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PAPER

Rapid fading of 3*H*-naphtho[2,1-*b*]pyrans with protonation of *N*,*N*-disubstituted group

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We present the rapid fading of photochromic 3*H*-naphtho[2,1-*b*]pyrans at ambient temperature by protonation of *N*,*N*-disubstituted group. It is found that photochromic 3*H*-naphtho[2,1-*b*]pyrans with a *N*,*N*-disubstituted group are converted to protonated 3*H*-naphtho[2,1-*b*]pyran by treatment with acid, and the protonated 3*H*-naphtho[2,1-*b*]pyrans show rapid fading in both solution and a rigid polymer matrix at ambient temperature. It is also found that the protonated 3*H*-naphtho[2,1-*b*]pyrans exhibit similar absorption and fatigue resistance compared to their original compounds.

Introduction

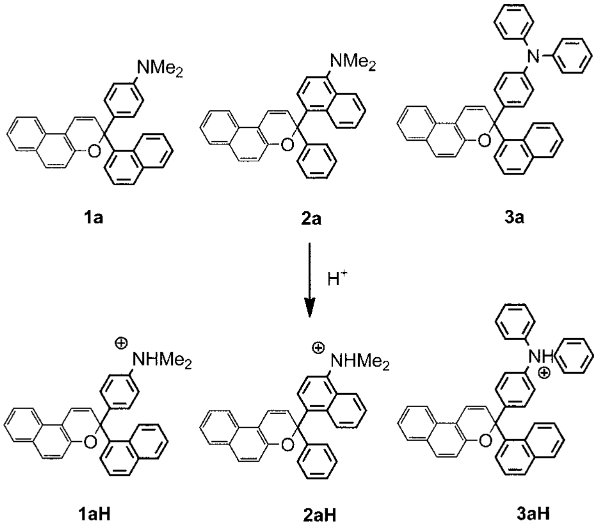
Photochromic naphthopyrans with rapid fade at ambient temperature are of great importance with regards to commercial application used as ophthalmic lenses.[1–8] Consequently, a variety of strategies have been employed to achieve this purpose. There are two strategies extensively explored for enhancement of fading speed of naphthopyrans at ambient temperature, one is to modify the intrinsic properties of molecules including electronic nature of substituents and structure of naphthopyrans,[9–11] the other is to change the local host environment and the media that incorporate them.[12–15]

One of the major interests in our group has focused on developing new strategy for increasing fading speed of naphthopyrans at ambient temperature. In our previous studies,[16,17] we found that 3*H*-naphtho[2,1-*b*]pyrans containing *N*,*N*-disubstituted group in the *para* position of aryl ring at 3-position showed faster fade than that of 3*H*-naphtho[2,1-*b*]pyrans without *N*,*N*-disubstituted group at ambient temperature. Herein we disclose the first example of increasing the fading speed of 3*H*-naphtho[2,1-*b*]pyrans by protonation of *N*,*N*-disubstituted group in the *para* position of aryl ring at 3-position at ambient temperature. As illustrated in Scheme 1, 3*H*-naphtho[2,1-*b*]pyrans containing *N*,*N*-disubstituted group (**1a–3a**) are easily converted to protonated 3*H*-naphtho[2,1-*b*]pyrans (**1aH–3aH**) by protonation of *N*,*N*-disubstituent group with acid. It is found that the protonated 3*H*-naphtho[2,1-*b*]pyrans exhibit photochromism in both solution and a rigid polymer matrix, and the fading speed of steady-state is significantly increased at ambient temperature in comparison to the original compounds. Moreover, it is also found that the protonated naphthopyrans show similar absorption properties and fatigue resistance to their original compounds in solution as well as in rigid polymer matrix, which provides a new strategy for increasing the fading speed of 3*H*-naphtho[2,1-*b*]pyrans at ambient temperature without changing their absorption and fatigue resistance.

Experimental

General

^{1}H NMR spectra were recorded at 400 MHz with tetramethylsilane (TMS) as an internal reference and $CDCl_3$ as solvent. Mass spectra were recorded with a GC–TOF MS spectrometer. UV absorption spectra were measured on an absorption spectrophotometer (Hitachi U-3010). Coloration was carried out



Scheme 1 Protonated 3*H*-naphtho[2,1-*b*]pyrans **1aH–3aH** resulted from the protonation of 3*H*-naphtho[2,1-b]pyrans **1a–3a** by treatment with acid.

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with a UV light (λ = 254 nm, intensity: 4.3 mW cm^{-2}). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reactions were monitored by TLC silica gel plate 60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). PMMA thin film was prepared as following: naphthopyrans (1.0 mg) was dissolved in 2.0 ml PMMA–cyclohexanone solution (10%, w/w). The film was obtained by spin coating on quartz glass with a gradient of 700 rpm (10 s) followed 1200 rpm (30 s) (25 °C) and dried in air and kept in the darkness at room temperature. The concentration of thin film is about 1.2×10^{-5} mol/g.

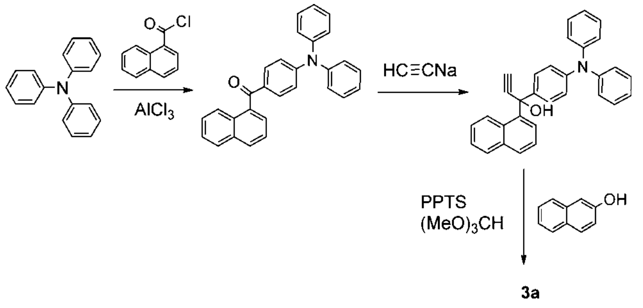
Material

Naphthopyrans **1a**[18] and **2a**[17] were prepared previously in our laboratory, and **3a** was prepared according to the synthetic route described in Scheme 2 and the detailed procedures were according to the literature[19] which summarized as follows: 1,2-Diaryl-2-ol was synthesized by starting from 1-naphthoyl chloride, which reacted with *N*,*N*-diphenylaniline by Friedel–Crafts reaction to afford 1,1-diarylketone, followed by treatment with soldium acetylide in an ether solvent at ambient temperature. The target compound **3a** was obtained by the condensation of 1,2-diaryl-2-propyn-1-ol with 2-naphthol in the presence of pyridinium *para*-toluenesulfonate (PPTS) as the catalyst. The general procedure is as follows: treatment of 1,2-diaryl-2-propyn-1-ol (1.1 equiv) and 2-naphthol in 1,2-dichloroethane with 2 equivalent of $(MeO)_3CH$ and 5 mol % PPTS (pyridinium *para*-toluensulfonate) furnished the desired product.

1a: Total yield: 28%. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.31 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 8.9 Hz, 1H), 7.46–7.44 (t, J = 3.7, 3.8 Hz, 1H), 7.39–7.36 (m, 2H), 7.34–7.30 (m, 5H), 7.12 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 8.9 Hz, 2H), 6.31 (d, J = 9.9 Hz, 1H), 2.91 (s, 6H). HRMS: m/z (M^+ + 1): 428.2.

2a: Total yield: 38%. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.32 (d, J = 8.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.54–7.27 (m, 11H), 7.10 (d, J = 8.8 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 9.9 Hz, 1H), 2.85 (s, 6H). MS: m/z [M^+ + 1]: 428.4.

3a: Total yield: 30%. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.36 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.84–7.69 (m, 4H), 7.60 (d, J = 8.9 Hz, 1H), 7.50–7.30 (m, 8H), 7.22 (dd, J = 8.3, 7.5 Hz, 4H), 7.09 (dd, J = 14.5, 8.2 Hz, 5H), 6.99 (t, J = 7.9 Hz, 4H), 6.29 (d, J = 9.9 Hz, 1H). HRMS: m/z (M^+): 551.22.



Scheme 2 Synthesis of **3a**.

Protonated compounds **1aH–3aH** were prepared as follows: To solution of **1a–3a** (10 mmol) in CH_2Cl_2 (10 ml) was added CF_3COOH (1.2 mmol), the mixture solution was stirred at room temperature for 10 min in the dark. The target compound **1aH–3aH** were obtained after evaporation of the solvent under reduced pressure without further purification.

1aH: ^1H NMR (400 MHz, $CDCl_3$, δ): 8.21 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.82 (t, J = 8.9 Hz, 2H), 7.66 (ddd, J = 22.9, 14.8, 8.5 Hz, 5H), 7.54–7.31 (m, 8H), 7.09 (d, J = 8.8 Hz, 1H), 3.19 (s, 6H). HRMS: 427.955.

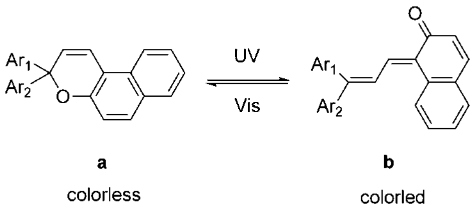
2aH: ^1H NMR (400 MHz, $CDCl_3$, δ): 8.45 (d, J = 8.7 Hz, 1H), 8.27 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.72 (d, (d, J = 8.2 Hz, 1H), 7.60 (t, J = 8.9, 8.8 Hz, 1H), 7.62 (d, J = 8.9 Hz, 1H), 7.50–7.34 (m, 10H), 7.07 (d, J = 8.8 Hz, 1H), 6.17 (d, J = 3.7 Hz, 1H), 3.40 (s, 6H).

3aH: ^1H NMR (400 MHz, $CDCl_3$, δ): 8.37 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.8 Hz, 1H), 7.48–7.31 (m, 8H), 7.22 (t, J = 8.3, 8.1 Hz, 4H), 7.08–7.06 (m, 5H), 6.99–6.97 (m, 4H), 6.30 (d, J = 9.9 Hz, 1H).

Results and discussion

Treatment of naphthopyrans **1a–3a** with CF_3COOH in CH_2Cl_2 yielded protonated naphthopyrans **1aH–3aH** in quantitativity, and their structures were characterized by ^1H NMR spectra. As it is known,[20–22] the signals arising from the protons of *N*,*N*-disubstituted groups shift downfield, and the signals arising from the protons of benzene ring shift upfield when *N*,*N*-disubstituted groups are protonated. As compared to **1a**, the signals arising from the protons of *N*,*N*-disubstituted groups of **1aH** shifted downfield from 2.91 ppm to 3.19 ppm, and the signals arising from the protons of benzene ring of **1aH** shifted upfield from 8.31 ppm to 8.21 ppm. Similar results were obtained with compounds **2aH** and **3aH**.

All protonated compounds **1aH–3aH** showed photochromism in both solution and PMMA thin film. The ring-opening and ring-closing isomerization was illustrated in Scheme 3,[23,24] and their absorption data were presented in Table 1. By comparison with the absorption of naphthopyrans **1b–3b**, it was found that the absorption spectral of protonated naphthopyrans **1bH–3bH** showed similar profile to these of **1b–3b** in both solution and in PMMA thin film (Fig. 1), and no significant change was detected except for optical density (O.D.). As presented in Table 1, it was found that the optical density of **1bH** (O.D.[a] = 0.390) is much smaller than that of **1b** (O.D.[a] = 0.577) in the solution at



Scheme 3 Photochromism of **1a–3a** and **1aH–3aH** in both solution and in PMMA thin film.

Table 1 Absorption data of **1b–3b** and **1bH–3bH** in both solution (CH_3CN, 2×10^{-5} M) and in PMMA thin film (1.2×10^{-5} mol g^{-1})

Compound	Media	λ_{max} (nm)	O. D.[a]	O. D.[b]
1b	Solution	542	0.577	0.640
	Film	550	1.074	1.074
1bH	Solution	542	0.390	0.553
	Film	550	0.832	0.832
2b	Solution	415	0.229	0.240
	Film	420	0.569	0.569
2bH	Solution	415	0.142	0.232
	Film	420	0.427	0.427
3b	Solution	518	0.525	0.531
	Film	526	0.714	0.714
3bH	Solution	518	0.375	0.526
	Film	526	0.60	0.60

[a] Optical density was measured by scanning the full absorption spectral (200–700 nm) at ambient temperature (15 °C). [b] Optical density was measured by detection of local maximum absorption (λ_{max}) at ambient temperature (15 °C).

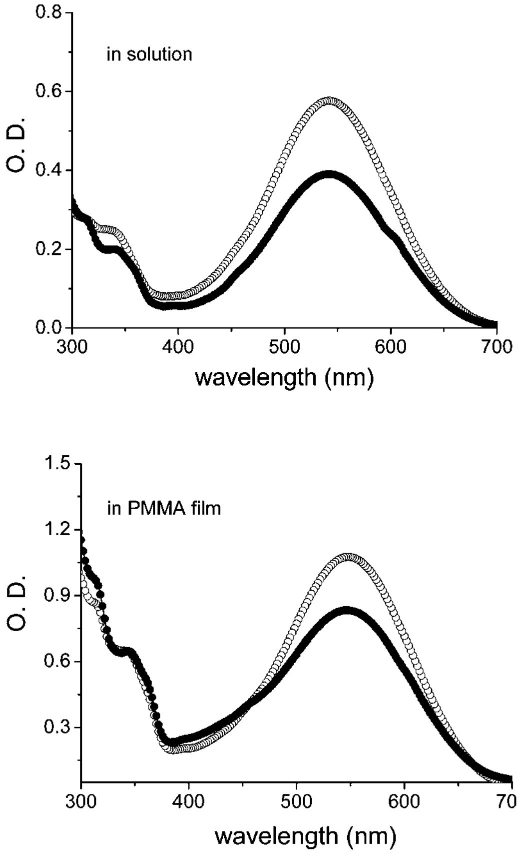


Fig. 1 Absorption of **1bH** (white) and **1b** (black) in solution (2×10^{-5} M, CH_3CN) and in PMMA thin film (1.2×10^{-5} mol g^{-1}) at photo-steady state.

photo-steady state, and similar results were obtained by comparison of **2bH** and **3bH** with **2b** and **3b**. The large decrease in optical density of **1bH** is probably due to faster fade of **1bH** than that of **1b** at ambient temperature, and time consumption of scanning absorption spectrum results in the decrease of optical density. The suggestion was confirmed by the control experiments. As presented in Table 1, a little small decrease of optical density of **1bH** (O. D.^{b} = 0.553) was obtained as compared to **1b** (O.D.^{b} = 0.577) when optical density was detected at local wavelength (λ_{max}). Similarly, a small decrease in optical density of **1bH–3bH** was also obtained in PMMA thin film as compared to their original compounds **1b–3b** due to slower fading speed in a rigid polymer matrix than in solution at ambient temperature.

It is known[23] that the colored forms of naphthopyrans fade back to colorless forms *via* two steps: transoid-*cis* to colorless form (k_1) and transoid-*trans* to colorless form (k_2). Convenient measures of fade speed are the $T_{1/2}$ and $T_{3/4}$ values,[25] which are the time it takes from the optical density to reduce by 1/2 and 3/4 of the initial optical density of the colored form, and the smaller $T_{1/2}$ and $T_{3/4}$, the faster the fade. Table 2 represents the fading kinetics of **1bH–3bH** in both solution and PMMA thin film at ambient temperature. As compared to naphthopyrans **1b–3b**, the fading speed of protonated naphthopyrans **1bH–3bH** was much faster than that of **1b–3b** in both solution and in PMMA thin film. It was found that the fading time of **1bH** ($T_{1/2} = 8$ s, $T_{3/4} = 16$ s) is much shorter than that of **1b** ($T_{1/2} = 62$ s, $T_{3/4} = 220$ s), and only about 1/8 original fading time was obtained. Similar results were observed when the media was changed from solution to a rigid polymer. The fading time of **1bH** ($T_{1/2} = 24$ s, $T_{3/4} = 43$ s) was also much shorter than that of **1b** ($T_{1/2} = 70$ s and $T_{3/4} = 195$ s) in PMMA thin film. The data presented in Table 2 indicated that the protonated naphthopyrans show much faster fade than their original naphthopyrans in both solution and in a rigid polymer matrix.

The fading speed of protonated naphthopyrans **1bH–3bH** being much faster than that of naphthopyrans **1b–3b** was also confirmed by the fading rate constant. Comparing the kinetics of fading speed found that the fading rate constants of **1bH** (in solution: $k_1 = 6.0 \times 10^{-2}$ s^{-1}, in film: $k_1 = 2.3 \times 10^{-2}$ s^{-1}) are larger than these of **1b** (in solution: $k_1 = 0.92 \times 10^{-2}$ s^{-1}, in film: $k_1 = 0.8 \times 10^{-2}$ s^{-1}) in both solution and in PMMA thin film (Fig. 2), which resulted in the fading speed of **1bH** being much faster than that of **1b**. Similar results were obtained with other protonated naphthopyrans **2bH** and **3bH**, as compared to naphthopyrans **2b** and **3b**, the fading rate constants of **2bH** and **3bH** are much larger than these of **2b** and **3b**, respectively, in both solution and a rigid polymer matrix (Table 2).

Further investigation of protonated naphthopyrans **1bH–3bH** being faster fade than that of **1b–3b** at ambient temperature was explored. Control experiments found that **1bH–3bH** showed more thermal instablity than that of **1b–3b** at ambient temperature. As presented in Fig. 3, it took about 20 min for **1bH** to completely bleach to colorless in PMMA thin film at 20 °C, but it took 80 min for **1b** to bleach to colorless under the same conditions. The time for completed bleach of both is shortened with raising the temperature, and it was found that the bleach time is almost the same (less than 1 min) when the temperature is over 70 °C. It was noted that different results were obtained when both the protonated compounds **1bH–3bH** and their original compounds **1b–3b** were bleached with visible light irradiation, as presented in Fig. 4, the fading rate constant of **1bH** ($k_1 = 5.1 \times 10^{-2}$ s^{-1}) is smaller than that of **1b** ($k_1 = 7.6 \times 10^{-2}$ s^{-1}) in the same conditions with visible light irradiation, which is contrary to that with thermal bleach. In addition, control experiments also

Table 2 Kinetics data of **1b–3b** and **1bH–3bH** in both solution (CH_3CN, 2 × 10^{-5} M) and in PMMA thin film (1.2 × 10^{-5} mol g^{-1})

Compound	Media	λ_{max}/nm	O. D.[c]	[a]$T_{1/2}$ (s)	[a]$T_{3/4}$ (s)	[b]K_1 (× 10^{-2})	[b]K_2 (× 10^{-4})
1b	Solution	542	0.640	62	220	0.9	1.8
	Film	550	1.074	70	195	0.8	2.0
1bH	Solution	542	0.553	8	16	6.0	7.2
	Film	550	0.832	24	43	2.3	2.9
2b	Solution	415	0.240	58	135	1.0	4.5
	Film	420	0.569	64	162	0.9	4.6
2bH	Solution	415	0.232	7	15	6.4	4.1
	Film	420	0.427	14	32	4.0	2.8
3b	Solution	518	0.531	110	238	0.6	1.1
	Film	526	0.714	420	1230	0.2	0.7
3bH	Solution	518	0.526	31	61	2.2	1.9
	Film	526	0.60	115	350	0.5	3.2

[a] Samples initially irradiated at 254 nm till photo-steady state (40 s), then thermal decoloration monitored at λ_{max} of the colored form at room temperature in the dark. [b] The fading rate constant was obtained using the biexponetial decoloration model according to the standard biexponential equation.[26,27] [c] The optical density was obtained by measuring the local maximum wavelength at ambient temperature (15 °C).

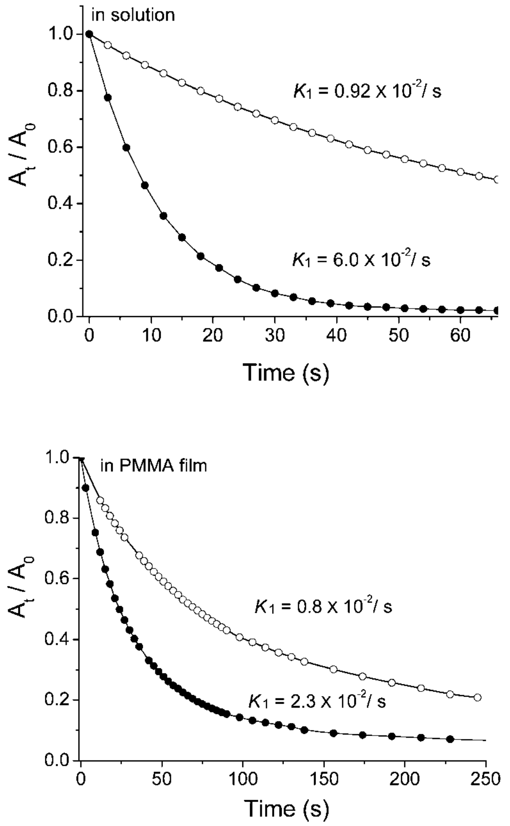


Fig. 2 The fading kinetics of **1bH** (black) and **1b** (white) in both solution (CH_3CN) and PMMA thin film at ambient temperature (15 °C).

confirmed that the protonation of naphthopyran with amino group also produced the protonated compound **4aH** (Scheme 4), whose fading speed was also increased significantly in both solution (**4a**: $k_1 = 1.3 \times 10^{-2}$ s^{-1}, **4aH**: $k_1 = 2.1 \times 10^{-2}$ s^{-1}) and PMMA thin film (**4a**: $k_1 = 1.2 \times 10^{-2}$ s^{-1}, **4aH**: $k_1 = 1.8 \times 10^{-2}$ s^{-1}), but no significant change of fading speed was detected when naphthopyrans without amino substituent group such as **5a** and **6a** (Scheme 4) were treated with acid.

The preliminary investigation showed that the protonated naphthopyrans **1bH–3bH** exhibited similar fatigue resistance to

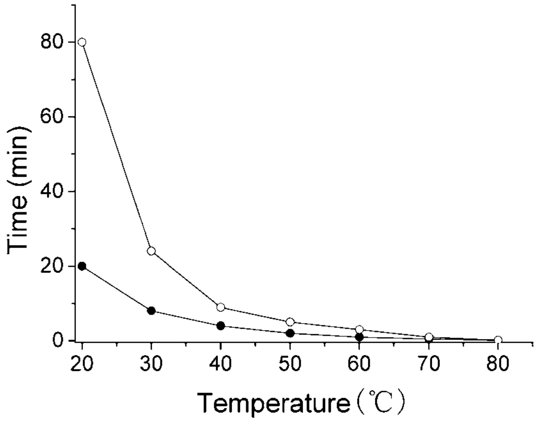


Fig. 3 The completed bleach of **1bH** (black) and **1b** (white) in PMMA thin film at different temperature.

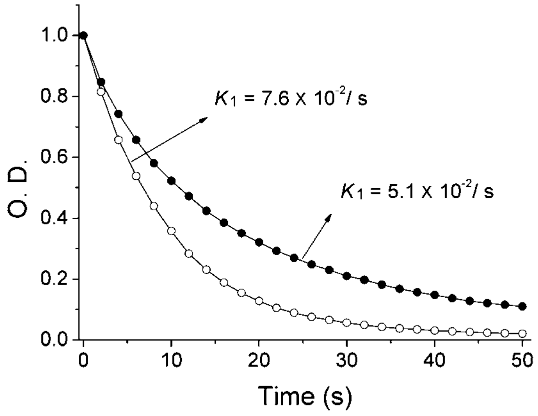
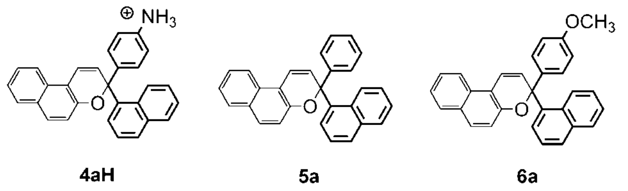


Fig. 4 The fading kinetics of **1bH** (black) and **1b** (white) in PMMA thin film with visible light irradiation (λ ≥ 400 nm).

1b–3b in both solution and a rigid polymer matrix. No significant degradation was detected after 5 cycles of coloration/decoloration when **1aH** was irradiated up to photosteady state (**1bH**) with UV light, and the colored **1bH** was completely bleached back (kept in the dark) to colorless (**1aH**) at ambient temperature



Scheme 4 Chemical structures of naphthopyrans **4a**, **4aH**, **5a** and **6a**.

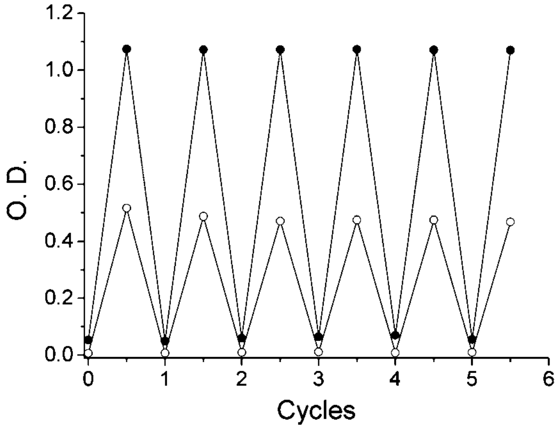


Fig. 5 The fatigue resistance of **1bH** in CH_3CN (white) and in PMMA thin film (black) (detecting optical denisty at $\lambda_{max} = 542$ nm in solution, and $\lambda_{max} = 550$ nm in PMMA thin film).

(Fig. 5). Similar results were obtained with other protonated naphthopyrans **2aH** and **3aH**. In addition, control experiments demonstrated that counter anion CF_3COO^- had no effect on the fading speed of naphthopyrans, and no significant change in fading speed of **1bH** was detected when CF_3COONa was added to the solution of **1a**. Furthermore, **1aH–3aH** could be obtained by treatment of **1a–3a** with other strong acids (acetic acid, 4-chlorobenzoic acid, 4-nitrobenzoic acid), and the protonated **1bH–3bH** also showed rapid fading speed at ambient temperature in both solution and a rigid polymer matrix.

Conclusion

A new strategy for increasing the fading speed of photochromic 3*H*-naphtho [2,1-*b*]pyrans with *N*,*N*-disubstituted groups has been developed. It has demonstrated that 3*H*-naphtho [2,1-*b*] pyrans with *N*,*N*-disubstituted groups can be converted to protonated naphthopyrans whose fading speed is increased significantly in both solution and in a rigid polymer matrix at ambient temperature. The protonated naphthopyrans shows similar absorption and fatigue resistance to their corresponding naphthopyrans, which provides a simple and efficient method for enhancing the fading speed of naphthopyrans without changing the color and fatigue resistance.

Acknowledgements

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Notes and references

1 M.-J. P. R. Queiroz, A. S. Abreu, P. M. T. Ferreira, M. Manuel Olievira, R. Dubest, J. Aubard and A. A. Samat, *Org. Lett.*, 2005, **7**, 4811.
2 J. N. Moorthy, P. Venkatakrishnan, S. Samanta and D. K. Kumar, *Org. Lett.*, 2007, **9**, 919.
3 W. Zhao and E. M. Carreira, *J. Am. Chem. Soc.*, 2002, **124**, 1582.
4 N. F. S. A. Cerqueria, A. M. F. Oliveria-Campos, P. J. Coelho, L. H. Melode Carvalho, A. Samat and R. Gugliemetti, *Helv. Chim. Acta*, 2002, **85**, 442.
5 B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington, D. A. Clarke and S. N. Corns, *WO*, 2001/12619A1, 2001.
6 D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington and S. N. Corns, *US Pat.*, 6 248 264 B241, 2001.
7 D. B. Knowles, *US Pat.*, 5384077, 1995.
8 B. Van Gemert, M. P. Bergomi, *US Pat.*, 5066818, 1991.
9 M. Frigoli, C. Moustrou, A. Samat and R. Guglielmetti, *Eur. J. Org. Chem.*, 2003, 2799.
10 W. Zhao and E. M. Carreira, *Chem.–Eur. J.*, 2007, **13**, 2671.
11 J.-L. Coelho, M. A. Salvador, M. Manuel Oliveira and L. M. Carvalho, *J. Photochem. Photobiol., A*, 2005, **172**, 300.
12 R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball and D. A. Lewis, *Nat. Mater.*, 2005, **41**, 249.
13 F. Ercole, N. Malic, S. Harrisson, T. P. Davis and R. A. Evans, *Macromolecules*, 2010, **43**, 249.
14 N. Malic, J. A. Campbell and R. A. Evans, *Macromolecules*, 2008, **41**, 1206.
15 F. Ercole, T. P. Davis and R. A. Evans, *Macromolecules*, 2009, **42**, 1500.
16 K. Guo and Y. Chen, *J. Mater. Chem.*, 2010, **20**, 4193.
17 S. Han and Y. Chen, *J. Mater. Chem.*, 2011, **21**, 4961.
18 K. Guo and Y. Chen, *J. Phys. Org. Chem.*, 2010, **23**, 207.
19 W. Zhao and E. M. Carreia, *Org. Lett.*, 2006, **8**, 99.
20 X. Meng, W. Zhu, Z. Guo, J. Wang and H. Tian, *Tetrahedron*, 2006, **62**, 9840.
21 K. Yang, L. P. Chen, Y. Q. Cai, N. Hiraoka, S. Li, J. F. Zhao, D. W. Shen, H. F. Song, H. Tian, L. H. Bai, Z. H. Chen, Z. G. Shuai and D. L. Feng, *Phys. Rev. Lett.*, 2007, **98**, 036404.
22 J. T. C. Wojtyk, A. Wasey, N.-N. Xiao, P. M. Kazmaier, S. Hoz, C. Yu, R. P. Lemieux and E. Buncel, *J. Phys. Chem. A*, 2007, **111**, 2511.
23 *Organic Photochromic and Thermochromic Compounds.* ed. J. C. Crano and R. J. Gugliemetti, Plenum Press, New York, 1999.
24 *Photochromism: Molecules and Systems*, ed. H. Duerr and H. Bouas-Laurent, Elsevier, Amsterdam, The Netherlands, 2003.
25 R. W. Walters and H. Van Gemert, *WO*, 2001/70719A2, 2001.
26 B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani and J. A. Delaire, *J. Mater. Chem.*, 1997, **7**, 61.
27 J. Hobley, U. Pfeifer-Fukumura, M. Bletz, T. Asahi, H. Masuhara and H. Fukumura, *J. Phys. Chem. A*, 2002, **106**, 2265.