Optimizing the photochromic performance of naphthopyrans in a rigid host matrix using poly(dimethylsiloxane) conjugation. J Mater Chem

ARTICLE *in* JOURNAL OF MATERIALS CHEMISTRY · JULY 2009

Impact Factor: 7.44 · DOI: 10.1039/b904345d

4 AUTHORS, INCLUDING:

Francesca Ercole
Monash University (Australia)
32 PUBLICATIONS **3,557** CITATIONS
SEE PROFILE

Thomas P Davis
Monash University (Australia)
498 PUBLICATIONS **19,763** CITATIONS
SEE PROFILE

Optimizing the photochromic performance of naphthopyrans in a rigid host matrix using poly(dimethylsiloxane) conjugation†

Francesca Ercole,[abc] Nino Malic,[ab] Thomas P. Davis[c] and Richard A. Evans*[abc]

Received 4th March 2009, Accepted 8th May 2009
First published as an Advance Article on the web 19th June 2009
DOI: 10.1039/b904345d

A series of methoxy substituted 2,2-diaryl-2*H*-naphthopyran photochromic dyes were assembled incorporating hydroxy functionality to allow their subsequent attachment to flexible poly(dimethylsiloxane) oligomers. The photochromic performance of the generated PDMS–naphthopyran conjugates was studied in a thermoset host matrix and compared to non-conjugated, electronically equivalent control dyes. Both coloration and decoloration speeds were found to be greatly improved with critical $T_{1/2}$ decoloration times reduced by 42–80%. The extent of solution-like performance provided by PDMS conjugation in the rigid host was examined with reference to the fade performance of control dyes in solution, and found to range from 20 to 90%. These measures are believed to be influenced by the electronic nature and steric interactions of the photochromic dyes.

Introduction

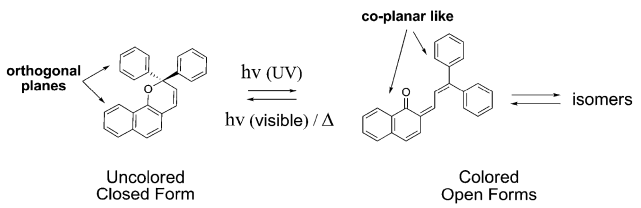
Naphthopyrans are an important class of photochromic dyes which display a reversible color change when exposed to UV light and are well known for their commercial application in the ophthalmic lens industry.[1–5] Potential application of photochromics in other areas such as electronic devices, optical memories and photo-switches continues to grow and motivate interesting research.[6–11]

The photochromic reaction proceeds by UV irradiation of the colorless closed form resulting in the electrocyclic ring opening of the pyran moiety *via* cleavage of the C(sp^3)–O bond (Scheme 1).[12] This produces a distribution of open geometrical isomers (merocyanines) which are intensely colored due to their extended conjugation and quasi-planar conformations. In the absence of UV irradiation, the colored isomers gradually thermally or photochemically revert back to the closed naphthopyran form, undergoing a significant intramolecular rotation during the conversion.

The optical lens market continues to be the largest consumer of photochromic dyes in which substituted 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans, with the base structure shown in Scheme 1, are highly represented.[1–3,13] Chemical developments aimed at optimizing performance characteristics such as intensity of coloration, fade (reversibility) rate, fatigue resistance and photogenerated color have been extensive. For example, 5-alkoxycarbonyl substitution,[14,15] heterocyclic fused moieties (*e.g.* an indeno group),[16,17] judiciously positioned electron donating substituents (*e.g.* methoxy or dialkyl amino)[18] and concurrent steric effects of substituents have all been found to influence photochromic characteristics such as de/coloration rates and photogenerated color.[12]

The photochemical as well as the thermal behavior of the photochromic molecules is also profoundly influenced by the media in which they are incorporated into. Within rigid, optically clear matrices, such as ophthalmic lens material, viscosity and free volume of the host environment become major factors governing the speed of the photochromic reaction.[19–21] Photochromic switching involves substantial mechanical movement, the transition requiring a large intramolecular rotation during coloration and decoloration. Therefore, in solid media the molecules are restricted in their movement rendering the speed of photochromic switching significantly slower. This is frequently referred to as the matrix effect.[19] We have been motivated to develop strategies that enable fast switching of photochromic dyes to occur even within the rigid material of a lens.[22–24]

The methodology developed in our laboratory which has provided considerable control and improvement to photochromic behavior in a host matrix is the use of polymer conjugation.[22,25–27] Covalent attachment of oligomers directly to the dye acts to alter the local environment in the vicinity of the photochromic molecule. When incorporated within a host matrix, entanglement and partitioning of polymer tails provide encapsulation and insulation from the rigid bulk environment, presenting the dye and its aggregates with a localized



Scheme 1 Generic photochromic reaction for substituted 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans.

[a]*CSIRO Molecular & Health Technologies, Bag 10, Clayton, VIC 3169, Australia. E-mail: Richard.Evans@csiro.au; Fran.Ercole@csiro.au; Nino.Malic@csiro.au*
[b]*The Cooperative Research Centre for Polymers, 8 Redwood Drive, Notting Hill, VIC 3168, Australia*
[c]*Centre for Advanced Macromolecular Design, School of Chemical Sciences and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia*

† Electronic supplementary information (ESI) available: Synthesis details and thermal decoloration pathway scheme. See DOI: 10.1039/b904345d.

environment of controlled viscosity. Attachment of PDMS (poly(dimethylsiloxane)) oligomers manifests a strong lubricating effect by introducing a local environment of low viscosity and higher mobility, effectively improving switching ability.

The purpose of the work presented in this article was to exploit PDMS conjugation to investigate its capacity to influence the photochromic behavior of a variety of known methoxy substituted 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans within a rigid host matrix. An OH group on the naphthopyran was used as the tethering moiety for subsequent conjugation *via* condensation chemistry. Practical strategies for synthesizing and accessing appropriate starting materials and conjugates were also presented. Photochromic spectrokinetic properties of PDMS-conjugated dyes within a rigid host matrix were compared to those of electronically equivalent control dyes which lacked PDMS tailing. The extent of the solution-like performance provided in the host matrix by PDMS conjugation was investigated by comparing their fade performance with that of their control dyes in solution.

Experimental

Materials

All chemicals (reagents and solvents) were of high purity and used as received unless otherwise stated. Reagents for synthesis were obtained from Aldrich at the highest purity available and used without further purification. Carbinol (hydroxyl-terminated) poly(dimethylsiloxane) was purchased from Gelest Inc. All chromatography was performed using silica gel (Kieselgel Merck 60, 0.040–0.063 mm) and TLC was performed on Merck Silica 60F254 plates.

Methyl 1,4-dihydroxy-2-naphthoate (**2a**) and methyl 4-hydroxy-6-methoxy-2-naphthoate (**6a**) were prepared using literature procedures.[28,29] The synthesis of 4-hydroxy-1-phenyl-2-naphthoic acid (**7**) was performed using a patent procedure.[30] 5-Hydroxy-7*H*-benzo[*c*]fluoren-7-one (**9**) was synthesized using the procedure of Aki *et al.*[31] 5-Hydroxy-7*H*-benzo[*c*]-fluoren-7-ol (**10**) was synthesized using the procedure of Zeynizadeh and Behyar.[32] 4-Hydroxy-4′-methoxybenzophenone (**11**) was synthesized using a procedure adapted from the literature.[33] 4-(3-Hydroxypropoxy)-phenyl-4′-methoxybenzophenone (**12**) was synthesized as reported in patent literature.[34] Propynols **13**, **14** and **15** were prepared using lithium trimethylsilylacetylide, as in the literature.[35] Complete characterization and additional details of synthetic procedures are outlined in ESI†.

General experimental measurements

^{1}H (400 MHz/200 MHz) and ^{13}C (100 MHz/50 MHz) NMR spectra were obtained with a Bruker AV400 or a Bruker AC200 spectrometer at 25 °C. Spectra were recorded for samples dissolved in deuterated solvent and chemical shifts are reported in parts per million from external tetramethylsilane and *J* values are given in Hz. Positive ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using ionization energy of 70 eV. Accurate mass measurements were obtained with a high resolution of 5000–10 000 using PerFluoroKerosene (PFK) as the reference sample. Positive and negative ion electrospray mass spectra (ESI-MS) were acquired with a VG Platform mass spectrometer using a cone voltage of 50 V with the source maintained at 80 °C. Methanol was used as solvent system with a flow rate of 0.04 mL min^{-1}.

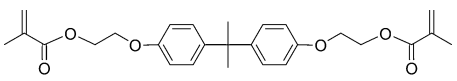
Molecular weights of PDMS were obtained from ^{1}H NMR spectra from integration values of CH_2 resonances along the backbone with respect to those of $Si(CH_3)_2$. Final molecular weights of PDMS–naphthopyran conjugates were additionally confirmed from integration of characteristic naphthopyran end groups.

Photochromic analyses were performed on lenses composed of PDMS–naphthopyran conjugates and their corresponding controls dissolved individually in a standard industrial lens formulation comprising 1 : 4 weight ratio of poly(ethylene glycol)(400) dimethacrylate (PEGDMA) and 2,2′-bis((4-methacryloxyethoxy)phenyl)propane (EBPDMA) with 0.4% azobis(isobutyronitrile) (AIBN) (Fig. 1). The formulation was then cured at 80 °C for 16 h in a standard mold to give optically clear test samples of equivalent thickness (~2.4 mm). The doping concentrations were chosen in order to maintain optical densities in a meaningful detector range for photochromic kinetic tests (refer to those entries in Table 2).

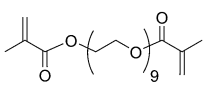
Under continuous irradiation, the photochromic responses of the lenses were analyzed on a light table (schematic representation available in literature)[24] comprising a Cary 50 spectrophotometer to measure absorbance values and a 160 W Oriel xenon lamp as an incident light source. A series of two filters (Edmund Optics WG320 and Edmund Optics band-pass filter U-340) were used to restrict the output of the lamp to a narrow band (350–400 nm). The samples were maintained at 20 °C and monitored at the maximum absorbance of the colored form for a period of 1000 s. Then the thermal decoloration was monitored in the dark for a further 4800 s (maximum). Control samples were also analyzed in solution using toluene as the solvent in a quartz cell with 1 cm path length. Concentrations ranged from 10^{-4} to 10^{-5} M, refer to entries in Table 2.

Preparation of starting materials

Methyl 4-hydroxy-1-methoxy-2-naphthoate (2b). 1,4-Dihydroxy-2-naphthoic acid (**1**) (2.00 g, 9.80 mmol) and K_2CO_3 (5.40 g, 39.18 mmol) were dissolved in a mixture of water (50 mL) and i-PrOH (10 mL). The solution was cooled to −15 °C in an EtOH–dry ice bath and propionyl chloride (1.30 mL, 1.36 g, 14.7 mmol) was added dropwise with vigorous stirring over a period of 5 min. The mixture was left to stir at −15 °C for an additional 15 min and then quenched by the dropwise addition of aqueous 6 M HCl to pH ~5 (**caution** – foaming). The solid was then collected by filtration, washed with water and dried under



EBPDMA



PEGDMA

Fig. 1 Structures of monomers of thermally curable host matrix formulation.

vacuum overnight at 40 °C to give 1-hydroxy-4-(propionyloxy)-2-naphthoic acid (2.20 g, 75% pure by ^{1}H NMR). The solid was dissolved in dry acetone (180 mL) and then treated with finely ground anhydrous K_2CO_3 (7.20 g, 52.1 mmol). The mixture was heated to reflux for 30 min and then cooled to 0 °C with an ice bath. Iodomethane (4.5 mL, 10.3 g, 72.3 mmol) was then added dropwise over 5 min *via* syringe and the resulting mixture was left to stir at room temperature for 16 h. Removal of the solvent and excess reagents under vacuum gave a brown paste that was re-dissolved in diethyl ether and filtered through a plug of silica gel to remove baseline material. The solvent was then removed under vacuum and the brown gum was collected to afford methyl 1-methoxy-4-(propionyloxy)-2-naphthoate as a crude product. Finely ground K_2CO_3 (1.64 g, 11.9 mmol) was added to a suspension of the crude material (2.74 g) in methanol (15 mL) and the resulting suspension was stirred at room temperature for 3 h. The mixture was then diluted with water (100 mL), acidified by the addition of aqueous 2 M HCl and extracted into diethyl ether (3 × 75 mL). The combined organic extracts were washed with 10% $NaHCO_3$ (3 × 75 mL) and water (1 × 100 mL). The product was then extracted from the organic layer into an aqueous basic layer using 0.1 M NaOH (5 × 50 mL). The combined basic aqueous layers were then acidified with aqueous 2 M HCl to pH ~5 and extracted with diethyl ether (3 × 75 mL). The combined organic layers were then washed with saturated brine and dried with $MgSO_4$. Solvent removal yielded the pure final product, methyl 4-hydroxy-1-methoxy-2-naphthoate (**2b**), as a tan solid (1.70 g, 75%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 3.90 (s, 3H, $ArOCH_3$), 3.96 (s, 3H, $COOCH_3$), 7.22 (s, 1H, ArH), 7.59–7.64 (m, 2H, ArH), 8.17–8.21 (m, 1H, ArH), 8.22–8.27 (m, 1H, ArH), 9.07 (s, 1H, ArOH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 52.4, 63.5, 108.3, 120.6, 123.5, 124.2, 127.9, 128.2, 129.0, 130.3, 149.9, 151.5, 167.1 ppm. Mass spec (EI): *m*/*z* 232.1 ([M]$^+$, 100%), 217.1 (68), 201.1 (22), 170.0 (20), 161.1 (27), 142.1 (17), 131.0 (18), 115.1 (24), 102 (24), 83.9 (89), 69.1 (54). Mass spec (HR, EI): *m*/*z* 232.0729 ($C_{13}H_{12}O_4$ requires 232.0736).

4-Hydroxy-6-methoxy-2-naphthoic acid (5). The Stobbe condensation of 4-methoxybenzaldehyde with diethyl succinate was affected either by *t*-BuOK (2.2 equivalents, toluene, room temperature, 16 h)[36] or by sodium ethylate (Na in dry ethanol (NaOEt), 2 equivalents, reflux 3 h).[37] Both methods resulted in a considerable proportion (~35%) of by-product, 2,3-bis(4-methoxybenzylidene)succinic acid (**3b**), isolated as a pale yellow crystalline material, as well as the desired half ester product, **3a**.[29] The ^{1}H NMR for **3b** showed a mixture of geometrical isomers (both *E*/*E* and *Z*/*Z*, inconsistent proportions): ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ: 3.73 and 3.79 (2 × s, 6H, $ArOCH_3$), 6.89 (d, *J* 8.8 Hz, 2H, ArH), 7.01 (d, *J* 8.8 Hz, 2H, ArH), 7.38 (d, *J* 8.4 Hz, 2H, ArH), 7.50 (d, *J* 8.4 Hz, 2H, ArH), 7.68 and 7.72 (2 × s, 2H, olefinic H) ppm. A second alternative literature procedure[38] was also used to prepare the half ester **3a** which resulted in no by-product: to a mixture of 4-methoxybenzaldehyde (2.00 g, 14.7 mmol) and diethyl succinate (2.56 g, 14.7 mmol) was added powdered *t*-BuOK (2.17 g, 17.7 mmol). The mixture was ground with a mortar and pestle for 10 min and then left to sit at room temperature for 3 h. The thick paste was then dissolved in water and the resulting basic solution washed with diethyl ether (3 × 100 mL). The basic solution was neutralized with 2 M HCl and re-extracted back into diethyl ether (3 × 100 mL). The organic layers were combined and washed with saturated brine, dried with $MgSO_4$ and the solvent removed under reduced pressure to give a thick amber oil (**3a**, 2.9 g, 75%) in sufficient purity for subsequent steps. Friedel–Crafts acylation of the crude half ester mixture (**3a**), using procedures outlined in the literature,[29,36,37,39] followed by saponification yielded 4-hydroxy-6-methoxy-2-naphthoic acid (**5**) as a pale pink powder (35% overall yield for the three steps). ^{1}H NMR (400 MHz, d_6-acetone) δ: 3.95 (s, 3H, $ArOCH_3$), 7.22 (dd, *J* 8.7, 1.5 Hz, 1H, ArH), 7.49 (br d, *J* 1.5 Hz, 1H, ArH), 7.58 (d, *J* 1.5 Hz, 1H, ArH), 7.92 (d, *J* 8.7 Hz, 1H, ArH), 8.12 (s, 1H, ArH), 9.21 (s, 1H, ArOH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 55.1, 100.7, 108.0, 119.8, 122.6, 126.1, 128.8, 129.5, 131.0, 152.4, 159.4, 167.3 ppm. ESI-MS *m*/*z* 217.2 [M − H]$^-$.

3-Hydroxypropyl 4-hydroxy-6-methoxy-2-naphthoate (6b). The title compound was synthesized using an alkylation procedure adapted from that of Hattori *et al.*[28] 4-Hydroxy-6-methoxy-2-naphthoic acid (**5**) (4.82 g, 22.1 mmol) and anhydrous sodium bicarbonate (1.86 g, 22.1 mmol) were added to DMF (20 mL) and stirred at 100 °C for 30 min under argon. The solution was cooled with an ice bath and sodium iodide (6.63 g, 44.2 mmol) was added, followed by the dropwise addition of 3-chloropropanol (4.20 g, 44.2 mmol, 3.80 mL). The mixture was stirred for an additional 3 h at 100 °C and then poured into dilute aqueous HCl and extracted into diethyl ether (3 × 75 mL). The combined organic extracts were washed with 10% $NaHCO_3$ (3 × 75 mL) and water (1 × 100 mL). The product was extracted from the organic layer with 0.1 M NaOH (5 × 50 mL). The combined basic aqueous layers were then acidified with aqueous 2 M HCl, extracted with diethyl ether (3 × 75 mL), washed with saturated brine and dried ($MgSO_4$). Solvent removal under vacuum yielded the pure final product, 3-hydroxypropyl 4-hydroxy-6-methoxy-2-naphthoate (**6b**), as an off-white solid (3.95 g, 65%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 1.98 (p, *J* 6.2 Hz, 2H, $CH_2CH_2CH_2$), 3.68 (br s, OH), 3.75 (t, *J* 6.2 Hz, 2H, CH_2OH), 3.95 (s, 3H, $ArOCH_3$), 4.42 (t, *J* 6.2 Hz, 2H, $CH_2CH_2CH_2$) 7.22 (dd, *J* 8.7, 2.5 Hz, 1H, ArH), 7.47 (br d, *J* 1.5 Hz, 1H, ArH), 7.57 (d, *J* 1.5 Hz, 1H, ArH), 7.92 (d, *J* 8.7 Hz, 1H, ArH), 8.09 (s, 1H, ArH), 9.19 (br s, 1H, ArOH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 32.0, 54.8, 58.1, 61.7, 100.4, 107.4, 119.6, 122.0, 125.8, 128.5, 129.2, 130.7, 152.2, 159.1, 166.2 ppm. Mass spec (EI): *m*/*z* 276.1 ([M]$^+$, 100%), 218.0 (69), 201.0 (58), 175.0 (41), 145.1 (13), 130.0 (12), 115.1 (10), 102 (22). Mass spec (HR, EI): *m*/*z* 276.0988 ($C_{15}H_{16}O_5$ requires 276.0988).

2-Hydroxyethyl 4-hydroxy-1-phenyl-2-naphthoate (8). The synthesis of the title compound was also performed using the alkylation procedure of Hattori *et al.*[28] 4-Hydroxy-1-phenyl-2-naphthoic acid (**7**) (2.00 g, 7.57 mmol) and $NaHCO_3$ (0.636 g, 7.57 mmol) were added to DMF (20 mL) and stirred at 60 °C for 2 h under nitrogen, then at 100 °C for 15 min. Freshly distilled and acid-free 2-bromoethanol (1.14 g, 9.08 mmol, 0.64 mL) was then added and the mixture stirred for an additional 1.25 h at 100 °C. The mixture was poured into dilute aqueous HCl and extracted with diethyl ether. The ether layer was washed several times with water, then with saturated brine and dried with $MgSO_4$. The solvent was removed under vacuum to give the pure

product as an off-white solid (2.16 g, 93%). ^{1}H NMR (200 MHz, d_6-acetone) δ: 3.43 (t, J 5.2 Hz, 2H, CH_2OH), 4.00 (t, J 5.2 Hz, 2H, OCOCH_2CH$_2$), 7.26–7.31 (m, 2H, ArH), 7.35 (s, 1H, ArH), 7.40–7.62 (m, 6H, ArH), 8.35 (dd, J 8.3, 1.1 Hz, 1H, ArH) ppm. ^{13}C NMR (50 MHz, d_6-acetone) δ: 60.3, 67.0, 108.1, 123.0, 127.1, 127.2, 127.8, 127.9, 128.0, 128.7, 129.9, 131.1, 133.1, 134.6, 140.4, 153.3, 168.7 ppm. ESI-MS m/z 307.4 [M − H]$^-$.

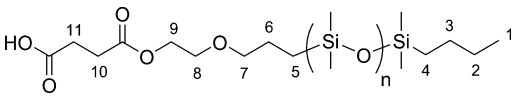
Typical synthesis of hydroxyl naphthopyran

The synthesis of methyl 6-hydroxy-2,2-bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran-5-carboxylate (**16**)[13] from methyl 1,4-dihydroxy-2-naphthoate (**2a**) and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**14**) has been described by us elsewhere[24] using a procedure adapted from the literature.[40] The product was isolated by crystallization from diethyl ether as a bright yellow solid (0.97 g, 45%). ^{1}H NMR (400 MHz, d_6-acetone) δ 3.73 (s, 6H, 2 × ArOCH_3), 4.05 (s, 3H, COOCH_3), 6.32 (d, J 10.0 Hz, 1H, pyran-CH), 6.86 (d, J 8.8 Hz, 4H, Ar-H), 7.45 (d, J 8.8 Hz, 4H, ArH), 7.48 (d, J 10.0 Hz, 1H, pyran-CH), 7.59 (m, J 8.4 and 1.5 Hz, 1H, Ar-H), 7.75 (m, J 8.4 and 1.5 Hz, 1H, ArH), 8.31 (d, J 8.4 Hz, 1H, ArH), 8.39 (d, J 8.4 Hz, 1H, ArH), 12.18 (s, 1H, ArOH) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ: 53.8, 56.2, 82.6, 104.0, 115.0, 115.2, 123.5, 125.0, 125.6, 126.7, 128.4, 129.5, 129.9, 130.3, 131.5, 138.7, 142.7, 157.8, 160.7, 173.7 ppm. Mass spec (EI): m/z 468.2 ([M]$^+$, 92%), 436.2 (100), 408.2 (38), 391.2 (18), 377.1 (13), 330.1 (39), 218.1 (16). Mass spec (HR, EI): m/z 468.1564 ($C_{29}H_{24}O_6$ requires 468.1573).

Typical synthesis of naphthopyran control

Methyl 2,2-bis(4-methoxyphenyl)-6-(propionyloxy)-2H-naphtho[1,2-b]pyran-5-carboxylate (16a). To a solution of methyl 6-hydroxy-2,2-bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran-5-carboxylate (**16**) (0.20 g, 0.427 mmol) in dry dichloromethane (10 mL) was added triethylamine (0.178 mL, 0.13 g, 1.28 mmol), under nitrogen. Propionyl chloride (0.04 g, 0.427 mmol, 0.037 mL) was added dropwise *via* a syringe and the mixture stirred at ambient temperature until TLC analysis showed the reaction to be complete (*ca.* ~15 min). The solvent and excess reagents were evaporated under vacuum and the residue re-dissolved in diethyl ether (20 mL) and washed successively with 0.1 M HCl, water, 0.1 M NaHCO_3, water and brine. The organic layer was dried with MgSO_4 and the solvent removed under vacuum. The crude glassy residue was then purified by column chromatography (silica gel, diethyl ether–hexane, 2 : 1), giving the pure product as a pale pink solid (0.180 g, 79%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 1.26 (t, J 7.5 Hz, 3H, propionyl-CH_3), 2.76 (q, J 7.5 Hz, 2H, propionyl-CH_2), 3.76 (s, 6H, 2 × ArOCH_3), 3.93 (s, 3H, COOCH_3), 6.41 (d, J 10.0 Hz, 1H, pyran-CH), 6.89 (d, J 8.9 Hz, 4H, ArH), 6.96 (d, J 10.0 Hz, 1H, pyran-CH), 7.45 (d, J 8.9 Hz, 4H, ArH), 7.59 (m, 1H, ArH), 7.67 (m, 1H, ArH), 7.85 (d, J 8.4 Hz, 1H, ArH), 8.41 (d, J 8.4 Hz, 1H, ArH) ppm. ^{13}C NMR (50 MHz, d_6-acetone) δ: 9.4, 27.7, 52.8, 55.5, 83.5, 114.3, 114.4, 120.8, 121.6, 123.0, 123.5, 127.1, 128.3, 128.6, 128.8, 128.9, 130.2, 137.7, 140.3, 146.7, 160.1, 166.3, 173.1 ppm. Mass spec (EI): m/z 524.2 ([M]$^+$, 36%), 568.2 (54), 436.2 (100), 407.1 (28), 391.1 (11), 372.1 (39). Mass spec (HR, EI): m/z 524.1835 ($C_{32}H_{28}O_7$ requires 524.1819).

Preparation of PDMS-conjugated naphthopyrans



COOH-terminated poly(dimethylsiloxane), n = 12.6. Hydroxy end-terminated poly(dimethylsiloxane) (25 g, *ca.* 0.0221 mol) and succinic anhydride (2.65 g, 0.0265 mol) were added to dry CH_2Cl_2 (*ca.* 40 mL) under nitrogen. Triethylamine (3.35 g, 4.6 mL, 0.033 mol) was then added in one portion, the mixture stirred at room temperature for 30 min followed by heating at 35 °C for 1 h. Polyethylene glycol methyl ether (3.86 g, 0.011 mol) was added and the mixture stirred for an additional 30 min at 35 °C. Hexane (*ca.* 40 mL) was then added, the mixture washed with several portions of 1 M HCl and then dried with MgSO_4. The solvent was removed under vacuum giving the pure product as a colorless oil (26.34 g, 97%). ^{1}H NMR (400 MHz, CDCl_3) δ: 0.04–0.08 (m, SiCH_3), 0.50–0.55 (m, 4H, CH_2-4,5), 0.88 (t, J 7.0 Hz, 3H, CH_3-1), 1.26–1.36 (m, 4H, CH_2-2,3), 1.57–1.65 (m, 2H, CH_2-6), 2.68 (br s, 4H, CH_2-10,11), 3.42 (t, J 7.3 Hz, 2H, CH_2-7), 3.63 (t, J 4.8 Hz, 2H, CH_2-8), 4.25 (t, J 4.8 Hz, 2H, CH_2-9) ppm. Refer to graphic above for corresponding numbering system used for CH_2 NMR assignments.

Succinoyl chloride terminated poly(dimethylsiloxane). Carboxylic acid terminated poly(dimethylsiloxane) (1.0 g, *ca.* 0.811 mmol) was dissolved in dry dichloromethane (10 mL) under nitrogen and 1 small drop of DMF was added. To the mixture was added oxalyl chloride (0.41 g, 0.28 mL, 3.24 mmol) in one portion. The mixture was stirred at ambient temperature for no more than 30 min whilst maintaining a slow nitrogen flow above the reaction by means of a syringe needle through a rubber septum. The solvent and excess reagents were removed under vacuum with residual traces of oxalyl chloride removed with the aid of 1,2-dichloroethane. The acid chloride product was used immediately. Analysis by ^{1}H NMR in d-chloroform showed quantitative conversion. ^{1}H NMR (400 MHz, CDCl_3) δ: 0.04–0.08 (m, av. 80H, SiCH_3), 0.50–0.55 (m, 4H, CH_2-4,5), 0.88 (t, J 7.0 Hz, 3H, CH_3-1), 1.26–1.36 (m, 4H, CH_2-2,3), 1.57–1.65 (m, 2H, CH_2-6), 2.72 (t, J 6.6 Hz, 2H, CH_2-10), 3.22 (t, J 6.6 Hz, 2H, CH_2-11), 3.42 (t, J 7.0 Hz, 2H, CH_2-7), 3.63 (t, J 4.8 Hz, 2H, CH_2-8), 4.26 (t, J 4.8 Hz, 2H, CH_2-9) ppm. Refer to graphic above (where n = 12.6) for corresponding numbering system used for CH_2 NMR assignments.

Typical synthesis of PDMS–naphthopyran conjugates

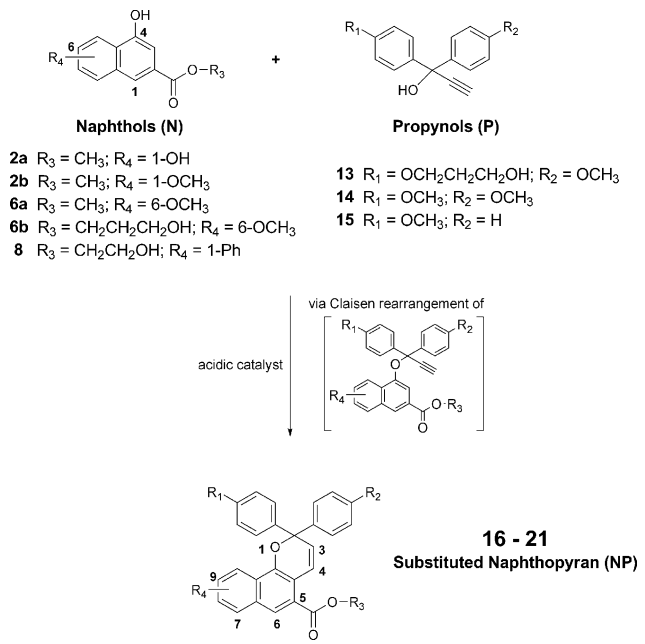
Methyl 2,2-bis(4-methoxyphenyl)-6-(butyl(PDMS)propyloxyethoxy-succinoyloxy)-2H-naphtho[1,2-b]pyran-5-carboxylate (16b). Methyl 6-hydroxy-2,2-bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran-5-carboxylate (**16**) (0.25 g, 0.534 mmol) was dissolved in dry dichloromethane (10 mL) followed by the addition of triethylamine (119 mg, 0.16 mL, 1.17 mmol), under an atmosphere of argon. Succinoyl chloride end-functionalised PDMS, synthesized as described above, was then added dropwise (0.485 mmol) and the mixture was left to stir at room

temperature for 1 h. The solvent was then removed under vacuum, the residue re-dissolved in diethyl ether–hexane (1 : 1) and the mixture filtered through a plug of silica gel. The solvent was removed and the remaining oily residue was purified by column chromatography (silica gel, CH_2Cl_2–petroleum ether, 4 : 1) to give the pure PDMS conjugate as a viscous red oil (759 mg, 80%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 0.07–0.13 (m, $SiCH_3$), 0.57 (m, 4H, CH_2-4,5), 0.89 (br t, J 7.0 Hz, 3H, CH_3-1), 1.35 (m, 4H, CH_2-2,3), 1.59 (m, 2H, CH_2-6), 2.78 (m, 2H, CH_2-10 overlap with H_2O and HDO signals), 3.04 (t, J 6.5 Hz, 2H, CH_2-11), 3.41 (t, J 6.8 Hz, 2H, CH_2-7), 3.62 (t, J 5.0 Hz, 2H, CH_2-8), 3.75 (s, 6H, 2 × $ArOCH_3$), 3.95 (s, 3H, $COOCH_3$), 4.23 (t, J 5.0 Hz, 2H, CH_2-9), 6.40 (d, J 10 Hz, 1H, pyran-CH), 6.88 (d, J 8.8 Hz, 4H, ArH), 6.96 (d, J 10 Hz, 1H, pyran-CH), 7.44 (d, J 8.8 Hz, 4H, ArH), 7.59 (t, J 7.5 Hz, 1H, ArH), 7.66 (t, J 7.5 Hz, 1H, ArH), 7.94 (d, J 8.5 Hz, 1H, ArH), 8.40 (d, J 8.5 Hz, 1H, ArH) ppm. Refer to Fig. 4 for corresponding numbering system used for CH_2 NMR assignments.

Results and discussion

Naphthopyrans

Substituted 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans (NP) are synthesized by reacting a 1-naphthol (N) with a diaryl prop-2-yn-1-ol (P) in the presence of an acidic catalyst (Scheme 2). The formation of the naphthopyran is confirmed by the appearance of characteristic resonances in the ^{1}H NMR spectrum between 6 and 8 ppm with coupling constants of $J \approx 10$ Hz due to pyran ring protons H-3 and H-4. The mechanisms involved in formation are well known, involving the Claisen rearrangement of the generated naphthyl propargyl ether.[35] The reaction can be carried out in a solvent (*e.g.* toluene) or in solid state (grinding reagents in silica gel), with varying degrees of acid strength of catalyst (*e.g.* *p*-toluene sulfonic acid or refluxing in acidic alumina) or with the addition of a dehydrating agent (trimethyl orthoformate) to react with the generated water.[40,41]



Scheme 2 Synthesis of naphthopyran from substituted starting materials.

It has been shown previously that the substitution patterns can dramatically influence photogenerated color and switching speed by effecting the stability of the generated ring-opened forms, as investigated by Gabbutt *et al.*[18,29] Alkoxycarbonyl substitution at position 5 assists fade rate; 9-methoxy substitution results in a faster fade rate compared to 6-methoxy substitution due to large disparities in the stability of their open forms; bis *vs.* mono *p*-methoxy substitution on the diaryl portion of the naphthopyran increases the fade rate and bathochromically shifts the absorption of the colored form.[18,42,43] An extra 6-phenyl moiety substituted on the already bulky naphthol ring also poses further steric considerations. Finally, an indeno moiety joining positions 5 and 6 is another significant structural modification of the 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans.[16,17,30] Along with *p*-methoxy substitution on the diaryl rings, such naphthopyrans produce open forms containing an extended π-electron system that are significantly shifted to higher wavelengths and capable of displaying faster bleaching kinetics.

The naphthopyran dyes exploited in this study were chosen to display a broad range of switching speeds both in solution and in a host matrix by variation of these known substitution patterns. The preliminary requirement of this work was therefore the synthesis of such naphthopyrans incorporating a free hydroxyl group for subsequent attachment of PDMS oligomers. Overall, the conditions for final assembly of the dyes were optimized in order to achieve synthesis yields comparable to those found in the literature for equivalent non-hydroxyl functionalized dyes (30–70%).

Hydroxyl functionalized naphthopyrans **16–21**, listed in Table 1, were assembled from relevant starting materials and then converted to their corresponding ester derivatives which are displayed in Fig. 3. The naphthopyrans (NP) each contain 5-alkoxycarbonyl substitution, shown in the base structure in Scheme 2. Hydroxyl indeno-fused naphthopyran, **22**, shown in Fig. 2, was also synthesized accordingly and converted to its esterified derivatives also displayed in Fig. 3.

Starting materials

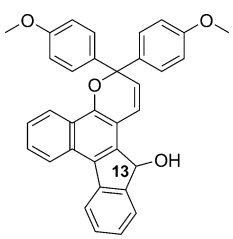
Naphthols. Methyl 1,4-dihydroxy-2-naphthoate, **2a** (Scheme 3), was prepared from commercially available 1,4-dihydroxy-2-naphthoic acid, **1**.[28] Carboxyl substitution present in **2a** precludes the formation of possible di-naphthopyran species,[12] affording naphthopyrans substituted with a free 6-hydroxy group. Such by-products can be produced in significant proportion from dihydroxy naphthalenes due to the presence of two reactive centers.

The 6-hydroxy moiety present in, for example, naphthopyrans **16** and **17** can then be methylated as a way to access a 6-methoxy substitution. However, this direct conversion also affords a major ring-opened and non-photochromic by-product, as reported by Gabbutt *et al.*[29] We therefore explored an alternative strategy *via* the assembly of the appropriate starting material, methyl 4-hydroxy-1-methoxy-2-naphthoate (**2b**), using the series of transformations as shown in Scheme 3. Reaction of **1**, in cold and basic water–isopropanol solution, with one and a half

Table 1 Substituted hydroxyl naphthopyrans (NP) synthesized from corresponding reactants, naphthol (N) and propynol (P)

Naphthopyrans NP	Reactants		Naphthopyran substituents[a]			
	N	P	R_1	R_2	R_3	R_4
16	**2a**	**14**	OCH_3	OCH_3	CH_3	6-OH
17	**2a**	**15**	OCH_3	H	CH_3	6-OH
18	**2b**	**13**	OCH_3	$-OCH_2CH_2CH_2OH$	CH_3	6-OCH_3
19	**6b**	**14**	OCH_3	OCH_3	$-CH_2CH_2CH_2OH$	9-OCH_3
20	**6b**	**15**	OCH_3	H	$-CH_2CH_2CH_2OH$	9-OCH_3
21	**8**	**14**	OCH_3	OCH_3	$-CH_2CH_2OH$	6-Ph

[a] Substituents R_1 to R_4 refer to substituted naphthopyrans (NP) in Scheme 2.



22

Fig. 2 Substituted hydroxyl indeno-fused naphthopyran **22** synthesized from propynol **14** and naphthol **10**.

equivalents of propionyl chloride selectively acylated the phenol, affording 1-hydroxy-4-(propionyloxy)-2-naphthoic acid in 75% crude yield (with 25% of starting material **1** remaining present). The crude mixture was alkylated with an excess of methyl iodide and K_2CO_3 in dry acetone to give methyl 1-methoxy-4-(propionyloxy)-2-naphthoate in the same proportions, followed by the removal of the propionyl group using an alcoholic solution of K_2CO_3. Importantly, **2b** could then be isolated from the crude organic mixture by selective extraction using 0.1 M NaOH, with an overall isolatable yield of 70% from **1**.

4-Hydroxy-6-methoxy-2-naphthoic acid **5** was required for the synthesis of **6a** and **6b**. As shown in Scheme 4, the strategy used to assemble **5** firstly involved the Stobbe condensation of 4-methoxybenzaldehyde with diethyl succinate (using NaOEt–*t*-BuOK)[29,36,37,44] to produce the required half ester **3a**. The crude yield of this reaction was consistently 70% and comparable to literature values. A pale yellow precipitate, however, formed on standing from the amber viscous oil (~13% by mass) and was found to be an isomeric mixture (both *E*/*E* and *Z*/*Z* isomers) of **3b**, forming as a result of a second molecule of benzaldehyde condensing with the generated half ester, **3a**. The use of anhydrous ethanol gave a cleaner product[29] with no by-product evident by ^{1}H NMR, but we found yields to be disappointing (35%). Removal of the by-product could be easily carried out *via* filtration, being insoluble in most solvents, however, the use of solvent-free conditions[38] provided us with the half ester in higher yields and exclusive of **3b**. Friedel–Crafts acylation of the resulting crude half ester, **3a**, gave the cyclized product **4**, followed by base hydrolysis to afford **5**.

1-Phenyl substituted naphthoic acid, **7**, was also synthesized from benzophenone using Stobbe condensation chemistry though no analogous by-product was ever formed during its synthesis.

Condensation of a large excess of a diol, such as ethylene glycol, with the generated substituted naphthoic acids (**5** and **7**) was a logical approach to introduce hydroxyl functionality to naphthol derivatives.[45] Esterification with methanol using Fischer esterification conditions (high excesses of methanol and catalytic quantities of acid) was straightforward, quantitatively generating the methyl ester derivative, **6a** (Scheme 5). However, numerous attempts to condense ethylene glycol to **5** in an equivalent manner proved futile, with numerous etherified and inseparable by-products formed during the reaction. Lower temperatures only resulted in low conversion to products. A much more successful strategy was found to be the nucleophilic displacement of a halogen by the selectively deprotonated naphthoic acid. With one equivalent of $NaHCO_3$ and dry DMF, two equivalents of 3-chloropropanol and sodium iodide, **6b** could be synthesized in 65% yield and with exceptional purity (Scheme 5). The use of 2-bromoethanol proved even more successful giving yields in excess of 90% for **8** (Scheme 6).

Friedel–Crafts cyclization[31] of **7**, followed by the reduction of the carbonyl group[32] of the resultant fluorenone derivative, **9**, gave the hydroxyl substituted benzofluorenol **10**, as shown in Scheme 6.

Propynols. Diaryl prop-2-yn-1-ols can be conveniently prepared by the addition of lithium trimethylsilylacetylide to a benzophenone following the removal of the trimethylsilyl group.[35,46] In this work **13** and **14** were easily accessed from commercially available benzophenones. Hydroxyl substitution can also be introduced to the naphthopyran *via* the diaryl prop-2-yn-1-ol,[33,34] as exemplified with naphthopyran **18**. Williamson etherification of **11** with 3-chloropropanol[33] generated **12** which was then converted to diaryl propynol **13** (Scheme 7). However, attempts to generate a propynol directly from the phenolic benzophenone **11** were unsuccessful. Meyer–Schuster rearrangement of the propynol[46,47] resulted in its degradation and the material formed an intractable gum on standing. The generation of propynol **13** from **12** was therefore preferable for our investigations.

Conjugated naphthopyrans

The condensation of naphthopyrans **16–22** to their corresponding ester derivatives was carried out using standard acid chloride chemistry, as shown in Scheme 8.

Carboxylic acid terminated PDMS was prepared from commercially available OH terminated PDMS by acylation with

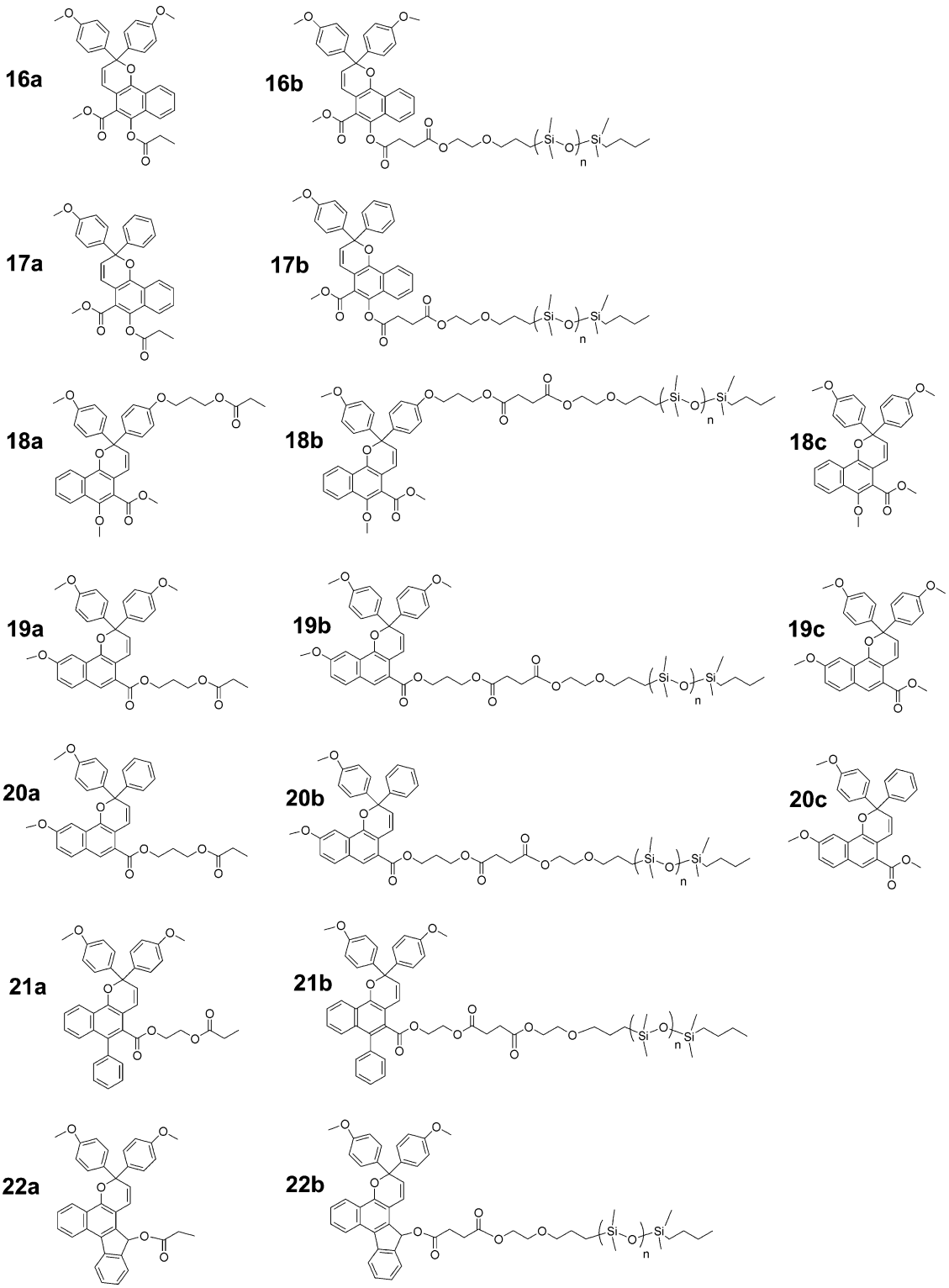
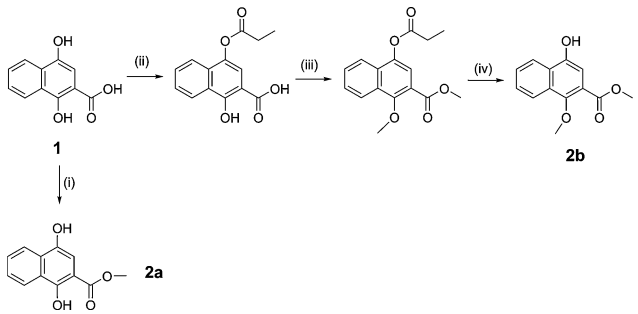


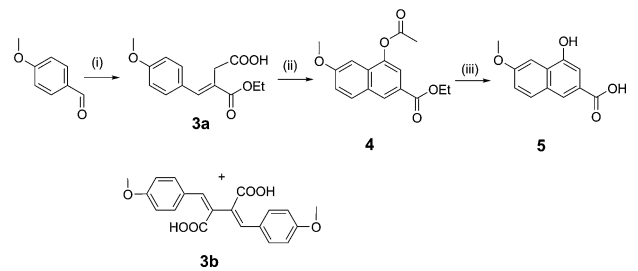
Fig. 3 Molecular glossary of substituted naphthopyrans tested.

succinic anhydride. The oligomeric product was shown by ^{1}H NMR to have an average molecular weight of approx. 1200 g mol^{-1} where $n = \sim 13$. Esterification reactions generated both PDMS conjugates (**16b–22b**) and propionate control naphthopyrans (**16a–22a**) in high yields, with products easily purified by chromatography. The final substituted naphthopyrans (both propionate controls and PDMS conjugates) and control dyes **18c**, **19c** and **20c** are displayed in a glossary as Fig. 3.

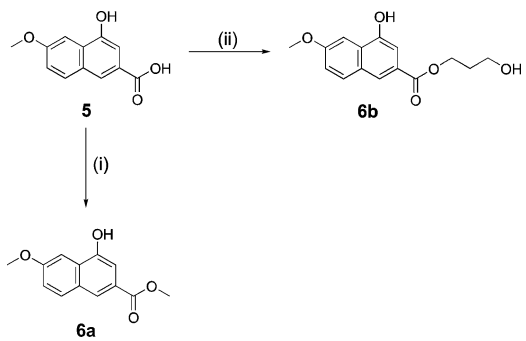
Each PDMS conjugate produced displayed a high level of purity; every methylene proton was accounted for, correct integral ratios and expected peak shifts associated with ester bond formation were exhibited (refer to ESI† for all ^{1}H NMR



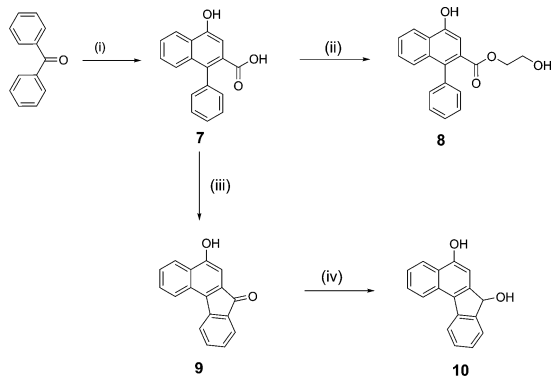
Scheme 3 (i) MeI, DMF, $NaHCO_3$ (1 equiv.), 100 °C; (ii) K_2CO_3 (4 equiv.), H_2O–i-PrOH (5 : 1), propionyl chloride (1.5 equiv.), −15 °C, neutralization; (iii) K_2CO_3 (4 equiv.), dry acetone, MeI (8 equiv.); (iv) K_2CO_3 (1.5 equiv.), MeOH.



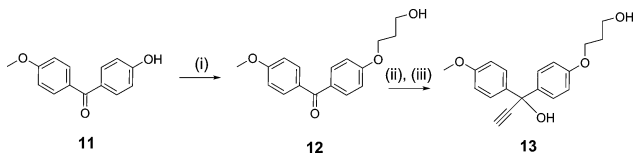
Scheme 4 (i) Diethyl succinate, Na ethylate (2 equiv.), reflux; (ii) anhydrous NaOAc (1.1 equiv.), acetic anhydride; (iii) 5% NaOH in EtOH–H_2O (4 : 1).



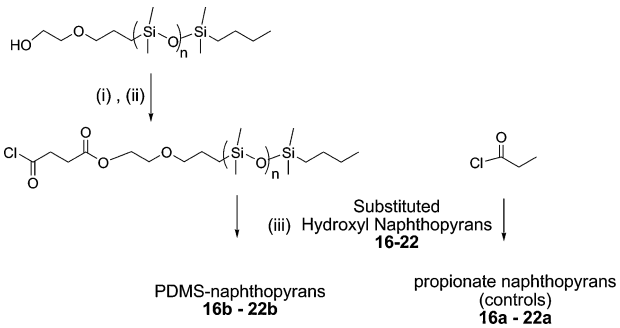
Scheme 5 (i) MeOH, H_2SO_4 (catalytic); (ii) 3-chloropropanol (2 equiv.), NaI (2 equiv.), dry DMF, $NaHCO_3$ (1 equiv.), 100 °C.



Scheme 6 (i) Stobbe condensation with dimethyl succinate, Friedel–Crafts acylation, base hydrolysis; (ii) 2-bromoethanol (2 equiv.), dry DMF, $NaHCO_3$ (1 equiv.), 100 °C; (iii) methanesulfonic acid, 60 °C; (iv) $NaBH_4$, wet THF, 50 °C.



Scheme 7 (i) 3-Chloropropanol (2 equiv.), NaI (2 equiv.), DMF, K_2CO_3 (2 equiv.), 100 °C; (ii) lithium trimethylsilylacetylide, anhyd. THF, 0 °C to rt; (iii) KOH, MeOH, then AcOH.



Scheme 8 Condensation chemistry for synthesizing propionate naphthopyran controls (**16a–22a**) and PDMS–naphthopyran conjugates (**16b–22b**); (i) succinic anhydride, TEA, DCM, rt; (ii) $(COCl)_2$, DCM, DMF (1 drop), rt; (iii) DCM, TEA, rt. See experimental in ESI† for n values (normally $n = \sim 13$).

assignments and final n values for PDMS-conjugated tail (normally $n = \sim 13$)). An example ^{1}H NMR spectrum for PDMS conjugate **19b** with final peak assignments is shown below (Fig. 4).

The final photochromic test samples were prepared by dissolving the photochromic conjugates and controls individually in a lens monomer formulation. Previous 2D NMR investigations have confirmed intramolecular and localized associations between PDMS oligomer chains and covalently bound spirooxazine photochromic dyes in solution.[27] Within the environment of a rigid matrix stronger interactions are envisaged due to the reduced miscibility and chemical compatibility of the PDMS with the host matrix. The partitioning of oligomer tails around bound dye moieties is believed to provide an overall insulation and encapsulation effect. Visibly obvious hazing in the cured lens sample, as a result of undesirable phase separation of PDMS–dye conjugates, was not observed throughout our sample preparation. This indicated an appropriate level of miscibility of the PDMS with the lens host with the concentration levels used (Table 2).

Photochromic properties

When irradiated with UV light an initially colorless photochromic test sample becomes highly colored. Upon cessation of the incident UV light, the thermal back reaction occurs as the naphthopyran open form undergoes ring closure and samples decolorize spontaneously in the dark. Spectrokinetic properties are studied by monitoring absorption density with time at the λ_{max} of the colored form. Firstly the sample is continuously

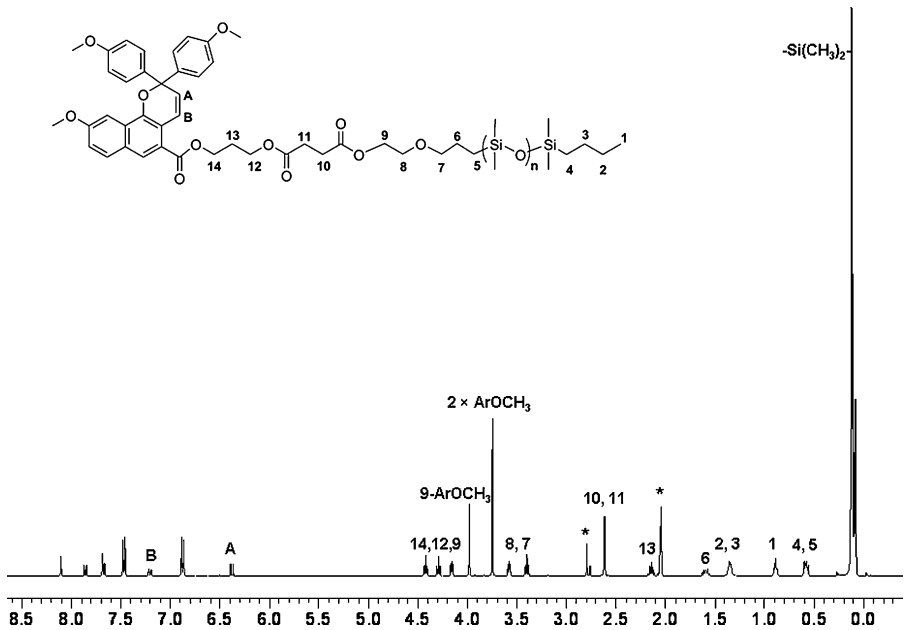


Fig. 4 ^{1}H NMR spectrum (d_6-acetone) of PDMS conjugate **19b** with peak assignments. *HDO, H_2O (2.84 ppm) and acetone (2.05 ppm).

Table 2 Photokinetic analysis of the decoloration of control and PDMS-conjugated naphthopyrans in host lens matrix (PEGMA–EBPDMA 1 : 4 mass composition) *vs.* control naphthopyrans in toluene[a]

	A_0[b]	A_1	k_1/min^{-1}	A_2	k_2/min^{-1}	A_{th}	$T_{1/2}$/s[c]	Host (conc.)[d]	λ_{max}[a]/nm
16a	1.22	0.69	1.209	0.13	0.077	0.16	55	Lens (6×10^{-7})	510
16b	1.35	0.80	1.837	0.06	0.096	0.14	31	Lens (6×10^{-7})	510
16a	1.85	0.82	3.691	0.20	0.039	0.04	19	Toluene (9.5×10^{-3})	499
17a	0.91	0.64	0.638	0.10	0.072	0.24	120	Lens (1.5×10^{-7})	500
17b	1.10	0.72	1.034	0.04	0.103	0.23	63	Lens (1.5×10^{-7})	500
17a	1.42	0.69	1.036	0.24	0.005	0	52	Toluene (5.0×10^{-5})	485
18c	1.24	0.60	0.401	0.13	0.072	0.26	212	Lens (1.5×10^{-7})	511
18a	1.15	0.64	0.463	0.10	0.077	0.24	167	Lens (1.5×10^{-7})	511
18b	1.23	0.70	0.567	0.06	0.110	0.24	123	Lens (1.5×10^{-7})	511
18c	0.84	0.70	0.724	0.18	0.025	0.05	74	Toluene (3.0×10^{-5})	501
19c	1.45	0.68	3.197	0.12	0.072	0.17	20	Lens (1.2×10^{-6})	519
19a	1.12	0.71	4.038	0.11	0.077	0.16	15	Lens (1.2×10^{-6})	519
19b	1.24	0.88	8.852	0.03	0.040	0.14	6	Lens (1.2×10^{-6})	519
19c	0.49	0.98	12.622	0.08	0.782	0	4	Toluene (2.0×10^{-4})	508
20c	1.98	0.70	2.186	0.08	0.072	0.19	28	Lens (1.2×10^{-6})	507
20a	1.79	0.73	2.878	0.08	0.075	0.18	26	Lens (1.2×10^{-6})	507
20b	1.09	0.85	4.928	0.03	0.024	0.16	11	Lens (1.2×10^{-6})	507
20c	0.87	0.89	5.479	0.13	0.041	0.01	10	Toluene (6.4×10^{-5})	497
21a	0.62	0.51	0.853	0.20	0.064	0.24	129	Lens (1.5×10^{-7})	515
21b	0.83	0.62	1.228	0.15	0.082	0.20	60	Lens (1.5×10^{-7})	515
21a	1.19	0.94	5.247	0.13	0.662	0.01	11	Toluene (6.5×10^{-5})	507
22a	0.53	0.43	0.390	0.31	0.047	0.21	355	Lens (1.5×10^{-7})	560
22b	0.73	0.71	0.776	0.16	0.083	0.10	76	Lens (1.5×10^{-7})	560
22a	1.01	0.82	1.052	0.15	0.138	0.001	45	Toluene (4.7×10^{-5})	553

[a] Samples initially irradiated at 350–400 nm for 1000 s, then thermal decoloration monitored at λ_{max} of the colored form (determined by wavelength scan of colored form[d]) at 20 °C in the dark for 4800 s. [b] Measured absorbance intensity at onset of thermal decoloration period. [c] Time taken for the initial absorbance value A_0 to decay to half. [d] Concentration in mole (naphthopyran) per gram matrix formulation (for lens); M (in toluene).

irradiated for 1000 s and then the decoloration kinetics of the naphthopyrans in solution and in the host matrix is investigated in the dark at 20 °C upon cessation of UV irradiation. The following empirical biexponential equation[48,49] was used to analyze the thermal ring closure kinetics within the host matrix:

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th} \quad (1)$$

where $A(t)$ is the optical density at λ_{max} of the open form; A_1 and A_2 are the contributions to the initial optical density A_0; k_1 and k_2 are exponential decay rate constants of fast and slow components, respectively, and A_{th} is the residual coloration (offset).

The other standard photochromic parameters presented were the λ_{max} of the photocolored form and colorability, A_0, which is

the absorbance level achieved after 1000 s of continuous irradiation. This equation has been used frequently to represent and compare the decoloration behavior of both spirooxazines and naphthopyrans within solid media[33,48,50,51] and has consistently fitted our decoloration curves with correlation coefficients (R) greater than 0.99.[23,24,52,53] An evaluation of $T_{1/2}$ value, which is the time taken for the sample to fade to half of the initial absorbance value, is also insightful for comparing overall kinetics.

As depicted in Scheme 1 (and specifically in ESI†), exposure of the naphthopyran closed form (CF) to continuous UV irradiation results in a distribution of colored merocyanine isomers. Spectroscopy studies have underlined the formation of two main classes of transoid open isomers: a short-lived and major component, namely *trans–cis* (TC) geometrical isomers and a longer-lived and minor *trans–trans* (TT) population. The latter reverts to the closed form through a two-step process (TT → TC → CF), with the TC isomers being the intermediates. The thermal decoloration behavior in solution can be attributed to these two main classes of open isomers decaying with different first-order rate constants, k_1 and k_2.[49,54–56] Kinetics within a solid substrate can be complicated by a more disperse environment in terms of distributions of free volume and variations in chemical composition within the matrix environment. Therefore, separated constants k_1 and k_2, in the equation above, along with their allocated contributions to initial optical density, are overall empirical values representing only *fast* and *slow* components. It is noteworthy, however, that PDMS conjugates tested in this study displayed a diminished contribution term, A_2, which is associated with the slower kinetic component k_2, compared to their control samples. Their kinetics more closely approached the simplified decays displayed by naphthopyrans in solution. We believe that this trend is indicative of a more homogenous and less disperse local environment created for naphthopyran molecules within the matrix as a result of PDMS tailing.

Table 2 summarizes the data obtained for kinetic fitting for all samples tested. For visual convenience, data for the PDMS conjugates are listed between that of the controls in solution (which are fastest and at the bottom of each set) and that of the controls in the host matrix (which are slowest and at the top of each set).

On the whole, all naphthopyran dyes tested displayed accelerated switching speeds in the host matrix (both coloration and decoloration) when conjugated to PDMS compared to their controls. This was evidenced by reduced $T_{1/2}$ values and increasing rate constants throughout (see Table 2); $T_{1/2}$ values were 1.3–4.7 times lower (reduced by 42–80%) and fast rate constants, k_1, were 1.2–2.8 times greater for PDMS conjugates compared to their non-conjugated controls. This is particularly apparent in Fig. 5 which shows the overlaid coloration and decoloration curves for indeno-fused naphthopyrans **22a** and **22b**.

A comparison of the kinetics of naphthopyran controls **18c**, **19c** and **20c** with respect to their alkyl extended and electronically equivalent versions (**18a**, **19a** and **20a**) showed some additional improvement to rates with an additional spacer (1.1–1.3 times higher $T_{1/2}$ values for controls containing extra spacer). However, this effect was insignificant compared to that displayed by PDMS conjugation. Fig. 6 shows the overall

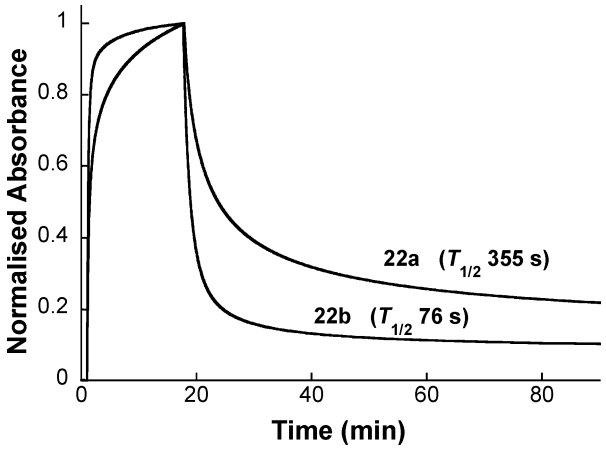


Fig. 5 Normalized absorbance *vs.* time for the coloration and decoloration of indeno-fused naphthopyran control dye **22a** and corresponding PDMS conjugate **22b** in a rigid polymeric host matrix PEGDMA–EBPDMA (1 : 4).

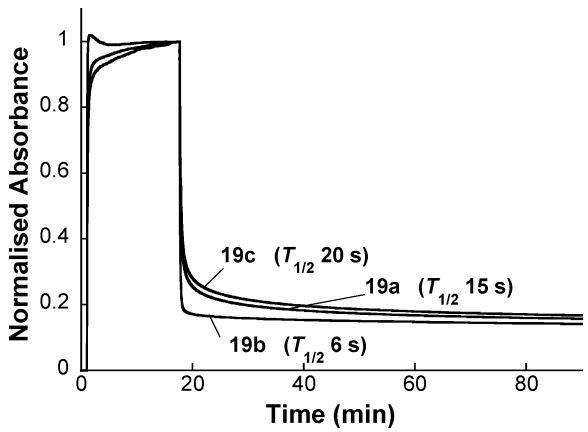


Fig. 6 Normalized absorbance *vs.* time for the coloration and decoloration of 9-methoxy substituted naphthopyran control dyes **19a** and **19c** compared to corresponding PDMS conjugate **19b** in a rigid polymeric host matrix PEGDMA–EBPDMA (1 : 4).

improvement to the switching kinetics displayed by PDMS-conjugated **19b** compared to the slower controls **19a** and **19c**, the latter displaying only minor differences with respect to one another.

All naphthopyran controls showed slower kinetics in the matrix compared to their solution behavior. This is expected due to the restricted rotational mobility of the photochromic molecules in the rigid host. The major fast decay constant, k_1, for 6-phenyl substituted naphthopyran control **21a**, dropped to a sixth of the value in the matrix compared to solution, evidenced also by significantly different $T_{1/2}$ values (129 s for matrix compared to 11 s for solution). Indeno-fused **22a** also showed considerably slower switching speed in the matrix ($T_{1/2}$ 355 s) compared to its behavior in solution ($T_{1/2}$ 45 s).

The extent to which PDMS conjugation offers solution-like behavior was estimated by directly comparing the $T_{1/2}$ values of the PDMS conjugate in the matrix to those of the control in solution (set as the lowest limit). Overall this measure ranged

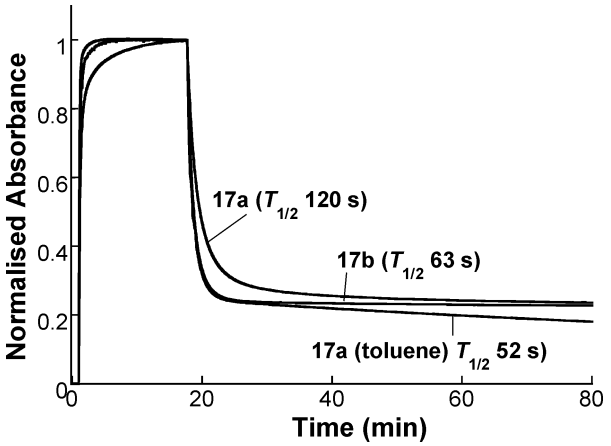


Fig. 7 Normalized absorbance *vs.* time for the coloration and decoloration of naphthopyran control dye **17a** and corresponding PDMS conjugate **17b** in host matrix PEGDMA–EBPDMA (1 : 4), 1.50×10^{-7} mol g^{-1}, compared to the behavior of **17a** in toluene (5.0×10^{-5} M).

from 20% for **21b** to 90% for **20b** with conjugates **17b**, **19b**, **20b** and **22b** being particularly impressive. Several factors are likely to be involved; the 6-phenyl substituted naphthopyran **21a** is more likely to experience steric hindrance to bond rotation within the matrix due to an additional aromatic moiety whereas naphthopyran dyes **19c** and **20c** have the benefit of a 9-methoxy moiety which acts to positively influence the energetics of the system for ring closure.[29] Interestingly the indeno-fused naphthopyran **22b**, also containing an extra bulky heterocyclic moiety, showed superior performance by more closely approaching its solution-like behavior in the matrix, in contrast to **21b**. Fig. 7 also displays superior performance for the coloration and decoloration behavior of PDMS dye **17b** in the host matrix compared to the control **17a** and its ability to restore solution-like kinetics. Inspection of the overlaid curves also indicates a weak yet residual coloration in the matrix which could only be removed in a reasonable period of time on exposure to visible light. In solution, however, this eventually faded completely in the dark. This was also evident in all other samples tested and is likely to be due to stable isomer populations whose conversion back to their closed forms is particularly unfavorable within the matrix, even in the presence of a lubricating tail.

Attachment of PDMS does not aim to modulate photochromic speed by manipulating electronic characteristics of the naphthopyran; it simply aims to restore the dye's switching potential when incorporated into a rigid media. Therefore, the methodology cannot make an inherently slow dye become fast and certainly not faster than its solution speed at a given temperature. For example, PDMS-conjugated dye **18b**, containing a 6-methoxy moiety, could never achieve the decoloration speeds in the matrix that are displayed by 9-methoxy substituted control dyes **19c** and **20c**, despite the presence of a lubricating tail—its electronic nature renders the dye inherently slow. Therefore, the overall speed of the PDMS–naphthopyran dye conjugate within the host is determined by many interplaying factors: the thermodynamics of the photochromic transition, influenced by electronic substitution, simultaneous steric affects, as well as the overall rigidity imposed by the local environment. We therefore do not expect the impact on kinetics offered by PDMS conjugation to be the same for each dye.

In previous investigations, the attachment of low T_g radically polymerized tails, such as poly(*n*-butyl acrylate) to naphthopyran dyes of base structures **16a** and **17a**, displayed not only improved de/coloration speeds but also enhanced optical densities (colorabilities) compared to their unconjugated controls.[24,57] These concurrent *fast* and *dark* effects were not evidenced throughout our entire investigations. Whilst a larger proportion of PDMS–naphthopyrans tested did display higher colorabilties some showed the contrary, such as the 9-methoxy substituted PDMS conjugates (**19b** and **20b**). It is well known that the photocoloration period involves both thermal and photochemical pathways inter-converting between the isomers.[49,54,55] A diminished colorability is likely to be the result of competitive thermal reverse processes which can affect the amount of colorless form able to convert during irradiation.[58] Nonetheless, all coloration curves comprehensively displayed an overall positive effect from PDMS conjugation with samples achieving a photostationary state very quickly (mostly within 10 min) compared to the controls which all showed reduced coloration speeds.

It is noteworthy that all naphthopyran samples also exhibited a bathochromic shift (10–15 nm) in the wavelength of their open forms within the lens matrix with respect to that in toluene. This can be accounted for by the partly polar nature of the lens matrix incorporating substantial PEG units and its interaction with their more polar transition states. Such effects are likely to have little consequence on the overall speed, with all samples displaying significantly slowed kinetics compared to those in toluene as a result of the rigidity of the matrix.

Conclusions

In conclusion, we have shown that the attachment of PDMS to various methoxy substituted naphthopyrans gives markedly superior photochromic performance in coloration and decoloration speeds and, for a majority of the samples tested, greater colorabilties within a rigid host matrix. This is made possible by providing a localized and favorable environment for switching of attached dyes and their aggregates, all acting to overcome the restrictions imposed on mobility by a rigid matrix.

Efficient routes that were used to access the relevant starting materials necessary to generate the hydroxyl functionalized naphthopyrans and subsequent conjugates were also presented as part of the investigation.

Acknowledgements

FE thanks the CRC for Polymers for funding the research in association with CAMD, School of Chem. Eng. and Ind. Chem. and CSIRO Molecular and Health Technologies for providing laboratory space. FE also acknowledges the assistance of Dr Jonathan Campbell (University of New South Wales) for the set-up and maintenance of photochromic testing equipment. TPD acknowledges the receipt of a Federation fellowship from the ARC.

References

1 B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington, D. A. Clarke and S. N. Corns, Rapid fading photo-responsive materials, WO 01/12619 A1, 2001.
2 D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington and S. N. Corns, Neutral coloring photochromic 2*H*-naphtho[1,2-*b*]pyrans and heterocyclic pyrans, *US Pat.*, 6 248 264 B1, 2001.
3 D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington and S. N. Corns, Intense colouring photochromic 2*H*-naphtho[1,2-*b*]pyrans and heterocyclic pyrans, WO 98/42695, 1998.
4 I. Calderara, Process for the manufacture of a crosslinked, transparent, hydrophilic and photochromic polymeric material, and optical and opthalmic articles obtained, *US Pat.*, 6 224 945, 2001.
5 O. Breyne and Y.-P. Chan, Naphthopyran derivatives, compositions and (co) polymer matrices containing same, *US Pat.*, 6 399 791 B1, 2002.
6 G. Berkovic, V. Krongauz and V. Weiss, *Chem. Rev.*, 2000, **100**, 1741–1753.
7 J. Delaire and K. Nakatani, *Chem. Rev.*, 2000, **100**, 1817–1845.
8 S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777–1788.
9 H. i. Lee, W. Wu, J. K. Oh, L. Mueller, G. Sherwood, L. Peteanu, T. Kowalewski and K. Matyjaszewski, *Angew. Chem., Int. Ed.*, 2007, **46**, 2453–2457.
10 M. Yamada, M. Kondo, J.-i. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett and T. Ikeda, *Angew. Chem., Int. Ed.*, 2008, **47**, 1–4.
11 V. Lemieux, D. M. Spantulescu, K. K. Baldridge and N. R. Branda, *Angew. Chem., Int. Ed.*, 2008, **47**, 5034–5037.
12 B. Van Gembert., Benzo and naphthopyrans (chromenes), in *Organic Photochromic and Thermochromic Compounds*, ed. J Crano and R Guglielmetti, Plenum Publishing, New York, 1998, vol. 1, ch. 3.
13 A. Kumar, B. Van Gemert and D. B. Knowles, Novel substituted naphthopyrans, WO 95/16215, 1995.
14 A. Kumar, B. Van Gemert and D. B. Knowles, Substituted naphthopyrans, US Pat., 5 458 814, 1995.
15 B. Van Gemert, A. Kumar and D. Knowels, *Mol. Cryst. Liq. Cryst.*, 1997, **297**, 131–138.
16 B. Van Gemert, Photochromic indeno-fused naphthopyran compounds, US Pat., 5 645 767, 1997.
17 B. Van Gemert, Novel photochromic indeno-fused naphthopyrans, WO 96/14596, 1995.
18 R. M. Christie, J. D. Hepworth, C. D. Gabbut and S. Rae, *Dyes Pigm.*, 1997, **35**(4), 339–346.
19 V. Krongauz, *Environmental Effects on Organic Photochromic Systems*, 1st edn, Elsevier House Publishing House, Amsterdam, 1990, vol. 40, pp. 793–820.
20 A. V. Lyubimov, N. L. Zaichenko and V. S. Marevtsev, *J. Photochem. Photobiol., A*, 1999, **120**, 55–62.
21 K. Ichimura, Photochromic polymers, in *Organic Photochromic and Thermochromic Compounds*, ed. J. Crano and R. Guglielmetti, 1st edn 1999, vol. 2, pp. 9–64.
22 R. A. Evans, T. L. Hanley, M. A. Skidmore, L. H. Yee and D. A. Lewis, Fast fade photochromic dyes through nano-encapsulation. Photochromic compositions and light transmissible articles, WO 2004/041961 A1, 2003.
23 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2006, **39**(4), 1392–1396.
24 N. Malic, J. A. Campbell and R. A. Evans, *Macromolecules*, 2008, **41**, 1206–1214.
25 R. A. Evans, G. K. Such, N. Malic, T. P. Davis, D. A. Lewis and J. A. Campbell, Photochromic compounds comprising polymeric substituents and methods for preparation and use thereof, WO 2006 024 099, 2006.
26 R. A. Evans and G. K. Such, *Aust. J. Chem.*, 2005, **58**, 825–830.
27 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**(3), 249–254.
28 T. Hattori, H. Nobuyuki, S. Oi, H. Abe and S. Miyano, *Tetrahedron: Asymmetry*, 1995, **6**(5), 1043–1046.
29 C. D. Gabbutt, J. D. Hepworth, M. Heron, D. A. Thomas and S. M. Partington, *Heterocycles*, 2004, **63**(3), 567–582.
30 B.-K. Kim, J. Deng; W. Xiao, B. Van Gemert, A. Chopra, F. Molock and S. Mahadevan, Opthalmic devices comprising photochromic materials having extended PI-conjugated systems, *US Pat.*, 2006/0226402, 2006.
31 S. Aki, Y. Haraguchi, H. Sakikawa, M. Ishigami, T. Fujioka, T. Furuta and J.-i. Minamikawa, *Org. Process Res. Dev.*, 2001, **5**, 535–538.
32 B. Zeynizadeh and T. Behyar, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 307.
33 W. Sriprom, M. Néel, C. D. Gabbutt, M. Heron and S. Perrier, *J. Mater. Chem.*, 2007, **17**, 1885–1893.
34 B. Van Gemert, A. Chopra and A. Kumar, Polymerizable polyalkoxylated naphthopyrans, WO 00/15629, 2000.
35 C. D. Gabbutt, M. B. Heron, A. C. Instone, D. A. Thomas, S. M. Partington, M. B. Husthouse and T. Gelbrich, *Eur. J. Org. Chem.*, 2003, 1220–1230.
36 A. M. Asiri, *J. Photochem. Photobiol., A*, 2003, **159**, 1–5.
37 S. Doulut, I. Dubuc, M. Rodriguez, F. Vecchini, H. Fulcrand, H. Barelli, F. Checler, E. Bourdel, A. Aumelas, J. C. Lallement, P. Kitabgi, J. Costentin and J. Martinez, *J. Med. Chem.*, 1993, **36**, 1369–1379.
38 K. Tanaka, T. Sugino and F. Toda, *Green Chem.*, 2000, **2**, 303–304.
39 D. L. Boger, N. Han, C. M. Tarby, C. W. Boyce, H. Cai, Q. Jin and P. A. Kitos, *J. Org. Chem.*, 1996, **61**, 4894–4912.
40 K. Tanaka, H. Aoki, H. Hosomi and S. Ohba, *Org. Lett.*, 2000, **2**(14), 2133–2134.
41 W. Zhao and E. M. Carreira, *Org. Lett.*, 2003, **5**(22), 4153–4154.
42 B. Van Gemert, M. Bergomi and D. B. Knowles, *Mol. Cryst. Liq. Cryst.*, 1994, **246**, 67–73.
43 A. Kumar, B. Van Gemert and D. Knowels, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 217–222.
44 D. L. Boger, N. Han, C. M. Tarby, C. W. Boyce, H. Cai, Q. Jin and P. A. Kitos, *J. Org. Chem.*, 1996, **61**, 4894–4912.
45 R. W. Walters and B. Van Gemert, Hydroxylated/carboxylated naphthopyrans, WO 01/70719, 2001.
46 C. D. Gabbut, B. M. Heron, A. C. Instone, P. N. Horton and M. B. Hursthouse, *Tetrahedron*, 2005, **61**, 463–471.
47 M. Edens, D. C. R. Boerner, D. N. Chase and M. D. Schiavelli, *J. Org. Chem.*, 1977, **42**(21), 3403–3407.
48 J. Biteau, F. Chaput and J. Boilot, *J. Phys. Chem.*, 1996, **100**, 9024–9031.
49 S. Delbaere, B. Luccioni-Huoze, C. Bochu, Y. Teral, M. Campredon and G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1153–1157.
50 M. Zayat and D. Levy, *J. Mater. Chem.*, 2003, **13**, 727–730.
51 G. K. Such, R. A. Evans, L. H. Yee and T. P. Davis, *J. Macromol. Sci., Polym. Rev.*, 2003, **C43**(4), 547–579.
52 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2004, **37**(26), 9664–9666.
53 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2006, **39**, 9562–9570.
54 G. Ottavi, G. Favaro and V. Malatesta, *J. Photochem. Photobiol., A*, 1998, **115**, 123–128.
55 S. Delbaere, J.-C. Micheau and G. Vermeersch, *J. Org. Chem.*, 2003, **68**, 8968–8973.
56 P. J. Coelho, M. A. Salvador, M. Oliveira and L. M. Carvalho, *J. Photochem. Photobiol., A*, 2005, **172**, 300–307.
57 F. Ercole, T. P. Davis and R. A. Evans, *Macromolecules*, 2009, **42**(5), 1500–1511.
58 G. Favaro, V. Malatesta, U. Mazzucato, G. Ottavi and A. Romani, *J. Photochem. Photobiol., A*, 1995, **87**, 235–241.