Found C 77.67, H 7.08, N 14.96.

2.1.5. 2-(5,5-Dimethyl-3-(2-(1-(4-nitrophenyl)-1H-pyrrol-2-yl)vinyl)cyclohex-2-enylidene)malononitrile (NP)

^1H NMR (CDCl_3 , δ): 1.03 (6H, s, – CH_3), 2.23 (2H, s, – CH_2 –), 2.56 (2H, s, – CH_2 –), 6.46 (1H, m, – $\text{C}=\text{CH}$ –), 6.75 (1H, m, Py-H), 6.87 (1H, m, Py-H), 7.01 (1H, m, Py-H), 6.68–6.72 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –), 6.79–6.83 (1H, d, $J = 16$ Hz, – $\text{CH}=\text{CH}$ –), 7.47–7.49 (2H, d, $J = 9.2$ Hz, Ar-H), 8.38–8.41 (2H, d, $J = 9.2$ Hz, Ar-H). Elemental analysis for $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_2$: (%) Calcd. C 71.86, H 5.24, N 14.57, O 8.32; Found C 71.57, H 5.40, N 14.34.

3. Results and discussion

3.1. Design of new pyrrolic chromophores

The chemical structures of newly designed asymmetric chromophores are shown in Fig. 1, together with their abbreviations. Asymmetric chromophores consist of the configurationally locked π -conjugated hexatriene bridge linked between heteroaromatic *N*-substituted pyrrole electron donor and dicyanomethylidene electron acceptor. We employ the configurationally locked π -conjugated hexatriene bridge, since it exhibits efficient charge

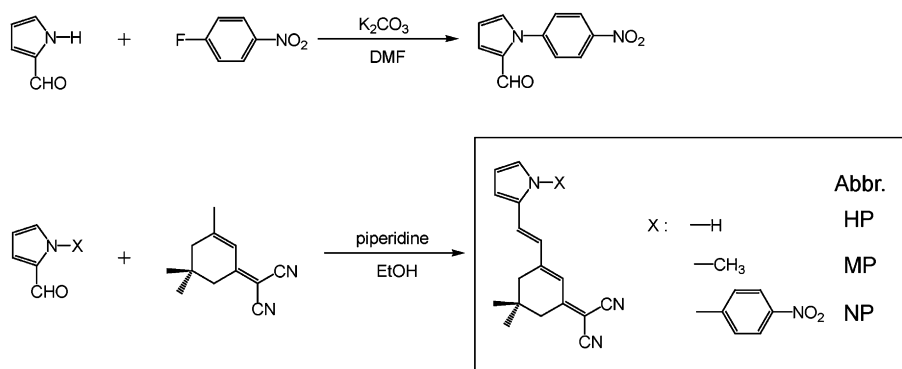


Fig. 1. Synthetic route for the investigated chromophores.

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