RESEARCH FRONT

CSIRO PUBLISHING

Aust. J. Chem. **2013**, *66*, 172–177
http://dx.doi.org/10.1071/CH12435

Full Paper

A Two-Stage Continuous-Flow Synthesis of Spirooxazine Photochromic Dyes

Mark York[A,B,C,D] *and Adriana Edenharter*[A]

[A]CSIRO Materials Science and Engineering, Clayton, Vic. 3169, Australia.
[B]Cooperative Research Centre for Polymers, Notting Hill, Vic. 3168, Australia.
[C]Advanced Polymerik Pty Ltd, Notting Hill, Vic. 3168, Australia.
[D]Corresponding author. Email: mark.york@csiro.au

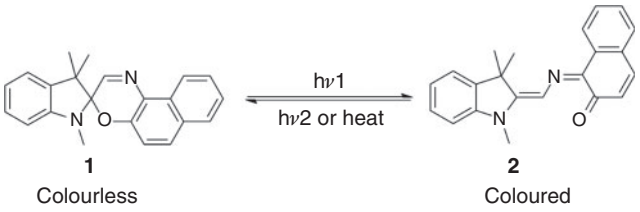
A continuous-flow process for the synthesis of several known and previously unreported spirooxazine photochromic dyes is reported. The process proceeds via an initial copper catalysed addition of substituted anilines to naphthalene-1,2-dione. This is followed by reaction with 1,3,3-trimethyl-2-methyleneindoline in the presence of hydroxylamine hydrochloride to give the desired spirooxazine products. The photochromic dyes were then cast into lenses to allow a preliminary evaluation of their properties.

Manuscript received: 25 September 2012.
Manuscript accepted: 9 November 2012.
Published online: 28 November 2012.

Introduction

The performance of synthetic transformations under continuous-flow conditions (on either a micro- or mesoscale) is an area of intense current interest. This interest can be explained, at least in part, by the array of potential advantages that continuous-flow processing presents over traditional batch processing. Such advantages include the ease of scale-up, high reproducibility, rapid mixing and heat transfer, and inherently higher safety due to smaller reactor volumes and the containment of hazardous intermediates.[1–3]

Spirooxazines are a commercially relevant class of photochromic dyes which upon exposure to ultraviolet light undergo a reversible colour change from the colourless spirocyclic isomer, **1** to the conjugated, coloured merocyanine isomer, **2** (Scheme 1).[4–8] Amongst these dyes, those substituted with an arylamino functionality in the 6′ position are of particular interest due to their green coloration,[9–11] which contrasts with the dark blue to purple coloration exhibited by most spirooxazines reported.[4]



Scheme 1.

Results and Discussion

The published syntheses of such dyes are generally performed as a three step process beginning with reaction of Folin's reagent (sodium 1,2-naphthoquinone-4-sulfonate, **3**, $R_1 = SO_3^-Na^+$) with a *N*,*N*-disubstituted aniline **4** (Scheme 2).[9–11]

During the course of our research into organic photochromism we had reason to prepare several green colouring spirooxazine dyes. We were initially drawn to investigate the continuous-flow synthesis of these dyes due to the low yields observed and the requirement for extended reaction times in the initial coupling reaction between Folin's reagent and substituted anilines **4**. These yields are typically less than 50 % with reaction times in excess of 18 h and are performed by addition of the aniline to a suspension of Folin's reagent in aqueous methanol.[9,10] Furthermore, such a method is not suitable for use with sterically hindered anilines, giving no detectable amounts of product even after extended reaction times for reaction with *N*,*N*,3,5-tetramethylaniline.[12] A single report exists of the formation of substituted naphthoquinones **5** under similar conditions in >80 % yield with a reaction time of 4–5 h.[11] However, in our hands, this protocol gave a <20 % yield of the desired products. The synthesis of 1,2-naphthoquinones of the general structure **5** has also been reported from the reaction of the corresponding anilines in the presence of stoichiometric amounts of copper or nickel, with the products being isolated in ~50 % yield.[13–15]

Our synthesis of substituted 1,2-naphthoquinones **5** was performed by heating a solution of 1,2-naphthoquinone **3** ($R_1 = H$), aniline **4** and 10 mol-% copper (II) chloride in *N*,*N*-dimethylacetamide (DMAc) at 140°C for 10 min using a commercially available Vapourtec flow reactor (Scheme 3).[16]

In this way, reaction with *N*,*N*-diethylaniline gave an 80 % yield of the corresponding naphthoquinone **5a**. In the absence of catalytic copper only 18 % of the product was isolated (Table 1, entry 1). Performance of the reaction in a sealed tube under microwave irradiation gave only a 54 % yield of the product (Table 1, entry 1). The reason for this reduction in yield is unknown although it may be a reflection of the greater operating

pressure of the continuous-flow system. The presence of a free hydroxyl group in the aniline was well tolerated (Table 1, entries 2 and 5) as were substituents in the 3 position, which could have been expected to provide a steric barrier to the coupling reaction (Table 1, entries 2–4 and 6). Notably *N*,*N*,3,5-tetramethylaniline, which failed to react under the standard literature conditions,[12] gave the corresponding product **5f** in 51 % yield (Table 1, entry 5).

With naphthoquinone derivatives **5** in hand we then turned our attention to the conversion of these into the spirooxazine photochromic dyes **7**. This is typically done in two discreet stages, with an initial conversion of the 4-substituted naphthoquinone **5** to the corresponding oxime **6** by treatment with hydroxylamine hydrochloride, before reaction with a substituted methylene indoline to deliver the spirooxazine photochromic **7** (Scheme 2).[10,11]

In order to avoid the necessity of two separate steps a combined protocol was developed whereby a mixture of the naphthoquinone **5** and hydroxylamine hydrochloride in 3 : 1 v/v MeOH : THF was mixed with a second reagent stream containing a solution of *N*,*N*-diisopropylethylamine (DIPEA) and 1,3,3-trimethyl-2-methyleneindoline in MeOH. The combined reagent stream was then pumped through a series of four 10 mL tube reactors at 120°C with a total residence time of 20 min allowing the synthesis of the desired photochromics **7** without the need to isolate the intermediate oximes **6** (Scheme 4). The presence of DIPEA was required to deprotonate the oxime hydrochloride salt formed in the reaction. In its absence only traces of product were observed.

As can be seen, the continuous flow method was successful for the synthesis of both known (Table 2, entry 1) and novel (Table 2, entries 2–3 and 5–8) spirooxazine photochromic dyes in moderate yields. In this way oxime **5a** gave the corresponding spirooxazine in 55 % yield (Table 2, entry 1). The process could also be performed in a sealed tube under microwave irradiation, although in this case the yield was slightly lower than that obtained under continuous-flow conditions (Table 2, entry 1).

In the case of the naphthoquinone bearing a free hydroxyl functionality (**5e**) the reaction was not successful due to insufficient solubility of the starting quinone in the reaction medium (Table 2, entry 4).

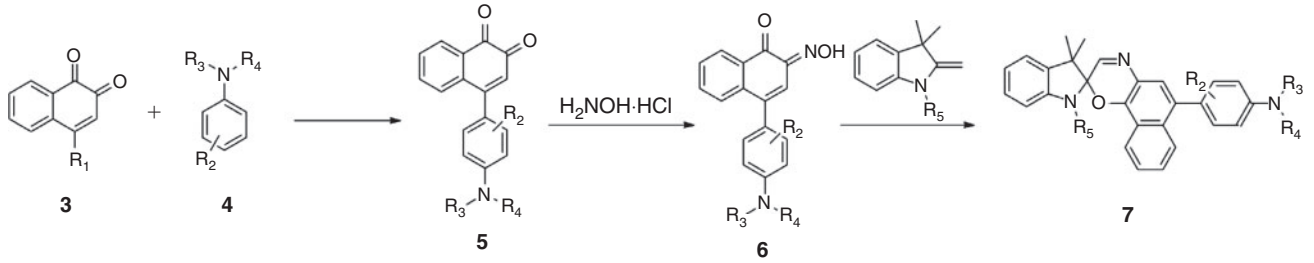
In order to undertake a preliminary evaluation of the photochromic properties of novel compounds **7b**, **7c**, and **7e** to **7h**, in comparison to known dye **7a**, test lenses were prepared. The lenses were composed of a matrix containing polyethyleneglycol 400 dimethacrylate and bisphenol A ethoxylate dimethacrylate in a 1 : 4 weight ratio with 0.4 % AIBN by mass as initiator. The monomer was thoroughly mixed with 1.5×10^{-6} mol of spirooxazine per gram of matrix and the lenses thermally cured. The lenses, after irradiation at 365 nm with a handheld UV source, can be seen in Fig. 1. Variations in the nitrogen substituents of the aniline gave only very subtle changes in the green coloration of the dyes (Fig. 1; **7a**, **7g**, and **7h**). Substituents in either the 3 or 5 position of the aniline tended to produce dyes which were blue shifted (Fig. 1; **7b**, **7c**, **7e**, and **7f**).

Conclusion

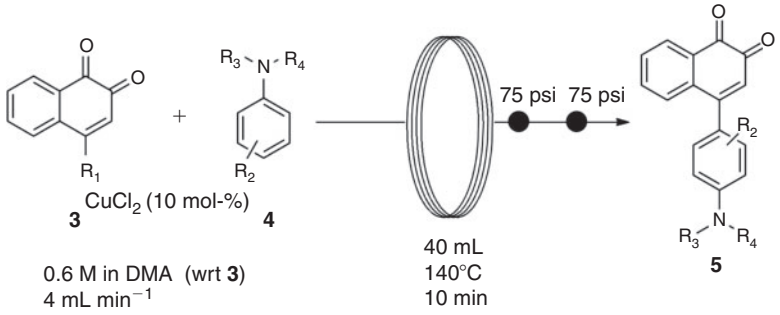
In conclusion, a two stage, continuous-flow process for the synthesis of spirooxazine photochromic dyes has been developed including a copper catalysed addition of substituted anilines to 1,2-naphthoquinone. This method provides convenient access to several both novel and previously unreported dyes, including some which are not accessible using previously published syntheses.

Experimental

Continuous-flow chemistry was performed on a Vapourtec R-4 flow reactor heater with a connected R2+ pumping module using either DMAc (**5**) or MeOH (**7**) as flow solvent. NMR data were collected on a Bruker AV200 (200 MHz) or Bruker AV400 (400 MHz) spectrometer using $CDCl_3$ as the solvent and TMS as internal standard. Positive ion EI mass spectra were collected using a ThermoQuest MAT95XL mass spectrometer with an

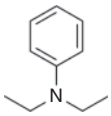
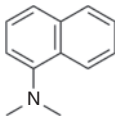
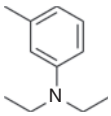
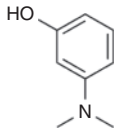
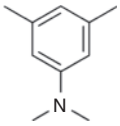
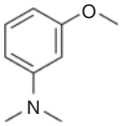
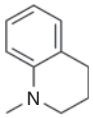
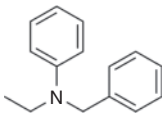


Scheme 2.



Scheme 3.

Table 1. Continuous-flow synthesis of substituted 1,2-naphthoquinones 5

Entry	Aniline	Product	Yield [%]
1		**5a**	80 18[A] 54[B]
2		**5b**	65
3		**5c**	82
4		**5d**	64
5		**5e**	51
6		**5f**	86
7		**5g**	81
8		**5h**	66

[A]Reaction performed in the absence of $CuCl_2$.
[B]Reaction performed in a sealed tube under microwave irradiation.

ionisation energy of 70 eV. UV-Vis spectra were recorded using a Hewlett Packard 8453 diode array spectrophotometer. Melting points were obtained using a Gallenkamp capillary melting point apparatus and are uncorrected. The anilines used to prepare **5f** and **5g** were synthesised according to published procedures.[17,18] All other starting materials were purchased from commercial sources and used without further purification.

*General Procedure for the Preparation of 4-Substituted 1,2-Naphthoquinones, **5***

A solution of substituted aniline (3.35 mmol), copper (II) chloride (35 mg, 0.335 mmol) and 1,2-naphthoquinone (1.06 g, 6.70 mmol) in DMAc (total volume of solution = 11.5 mL) was pumped at a rate of 4 mL min^{-1} through a series of 4 × 10 mL reactor coils (PFA tubing, 1 mm i.d.) heated to 140°C. The reagent stream was eluted through 2 × 75 psi back pressure regulators into a mixture of ethyl acetate (50 mL) and water (50 mL). The organic phase was separated, washed with a further portion of water (30 mL), dried over magnesium sulfate and evaporated under vacuum. The residue was then purified by column chromatography over silica gel eluting with 0–20 % v/v ethyl acetate/light petroleum 40–60°C.

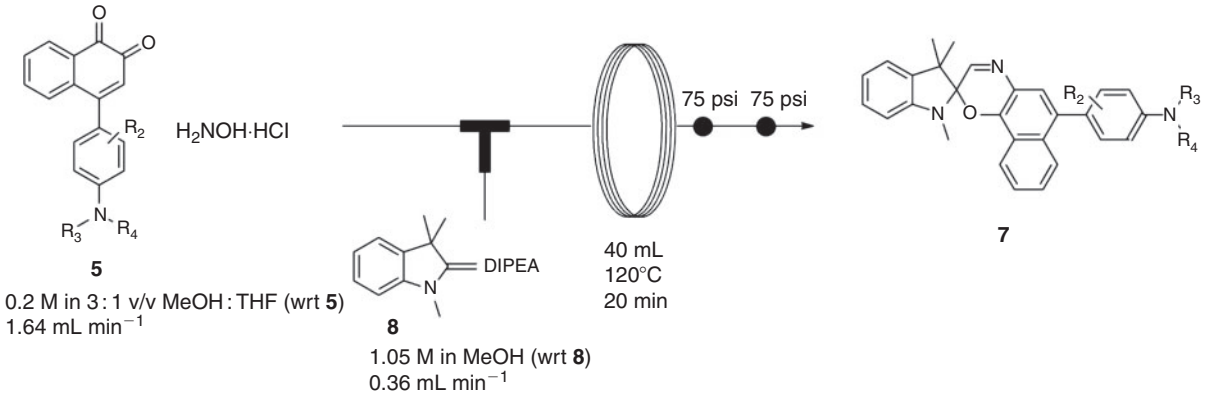
4-(4-(Diethylamino)phenyl)naphthalene-1,2-dione **5a** is a known compound; analytical data was in good agreement with that reported previously.[9]

*4′-(Dimethylamino)-[1,1′-binaphthalene]-3,4-dione **5b***

Obtained as a dark brown solid in 65 % yield; mp 66–68°C. δ_H (400 MHz) 8.30 (d, *J* 8.4, 1H), 8.20 (dd, *J* 7.6 and 1.5, 1H), 7.65 (d, *J* 8.4, 1H), 7.53–7.49 (m, 1H), 7.49–7.44 (dt, *J* 7.6 and 1.2, 1H), 7.42–7.35 (m, 3H), 7.11 (d, *J* 7.7, 1H), 6.89 (dd, *J* 7.6 and 1.1, 1H), 6.52 (s, 1H), 2.97 (s, 6H). δ_c (100 MHz) 180.9, 179.8, 157.3, 152.7, 136.4, 135.5, 132.5, 131.5, 130.8, 130.3, 130.2, 129.1, 128.8, 128.6, 126.8, 126.4, 126.3, 125.8, 125.1, 113.3, 45.2. *m/z* (HREI) calc. for $C_{22}H_{17}NO_2$ 327.1254 ($M^{+\bullet}$), found 327.1255.

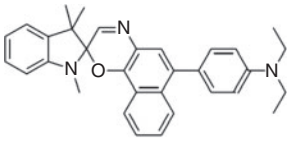
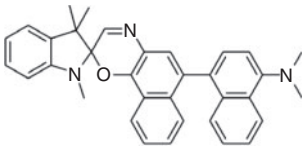
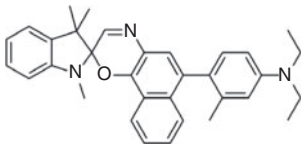
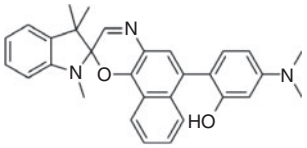
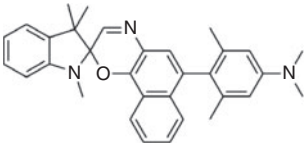
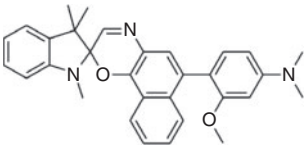
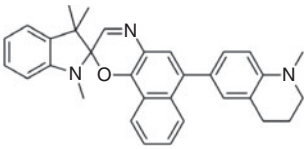
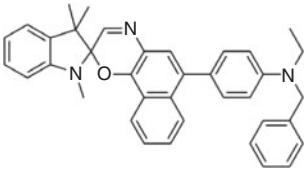
*4-(4-(Diethylamino)-2-methylphenyl) naphthalene-1,2-dione **5c***

Obtained as a dark blue solid in 82 % yield; mp 148–149°C. δ_H (400 MHz) 8.15 (dd, *J* 7.5 and 1.6, 1H), 7.54–7.49 (dt, *J* 7.6 and 1.5, 1H), 7.49–7.44 (dt, *J* 7.5 and 1.3, 1H), 7.12 (dd, *J*7.6 and 1.2, 1H), 7.05–7.00 (m, 1H), 6.60–6.55 (m, 2H), 6.35 (s, 1H), 3.39 (q, *J* 7.1, 4H), 2.16 (s, 3H), 1.20 (t, *J* 7.1, 6H). δ_c (100 MHz) 180.9, 180.2, 158.5, 148.6, 136.8, 136.4, 135.4, 131.6, 130.6,



Scheme 4.

Table 2. Continuous-flow synthesis of substituted spirooxazines 7

Entry	Oxime	Product	Yield [%]
1	**5a**	 **7a**	55 41[A]
2	**5b**	 **7b**	71
3	**5c**	 **7c**	63
4	**5d**	 **7d**	ND[B]
5	**5e**	 **7e**	68
6	**5f**	 **7f**	45
7	**5g**	 **7g**	59
8	**5h**	 **7h**	53

[A]Reaction performed in a sealed tube under microwave irradiation.
[B]Reaction unsuccessful, starting material insufficiently soluble. ND = not determined.

130.1, 130.0, 128.1, 123.1, 113.2, 109.1, 44.5, 21.1, 12.8. *m/z* (HREI) calc. for $C_{21}H_{21}NO_2$ 319.1567 ($M^{+\bullet}$), found 319.1562.

4-(4-(Dimethylamino)-2-hydroxyphenyl) naphthalene-1,2-dione ***5d***

Obtained as a dark purple solid in 64 % yield; mp 182–185°C. δ_H (400 MHz) 8.16 (dd, *J* 7.4 and 1.6, 1H), 7.58–7.53 (dt, *J* 7.6 and 1.6, 1H), 7.52–7.47 (m, 1H), 7.34 (dd, *J* 7.8 and 1.2, 1H), 7.10 (d, *J* 8.6, 1H), 6.47 (s, 1H), 6.41 (dd, *J* 8.6 and 2.5, 1H), 6.27 (d, *J* 1.5, 1H), 4.89 (br s, 1H), 3.02 (s, 6H). δ_c (100 MHz) 180.6, 180.2, 155.2, 154.4, 153.2, 135.4, 135.2, 131.8, 131.1, 130.8, 130.2, 130.1, 127.8, 111.2, 105.3, 99.7, 40.4. *m/z* (HREI) calc. for $C_{18}H_{13}NO_3$ 291.0890 ($M^{+\bullet}$), found 218.0899.

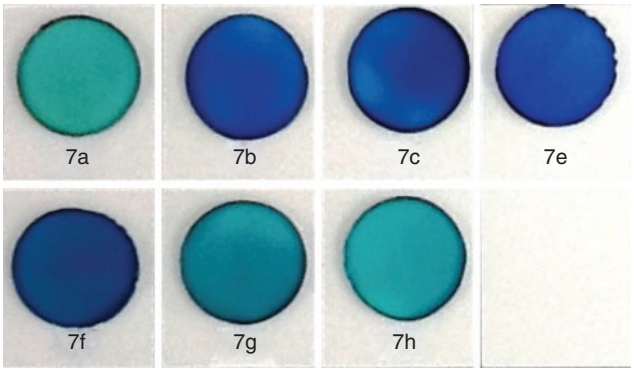


Fig. 1. Test lenses containing spirooxazine compounds **7a**–**7c** and **7e**–**7h** after UV irradiation.

4-(4-(Dimethylamino)-2,6-dimethylphenyl) naphthalene-1,2-dione ***5e***

Obtained as a dark brown solid in 51 % yield; mp 180–182°C. δ_H (400 MHz) 8.18–8.15 (m, 1H), 7.50–7.46 (m, 2H), 6.92–6.88 (m, 1H), 6.50 (s, 2H), 6.32 (s, 1H), 2.99 (s, 6H), 2.11 (s, 6H). δ_c (100 MHz) 180.9, 179.9, 158.2, 150.6, 136.1, 136.0, 135.8, 131.6, 130.8, 130.1, 129.0, 128.7, 123.8, 111.5, 40.4, 20.6. *m/z* (HREI) calc. for $C_{20}H_{19}NO_2$ 305.1410 ($M^{+\bullet}$), found 305.1409.

4-(4-(Dimethylamino)-2-methoxyphenyl) naphthalene-1,2-dione ***5f***

Obtained as a dark purple solid in 86 % yield; mp 172–174°C. δ_H (400 MHz) 8.10 (dd, *J* 7.6 and 1.4, 1H), 7.52–7.46 (dt, *J* 7.6 and 1.5, 1H), 7.45–7.39 (dt, *J* 7.5 and 1.2, 1H), 7.17 (dd, *J* 7.6 and 1.0, 1H), 7.10 (d, *J* 8.5, 1H), 6.40 (s, 1H), 6.37 (dd, *J* 8.5 and 2.2, 1H), 6.27 (d, *J* 2.2, 1H), 3.73 (s, 3H), 3.04 (s, 6H). δ_c (100 MHz) 180.8, 180.4, 158.1, 156.2, 153.2, 136.0, 134.8, 131.5, 130.9, 130.2, 129.9, 129.7, 127.9, 113.5, 104.6, 95.4, 55.4, 40.5. *m/z* (HREI) calc. for $C_{19}H_{17}NO_3$ 307.1203 ($M^{+\bullet}$), found 307.1203.

4-(1-Methyl-1,2,3,4-tetrahydroquinolin-6-yl) naphthalene-1,2-dione ***5g***

Obtained as a dark blue solid in 81 % yield; mp 165°C. δ_H (400 MHz) 8.14 (d, *J* 7.4, 1H), 7.59–7.53 (m, 2H), 7.50–7.44 (m, 1H), 7.20 (dd, *J* 8.5 and 2.2, 1H), 7.09–7.06 (m, 1H), 6.60 (d, *J* 8.6, 1H), 6.38 (s, 1H), 3.33 (t, *J* 5.7, 2H), 2.97 (s, 3H), 2.78 (t, *J* 6.3, 2H), 2.04–1.95 (m, 2H). δ_c (100 MHz) 180.6, 180.3, 157.6, 148.4, 135.5, 134.8, 132.1, 130.5, 130.3, 130.0, 129.2, 128.4, 125.5, 123.3, 122.6, 110.2, 51.2, 38.9, 28.0, 22.0. *m/z* (HREI) calc. for $C_{20}H_{17}NO_2$ 303.1254 ($M^{+\bullet}$), found 303.1251.

4-(4-(Benzyl(ethyl)amino)phenyl)naphthalene-1,2-dione ***5h***

Obtained as a dark violet gum in 66 % yield. δ_H (400 MHz) 8.14 (d, *J* 7.7, 1H), 7.59–7.51 (m, 2H), 7.50–7.44 (m, 1H), 7.35–7.30 (m, 4H), 7.28–7.21 (m, 3H), 6.75 (d, *J* 9.0, 2H), 6.38

(s, 1H), 4.60 (s, 2H), 3.56 (q, *J* 7.1, 2H), 1.27 (t, *J* 7.5, 3H). δ_c (100 MHz) 180.5, 180.3, 157.4, 150.1, 138.1, 135.4, 134.8, 132.0, 130.5, 130.4, 130.3, 129.9, 128.9, 127.2, 126.4, 125.7, 123.5, 111.7, 53.8, 45.5, 12.3. *m/z* (HREI) calc. for $C_{25}H_{21}NO_2$ 367.1567 ($M^{+\bullet}$), found 367.1560.

General Procedure for the Preparation of Substituted Spirooxazines, 7

A solution of substituted 1,2-naphthoquinone **5** (0.98 mmol) and hydroxylamine hydrochloride (75 mg, 1.08 mmol) in 3 : 1 v/v MeOH : THF (total volume of solution = 5 mL), pumped at a rate of 1.64 mL min^{-1} was mixed at ambient temperature via a T-piece with a solution of 1,3,3-trimethyl-2-methyleneindoline (204 mg, 1.18 mmol) and DIPEA (188 µL, 1.08 mmol) in MeOH (total volume of solution = 1.1 mL), pumped at a rate of 0.36 mL min^{-1}. The combined reagent stream was then passed through a series of series of 4 × 10 mL reactor coils (PFA tubing, 1 mm i.d.) heated to 120°C before elution through 2 × 75 psi back pressure regulators. The eluent was then evaporated under vacuum and the residue was then purified by column chromatography over silica gel eluting with 0–10 % v/v ethyl acetate/light petroleum 40–60°C.

N,*N*-Diethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl)aniline **7a** is a known compound; analytical data was in good agreement with that reported previously.[9]

N,N-*Dimethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl)naphthalen-1-amine* ***7b***

Obtained as a sage foam in 71 % yield; mp 171–173°C. λ_{max} 607 nm. δ_H (400 MHz) 8.39 (d, *J* 8.4, 1H), 8.13 (d, *J* 8.5, 1H), 7.78 (d, *J* 2.5, 1H), 7.60 (d, *J* 2.7, 1H), 7.51–7.44 (m, 3H), 7.35–7.16 (m, 7H), 6.96 (dt, *J* 8.9 and 1.2, 1H), 6.66 (t, *J* 7.6, 1H), 3.04 (s, 6H), 2.92 and 2.86 (2 s, 3H), 1.47–1.13 (m, 6H). δ_c (100 MHz) 152.8, 152.5, 147.9, 141.3, 136.2, 134.4, 134.3, 131.6, 128.9, 128.3, 128.2, 127.9, 127.3, 127.0, 126.9, 125.6, 125.2, 124.7, 124.5, 123.7, 122.2, 121.7, 120.0, 113.8, 107.3, 99.7, 99.4, 52.1, 52.0, 45.5, 30.0, 29.9, 25.7, 21.2. *m/z* (HREI) calc. for $C_{34}H_{31}N_3O$ 497.2462 ($M^{+\bullet}$), found 497.2463.

N,N-*Diethyl-3-methyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl)aniline* ***7c***

Obtained as a pale green solid in 63 % yield; mp 147–148°C. λ_{max} 612 nm. δ_H (400 MHz) 8.10–8.07 (m, 1H), 7.76 (d, *J* 3.7, 1H), 7.56–7.51 (m, 1H), 7.45 (d, *J* 3.3, 1H), 7.38–7.35 (m, 2H), 7.27 (t, *J* 7.6, 1H), 7.16–7.12 (m, 2H), 6.95 (t, *J* 7.4, 1H), 6.68–6.62 (m, 3H), 3.45 (q, *J* 7.0 4H), 2.87 and 2.83 (2 s, 3H), 2.07 (s, 3H), 1.46–1.31 (m, 6H), 1.27 (t, *J* 7.1, 6H). δ_c (100 MHz) 152.7, 152.3, 147.9, 147.5, 140.7, 138.0, 136.2, 134.1, 133.2, 131.9, 128.1, 127.0, 126.8, 125.4, 124.6, 123.7, 122.2, 121.7, 119.9, 112.9, 109.2, 107.3, 99.5, 99.2, 52.0, 51.8, 44.5, 29.9, 25.6, 21.1, 13.0. *m/z* (HREI) calc. for $C_{33}H_{35}N_3O$ 489.2775 ($M^{+\bullet}$), found 497.2764.

N,N,*3,5-Tetramethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl)aniline* ***7e***

Obtained as a pale green foam in 68 % yield; mp 190–192°C. λ_{max} 605 nm. δ_H (400 MHz) 8.09 (dt, *J* 7.7 and 1.5, 1H), 7.76 (s, 1H), 7.39–7.26 (m, 5H), 7.15 (dd, *J* 7.3 and 0.9, 1H), 6.96 (dt, *J* 7.4 and 0.9, 1H), 6.66–6.62 (m, 3H), 3.05 (s, 6H), 2.87 (s, 3H), 1.97 (d, *J* 6.0, 6H), 1.44 (d, *J* 12.6, 6H). δ_c (100 MHz) 152.6, 147.8, 140.7, 138.3, 136.2, 133.9, 131.9, 128.1, 127.0, 126.0, 125.5, 125.0, 124.0, 122.23, 121.7, 119.9, 111.8, 107.3, 99.4, 52.0, 40.9, 29.9, 25.6, 21.2, 21.1. *m/z* (HREI) calc. for $C_{32}H_{33}N_3O$ 475.2618 ($M^{+\bullet}$), found 475.2614.

*3-Methoxy-*N,N-*dimethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl) aniline* ***7f***

Obtained as a khaki foam in 45 % yield; mp 108–110°C. λ_{max} 614 nm. δ_H (400 MHz) 8.09–8.04 (m, 1H), 7.75 (d, *J* 6.2, 1H), 7.64–7.60 (m, 1H), 7.51 (d, *J* 4.3, 1H), 7.40–7.30 (m, 2H), 7.26 (t, *J* 7.7, 1H), 7.20 (dd, *J* 8.3 and 1.2, 1H), 7.14 (t, *J* 7.4, 1H), 6.95 (dt, *J* 7.3 and 2.0, 1H), 6.64 (t, *J* 8.2, 1H), 6.54–6.42 (m, 2H), 3.72 (s, 3H), 3.07 (s, 6H), 2.87 and 2.83 (2 s, 3H), 1.46–1.41 (m, 6H). δ_c (100 MHz) 158.3, 152.5, 151.9, 148.0, 140.8, 136.3, 133.9, 132.8, 130.2, 128.1, 127.5, 127.0, 126.6, 125.3, 124.6, 123.8, 122.1, 121.7, 119.9, 107.3, 104.9, 99.6, 99.1, 66.0, 55.7, 52.0, 51.7, 40.9, 30.0, 25.8, 23.3, 21.3. *m/z* (HREI) calc. for $C_{31}H_{31}N_3O_2$ 477.2411 ($M^{+\bullet}$), found 477.2401.

*1,3,3-Trimethyl-6′-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)spiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazine]* ***7g***

Obtained as a cream solid in 59 % yield; mp 205–206°C. λ_{max} 628 nm. δ_H (400 MHz) 8.06 (dd, *J* 7.7 and 2.1, 1H), 7.98 (dd, *J* 7.7 and 2.0, 1H), 7.74 (s, 1H), 7.50 (s, 1H), 7.43–7.35 (m, 2H), 7.26–7.22 (m, 2H), 7.15–7.13 (m, 2H), 6.95 (t, *J* 6.1, 1H), 6.73 (d, *J* 8.4, 1H), 6.62 (d, *J* 7.7, 1H), 3.33 (t, *J* 5.6, 2H), 2.98 (s, 3H), 2.86 (t, *J* 6.3, 2H), 2.82 (s, 3H), 2.11–2.05 (m, 2H), 1.41 (d, *J* 6.5, 6H). δ_c (100 MHz) 152.5, 147.8, 146.0, 140.5, 136.2, 133.7, 133.1, 130.8, 129.0, 128.1, 127.9, 126.8, 126.6, 126.3, 125.5, 124.6, 122.8, 122.2, 121.7, 119.9, 110.8, 107.3, 99.4, 51.8, 51.5, 39.3, 29.9, 28.0, 25.6, 22.6, 21.1. *m/z* (HREI) calc. for $C_{32}H_{31}N_3O$ 473.2462 ($M^{+\bullet}$), found 473.2441.

N-*Benzyl-*N-*ethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-*b*][1,4]oxazin]-6′-yl)aniline* ***7h***

Obtained as a dark green foam in 53 % yield; mp 116–117°C. λ_{max} 623 nm. δ_H (400 MHz) 8.07 (dd, *J* 6.9 and 1.8, 1H), 7.98 (dd, *J* 7.1 and 1.6, 1H), 7.74 (s, 1H), 7.52 (s, 1H), 7.42–7.25 (m, 11H), 7.14 (dd, *J* 7.3 and 0.9, 1H), 6.95 (t, *J* 7.5, 1H), 6.84 (d, *J* 8.8, 1H), 6.62 (d, *J* 7.7, 1H), 4.64 (s, 2H), 3.59 (q, *J* 7.1, 2H), 2.83 (s, 3H), 1.42 (d, *J* 7.0, 6H), 1.33 (t, *J* 6.0, 3 H). δ_c (100 MHz) 152.6, 147.9, 147.8, 140.5, 139.4, 136.2, 133.6, 133.1, 131.2, 128.8, 128.1, 127.8, 127.0, 126.8, 126.7, 126.5, 126.4, 125.5, 124.7, 124.0, 122.2, 121.7, 199.9, 112.0, 107.3, 99.4, 54.2, 51.9, 45.4, 29.9, 25.7, 21.1, 12.4. *m/z* (HREI) calc. for $C_{37}H_{35}N_3O$ 537.2775 ($M^{+\bullet}$), found 537.2767.

General Procedure for the Preparation of Test Lenses

A matrix composed of polyethyleneglycol 400 dimethacrylate and bisphenol A ethoxylate dimethacrylate in a 1 : 4 weight ratio with 0.4 % AIBN by mass as initiator was thoroughly mixed with 1.5×10^{-6} mol of spirooxazine per gram of matrix. The lenses were then added to a mould and thermally cured with a gradient heating profile (40°C for 60 min followed by an increase of 0.2°C per minute for 275 min followed by 95°C for 180 min). The lenses thus formed had a diameter of 15 mm and a thickness of 1 mm.

Supplementary Material

^{1}H and ^{13}C NMR for compounds **5a**–**5h**, **7b**–**7c**, and **7e**–**7h** and UV-Vis spectra for compounds **7a**–**7c** and **7e**–**7h** are available on the Journal's website.

Acknowledgements

The authors thank the Co-operative Research Centre for Polymers, Advanced Polymerik Pty Ltd, and CSIRO Materials Science and Engineering for their support.

References

[1] J. Yoshida, H. Kim, A. Nagaki, *ChemSusChem* **2011**, *4*, 331. doi:10.1002/CSSC.201000271

[2] D. Webb, T. F. Jamison, *Chem. Sci.* **2010**, *1*, 675. doi:10.1039/C0SC00381F

[3] J. Wegner, S. Ceylan, A. Kirschning, *Chem. Commun.* **2011**, *47*, 4583. doi:10.1039/C0CC05060A

[4] V. Lokshin, A. Samat, A. V. Metelitsa, *Russ. Chem. Rev.* **2002**, *71*, 893. doi:10.1070/RC2002V071N11ABEH000763

[5] H. Bouas-Laurent, H. Durr, *Pure Appl. Chem.* **2001**, *73*, 639. doi:10.1351/PAC200173040639

[6] N. Malic, J. A. Campbell, A. S Ali, M. York, A. D'Souza, R. A. Evans, *Macromolecules* **2010**, *43*, 8488. doi:10.1021/MA101051M

[7] M. York, R. A. Evans, *Tetrahedron Lett.* **2010**, *51*, 2195. doi:10.1016/J.TETLET.2010.02.105

[8] M. York, *Tetrahedron Lett.* **2012**, *53*, 2226. doi:10.1016/J.TETLET.2012.02.082

[9] M. York, R. A. Evans, *Synth. Commun.* **2010**, *40*, 3618. doi:10.1080/00397910903457423

[10] D. A. Clarke, B. M. Heron, C. D. Gabbutt, J. D. Hepworth, S. M. Partington, S. N. Corns, *U. S. Patent 6 303 673* **2001**.

[11] M. Rickwood, S. D. Marsden, V. E. Askew, *U. S. Patent 5 446 150* **1995**.

[12] A mixture of sodium 1,2-naphthoquinone-4-sulfonate (0.3 g, 1.153 mmol) and *N*,*N*,3,5-tetramethylaniline (0.17 g, 1.153 mmol) in 20 % aqueous methanol (8.5 mL) was stirred for 72 h at room temperature. Analysis of the mixture showed none of the desired product had formed.

[13] Y. Ooyama, T. Okamoto, T. Yamaguchi, T. Suzuki, A. Hayashi, K. Yoshida, *Chem. – Eur. J.* **2006**, *12*, 7827. doi:10.1002/CHEM.200600094

[14] Y. Ooyama, S. Nagano, K. Yoshida, *Tetrahedron* **2009**, *65*, 1467. doi:10.1016/J.TET.2008.12.003

[15] Y. Ooyama, Y. Kagawa, Y. Harima, *Eur. J. Org. Chem.* **2007**, 3613. doi:10.1002/EJOC.200700247

[16] www.vapourtec.co.uk.

[17] P. R. de Oliveira, D. S. Ribeiro, R. Rittner, *J. Phys. Org. Chem.* **2005**, *18*, 513. doi:10.1002/POC.896

[18] H. Ahlbrecht, E. O. Dueber, J. Epsztajn, R. M. K. Martcinowski, *Tetrahedron* **1984**, *40*, 1157. doi:10.1016/S0040-4020(01)99321-4