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Synthesis and photochromic properties of substituted naphthopyran compounds

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ABSTRACT

A group of 3,3-diaryl-3*H*-naphtho[2,1-b]pyran compounds with functional substituents at the 5- and 6-positions of the naphthopyran skeleton and the *para* positions at the 3-aryl moieties were prepared through condensation reactions between 2-naphthol derivatives and 1,1-diarylprop-2-yn-1-ol derivatives. The chemical structures of the compounds were confirmed by NMR and MS. The crystal structure of 3,3-diphenyl-6-morpholino-3*H*-naphtho[2,1-b]pyran (**4b**) was determined and the relationship between the pyran substructure and photochromism was discussed. The photochromic properties were studied as well, and decoloration kinetics of colored forms was fitted to the biexponential model. Among these compounds, **4b** was considered to be the best one due to the large ΔOD of colored form, which is one of the most important properties used in the photochromic material.

1. Introduction

The photochromism is an interesting phenomenon that has been drawing various attentions for several decades. It is a reversible photochemical reaction of a compound, which quickly changes its color when irradiated with light, such as UV light, sunlight or light from a fluorescent lamp and resumes its initial color when no irradiation. Various compounds have so far been synthesized and used in ophthalmic lenses,[1–5] imaging devices, and smart windows.[6,7] The photochromic compounds working through external light stimulus can also be the basis for molecular photoswitches,[8–11] sensors,[12–14] and the photo-control nano surface topology.[15] Furthermore, the application of photochromic compounds in other fields, e.g., fuel markers[16] and security markers,[17] continues to grow.

In the field of photochromic ophthalmic lenses, there are many requirements on photochromic dyes, such as optical density and fading speed in the dark, and so on.[18] In particular, the color tone that greatly affects the liking of the customers serves as an important factor, and a neutral tint like grey or brown is generally considered to be the most desired color tone for most people at any step of developing and fading during photochromism. However, it is difficult to obtain the above neutral tint relying upon one photochromic compound only. Practically, it could be obtained by mixing two or more photochromic compounds, which acts as the complimentary colors in the color gamut. For example, a neutral tint was obtained from a photochromic compound that develops yellowish or reddish color and a photochromic compound that develops blue color. Recently, our research interest has been focused on the naphthopyran compounds. The reversible color generation mechanism of the naphthopyran compounds operates through a facile electrocyclic ring-opening of the 2*H*-pyran moiety to afford an equilibrium mixture of colored geometrical isomers that gradually electrocyclise to the colorless pyran ring on cessation of irradiation.[19,26] Compared to other photochromic families, the naphthopyran compounds have the advantages of the low initial color, low solvachromism, high color density and large color gamut provided by the ring open form when substituted with various electron donating and withdrawing groups.[20] Furthermore, we realize that it will be great beneficial to the composites compatibility in the formula and the color balance at steps of developing and fading, if the neutral tint is obtained by the mixture of compounds selected from the same structural family. In order to accomplish the above object, the present paper has conducted keen study concerning on the synthesis of a number of naphthopyran compounds with various substituted groups and the effects of these groups on the optical properties of the compounds.

Thus, we prepared the 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran compounds (Scheme 1), with substituents at the 5- and 6-positions of the naphthopyran skeleton and the *para* positions of the 3-aryl moieties. The substituents were selected form the substituted amino groups and heterocyclic groups bonded to the skeleton structure of chromophores through the nitrogen atom, and the substituted amido groups as well. The starting materials, such as naphthol derivatives and ketones were commercially available. The chemical structures and photochromic properties were characterized, and the decoloration kinetics was studied as well.

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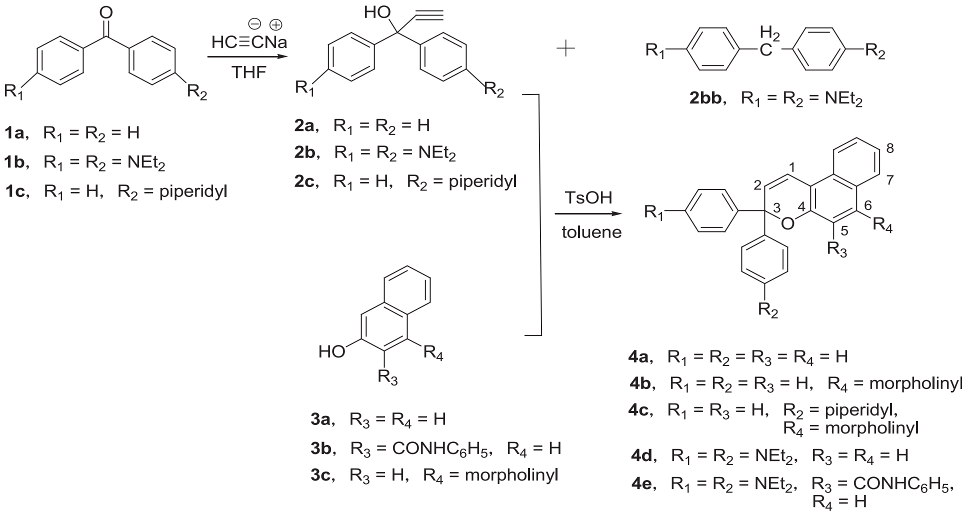


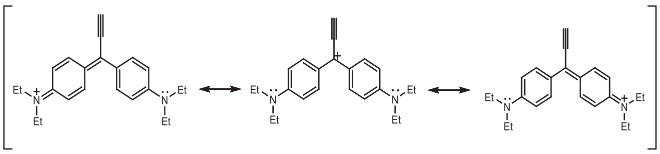
Scheme 1. Preparation of the 3,3-diaryl-3*H*-naphtho[2,1-b]pyran compounds.

2. Results and discussion

2.1. Synthesis and structures

The preparation of the 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran compounds as outlined in Scheme 1, With the purpose of enhancement of the color density, the benzophenone was replaced by 4,4′-bis(diethylamino)benzophenone (**1b**) at the case of **2b**, which having diethylamino groups at the *para* positions of both phenyl moieties. Interestingly, 4,4′-bis(diethylamino)diphenylmethane (**2bb**) was identified as a minor amount of byproduct as well as the principal intermediate product of propargyl alcohol (**2b**) in the reaction mixture using analysis methods of ESI-MS and HR-ESIMS (**2bb**, calcd for $C_{21}H_{31}N_2$, 311.2482, found 311.2486.), which might result from reduction of 4,4′-bis(diethylamino)benzophenone (**1b**) with sodium acetylide, perhaps in a similar way of reduction using $LiAlH_4$.[21]

A carbocation generated by the protonation of the propynol and following loss of water acts as an important intermediate to interact with 2-naphthol, then continues to undergo the Claisen rearrangement, tautomerisation to the allenyl naphthol, a 1,5-hydrogen shift and finally a 6p electrocyclisation to complete the sequence to afford the 3*H*-naphtho[2,1-*b*]pyran.[22] The yields of **4d** and **4e** were relatively low, which may be explained by the resonance-stabilized carbocation affected by diethylamino groups at the *para* positions of the phenyl groups. Obviously, the positive charge was delocalized throughout the resonance system, which extended by p−π conjugation (Scheme 2), and the selectivity of the reaction was decreased when reaction with 2-naphthol and then led to the low yield.



Scheme 2. The resonance of carbocation stabilized by electron donating substituted amino groups.

The X-ray crystal analysis was a good tool to investigate the effect of substitutes on the geometrical configuration and thus the single crystal of **4b** among the naphthopyran compounds was fortunately obtained by slow evaporation of the solvent. The molecular configuration was shown in Fig. 1 and the two phenyl groups substituted at the spiro carbon atom were repelling to both sides of the naphthopyran plane, which indicated an unconjugation relationship of them and assured the colorless state of naphthopyran compound in the closed form. On the other hand, it would prevent the intermolecular π−π interaction, which often leading to the compact stacking and poor solubility in solvents or polymer matrix. The morpholinyl group was directly substituted to the naphthalene backbone, which led to the p−π conjugation and therefore resulted in an enhanced hyperchromic effect with the value of ΔOD increasing to six times than that of **4a** (Table 1).

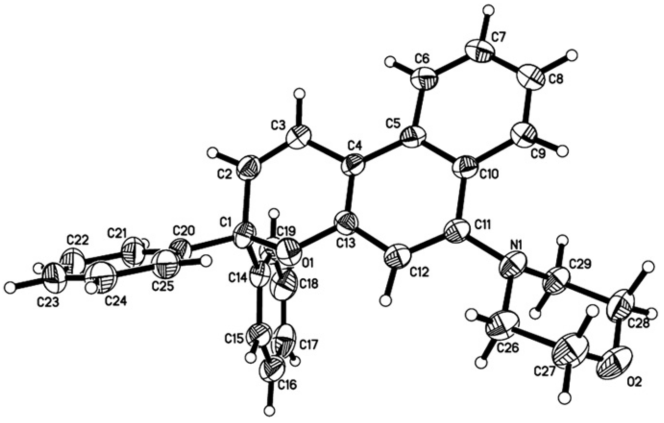


Fig. 1. The molecular configuration of **4b**.

Table 1
The photochromic characteristics of the colored (open) forms

Entry	λ_{max} (nm)	Colors	ΔOD	$\tau_{1/2}$ (min)
4a	430	Yellow	0.06	17
4b	420	Yellow	0.36	15
4c	490	Red	0.18	11
4d	580	Violet	0.01	6
4e	640	Blue	0.01	<1

In the molecular structure of naphthopyran compounds, the pyran ring did not fit into a perfect plane like the naphthalene plane and the rms deviation of fitted atoms from the least-squares plane was as large as 0.1307, which actually indicated as a non-aromatic ring but as the core unit for photochromism. The pyran ring of **4b**, as well as the bond lengths, were clarified and shown in Fig. 2. The bond length of O(1)–C(1) was measured as 1.456 Å, and O(1)–C(13) was 1.362 Å, which indicated the later one could be regarded as the double bond and the previous one as a single bond. Thus the weak bond of O(1)–C(1) was reasonably considered as the cleavable bond during the photochromic process. The bond length of C(2)–C(3) was 1.300 Å, which was a typical double bond and conjugated to the naphthalene plane. The angle of O(1)–C(1)–C(2) was measured as 109.7°, which indicated a typical sp^3 carbon structure for C(1) and drove the C(2)–C(1) bond stretching outside from the main π conjugation plane of the molecule.

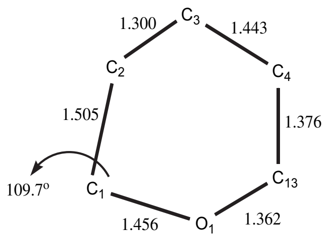
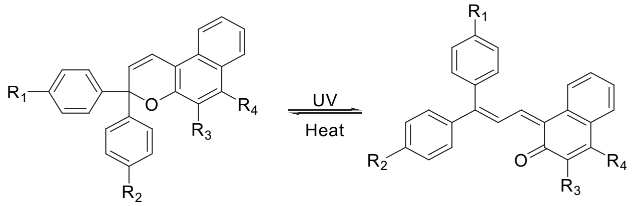


Fig. 2. The clarified structure of the pyran ring in **4b**.

2.2. The photochromic properties

In the reversible transformation upon exposure to UV radiation (Scheme 3), the derivatives of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran compounds indicated the typical absorption peaks in the visible area like **4c** shown in Fig. 3, and their photochromic characteristics of the colored forms (open forms) were listed in Table 1. From the wavelengths of the absorption maximum of **4d** and **4e**'s colored forms in the visible area, the electron donating groups at the *para* positions of both 3-phenyls gives a much bigger bathochromic shift than those derivatives, which had substitutes on the naphthalene, and this kind of shift seems additive. Interestingly, the electron donating group, such as morpholinyl at the 6-position on the naphthalene (**4b**) led to a minor hypsochromic rather than bathochromic shift, but the color density was still found to be enhanced at the same case. However, the changes of color density (ΔOD) of **4d** and **4e** were really low and the initial color densities were high, which limit their practical application. From the data of the $\tau_{1/2}$ of the colored forms, the fading speeds were increased by introduction of the electron donating groups not only at the *para* positions of 3-phenyl, but also on the naphthalene.



Scheme 3. The reversible transformation upon exposure to UV radiation.

2.3. The decoloration kinetics

The colored form reverting back to the thermodynamically stable closed form, with a decay kinetics strongly dependent on the environment and kinetics in solid media is normally quite complex due to the rigidity of the environment.[23] Fig. 4 presented the first-order plots for the decoloration of **4a**, **4b**, and **4c** in PS coating at room temperature and the kinetic behaviors of all three PS coatings indicated the obvious deviation from the monoexponential decay kinetics. It could be clearly seen that the decoloration was largely retarded by the PS matrix and was by no means a first-order reaction. This is because the high rigidity of the polymer matrix greatly restricted the degrees of freedom of the dye molecules at room temperature, whereas the glass transition temperature (T_g) of the polymer was measured as high as 107 °C.

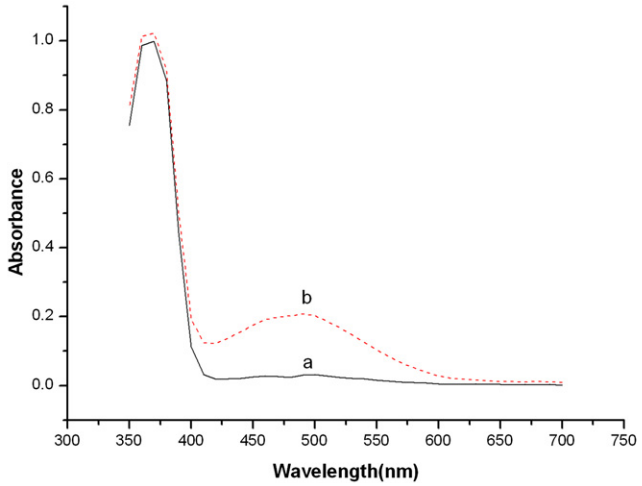


Fig. 3. The absorption spectra of **4c** doped PS film in dark (a) and irradiated by UV light (b).

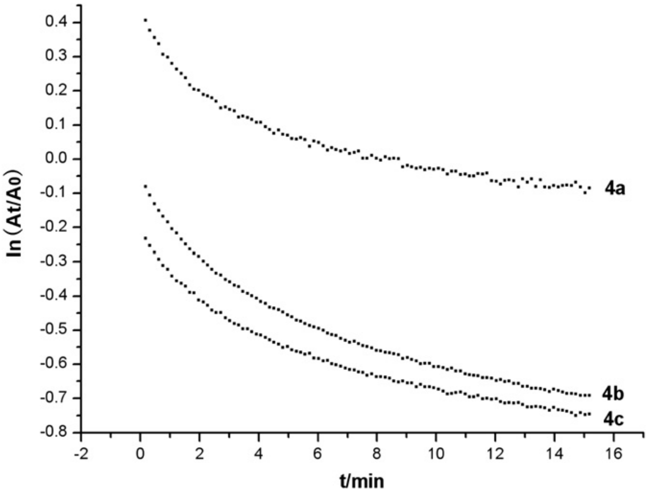


Fig. 4. First-order plots for the decay of colored forms in PS film.

The origins for the non-monoexponential decay kinetics could be described by a kinetic model taking into account the simultaneous relaxation of the matrix and the colored form of the compound,[24] and a biexponential model was used for analyzing the kinetic data of the thermal back reaction, which had been applied to the spirooxazine-doped organically modified doped gels by Boilot and co-workers.[25] The basic assumption of the model is that the distribution of rate constants, *k*, is due to a normal distribution of free energies. In this case, the thermal ring closure of the compound was described by the following equation:

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$$

where $A(t)$ is the optical density at the wavelength of the absorption maximum and A_1 and A_2 are contributions to the initial optical density A_0, A_{th} reflects the thermal equilibrium between the two forms, and k_1, k_2 are kinetic constants.

In our study of the PS coatings doped by **4a**, **4b**, and **4c**, the decay kinetics of colored forms indicated the excellent agreement between this biexponential model and the experimental data, and the agreement of thermal decoloration of **4c** doped PS coating was shown as an example in Fig. 5. Table 2 presented constant values deduced from the fit of the experimental data of the **4a**, **4b**, and **4c** doped PS coating samples by using biexponential process. The kinetic constants of k_1 and k_2 were obtained in range of 0.74 ~ 0.96 and 0.13 ~ 0.16, respectively. From the viewpoint of the distribution of free volume, the separated constants k_1 and k_2 were thus understood as empirical mean values of 'the fast' and 'the slow' kinetic constants, which represented by different degrees of freedom for the colored molecule restricted by the rigid polymer matrix. The contribution of two different dynamic paths were approximately evaluated using the values of the A_1/A_2 ratio in range of 0.44 ~ 0.58 for the three samples, which might be considered that the slow kinetics was relatively predominant dynamic path in the decoloration process. Thus, the shrinking cage around the trapped molecules rendered the thermal ring closure more difficult and less effect of substitutes on the fading kinetics was observed in PS matrices.

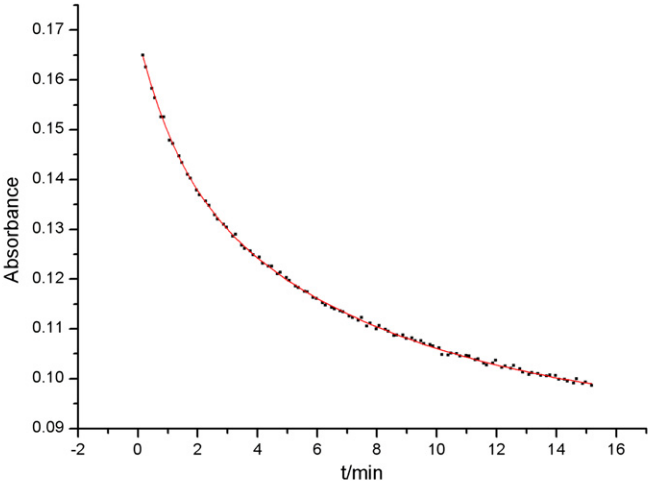


Fig. 5. The biexponential model and the experimental thermal decoloration of **4c** doped PS film (····: data measured; —: the biexponential model fitted).

Table 2
The parameters of fitted biexponential models for **4a**, **4b**, and **4c** in PS film

Entry	Fast path		Slow path		A_1/A_2	A_{th}
	k_1/min^{-1}	$\tau_{1/2}$/min	k_2/min^{-1}	$\tau_{1/2}$/min		
4a	0.96	0.7	0.16	4.3	0.58	0.056
4b	0.77	0.9	0.14	5.0	0.44	0.182
4c	0.74	0.9	0.13	5.3	0.46	0.092

3. Conclusion

Five photochromic naphthopyran compounds with functional substituents were prepared. The chemical structures of the compounds were confirmed by NMR and MS. The crystal structure of 3,3-diphenyl-6-morpholinyl-3*H*-naphtho[2,1-*b*]pyran (**4b**) was determined and the relationship between the pyran structure and photochromism was discussed. **4c**, **4d**, and **4e** showed significant bathochromic shifts in the spectra of the open forms. Among them, **4b** was considered to be the best one due to the large ΔOD of colored forms. The decoloration kinetics of colored forms of the **4a**, **4b**, and **4c** doped in PS coating were fitted to the biexponential model.

4. Experiment

4.1. General

All chemicals were commercial available. NMR spectra were recorded on a Mercury plus 400 instrument (Varian) for solutions in $CDCl_3$ unless otherwise stated using $(CH_3)_4Si$ as an internal standard, and *J* values are given in Hertz. LC–MS was performed on an HP 1100 HPLC (Agilent), interfaced with a triple–quadruple mass spectrometer equipped with an ESI or EI ion source and an in-line diode-array UV–vis detector. HRMS were recorded on a MAT95XP instrument (Thermo).

4.2. Preparation of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans (4), general procedure

Preparation methods of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans were generally based on condensation reactions taking place in the apolar solvent as toluene under acid catalysis, which starting from suitable naphthols and propargyl alcohols.[26–28]

The propargyl alcohol (**2**) was prepared from the diaryl ketone (**1**) as outlined in Scheme 1. 10 mmol diaryl ketone (**1**) was dissolved in 50 mL dry THF and was added dropwise to a solution of 50 mmol sodium acetylide in THF below 0 °C. The mixture was then allowed to stir at room temperature for about 3 h until none of the diaryl ketone (**1**) remained by TLC examination of the reaction mixture. The reaction mixture was poured into iced water for separation. The organic phase was collected and followed by washing with water (3×50 mL) and then dried (anhyd Na_2SO_4). The propargyl alcohol was then obtained in the yield of about 80% after the short flash chromatography and was used for subsequent procedure directly.[27]

3 mmol propargyl alcohol (**2**), 3 mmol 2-naphthol derivative (**3**), and 1.0 g *p*-toluenesulfonic acid (TsOH) were dissolved in 50 mL toluene. The reaction mixture was refluxed for about 2 h until TLC examination indicated that none of the propargyl alcohol remained. The mixture was cooled to room temperature and washed with 1 mol L^{-1} NaOH solution (2×50 mL) and water. After drying with anhyd Na_2SO_4, removal of the toluene by vacuum evaporation gave a dark gum. The pure naphthopyran product was obtained by elution from silica using 10% ethyl acetate/hexane. The following naphthopyrans were prepared using this method:

*4.2.1. 3,3-Diphenyl-3H-naphtho[2,1-b]pyran (**4a**).* Compound **4a** was prepared from **2a** and **3c** as the white microcrystal, (0.75 g, 75% yield), mp 158–160 °C (Lit. mp 158–159 °C[28]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J*=7.6 Hz, 1H), 7.76–7.80 (t, *J*=8.0 Hz, 2H), 7.47 (m, 6H), 7.29–7.36 (m, 6H), 7.23 (m, 2H), 6.58 (d, *J*=10 Hz, 2H); ESI-MS (*m*/*z*): 334.2 (M+1).

*4.2.2. 3,3-Diphenyl-6-morpholino-3H-naphtho[2,1-b]pyran (**4b**).* Compound **4b** was prepared from **2a** and **3c** as the light yellow microcrystal, (0.74 g, 59% yield), mp 156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J*=8.8 Hz, 1H), 7.94 (d, *J*=8.0 Hz, 1H), 7.42–7.50 (m, 2H), 7.24–7.30 (m, 10H), 7.24 (d, *J*=2.8 Hz, 1H), 6.83 (s, 1H), 6.20 (d, *J*=10.0 Hz, 1H), 3.95 (t, *J*=5.2 Hz, 4H), 3.09 (t, *J*=4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 151.1, 145.2, 131.2, 128.3, 127.7, 127.2, 126.9, 125.9, 124.7, 124.1, 123.3, 122.1, 119.6, 110.1, 107.7, 82.9, 67.5, 53.6; ESI-MS (*m*/*z*): 420.1 (M+H); HR-EIMS calcd for $C_{29}H_{25}NO_2$, 419.1885, found 419.1884.

Slow evaporation of ethyl acetate solution of **4b** gave crystals after several days. The single crystal was collected by filtration and used in the X-ray crystal analysis. X-ray diffraction data were collected at 293 K on a CAD4 DIFFACTIS 586 diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å), μ=0.080 mm^{-1}. Crystal data for **4b**: $C_{29}H_{25}NO_2$, monoclinic, space group P2$_1$/c, *a*=16.110(5) Å, *b*=6.511(2) Å, *c*=23.934(6) Å, β=119.984(15)°, Volume=2174.5(11) Å^3, *Z*=4, D_{calcd}=1.281 Mg/m^3, 10099 reflections collected, 4677 reflections independent, *R*(int)=0.0919, 1874 observed reflections (>2σ), R_1=0.1297 [$F^2>2\sigma(F^2)$], ωR_2=0.1591 (all data). The crystal structure was solved and refined with standard techniques.[29] All U values of H-atoms were refined to realistic values. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC804456.

*4.2.3. 3-(4-Piperidinophenyl)-3-phenyl–6-morpholino-3H-naphtho-[2,1-b]pyran, (**4c**).* Compound **4c** was prepared from **2c** and **3c** as the light orange microcrystal, 0.77 g, 51% yield, mp 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J=6.4 Hz, 1H), 7.20–7.60 (m, 8H), 7.02 (d, J=8 Hz, 1H), 6.80 (d, J=6 Hz, 1H), 6.14 (s, 1H), 6.10 (s, 1H), 3.96 (t, J=10 Hz, 4H), 2.22 (t, J=8 Hz, 8H), 1.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 151.1, 146.2, 131.2, 128.3, 127.5, 127.1, 126.9, 126.6, 124.6, 124.1, 123.3, 122.4, 119.1, 116.0, 110.2, 83.1, 67.5, 54.0, 50.4, 26.0, 24.2; ESI-MS (m/z): 503.2 (M+H); HR-ESIMS calcd for $C_{34}H_{35}N_2O_2$, 503.2699, found 503.2697.

*4.2.4. 3,3-Di(4-diethylaminophenyl)-3H-naphtho[2,1-b]pyran, (**4d**).* Compound **4d** was prepared from **2b** and **3a** as the light green solid, 0.25 g, 18%, yield, mp 193–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J=6.4 Hz, 1H), 7.59–7.72 (m, 5H), 7.10–7.25 (m, 8H), 6.58 (d, J=8 Hz, 1H), 6.24 (d, J=8.8 Hz, 1H), 3.31 (m, 8H), 1.12 (t, J=4.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 147.3, 132.2, 130.1, 129.9, 129.2, 129.0, 128.2, 126.3, 122.2, 121.5, 114.0, 112.3, 111.2, 82.6, 77.1, 44.6, 12.8; ESI-MS (m/z): 477.3 (M+H); HR-ESIMS calcd for $C_{33}H_{37}N_2O$, 477.2906, Found 477.2900.

*4.2.5. 3,3-Di(4-diethylaminophenyl)-5-(N-phenylamido-3H-naphtho [2,1-b]pyran), (**4e**).* Compound **4e** was prepared from **2b** and **3b** as the light blue microcrystal, 0.21 g, 12%, yield, mp 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.98 (s, 1H), 7.30–7.60 (m, 5H), 7.22 (m, 4H), 7.05 (m, 8H), 6.60 (d, J=10 Hz, 1H), 6.32 (d, J=10 Hz, 1H), 3.30 (m,8H), 1.12 (t, J=8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 148.2, 132.9, 132.4, 131.8, 130.7, 129.9, 129.2, 129.1, 128.1, 124.2, 124.0, 122.0, 121.6, 121.0, 118.9, 111.4, 77.1, 44.5, 12.5; ESI-MS (m/z): 596.3 (M+H); HR-ESIMS calcd for $C_{40}H_{42}N_3O_2$, 596.3272, found 596.3264.

*4.2.6. 4-(4-(Diethylamino)benzyl)-N,N-diethylbenzenamine, (**2bb**).* The byproduct of the less polar fraction during preparation of **2b** from **1b**, brown oil, 0.11 g, 3%, yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J=8 Hz, 4H), 6.50 (d, J=8 Hz, 4H), 3.80 (s, 2H), 3.31 (m, 8H), 1.15 (t, J=6 Hz, 12H); ESI-MS (m/z): 311.2 (M+H); HR-ESIMS, calcd for $C_{21}H_{31}N_2$, 311.2482, found: 311.2486.

4.3. Preparation of polymer films doped by the photochromic compounds

The polystyrene (PS) with the T_g of 107 °C and the photochromic compounds were weighted and dissolved in toluene. The solution was placed on a glass slide in horizontal and the solvent was allowed to evaporate overnight at room temperature. Then the film was removed from the glass slide and the film thickness was measured with a micrometer. The thickness of the film was kept about 10 μm by controlling the solution used, and the concentrations of the photochromic compounds in the polymer film were maintained in 0.1% w/w.

4.4. The spectral and kinetic measurements

The spectral and kinetic measurements were performed in doped polymer films using a TU1901 UV–vis spectrophotometer (PG Instruments Limited) coupled with flash photolysis and the film was placed in a holder room temperature. The photochromic optical density ΔOD is defined as the change of absorbance (A) at the photostationary state under UV irradiation (8 W lamp, 365 nm). The decoloration rate (k) and half-life time ($\tau_{1/2}$) were deduced from the coloring-fading curve.

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