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A simple, novel method for the preparation of *polymer-tetherable*, zwitterionic merocyanine NLO-chromophores

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A suite of polymer-ready nonlinear optical merocyanines has been synthesised and characterised. The tethering functionality—a vicinal dihydroxypropyl residue—is introduced onto the donor nitrogen of the chromophore precursor without the need for protection/deprotection steps, thereby giving ready access to potentially high T_g condensation polymer systems. An X-ray crystal structure determination on a representative chromophore **5** confirms the largely zwitterionic nature of these systems and experimental measurements of second-order nonlinear response [$\beta(0)$], by hyper-Raleigh scattering, indicate that a pyridylidene donor–quinomethide acceptor combination gives rise to the largest nonlinearity.

1. Introduction

In the search for optically nonlinear organic chromophores and $\chi^{(2)}$ materials that will find use in photonics applications, a great deal of research has focused upon the molecular engineering requirements to optimise optical nonlinearities in *push–pull* compounds (*i.e.* molecules that contain electron-donating and electron-withdrawing substituents flanking a conjugating π-framework).[1–3] In realising ever-increasing values of the first hyperpolarisability $\beta(0)$ in these systems, the chromophores have become more extensively and efficiently conjugated and structurally elaborate[4] with the concomitant result of having intense intramolecular charge-transfer absorption in the visible spectrum. This phenomenon greatly minimises the optical transparency range of these chromophores, a fact that is clearly of critical importance, for example, to the process of successfully interfacing plastic optical fibres to plastic optoelectronic devices.

As a means of overcoming this dilemma and, at the same time, seeking synthetic expediency, we became interested in exploring the possibility of preparing polymers containing chromophores with increased ground state zwitterionic character (*e.g.* Brooker-type merocyanines, $n \leqslant 1$, Fig. 1) reasoning that acceptable figures of merit $\mu\beta(0)$ might be realisable by trading some β for some μ. Hence, by 'blue-shifting' λ^{CT} and increasing the chromophore dipole moment, this would enhance the figures of merit of such molecules for poled materials applications that might use any second-order effects.

As has been previously recognised,[5–7] merocyanines of this type and other amphiphilic systems are classes of NLO chromophores that are known[8–12] to have large second-order hyperpolarisabilties and yet have received comparatively scant attention from a materials point of view, a fact that is surprising particularly because stabilisation of the charge-separated state is relatively easily achieved. To our knowledge, there has only been the one high-β zwitterionic chromophore system—the pyridino-phenolate (Fig. 1, $n=0$)—that has been covalently incorporated into a polymer matrix;[13,14] albeit to give a low T_g (*co*)methacrylate.

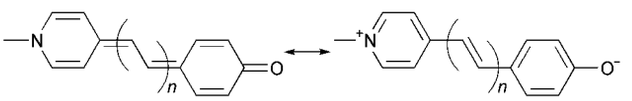

Fig. 1 Limiting ground state geometries of merocyanines.

Here we report a simple and efficient strategy that enables ready access to potentially high T_g condensation polymers that contain the more zwitterionic merocyanine-type chromophores as mainchain components of the polymer. With pyridylidene and benzothiazolylidene donor systems, in particular, the chemistry is achievable *without* the need for protection/deprotection of the tethering functionality and polyurethanes, for example, are easily accessible.

2. Results and discussion

Chromophore syntheses

The synthesis of the dihydropyridylidene donor moiety common to both the stilbazolium and heterocyclic merocyanine systems was accomplished by alkylating 4-picoline (4-methylpyridine) with either 3-iodo- or 3-chloropropane-1,2-diol to give the *N*-(dihydroxypropyl)picolinium salts **1a,b** as stable, colourless materials that required no purification prior to subsequent reaction. Only the picolinium chloride was able to be purified by recrystallisation. Alkylation with the isopropylidene 1,2-protected iododiol was successful but ultimately unnecessary. Our initial attempts to functionalise 4-picoline by alkylation with a symmetrical (protected) diol, 2-*O*-tosyl-1,3-*O*-benzylideneglycerol, for example, were unsuccessful, presumably as a result of steric hindrance to underside S_N2 approach through nonbonded interactions by the 1,3-dioxane ring oxygens.

Condensation of the picolinium salts **1a,b** with the 4-hydroxybenzaldehydes **2a–d** was effected in refluxing ethanol containing stoichiometric amounts of piperidine. The resulting stilbazolium salts **3a–d** were recovered by filtration and deprotonated by suspension in aqueous ammonia at 70 °C for 30 minutes to give the new merocyanines **4a–d** (Scheme 1) as sparingly soluble, high melting microcrystalline solids. As such, the syntheses represent no major departure from those previously published.[15,16] The new merocyanines were, how-

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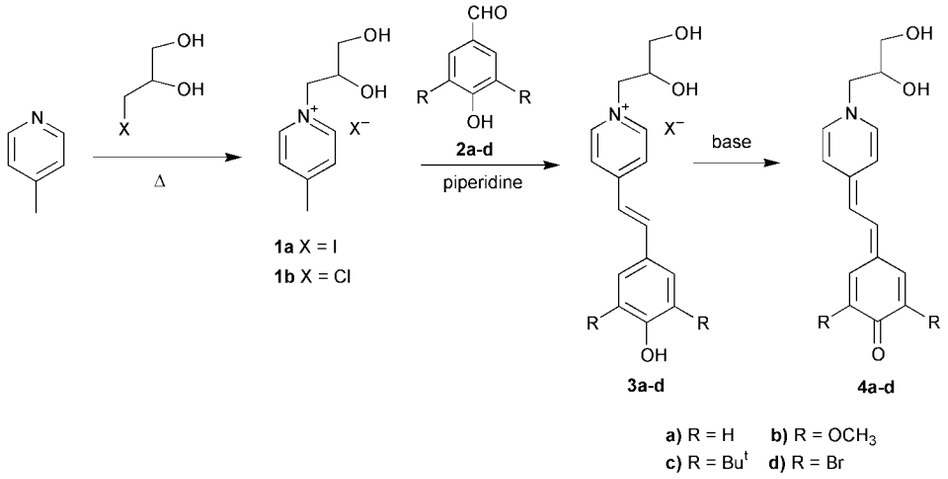
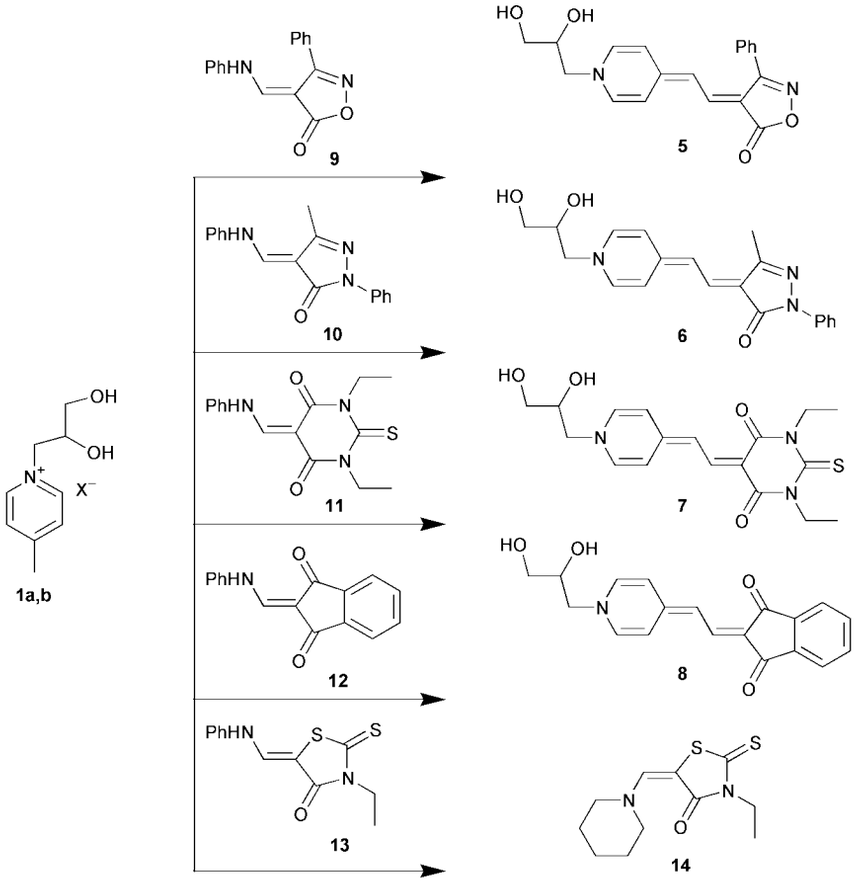


Scheme 1 Syntheses of merocyanines **4a–d**.

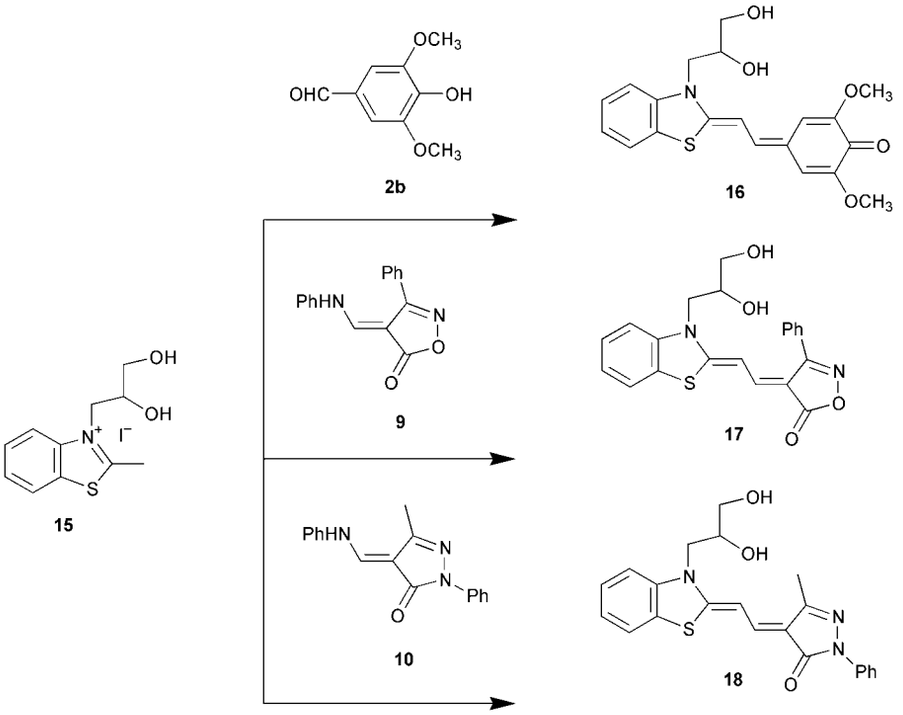
ever, not purifiable to analytical standard (as is typical[16]) but were characterised adequately by ^{1}H NMR spectroscopy, HRMS and UV-vis spectroscopy.

In essentially the same manner the heterocyclic merocyanines **5–7** as well as the indanedione analogue **8** were obtained as coloured, high melting, microcrystalline solids (Scheme 2) from the reaction of the picolinium salts **1a,b** and piperidine with the anilinomethylene functionalised molecules **9–12**.[17] The reaction of the 4-anilinomethylenerhodanine **13** furnished only the corresponding piperidinomethylene substituted heterocycle **14**, clear testimony to the fact that the rhodanine nucleus is a weaker electron acceptor than the acceptor systems present in compounds **9–12**.

Polymer-tetherable chromophores that contain the benzothiazolylidene donor nucleus **16–18** are also directly accessible, albeit in moderate yields, from the reaction of the 2-methylbenzothiazolium iodide salt **15** with 3,5-dimethoxy-4-hydroxybenzaldehyde, for example, and with the anilinomethylene functionalised heterocycles **9** and **10** (Scheme 3). In our hands the salt **15** could not be obtained pure, so no attempts were made subsequently to isolate it. Rather, the crude product was reacted directly with each of the acceptor precursors in solution in methanol. Whilst chromophore **17** was recovered, after a single crystallisation, as a single stereoisomer presumed to have the *trans* interconnect, chromophore **18** was clearly not. On the basis of ^{1}H NMR



Scheme 2 Syntheses of merocyanines **5–8**.



Scheme 3 Syntheses of merocyanines **16–18**.

data, compound **18** is presumed to be a mixture of regioisomers in which the interconnect stereochemistry is again presumed to be *trans* but in which the pyrazolone carbonyl is either *syn* or *anti* to the *N*-(dihydroxypropyl) residue. Resonances attributable to the olefinic methine protons in compounds **4a–c** and **5–8** clearly show coupling constants consistent with the *trans* stereochemistry (*viz.* 13–16 Hz), but in compounds **16–18** these are not discernible.

With the exception of merocyanine **4b**, all of the new, tetherable chromophores are high melting solids and, consequently, their thermal stabilities (T_D) are likely to be high also. In fact, T_D values measured by differential scanning calorimetry (10 °C min^{-1}) on compounds **5** and **6** were found to be 253 °C and 275 °C, respectively.

All compounds exhibit the negative solvatochromic behavior[18] characteristic of zwitterionic stilbazolium merocyanines.[19] That the predominant resonance contributors to the ground states of these chromophores, albeit in the solid state, are zwitterionic is evidenced from the X-ray crystal structure parameters for chromophore **5** (Fig. 2). Most significantly, the chromophore is only 4.2° from systemic planarity and the 'pyridylidene' donor ring is pyridinium rather than quinoid as all bond angles around N1 are between 119 and 121°. Remarkably, the C9–C10 bond in the bridging ethylidene moiety is shortened markedly to 1.33 Å from that expected of a simple sp^2–sp^2 carbon–carbon single bond (1.48 Å). Negative charge is considered to be delocalised over the (aryl)isoxazole nucleus. With regard to the ^{1}H NMR characteristics of all the

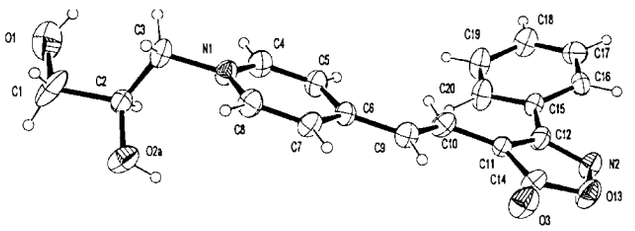


Fig. 2 View of the molecular structure of **5** using 30% probability ellipsoids for non-hydrogen atoms.[20,21] Atom numbering is non-standard (IUPAC) but is concurrent with that used in Table 2.

chromophores, the *N*-methylene AB quartet appears at lower field than that attributable to the terminal *O*-methylene AB system; this clearly must be due to the deshielding effect of a contiguous pyridinium nitrogen atom.

Polymer synthesis

Novel TDI-based polyurethanes containing various of the functionalised chromophores were synthesised cleanly and in high yields employing standard condensation polymerisation techniques.[22] Whilst no attempt has been made to structurally characterise these systems, two of the polymers, those that contain **5** and **6**, recorded high T_g values at 220 °C and 230 °C, respectively. In addition, excellent spin-coated thin films of several of these polymers could be prepared from solutions in *N,N*-dimethylacetamide. These are now under investigation.

Nonlinear optical characterisations

The first order hyperpolarisability coefficients of selected members of the compound sets as measured by hyper-Raleigh scattering in solution in methanol at 1064 nm are shown in Table 1. Because of the proximity of the respective absorption maxima to the second harmonic, the measured nonlinearities will almost certainly contain contributions from resonance-enhancement.[25] Table 1 also presents calculated ground state dipole moments (μ) for this suite of molecules from the semiempirical AM1 procedure contained in the MOPAC 97 package (employing the PRECISE keyword). With respect to dipole moments calculated for other more zwitterionic chromophores, these values are perhaps best described as modest. The extent of intramolecular charge transfer between donor and acceptor termini is clearly sufficient to produce the negative solvatochromic behavior but not as great as that calculated and observed for zwitterionic amino substituted dicyanoquinodimethanes, for example.[26] Within the entire series, the 'pyridylidene–quinone' system clearly yields $|\beta(0)|$ values and overall figures-of-merit (*i.e.* the $\mu\beta(0)$ product) that are larger than those observed for the chromophore systems that contain the heterocyclic acceptors. Furthermore, because the extent of conjugation is common to all, it is evident also

Table 1 First-order hyperpolarisabilities and calculated dipole moments of selected merocyanines

Chromophore	λ_{max}/nm	Solvent	$\beta/10^{-30}$ esu[a]	$\beta(0)/10^{-30}$ esu[b]	$\mu/10^{-18}$ esu	$\mu\beta(0)/10^{-48}$ esu
4a	452	Aq. NaOH	799	−420	9.88	−4150
4b	500	Aq. NaOH	2508	−741	9.33	−6914
5	476	Methanol	467	−205	10.34	−2120
6	501	Methanol	1500	−432	7.64	−3300
17	490	Methanol	<30	12[c]	10.03	120
18	486	Methanol	153	−56	7.54	−422

[a] β Values are calculated with respect to a *p*-nitroaniline reference ($\beta = 34 \times 10^{-34}$ esu).[23] [b] $\beta(0)$ calculated using the formula: $\beta = \beta(0) \times (1/\lambda_{max})^4 / \{[(1/\lambda_{max}^2) - (4/\lambda^2)] \times [1/\lambda_{max}^2) - (1/\lambda^2)]\}$.[24] [c] β Assumed to be 30 for this calculation.

that the benzothiazolylidene nucleus is a less effective electron donor than the pyridylidene nucleus and that the heterocyclic electron acceptors are less effective than the quinone methide system.

Conclusion

This work has shown that tetherable 'polymer-ready' zwitterionic merocyanine type NLO chromophores that contain the pyridyl and benzothiazolyl donor nuclei can be synthesised without the need for any protection/deprotection steps prior to polymerisation. This finding now enables ready access to potentially high T_g condensation polymers (*e.g.* polyurethanes) that might find use as stable, polable polymer $\chi^{(2)}$ materials. Hyper-Raleigh scattering estimates of $\beta(0)$ for selected members of this suite indicate that the 'quinomethide' acceptor is more effective than the heterocyclic equivalents and, furthermore, that the pyridylidene donor is more effective than the benzothiazolylidene equivalent.

Experimental

Nuclear magnetic resonance spectra and two-dimensional correlation data were recorded on a Bruker AVANCE 300 spectrometer and UV-vis absorption spectra were recorded using an HP 8452A diode array spectrophotometer. Mass spectra were recorded, unless otherwise stated, in the FAB(+) mode on a VG Micromass ZAB IF instrument. Elemental analyses were performed by the Campbell Microanalytical Laboratory in the Chemistry Department, University of Otago. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. First-order hyperpolarisabilities were measured by hyper-Raleigh scattering at 1064 nm using a seed-injected Nd:YAG pulsed laser operating at 10 Hz and producing 10–15 ns pulses. The scattered radiation from the solution was passed through either a 10 nm FWHM interference filter centred at 532 nm or through a monochromater to a Philips 56 UVP photomultiplier tube.

X-Ray crystallography

Single crystals of compound **5** were crystallized from methanol (Table 2).

Crystal data. $C_{19}H_{18}N_2O_4$, $M_r = 338.35$, triclinic, $a = 7.761(6)$, $b = 10.257(7)$, $c = 11.119(8)$ Å, $\alpha = 73.408(12)$, $\beta = 80.744(12)$, $\gamma = 70.240(14)^\circ$, $U = 796.3(10)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$ (No. 2); $Z = 2$, $\rho_c = 1.411$ g cm^{-3}, Radiation MoKα, $\lambda = 0.7107$ Å, μ (Mo Kα) = 0.100 mm^{-1}, 4056 reflections collected, 2902 unique ($R_{int} = 0.081$) used in all calculations. The final $wR(F^2)$ (all data) & $R(F)$ ($I > 2\sigma(I)$) were 0.172 & 0.072 respectively. CCDC reference number 1145/276. See http://www.rsc.org/suppdata/jm/b0/b008316j/ for crystallographic files in .cif format.

2,3-Dihydroxy-1-iodopropane

With vigorous stirring, hydriodic acid (57%, 133 mL, 1.0 mol) was added dropwise to neat glycidol (74.0 g, 1.0 mol) at ambient temperature. After stirring overnight the mixture was concentrated and then pumped to dryness under high vacuum. The crude oily product was purified by flash chromatography over silica using gradient elution with ethyl acetate–hexane mixtures (50–100% ethyl acetate) to give the iodopropanediol (125 g, 65%) as a colourless solid, mp 46–47 °C (lit.[27] mp 48–49 °C). ^{1}H NMR (D_2O) δ 3.60, m, 3H, -C*H*(OH)C*H*$_2$I; 3.56, dd, *J* 10.8, 4.2 Hz, 1H, lower field branch of AB quartet, -C*H*$_2$OH; 3.26, dd, *J* 10.8, 6.0 Hz, 1H, higher field branch of AB quartet, -C*H*$_2$OH. ^{13}C NMR (D_2O) δ 71.2 (CH), 65.0 (CH_2OH), 9.2 (CH_2I).

1-(2,3-Dihydroxypropyl)-4-methylpyridinium iodide, 1a

To a stirred solution of 2,3-dihydroxy-1-iodopropane (10.0 g, 49.5 mmol) in dry isopropyl alcohol (50 mL) was added dropwise, freshly distilled 4-methylpyridine (5.07 g, 54.5 mmol) and the resulting mixture refluxed overnight under an atmosphere of nitrogen. The solution was then cooled and concentrated to afford **1a** as a viscous, off-white oil (12.2 g) that was used as such after the removal of the volatiles under high vacuum. ^{1}H NMR (D_2O) δ 8.81, d, *J* 6.5 Hz, 2H, aromatic; 7.98, d, *J* 6.5 Hz, 2H, aromatic; 4.73, dd, *J* 13.1, 3.0 Hz, 1H, lower field branch of AB quartet, -NC*H*$_2$; 4.41, dd, *J* 13.1, 8.5 Hz, 1H, higher field branch of AB quartet, -NC*H*$_2$; 3.87, m, 1H, C*H*OH; 3.49, dd, *J* 11.1, 4.9 Hz, 1H, lower field branch of AB quartet, -C*H*$_2$OH; 3.31, dd, *J* 11.1, 6.3 Hz, 1H, higher field branch of AB quartet, -C*H*$_2$OH; 2.61, s, 3H, C*H*$_3$. ^{13}C NMR (D_2O) δ 159.2 (C_Q), 144.8 (CH), 128.2 (CH), 70.6 (CH), 63.2 (CH_2), 63.1 (CH_2), 21.9 (CH_3).

1-(2,3-Dihydroxypropyl)-4-methylpyridinium chloride, 1b

A mixture of freshly distilled 4-methylpyridine (10.0 g, 108 mmol) and 2,3-dihydroxy-1-chloropropane (10.0 g, 91 mmol) was heated at 80–100 °C for 72 h whilst protected from moisture by a calcium chloride drying tube. After cooling a solid formed which was broken up with the aid of a spatula and then ethyl acetate (20 mL) added. The solid mass was collected by filtration and washed with ethyl acetate to give **1b**

Table 2 Selected geometric parameters for **5** (Å, °)

N1–C8	1.340 (6)	C10–C11	1.423 (7)
N1–C4	1.337 (6)	C11–C12	1.418 (6)
N2–C12	1.318 (6)	C11–C14	1.426 (7)
N2–O13	1.423 (5)	C14–O13	1.391 (6)
C4–C5	1.348 (7)	C8–N1–C4	118.7 (5)
C5–C6	1.401 (6)	C8–N1–C3	119.9 (5)
C6–C7	1.395 (6)	C5–C6–C9–C10	5.9 (5)
C6–C9	1.431 (7)	C6–C9–C10–C11	−178.4 (5)
C7–C8	1.354 (7)	C9–C10–C11–C12	178.9 (6)
C9–C10	1.328 (6)	C9–C10–C11–C14	−3.2 (9)

as a moisture sensitive pale-brown solid (17.81 g, 97%). Recrystallisation (ethanol) gave beige microcrystals, mp 157–158 °C. ^{1}H NMR (d_6-DMSO) δ 8.88, d, J 6.5 Hz, 2H; 7.97, d, J 6.5 Hz, 2H; 5.66, br s, 1H, -CHO*H* (exchangeable in D_2O); 5.20, br s, 1H, -CH_2O*H* (exchangeable in D_2O); 4.77, dd, J 13.0, 3.1 Hz, 1H, lower field branch of AB quartet, -NCH_2; 4.47, dd, J 13.0, 8.1 Hz, 1H, higher field branch of AB quartet, -NCH_2; 3.89, m, 1H, C*H*OH; 3.47–3.53, m, 1H, lower field branch of AB quartet, -CH_2OH; 3.27–3.33, m, 1H, higher field branch of AB quartet, -CH_2OH; 2.60, s, 3H, CH_3. ^{13}C NMR (d_6-DMSO) δ 159.1 (C_Q), 144.9 (CH), 128.1 (CH), 70.7 (CH), 63.0 (due to 2 × CH_2), 21.7 (CH_3). The signal at δ 63.0 is able to be resolved as two separate signals at δ 63.1 and 62.9 with D_2O as solvent.

General procedure for the preparation of 2,6-disubstituted 4-{2-[1-(2,3-dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene} cyclohexa-2,5-dien-1-ones, Brooker's merocyanines, 4a–d

To a stirred solution of 1-(2,3-dihydroxypropyl)-4-methylpyridinium iodide **1a** (14.75 g, 50 mmol) (or an equimolar amount of **1b**) in absolute ethanol (150 mL) was added the appropriate 4-hydroxybenzaldehyde **2a–d** (50 mmol), and the mixture heated to reflux. To the mixture was then added piperidine (4.5 g, 5.2 mL, 53 mmol) at which point an intense red colour developed. The solution was refluxed overnight, cooled and the resulting precipitate recovered by filtration and washed with a little cold ethanol. The precipitate was then suspended in aqueous ammonia (35%, 400 mL), and heated to *ca.* 70 °C with stirring for 30 min. The solid was again recovered by filtration and recrystallised from water, to which isopropyl alcohol (*ca.* 20% final volume) was later added to facilitate crystallisation. The product was pistol dried at *ca.* 75 °C under high vacuum.

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene} cyclohexa-2,5-dien-1-one, 4a[28]

From the reaction of the 4-methylpyridinium iodide with 4-hydroxybenzaldehyde, **4a** was isolated as bright red platelets (10.57 g, 78%), mp 227–229 °C (Found: MH^+ m/z 272.12813. $C_{16}H_{17}NO_3$ requires MH^+ m/z 272.12867 Δ = 1.8 ppm). λ_{max} 456 (H_2O); 490 (methanol) $\log_{10}\varepsilon$ 4.57; 578 (DMSO); 574 (pyridine).^{1}H NMR (D_2O) δ 8.34, d, J 6.3 Hz, 2H; 7.80, d, J 6.3 Hz, 2H; 7.61, d, J 13.2 Hz, 1H; 7.47, d, J 8.4 Hz, 2H; 6.91, d, J 13.2 Hz, 1H; 6.70, d, J 8.4 Hz, 2H; 4.52, d, J 13.5 Hz, 1H, lower field branch of AB quartet, -NCH_2; 4.27, dd, J 13.5, 9.0 Hz, 1H, higher field branch of AB quartet, -NCH_2; 4.08, m, 1H, -C*H*OH, 3.63–3.65, m, 2H, -CH_2OH. Solubility precluded the recording of complete, meaningful^{13}C NMR data. Microanalytical data were inconsistent with the expected formula and NMR spectra consistently confirmed the presence of both water and propan-2-olate of crystallization.

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene} -2,6-dimethoxycyclohexa-2,5-dien-1-one, 4b

From the reaction of the 4-methylpyridinium iodide with 3,5-dimethoxy-4-hydroxybenzaldehyde, **4b** was isolated as a dark green microcrystalline solid (10.43 g, 63%), mp 170–172 °C (Found: C, 61.2; H, 6.5; N, 4.0. $C_{18}H_{21}NO_5{\cdot}H_2O$ requires C, 61.7; H, 6.9; N, 4.0%. Found: MH^+ m/z 332.14939. $C_{18}H_{21}NO_5$ requires MH^+ m/z 332.14980 Δ = 1.2 ppm). λ_{max} 502 (H_2O); 558 (methanol) $\log_{10}\varepsilon$ 4.64; 640 (DMSO); 654 (pyridine). ^{1}H NMR (d_6-DMSO) δ 7.70, d, J 5.7 Hz, 2H; 7.58, d, J 14.7 Hz, 1H; 7.27, d, J 5.7 Hz, 2H; 6.79, s, 2H; 6.42, d, J 14.7 Hz, 1H; 4.18, d, J 13.2 Hz, 1H, lower field branch of AB quartet -NCH_2; 3.91, m, 1H, higher field branch of AB quartet -NCH_2; 3.77, s, 6H, -OCH_3; remaining methine and methylene resonances of the *N*-(dihydroxypropyl) substituent were concealed by a broad water signal. Solubility precluded the recording of full ^{13}C NMR spectral details.

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene} -2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one, 4c

From the reaction of the 4-methylpyridinium iodide with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, **4c** was isolated as a pale green microcrystalline solid (7.09 g, 37%), mp 292–294 °C (Found: MH^+ m/z 384.25274. $C_{24}H_{35}NO_3$ requires MH^+ m/z 384.25387 Δ = 2.9 ppm). λ_{max} 538 (H_2O); 590 (methanol) $\log_{10}\varepsilon$ 4.70; 618 (DMSO); 630 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.75, d, J 6.0 Hz, 2H; 8.20, d, J 6.0 Hz, 2H; 8.02, d, J 16.1 Hz, 1H; 7.54, s, 2H; 7.32, d, J 16.1 Hz, 1H; 5.36, br s, -CHO*H*; 4.97, br s, -CH_2O*H*; 4.64, apparent d, J 12.4 Hz, 1H, lower field branch of AB quartet, -NCH_2; 4.30–4.37, m, 1H, higher field branch of AB quartet, -NCH_2; 3.91, m, 1H, -C*H*OH; 3.50, m, 1H, lower field branch of AB quartet, -CH_2OH; 3.35, m, 1H, higher field branch of AB quartet, -CH_2OH; 1.43, s, 18H, -C(CH_3)$_3$. ^{13}C NMR (d_6-DMSO) δ 157.6 (C_Q), 154.0 (C_Q), 144.9 (CH), 142.9 (CH), 139.6 (C_Q), 126.7 (C_Q), 125.9 (CH), 122.8 (CH), 119.7 (CH), 70.7 (CH), 63.2 (CH_2), 62.8 (CH_2), 35.0 (C_Q), 30.8 (CH_3) ppm

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene} -2,6-dibromocyclohexa-2,5-dien-1-one, 4d

From the reaction of the 4-methylpyridinium iodide with 3,5-dibromo-4-hydroxybenzaldehyde, **4d** was isolated as a reddish-brown microcrystalline solid (12.63 g, 59%), mp 256–258 °C (Found: MH^+ m/z 429.94866. $C_{16}H_{15}NO_3Br_2$ requires MH^+ m/z 429.94777 Δ = 2.1 ppm). λ_{max} 448 (H_2O); 490 (methanol) $\log_{10}\varepsilon$ 4.63; 540 (DMSO); 578 (pyridine). The low solubility of **4d** in common NMR solvents precluded the acquisition of satisfactory ^{1}H and ^{13}C NMR data.

2-Anilinomethylideneindane-1,3-dione, 12

Indane-1,3-dione (4.38 g, 30 mmol) and *N,N*′-diphenylformamidine (6.48 g, 33 mmol) were stirred together at 120 °C for 20 min, and the mixture then allowed to cool to room temperature to give a green–black paste. To this was added isopropyl alcohol (50 mL) and the resultant slurry refluxed for 10 min and then cooled, whereupon a dark-green precipitate formed. This was collected by filtration and washed with isopropyl alcohol (3 × 15 mL) to give 2-anilinomethylideneindane-1,3-dione **12** as an olive-green powder (6.61 g, 88%). Recrystallisation (1 : 1 ethanol–isopropyl alcohol) gave yellow–green microcrystals, mp 200–201 °C (Found: MH^+ m/z 250.08501. $C_{16}H_{21}NO_2$ requires MH^+ m/z 250.08626 Δ = 5.0 ppm). ^{1}H NMR (d_6-DMSO) δ 8.31, s, 1H; 7.76, s, 4H; 7.58–7.60, m, 2H; 7.41–7.46, m, 2H; 7.21–7.26, m, 1H. ^{13}C NMR (d_6-DMSO) δ 144.7 (CH), 139.8 (C_Q), 139.4 (C_Q), 134.4 (CH), 130.0 (CH), 126.0 (CH), 121.7 (CH), 121.7 (C_Q), 118.7 (CH), 106.0 (C_Q).

General procedure for the preparation of chromophores 5–8 and the piperidinomethylene substituted rhodanine 14

To a stirred solution of the 4-methylpyridinium iodide **1a** (5.0 g, 16.9 mmol) (or an equimolar amount of **1b**) in ethanol (25 mL) was added the appropriate *N*-phenylamino substituted acceptor **9–13** (16.9 mmol). The mixture was then refluxed under nitrogen for 5 min and then piperidine (1.70 g, 2.0 mL, 20 mmol) was added and the resulting solution refluxed overnight under an atmosphere of nitrogen. After cooling the brightly coloured solid was recovered by filtration and washed with a little cold methanol. A further concentration and cooling of the mother liquors afforded more of the desired product. These materials were pistol dried and were generally suitable for use without

further purification. Analytical samples were obtained by recrystallisation from methanol.

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene}-3-phenylisoxazol-5(4*H*)-one, 5

From the reaction of **1a** with 4-anilinomethylidene-3-phenylisoxazol-5(4*H*)-one **9**, the product was isolated as an orange microcrystalline solid (3.40 g, 61%), mp 253–255 °C (Found: MH^+ *m/z* 339.13435. $C_{19}H_{18}N_2O_4$ requires MH^+ *m/z* 339.13448 $\Delta = 0.4$ ppm). λ_{max} 446 (H_2O); 476 (methanol) $\log_{10}\varepsilon$ 4.52; 500 (acetonitrile); 500 (DMSO); 514 (acetone); 518 (pyridine) $\log_{10}\varepsilon$ 4.84. ^{1}H NMR (d_6-DMSO) δ 8.07, d, *J* 7.1 Hz, 2H; 7.48–7.59, m, 6H; 7.43, d, *J* 7.0 Hz, 2H; 7.04, d, *J* 14.7 Hz, 1H; 5.28, d, *J* 5.5 Hz, 1H, -CHO*H*; 4.91, t, *J* 5.4 Hz, 1H, -CH_2O*H*; 4.32, dd, *J* 13.4, 2.9 Hz, 1H lower field branch of AB quartet, -NCH_2; 4.05, dd, *J* 13.4, 8.1 Hz, 1H, higher field branch of AB quartet, -NCH_2; 3.77, m, 1H, -C*H*OH; 3.45, m, 1H, lower field branch of AB quartet, -CH_2OH; 3.26, m, 1H, higher field branch of AB quartet, -CH_2OH. ^{13}C NMR (d_6-DMSO) δ 174.1 (C_Q), 162.4 (C_Q), 155.1 (C_Q), 142.5 (CH), 137.0 (CH), 131.6 (C_Q), 129.4 (CH), 129.1 (CH), 128.3 (CH), 118.5 (CH), 107.8 (CH), 90.4 (C_Q), 70.8 (CH), 63.2 (CH_2), 61.0 (CH_2).

4-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene}-3-methyl-1-phenylpyrazol-5(4*H*)-one, 6

From the reaction of **1a** with 4-anilinomethylidene-3-methyl-1-phenylpyrazol-5(4*H*)-one **10**, the product was isolated as a red powder (4.21 g, 71%), mp 276–278 °C (Found: MH^+ *m/z* 352.16527. $C_{20}H_{21}N_3O_3$ requires MH^+ *m/z* 352.16612 $\Delta = 2.4$ ppm). λ_{max} 462 (H_2O); 488 (methanol) $\log_{10}\varepsilon$ 4.88; 516 (acetonitrile); 520 (DMSO); 524 (acetone); 534 (pyridine) $\log_{10}\varepsilon$ 4.88. ^{1}H NMR (d_6-DMSO + D_2O) δ 8.05, d, *J* 7.8 Hz, 2H; 7.92, d, *J* 7.1 Hz, 2H; 7.60, d, *J* 14.5 Hz, 1H; 7.14–7.48, m, 5H; 6.98, m, 1H; 4.24, dd, *J* 13.5, 3.0 Hz, 1H, lower field branch of AB quartet, -NCH_2; 3.97, dd, *J* 13.5, 8.4 Hz, 1H, higher field branch of AB quartet, -NCH_2; 3.77, m, 1H, -C*H*OH; 3.45, dd, *J* 11.1, 4.8 Hz, 1H, lower field branch of AB quartet, -CH_2OH; 3.28, dd, *J* 11.1, 6.3 Hz, higher field branch of AB quartet, -CH_2OH; 2.18, s, 3H. ^{13}C NMR (d_6-DMSO) δ 154.8 (C_Q), 141.6 (CH), 141.0 (C_Q), 137.5 (CH), 128.6 (CH), 122.3 (CH), 117.4 (CH), 105.8 (CH), 104.5 (C_Q), 70.9 (CH), 63.2 (CH_2), 60.4 (CH_2), 13.2 (CH_3). One quaternary carbon signal not observed due to line broadening arising from ^{14}N–^{13}C coupling. Furthermore, as the signal to noise ratio for the ^{13}C measurements is low one CH carbon signal is not observed.

5-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene}-1,3-diethyl-2-thiobarbituric acid, 7

From the reaction of **1a** with 5-anilinomethylidene-1,3-diethyl-2-thiobarbituric acid **11**, the product was isolated as an orange–red microcrystalline solid (4.91 g, 77%), mp 233–236 °C (Found: MH^+ *m/z* 378.14906. $C_{18}H_{23}N_3O_4S$ requires MH^+ *m/z* 378.14875 $\Delta = 0.8$ ppm). λ_{max} 452 (H_2O); 482 (methanol) $\log_{10}\varepsilon$ 4.77; 496 (acetonitrile); 490 (DMSO); 500 (acetone); 510 (pyridine) $\log_{10}\varepsilon$ 4.99. ^{1}H NMR (d_6-DMSO) δ 8.27, d, *J* 6.1 Hz, 2H; 8.05, d, *J* 15.4 Hz, 1H; 7.62, d, *J* 6.1 Hz, 2H; 7.58, d, *J* 15.4 Hz, 1H; 5.34, d, *J* 4.6 Hz, 1H, -CHO*H*; 4.94, br s, 1H, -CH_2O*H*; 4.44–4.46, m, 5H, -NCH_2CH_3 and lower field branch of AB quartet –NCH_2; 4.10–4.17, m, 1H, higher field branch of AB quartet, –NCH_2; 3.82, m, 1H, -C*H*OH; 3.35–3.45, m, 2H, higher and lower field branches of AB quartet, -CH_2OH; 1.17, t, *J* 6.0 Hz, 6H, -NCH_2CH_3. ^{13}C NMR (d_6-DMSO) δ 176.4 (C_Q), 160.7 (C_Q), 156.5 (C_Q), 143.2 (CH), 140.5 (CH), 119.8 (CH), 112.6 (CH), 95.1 (C_Q), 70.8 (CH), 63.2 (CH_2), 61.5 (CH_2), 42.1 (CH_2), 12.9 (CH_3).

2-{2-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]ethylidene}-indane-1,3-dione, 8

From the reaction of **1a** with 2-anilinomethylideneindane-1,3-dione **12**, the product was isolated as a red–brown microcrystalline solid (3.06 g, 56%), mp 258–260 °C (Found: MH^+ *m/z* 324.12441. $C_{19}H_{17}NO_4$ requires MH^+ *m/z* 324.12304 $\Delta = 4.2$ ppm). λ_{max} 476 (H_2O); 502 (methanol) $\log_{10}\varepsilon$ 4.85; 524 (acetonitrile); 524 (DMSO); 530 (acetone); 534 (pyridine) $\log_{10}\varepsilon$ 5.05. ^{1}H NMR (d_6-DMSO) δ 8.06, d, *J* 7.1 Hz, 2H; 7.67, d, *J* 15.0 Hz, 1H; 7.40–7.52, m, 6H; 7.21, d, *J* 15.0 Hz, 1H; 5.30, d, *J* 5.4 Hz, 1H, -CHO*H*; 4.92, t, *J* 5.4 Hz, 1H, -CH_2O*H*; 4.32, dd, *J* 13.5, 2.9 Hz, 1H, lower field branch of AB quartet, -NCH_2; 4.05, dd, *J* 13.5, 8.1 Hz, 1H, higher field branch of AB quartet, -NCH_2; 3.79, m, 1H, -C*H*OH; 3.42–3.49, m, 1H, lower field branch of AB quartet, -CH_2OH; 3.26–3.32, m, 1H, higher field branch of AB quartet, -CH_2OH. ^{13}C NMR (d_6-DMSO) δ 190.3 (C_Q), 155.8 (C_Q), 142.3 (CH), 135.4 (CH), 132.0 (CH), 119.6 (CH), 118.3 (CH), 109.0 (C_Q), 108.2 (CH), 70.9 (CH), 63.2 (CH_2), 60.9 (CH_2).

5-Piperidinomethylidene-3-ethylrhodanine, 14

From the reaction of **1a** with 5-anilinomethylidene-3-ethylrhodanine **13**, or its 5-acetanilido-equivalent, the product was isolated as purple plates (2.85 g, 66%), mp 154–155 °C (Found: MH^+ *m/z* 257.08000. $C_{11}H_{16}N_2OS_2$ requires MH^+ *m/z* 257.07820 $\Delta = 7.0$ ppm). ^{1}H NMR (d_6-DMSO) δ 7.69, s, 1H; 4.00, q, *J* 7.1 Hz, 2H; 3.53, br s, 4H; 1.62, br s, 6H; 1.13, t, *J* 7.1 Hz, 3H. ^{13}C NMR (d_6-DMSO) δ 189.2 (C_Q), 167.3 (C_Q), 144.7 (CH), 86.3 (C_Q), 40.8 (CH_2), 26.3 (CH_2), 23.4 (CH_2), 12.4 (CH_3). One piperidinomethylene carbon signal not observed due to line broadening arising from ^{14}N–^{13}C coupling.

General procedure for the preparation of the (benzothiazol-ylidene)ethylidene functionalised chromophores, 16–18

A mixture of 2-methylbenzothiazole (3.0 g, 20.0 mmol) and 2,3-dihydroxy-1-iodopropane (4.0 g, 20.0 mmol) was stirred under an atmosphere of nitrogen at 100 °C for 16 h. The resulting mixture, which was presumed to contain 10 mmol of the requisite salt **15**, was cooled and diluted with a small volume of methanol. With stirring was then added a solution of either the *N*-phenylamino heterocycles, **9** or **10**, or 3,5-dimethoxy-4-hydroxybenzaldehyde, **2b**, (10.0 mmol) in methanol (30 ml) followed by triethylamine (2.1 ml, 15.0 mmol). The mixture was refluxed for 16 h and then cooled. After the addition of hexane (30 ml) the solution was cooled to –20 °C for several hours and the precipitate recovered by filtration, washed with hot water and then recrystallised from either ethanol or an isopropyl alcohol–methanol mixture.

4-{2-[3-(2,3-Dihydroxypropyl)-1,3-benzothiazol-2(3*H*)-ylidene]ethylidene}-2,6-dimethoxycyclohexa-2,5-dien-1-one, 16

From the reaction of **15** with 3,5-dimethoxy-4-hydroxybenzaldehyde **2b**, the initially isolated solid was suspended in isopropyl alcohol–triethylamine (5 : 1; 30 mL) and stirred at *ca.* 60 °C for 30 min, cooled and then collected by filtration to give an orange–red powder (1.53 g, 40%). Recrystallisation (ethanol) gave orange–red microcrystals, mp 262–264 °C (decomp.) (Found: MH^+ *m/z* 388.12065. $C_{20}H_{21}NO_5S$ requires MH^+ *m/z* 388.12132 $\Delta = 1.7$ ppm). λ_{max}[28] 566 (H_2O); 594 (methanol) $\log_{10}\varepsilon$ 4.96; 566 (acetonitrile); 594 (DMSO) $\log_{10}\varepsilon$ 4.99; 586 (acetone); 584 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.42, d, *J* 7.8 Hz, 1H; 8.12–8.19, m, 2H; 7.74–7.87, m, 3H; 7.35, s, 2H; 5.39, br s, 1H, -CHO*H*; 5.16, br s, 1H, -CH_2O*H*; 4.89–5.00, m, 2H, -NCH_2; 3.99, br s, 1H, -C*H*OH; 3.88, s, 6H, -OCH_3; 3.60–3.64, m, 2H, -CH_2OH. ^{13}C NMR (d_6-DMSO) δ 172.9 (C_Q), 149.6 (CH), 148.6 (C_Q), 142.2 (C_Q), 141.7 (C_Q),

129.4 (CH), 128.3 (CH), 127.9 (C_Q), 124.9 (C_Q), 124.5 (CH), 117.3 (CH), 111.5 (CH), 108.5 (CH), 70.3 (CH), 63.4 (CH_2), 56.8 (CH_3), 52.4 (CH_2).

4-{2-[3-(2,3-Dihydroxypropyl)-1,3-benzothiazol-2(3*H*)-ylidene]ethylidene}-3-phenylisoxazol-5(4*H*)-one, 17

From the reaction of **15** with 4-anilinomethylidene-3-phenylisoxazol-5(4*H*)-one **9**, the product was isolated as a microcrystalline orange solid (1.14 g, 29%), mp 240–241 °C (Found: MH^+ *m/z* 395.10696. $C_{21}H_{18}N_2O_4S$ requires MH^+ *m/z* 395.10601 $\Delta = 2.4$ ppm). λ_{max} 472 (99:1 H_2O–acetone); 486 (methanol) $\log_{10}\varepsilon$ 4.86; 492 (acetonitrile); 496 (DMSO) $\log_{10}\varepsilon$ 4.80; 496 (acetone); 502 (pyridine). ^{1}H NMR (d_6-DMSO) δ 7.96, d, *J* 7.1 Hz, 1H; 7.40–7.71, m, 10H; 5.26, br s, 1H, -CHO*H*; 5.00, br s, 1H, -CH_2O*H*; 4.30–4.43, m, 2H, -NCH_2; 3.97, br s, 1H, -C*H*OH; 3.53, m, 1H, lower field branch of AB quartet -CH_2OH; 3.32, m, 1H, higher field branch of AB quartet, -CH_2OH. ^{13}C NMR (d_6-DMSO) δ 172.9 (C_Q), 169.6 (C_Q), 162.3 (C_Q), 142.8 (CH), 142.4 (C_Q), 130.2 (CH), 129.4 (CH), 128.3 (CH), 128.0 (CH), 125.6 (CH), 125.1 (C_Q), 123.2 (CH), 114.9 (CH), 96.5 (CH), 95.7 (C_Q), 69.5 (CH), 63.9 (CH_2), 50.7 (CH_2).

4-{2-[3-(2,3-Dihydroxypropyl)-1,3-benzothiazol-2(3*H*)-ylidene]ethylidene}-3-methyl-1-phenylpyrazol-5(4*H*)-one, 18

From the reaction of **15** with 4-anilinomethylidene-3-methyl-1-phenylpyrazol-5(4*H*)-one **10**, the product was isolated as a microcrystalline red–brown solid (1.55 g, 38%), mp 244–245 °C (Found: MH^+ *m/z* 408.13854. $C_{22}H_{21}N_3O_3S$ requires 408.13764 $\Delta = 2.2$ ppm). λ_{max} 482 (99 : 1 H_2O–acetone); 488 (methanol) $\log_{10}\varepsilon$ 4.84; 492 (acetonitrile); 500 (DMSO) $\log_{10}\varepsilon$ 4.83; 494 (acetone); 502 (pyridine). Both ^{1}H and ^{13}C NMR spectra were clearly consistent with the appearance of structural isomers of **18**; these are assumed to be the compounds that contain the pyrazolone carbonyl *syn* and *anti* to the benzothiazolyl ring nitrogen.

General procedure for the preparation of chromophore: toluene-2,4-diisocyanate condensation polymers

To a stirred solution of anhydrous chromophore (10 mmol) in DMSO (20 mL) maintained at 80 °C under an atmosphere of nitrogen was added, in a single portion *via* syringe, toluene-2,4-diisocyanate (1.74 g, 1.43 mL, 10 mmol). This mixture was stirred at 80 °C for 16 h, and then cooled and filtered through an MSI glass fibre filter (1.0 micron). The filtrate was added dropwise to a vigorously stirred volume of methanol (100 mL). The coloured precipitate was recovered by filtration and/or centrifugation and washed thoroughly with hot methanol before being dried under vacuum. Polymers were purified by redissolution in a minimum volume of warm *N*,*N*-dimethylacetamide and reprecipitation in methanol. This purification procedure was repeated once more to give the polymers as fine, coloured powders in yields of 30–60% after vacuum drying. In preparation for spin-coating, the polymers were dissolved in dimethylacetamide optimally at 10–20% w/v and expressed through a 0.2 micron syringe filter onto glass or ITO-glass slides.

For compounds **5** and **6**, the resulting polyurethanes had T_g values at 220 °C and 230 °C when measured on a Rheometrics STA 1500 instrument operating from ambient to 320 °C at 10° min^{-1}.

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