Cite this: J. Mater. Chem., 2011, 21, 4961

www.rsc.org/materials

View Article Online / Journal Homepage / Table of Contents for this issue Dynamic Article Links

PAPER

Modification of a photochromic 3-aryl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*] pyran system with a fast fading speed in solution and in a rigid polymer matrix

Shulie Han and Yi Chen*

Received 11th January 2011, Accepted 26th January 2011 DOI: 10.1039/c1jm10139k

We have demonstrated that 3-aryl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*]pyrans photochromic system shows large optical density at photosteady state at ambient temperature. In this paper, we describe a strategy for modifying this photochromic system with a fast fading speed in both solution and in a rigid polymer matrix. It is found that the nature and position of the substituted groups attached to the aryl moiety at the 3-position play a key role in determining the fading speed of 3-aryl-3-(α naphthalene)-3*H*-naphtho[2,1-*b*]pyrans at ambient temperature. The fading speed of colored forms increase significantly when the electron-donating groups are attached to the *para*-position of aryl moieties at the 3-position. Further investigations find that (1) a strong electron-donating group is better than a weak electron-donating group for a fast fading speed, (2) an electron-donating group attached to the *para*-position of the naphthalene ring is better than one attached to the *para*-position of a benzene ring, and (3) with electron-donating groups at both *para*-positions of the naphthalene and benzene rings, the fading speed is dramatically increased in both solution and in the rigid polymer matrix.

Introduction

Organic photochromic materials have attracted considerable interest due to their color change upon irradiation with light.¹⁻³ In particular, thermally reversible photochromic molecules offer the opportunity to change and reset molecular properties by simply turning a light source on and off.⁴⁻⁷ Recently, novel photochromic molecules with instantaneous coloration upon exposure to UV light and rapid fading in the dark have attracted great attention for the development of optical switching devices, and a great progress has been achieved.⁸⁻¹¹

Photochromic naphthopyrans are being extensively explored for applications as optical switches^{12–16} and ophthalmic lenses,^{17–22} where a large steady-state optical density and rapid fading at ambient temperature is highly desired.^{23–26} It is known that photochromic 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans show thermal unstable colored forms at ambient temperature and rapidly fade back to a colorless form. Therefore, the optical density of colored forms is usually small at ambient temperature.^{27–30} The low optical density at ambient temperature is the main drawback of this system; therefore, the construction of a 3,3-diaryl-3*H*naphtho[2,1-*b*]pyran system with a large colored optical density and a rapid fading speed is crucial for their potential industrial applications. Recently, we reported³¹ that a 3*H*-naphtho[2,1-*b*] pyran bearing an α -naphthalene group at the 3-position (NPy) showed a large optical density at a photosteady state and a slow fading speed in both solution and in a rigid polymer matrix at ambient temperature by comparison with 3,3-diphenyl-3Hnaphtho[2,1-b]pyran (Py) in the same conditions (Scheme 1). In this paper, we extend our research on structure-photochromic activity relationships so as to develop a 3H-naphtho[2,1-b]pyranbased practical system with a large optical density at a photosteady state and a fast fading speed at ambient temperature. In terms of early reports^{32,33} and our previous findings³¹ that an electron-donating group in the para-position on the phenyl or naphthalene group of 3,3-diaryl-3H-naphtho[2,1-b]pyrans results in rapid fading, we have designed and prepared a class of 3-phenyl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*]pyrans with electron-donating groups in the para-position on both the benzene ring and the naphthalene ring as an extension of the 3H-naphtho [2,1-b]pyran system (Scheme 2). With such a system, a large optical density of the photosteady state and a fast fading speed were obtained in both solution and in a rigid polymer matrix at



Scheme 1 The structure of two 3-phenyl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*]pyrans.

Laboratory of Organic Optoelectronic Functional Materials and Molecular Engineering, Technical Institute of Physics and Chemistry, The Chinese Academy of Science, Beijing, 100190, China. E-mail: yichencas@yahoo. com.cn; Fax: +86 10 6487 9375; Tel: +86 10 8254 3595



Scheme 2 The structures of the target compounds.

ambient temperature, which provides a useful strategy for the design of 3H-naphtho[2,1-*b*]pyran-based naphthopyrans and benefits their future practical applications.

Experimental

General

¹H NMR spectra were recorded at 400 MHz with tetramethylsilane (TMS) as an internal reference and CDCl₃ as the solvent. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. UV absorption spectra were measured on an absorption spectrophotometer (Hitachi U-3010). Coloration was carried out with a UV light ($\lambda = 254 \text{ nm}$, 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 plates (60F-254). Column chromatography was performed on silica gel (Merck, 70-230 mesh). PMMA thin films were prepared as follows: the naphthopyran (1.0 mg) was dissolved in 1.0 mL of a PMMA-cyclohexanone solution (10%, w/w). A film was obtained by spin coating on quartz glass (diameter: 1.3 mm) with a gradient of 700 rpm (10 s), followed 1200 rpm (30 s) (25 °C), and dried in air and kept in the dark at room temperature. The concentration of the thin film was about 1.2×10^{-5} mol g⁻¹.

Material

Naphthopyrans **1a–6a** were synthesized according to the literature³⁴ using the synthetic method described in Scheme 3. The general procedure for their preparation is as follows. The treatment of the 1,2-diaryl-2-propyn-1-ol (1.1 equiv.) and β -naphthol



Scheme 3 Synthetic route to 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans.

(1.0 equiv.) in 1,2-dichloroethane with 2 equiv. of $(MeO)_3CH$ and 5 mol% PPTS (pyridinium *para*-toluensulfonate) furnished the desired product.

1a: Yield: 72%. ¹H NMR (400 MHz, CDCl₃, δ): 8.29 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.71–7.68 (m, 2H), 7.60 (d, J = 8.8 Hz, 1H), 7.47 (t, 1H), 7.41–7.31 (m, 7H), 7.11 (d, J = 8.8 Hz, 1H), 6.84–6.82 (m, 2H), 6.28 (d, J = 9.9 Hz, 1H), 3.76 (s, 3H). MS: m/z [M⁺]: 414. Anal. calc. for C₃₀H₂₂O₂: C, 86.93; H, 5.35. Found: C, 86.72; H, 5.49%.

2a: Yield: 28%. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.31$ (d, 1H, J = 8.6 Hz), 7.99 (d, 1H, J = 8.5 Hz), 7.82 (d, 1H, J = 8.0 Hz), 7.78 (d, 1H, J = 8.1 Hz), 7.60 (d, 2H, J = 7.6 Hz), 7.60 (d, 1H, J = 8.9 Hz), 7.46–7.44 (t, 1H, $J_1 = 3.7$ Hz, $J_2 = 3.8$ Hz), 7.39–7.36 (m, 2H), 7.34–7.30 (m, 5H), 7.12 (d, 1H, J = 8.8 Hz), 6.66 (d, 2H, J = 8.9 Hz), 6.31 (d, 1H, J = 9.9 Hz), 2.91 (s, 6H). HRMS: m/z [M⁺ + 1]: 428.2. Anal. calc. for C₃₁H₂₅NO: C, 87.09; H, 5.89. Found: C, 87.48; H, 5.80%.

3a: Yield: 76%. ¹H NMR (400 MHz, CDCl₃, δ): 8.27 (dd, J_1 = 8.3 Hz, J_2 = 7.3 Hz, 2H), 8.01 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.59 (dd, J_1 = 8.1 Hz, J_1 = 8.8 Hz, 2H), 7.51–7.45 (m, 3H), 7.46–7.24 (m, 7H), 7.10 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 6.21 (d, J = 9.9 Hz, 1H), 3.95 (s, 3H). MS: m/z [M⁺]: 414. Anal. calc. for C₃₀H₂₂O₂: C, 86.93; H, 5.35. Found: C, 86.57; H, 5.21%.

4a: Yield: 38%. ¹H NMR (400 MHz, CDCl₃, 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. Anal. calc. for C₃₁H₂₅NO: C, 87.09; H, 5.89. Found: C, 87.34; H, 5.78%.

5a: Yield: 70%. ¹H NMR (400 MHz, CDCl₃, δ): 8.28 (d, J = 9.8 Hz, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.47 (t, 1H), 7.45–7.29 (m, 6H), 7.09 (d, J = 8.8 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.2 Hz, 1H), 6.23 (d, J = 9.9 Hz, 1H), 3.95 (s, 3H), 3.77 (s, 3H). MS: m/z [M⁺]: 444. Anal. calc. for C₃₁H₂₄O₃: C, 83.76; H, 5.44. Found: C, 83.83; H, 5.38%.

6a: Yield: 10%. ¹H NMR (400 MHz, CDCl₃, δ): 8.31 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.47 (t, 1H), 7.45–7.29 (m, 6H), 7.11 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 7.9 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 6.25 (d, J = 9.9 Hz, 1H), 3.79 (s, 3H), 2.85 (s, 6H). MS: m/z [M⁺]: 457. Anal. calc. for C₃₂H₂₇NO₂: C, 84.00; H, 5.95. Found: C, 84.43; H, 5.63%.

Results and discussion

Compounds **1a–6a** showed typical photochromism in both solution and in a rigid polymer matrix upon irradiation with UV light. As a model compound, the photochromism and absorption spectral changes of **5a** in acetonitrile (A) and a PMMA matrix



Scheme 4 The photochromism of 5a in both solution and in a PMMA thin film.

thin film (B) with UV light irradiation are presented in Scheme 4 and Fig. 1, respectively. The absorption of the photosteady state (**5b**) appeared at 466 nm (in solution) and 476 nm (in PMMA matrix), respectively. Compared with the absorption in solution, **5b** showed a 10 nm red-shift in the PMMA matrix, which is probably due to the polarity of the medium. Similar results were obtained with other compounds, and the absorption data of **1a**– **6b** in both solution and in a PMMA matrix are presented in Table 1 and Table 2, respectively.

There are two open forms, **TC** (transoid-*cis*) and **TT** (transoid-*trans*), when 3*H*-naphtho[2,1-*b*]pyrans are irradiated with UV light to a photosteady state (Scheme 5); the **TC** form is the major and the **TT** form is the minor. The fading of the colored form back to the **FC** (colorless form) involve two steps, $TT \rightarrow TC \rightarrow$



Fig. 1 Absorption changes of **5b** in acetonitrile $(2 \times 10^{-5} \text{ M}, \text{ irradiating light: } \lambda = 254 \text{ nm}, \text{ intensity: 4.3 mW cm}^{-2}, \text{ irradiating periods: 0, 5, 10, 15, 20 and 25 s) and in a PMMA thin film <math>(1.2 \times 10^{-5} \text{ mol g}^{-1}, \text{ irradiating light: } \lambda = 254 \text{ nm}, \text{ intensity: 4.3 mW cm}^{-2}, \text{ irradiating periods: 0, 30, 60, 90, 120, 150, 180 and 210 s).}$

This journal is © The Royal Society of Chemistry 2011

Table 1 Kinetics data^b of **1a–6b** in MeCN solution $(2 \times 10^{-5} \text{ M})$ at 10 °C

Compound	$\lambda_{\rm max}/{\rm nm}$	0. D.	$T_{\frac{1}{2}}/s$	<i>T</i> ₄/s	$K_1 (\times 10^{-2})$	$K_2 (\times 10^{-4})$
$\mathbf{NPv(b)}^{a}$	422	0.384	125	405	0.33	7.20
1b	454	0.456	106	305	0.58	2.32
2b	540	0.554	51	118	1.18	8.06
3b	446	0.336	48	110	1.21	4.33
4b	414	0.215	43	104	1.54	4.46
5b	466	0.527	30	72	1.89	1.66
6b	466	0.311	25	68	2.09	2.68

^{*a*} NPy used as a reference compound $(2 \times 10^{-5} \text{ M}, \text{ in MeCN})$. ^{*b*} Samples initially irradiated at 254 nm until in a photosteady state (40 s). Thermal decoloration was then monitored at the λ_{max} of the colored form at 10 °C in the dark.

FC. The process of TC \rightarrow FC (k_1) is usually rapid and that of $TT \rightarrow TC (k_2)$ is slow.^{35–37} Convenient measures of the fading speed are the $T_{\frac{1}{2}}$ and $T_{\frac{1}{4}}$ values,^{38,39} which are the time it takes for the optical density to reduce by $\frac{1}{2}$ and $\frac{3}{4}$ of the initial optical density of the colored form, and the smaller are $T_{\frac{1}{2}}$ and $T_{\frac{1}{2}}$, the faster is the fading. Fig. 2 represented the fading kinetics of 5b in CH₃CN at ambient temperature (10 °C). It was found that the fading times $T_{\frac{1}{2}}$ and $T_{\frac{1}{4}}$ were 30 and 72 s, respectively, and the fading rate constant $(k_1 = 1.89 \times 10^{-2} \text{ s}^{-1}, k_2 = 1.66 \times 10^{-4} \text{ s}^{-1})$ was obtained using the biexponential decoloration model according to the standard biexponential equation.^{18,19,25} The fading kinetics of other compounds was analyzed using the same method, and the data are listed in Table 2. Compared with their parent compound, NPy, all the compounds showed a fast fading speed and a large fading rate constant, indicating that the electron-donating group attached to para-position of the aryl moiety at the 3-position improved the fading speed of the photosteady state of these naphthopyrans. A further investigation found the following results. First, the fading speed of **3b** ($T_{\frac{1}{2}} = 48$ s, $T_{\frac{1}{4}} =$ 110 s) and **4b** ($T_{\frac{1}{2}} = 43$ s, $T_{\frac{3}{4}} = 104$ s) were faster than that of **1b** $(T_{\frac{1}{2}} = 106 \text{ s}, T_{\frac{1}{4}} = 305 \text{ s})$ and **2b** $(T_{\frac{1}{2}} = 51 \text{ s}, T_{\frac{1}{4}} = 118 \text{ s})$, respectively, which suggests that the electron-donating group attached to the *para*-position of the naphthalene ring is better than that attached to the para-position of the benzene ring. Second, comparing 2b with 1b and 4b with 2b, it is found that the fading time of 2b is faster than that of 1b, and that of 4b is faster than that of 3b. This indicates that the fading speed is influenced by the strength of the electron-donating groups, and that the stronger the electron-donating group, the faster the fading speed. Third, by comparison of the data listed in Table 1, both 5b and 6b showed the fastest fading speed, which reveals that bearing electron-donating groups at both the para-position of the naphthalene ring and the benzene ring dramatically increases the fading speed.

The fading speed of **1a–6b** in a rigid polymer matrix were also investigated by doping naphthopyrans **1a–6a** in a polymethyl methacrylate (PMMA) matrix. A naphthopyran–PMMA thin film was obtained by spin coating a mixed solution of the naphthopyran and PMMA in cyclohexanone. As compared with **NPy (b)**, the fading speed of all the target compounds, **1a–6b**, increased significantly, and both $T_{\frac{1}{2}}$ and $T_{\frac{1}{4}}$ decreased greatly (Table 3), which reveals that the electron-donating group attached to the *para*-position of the aryl moiety at the 3-position increases the fading speed of the photosteady state of

Table 2 Kinetics data^b of **1a–6b** in a PMMA matrix $(1.2 \times 10^{-5} \text{ mol g}^{-1})$ at 10 °C

Compound	$\lambda_{\rm max}/{\rm nm}$	O. D.	$T_{1/2}/\mathrm{s}$	<i>T</i> :/ ₄ /s	$K_1 (imes 10^{-2})$	$K_2 (\times 10^{-4})$
NPv(b) ^a	426	0.73	300	>1000	0.32	2.43
1b	462	1.114	186	800	0.52	3.50
2b	548	1.330	65	150	1.03	5.59
3b	452	1.083	56	145	1.14	5.17
4b	420	0.780	50	125	1.20	4.62
5b	476	1.057	45	120	1.38	4.06
6b	476	0.769	40	94	1.58	3.43

^{*a*} NPy used as a reference compound (1.2×10^{-5} mol g⁻¹, in PMMA). ^{*b*} Samples initially irradiated at 254 nm until in a photosteady state (1.5 min). Thermal decoloration was then monitored at the λ_{max} of the colored form at 10 °C in the dark.



Scheme 5 The structures of the FC, TC and TT isomers.



Fig. 2 The fading kinetics of 5b in MeCN solution at 10 °C.

naphthopyrans. As presented in Table 3, the values of k of **5b** and 6b are larger than those of 1b-4b in a PMMA thin film, resulting in the fading speed of 5b and 6b being faster than those of 1b-4b. Also, it was found that the fading speed of 3b and 4b are faster than those of 1b and 2b, respectively, and that of 2b and 4b are faster than those of 1b and 3b, respectively, which confirms that the fading speed of 3-aryl-3-(α -naphthalene)-3H-naphtho[2,1-b] pyrans with a strong electron-donating group attached to the para-position of the aryl ring at the 3-position is dramatically increased; this result is in agreement with that obtained in solution. It is worth noting that although the switching performance of naphthopyrans is profoundly influenced by the local host environment and the media that incorporate them, 30,40 both the electronic and structural nature of naphthopyrans decides their intrinsic properties and plays a key role in their switching performance.

The fatigue resistance of compounds **1a-6a** in a PMMA thin film was evaluated, and it is found that all the compounds



Fig. 3 The fatigue resistance of 5a in a PMMA thin film.

showed very good fatigue resistance in a PMMA thin film. As presented in Fig. 3, after 10 cycles of coloration/decoloration, no distinct degradation was detected by UV-vis absorption for **5a** (detection optical density at $\lambda_{max} = 476$ nm). Other compounds also showed excellent fatigue resistance in PMMA thin films and less than 10% degradation was detected after 10 cycles.

Conclusion

A class of artificial photochromic 3-aryl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*]pyrans with fast fading speeds in both solution and in rigid polymer matrices has been developed. It was demonstrated that both the electronic properties and the position of substituents have a great influence over the fading speed of 3-aryl-3-(α -naphthalene)-3*H*-naphtho[2,1-*b*]pyrans, with the attachment of strong electron-donating groups at the *para*position of both the α -naphthalene ring and the benzene ring significantly increasing their fading speed at ambient temperature.

Acknowledgements

This work was supported by the National Basic Research Program of China (2010CB934103) and the National Nature Science Foundation of China (21073214).

References

- 1 M. Irie, Chem. Rev., 2000, 100, 1685.
- 2 Y. Yokoyama, Chem. Rev., 2000, 100, 1717.
- 3 G. Berkovic, V. Krongauz and V. Weiss, Chem. Rev., 2000, 100, 1741.
- 4 Organic Photochromic and Thermochromic Compounds, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999.

- 5 H. Duerr, H. Bouas-Laurent, *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 2003.
- 6 B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, Germany, 2001.
- 7 F. M. Raymo and M. Tomasulo, Chem.-Eur. J., 2006, 12, 3186.
- 8 Y. Harada, S. Hatano, A. Kimoto and J. Abe, *J. Phys. Chem. Lett.*, 2010, **1**, 1112.
- 9 Y. Kishimoto and J. Abe, J. Am. Chem. Soc., 2009, 131, 4227.
- 10 S. Hatano, K. Sakai and J. Abe, Org. Lett., 2010, 12, 4152.
- K. Fujita, S. Hatano, D. Kato and J. Abe, *Org. Lett.*, 2008, **10**, 3105.
 W. Sriprom, M. Neel, C. D. Gabbutt, B. Mark Heron and S. Perrier, *J. Mater. Chem.*, 2007, **17**, 1885.
- 13 A. R. Katritzky, R. Sakhuja, L. Khelashvili and K. Shanab, J. Org. Chem., 2009, 74, 3062.
- 14 C. D. Gabbutt, B. M. Heron, S. B. Kolla and M. Mcgivern, *Eur. J. Org. Chem.*, 2008, 2031.
- 15 S. Delbaere, G. Vermeersch, M. Frigoli and G. H. Mehl, Org. Lett., 2006, 8, 4931.
- 16 S. Delbaere, G. Vermeersch, M. Frigoli and G. H. Mehl, Org. Lett., 2010, 12, 4090.
- 17 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.
- 18 J. N. Moorthy, P. Venkatakrishnan, S. Samanta and D. K. Kumar, Org. Lett., 2007, 9, 919.
- 19 W. Zhao and E. M. Carreira, J. Am. Chem. Soc., 2002, 124, 1582.
- 20 N. F. S. A. Cerqueria, A. M. F. Oliveria-Campos, P. J. Coellho, L. H. Melode Carvalho, A. Samat and R. Gugliemetti, *Helv. Chim. Acta*, 2002, **85**, 442.
- 21 B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington, D. A. Clarke, S. N. Corns, *WO Pat.* WO 2001/12619 A1, 2001.

- 22 D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington, S. N. Corns, US Pat. 6,248,264 B241, 2001.
- 23 F. Ercole, N. Malic, S. Harrisson, T. P. Davis and R. A. Evans, Macromolecules, 2010, 43, 249.
- 24 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, **4**, 249.
- 25 N. Malic, J. A. Campbell and R. A. Evans, *Macromolecules*, 2008, 41, 1206.
- 26 F. Ercole, T. P. Davis and R. A. Evans, *Macromolecules*, 2009, **42**, 1500.
- 27 Organic Photochromic and Thermochromic Compounds, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999.
- 28 W. Zhao and E. M. Carriea, Chem.-Eur. J., 2007, 13, 2671.
- 29 W. Zhao and E. M. Carreia, Org. Lett., 2006, 8, 99.
- 30 J.-L. Pozzo, V. Lokshin, A. Samat, R. Guglielmetti, R. Dubest and J. Aubard, J. Photochem. Photobiol., A, 1998, **114**, 185.
- 31 K. Guo and Y. Chen, J. Mater. Chem., 2010, **20**, 4193.
- 32 B. Van Gemert, M. P. Bergomi, US Pat. 5,066,818, 1991.
- 33 B. Van Gemert, M. P. Bergomi and D. Knowles, *Mol. Cryst. Liq. Cryst.*, 1994, 246, 67.
- 34 W. Zhao and E. M. Carreira, Org. Lett., 2003, 5, 4153.
- 35 S. Delbaere, J.-C. Micheau and G. Vermeersch, J. Org. Chem., 2003, 68, 8968.
- 36 J. Hobley, V. Malatesta, K. Hatanaka, S. Kajimoto, S. L. Williams and H. Fukumura, *Phys. Chem. Chem. Phys.*, 2002, **4**, 180.
- 37 S. Delbaere and G. Vermeersch, J. Photochem. Photobiol., A, 2003, 159, 227.
- 38 R. W. Walters, B. Van Gemert, WO Pat. WO 2001/70719 A2, 2001.
- 39 F. Ercole, N. Malic, T. P. Davis and R. A. Evans, J. Mater. Chem., 2009, 19, 5612.
- 40 P. J. Coelho, M. A. Salvador, M. Manuel Oliveira and L. M. Carvalho, J. Photochem. Photobiol., A, 2005, 172, 300.