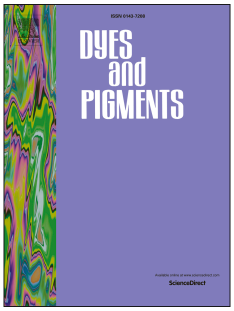

The Photochromic, Electrochemical and Third-order Nonlinear Optical Properties of the Novel Naphthopyran Derivatives

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PII: S0143-7208(20)31386-3

DOI: https://doi.org/10.1016/j.dyepig.2020.108689

Reference: DYPI 108689

To appear in: *Dyes and Pigments*

Received Date: 15 April 2020

Revised Date: 19 June 2020

Accepted Date: 3 July 2020

Please cite this article as: Zhao P, Gao H, Wang D, Yang Z, Cao H, He W, The Photochromic, Electrochemical and Third-order Nonlinear Optical Properties of the Novel Naphthopyran Derivatives, *Dyes and Pigments*, https://doi.org/10.1016/j.dyepig.2020.108689.

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Manuscript title: The Photochromic, Electrochemical and Third-order Nonlinear Optical Properties of the Novel Naphthopyran Derivatives

I have made substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work; AND I have drafted the work or revised it critically for important intellectual content; AND I have approved the final version to be published; AND I agree to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

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11th May, 2020

The Photochromic, Electrochemical and Third-order Nonlinear Optical Properties of the Novel Naphthopyran Derivatives

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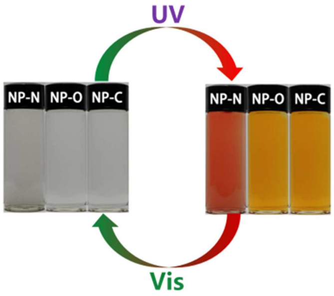

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A series of novel highly efficient photochromic naphthopyran dyes were synthesized and the photochromic behavior, electrochemical and third-order nonlinear optical properties of naphthopyran derivatives were fully investigated.

The Photochromic, Electrochemical and Third-order Nonlinear Optical Properties of the Novel Naphthopyran Derivatives

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Abstract

A series of novel naphthopyran derivatives featuring nonplanar and spiro-conjugation structure have been successfully synthesized and characterized. In this paper, we investigated the effects of the electron donating ability and volume of substituents on the photochromic and third-order nonlinear properties of novel naphthopyran derivatives. The UV-Vis absorption spectroscopy was used to analyse the photophysical and photochromic properties. Under the dual role of electron-donating group and bulky substituent group, maximum absorption peaks (λ_{max}) of the closed form and the open-form of the naphthopyran derivatives were both red shifted, and all molecules showed relatively good photochromic properties and fatigue resistance. The electrochemical properties have been investigated by the cyclic voltammetry (CV) measurement, the band gap of NP-C, NP-O and NP-N narrowed in sequence, and the level of HOMO decreased in turn. The third-order nonlinear optical (NLO) properties of the compounds were studied by the Z-scan techniques at 532 nm, which indicated that all molecules showed the reverse saturable absorption (RSA) behavior and the optical susceptibility $\chi^{(3)}$ reached 10^{-14}. These interesting findings provide a new insight on the practical application of naphthopyran molecules and the design of the NLO materials.

Key words: Naphthopyran, Photochromic properties, Third-order NLO properties, Electron donating ability

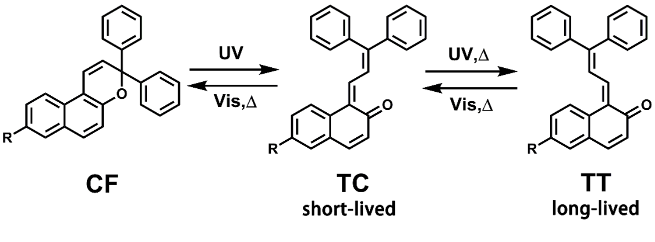
1. Introduction

Photochromism of chromenes was first reported by Becker and Michl in 1966[1]. Then the photochromic materials have attracted widespread research interest because of the physical and chemical properties could be changed by light irradiation, Among the classes of organic photochromic materials, azobenzenes and diarylethenes, spiropyrans and naphthopyran have received the most attention because of their excellent performance and broad utility. The photochromic materials have been used in many fields, such as optical switches[2-5, 35], photochromic lenses[6, 7], photochromic fibers and dyes[8-10], optical storage[11-13, 33] and molecule imaging[14-16], optical actuators[33]. Naphthopyrans as an important class of photochromic molecules which exhibit a reversible color change when exposed to UV light and are well known for the commercial application in the ophthalmic lens industry[17].

The exposure of the closed form (CF) of naphthopyrans to UV light or sunlight caused the opening of the C(sp3)-O bond of the pyran ring, that generates two isomers, the transoid-cis (TC) and transoid-trans (TT) forms. As shown in **Scheme 1**, The TC form is converted to the TT form by the rotation of the C═C bonds[18]. The TC form thermally returns to CF in a few seconds/minutes, whereas the thermal reversion of TT to CF is much slower (minutes/hour) because TT is thermostable and the relatively large activation energy isomerization barrier to TC must be overcome[6, 19]. Thus, although the coloration is very fast, the decolorization process is generally slower with an initial rapid discoloration and then a slower decolorization step, resulting in a residual color that lasts for a few minutes/hours.

The naphthopyrans with large optical density and fast return to the uncoloured closed form is a key requirement for their industrial application[20]. The slow thermal reversion of TT to CF and the residual colour of the TT form are considered to be one of the key issues that photochromic lenses and optical switches applications need to solve[6, 7, 18, 21]. One way to overcome the problem of the residual colour and avoid the formation of the TT isomer is to prevent the C═C isomerization of the short-lived TC isomer to the more stable TT isomer. Sousa reported that the formation of the TT form can be suppressed by incorporating an alkyl bridge between the pyran ring and the naphthalenic ring[20, 22, 23]. Yuki Inagaki found that the amount of the undesirable long-lived colored TT form could be reduced by introducing an alkoxy group at the 1-position of 8H-pyranoquinazolines. The alkoxy group effectively reduced the formation of the TT form due to C-H···O intramolecular hydrogen bonding in the TC form[6]. Céu M. Sousa synthesized a polycyclic photochromic fused-naphthopyran which could produce a single colored photoisomer under UV irradiation, and in the dark, the single colored photoisomer returned to the uncolored much faster than the parent unfused naphthopyran.[31] Stuart Aiken reported a series of bi-naphthopyrans, recorded the absorption spectra at lower temperature, bi-naphthopyrans showed an appreciable shoulder on the main absorption band accompanied by a change in colour. [32]

In this paper, we synthesized a series of novel highly efficient photochromic naphthopyran derivatives with different substituents, in order to study the effects of the volume of substituents and the electron donating ability of substituents on the photochromism, electrochemistry and third-order nonlinear optical properties of naphthopyran derivatives. Especially the third-order nonlinear optical properties of naphthopyrans, because in our previous work, we studied the third-order nonlinear properties of spiropyrans. Hong Zhao designed and synthesize two new photochromic cyclometalated (N^C^N)



Scheme 1 Photochromic reactions of naphthopyran

platinum(II) complexes, and the efficient photochromism allowed a significant NLO photomodulation, both in solution and in thin films[34]. we hope to explore this non-planar naphthopyrans with spiro conjugated whether the molecule has good third-order nonlinear performance. The volume of substituents and the electron donating ability of substituents on photochromism, electrochemistry and third-order nonlinear optical properties of naphthalpyran derivatives were fully studied in this paper.

2. Experimental

All the reagents were purchased as reagent grade from commercial sources and used without further purification. ^{1}H NMR spectra were measured on a BRAKER AVANCE III HD NMR spectrometer (500 MHz) at 20 °C. Chemical shifts were reported in ppm downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. FT-IR spectroscopy was recorded on a Perkin Elmer LR-64912C Fourier transform infrared spectrometer. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. Elemental analyses were performed at the Institute of Chemistry Chinese Academy of Sciences, with a Flash EA 1112 instrument. The UV/Vis spectra were recorded in a quartz cuvette on a JASCOV-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using glassy carbon working electrodes of 2 mm diameter, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI 660C instrument in dichloromethane/Bu_4NPF_6 at room temperature. All potentials were referenced to the ferrocenium/ferrocene (Fc/Fc^+) couple used as an internal standard. The NLO properties response measured by means of the Z-scan technique, employing 15 ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser, the intensity of the laser was 1 uj. The linearly polarized laser beam was focused with a 300 mm focal length lens and the sample was moved across the focus by means of a computer controlled micrometric translation stage. All the samples were studied from a 10^{-4} mol/L solution in dichloromethane, the thickness of the colorimetric dish was 1 mm. In addition, the NLO property of pure dichloromethane was also measured at the same conditions to clarify the solvent contribtion.

The synthetic routes and molecular structures are shown in **Scheme 2**.

Synthesis of 3,3-Diphenyl-8-[2-(trimethylsilyl)ethynyl]-3H-naphtho [2,1-b]pyran (2)

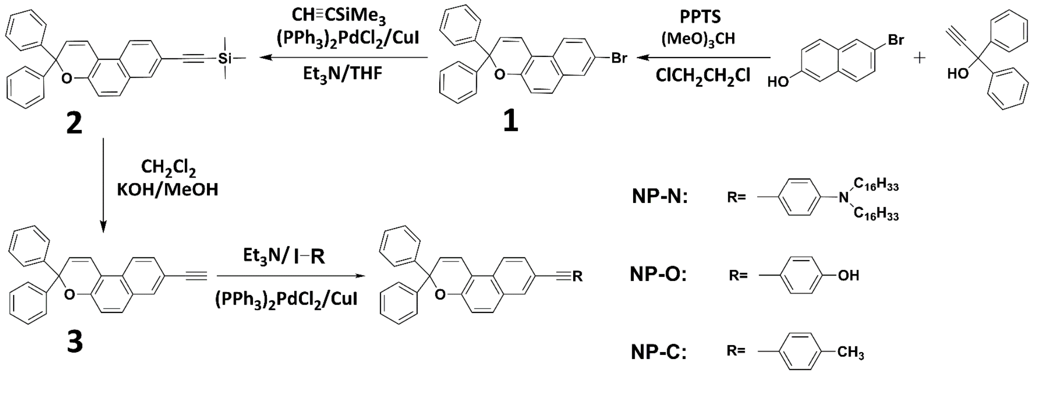
2 was prepared according to literature procedures[24]. **1** (1652 mg, 4.00 mmol) and ethynyltrimethylsilane (784 mg, 8.00 mmol) were added in the solvent of triethylamine (70 mL). After the mixture degassed under Ar. for 40 min, catalytic agents $Pd(PPh_3)_2Cl_2$ (563 mg, 0.80 mmol) and CuI (8.2 mg, 0.042 mmol, 3 mol%) were then added. The reaction mixture was stirred for 24h at 70 °C under Ar. atmosphere. After the evaporation of the solvent, the crude mixture was purified by silica gel column chromatography to give **2** as a white solid (1.38 g, 80%). R_f (dichloromethane: petroleum ether = 1:2): 0.45. ^{1}H NMR (500 MHz, Chloroform-d): δ 7.91-7.85 (m, 2H), 7.61 (d, J = 9.0 Hz, 1H), 7.55-7.48 (m, 5H), 7.38-7.32 (m, 4H), 7.30-7.26 (m, 3H), 7.24-7.21 (m, 1H), 6.29 (d, J = 10.0 Hz, 1H), 0.32 (s, 9H) ppm. The reaction phenomenon and chemical shifts of the resulting product are consistent with previous literature. **1** was also prepared according to literature procedures[25].

Synthesis of 8-Ethynyl-3,3-diphenyl-3H-naphtho[2,1-b] pyran (3)

3 was synthesized according to the previous literature[24]. To a stirred solution of 2 (1385 mg, 3.22 mmol) in CH_2Cl_2 (25 mL), A solution of KOH (540 mg, 9.66 mmol) in MeOH (17 mL) was added dropwise. And then stirred for 3 h at room temperature in the dark. The solvent was evaporated and the crude mixture was purified by silica gel column chromatography to give 3 as a white solid (1029mg, 89%), R_f (dichloromethane: petroleum ether = 2:3): 0.50. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.91-7.85 (m, 2H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.49-7.45 (m, 4H), 7.38-7.32 (m, 4H), 7.28 (d, *J* = 3.0 Hz, 2H), 7.25 (d, *J* = 1.0 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 6.29 (d, *J* = 10.0 Hz, 1H), 3.10 (s, 1H)ppm. The appearance and chemical shifts of the resulting product were consistent with previous literature[24].

Synthesis of 4-((3,3-diphenyl-3H-benzo[f]chromen-8-yl)ethynyl)-N, N-dihexadecylaniline (NP-N)

3 (790 mg, 2.21 mmol) and N,N-Dihexadecyl-4-iodoaniline (1472 mg, 2.21 mmol) were added in Et_3N (20 mL). After the



Scheme 2 Chemical structures and synthetic routes of **NP-N**, **NP-O**, **NP-C**.

mixture degassed under Ar for 40 min, catalytic agents $Pd(PPh_3)_2Cl_2$ (110 mg, 0.16 mmol) and CuI (31 mg, 0.16 mmol) were added successively in and stirred overnight under Ar at 90 °C. After cooling to room temperature, and the Et_3N was evaporated, the residue was purified by silica gel column chromatography to give **NP-N** as a light-yellow solid (1.506 g, 76%). R_f (PE:DCM = 3:2): 0.75; ^1H NMR (500 MHz, Chloroform-d): δ 7.87-7.81 (m, 2H), 7.57 (d, J = 8.5 Hz, 1H), 7.52 (dd, J = 8.9, 1.5 Hz, 1H), 7.49-7.44 (m, 4H), 7.38 (d, J = 9.0 Hz, 2H), 7.30 (t, J = 7.5 Hz, 4H), 7.24-7.22 (m, 2H), 7.22-7.19 (m, 1H), 7.17 (d, J = 9.0 Hz, 1H), 6.56 (d, J = 9.0 Hz, 2H), 6.24 (d, J = 10.0 Hz, 1H), 3.30-3.19 (m, 4H), 1.56 (s, 4H), 1.28 (d, J = 21.5 Hz, 52H), 0.87 (t, J = 7.0 Hz, 6H)ppm; FT-IR (KBr, cm^{-1}) : *v* = 3060, 2923, 2852, 2200, 1604, 1519, 1465, 1371, 1266, 1245, 1219, 1184, 1089, 1007, 812, 755, 730, 698; MALDI-TOF-MS (dithranol): m/z: calcd for $C_{65}H_{87}NO$: 897.7 g mol^{-1}, found: 896.5 g mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{65}H_{87}NO$ (897.7): C 86.90, H 9.76, N 1.56, O 1.78; found: C 86.92, H 9.74, N 1.56, O 1.78.

Synthesis of 4-((3,3-diphenyl-3H-benzo[f]chromen-8-yl)ethynyl) phenol (NP-O)

3 (345 mg, 0.96 mmol) and 4-iodophenol (212 mg, 0.96 mmol) were added in the mixed solvent of triethylamine (16 mL). After the mixture degassed under Ar for 40 min, catalytic agents $Pd(PPh_3)_2Cl_2$ (50 mg, 0. 07 mmol) and CuI (14 mg, 0.07 mmol) were added successively in and stirred overnight under Ar at 90 °C. After cooling to r. t. and the solvent was evaporated, the residue was purified by silica gel column chromatography to give **NP-O** as a white powder with a little purple (317 mg, 73%). R_f (PE:EAC = 3:1): 0.40; ^1H NMR (500 MHz, DMSO-d_6): δ 9.93 (s, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.05-7.99 (m, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.55 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 5H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 5H), 7.27 (t, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 10.0 Hz, 1H)ppm; FT-IR (KBr, cm^{-1}): *v* = 3386, 3060, 2955, 2925, 2853, 2204, 1893, 1633, 1605, 1582, 1512, 1465, 1447, 1379, 1265, 1245, 1220, 1168, 1091, 1054, 1006, 944, 891, 833, 761, 733, 699, 639, 582, 534; MALDI-TOF-MS (dithranol): m/z: calcd for $C_{33}H_{22}O_2$: 450.2 g·mol^{-1}, found: 450.5 g·mol^{-1} $[MH]^+$; Elemental analysis calcd (%) for $C_{65}H_{87}NO$ (450.2): C 87.98, H 4.92, O 7.10; found: C 87.97, H 4.92, O 7.11.

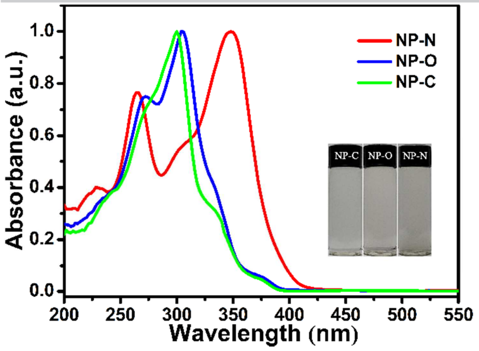


Fig. 1 UV-Vis absorption spectra and images of solution of the products **NP-N**, **NP-O** and **NP-C** in THF before UV irradiation.

Synthesis of 3,3-diphenyl-8-(p-tolylethynyl)-3H-benzo[f] chromene (NP-C)

3 (358 mg, 1.00 mmol) and 4-iodotoluene (218 mg, 1.00 mmol) were added in triethylamine (Et_3N/THF=1:1, 12 mL), 20 mL). After the mixture degassed under Ar for 40 min, catalytic agents $Pd(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol) and CuI (14 mg, 0.07 mmol) were added successively in and stirred overnight under Ar at 90 °C. After cooling to r. t. and the solvent was

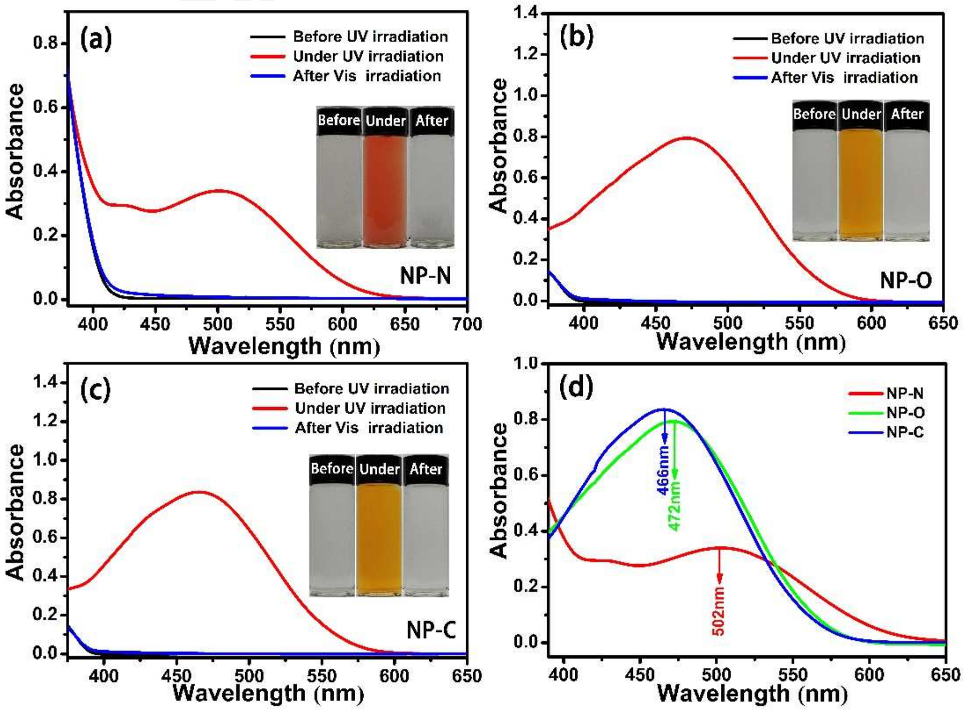


Fig. 2 The UV-Vis absorption spectra and the images of the solution of **(a) NP-N**, **(b) NP-O** and **(c) NP-N** in THF ($5x10^{-5}$ M) before UV irradiation, under UV irradiation (365nm, $100mW/cm^2$) and after visible light irradiation. **(d)** The UV-Vis absorption spectra of the three molecules in THF ($5x10^{-5}$ M) under UV irradiation.

evaporated, the residue was purified by silica gel column chromatography to give **NP-C** as a white solid (320 mg, 71%). R_f (PE:DCM = 2:1): 0.60; ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.53-7.47 (m, 5H), 7.46 (s, 1H), 7.34 (t, *J* = 7.5 Hz, 4H), 7.31-7.26 (m, 3H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.29 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H)ppm; FT-IR (KBr, cm^{-1}) : *ν* = 3059, 3028, 2920, 2851, 1900, 1629, 1580, 1511, 1492, 1465, 1447, 1381, 1353, 1266, 1246, 1217, 1183, 1158, 1084, 1054, 1006, 954, 889, 812, 757, 735, 699, 638, 523; MALDI-TOF-MS (dithranol): m/z: calcd for $C_{34}H_{24}O$: 448.2 g·mol^{-1}, found: 447.5 g·mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{34}H_{24}O$ (448.2): C 91.04, H 5.39, O 3.57; found: C 91.05, H 5.38, O 3.57.

3. Results and discussion

3.1 Photochromic behavior

Fig. 1 showed the absorption spectra and the images of the solution of molecules in THF. By comparing the absorption spectra of **NP-N**, **NP-O** and **NP-C**, it was found that the maximum absorption peaks (λ_{max}) of the closed-loop naphthopyran derivative shifted from **NP-C** (300 nm) to **NP-O** (304 nm) and **NP-N** (348 nm). Compared with **NP-C,** the absorption tails of the closed form of the **NP-N** showed a bathochromic shift of about 30 nm, because of the enhancement of the electron donating ability of the substituents which could conduce to the compounds becoming a more powerful and complicated intramolecular charge-transfer (ICT). As shown in the UV−Vis absorption spectra of the closed form of **NP-N**, the introduction of an amine group on the 3-position induced an intense absorption band in the region of 250-400 nm.

After stable ultraviolet irradiation (365 nm, 100 mW/cm^2), the solutions of **NP-N**, **NP-O** and **NP-C** in THF appeared photochromism, the naphthopyran derivatives changed from the closed-form to the open-form. As shown in **Fig. 2(a)**, **(b)** and **(c)**, the color of the THF solution of **NP-N** in THF changed from colorless to red, and that of the **NP-O** and **NP-C** changed from colorless to orange. By comparing the UV-Vis absorption spectra of the solutions before UV irradiation, under UV irradiation and after visible light irradiation, it was found that all three molecules could return to their original state after visible light irradiation, The THF solutions of these compounds actually showed bright and deep color changes before and after UV irradiation (**Movie S1**).

The open-form of the novel naphthopyran derivatives showed an intense absorption band in the region of 400-600 nm, the maximum absorption peaks (λ_{max}) of NP-C, NP-O and NP-N are 466 nm, 472 nm and 502 nm, respectively. All molecules behaved relatively good photochromic properties. As shown in **Fig. 2 (d)**, by comparing the UV-Vis absorption spectra of the open-form of the 3H-naphthopyran derivatives, it was found that the maximum absorption peaks (λmax) of the open-form of molecules bathochromically shifted from **NP-C** (466 nm) to **NP-O** (472 nm), and **NP-N** (502 nm), which could be reflected by the photography of products in **Fig. 2 (a)** , **(d)** and **(c)**, the color of the solutions had hanged from orange to red, because the enhancement of the electron donating ability of substituents which could conduce to the compounds becoming a more powerful and complicated ICT systems. The electron donating ability of alkylamine group was obviously stronger than that of hydroxyl group and methyl group, so **NP-N** showed a more obvious blue shift. With the enhancement of the electron donating ability of substituents, the absorbance of **NP-C**, **NP-O** and **NP-N** decreased in turn, the decrease in absorbance of **NP-N** was more obvious, the stronger the electron donating ability of substituents, the more difficult it is to transform from closed-form to open-form, because the steric repulsion of the bulky substitutes, it was more difficult for **NP-N** to switch from closed-form to open-form.

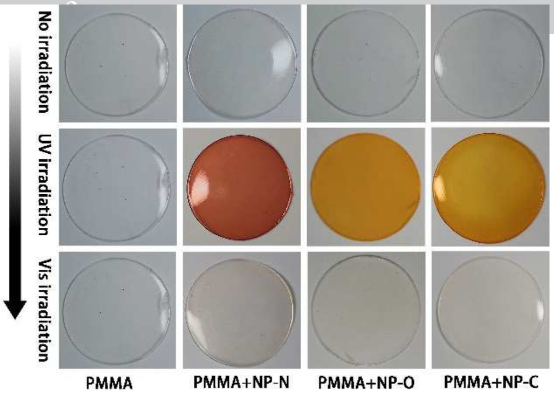


Fig. 3 The images of the films of PMMA doped with **NP-N**, **NP-O** and **NP-C** (3 wt%) before UV irradiation, under UV irradiation (365nm, 100mW/cm^2, 5min) and after visible light irradiation

Furthermore, the photochromic behavior of the polymer-doped films were investigated. The films of PMMA doped with the three novel molecules (3 wt%) were prepared by mold method, as shown in **Fig. 3**, the films exhibitd the same color change as in the solvent, the three novel molecules also behaved obvious photochromism, these molecules maybe be used in photochromic lenses, dyes and nail equipment.

3.2 Reversibility and fatigue resistance

Reversibility and stability are important factors for the application of naphthopyran. As portrayed in **Fig. 4 (a)**, **(b)** and **(c)**, The molecules were irradiated by ultraviolet light and visible light. After ten cycles of irradiation, the decreases of absorbance of the three molecules were almost negligible, so the **NP-N**, **NP-O** and **NP-C** performed relatively good fatigue resistance. The thermal fading curves after ceasing the UV irradiation were showed in **Fig. 4 (d)**, the thermal fading curves after ceasing the light irradiation consisted of an initial fast decay attributable to the thermal isomerization of the TC form to the CF and a following slow decay of the long-lived TT form. On the thermal fading curves, the absorbance of **NP-C**, **NP-O** and **NP-N** decreased in turn. As shown in **Fig. 4**, in the initial rapid decay phase, it could be inferred that the decay rates of **NP-O**, **NP-N** and

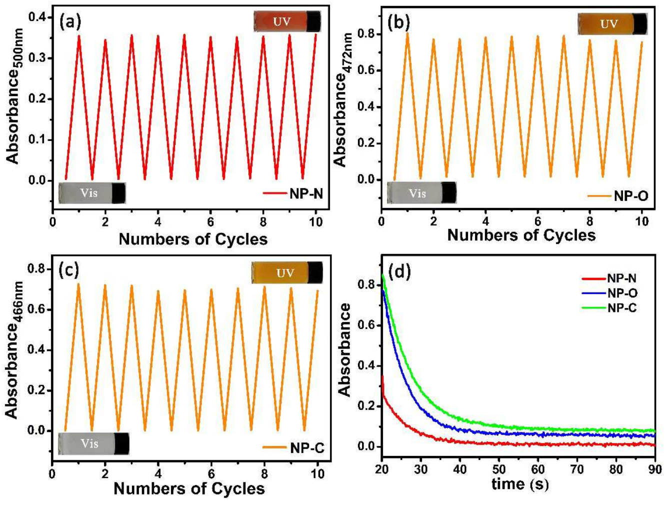


Fig. 4 Reversibility of **(a)** **NP-N**, **(b)** **NP-O** and **(c)** **NP-C** in THF solution upon UV-Vis cycles. **(d)** Time variation of the change in absorbance at λ_{max} of **NP-N**, **NP-O** and **NP-C** after continuous UV irradiation (365 nm, 100 mW/cm^2, 20 s) at 298 K.

NP-C decreased in sequentially, the reason for the phenomenon was strongly related to the half-life of the colored isomers. The half-lives ($\tau_{1/2}$) of the TC form were calculated from the fitting curves of the time variation of the absorbance using the double exponential function below[6, 8]:

$$f(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \qquad (1)$$

Where k_1 is the rate constant for the thermal back reaction of the TC form and k_2 is that of the TT form, A_1 and A_2 are the initial absorbances of the two species, the formation ratios of the TT form are defined as $A_2/(A_1+A_2)$ by assuming the molar extinction coefficients of the TC and TT forms are same.

Table 1 The λ_{max} for the colored form at the photostationary state, Half-Lives ($\tau_{1/2}$=ln(2)/K_1) of the TC forms, and formation ratios of the TT form in THF (5 × 10^{-5} M) at 298 K.

compound	λ_{max}/nm	A_1	A_2	k_1	k_2	$\tau_{1/2(TC)}$/ s	TT form /%
NP-N	502	0.257	0.015	0.166	0.002	4.17	5
NP-O	472	0.731	0.068	0.177	0.003	3.91	9
NP-C	466	0.766	0.085	0.137	0.004	5.06	10

These results were reported in **Table 1**. The $\boldsymbol{k_1}$ of **NP-O, NP-N** and **NP-C** decreased in sequentially, so in the initial rapid decay phase, the decay rates of **NP-O**, **NP-N** and **NP-C** decreased in turn. Formation ratio of the TT form of **NP-C, NP-O** and **NP-N** were 10%, 9% and 5%, respectively. The formation ratio **NP-C** is slightly higher than that of **NP-O**, but significantly higher than that of **NP-N**, because the volume of alkylamine group was larger than that of hydroxyl group and had a stronger electron donating ability electron donating ability, as shown on the thermal fading curves, the absorbance of NP-C, NP-O and NP-N reduced in turn. The half-life ($\tau_{1/2}$) of the TC form of **NP-C**, **NP-N** and **NP-O** were shortened in turn, **NP-O** had a longer half-life than **NP-C,** because of the electron donating ability of the hydroxyl group was greater than that of the methyl group. However, the half-life ($\tau_{1/2}$) of the TC form of **NP-N** was longer than that of **NP-O**, because of the double effect of the strong electron-donating ability and the steric repulsion of the bulky substitutes.

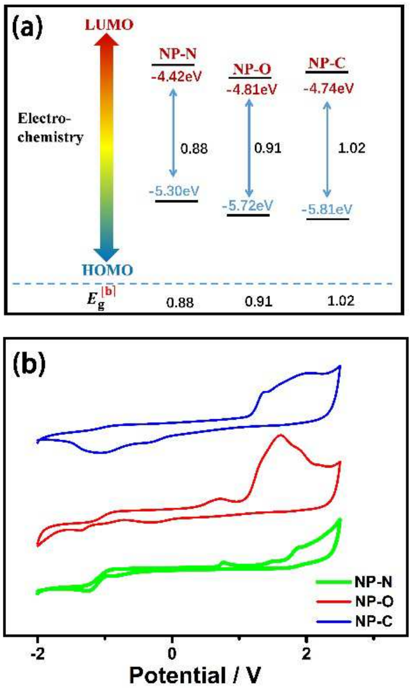


Fig. 5 (a) The diagrammatic sketch of HOMO and LUMO energy levels. **(b)** The cyclic voltammogram of the closed form of **NP-N**, **NP-O** and **NP-C** in dichloromethane.

3.3 Electrochemical properties

In order to investigate the electrochemical properties of the closed-form of the novel molecules, the cyclic voltammetry (CV) were performed in dichloromethane solution containing 0.1 M Tetrabuty-lammonium hexafluorophosphate (Bu_4NPF_6) as the supporting. Electrolyte (a standard ferrocene/ferrocenium (Fc/Fc^+) redox system as the internal standard) at room temperature. The HOMO and the LUMO energy levels of the molecules could be calculated by the following equations.

$$\mathrm{HOMO} = -\mathrm{e}[\mathrm{E}_{\mathrm{onset}}^{\mathrm{ox}} - E_{\mathrm{Fc}} + 4.8\mathrm{V}] \qquad (2)$$

$$\mathrm{LUMO} = -\mathrm{e}[\mathrm{E}_{\mathrm{onset}}^{\mathrm{red}} - E_{\mathrm{Fc}} + 4.8\mathrm{V}] \qquad (3)$$

Table 2 The electrochemical properties of the closed form of all products.

Sample	E_{onset}^{ox} [a] [V]	E_{onset}^{red} [a] [V]	HOMO [eV]	LUMO [eV]	E_g [b]
NP-N	0.68	-0.20	-5.30	-4.42	0.88
NP-O	1.10	0.19	-5.72	-4.81	0.91
NP-C	1.19	0.12	-5.81	-4.74	1.07

[a] Onset oxidation and reduction potentials determined from cyclic voltammograms in CH_2Cl_2/Bu4NPF6. [b] Band gaps estimated from the onset potentials.

Where E_{Fc} is the measured oxidation-reduction potential of Fc (vs Ag/AgCl) is 0.18 V. The experimental results were depicted in **Table 2** and **Fig. 5**. **Table 2** showed that the onset oxidation potential of the novel 3H-naphthopyran derivatives decreased with the enhancement of electron donating ability of substituents.

Fig. 5(b) visually reflect the same phenomenon. By comparing the band gaps and the HOMO levels of the closed form of **NP-C**, **NP-O** and **NP-N** in the diagrammatic sketch **(Fig. 5(a))**, it was clearly found that the HOMO energy level of the molecules increased and the band gap narrowed with the electron-donating ability of the substituent increased, because the electron-donating ability of substituents promoted the intramolecular electron transfer.

3.4 Third-order nonlinear optical properties

The Z-scan technique was performed to study the third-order nonlinear optical properties of the molecules, the nonlinear absorption coefficient (β) was measured by means of open-aperture Z-scan techniques, the nonlinear index (n_2) was measured by the closed-aperture Z-scan techniques in dichloromethane. However, the third-order nonlinear refractive properties of these novel molecules were so poor that can’t be discerned. Therefore, the third-order nonlinear optical susceptibility $\chi^{(3)}$ only involved the nonlinear absorption coefficient (β) in this paper. The normalized open aperture Z-scan traces of the molecules were shown in **Fig. 6 (a)**, **(b)** and **(c),** a trough of transmittance could be seen near the focus, as the sample moved toward the focus, the transmittance decreased and reached a minimum at the focus. All molecules exhibited the reverse saturable absorption (RSA) behavior, which could be used for optical limiting of laser protection and indicating that the nonlinear absorption coefficient is positive[26, 27].

The parameters of third-order nonlinear optical (NLO) property were summarized in **Table 3**, the third-order nonlinear

Fig. 6 The red lines are the theoretical fitting curves and the blue scatter dots are the Z-scan experimental data: the normalized open aperture Z-scan traces measured for **(a) NP-N**, **(b) NP-O**, **(c) NP-C**. **(d)** The comparison of the normalized open aperture Z-scan traces.

absorption coefficient (β) was calculated by the following equation[28, 29]:

$$\boldsymbol{\beta(m/W)=\frac{2\sqrt{2}[1-T(Z=0)]}{I_0L_{eff}}} \qquad (4)$$

Where, $\boldsymbol{T}$ is the normalized transmittance at the focus (Z=0), $\boldsymbol{I_0}$ is the intensity of the laser beam at the focal point. The effective thickness of the sample can be estimated as $\boldsymbol{L_{eff}=[1-\exp(-\alpha L)]/\alpha}$, $\boldsymbol{L}$ is the thickness of the sample and α is the linear absorption coefficient of the sample at the laser excitation wavelength.

Com- pounds	β ($\times10^{-13}$ m/W)	Im$\chi^{(3)}$ ($\times10^{-14}$ esu)	$\chi^{(3)}$ ($\times10^{-14}$ esu)
NP-N	11.80	2.55	2.55
NP-O	4.50	0.97	0.97
NP-C	4.00	0.86	0.86

The value of the third-order nonlinear optical susceptibility only includes the real parts in this paper, which can be calculated from the third-order nonlinear absorption coefficient (β) by the following equation[27]:

$$\mathbf{Re}\chi^{(3)}(\mathbf{esu})=\boldsymbol{\frac{n_0{}^2c^2\beta}{240\pi^2\omega}} \qquad (5)$$

Where, n_0 is the linear refractive index of solution, c is the speed of light and $\omega=\frac{2\pi}{\lambda}$ is the fundamental frequency in cycles s^{-1}. The value of the third-order nonlinear optical susceptibility $\chi^{(3)}$ could be calculated through the equation[28]:

$$\boldsymbol{\chi^{(3)}=\sqrt{|\mathrm{Re}\chi^{(3)}|^2}} \qquad (6)$$

Table 3 Third-order nonlinear optical parameters of compounds.

As shown in Table 3, the third-order absorption coefficient β of the molecules is positive, which in agreement with the **Fig. 6** The third-order nonlinear absorption coefficient (β) and optical susceptibility $\chi^{(3)}$ both increased with the enhancement of the electron donating ability of the substituent which could be visually observed in **Fig. 6 (d)**. Usually, the strong electron donating and the conjugated structures are the key factors for enhancing NLO properties. The abilities of π-electron delocalization and intramolecular charge transfer are the foundation for enhancing NLO properties. Comparing to **NP-C**, **NP-O** had a strong electron donating group, so **NP-O** showed better third-order nonlinear optical properties than **NP-C**. Comparing to **NP-C** and **NP-O**, **NP-N** exhibited much better third-order nonlinear optical properties, because the substituent of **NP-N** had the stronger electron-donating ability than that of **NP-C** and **NP-O**, which could promote the intramolecular electron transfer and enhance third-order NLO properties.

4. Conclusion

In summary, a series of novel highly efficient photochromic naphthopyran derivatives with different electron donating ability substituents were synthesized, and the effects of substituents on photochromic behavior, electrochemical and third-order nonlinear optical properties of naphthopyran derivatives have been studied in this paper. A very interesting phenomenon was found, with the enhancement of electron donating ability of substituents, the maximum absorption peaks (λ_{max}) and the absorption tails of the closed form and the open-form of the molecules both showed strong bathochromic shift, the absorbance at λ_{max} of the open-form decreased, the half-lives ($\tau_{1/2}$) of the compounds' TC form shorten and the formation ratios of the TT form increased, the HOMO energy level of the molecules decreased and the band gaps narrowed, the third-order nonlinear absorption coefficient (β) and optical susceptibility $\chi^{(3)}$ both increased. These findings provide a guidance for the design of naphthopyran molecules and are of great significance for the practical application of naphthopyran molecules.

Conflicts of interest

There are no conflicts to declare

Acknowledgments

This work was supported by the National Key Basic Research Program of China (2014CB931804), the National Natrual Science Foundation of China (Grant No. 51673023, 51773017, 61370048, 51333001), the State Key Laboratory for Advanced Metals and Materials (No. 2018Z-06), the Fundamental Research Funds for the Central Universities (Grant No. FRF-GF-17-B8).

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Highlights:

1. A series of novel naphthopyran derivatives with different substituents was synthesized.
2. The novel naphthopyran derivatives showed excellent photochromic behavior.
3. The photochromic behavior, electrochemical and third-order nonlinear optical properties of naphthopyran derivatives have been fully studied.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: