Synthesis and photochromic properties of conjugated naphthopyran derivatives

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Three novel types of naphthopyran derivatives containing alkoxyl and phenyl moieties, 13-butyl -6,11-dimethyl-3,3-diphenyl-3,13-dihydrobenzo[h]indeno[2,1-f]chromen-13-ol (**NP**), 13-butyl-3,3-bis(6-methoxy-[1,1′-biphenyl]-3-yl)-6,6-dimethyl-3,13-dihydrobenzo[h]indeno[2,1-f]chromen-13-ol (**NP1**) and 13-butyl-3,3-bis(6-methoxy-4′-naphthalenyl-[1,1′-biphenyl]-3-yl)-6,11-dimenthyl-3,13-dihydrobenz[h]indeno[2,1-f]chromen-13-ol (**NP2**), were synthesised and characterised. Measurements indicated that they possessed an excellent photochromic response, a rapid thermal bleaching rate and good fatigue resistance. Meanwhile, the UV maximum absorption wavelengths of **NP1** (562 nm) and **NP2** (597 nm) appeared bathochromically shifted compared with **NP** (536 nm). The bleaching rate of **NP1** was found to be approximately twice that of **NP**. The results indicated that the UV maximum absorption wavelength and bleaching rate increase with increasing length of the phenyl side chain moieties. In PMMA film, the compounds showed almost the same photochromic properties in the solid state as in dichloromethane solution. The UV absorbance with high-contrast switching in solid film could be beneficial for practical applications.

Keywords: photochromic, naphthopyran derivatives, fading rate, absorption wavelength

Photochromic materials have attracted considerable attention due to their potential application in optical switch memories, precision machining triaxial data storage and nonlinear devices.[1–3] Photochromic compounds, such as diarylethenes, spiropyrans, spirooxazines and azobenzenes, have attracted considerable research attention in recent years.[4–9] Naphthopyrans also play a significant role in photochromic materials, due to the versatility of the naphthopyran entity. There has been intense research interest in this class of molecules. Naphthopyrans show high resistance to photodegradation and different colours can be produced after UV irradiation, and the thermal bleaching kinetics can also be controlled by introducing appropriate substituents in the structure.[10–12] Under UV light irradiation, the uncoloured naphthopyran undergoes an electrocyclic pyran-ring opening with cleavage of the (sp^3) C–O bond to form a merocyanine (**NP**–**MC**) structure, as shown in Scheme 1. There are two open forms,[13,14] TT (transoid-*trans*) and TC (transoid-*cis*): while the TC isomer rapidly returns to the uncoloured closed form (CF), the TT isomer is thermally more stable (Scheme 2). The TC form photochemically isomerises to the TT form (and *vice versa*) through C=C bond rotation. The TC form thermally reverts to the CF in a few seconds or minutes, whereas the thermal back reaction from the TT form to the CF is much slower (minutes or hours) because the TT form is thermally stable and must overcome a relatively large activation energy barrier to isomerise to the TC form. The residual colour of the TT form and the slow thermal back reaction of the TC form are considered as one of the inconvenient problems to solve for photoswitching applications. Sousa and co-workers also reported recently that the formation of the TT form of naphthopyrans can be suppressed by using a fused alkane chain as a bridge between the pyran ring and the naphthalene core.[15,16]

Though this technique effectively suppresses the formation of the TT form, much time and effort is required to prepare these compounds.[17,18] To reduce the formation of the TT form, we designed and synthesised three novel naphthopyran derivatives with methoxy, phenyl and 4-(1-naphthyl)phenyl groups at the *para*- and *ortho*-positions with the substituents R_3 (phenyl) and R_4 (4-(1-naphthyl)phenyl) in **NP1** and **NP2** respectively (Scheme 3). These compounds are based on the inexpensive 4,4′-dimethylbenzophenone as a raw material; the synthesis route is relatively simple and the product is easy to separate and purify, the yield is high and it has potential industrial production capacity. At the same time, the synthesised structure is novel and the conjugated system is extended to have good fatigue resistance, fast bleaching rate and wide photochromic response range of the visible spectrum.

Results and discussion

The naphthopyrans showed good photochromic properties and could be toggled between their colourless closed-ring and coloured open-ring isomers by UV (365 nm, 20 mW cm^{-2}) irradiation. After 365 nm UV light irradiation, a new absorption band in the visible region around 525 nm appeared due to the open-isomer **NP**–**MC**. The red coloured solution faded to colourless in the dark within 3 min. **NP**, **NP1** and **NP2** had similar properties; however, the absorbance of **NP**, **NP1** and **NP2** were different to one another both before and after UV light irradiation (Figs S1–S3 in the Electronic Supplementary Information (ESI)). The relevant parameters of the three compounds before and after irradiation are summarised in Table 1.

In the PMMA film, the three compounds also showed similar photochromic activity (Figs S10–S13 in the ESI). The absorbance band of the open-form **NP**–**MC** in PMMA film was broadened in the range 410–660 nm, and was broader than in the solution. The redshift values of the closed-ring isomers were consistent with those of reported diarylethenes,[19,20] and might be attributed to the polar effect of the polymer matrix in the amorphous solid state. Furthermore, the film's absorbance curve is broad and weak. Because of the stabilisation of molecular alignment in solid media, the movement of molecules at their photochromic switching speeds is significantly slower. Colouration and discolouration of each compound are relatively slow. So when the exposed film is placed in the dark, these films take about 7–15 min to fade (Fig. 1), and may even require a longer time.

The fading of the coloured form back to **NP** (colourless form) involves two steps, TT→TC→**NP**. The process of TC→**NP** (k_1) is usually rapid, while TT→NP (k_2) is slow. Convenient measurement of the fade speed is obtained from the $t_{1/2}$ value,[21–23] which is the time taken for the optical density to reduce by one half of the initial optical density of the coloured form, and the smaller $t_{1/2}$, the faster the fade rate (as shown in Fig. 2).

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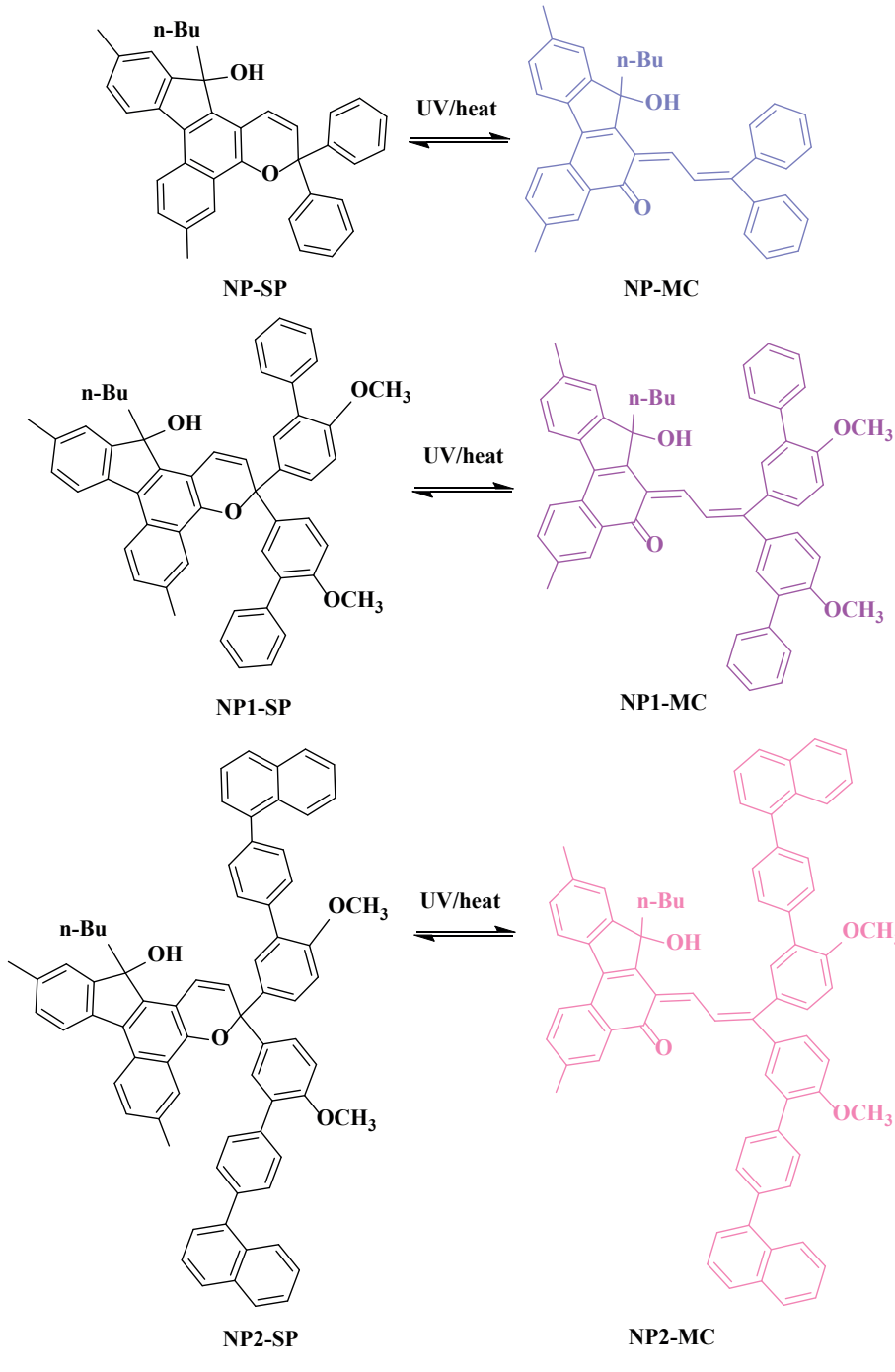
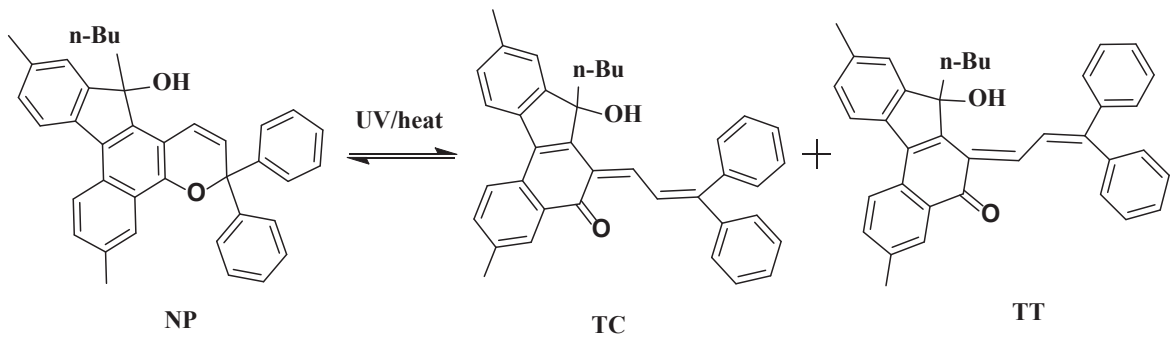
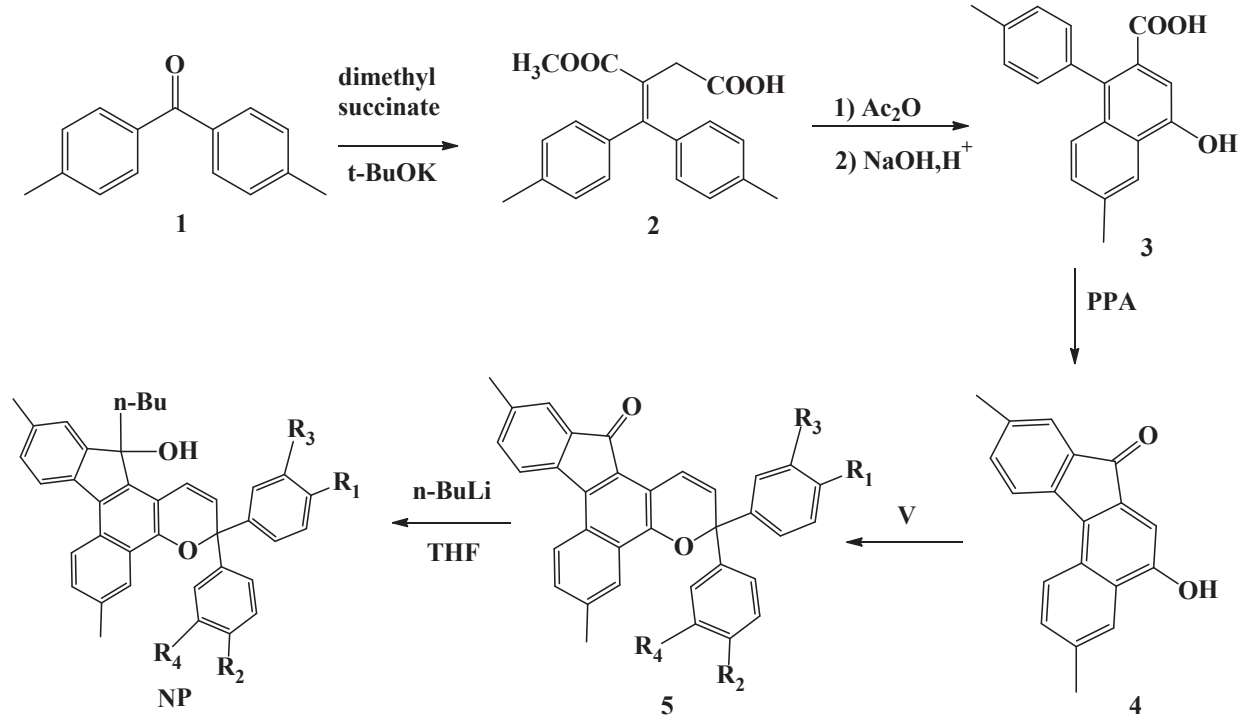


Scheme 1 Photochromism of **NP**, **NP1** and **NP2**.



Scheme 2 Photochromism of **NP**, and TC and TT isomers.



NP: $R_1=R_2=R_3=R_4=H$
NP1: $R_1=R_2=OMe$, $R_3=R_4=Ph$
NP2: $R_1=R_2=OMe$, $R_3=R_4=4$-(naphthyl)phenyl

5a: $R_1=R_2=R_3=R_4=H$
5b: $R_1=R_2=OMe$, $R_3=R_4=Ph$
5c: $R_1=R_2=OMe$, $R_3=R_4=4$-(naphthyl)phenyl

Scheme 3 Synthetic route for naphthopyrans **NP–NP2**.

Table 1 The biexponential decay data and $t_{1/2}$ data for **NP–NP2** in CH_2Cl_2 (1×10^{-4} mol L^{-1}) and PMMA film (13%, w/w) at 293 K

Compound	λ_{max} before		λ_{max} after		A_1		k_1		$t_{1/2}$	
	CH_2Cl_2	PMMA	CH_2Cl_2	PMMA	CH_2Cl_2	PMMA	CH_2Cl_2	PMMA	CH_2Cl_2	PMMA
NP	360	300	525	536	1.49	0.05	245.23	144.04	151	451
NP1	359	298	542	562	0.47	0.02	39.78	53.93	112	402
NP2	362	302	572	597	0.62	0.02	42.23	11.99	105	343

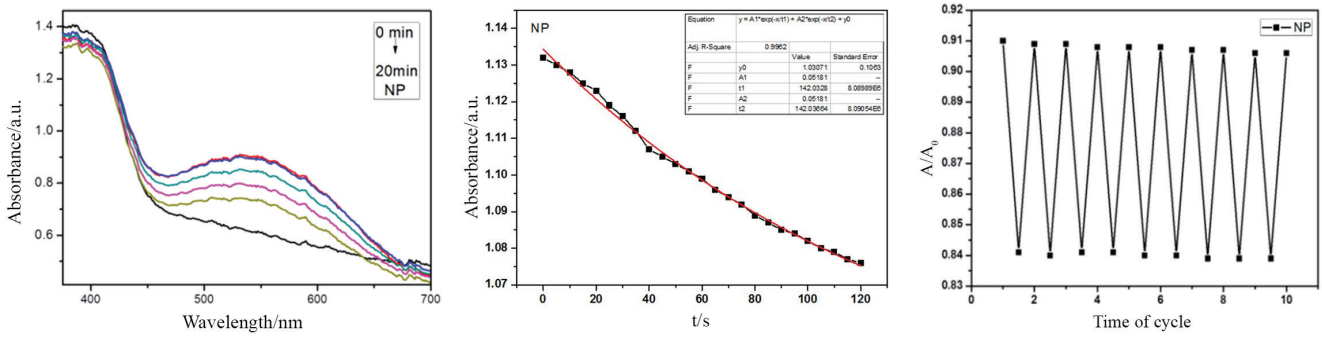


Fig. 1 Absorption decay curves of NP (left), the experimental thermal fading kinetic of **NP** (middle) and the change of the optical density value with the number of cycles **NP** (right) in PMMA film (13%, w/w).

The thermal fading kinetics, which was determined from the absorption–time dataset, were analysed using the biexponential equation[24] $y = A_1\exp(-t/k_1) + A_2\exp(-t/k_2) + y_0$ to evaluate the photochromic fade rate, where 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 colouration.[25] Figures 1 and 3 show y–t decay and ExpDec2 curves produced using Origin Software. R^2 and Chi^2/DoF (variance) were used to measure the degree of fitting. R^2 was extremely close to 1 (0.999) and Chi^2/DoF was close to 0 (0.00045). This revealed that the fitting curve was successfully simulated with the equation. As a result, the discolouration process followed a biexponential attenuation law, and had both fast and slow processes.[26,27]

It was found that the fading rate constant of **NP1** (k_1 = 39.78) was smaller than that for **NP** (k_1 = 245.23). The fading kinetics data confirmed that the donating group at the conjugative position of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran increased the

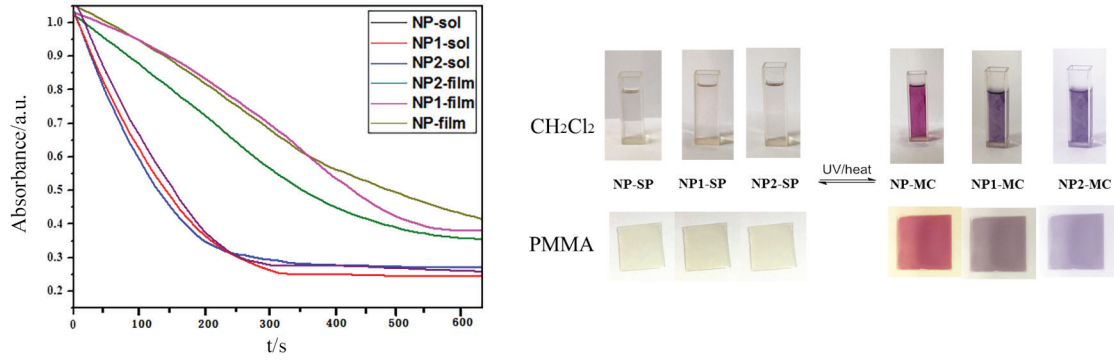


Fig. 2 The $t_{1/2}$ curves and the colour changes of **NP–NP2** by UV irradiation in CH_2Cl_2 (1×10^{-4} mol L^{-1}) and PMMA film (13%, w/w) at 293 K.

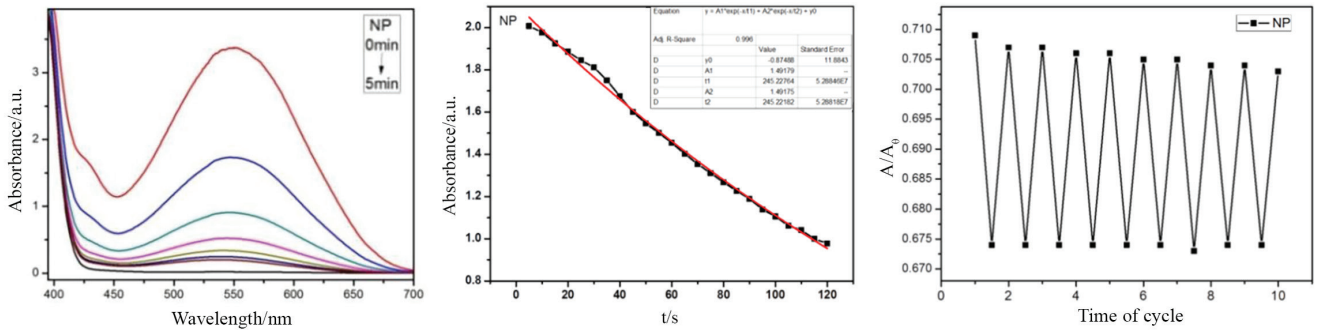


Fig. 3 Absorption decay curves of NP (left), the experimental thermal fading kinetic of **NP** (middle) and the change of the optical density value with the number of cycles **NP** (right) in CH_2Cl_2 (1×10^{-4} mol L^{-1}).

fading speed because of an electronic effect.[28,29] Compared with **NP1**, the fading speed of **NP2** was increased and $t_{1/2}$ was decreased. As presented in Table 1, the k_1 value of **NP2** (k_1 = 42.23) was larger than that of NP1 (k_1 = 39.78) in CH_2Cl_2, which resulted in the fading speed of **NP2** ($t_{1/2}$ = 105 s) being faster than that of **NP1** ($t_{1/2}$ = 112 s) under the same conditions. It is noteworthy that the fading speed increased with increasing length of the aryl group moieties. With increasing length, the fading speed of $t_{1/2}$ decreased from 151 s to 112 s. This result suggests that the fading speed of the coloured form was promoted by the electronic effects of the phenyl group and the length of the attached phenyl/aryl group chain. At the same time, the above conclusions also apply to the PMMA films of these compounds.

The fatigue resistances of naphthopyran were also tested. Figures 1 and 3 show the photochromic on–off switching trend over 10 cycles of **NP** in both PMMA film and CH_2Cl_2 solution, respectively. When the compounds were excited by UV light (365 nm) for 100 s, and then put in the dark for 5–30 min, the absorption intensity decreased to 83–94% of its original value. **NP1** was also excited in the same manner and its absorption intensity decreased to 94% of its original value. **NP2** decreased to 93.4% compared with its original value. These compounds also have good fatigue resistance.

Conclusion

Three naphthopyrans bearing conjugated substituents were synthesised and characterised by NMR. The experimental results show that the design and synthesis of these structures suppresses participation of the TT form in the ring-opening reaction. The introduction of an alkoxy group and a phenyl moiety was found to make a significant contribution to the reduction of the formation of the TT form, and endow the naphthopyrans with some new properties. These findings will lead to fast light-responsive photochromic lenses, smart windows, fast optical switching applications and molecular actuators.

Experimental

The NMR spectra were recorded on a Bruker Avance 400 spectrometer at resonant frequencies of 400 MHz for ^{1}H and 101 MHz for ^{13}C nuclei using DMSO-d_6 or $CDCl_3$ as the solvent. Uncorrected melting points were observed in sealed capillaries. Elemental analysis was performed on a PerkinElmer 240 C elemental analyser. UV-Vis absorption spectra were obtained on a UV-2550 UV-Vis spectrophotometer. Fourier transform infrared (FTIR) spectra of intermediates and monomers were obtained from KBr pellets with a Nicolet NEXUS-470 FTIR spectrophotometer.

4,4′-Dimethylbenzophenone (99%, Changzhou Nock Chemical Technology Co. Ltd., Jiangsu, China), 4-(1-naphthyl)phenylboronic acid (99%, Aladdin, Shanghai, China), phenylboronic acid (99%, Aladdin Shanghai, China), palladium(II) chloride (59.5% Pd, Shanxi Kaida Chemicals, Co. Ltd., Shanxi, China) and *n*-butyllithium (Aladdin, 2.5 mol L–1 in *n*-hexane) were used as received. $Pd(PPh_3)_4$ was synthesised following a literature procedure.[30] THF was distilled from sodium and benzophenone under pure nitrogen before use. All the other solvents and reagents of analytical grade were used without further purification.

Synthesis of naphthopyrans **NP–NP2***; general procedure*

The target compounds were synthesised by bromination followed by Suzuki reaction with phenylboronic acid and 4-(naphthyl) phenylboronic acid, respectively (detailed synthetic route is given in the ESI). 4,4′-Dimethylbenzophenone was subjected to Stobbe condensation to give compound **2**, and thence compound **4**. Subsequent treatment with each of the three alkynols (**Va–Vc**) proceeded under acid catalysis to give compounds **5a–c**. These compounds were then treated with *n*-butyllithium (Scheme 3). **NP1** and **NP2** contain large conjugated moieties and exhibit excellent electron-donor units and were obtained in good yield.

Synthesis of 3-(ethoxycarbonyl)-4,4-di-p-tolylbut-3-enoic acid[31] (**2**)

A mixture of *t*-BuOK (8.81 g, 0.07 mol), 4,4′-dimethylbenzophenone (15.00 g, 0.07 mol, purchased from Aladdin), dimethyl succinate (11.50 g, 0.08 mol) and toluene (120 mL) were stirred for 4 h with heating to 110 °C. After completion of the reaction, the mixture was cooled to 40 °C. The crude product was extracted with toluene (3 × 30 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The purified product was obtained by recrystallisation from ethyl acetate and *n*-hexane (5:1) to give compound **2** as a yellow solid; yield 16.86 g (73%); m.p. 211–213 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.44 (s, 1H, –COOH), 7.14 (d, *J* = 9.4 Hz, 2H, ArH), 7.04 (d, *J* = 8.4 Hz, 2H, ArH), 6.90 (d, *J* = 9.2 Hz, 2H, ArH), 6.82 (d, *J* = 8.4 Hz, 2H, ArH), 3.53 (s, 5H, –CH_2–, –CH_3), 2.22 (s, 6H, –CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 172.5, 169.7, 150.6, 139.4, 138.3, 137.6, 129.5, 129.2, 129.1, 128.8, 124.8, 51.7, 40.4, 40.2, 21.2. Anal. calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.22; found: C, 74.08; H, 6.23%.

Synthesis of 4-hydroxy-6-methyl-1-p-tolyl-2-naphthoic acid (**3**)

A 250 mL three-necked flask was charged with compound **2** (3-(ethoxycarbonyl)-4,4′-di-*p*-tolybut-3-enoic acid) (10.00 g, 0.03 mol) and Ac_2O (130 mL). The reaction mixture was heated to 135 °C for 4 h under a nitrogen atmosphere. When the reaction was completed, the apparatus was converted to vacuum distillation to remove the remaining acetic anhydride. When the temperature cooled to 40 °C, the reaction mixture was poured into sodium bicarbonate and the pH adjusted to alkaline. The product was dissolved in sodium hydroxide (5.00 g, 0.12 mol, in water (30 mL)) and ethanol (20 mL) solution. The mixture was stirred for 10 h and heated at 85 °C. After completion of the reaction, the mixture was cooled to room temperature. The organic phase was washed with hydrochloric acid solution three times and dried with anhydrous sodium sulfate. The purified product was obtained by recrystallisation from ethyl acetate and *n*-hexane to give compound **3** as a white solid; yield 6.50 g (72%); m.p. 190–192 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H, –COOH), 8.04 (s, 1H, –OH), 7.34 (s, 2H, ArH), 7.28 (d, *J* = 9.0 Hz, 2H, ArH), 7.23 (s, 1H, ArH), 7.14 (d, *J* = 9.4 Hz, 2H, ArH), 2.52 (s, 3H, –CH_3), 2.44 (s, 3H, –CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 169.8, 152.3, 136.5, 136.2, 135.7, 132.0, 130.8, 130.5, 129.4, 128.9, 127.2, 126.2, 121.4, 107.56, 21.8, 21.3. Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52; found: C, 78.04; H, 5.56%.

Synthesis of 5-hydroxy-3,9-dimethylbenzo[c]fluoren-7-one[32] (**4**)

4-Hydroxy-6-methy-tolyl-2-naphthoic acid (**3**) (5.00 g, 0.02 mol) and methanesulfonic acid (60 mL) were heated to 50 °C and kept at this temperature for 10 h. After cooling to room temperature, the reaction mixture was poured into ice water (200 mL) and washed with sodium hydroxide solution (3 × 50 mL) to adjust the pH to alkaline. The compound was dried at 100 °C under vacuum to afford compound **4** as a black solid; yield 4.10 g (87%); m.p. 200–202 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.74 (s, 1H, –OH), 8.39 (d, 1H, ArH), 7.98 (s, 1H, ArH), 7.90 (d, *J* = 9.2 Hz, 1H, ArH), 7.49 (s, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 6.95 (s, 1 H, ArH), 2.48 (s, 6H, –CH_3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 193.6, 153.6, 141.7, 136.5, 136.4, 134.4, 132.4, 130.5, 129.9, 127.8, 126.7, 124.1, 123.6, 122.5, 121.5, 101.05, 19.9. Anal. calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14; found: C, 83.17; H, 5.12%.

Synthesis of 6,11-dimethyl-3,3-diphenylbenzo[h]indeno [2,1-f]chromen-13(3H)-one (**5a**)

5-Hydroxy-3,9-dimethylbenzo[*c*]fluoren-7-one (**4**) (0.30 g, 1.10 mmol) in toluene (20 mL) was heated to 60 °C; after 30 min, an equivalent of pyridine hydrochloride (0.02 g, 0.30 mmol), trimethyl orthoformate (1.00 mL, 0.07 mmol) and 3,3-diphenylprop-2-yn-1-ol (**Va**) (0.25 g, 1.20 mmol) were added and the mixture was heated to 110 °C for 8 h. TLC examination indicated that no starting material remained. Water (30 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with water (5 × 50 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate 10: 1) to afford compound **5a** as a red solid; yield 0.35 g (70%); m.p. 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8 Hz, 1H, ArH), 8.11 (s, 1H, ArH), 7.86 (d, *J* = 12 Hz, 1H, ArH), 7.66 (d, *J* = 8 Hz, 1H, ArH), 7.50 (d, *J* = 8 Hz, 4H, ArH), 7.33–7.36 (m, *J* = 8.9 Hz, 6H, ArH), 7.18 (d, *J* = 8 Hz, 1H, ArH), 6.32 (d, *J* = 9.6 Hz, 1H, ArH), 2.53 (s, 3H, –CH_3), 2.33(s, 3H, –CH_3); ^{13}C NMR (101MHz, $CDCl_3$): δ 196.1, 148.2, 144.7, 142.1, 138.0, 137.6, 136.0, 135.0, 134.4, 130.1, 129.6, 128.2, 127.7, 126.9, 124.6, 124.4, 122.3, 122.0, 119.8, 113.6, 83.5, 22.1, 20.9. Anal. calcd for $C_{34}H_{24}O_2$: C, 87.90; H, 5.21; found: C, 87.92; H, 5.31%.

Synthesis of 3,3-bis(2-methoxy-[1,1′-biphenyl]-4-yl)-6,11-dimethylbenzo[h]indeno[2,1-f]chromen-13(3H)-one (**5b**)

The synthesis was similar to that used for **5a**. Compound **5b** was obtained as a red solid; yield 0.39 g (78%); m.p. 222–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.3 Hz, 1H, ArH), 8.16 (s, 1H, ArH), 7.86 (d, *J* = 12 Hz, 1H, ArH), 7.70 (d, *J* = 8 Hz, 2H, ArH), 7.51 (s, 2H, ArH), 7.36–7.43 (m, 5H, ArH), 7.28–7.32 (m, 6H, ArH), 7.20 (d, *J* = 7.1 Hz, 1H, ArH), 6.89–6.91 (m, 2H, ArH), 6.38 (d, *J* = 8.8 Hz, 1H, ArH), 6.24 (d, *J* = 24.6 Hz, 1H, ArH), 3.78 (d, *J* = 12.4 Hz, 6H, –OCH_3), 2.54 (s, 3H, –CH_3), 2.35 (s, 3H, –CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.1, 155.9, 148.3, 142.2, 138.4, 137.1, 135.1, 134.4, 132.1, 130.5, 130.2, 129.8, 129.5, 127.9, 127.3, 126.9, 124.7, 124.5, 122.5, 122.0, 119.6, 110.6, 83.1, 55.6, 31.0, 21.1. Anal. calcd for $C_{48}H_{36}O_4$: C, 85.18; H, 5.36; found: C, 85.16; H, 5.37%.

Synthesis of 3,3-bis(2-methoxy-4′-(naphthalen-1-yl)- [1,1′-biphenyl]-4-yl)-6,11-dimethylbenzo[h]indeno[2,1-f]chromen-13-(3H)-one (**5c**)

The synthesis was similar to that used for **5a**. Compound **5c** was obtained as a red solid; yield 0.50 g (74%); m.p. 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 2H, ArH), 8.06 (s, 2H, ArH), 7.85–7.93 (m, 8H, ArH), 7.72–7.78 (m, 7H, ArH), 7.49–7.51 (m, 6H, ArH), 7.40 (d, *J* = 8 Hz, 2H, ArH), 7.22 (d, *J* = 8 Hz, 1H, ArH), 6.94–6.97 (m, 1H, ArH), 6.40 (d, *J* = 8.8 Hz, 1H, ArH), 3.82 (d, *J* = 9.6 Hz, 6H, –OCH_3), 2.58 (s, 3H, –CH_3), 2.35 (s, 3H, –CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.2, 156.0, 148.4, 137.5, 137.2, 135.1, 134.5, 133.7, 132.7, 130.5, 129.9, 128.4, 128.2, 127.5, 127.1, 126.3, 125.9, 125.8, 125.6, 124.6, 122.6, 122.1, 110.7, 83.3, 55.1, 22.2, 21.2. Anal. calcd for $C_{68}H_{48}O_4$: C, 87.90; H, 5.21; found: C, 87.88; H, 5.23%.

Synthesis of 13-butyl-6,11-dimethyl-3,3-diphenyl- 3,13–dihydrobenzo[h]indeno[2,1-f]chromen-13-ol (**NP**)

Dry THF (15 mL) was placed in a three-necked flask and cooled to –30 °C. *n*-Butyllithium in hexane (2.5 M, 9 mL) was gradually added and the resulting mixture was stirred at this temperature for 1 h. 6,11-Dimethyl-3,3-diphenylbenzo[*h*]indeno [2,1-*f*] chromen-13(3*H*)-one (**5a**) (0.20 g, 0.43 mol) in THF (10 mL) was added gradually, and the resulting mixture was stirred for 1 h then warmed gradually to room temperature over 2 h. The organic layer was separated, washed with water and ethyl acetate three times and dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel, (*n*-hexane: ethyl acetate 15:1) to give the pure product **NP** as a red solid; yield 0.15 g (67 %); m.p. 222–224 °C; FTIR (KBr) (ν_{max} cm^{-1}): 3326 (–OH, stretching), 3052 ($\upsilon_{=C-H}$, stretching), 2953 (–CH_3, stretching), 2858 (–CH_2–, stretching), 1447 (δ_{C-H}, bending), 1492 ($\upsilon_{C=C}$, stretching), 769 ($\gamma_{=C-H}$, bending); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.4 Hz, 1H, ArH), 8.19 (s, 1H, ArH), 7.88 (d, *J* = 8.6 Hz, 2H, ArH), 7.51–7.56 (m, 5H, ArH), 7.34–7.38 (m, 5H, ArH), 7.18–7.23 (m, 3H, ArH), 6.23 (d, *J* = 12.6 Hz, 1H, ArH), 2.55 (s, 3H, –CH_3), 2.41 (s, 3H, –CH_3), 2.21–2.33 (m, 4H, –CH_2CH_2–), 1.02 (m, 2H, –CH_2–), 0.56 (t, *J* = 8.0 Hz, 3H, –CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.8, 145.5, 144.1, 138.1, 135.0, 129.3, 128.2, 127.9, 127.6, 127.4, 127.2, 126.8, 123.9, 123.4, 122.1, 121.5, 121.3, 113.9, 83.5, 82.7, 39.1, 30.9, 25.7, 22.82, 21.9, 21.42, 13.7. Anal. calcd for $C_{38}H_{34}O_2$: C, 87.32; H, 6.56; found: C, 87.30; H, 6.57%.

*Synthesis of 13-butyl-3,3-bis(2-methoxy-[1,1′-biphenyl]-3-yl)-6,11-dimethyl-3,13-dihydrobenzo[h]indeno[2,1-f]chromen-13-ol (***NP1***)*

The synthesis route was similar to that used for **NP**. Compound **NP1** was obtained as a green solid; yield 0.14 g (65%); m.p. 222–224 °C; FTIR (KBr) (ν_{max} cm^{-1}): 3484.73 (–OH, stretching), 3439 ($\upsilon_{=C-H}$, stretching), 2926 (υ_{C-H}, stretching), 2924 (υ_{C-H}, stretching), 2853 ($-CH_2-$, stretching), 1486 (δ_{C-H}, bending), 1262 ($\upsilon_{C=C}$, stretching), 755 ($\gamma_{=C-H}$, bending); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.6 Hz, 1H, ArH), 8.24 (s, 1H, ArH), 7.90 (d, *J* = 8.8 Hz, 1H, ArH), 7.32–7.47 (m, 16H, ArH), 7.18 (d, *J* = 12.4 Hz, 1H, ArH), 6.94 (d, *J* = 8.2 Hz, 1H, ArH), 6.80 (d, *J* = 8 Hz, 1H, ArH), 6.26 (d, *J* = 12.6 Hz, 1H, ArH), 3.71 (s, 3H, $-OCH_3$), 3.80 (s, 3H, $-OCH_3$), 2.56 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 2.10–2.42 (m, 4H, $-CH_2CH_2-$), 0.96–1.05 (m, 2H, $-CH_2-$), 0.56 (br. t, 3H, $-CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 134.8, 133.9, 129.2, 128.5, 128.2, 128.1, 126.9, 126.1, 125.8, 122.1, 122.3, 121.3, 120.5, 109.6, 109.2, 82.5, 81.4, 54.6, 54.4, 28.6, 24.7, 21.7, 20.40, 12.1. Anal. calcd for $C_{52}H_{46}O_4$: C, 84.98; H, 6.31; found: C, 85.01; H, 6.37%.

*Synthesis of 13-butyl-3,3-bis(2-methoxy-4′-(naphtha len-1-yl)-[1,1′-biphenyl]-4-yl)-6,11-dimethylbenzo[h]indeno[2,1-f]chromen-13-ol (***NP2***)*

The synthesis route was similar to that used for **NP**. Compound **NP2** was obtained as a white solid; yield 0.13 g (62%); m.p. 222–224 °C; FTIR (KBr) (ν_{max} cm^{-1}): 3435 (–OH, stretching), 3052 ($\upsilon_{=C-H}$, stretching), 2932 (υ_{C-H}, stretching), 2953 (υ_{C-H}, stretching), 2932, 2858 ($-CH_2-$, stretching), 1462 (δ_{C-H}, bending), 1492 ($\upsilon_{C=C}$, stretching), 754 ($\gamma_{=C-H}$, bending); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.4 Hz, 1H, ArH), 8.29 (s, 1H, ArH), 8.06 (d, *J* = 8.4 Hz, 2H, ArH), 7.91–7.92 (m, 8H, ArH), 7.69–7.88 (m, 8H, ArH), 7.62 (d, *J* = 8 Hz, 5H, ArH), 7.52 (d, *J* = 8 Hz, 2H, ArH), 7.49–7.51 (m, 9H, ArH), 7.34 (s, 1H, ArH), 7.18 (d, *J* = 8.8 Hz, 1H, ArH), 6.99 (d, *J* = 24.6 Hz, 1H, ArH), 6.85 (d, 1H, ArH), 6.32 (d, 1H, ArH), 3.85 (s, 3H, $-OCH_3$), 3.77 (s, 3H, $-OCH_3$), 2.60 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 2.22–2.35 (m, 4H, $-CH_2CH_2-$), 1.02 (m, 2H, $-CH_2-$), 0.57 (t, *J* = 8.3 Hz, 3H, $-CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 155.9, 149.9, 149.9, 141.2, 139.7, 139.6, 138.3, 138.2, 138.0, 137.6, 136.0, 148.6, 139.9,137.4, 134.6, 129.2, 129.1, 128.9, 128.7, 128.5, 128.4, 135.9, 135.1, 133.7, 132.6, 130.1, 130.0, 129.7, 129.6, 129.4, 128.4, 128.2, 127.6, 127.0, 126.9, 126.3, 125.9, 125.7, 125.6, 125.5, 114.2, 110.8, 110.3, 83.6, 82.5, 55.7, 55.6, 39.2, 25.8, 22.8, 21.9, 21.6, 13.8. Anal. calcd for $C_{72}H_{58}O_4$: C, 87.60; H, 5.92; found: C, 87.63; H, 5.87%.

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Electronic Supplementary Information

UV-Vis spectra and spectrokinetic data for **NP**, **NP1** and **NP2** as well as ^{1}H and ^{13}C NMR spectra for all intermediates and novel pyrans are available in the ESI through http://ingentaconnect.com/content/stl/jcr/2018/00000042/00000008/art00006

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