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Synthesis and photochromic properties of new naphthopyrans

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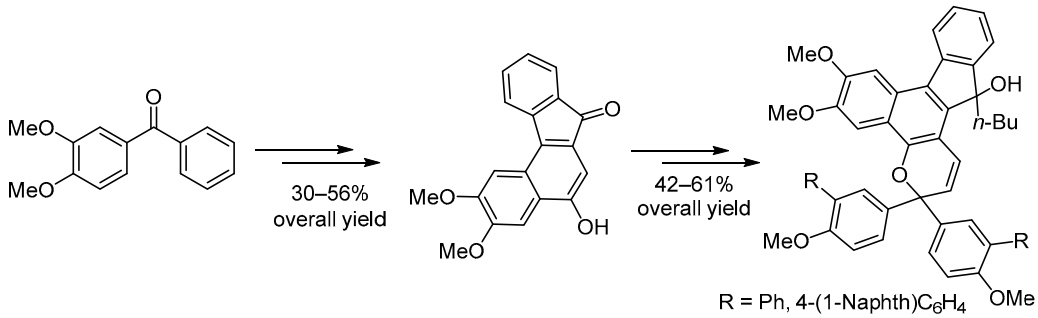


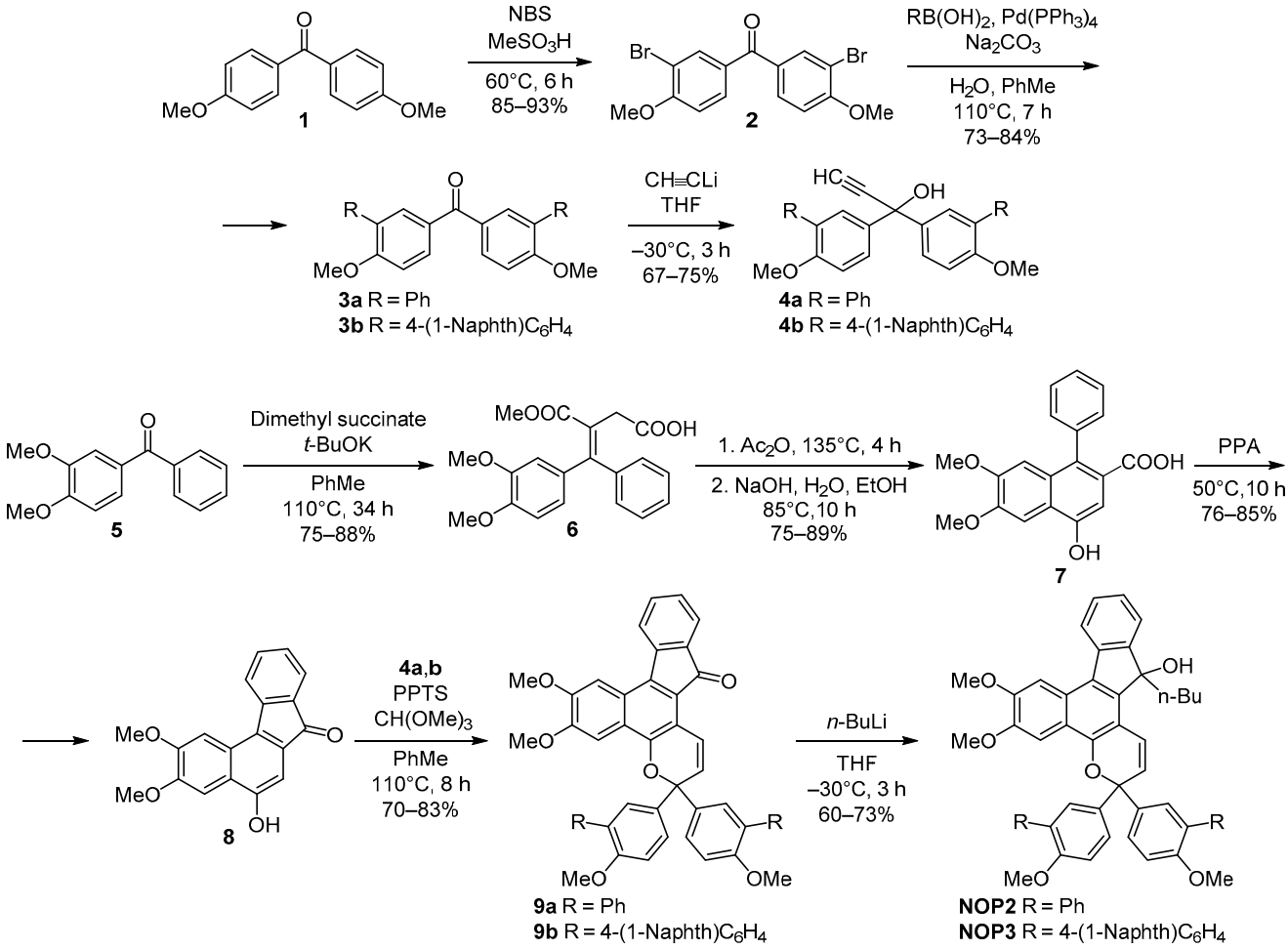
Two novel isomeric naphthopyrans substituted with phenyl (13-butyl-6,7-dimethoxy-3,3-bis(6-methoxybiphenyl-3-yl)-3,13-dihydrobenzo[*h*]indeno[2,1-*f*]chromen-13-ol) and 4-(naphthalen-1-yl)phenyl (13-butyl-6,7-dimethoxy-3,3-bis[6-methoxy-4'-(naphthalenyl)-biphenyl-3-yl]-3,13-dihydrobenzo[*h*]indeno[2,1-*f*]chromen-13-ol) moieties were synthesized. Their photochromism, electrochemical and fluorescent properties were investigated. They displayed faster color fading rate and larger fluorescence quantum yield than 13-butyl-6,7-dimethoxy-3,3-bis(4-methoxyphenyl)-3,13-dihydrobenzo[*h*]indeno[2,1-*f*]chromen-13-ol. Moreover, they showed excellent photochromic and fluorescent properties both in solution and in polymethylmethacrylate film. In addition, cyclic voltammetry tests showed that the aromatic substituents had a significant effect on the electrochemical behavior of the naphthopyran derivatives.

Keywords: naphthopyran, electrochemistry, fluorescence, photochromism, wavelength.

Photochromic materials find application in various photonic devices, such as erasable memory media, photo-optical switch components, and displays.[1,2] Among various photochromic systems, naphthopyran plays a great role because of the excellent photochromic response, good colorability, and rapid color fading rate.[3] UV light irradiation of the closed form of naphthopyran (NOP) promotes the cleavage of the C(sp^3)–O bond of the pyran ring to afford the *transoid-cis* (TC) form and *transoid-trans* (TT) form. The TC form thermally reverts to the NOP form in a few seconds/minutes, whereas the TT form reverts to the NOP form much slower (minutes/hours).[4] Although hundreds of naphthopyrans have been prepared over the past two decades, there are still problems with these molecules. Most of the coloration disappears rapidly in few seconds, but 10–20% slowly fades (minutes/hour) because of the formation of a more stable TT isomer.[5–9] In the dark it fades very slowly, and does not disappear completely.[10,11] The residual color of the TT form and the slow thermal back reaction of the TC form have been considered as one of the inconvenient problems to solve for the photo-switching applications. This can be solved by incorporating some alkyl or phenyl groups to the pyran or naphthalene ring of the naphthopyran ring system.[12] Recently, Liwen Song and coworkers explored new excellent fluorescent switching with naphthopyran as photochromic group;[13] they studied different *N*-substituted imide groups at the naphthopyran moiety, indicating that the photochromic properties can be affected by the different functional groups of the naphthopyran unit. It has been revealed that the aryl moieties and functional substituents imposed significant influence on its photochromic properties.

Based on the previous research, we introduced the methoxy, phenyl, and 4-(naphthalen-1-yl)phenyl substituents into naphthopyran ring system. The molecular structures and synthetic routes are shown in Scheme 1. Benzophenone derivative **2** was synthesized by bromination of compound **1**, while biphenylmethanones

Scheme 1. Synthesis of compounds **NOP2**,**3**



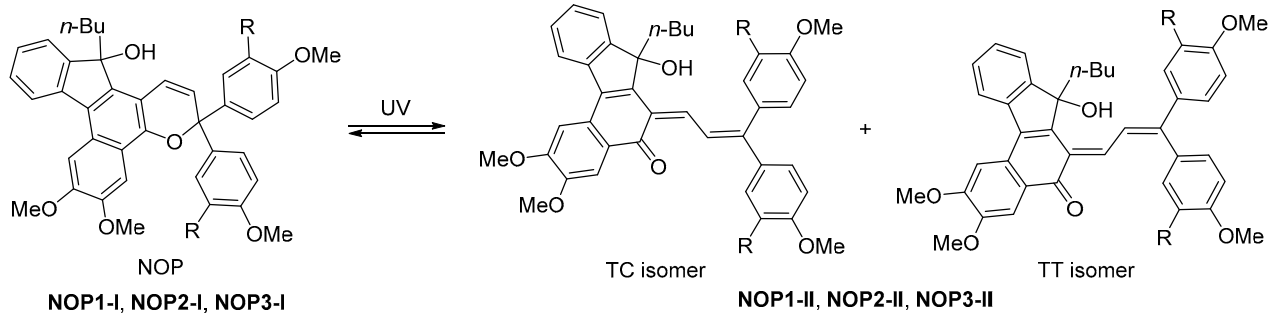
3a,**b** were synthesized using Suzuki reaction with phenylboronic acid and 4-(naphthalenyl)phenylboronic acid, respectively. The synthesis of alkynols **4a**,**b** was carried out by reaction of compounds **3a**,**b** with ethynyllithium at low temperature. (3,4-Dimethoxyphenyl)(phenyl)methanone (**5**) as a starting material was subjected to the Stobbe condensation to get compound **6**. Phenylbutenoic acid **6** underwent cyclodehydration by acetic anhydride and then was hydrolyzed by sodium hydroxide to give compound **7**, which in reaction with polyphosphoric acid (PPA) afforded fluorenone **8**. Compound **8** and two alkynols **4a**,**b** through Claisen condensation reaction in the presence of pyridinium *p*-toluenesulfonate (PPTS) gave chromenones **9a**,**b**. These reacted with *n*-butyllithium to give products **NOP2** and **NOP3**. They contain large conjugated moieties and excellent electron-donating units and were obtained with good yield. In order to better explain the effect of introducing conjugated benzene ring on the photochromic properties, we refer to a patent on the synthesis of naphthopyran (**NOP1**) without a benzene moiety on the pyran ring for comparison (see Supplementary information file, Scheme SI).[14] Compounds were characterized by ^{1}H and ^{13}C NMR spectra, IR spectra, and elemental analysis. To the best of our knowledge, this kind of naphthopyran photoswitching in solution and film has never been reported previously. The NMR spectra, IR data, and the synthetic route to compound **NOP1** are given in the Supplementary information file.

Under UV light irradiation, naphthopyrans **NOP1**–**NOP3** underwent an electrocyclic pyran ring opening with cleavage of the C(sp^3)–O bond and a subsequent structural reorganization allowing the photogenerated species to adopt more planar structures (open form) with greater conjugation, which is responsible for the increased absorption in the visible part of the spectrum. Their molecular structures are shown in Scheme 2.

Compound **NOP1-I** exhibited a small absorption peak at 350 nm, which arose from π–π* transition;[15] after 365 nm UV light irradiation, a new absorption band in the visible region around 550 nm appeared belonging to the open form **NOP1-II** (Fig. 1). The purple color of the solution could fade to colorless in dark within 7 min. After UV irradiation, it turned purple again. In a similar manner, the colorless solution of **NOP2-I** and **NOP3-I** turned blue (**NOP2-II**) and green (**NOP3-II**) by 365 nm UV irradiation (Fig. 2c).

In polymethylmethacrylate (PMMA) films, **NOP1**–**3** also showed similar photochromic activity (Fig. 1). The absorbance band of open form **NOP1**–**3** in PMMA film broaden at 410–660 nm, which was broader than in the solution. The red shift values of the closed-ring isomers

Scheme 2. Structural reorganization of compounds **NOP1-I–3-I** under UV light irradiation



NOP1 R = H, **NOP2** R = Ph, **NOP3** R = 4-(1-Naphth)C_6H_4

were consistent with those of reported for diarylethenes[16,17] and may be attributed to the polar effect of the polymer matrix in amorphous solid state. The absorbance bands of the film were broadened, because the movement of the molecules in solid medium is restricted rendering the speed of photochromic switching significantly slower.

The fluorescence was also investigated at room temperature (Fig. 2); the fluorescence quantum yields and optical properties of three compounds are summarized in Table 1. The emission wavelengths going from **NOP1** to **NOP3** were red-shifted because of the extended π-conjugation in the molecule. We calculated quantum yield values of naphthopyrans by reference to literature[18] using fluorescein as a standard (Φ_{std} 0.55, quinine sulfate, 1 μg/ml, H_2SO_4, 0.1 mol/l, see Supplementary information file). As shown in Table 1, the fluorescence quantum yields of **NOP2** and **NOP3** were higher than that of **NOP1** for both open- and closed-ring isomers. The possible explanation is that benzene ring could notably enhance the fluorescence quantum yield and influence the fluorescence emission intensity of naphthopyrans.

The colored forms TT and TC fade back to colorless form NOP. The process TC→NOP (k_1) is usually rapid, while TT→NOP (k_2) is slow. The thermal fading kinetics which is determined from the absorption–time dataset is analyzed to evaluate the photochromic fade rate using the following biexponential equation:[19]

$$y = A_1\exp(-t/k_1) + A_2\exp(-t/k_2) + y_0.$$

A_1 and A_2 are the contributions to the initial optical density, k_1 and k_2 are exponential decay rate constants of fast and slow components, respectively, and y_0 is the residual coloration.[20] Figure 2 shows $y - t$ decay and two-phase exponential decay curve for compound **NOP1**, obtained using the Origin software (OriginLab Co., Northampton, MA, USA). Convenient feature of the fading speed is the $T_{1/2}$ value,[21–23] which is the time required to reduce the optical density by half of the initial optical

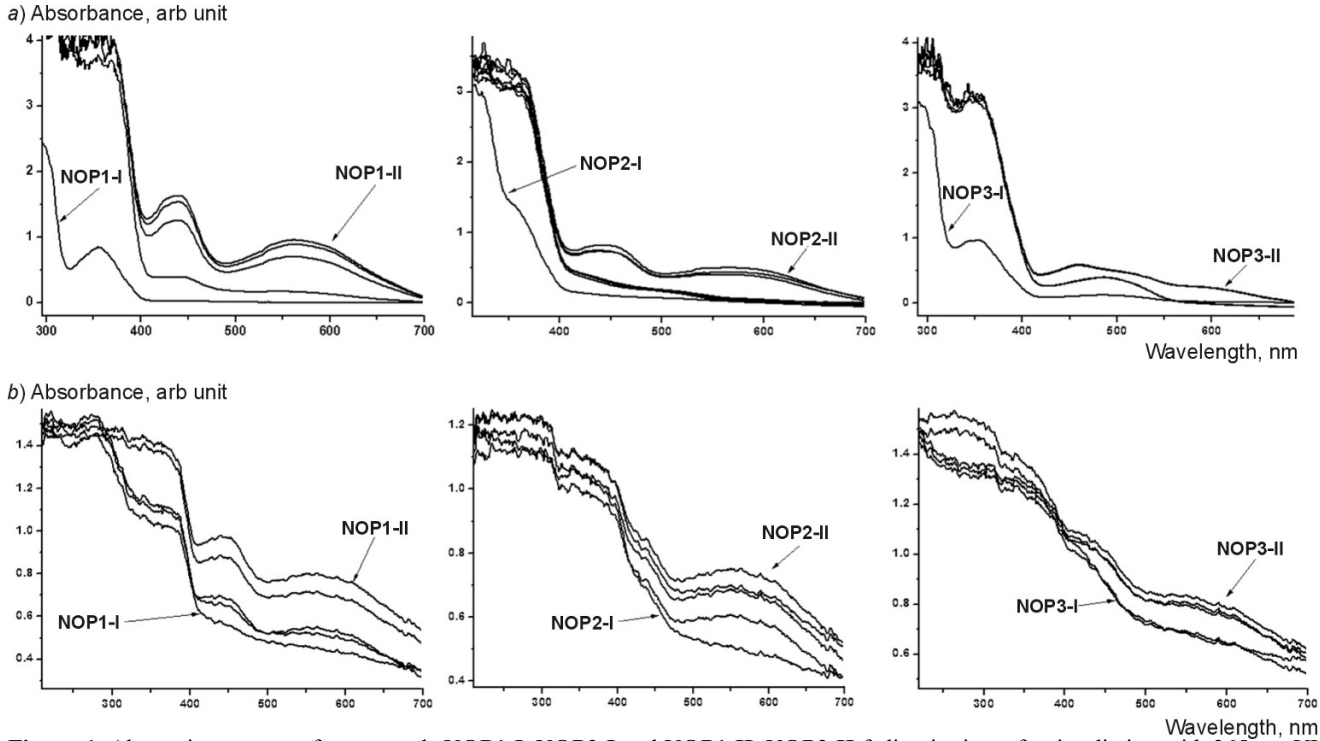


Figure 1. Absorption spectra of compounds **NOP1-I–NOP3-I** and **NOP1-II–NOP3-II** fading in time after irradiation with 365 nm UV light in *a*) CH_2Cl_2 solution (2×10^{-5} mol/l), 0–7 min, and *b*) PMMA film (13%, w/w), 0–13 min, at 293 K.

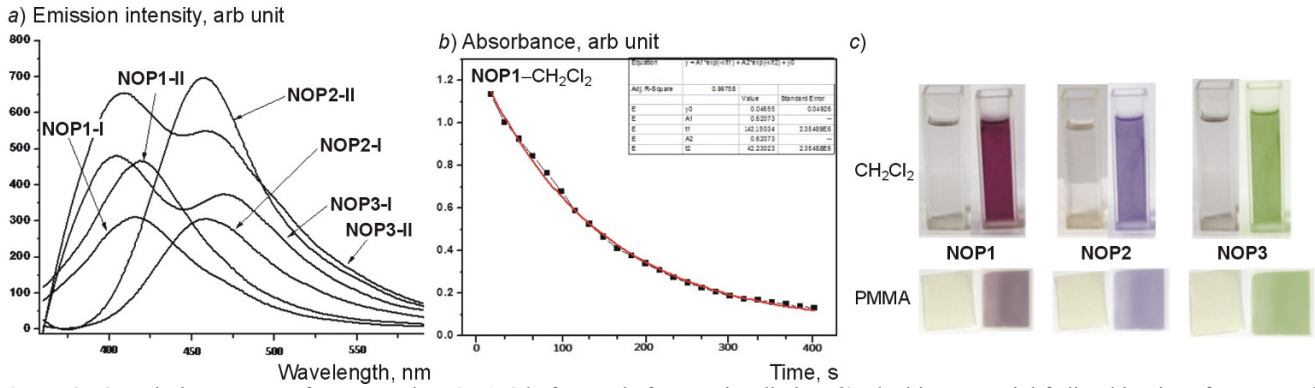


Figure 2. *a*) Emission spectra of compounds **NOP1**–**3** before and after UV irradiation, *b*) The biexponential fading kinetics of compound **NOP1** in CH_2Cl_2 at 352 nm, and *c*) the color change in CH_2Cl_2 (2×10^{-5} mol/l) and PMMA film (13%, w/w) at 293 K before (left) and after (right) irradiation with 365 nm UV light.

density of the colored form, and the smaller $T_{1/2}$, the faster is fading. That was reflected by the fitting curve which was successfully simulated with the above equation. As a result, the discoloration process followed a biexponential attenuation law, which included fast and slow components.[24,25]

As shown in Table 1, the fading rate constant of **NOP3** (k_1 617.48) was about six times larger as compared with the value of **NOP1** (k_1 142.18). The data of fading kinetics confirmed that the colored form of naphthopyran with a naphthyl group was more thermally stable than this without it. It had been demonstrated that donating group at the conjugative position of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran increased fading speed because of electronic effect.[26,27] As compared to **NOP1** ($T_{1/2}$ 187 s), the fading speed of **NOP3** ($T_{1/2}$ 100 s) was increased significantly under the same conditions. Similar results were obtained with **NOP2** ($T_{1/2}$ 103 s). It is worth noting that the fading speed is increased for compounds with the phenyl group attached to a longer chain. The results suggest that the fading speed of colored form is promoted by the electronic effect of the phenyl group and the length of the attached phenyl group chain.

We also tested the fatigue resistance of naphthopyran derivatives (Figure S1 in the Supplementary information file shows the trend of photochromic switching on-off 10 cycles of **NOP1**–**3** in CH_2Cl_2 solution and in PMMA film.) When the compounds were excited by UV light of 365 nm for 200 s and left in the dark for 5–30 min, the absorption intensity decreased to 83–94% of its original value. Absorption intensity of **NOP1** decreased to 94% of the **NOP1** original value and that of **NOP2** was decreased to 93.4% compared to the **NOP2** original value, showing that the tested compounds have good fatigue resistance.

Table 1. The UV absorption and fluorescence, biexponential decay values, and $T_{1/2}$ data of **NOP1**–**3** in CH_2Cl_2 ($2\cdot10^{-5}$ mol/l) and PMMA film (13%, w/w) at 293 K

Compound	λ_{max}^{abs}, nm		Φ	λ_{max}^{em}, nm	k_1		$T_{1/2}$	
	CH_2Cl_2	PMMA	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	PMMA	CH_2Cl_2	PMMA
NOP1-I	352*	300	0.43	408	142.18	23.98	187	503
NOP1-II	560	595	0.31	418				
NOP2-I	363*	356	0.52	455	424.68	66.92	103	499
NOP2-II	598	587	0.44	459				
NOP3-I	378*	312	0.57	477	617.48	120.33	100	492
NOP3-II	600	600	0.46	475				

* The fluorescence excitation wavelength for the respective compound.

The electrochemical properties of naphthopyran derivatives have attracted a great attention for potential application in molecular switches.[28–32] Figure 3 shows the CV curves of **NOP1**–**3** with the scanning rate of 50 mV/s. The onset potentials (E_{onset}) of oxidation and reduction for **NOP1-I** were initiated at +1.89 and –0.51 V, and **NOP1-II** at +1.86 and –0.48 V, respectively. According to the reported method,[33,34] the ionization potential (IP) and electron affinity (E_A) of **NOP1-I** were calculated to be –6.23 and –3.77 eV, and those of **NOP1-II** were –6.02 and –3.35 eV. Based on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level, the band gap E_g ($E_g = E_{LUMO} - E_{HOMO}$) of **NOP1-I** and **NOP1-II** can be determined as +2.46 and

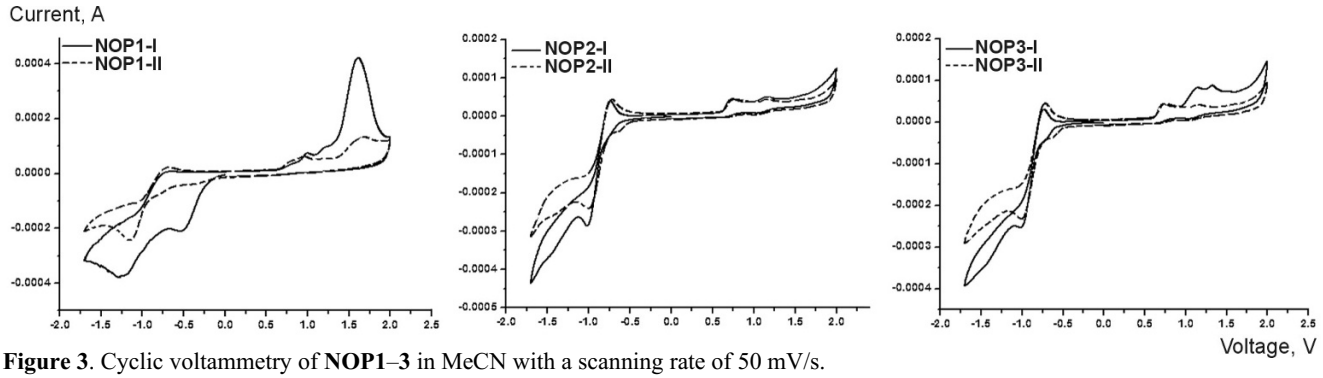


Figure 3. Cyclic voltammetry of **NOP1**–**3** in MeCN with a scanning rate of 50 mV/s.

Table 2. Electrochemical properties of naphthopyrans **NOP1**–**3**

Compound	Oxidation		Reduction		Band gap
	E_{onset}, V	IP, eV	E_{onset}, V	E_A, eV	E_g, eV
NOP1-I	1.89	–6.23	–0.51	–3.77	2.46
NOP1-II	1.86	–6.02	–0.48	–3.35	2.67
NOP2-I	1.92	–6.45	–0.52	–4.27	2.18
NOP2-II	1.90	–6.36	–0.43	–3.99	2.37
NOP3-I	1.87	–6.12	–0.64	–4.06	2.06
NOP3-II	1.86	–6.24	–0.65	–4.13	2.11

+2.67 eV. The corresponding values for **NOP1**–**3** are summarized in Table 2.

From the Table 2, it can be clearly seen that the electrochemical parameters of the compounds are remarkably dependent on the substituent effects. The oxidation process for the open-ring isomers **NOP1-II**–**3-II** occurs at lower potentials than the corresponding closed-ring isomers **NOP1-I**–**3-I**. This is because the longer conjugation length of the open-ring isomers generally leads to a less positive potential.[35] For the band gap of three compounds, the values of E_g of the open-ring isomers are higher than those of the closed-ring isomers. Among these compounds, the E_g of **NOP3-I** is the smallest, which implies that the charge transfer in **NOP3** is the fastest.[36] The results of electrochemical calculations generally correspond to the band gap which is determined from the UV-visible spectrum. These data indicate that the effect of the substituent on the electron-conjugated structure has an influence on the photochromic properties of naphthopyrans.

In conclusion, two naphthopyrans bearing conjugated substituents were synthesized using a (3,4-dimethoxyphenyl)-(phenyl)methanone as starting material. The experimental results indicate that that there is a correlation between electronic nature of substituents and fatigue, fading rate, and electrochemical behavior of naphthopyran photochromes. These findings may lead to fast light-responsive photochromic lenses, smart windows, and fast optical switching applications and molecular actuators.

Experimental

Fourier transform infrared spectra were obtained on a Nicolet NEXUS-470 FT-IR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 and 101 MHz, respectively) in DMSO-d_6 (compounds **2**, **7**, **8**) or $CDCl_3$ (compounds **3a**, **3b**, **4a**, **4b**, **6**, **9a**, **9b**, **NOP2**, **NOP3**) as solvents and TMS as internal standard. Elemental analysis was performed on a PerkinElmer 240 C elemental analyzer. UV-Vis absorption spectra were obtained on a Shimadzu UV-2550 UV-Vis spectrophotometer. Samples were irradiated with 365 nm, 20 mW·cm^{-2} UV light at a distance of 7 cm from the Nitecore CU6 UV lamp for 200 s. Fluorescence spectra were recorded by a Varian Cary Eclipse fluorescence spectrophotometer in films. Films were prepared using a Chemat Technology KW-4A spin coater. Melting points were obtained in open capillaries in H_2SO_4 bath and were not corrected. Cyclic voltammetry curves were measured by a CH Instruments 660C electrochemical analyzer. Typical electrolyte was tetrabutylammonium perchlorate (0.1 mol/l) in MeCN (20 ml), platinum electrode, Hg/Hg_2Cl_2 as the reference electrode. The working electrode preparation method: the naphthopyrans in CH_2Cl_2 ($2\cdot10^{-5}$ mol/l) solution were dropped on a polished glassy carbon electrode and dried in air. Open-ring isomers were obtained by irradiation of a coated glassy carbon electrode by UV light for testing.

The PMMA films were prepared by the following procedure: PMMA (2 g) and $CHCl_3$ (15 ml) were stirred for 30 min, the solution of **NOP1**–**3** (5 mg) in $CHCl_3$ (2 ml) was added. The resulting solution was dripped onto the glass slide to form the film by spin-coating at 100 rpm for 30 s. The film was put in a dark place to dry in air.

THF was distilled from sodium and benzophenone under pure nitrogen. All the other solvents and reagents of analytical grade were used as purchased without further purification.

Bis(3-bromo-4-methoxyphenyl)methanone (2). Bis-(4-methoxyphenyl)methanone (**1**) (5.00 g, 0.02 mol), methanesulfonic acid (50 ml), and NBS (7.75 g, 0.04 mol) were stirred for 6 h at 60°C. When the reaction was completed, ice water (60 ml) was added and precipitate collected by filtration. The solid was washed with aqueous solution of NaOH (4.5 mol/l, 3 × 50 ml), compound **2** was obtained by recrystallization from *n*-hexane–EtOAc, 5:1. Yield 7.20 g (86%), yellow solid, mp 174–178°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.97 (6H, s, OCH_3); 7.25–7.30 (2H, m, H Ar); 7.71–7.78 (2H, m, H Ar); 7.92 (2H, d, *J* = 2.1, H Ar).^{13}C NMR spectrum, δ, ppm: 57.3; 111.3; 112.7; 131.2; 131.9; 134.6; 159.3; 191.4. Found, %: C 45.01; H 3.01. $C_{15}H_{12}Br_2O_3$. Calculated, %: C 45.03; H 3.02.

Synthesis of biphenylmethanones 3a,b (General method). A solution of bis(3-bromo-4-methoxyphenyl)-methanone (**2**) (2.00 g, 0.005 mol), phenylboronic acid (1.34 g, 0.01 mol) or [4-(naphthalen-1-yl)phenyl]boronic acid (2.73 g, 0.01 mol), $Pd[P(C_6H_5)_3]_4$ (0.17 g, 0.015 mmol), and Na_2CO_3 (2.12 g, 0.02 mol) in water (10 ml) and toluene (20 ml) was stirred at 110°C for 7 h. After TLC examination indicated that no starting material remained, the aqueous phase was extracted with EtOAc (3×35 ml). The organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, the product was recrystallized from appropriate solvent mixture.

Bis(6-methoxybiphenyl-3-yl)methanone (3a) was recrystallized from *n*-hexane–EtOAc, 4:1. Yield 1.74 g (82%), yellow solid, mp 143–145°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.90 (6H, s, OCH_3); 7.04 (2H, d, *J* = 8.4, H Ar); 7.33–7.36 (2H, m, H Ar); 7.42 (4H, t, *J* = 7.4, H Ar); 7.55 (4H, d, *J* = 8.4, H Ar); 7.82–7.87 (4H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.9; 110.5; 127.4; 128.1; 129.6; 130.6; 130.8; 131.5; 133.1; 137.6; 159.8; 194.5. Found, %: C 82.21; H 5.61. $C_{27}H_{22}O_3$. Calculated, %: C 82.21; H 5.62.

Bis[6-methoxy-4'-(naphthalen-1-yl)biphenyl-3-yl]-methanone (3b) was recrystallized from *n*-hexane–EtOAc, 5:1. Yield 2.80 g (84%), white solid, mp 145–146°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.95 (6H, s, OCH_3); 7.09 (2H, d, *J* = 8.6, H Ar); 7.48–7.51 (4H, m, H Ar); 7.68–

7.70 (4H, m, H Ar); 7.79–7.81 (6H, m, H Ar); 7.85–7.97 (10H, m, H Ar); 8.09 (2H, s, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.9; 110.6; 125.6; 125.8; 126.0; 126.3; 127.2; 127.7; 128.3; 128.5; 130.1; 130.9; 131.6; 132.7; 133.0; 133.1; 133.7; 136.7; 138.2; 140.1; 159.9; 194.5. Found, %: C 87.26; H 5.30. $C_{47}H_{34}O_3$. Calculated, %: C 87.28; H 5.30.

Synthesis of alkynols 4a,b (General method). Under a nitrogen atmosphere, ethynyllithium (30 mmol) in dry THF (30 ml) was slowly added (5 min) to a cold (–30°C) solution of compound **3a** (5.0 g, 12.67 mmol) or compound **3b** (5.00 g, 7.73 mmol) in dry THF (15 ml). After being stirred for 3 h, water (50 ml) was added, and the aqueous phase was extracted with EtOAc (3×30 ml). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude product was purified by recrystallization from *n*-hexane– EtOAc, 8:1.

1,1-Bis(6-methoxybiphenyl-3-yl)prop-2-yn-1-ol (4a). Yield 4.01 g (75%), white solid, mp 93–95°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.82 (1H, s, OH); 2.89 (1H, s, ≡CH); 3.81 (6H, s, OCH_3); 6.95 (2H, d, *J* = 8.6, H Ar); 7.31–7.33 (2H, m, H Ar); 7.39–7.43 (4H, m, H Ar); 7.52–7.54 (4H, m, H Ar); 7.56–7.58 (2H, m, H Ar); 7.62 (2H, d, *J* = 2.4, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.7; 73.8; 75.4; 86.7; 110.9; 126.3; 127.1; 128.0; 128.8; 129.6; 130.4; 137.1; 138.4; 156.1. Found, %: C 82.83; H 5.73. $C_{29}H_{24}O_3$. Calculated, %: C 82.83; H 5.75.

1,1-Bis[6-methoxy-4'-(naphthalen-1-yl)biphenyl-3-yl]-prop-2-yn-1-ol (4b). Yield 3.42 g (67%), white solid, mp 94–96°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.91 (1H, s, ≡CH); 3.85 (3H, s, OCH_3); 3.88 (3H, s, OCH_3); 6.86 (1H, d, *J* = 8.6, H Ar); 6.97 (1H, d, *J* = 8.8, H Ar); 7.49–7.51 (6H, m, H Ar); 7.63–7.78 (6H, m, H Ar); 7.80–7.84 (6H, m, H Ar); 7.87 (1H, d, *J* = 8.0, H Ar); 7.90–7.93 (5H, m, H Ar); 8.08 (2H, s, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.0; 73.2; 74.5; 86.6; 109.6; 124.6; 124.8; 125.0; 125.4; 126.2; 126.7; 127.3; 127.5; 129.1; 130.0; 130.6; 131.7; 132.1; 132.8; 135.7; 137.2; 141.1; 158.4. Found, %: C 87.45; H 5.37. $C_{49}H_{36}O_3$. Calculated, %: C 87.47; H 5.39.

4-(3,4-Dimethoxyphenyl)-3-(methoxycarbonyl)-4-phenyl-but-3-enoic acid (6). Potassium (3.10 g, 0.08 mol) and *t*-BuOH (110 ml) were stirred at 60°C for 3 h under nitrogen until the potassium disappeared. *t*-BuOH was evaporated under reduced pressure to obtain the white solid (*t*-BuOK). Then (3,4-dimethoxyphenyl)(phenyl)methanone (**5**) (15.00 g, 0.06 mol), dimethyl succinate (11.50 g, 0.07 mol), and toluene (100 ml) were added and stirred at 110°C for 34 h. After completion of the reaction, water (100 ml) was added, and the aqueous phase was extracted with toluene (3×50 ml). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and product **6** was purified by recrystallization from *n*-hexane–EtOAc, 4:1. Yield 18.86 g (85%), yellow solid, mp 211–212°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 (3H, d, *J* = 2.4, OCH_3); 3.59 (2H, s, CH_2); 3.78 (3H, s, OCH_3); 3.89 (3H, s, OCH_3); 6.68–6.73 (2H, m, H Ar); 6.83–6.87 (1H, m, H Ar); 7.10–7.14 (2H, m, H Ar); 7.26–7.29 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.4; 38.4; 51.7; 55.9; 81.2; 110.9; 112.5; 122.2; 123.4; 127.9; 128.8; 133.8; 141.9; 148.7; 149.3; 152.8; 169.2; 170.2; 177.2. Found, %: C 67.26; H 5.73. $C_{20}H_{20}O_6$. Calculated, %: C 67.41; H 5.66.

4-Hydroxy-6,7-dimethoxy-1-phenyl-2-naphthoic acid (7). Compound **6** (10.00 g, 0.03 mol) and Ac_2O (130 ml) were stirred at 135°C for 4 h under a nitrogen atmosphere. When the reaction was completed, the Ac_2O was evaporated under reduced pressure. When the temperature decreased to 40°C, a solution of $NaHCO_3$ (5.00 g, 0.060 mol) in water (100 ml) was added to the residue, in order to neutralize the remaining Ac_2O and adjust the pH to weakly basic. The product was dissolved in NaOH (5.00 g, 0.12 mol, 30 ml of water) and EtOH (20 ml) solution. The mixture was stirred at 85°C for 10 h. HCl (12 mol/l, 17 ml) was added, and the aqueous phase was extracted with EtOAc (3×50 ml), The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The purified product was obtained by recrystallization from *n*-hexane–EtOAc, 5:1. Yield 7.41 g (82%), white solid, mp 242–243°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.53 (3H, s, OCH_3); 3.90 (3H, s, OCH_3); 6.68 (1H, s, H Ar); 7.13 (1H, s, H Ar); 7.22–7.24 (2H, m, H Ar); 7.38–7.44 (3H, m, H Ar); 7.49 (1H, s, H Ar); 10.29 (1H, s, OH); 12.32 (1H, s, COOH). ^{13}C NMR spectrum, δ, ppm: 55.9; 56.1; 101.3; 102.8; 103.7; 122.5; 123.6; 124.8; 125.6; 127.7; 131.2; 131.8; 134.4; 135.5; 145.6; 150.8; 151.8; 154.3; 164.3. Found, %: C 70.29; H 5.02. $C_{19}H_{16}O_5$. Calculated, %: C 70.36; H 4.97.

5-Hydroxy-2,3-dimethoxy-7*H*-benzo[*c*]fluoren-7-one (8). Compound **7** (7.00 g, 0.02 mol) and polyphosphoric acid (60 ml) were stirred at 50°C for 10 h, ice water (200 ml) was added. The product was filtered off, washed with water three times and then with aqueous solution of NaOH (4.5 mol/l, 3×100 ml) to adjust pH to alkaline. The purified product was obtained by recrystallization from *n*-hexane–EtOAc, 4:1. Yield 5.13 g (84%), red solid, mp 270–271°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.82 (3H, s, OCH_3); 3.92 (3H, s, OCH_3); 6.81 (1H, s, H Ar); 7.10–7.14 (1H, m, H Ar); 7.37–7.39 (2H, m, H Ar); 7.41–7.43 (1H, m, H Ar); 7.47 (1H, s, H Ar); 7.84 (1H, d, *J* = 8.6, H Ar); 10.58 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 55.9; 56.2; 101.4; 102.9; 103.7; 122.6; 123.7; 125.6; 127.7; 131.2; 135.5; 145.6; 150.7; 151.7; 154.2; 194.4. Found, %: C 74.86; H 4.87. $C_{19}H_{14}O_4$. Calculated, %: C 74.50; H 4.61.

Synthesis of chromenones 9a,b (General method). A solution of 5-hydroxy-2,3-dimethoxy-7*H*-benzo[*c*]-fluoren-7-one (**8**) (0.20 g, 0.67 mmol), PPTS (0.02 g, 0.24 mmol), and trimethoxymethane (1 ml, 0.07 mmol) in toluene (20 ml) was stirred at 60°C. 1,1-Bis(6-methoxy-biphenyl-3-yl)prop-2-yn-1-ol (**4a**) (0.31 g, 0.80 mmol, 1.2 equiv) or 1,1-bis[6-methoxy-4'-(naphthalen-1-yl)bi-phenyl-3-yl]prop-2-yn-1-ol (**4b**) (0.50 g, 0.75 mmol, 1.2 equiv) was added after 30 min and the solution stirred at 110°C for 8 h. After the reaction was complete, the aqueous phase was extracted with EtOAc (3×30 ml) and the combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The purified product was obtained by silica gel column chromatography (*n*-hexane–EtOAc, 10:1).

6,7-Dimethoxy-3,3-bis(6-methoxybiphenyl-3-yl)benzo-[*h*]indeno[2,1-*f*]chromen-13(3*H*)-one (9a). Yield 0.37 g

(78%), red solid, mp 222–224°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.77 (6H, s, OCH_3); 3.97 (3H, s, OCH_3); 4.09 (3H, s, OCH_3); 6.34 (1H, d, *J* = 8.8, H-1(2)); 6.90 (2H, d, *J* = 8.0, H Ar); 7.18–7.20 (1H, m, H Ar); 7.29–7.33 (2H, m, H Ar); 7.35–7.37 (4H, m, H Ar); 7.42–7.44 (7H, m, H Ar); 7.50 (2H, s, H Ar); 7.58–7.59 (2H, m, H Ar), 7.61 (1H, s, H Ar); 7.72–7.73 (1H, m, H Ar); 7.88 (1H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.6; 55.9; 83.4; 101.9; 103.5; 110.5; 119.6; 121.6; 123.6; 127.1; 127.3; 127.4; 127.9; 129.5; 129.9; 130.4; 133.9; 134.1; 135.1; 137.0; 138.4; 145.0; 148.1; 151.1; 151.3; 155.9; 195.7. Found, %: C 81.26; H 5.32. $C_{48}H_{36}O_6$. Calculated, %: C 81.34; H 5.12.

6,7-Dimethoxy-3,3-bis[6-methoxy-4'-(naphthalen-1-yl)-biphenyl-3-yl]benzo[*h*]indeno[2,1-*f*]chromen-13(3*H*)-one (9b). Yield 0.49 g (74%), red powder, mp 218–200°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (6H, s, OCH_3); 4.03 (3H, s, OCH_3); 4.10 (3H, s, OCH_3); 6.39 (1H, d, *J* = 8.6, H-1(2)); 6.95 (2H, d, *J* = 8.4, H Ar); 7.47–7.50 (7H, m, H Ar); 7.56 (1H, s, H Ar); 7.57–7.59 (5H, m, H Ar); 7.67 (1H, s, H Ar); 7.72–7.74 (6H, m, H Ar); 7.75–7.77 (2H, m, H Ar); 7.84–7.93 (9H, m, H Ar); 8.05 (2H, s, H Ar). ^{13}C NMR spectrum, δ, ppm: 55.7; 56.0; 56.1; 83.4; 99.9; 102.0; 103.5; 110.6; 113.2; 119.7; 123.6; 124.4; 125.5; 125.7; 125.9; 126.2; 127.0; 127.4; 127.6; 128.2; 128.4; 129.8; 129.9; 130.0; 130.3; 132.6; 133.7; 134.1; 135.0; 135.1; 137.1; 137.5; 138.2; 139.8; 145.0; 148.1; 151.1; 151.3; 156.1; 195.7. Found, %: C 85.12; H 5.23. $C_{68}H_{48}O_6$. Calculated, %: C 84.98; H 5.03.

Synthesis of naphthopyrans NOP2,3 (General method). *n*-Butyllithium (10 ml, 0.25 M in hexane) was slowly added (3 min) to a cold (–30°C) solution of compound **9a** (0.22 g, 0.31 mmol) or compound **9b** (0.21 g, 0.22 mmol) in dry THF (25 ml). The mixture was stirred at –30°C for 1 h and warmed up gradually to room temperature in 2 h. Water (50 ml) was added, and the aqueous phase was extracted with EtOAc (3×30 ml). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The purified product was obtained by column chromatography on silica gel (*n*-hexane–EtOAc, 15:1).

13-Butyl-6,7-dimethoxy-3,3-bis(6-methoxybiphenyl-3-yl)-3,13-dihydrobenzo[*h*]indeno[2,1-*f*]chromen-13-ol (NOP2). Yield 0.15 g (62%), green powder, mp 196–198°C. IR spectrum, cm^{-1}: 3493 (–OH), 2929 (–CH_3), 2859 (–CH_2–), 1492 ($\delta_{C–H}$), 816 ($\gamma_{=C–H}$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.38–0.48 (2H, m, CH_2); 0.54–0.58 (3H, m, CH_3); 2.23–2.35 (4H, m, CH_2CH_2); 3.69 (3H, s, OCH_3); 3.79–3.84 (6H, m, OCH_3); 4.04 (3H, s, OCH_3); 5.35 (1H, s, OH); 6.23 (1H, d, *J* = 9.6, H-1(2)); 6.77 (1H, d, *J* = 8.8, H Ar); 6.96 (1H, d, *J* = 9.2 H Ar); 7.20–7.64 (20H, m, H Ar); 7.88 (1H, d, *J* = 8.4, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.8; 22.8; 25.7; 39.1; 55.4; 55.5; 55.7; 55.9; 82.6; 83.3; 101.8; 103.1; 109.9; 113.2; 121.3; 122.7; 125.8; 126.1; 126.9; 127.1; 127.4; 127.8; 128.1; 128.6; 129.5; 129.6; 130.3; 130.4; 136.3; 138.2; 138.5; 140.7; 140.9; 147.7; 148.4; 150.0; 155.8; 155.9. Found, %: C 81.47; H 6.12. $C_{52}H_{46}O_6$. Calculated, %: C 81.44; H 6.05.

13-Butyl-6,7-dimethoxy-3,3-bis[6-methoxy-4'-(naphthalen-1-yl)biphenyl-3-yl]-3,13-dihydrobenzo[*h*]indeno[2,1-*f*]-chromen-13-ol (NOP3). Yield 0.14 g (61%), white powder, mp 196–198°C. IR spectrum, cm^{-1}: 3484 (–OH), 2955 (–CH_3), 2933, (–CH_2–), 1486 ($\delta_{C–H}$), 812 ($\gamma_{=C–H}$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.32–0.46 (2H, m, CH_2); 0.58 (3H, t, *J* = 9.6, CH_3); 1.02–1.04 (2H, m, CH_2); 2.22–2.26 (2H, m, CH_2); 3.71 (3H, s, OCH_3); 3.84–3.85 (6H, m, OCH_3); 4.06 (3H, s, OCH_3); 5.35 (1H, br. s, OH); 6.29 (1H, d, *J* = 9.8, H-1(2)); 6.82 (1H, d, *J* = 8.4, H Ar); 7.02–7.03 (1H, m, H Ar); 7.22–7.23 (1H, m, H Ar); 7.27–7.29 (1H, m, H Ar); 7.47–7.67 (18H, m, H Ar); 7.70–7.78 (4H, m, H Ar); 7.85–7.92 (7H, m, H Ar); 8.05 (2H, d, *J* = 8.0, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.5; 22.8; 25.8; 39.1; 55.5; 55.7; 55.8; 82.6; 83.5; 101.9; 103.9; 110.1; 110.8; 113.3; 121.1; 122.7; 125.5; 125.7; 125.9; 126.3; 126.6; 126.9; 127.1; 127.6; 128.2; 128.4; 128.7; 129.8; 129.9; 130.1; 130.2; 132.6; 133.7; 136.5; 138.2; 139.7; 140.8; 147.8; 148.6; 148.7; 149.9; 155.9; 156.1. Found, %: C 84.91; H 5.66. $C_{72}H_{58}O_6$. Calculated, %: C 84.85; H 5.74.

Supplementary information file containing IR, ^{1}H and ^{13}C NMR spectral data of all synthesized compounds, synthetic procedure of compound **NOP1**, and optical density change curves of compounds **NOP1**–**3** in CH_2Cl_2 and PMMA is available on the journal website at http://link.springer.com/journal/10593.

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