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Simple zwitterionic merocyanines as potential NLO chromophores

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A suite of zwitterionic pyridylidene-based merocyanines that contain no interconnecting π-bridge between the donor and acceptor rings has been synthesised and their second-order NLO properties evaluated largely by semi-empirical computational methods (MOPAC 97/AM1). Contrary to expectation, increasing the degree of inter-ring twist (θ), at least up to 55°, in these new pyridylideneazolone chromophores is found to have little or no effect on the figure of merit [$\mu\beta(0)$]. An X-ray crystallographic appraisal of one of these chromophores, **14**, reveals however that the twist angle (albeit in the solid state) is greater than that predicted by computation and that all other features are consistent with the highly zwitterionic nature of these systems. In spite of this, a combination of factors—insufficient acceptor strength, insufficient extent of conjugation and perhaps insufficient twist angle, in particular—clearly leads to the low values of the quadratic hyperpolarisabilities. The trade-off between targeting a more modest β from a minimum of π-conjugating framework between D and A (and therefore synthetic expediency) and seeking a moderate-to-high dipole moment has therefore resulted in only low figures of merit for these systems.

Calculations performed on a suite of readily accessible, *isoelectronic* cyanines, in which the acceptor is a stabilised cyclopentadienide carbocycle rather than a heterocycle, have revealed the potential that these systems, exemplified by **27**, have as NLO chromophores. Representative polymer-tetherable derivatives of this system have been prepared as have the corresponding TDI-based polyurethanes.

Introduction

Organic molecules that give rise to large second-order nonlinear figures of merit ($\mu\beta$) consist of electron donor and electron acceptor groups that flank a π-conjugating bridge.[1–4] The magnitudes of the nonlinearities depend upon donor and acceptor strengths and upon the length and effectiveness of the π-interconnect in the chromophore and are due principally to the hyperpolarisability term (β) rather than to the dipole moment term (μ). In general, the chromophores that yield these large nonlinearities are also structurally 'large', there being extensive conjugation between the donor and acceptor groups.[5–7] Not only does this make the molecule less readily accessible synthetically but, because of this structural complexity, thermal and particularly photochemical stability issues might therefore preclude any practical application in either host polymer or backbone polymer matrices.

Chromophores whose ground states are predominantly zwitterionic present a class of NLO molecules capable of yielding large figures of merit.[8–11] Theoretically it is possible to design structurally less complex chromophores, with perhaps more modest β (and concomitantly lower λ^{CT}), but that have more appreciable dipole moments. In fact, computational modelling on a number of simple, zwitterionic merocyanines (*e.g.* the TICTOID quinopyridines **1**, Fig. 1) and merocyanine-type compounds (*e.g.* the quinopyrans **2** and analogues[8] and diaminodicyanoquinodimethanes **3**[11,12]) has shown that β can be optimised by way of substantial modifications of the dihedral angle between each of the ring planes. This twisting around the central double bond in **1** and **2** leads to charge separation and this, in turn, leads to aromatic stabilisation of the resulting pyridinium and pyrylium phenolate rings.

For example,[12] in an AM1-optimised structure for **3** (which closely resembled the structure obtained by crystallography) the normalised molecular hyperpolarisability coefficient $\beta(0)$ approaches its maximum (*ca.* -40×10^{-30} esu) when θ is between 40–50°. Of the simple (stunted) merocyanine class, only the quinopyridine system **1** has been studied experimentally as an NLO chromophore and, for the 3,5-di-*tert*-butyl-homologue (R = R′ = H; R″ = Bu^t), been shown by NMR spectroscopy to have a tilt angle of 42 ± 7° and to possess a $\beta(0)$ approaching -30×10^{-30} esu.[13,14]

Recently, we embarked upon a study of the quadratic NLO properties of some planar Brooker-type merocyanines (*e.g.* **4** and **5**, $n = 1$) and, at the same time, devised a simple method to render these chromophores polymer-tetherable [R = -CH_2CH-(OH)CH_2OH].[15] This study showed, amongst other things, that the quinoid acceptor was more effective than any of the aromatisable heterocyclic acceptor systems investigated.

Nonetheless, with a view to further minimising the structural

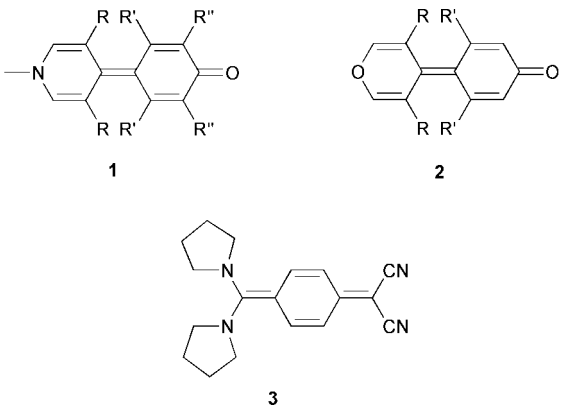

Fig. 1 Simple zwitterionic merocyanines.

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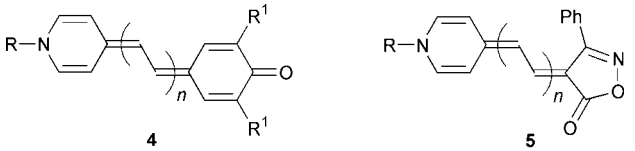
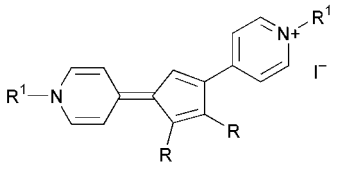


4 5

R=-$CH_2CH(OH)CH_2OH$; R^1=H,Bu^t,OCH_3,Br



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R=alkyl or aryl

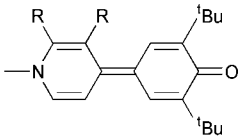
R^1=-CH_2CH_2OH, for example

complexity of the chromophore, we were interested in exploring the syntheses and NLO properties of the 'simple' merocyanines (*e.g.* **5**, $n = 0$) that contained the pyridylidene donor nucleus, reasoning that through the incorporation of a tilt between the two sp^2 connected ring planes, it might be possible to realise β values comparable to or better than those observed for the planar chromophores **4** and **5** ($n = 1$) and perhaps the quinopyridine system **1** ($R'' = Bu^t$). We were also interested in the related pyridinium cyclopentadiene (cyanine) system **6**, which has been reported[16–19] before but not in an NLO capacity; our interest was triggered by the results of a computational study on selected members of this class of zwitterionic chromophore.

In this paper, we present details of the syntheses of representative, polymer-ready, 'stunted' merocyanines and cyanines together with a theoretical estimate of μ and $\beta(0)$ for these systems.

Results and discussion

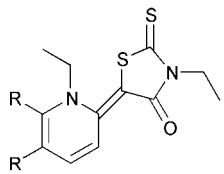
In spite of the theoretical interest that the stunted or 'simple' merocyanines **1** and the analogous quinopyrans **2** have generated as potential NLO chromophores,[8,20] examples of them are few and far between. In fact, to our knowledge only the merocyanine chromophores **7** and **8**, that bear substituents in the 3′ and 5′ positions of the quinone ring, have been synthesised (electrochemically) and their NLO properties evaluated.[21–23]



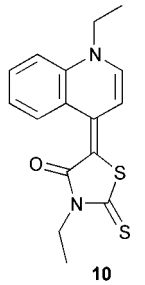
7 R=H
8 R=$(CH)_4$

Modest figures of merit [$\mu\beta(0)$] in the range 500–700 $\times$ 10^{-48} have been measured by EFISH for these chromophores, which have been described as having twist angles between 40–50° from proton NMR spin-relaxation rate data on the two sets of hydrogen atoms *ortho* to the interconnect. Computational modelling on systems **1** and **2**, on the other hand, implies that as the twist angle increases from near zero (when R = R′ = H in **1**) to near 90°, large and sudden enhancements (two orders of magnitude, for example) in NLO response are to be expected. Chromophore **1** (R = R′ = Bu^t; R″ = H), for example, has a calculated twist angle of 83° and an impressive $\mu\beta$ at 0.65 eV of about $-30\,000 \times 10^{-48}$ esu.

In view of the obvious potential that these stunted systems have, we were interested to explore the synthetic accessibility of heterocyclic equivalents of the parent **1** because the introduction of the R and R′ substituents required to bring about the inter-ring twist should be reasonably achievable in these systems. Brooker's group's pioneering work[24] on merocyanines is the only literature that details the synthesis of this type of stunted chromophore. Only one example each of chromophores containing the 2(1*H*)-pyridylidene **9a** and 2(1*H*)- and 4(1*H*)-quinolylidene donor nuclei **9b** and **10** have been reported and each of these contains only the weak ethylrhodanine acceptor.



9a R=H
9b RR=–$(CH)_4$–



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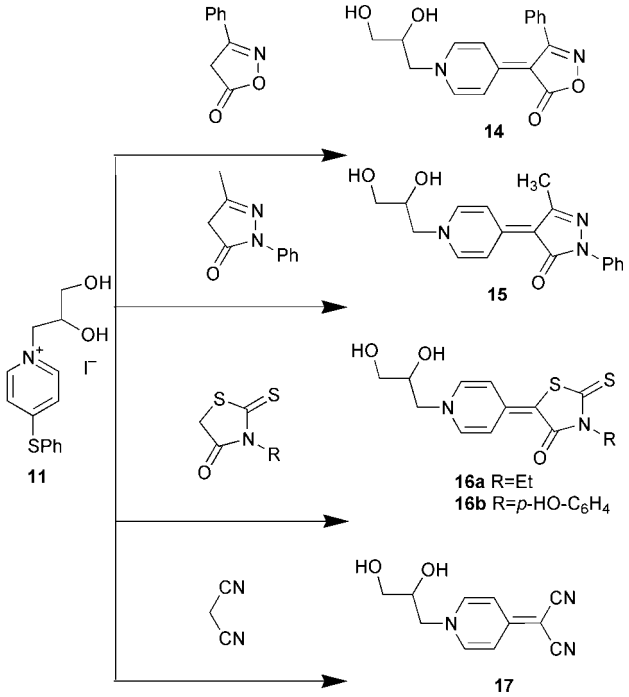
By employing, in essence, the same chemistry, heterocyclic acceptors were condensed with the 4-(phenylthio)pyridinium halides **11**–**13** to give the respective merocyanines in moderate yields (Schemes 1–3). In most instances, the 2,3-dihydroxypropyl halides were used to directly quaternise the pyridine nitrogen since we had previously shown that it was unnecessary to protect this polymer-tethering substituent.[15] As the means of introducing bulky substituents into the donor moiety, the 3,5-diiodopyridinium nucleus was elected as the target system principally because of the accessibility and availability of suitable precursors. To this end also, consideration was given to the synthesis of the 3,5-bis(trimethylsilyl)pyridinium analogue employing the recently published 'bromine–magnesium exchange' methodology.[25] Even though we were able to prepare the corresponding 4-(phenylthio)methylpyridinium iodide, attempts to couple heterocycles and to isolate product cleanly were unsuccessful.

Consistent with expectation, all of the compounds, **14**–**24**,



11

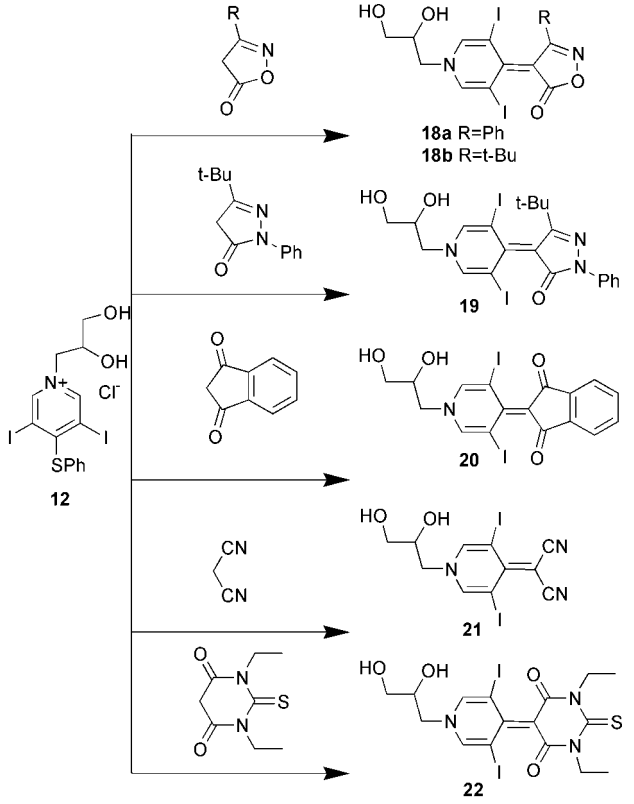
14

15

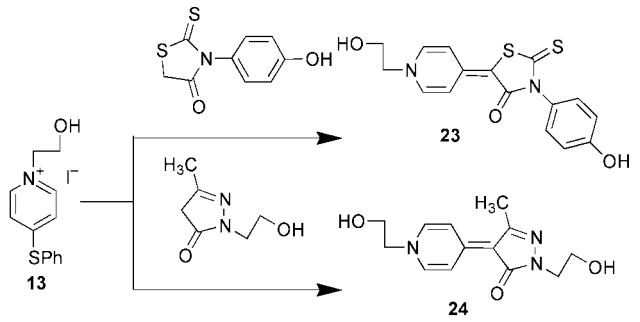
16a R=Et
16b R=*p*-HO-C_6H_4

17

Scheme 1 Syntheses of merocyanines **14**–**17**.



Scheme 2 Syntheses of merocyanines **18**–**22**.



Scheme 3 Syntheses of doubly-tetherable merocyanines **23**,**24**.

exhibited negative solvatochromic behaviour but to a lesser degree than their more conjugated homologues.[15] No significant differences in behaviour were observed between the three suites of chromophores. However, the extinction coefficients for the three compounds that would be expected to have the largest twist angles, namely **18a**,**b** and **19**, are an order of magnitude less than almost all of those for which an angle of $<5^\circ$ is calculated. This is clearly a result of a much less effective extent of π-orbital overlap between the rings.

Table 1 presents the results of twist angle (θ), ground state dipole moment (μ_g) and average static hyperpolarisability [$\beta(0)$] computations on the three suites of chromophores using the MOPAC97 programme. Structure optimisations were performed using the semi empirical AM1 method with the PRECISE keyword.

Immediately obvious from this table are the modest figures of merit [$\mu_g\beta(0)$], most particularly when compared to those reported for the quinopyridines **9a**,**b**, for which values in the vicinity of -500×10^{-48} esu have been measured by EFISH.[21] This is entirely reminiscent of the situation that emerged from a study[15] of the next highest homologues **4** and **5**; molecules containing the quinonoid acceptor, *viz.* **4** ($n = 1$), consistently exhibited higher figures of merit than those containing the heterocyclic acceptors, *e.g.* **5** ($n = 1$). The stunted

Table 1 Calculated dipole moment, static field hyperpolarisability and inter-ring dihedral angle values for chromophores **14**–**24**

Compound	μ_g/D	$\beta(0)$/ 10^{-30} esu	$\mu\beta(0)$/ 10^{-48} esu	Twist angle/°[a]
14	9.62	2.4 (*27*)[b]	23.1	0.22
15	7.10	3.4 (*31*)[b]	24.1	0.89
16a	7.37	14.3	105.4	0.00
16b	7.35	14.3	105.1	0.00
17	8.05	1.5	12.1	0.00
18a	11.04	6.7 (*20*)[b]	74.0	44.8
18b	11.20	9.3 (*16*)[b]	104.2	52.5
19	8.85	11.0	97.4	54.2
20	1.38	3.5	4.8	4.65
21	7.71	2.1	16.2	1.72
22	6.29	3.9	24.5	3.01
23	8.44	13.9	117.3	0.00
24	8.15	3.7	30.2	1.91

[a]Average of the two dihedral angles between the donor–acceptor moieties. [b]Measured values using HRS.

chromophores we describe herein are clearly zwitterionic, as judged from the small but consistent negative solvatochromism, but the extent of this status is probably only marginal.

Interestingly, a crystallographic appraisal of one of these chromophores, the pyridylideneisoxazolone **14** (Fig. 2) reveals quite clearly that, in addition to the conformational flexibility in the dihydroxypropyl tether, there is considerable benzenoid, *i.e.* pyridinium, character in the donor nucleus of the chromophore system. Bond lengths in the azine ring mimic the trends observed in *N*-methylpyridinium iodide[26] and not those in either the cyclopentadienylidene-1,4-dihydropyridine **25**[27] or the benzylidene-1,4-dihydropyridine **26**.[28] In precisely the same manner, the same is true of the bond angles about the azine nitrogen in **14**; all are within the tight range 119.4–120.7°, which confirms the existence of systemic planarity about the nitrogen, whereas in **25** the angles are in the range 117–123°. Furthermore, at 1.436 Å, the interconnect between the two rings in **14** is markedly lengthened when compared to those in **25** (at 1.388 Å) and **26** (at 1.360 Å) and, as such, clearly implies that there is considerable charge separation within the chromophore.

A twist angle of 14.5° is observed in the crystal geometry of **14**, compared to that of 0.2° suggested through the application of the AM1 method.

This particular observation is entirely consistent with the findings of Ravi *et al.*[29,30] who found that crystallographic geometries of chromophores belonging to the dicyanodiaminoquinodimethane system **3** were more benzenoid than was

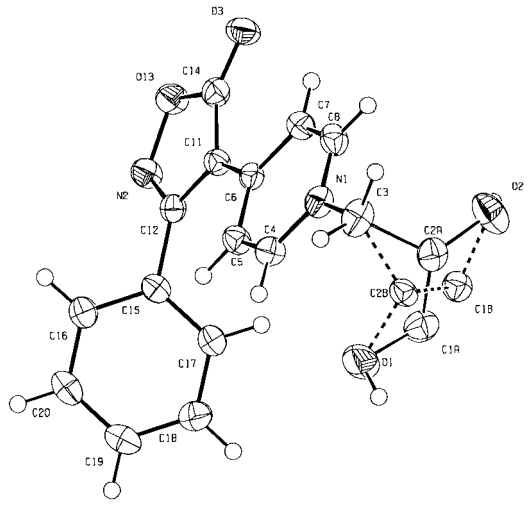
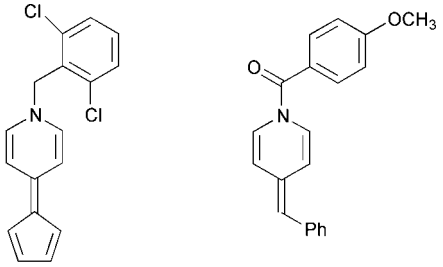


Fig. 2 View of the molecular structure of **14** showing the two conformations for the C1 and C2 atoms. 30% probability ellipsoids for non-hydrogen atoms are used.[37,38]



25 26

otherwise predicted at the AM1 level because the former are the optimal geometries for those molecules in a strongly polar crystal environment. From Table 1, it can also be seen that the measured values of $\beta(0)$ for **14** and **15** (the only compounds for which measurements were made) are larger than those predicted.

The introduction of substituents into each of the rings as a means of twisting the donor and acceptor rings out of coplanarity appears to have little real effect on $\beta(0)$. However, the larger measured $\beta(0)$ for compounds **14** and **15** might suggest that the AM1 derived values are consistently low but, even with this factor applied to other chromophores, $\mu\beta(0)$ values are still $<300 \times 10^{-48}$ esu and much less than that for the parent quinone system **7**, for example. With the exception of the thiobarbituric acid derivative **22**, which has only *ortho* carbonyl functionalities and the acyclic dicyanomethylidene containing compounds **17** and **21**, all the chromophore acceptor systems contain 5-membered heterocyclic rings. As a consequence, it is conceivable that twist angles of the magnitude putatively required to maximise β in 6–6 D–A ring systems might not be as achievable by synthetic manipulation in 6–5 D–A ring systems.

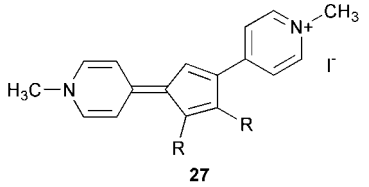
In any event, at the AM1 level, the dipole moment and hyperpolarisability terms are smaller than expected for zwitterionic species but are, nonetheless, features which imply that the extent of charge transfer and/or acceptor strength are insufficient to produce significant figures of merit in these stunted systems.

In connection with some of our earlier studies[15] on merocyanines **4** and **5** ($n = 1$), we had reason to explore the syntheses of double salts of 1,3-di(4-pyridyl)propane as a potential means of gaining access to bridged dimers of **4** and of **5**. This search revealed that such double (methiodide) salts were, in fact, precursors to stunted donor–acceptor functionalised molecules belonging to the *cyanine* class of chromophore.[17–19]

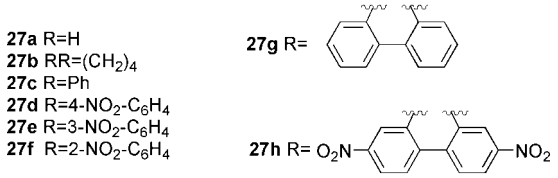
In view of the fact that this system can be viewed simplistically as a push–pull azasesquifulvalene chromophore that is isoelectronic with the stunted merocyanines above (albeit bearing a pyridinium substituent), we calculated the ground state dipole moment and static hyperpolarisability data from optimised AM1 geometries of a number of derivatives of **27** and the results are presented in Table 2. Even though the system is symmetrical or fluxional, there is an unexpectedly high ground state dipole moment that increases with increasing acceptor strength in R. For compound **27d** as a positively charged chromophore (without its counterion), for example, a dipole moment of 26.4 D is calculated together with a static hyperpolarisability of 51.2×10^{-30} esu. When optimised in the presence of its counterion, values of 13.2 D and 25.0×10^{-30} esu, respectively, are calculated.

Encouraged by the results of our computational study, we prepared the 'polymer-tetherable' cyanines **29a–d** as outlined in Scheme 4. Attempts to prepare the corresponding cyanine from 4,4′-dinitrobenzil were unsuccessful due to the extremely poor solubility of the requisite dione in methanol. In addition, a blue solid was obtained from reaction of **28** with 2,7-dinitrophenanthrenequinone but this has proved to be too insoluble to be

Table 2 Calculated dipole moment and static hyperpolarisability values for selected members of the cyanine series **27**



27



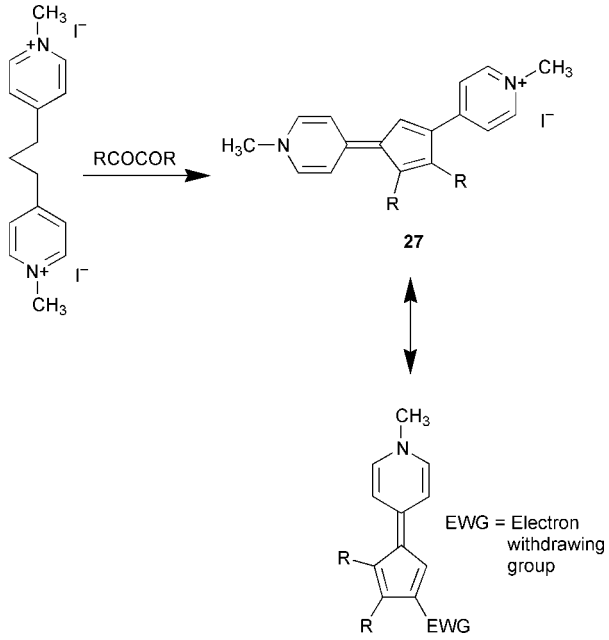
27a R=H
27b RR=$(CH_2)_4$
27c R=Ph
27d R=4-NO_2-C_6H_4
27e R=3-NO_2-C_6H_4
27f R=2-NO_2-C_6H_4

27g R=

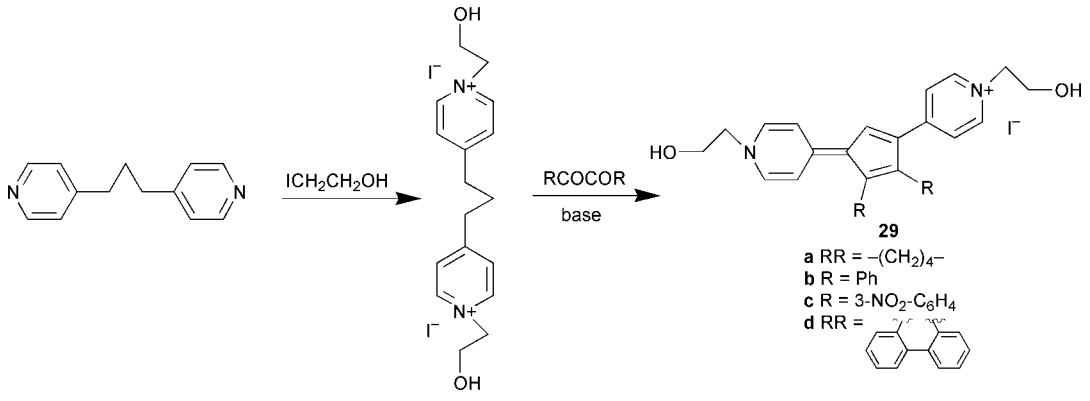
27h R= O_2N NO_2

Compound	μ_g/D[a]	$\beta(0)/10^{-30}$ esu[a]	$\mu\beta(0)/10^{-48}$ esu[a]
27a	4.08 (2.46)	35.9 (3.4)	146.5 (8.3)
27b	7.65 (5.47)	43.9 (34.7)	335.8 (189.8)
27c	12.00 (3.54)	51.6 (10.0)	619.2 (35.4)
27d	26.37 (13.17)	51.2 (25.0)	1350.1 (329.3)
27e	21.70 (8.03)	50.5 (36.4)	1095.9 (292.3)
27f	14.28 (8.35)	49.2 (35.3)	702.6 (294.9)
27g	12.65 (5.78)	62.1 (7.8)	785.6 (45.1)
27h	18.46 (8.83)	49.7 (17.1)	917.5 (150.7)

[a]Values given first are calculations performed without the iodide counterion, while those in parentheses are for the neutral molecules.



meaningfully characterised. The negative solvatochromic effect observed for these compounds is a little more pronounced than it is for the stunted merocyanines above and again suggests that the chromophore moiety is zwitterionic, the negative charge being associated with the cyclopentadienyl(ide) system or further delocalised by the Ar and pyridinium substituents. In fact, in all but compound **29d**, the systemic simplicity of the cationic chromophore is confirmed from ^{13}C- and ^{1}H-NMR spectroscopy, thereby attesting to the fluxional nature of the entire pyridinium–sesquifulvalene nucleus in solution. These cyanine dyes are, however, known to be protonated on the central cyclopentadienide ring in strongly acid media.[17] With regard to the NMR spectra of compounds **29a–c**, in which the two pairs of vicinal methylene groups are observed as two discrete multiplets [at δ 4.16 (NCH_2) and 3.72 (CH_2OH) for **29b**



Scheme 4 Synthesis of polymer-tetherable cyanines **29a–d**.

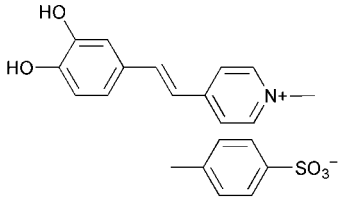
for example] and as a coincident signal at 60.2 ppm (for **29b**), the corresponding signals in compound **29d** are all non-equivalent, appearing as four two-proton multiplets at δ 4.21 and 4.00 (NCH_2) and δ 3.76 and 3.62 (CH_2OH). The ^{13}C-NMR spectrum displays three discrete signals in the ratio 1 : 2 : 1 at 60.6, 60.3 and 60.1 ppm indicating most probably that the two *N*-methylenes are no longer equivalent. This indicates that there is a lack of symmetry in **29d**, most likely as a result of distortion in the phenanthrenyl nucleus caused by its close proximity to the azine rings.

As NLO materials, molecular salts, in which one ion possesses a large molecular hyperpolarisability, are known to exhibit large second-order optical nonlinearities.[31,32] Stilbazolium tosylate salts **30** in the solid state, for example, can form macroscopically polar (*i.e.* noncentrosymmetric) structures as a result of alternating cation and anion sheets in the crystal lattice.[31] Analogues containing an 'internal salt', *e.g.* **31**, have also been shown to possess a large permanent dipole moment (16 D) and an high static nonlinear coefficient $\beta(0)$ of 37×10^{-30} esu. These systems have been considered as chromophores for inclusion in side-chain polymers and in LB films.[32]

As both **30** and **31** crystallise in noncentrosymmetric space groups ($P1$ and $Pc2_1b$, respectively), we were interested to see whether or not the same might have been true of a representative of the azasesquifulvalene system. Large crystals of chromophore **29a** were prepared, but these showed poor refinement in the structure analysis. The molecular structure could not be definitely established even though a space group and unit cell dimensions could be assigned ($P2_1/c$; a = 9.120 Å, b = 24.34 Å, c = 9.659 Å, $\alpha = \gamma = 90°$, $\beta = 96°$; $z = 4$); this cell has been confirmed by X-ray powder diffraction studies which show that other phases may be present. With a space group of $P2_1/c$, the packing motif would be clearly centrosymmetric, an outcome that, if general for this class of compound, effectively precludes the use of them as NLO elements in the crystalline state. With respect to the position of the organic cation, the iodide ion is localised at a pyridinium terminus, the nearest neighbour in fact being the oxygen of the pyridinium hydroxyethyl substituent.

In an earlier crystallographic study of the *N*,*N*′-dimethyl (bromide) analogue of **27**, namely **32**, in which one of the azine rings is present as a 2- rather than as a 4-substituent, Ammon and Erhardt[33] found no evidence for the existence of a tripolar structure, *i.e.* a bis(pyridiniumyl)cyclopentadienide; rather, that the compound is a hybrid of two monopolar cationic forms that exists in the centrosymmetric $P\bar{1}^c$ space group.

Even though only computational findings suggested nonlinear optical behaviour in these cyanine systems, we were interested to explore the possibility of synthesising a polymer containing this genuinely ionic NLO chromophore as either a side- or main-chain component of the backbone. In addition, we are interested to see whether or not a satisfactory level of chromophore alignment can be achieved by electric field poling and this will be reported in due course.



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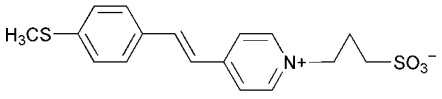
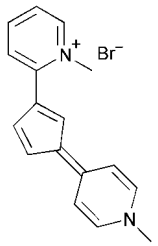


31

Utilising standard procedures[34] for novel polyurethane synthesis, we prepared a polymer of **29c** with a 1 : 1 stoichiometry with tolylene diisocyanate (TDI) and purified it easily twice by redissolution (DMSO–cyclohexanone)–reprecipitation (MeOH). Whilst we have no molecular weight data on this and other mainchain cyanine polymers, the integrity of this particular chromophore in this polymer was confirmed from UV–vis spectroscopy and an elemental analysis revealed an almost stoichiometric retention of iodide ion. The T_g recorded for this polymer was 240 °C.

In like manner, each of the multiply-tetherable chromophores **16b**, **23** and **24** (Schemes 1 and 3) was found to form, very cleanly, stoichiometric polyurethanes with TDI. T_g values are again high at 234 °C for **23** and 243 °C for **16b**. However, as these new materials are genuine mainchain polymer systems we envisage the need to further space and/or crosslink these types of chromophore elements using the triethanolamine methodology,[35] for example.

Finally, we believe there is scope to study the preparation of non-centrosymmetric crystals of derivatives of **27** and this



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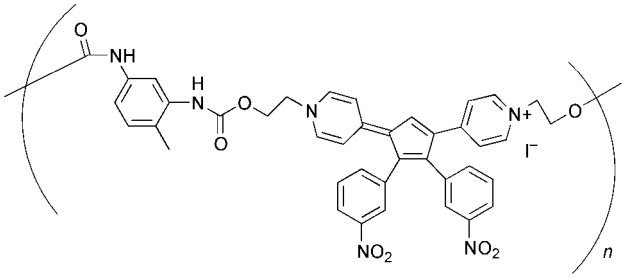

should be readily achieved by incorporating a chiral substituent onto one of the pyridinium N atoms; this will form the basis of our future studies. Thus, while polymers derived from **28** may yet prove unsuitable for spin-coating and 'utilisation' due to the tendency of ionic polymers to promote hole-burning on poling, non-centrosymmetric crystals of large $\beta(0)$ organic salts are known to have high second harmonic generation efficiencies.[36]

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. ^{1}H NMR multiplicities are defined by the usual notation and coupling constants are in hertz. The assignments of resonances were made with the aid of DEPT, ^{1}H–^{1}H COSY and ^{13}C–^{1}H HSQC experiments and heteronuclear multiple bond connectivity (HMBC) experiments. UV–vis absorption spectra were recorded on an Hewlett-Packard 8452A diode array spectrophotometer. Accurate mass measurements were made on a PE Biosystems Mariner operating in the electrospray mode and used in preference to microanalytical data since these were consistently marred by the retention of variable amounts of solvent of crystallisation.

Thin layer chromatography was performed on Merck Alufoilen 60 F_{254} analytical plates and flash chromatography performed over Riedel-de Haen silica gel S (230–400 mesh).

Measurements of the first hyperpolarisability were measured at the University of Otago using the hyper-Raleigh scattering technique with a fundamental wavelength of 1064 nm (seed-injected Nd:YAG pulsed laser; energy 20–25 μJ, width 70 ps, repetition rate 2 kHz) and with a series of concentrations (c 1–5 μM) in 0.2 micron-filtered methanol. Scattered SH light was detected by interference filtration and shown to have a quadratic dependence upon I^2 (1064).

X-Ray crystallography

Single crystals of compound **14** were crystallized from an acetone–hexane mixture.

Crystal data. $C_{17}H_{16}N_2O_4$, $M_r = 312.32$, triclinic, $a = 7.987(2)$, $b = 10.300(3)$, $c = 10.806(3)$ Å, $\alpha = 118.308(4)$, $\beta = 106.121(4)$, $\gamma = 94.752(4)^\circ$, $U = 727.3(4)$ Å^3, $T = 158(2)$ K, space group $P\bar{1}$ (No. 2); $Z = 2$, $\rho_c = 1.426$ g cm^{-3}, radiation MoKα, $\lambda = 0.71073$ Å, μ (Mo Kα) = 0.103 mm^{-1}, 8989 reflections collected, 2897 unique ($R_{int} = 0.0217$) used in all calculations. The final $wR(F^2)$ (all data) and $R(F)$ ($I > 2\sigma(I)$) were 0.112 and 0.0392 respectively. Selected bond lengths and angles are given in Table 3.

CCDC reference number 164244. See http://www.rsc.org/suppdata/jm/b1/b103148c/ for crystallographic files in .cif or other electronic format.

3-(*p*-Hydroxyphenyl)rhodanine

4-Aminophenol (10.9 g, 0.1 mol) was dissolved in aqueous NaOH (1 M, 100 mL) and the solution refluxed for 10 min and then allowed to cool. Bis(carboxymethyl) trithiocarbonate (22.6 g, 0.1 mol) was added and the mixture refluxed overnight. After cooling, the resulting solid was recovered by filtration, washed with water (3 × 100 mL), suspended in methanol–isopropanol (propan-2-ol) (1 : 1) (150 ml) and the mixture refluxed for 10 min before being cooled and filtered. The solid was dried in air to give the hydroxyphenyl rhodanine as a beige powder (14.4 g, 64%). Recrystallisation (methanol) gave beige crystals, mp 237.5–241 °C (dec.) (Found: C, 48.13; H, 3.01; N, 6.31. $C_9H_7NO_2S_2$ requires C, 47.98; H, 3.13; N, 6.22%) (Found: MH$^-$ m/z 223.98396; $C_9H_7NO_2S_2$ requires MH$^-$ m/z 223.98345; $\Delta = 2.3$ ppm). ^{1}H NMR (d_6-DMSO) δ 9.80 (s, 1H, -O*H*), 7.02 (d, *J* 8.7 Hz, 2H), 6.86 (d, *J* 8.7 Hz, 2H), 4.35 (s, 2H). ^{13}C NMR (d_6-DMSO) δ 204.3 (C_Q), 174.5 (C_Q), 158.3 (C_Q), 130.1 (CH), 126.8 (C_Q), 116.1 (CH), 37.0 (CH_2).

1-(2-Hydroxyethyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

To a stirred solution of ethyl acetoacetate (10.0 g, 58 mmol) at 0–5 °C was added dropwise over 10 min 2-hydroxyethylhydrazine (5.0 g, 60 mmol) and then acetic acid (1 mL). [The addition of the hydrazine results in a vigorous reaction and the addition should be done at such a rate so as to minimise sudden elevations in the reaction temperature.] The mixture was then stirred together for 1 h at 100 °C, cooled and, while still slightly warm, diluted with ether (30 mL) and triturated to give a tarry brown syrup (14.4 g) that was used as such in subsequent reactions; all attempts to crystallise the product failed. ^{1}H NMR ($CDCl_3$) δ 3.72–3.84 (m, 4H, -NC*H*$_2$ and -C*H*$_2$OH), 3.17 (s, 2H, -C*H*$_2$-), 2.04 (s, 3H, -C*H*$_3$). ^{13}C NMR ($CDCl_3$) δ 173.3 (C_Q), 156.7 (C_Q), 61.5 (CH_2), 47.5 (CH_2), 42.1 (CH_2), 17.3 (CH_3). NMR spectroscopy indicated significant impurities to be present in the crude tar, and while suitable for use without further purification it was presumed to be only 75% pure. Confirmation of the proposed structure was obtained by

Table 3 Selected geometric parameters for chromophore **14** (Å, °)

O(3)–C(14)	1.245(2)	O(13)–N(2)	1.4455(19)
O(13)–C(14)	1.3859(16)	N(1)–C(4)	1.3605(17)
N(1)–C(8)	1.3589(17)	N(2)–C(12)	1.3166(17)
C(4)–C(5)	1.3674(18)	C(5)–C(6)	1.419(2)
C(6)–C(11)	1.4359(17)	C(6)–C(7)	1.4207(17)
C(7)–C(8)	1.3698(18)	C(11)–C(12)	1.435(2)
C(12)–C(15)	1.494(2)	N(2)–O(13)–C(14)	109.58(10)
C(3)–N(1)–C(4)	119.62(13)	C(5)–C(6)–C(7)	115.88(11)
C(4)–C(5)–C(6)	120.89(13)	C(6)–C(11)–C(14)	124.01(13)
C(6)–C(11)–C(12)	130.83(13)	C(11)–C(12)–C(15)	130.82(11)
C(12)–C(11)–C(14)	104.97(11)	O(3)–C(14)–C(11)	105.9(3)
O(3)–C(14)–O(13)	118.67(12)	C(3)–N(1)–C(4)–C(5)	−176.29(13)
O(13)–C(14)–C(11)	107.12(13)	C(5)–C(6)–C(11)–C(12)	−10.6(2)
C(4)–N(1)–C(3)–C(2A)	94.4(2)	C(7)–C(6)–C(11)–C(12)	171.37(14)
C(11)–C(6)–C(7)–C(8)	−179.79(13)	C(6)–C(11)–C(14)–O(3)	3.9(3)
C(5)–C(6)–C(11)–C(14)	163.55(13)	C(12)–C(15)–C(16)–C(17)	−176.48(13)
C(7)–C(6)–C(11)–C(14)	−14.5(2)	N(2)–C(12)–C(15)–C(20)	−51.07(18)

reacting the crude tar with *N,N′*-diphenylformamidine to give the expected anilinomethylidene derivative as shown below.

4-Anilinomethylidene-1-(2-hydroxyethyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one

Crude 1-(2-hydroxyethyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (14.4 g) and *N,N′*-diphenylformamidine (14.9 g, 76 mmol) were stirred together at 120 °C for 1 h, and the mixture then allowed to cool to room temperature. To this was added firstly isopropanol (30 mL) and then water dropwise until a solid had formed. The resultant brown solid was collected by filtration and recrystallised (1 : 1 water–ethanol) to give brown-red needles (10.89 g, 58%), mp 117–119 °C (Found: MH^+ *m/z* 246.12279; $C_{13}H_{15}N_3O_2$ requires MH^+ *m/z* 246.12370; $\Delta = -3.7$ ppm). ^{1}H NMR ($CDCl_3$) δ 7.90 (s, 1H), 7.40–7.45 (m, 2H), 7.20–7.25 (m, 3H), 3.92–4.00 (m, 4H, -NCH_2 and -CH_2OH), 2.23 (s, 3H, -CH_3). ^{13}C NMR ($CDCl_3$) δ 166.9 (C_Q), 147.5 (C_Q), 143.6 (CH), 138.9 (C_Q), 130.4 (CH), 126.2 (CH), 117.7 (CH), 102.5 (C_Q), 62.4 (CH_2), 47.9 (CH_2), 12.9 (CH_3).

3-*tert*-Butylisoxazol-5(4*H*)-one

To a solution of ethyl pivaloylacetate (18.0 g, 0.105 mol) in ethanol (250 mL) was added a solution of hydroxylamine hydrochloride (7.92 g, 0.114 mol) in water (150 mL) followed by sodium acetate trihydrate (14.4 g, 0.105 mol). The mixture was refluxed for 1 h, cooled and concentrated and the resulting solid extracted with ether (3 × 150 mL). The ether extracts were pooled, dried (Na_2SO_4) and concentrated to give an off-white solid. A single recrystallisation from an ethyl acetate–hexane mixture afforded the isoxazolone as colourless needles (8.81 g, 60%), mp 110–111 °C (Found: MH^+ *m/z* 142.08561; $C_7H_{11}NO_2$ requires MH^+ *m/z* 142.08625; $\Delta = 4.5$ ppm). ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9H), 3.42 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 176.0 (C_Q), 174.1 (C_Q), 35.1 (C_Q), 33.7 (CH_2), 27.9 (CH_3).

3-*tert*-Butyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one

A mixture of ethyl pivaloylacetate (19.2 g, 0.112 mol), phenylhydrazine (12.5 g, 11.4 mL, 0.116 mol) and acetic acid (2 mL) was stirred for 1 h at 100 °C. The mixture was then cooled and, while still slightly warm, diluted with ether (30 mL) and then triturated with a glass rod. After cooling to −30 °C, the pale yellow solid was recovered by filtration and washed with cold ether (2 × 15 mL). Recrystallisation from isopropanol containing a few drops of ether afforded chunky colourless crystals (13.12 g, 54%), mp 117–119 °C (Found: C, 71.92; H, 7.45; N, 12.89. $C_{13}H_{16}N_2O$ requires C, 72.19; H, 7.46; N, 12.95%) (Found: MH^+ *m/z* 217.13291; $C_{13}H_{16}N_2O$ requires MH^+ *m/z* 217.13354; $\Delta = 2.9$ ppm). ^{1}H NMR ($CDCl_3$), δ 7.80–7.83 (m, 2H), 7.27–7.32 (m, 2H), 7.05–7.10 (m, 1H), 3.35 (s, 2H), 1.18 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 171.2 (C_Q), 167.0 (C_Q), 138.7 (C_Q), 129.1 (CH), 125.3 (CH), 119.2 (CH), 39.3, (CH_2), 35.3 (C_Q), 28.5, (CH_3).

1-(2,3-Dihydroxypropyl)-4-(phenylthio)pyridinium iodide, 11

A solution containing 4-(phenylthio)pyridine (2.0 g, 10.7 mmol) and 1-iodo-2,3-dihydroxypropane (2.2 g, 10.9 mmol) in ethanol (10 mL) was refluxed for 4 hours then cooled and concentrated to a yellow oil. Trituration with ethyl acetate afforded 1-(2,3-dihydroxypropyl)-4-(phenylthio)pyridinium iodide as a hygroscopic, off-white solid (3.95 g, 94%) which was used as such without further purification. ^{1}H NMR (D_2O) δ 8.36 (d, *J* 6.8 Hz, 2H), 7.56–7.66 (m, 5H), 7.48 (d, *J* 6.7 Hz, 2H), 4.61 (dd, *J* 3.0, 13.8 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.34 (dd, *J* 8.8, 13.7 Hz, 1H, higher field branch of AB quartet, -NCH_2), 4.07–4.14 (m, 1H, -C*H*OH), 3.65 (d, *J* 5.1 Hz, 2H, -CH_2OH). ^{13}C NMR (D_2O) δ 165.4 (C_Q), 143.3 (CH), 135.9 (CH), 132.1 (CH), 131.4 (CH), 126.0 (C_Q), 123.1 (CH), 70.9 (CH), 62.9 (CH_2), 62.6 (CH_2).

3,5-Diiodo-4-hydroxypyridine

This was prepared employing a slight modification to the previously reported method.[39] To a solution of 4-hydroxypyridine (15.0 g, 0.158 mol) in water (200 mL) was added a solution of sodium hydroxide (40.0 g, 1 mol) and sodium acetate trihydrate (200.0 g, 1.47 mol) in water (500 mL). The solution was stirred and heated to boiling and then powdered iodine (106 g, 0.417 mol) was added. The solution was acidified with acetic acid (50%) and then neutralised with aqueous sodium hydroxide (40%) and these steps repeated. The acidifications and neutralisations were made at the boiling point of the reaction mixture and each procedure was conducted over about 20 minutes. The final (third) acidification was made until free iodine was just precipitated. This was removed by boiling and the precipitated 3,5-diiodo-4-hydroxypyridine recovered by filtration, washed thoroughly with boiling water and dried to give the product as an off-white powder (47.8 g, 87%), mp 315 °C (dec.) (lit.[39] 317 °C (dec.)). ^{1}H NMR (d_6-DMSO) δ 8.28 (s, 2H). ^{13}C NMR (d_6-DMSO) δ 170.8 (C_Q), 143.3 (CH), 86.8 (C_Q).

4-Chloro-3,5-diiodopyridine

To a mixture of *dry* 3,5-diiodo-4-hydroxypyridine (40 g, 0.121 mol) in phosphoryl chloride (120 mL) was added phosphorus pentachloride (40 g, 0.192 mol) and the resultant slurry stirred at 100–110 °C for 16 h while protected from atmospheric moisture by a calcium chloride drying tube. The solution was then cooled and poured in *small* portions into water (1 L). Following each addition of the chlorinating mixture there followed a short induction period (*ca.* 1–2 min), after which considerable heat was generated: care was taken to ensure that the temperature of the aqueous solution did not rise above 70 °C. The hydrolysis step required 2–3 h in total. Once the mixture had cooled to room temperature it was chilled to *ca.* 5 °C and partially neutralised *via* the *cautious* addition of 30% aqueous sodium hydroxide (500–750 mL), after which a white precipitate formed in abundance. This was collected by filtration, suspended in water (500 mL) and the slurry made slightly basic to litmus. The solid was collected by filtration and washed thoroughly with water to give 4-chloro-3,5-diiodopyridine as a white powder (42.2 g, 96%), mp 174–176 °C (pentan-2-ol) (lit.[40] 175 °C). ^{1}H NMR (d_6-DMSO) δ 8.81 (s, 2H). ^{13}C NMR (d_6-DMSO) δ 157.3 (CH), 150.3 (C_Q), 99.1 (C_Q).

3,5-Diiodo-4-(phenylthio)pyridine

To a cooled (ice–water), stirred solution of 4-chloro-3,5-diiodopyridine (40 g, 0.11 mol) in triethylamine (150 mL) was added portion wise over 5 min neat thiophenol (15 g, 14 mL, 0.136 mol). The mixture was refluxed overnight, cooled and then diluted with water (150 mL) and stirred for 30 min. The precipitated solid was recovered by filtration,† washed with plenty of water and then recrystallised from an acetone–methanol (1 : 1) mixture to give the (phenylthio)pyridine as off-white microcrystals (38.5 g, 80%), mp 111–112.5 °C. A further 5–7 g of product was recovered from the mother liquor (Found: C, 30.38; H, 1.54; N, 3.15. $C_{11}H_7I_2NS$ requires C, 30.09; H, 1.61; N, 3.19%) (Found: MH^+ *m/z* 439.8454; $C_{11}H_7I_2NS$ requires MH^+ *m/z* 439.84615; $\Delta = 1.7$ ppm). ^{1}H NMR (d_6-DMSO) δ 8.99 (s, 2H), 7.32–7.37 (m, 2H), 7.23–7.28 (m, 1H), 7.04–7.07 (m, 2H). ^{13}C NMR (d_6-DMSO) δ 157.7

†Due to the presence of a thick oil filtration may require 5–6 hours until completion.

(CH), 150.6 (C_Q), 134.4 (C_Q), 130.0 (CH), 127.7 (CH), 127.0 (CH), 108.3 (C_Q).

1-(2,3-Dihydroxypropyl)-3,5-diiodo-4-(phenylthio)pyridinium chloride, 12

A mixture of 3,5-diiodo-4-(phenylthio)pyridine (5.0 g, 11.4 mmol) and α-chloroglycerol (15.0 g, 73.7 mmol) was stirred at 120 °C for 16 h after which time the resulting orange oil was added dropwise to a stirred volume of acetone (400 mL), whereupon a sticky orange-yellow solid precipitated. This was recovered by filtration and recrystallised (ethanol) to give 1-(2,3-dihydroxypropyl)-3,5-diiodo-4-(phenylthio)pyridinium chloride as air sensitive bright yellow microcrystals (3.68 g, 59%), mp 173.5–175 °C. ^{1}H NMR (d_6-DMSO) δ 9.42 (s, 2H), 7.35–7.45 (m, 3H), 7.25–7.28 (m, 2H), 5.56 (d, *J* 5.8 Hz, 1H, -CHO*H*), 5.05 (t, *J* 5.5 Hz, 1H, -CH_2O*H*), 4.67 (dd, *J* 2.6, 12.6 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.33–4.40 (m, 1H, higher field branch of AB quartet, -NCH_2), 3.95 (m, 1H, -C*H*OH), 3.48–3.57 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.38–3.46 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 161.7 (C_Q), 151.6 (CH), 133.1 (C_Q), 130.3 (CH), 129.8 (CH), 128.4 (CH), 105.5 (C_Q), 70.7 (CH), 63.4 (CH_2), 63.0 (CH_2).

General procedure for the preparation of pyridylidene-functionalised heterocycles

To a solution of 1-(2,3-dihydroxypropyl)-4-(phenylthio)pyridinium iodide (3.89 g, 0.01 mol) and the appropriate heterocyclic acceptor (0.01 mol) in ethanol (50 mL) was added triethylamine (1.5 mL, 1.09 g, 0.01 mol). The mixture was then refluxed for 1 h, cooled and the resulting chromophores isolated as outlined below. Reactions with the diiodopyridinium chloride analogue were performed in like stoichiometric manner at the 2.0 mmol scale and at reflux for 16 h. In all instances the crude condensation product was recovered by filtration of the cooled reaction liquor.

4-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]-3-phenylisoxazol-5(4*H*)-one, 14. Isolated by flash chromatography over silica using gradient elution of an acetone–hexane mixture (70–100%) and isolated as a yellow solid. Recrystallisation from acetone afforded bright yellow microcrystals (87 mg, 9%), mp 247–250 °C (Found: MH^+ *m*/*z* 313.11871; $C_{17}H_{16}N_2O_4$ requires MH^+ *m*/*z* 313.11828; Δ = 1.4 ppm). λ_{max} 370 (H_2O); 382 (methanol) $\log_{10}\varepsilon$ 4.45; 384 (10% aqueous acetonitrile); 394 (DMSO) $\log_{10}\varepsilon$ 4.50; 400 (acetone); 404 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.01 (d, *J* 7.2 Hz, 2H), 7.52–7.55 (m, 4H), 7.42–7.45 (m, 3H), 5.21 (d, *J* 5.4 Hz, 1H), 4.87 (t, *J* 5.4 Hz, 1H), 4.23 (dd, *J* 2.9, 13.5 Hz, 1H, lower field branch of AB quartet, -NCH_2), 3.94 (dd, *J* 8.2, 13.5 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.71–3.73 (m, 1H, -C*H*OH), 3.37–3.44 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.21–3.29 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 174.0 (C_Q), 162.3 (C_Q), 149.4 (C_Q), 141.9 (CH), 133.0 (C_Q), 129.6 (CH), 129.3 (CH), 128.8 (CH), 115.2 (CH), 85.6 (C_Q), 70.7 (CH), 63.2 (CH_2), 60.9 (CH_2).

4-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]-3-methyl-1-phenylpyrazol-5(4*H*)-one, 15. Isolated in the manner described for the isoxazolone analogue and purified by recrystallisation from an acetone–hexane mixture to give bright yellow crystals (214 mg, 22%), mp 242–245 °C (Found: C, 66.33; H, 6.02; N, 12.73. $C_{18}H_{19}N_3O_3$ requires C, 66.44; H, 5.89; N, 12.92%) (Found: MH^+ *m*/*z* 326.15083; $C_{18}H_{19}N_3O_3$ requires MH^+ *m*/*z* 326.14992; Δ = 2.8 ppm). λ_{max} 378 (H_2O); 390 (methanol) $\log_{10}\varepsilon$ 4.37; 392 (10% aqueous acetonitrile); 412 (DMSO) $\log_{10}\varepsilon$ 4.39; 404 (10% aqueous acetone); 418 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.82 (br s, 2H), 8.08 (apparent d, *J* 8.3 Hz, 2H), 8.00 (d, *J* 7.3 Hz, 2H), 7.32 (apparent t, *J* 7.86 Hz, 2H), 7.01 (apparent t, *J* 7.3 Hz, 1H), 5.26 (d, *J* 5.4 Hz, 1H, -CHO*H*), 4.90 (t, *J* 5.3 Hz, 1H, -CH_2O*H*), 4.26 (dd, *J* 2.8, 13.5 Hz, 1H, lower field branch of AB quartet, -NCH_2), 3.98 (dd, *J* 8.0, 13.5 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.77–3.78 (m, 1H; -C*H*OH), 3.41–3.48 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.26–3.33 (m, 1H, higher field branch of AB quartet, -CH_2OH), 2.38 (s, 3H, CH_3). ^{13}C NMR (d_6-DMSO) δ 165.2 (C_Q), 149.1 (C_Q), 147.0 (C_Q), 141.4 (CH), 140.8 (C_Q), 128.7 (CH), 122.6 (CH), 117.9 (CH), 114.7 (CH), 97.4 (C_Q), 70.9 (CH), 63.2 (CH_2), 60.4 (CH_2), 18.5 (CH_3).

5-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]-3-ethylrhodanine, 16a. Isolated as described above and purified by recrystallisation from an acetone–hexanes mixture to give orange rosettes (1.72 g, 55%), mp 220–222 °C (Found: MH^+ *m*/*z* 313.06793; $C_{13}H_{16}N_2O_3S_2$ requires MH^+ *m*/*z* 313.06751; Δ = 1.3 ppm). λ_{max} 454 (H_2O); 460 (methanol) $\log_{10}\varepsilon$ 4.79; 462 (acetonitrile); 466 (DMSO) $\log_{10}\varepsilon$ 4.78; 464 (acetone); 470 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.22–8.25 (m, 1H), 7.81–7.85 (m, 2H), 6.42–6.45 (m, 1H), 5.19 (br s, 1H, -CHO*H*), 4.85 (br s, 1H, -CH_2O*H*), 4.15 (dd, *J* 3.0, 13.6 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.00 (q, *J* 7.0 Hz, 2H, -NC$H_2$$CH_3$), 3.89 (dd, *J* 7.9, 13.6 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.74 (m, 1H, -C*H*OH), 3.42 (dd, *J* 4.9, 10.9 Hz, 1H, lower field branch of AB quartet, -CH_2OH), 3.26 (dd, *J* 6.5, 10.9 Hz, 1H, higher field branch of AB quartet, -CH_2OH), 1.14 (t, *J* 7.0 Hz, 3H, -NCH_2CH_3). ^{13}C NMR (d_6-DMSO) δ 185.6 (C_Q), 162.9 (C_Q), 143.7 (C_Q), 141.2 (CH), 140.6 (CH), 113.6 (CH), 113.3 (CH), 88.1 (C_Q), 70.8 (CH), 63.2 (CH_2), 60.0 (CH_2), 38.9 (CH_2), 12.6 (CH_3).

5-[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]-3-(*p*-hydroxyphenyl)rhodanine, 16b. Isolated as a crude precipitate that was purified by crystallisation from an acetone–hexane mixture to give bright orange microcrystals (1.55 g, 41%), mp 273–274 °C (Found: MH^+ *m*/*z* 377.06321; $C_{17}H_{16}N_2O_4S_2$ requires MH^+ *m*/*z* 377.06243; Δ = 2.1 ppm). λ_{max} 454 (H_2O); 460 (methanol) $\log_{10}\varepsilon$ 4.88; 464 (acetonitrile); 466 (DMSO) $\log_{10}\varepsilon$ 4.91; 464 (acetone); 470 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.68 (s, 1H, ArO*H*), 8.15–8.18 (m, 1H), 7.80–7.84 (m, 2H), 7.00 (d, *J* 8.7 Hz, 2H), 6.84 (d, *J* 8.7 Hz, 2H), 6.46–6.50 (m, 1H), 5.22 (d, *J* 5.3 Hz, 1H, -CHO*H*), 4.87 (t, *J* 5.4 Hz, 1H, -CH_2O*H*), 4.14 (dd, *J* 2.8, 13.6 Hz, 1H, lower field branch of AB quartet, -NCH_2), 3.88 (dd, *J* 7.9, 13.6 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.74 (m, 1H, -C*H*OH), 3.39–3.47 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.23–3.32 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 187.5 (C_Q), 163.6 (C_Q), 157.7 (C_Q), 143.6 (C_Q), 141.2 (CH), 140.5 (CH), 130.1 (CH), 128.6 (C_Q), 115.7 (CH), 113.4 (CH), 113.2 (CH), 88.2 (C_Q), 70.9 (CH), 63.2 (CH_2), 59.9 (CH_2).

[1-(2,3-Dihydroxypropyl)pyridin-4(1*H*)-ylidene]dicyanomethane, 17. Malononitrile (0.22 g, 3.3 mmol) was added to a solution of sodium ethoxide [prepared from sodium metal (0.08 g, 3.3 mmol)] in ethanol (10 mL) and the mixture stirred for 30 min after which time 1-(2,3-dihydroxypropyl)-4-(phenylthio)pyridinium iodide (1.30 g, 3.34 mmol) was added. The solution was refluxed for 1 h, and then cooled to –18 °C. The resulting solid was recovered by filtration, washed with water (10 mL) and then isopropanol (10 mL) to give a pale yellow powder (0.32 g, 44%). Recrystallisation from ethanol afforded light tan microcrystals, mp 183–184.5 °C (Found: C, 60.81; H, 5.07; N, 19.14. $C_{11}H_{11}N_3O_2$ requires C, 60.82; H, 5.10; N, 19.35%) (Found: MH^+ *m*/*z* 218.09261; $C_{11}H_{11}N_3O_2$ requires MH^+ *m*/*z* 218.09240; Δ = 0.9 ppm). λ_{max} 374 (H_2O–acetone; 20 : 1); 378 (methanol) $\log_{10}\varepsilon$ 4.24; 376 (acetonitrile); 378 (DMSO) $\log_{10}\varepsilon$ 4.27; 376 (acetone); 380 (pyridine). ^{1}H NMR (d_6-DMSO) δ 7.86 (d, *J* 7.0 Hz, 2H), 6.83

(d, J 7.0 Hz, 2H), 5.23 (d, J 5.1 Hz, 1H, -CHO*H*), 4.87 (t, J 5.2 Hz, 1H, -CH_2O*H*), 4.19 (dd, J 2.4, 13.5 Hz, 1H, lower field branch of AB quartet, -NCH_2), 3.92 (dd, J 8.0, 13.5 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.72 (m, 1H, -C*H*OH), 3.36–3.44 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.22–3.27 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 155.7 (C_Q), 141.4 (CH), 118.9 (C_Q), 112.6 (CH), 70.8 (CH), 63.1 (CH_2), 60.2 (CH_2), 43.5 (C_Q).

4-[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]-3-phenylisoxazol-5(4*H*)-one, 18a. Purified by recrystallisation from ethanol to give an orange-yellow microcrystalline powder (0.28 g, 25%), mp 223.5–225 °C (Found: MH^+ m/z 564.90888; $C_{17}H_{14}I_2N_2O_4$ requires MH^+ m/z 564.91159; Δ = 4.8 ppm). λ_{max} 432 (H_2O); 456 (methanol) $\log_{10}\varepsilon$ 3.51; 466 (10% aqueous acetonitrile); 492 (DMSO) $\log_{10}\varepsilon$ 3.71; 490 (5% aqueous acetone); 510 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.05 (s, 1H), 9.01 (s, 1H), 7.27–7.36 (m, 3H), 7.16–7.19 (m, 2H), 5.43 (d, J 5.7 Hz, 1H, -CHO*H*), 4.94 (t, J 5.4 Hz, 1H, -CH_2O*H*), 4.52 (dd, J 2.6, 13.0 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.23 (dd, J 8.7, 13.0 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.86–3.88 (m, 1H, -C*H*OH), 3.45–3.52 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.33 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 171.1 (C_Q), 161.8 (C_Q), 160.6 (C_Q), 150.2 (CH), 149.8 (CH), 134.3 (C_Q), 128.9 (CH), 128.8 (CH), 126.3 (CH), 99.1 (C_Q), 98.8 (C_Q), 91.9 (C_Q), 70.6 (CH), 63.4 (CH_2), 61.9 (CH_2).

4-[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]-3-*tert*-butylisoxazol-5(4*H*)-one, 18b. Purified by recrystallisation from methanol to give orange platelets (0.21 g, 19%), mp 278–280 °C (Found: C, 32.29; H, 3.35; N, 4.87. $C_{15}H_{18}I_2N_2O_4\cdot$½$H_2O$ requires C, 32.57; H, 3.46; N, 5.06%) (Found: MH^+ m/z 544.94108; $C_{15}H_{18}I_2N_2O_4$ requires MH^+ m/z 544.94289; Δ = 3.3 ppm). λ_{max} 448 (H_2O); 486 (methanol) $\log_{10}\varepsilon$ 2.81; 488 (10% aqueous acetonitrile); 554 (DMSO) $\log_{10}\varepsilon$ 3.09; 556 (5% aqueous acetone); 550 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.28 (s, 1H), 9.23 (s, 1H), 5.51 (d, J 5.7 Hz, 1H, -CHO*H*), 4.98 (t, J 5.4 Hz, 1H, -CH_2O*H*), 4.59 (dd, J 2.4, 12.8 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.31–4.35 (m, 1H, higher field branch of AB quartet, -NCH_2), 3.92 (m, 1H, -C*H*OH), 3.40–3.43 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.32–3.37 (m, 1H, higher field branch of AB quartet, -CH_2OH), 1.09 (9H, -CH_3). ^{13}C NMR (d_6-DMSO) δ 195.0 (C_Q), 167.3 (C_Q), 166.2 (C_Q), 150.0 (CH), 149.7 (CH), 105.9 (C_Q), 105.7 (C_Q), 93.0 (C_Q), 70.6 (CH), 63.4 (CH_2), 62.6 (CH_2), 33.4, (C_Q), 30.2, (CH_3).

4-[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]-3-*tert*-butyl-1-phenylpyrazol-5(4*H*)-one, 19. Obtained as a red powder, which on filtration and exposure to air gradually changed to a crimson, glassy-like solid (0.624 g, 50%) (Found: MH^+ m/z 619.99386; $C_{21}H_{23}I_2N_3O_3$ requires MH^+ m/z 619.99017; Δ = 6.0 ppm). λ_{max} 536 (3 : 1; H_2O–DMSO); 536 (methanol) $\log_{10}\varepsilon$ 2.99; 542 (49 : 1; acetonitrile–DMSO); 548 (DMSO) $\log_{10}\varepsilon$ 3.05; 542 (49 : 1; acetone–DMSO); 558 (49 : 1; pyridine–DMSO). Due to poor resolution ^{1}H and ^{13}C NMR spectra were not helpful and therefore are not reported here.

2-[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]-indane-1,3-dione, 20. Purified by recrystallisation from ethanol to give an orange powder (0.09 g, 8%), mp 235–237 °C (Found: C, 37.10; H, 2.88; N, 2.36. $C_{17}H_{13}I_2NO_4$ requires C, 37.19; H, 2.39; N, 2.55%) (Found: MH^+ m/z 549.89899; $C_{17}H_{13}I_2NO_4$ requires MH^+ m/z 549.90069; Δ = 3.1 ppm). λ_{max} 432 (H_2O); 444 (methanol) $\log_{10}\varepsilon$ 3.96; 468 (acetonitrile); 464 (DMSO) $\log_{10}\varepsilon$ 4.14; 470 (acetone); 476 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.02 (s, 2H), 7.33–7.43 (m, 4H), 5.44 (d, J 5.7 Hz, 1H, -CHO*H*), 4.95 (t, J 5.4 Hz, 1H, -CH_2O*H*), 4.53 (dd, J 2.1, 12.9 Hz, 1H, lower field branch of AB quartet, -NCH_2), 4.23 (dd, J 8.8, 12.9 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.89 (m, 1H, -C*H*OH), 3.46–3.53 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.31–3.39 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 184.1 (C_Q), 163.9 (C_Q), 149.7 (CH), 140.6 (C_Q), 130.8 (CH), 119.1 (CH), 110.9 (C_Q), 98.1 (C_Q) 70.8 (CH), 63.4 (CH_2), 61.7 (CH_2).

[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]dicyanomethane, 21. Purified by recrystallisation from ethanol to give yellow platelets (0.39 g, 49%), mp 263–264 °C (Found: MH^+ m/z 469.88491; $C_{11}H_9I_2N_3O_2$ requires MH^+ m/z 469.88571; Δ = 1.7 ppm). λ_{max} 404 (H_2O–acetone; 20 : 1); 410 (methanol) $\log_{10}\varepsilon$ 4.16; 410 (acetonitrile); 412 (DMSO) $\log_{10}\varepsilon$ 4.22; 412 (acetone); 416 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.53 (s, 2H), 5.24 (d, J 5.6 Hz, 1H, -CHO*H*), 4.85 (t, J 5.4 Hz, 1H, -CH_2O*H*), 4.23 (dd, J 2.6, 13.3 Hz, 1H, lower field branch of AB quartet, -NCH_2), 3.96 (dd, J 8.4, 12.3 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.73–3.75 (m, 1H, -C*H*OH), 3.38–3.46 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.24–3.31 (m, 1H, higher field branch of AB quartet, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 154.8 (C_Q), 149.5 (CH), 119.6 (C_Q), 83.2 (C_Q), 70.6 (CH), 63.2 (CH_2), 59.9 (CH_2). One quaternary carbon signal, -*C*$(CN)_2$, not observed.

5-[1-(2,3-Dihydroxypropyl)-3,5-diiodopyridin-4(1*H*)-ylidene]-1,3-diethyl-2-thiobarbituric acid, 22. Isolated by concentrating the crude product mixture to dryness and then stirring the residual solids in hot acetone–hexanes (1 : 1). The resulting precipitate was collected by filtration and washed with hot hexanes to give an orange-yellow powder (119 mg, 10%). Recrystallisation (isopropanol) afforded bright orange microcrystals, mp 265–266 °C (Found: MH^+ m/z 603.92656; $C_{16}H_{19}I_2N_3O_4S$ requires MH^+ m/z 603.92586; Δ = 0.7 ppm). λ_{max} 414 (H_2O); 438 (methanol) $\log_{10}\varepsilon$ 3.93; 458 (acetonitrile); 448 (DMSO) $\log_{10}\varepsilon$ 3.94; 462 (acetone); 468 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.19 (s, 2H), 5.48 (d, J 5.7 Hz, 1H, -CHO*H*), 4.97 (t, J 5.4 Hz, 1H, -CH_2O*H*), 4.61–4.64 (m, 1H, lower field branch of AB quartet, -NCH_2), 4.44 (q, J 6.4 Hz, 4H, -NC$H_2$$CH_3$), 4.32 (dd, J 9.0, 12.8 Hz, 1H, higher field branch of AB quartet, -NCH_2), 3.91 (m, 1H, -C*H*OH), 3.47–3.54 (m, 1H, lower field branch of AB quartet, -CH_2OH), 3.35–3.39 (m, 1H, higher field branch of AB quartet, -CH_2OH), 1.19 (t, J 6.7 Hz, 6H, -NCH_2CH_3). ^{13}C NMR (d_6-DMSO) δ 176.3 (C_Q), 166.4 (C_Q), 156.8 (C_Q), 150.2 (CH), 130.2 (C_Q), 103.0 (C_Q), 70.7 (CH), 63.5 (CH_2), 62.6 (CH_2), 41.6 (CH_2), 13.1 (CH_3).

1-(2-Hydroxyethyl)-4-(phenylthio)pyridinium iodide, 13

A mixture of 4-(phenylthio)pyridine (5.61 g, 0.03 mol) and 2-iodoethanol (5.16 g, 0.03 mol) in solution in isopropanol (15 mL) was refluxed for 3 days, after which time it was cooled and concentrated to give a yellow oil. This was triturated with ether (15 mL) and then cooled until a solid mass had formed. The solid was recovered by filtration and washed thoroughly with ether to afford 1-(2-hydroxyethyl)-4-(phenylthio)pyridinium iodide as a beige solid (10.57 g, 98%) which was acceptable for use without further purification. Recrystallisation from a methanol–isopropanol mixture gave the salt as off-white microcrystals, mp 166–167.5 °C (Found: C, 43.48; H, 3.82; N, 3.87. $C_{13}H_{14}INOS$ requires C, 43.46; H, 3.93; N, 3.90%); ^{1}H NMR ($CDCl_3$) δ 8.85 (d, J 7.1 Hz, 2H), 7.58–7.63 (m, 5H), 7.38 (d, J 7.1 Hz, 2H), 4.88 (t, J 4.8 Hz, 2H), 4.13 (br s, 1H), 4.05 (m, 2H). ^{13}C NMR ($CDCl_3$), δ 165.1 (C_Q), 143.6 (CH), 135.9 (CH), 132.2 (CH), 131.5 (CH), 125.7 (C_Q), 122.8 (CH), 62.3 (CH_2), 61.1 (CH_2).

5-[1-(2-Hydroxyethyl)pyridin-4(1*H*)-ylidene]-3-(*p*-hydroxyphenyl)rhodanine, 23

A mixture of 1-(2-hydroxyethyl)-4-(phenylthio)pyridinium iodide (3.59 g, 0.01 mol), 3-(*p*-hydroxyphenyl)rhodanine (2.25 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in ethanol (50 mL) was refluxed for 16 h and then cooled. The resulting precipitate was collected by filtration and washed with a little cool ethanol to give a deep orange powder (2.58 g, 75%). Recrystallisation from an acetone–hexane mixture gave orange microcrystals, mp > 320 °C (Found: C, 55.20; H, 3.99; N, 8.08. $C_{16}H_{14}N_2O_3S_2$ requires C, 55.47; H, 4.07; N, 8.09%) (Found: MH^+ *m/z* 377.06321; $C_{16}H_{14}N_2O_3S_2$ requires MH^+ *m/z* 377.06243; Δ = 2.1 ppm). λ_{max} 454 (H_2O); 460 (methanol) $\log_{10}\varepsilon$ 4.83; 462 (acetonitrile); 466 (DMSO) $\log_{10}\varepsilon$ 4.85; 464 (acetone), 470 (pyridine). ^{1}H NMR (d_6-DMSO) δ 9.67 (s, 1H, ArO*H*), 8.16–8.19 (m, 1H), 7.84–7.88 (m, 2H), 7.00 (d, *J* 8.7 Hz, 2H), 6.85 (d, *J* 8.7 Hz, 2H), 6.47–6.50 (m, 1H), 5.06 (t, *J* 5.1 Hz, 1H, -CH_2O*H*), 4.04 (t, *J* 4.9 Hz, 2H, -NCH_2), 3.67–3.72 (m, 2H, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 187.5 (C_Q), 163.6 (C_Q), 157.7 (C_Q), 143.6 (C_Q), 140.8 (CH), 140.1 (CH), 130.1 (CH), 128.6 (C_Q), 115.7 (CH), 113.6 (CH), 113.4 (CH), 88.2 (C_Q), 60.5 (CH_2), 59.4 (CH_2).

4-[1-(2-Hydroxyethyl)pyridin-4(1*H*)-ylidene]-1-(2-hydroxyethyl)-3-methylpyrazol-5(4*H*)-one, 24

A mixture of 1-(2-hydroxyethyl)-4-(phenylthio)pyridinium iodide (1.1 g, 3.0 mmol), crude 1-(2-hydroxyethyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (0.7 g, 4.9 mmol) and triethylamine (0.5 g, 4.9 mmol) in ethanol (20 mL) was refluxed for 16 h, cooled and concentrated to dryness. The product was dissolved in water (25 mL) and the solution reconcentrated with stirring under high vacuum to the point where *ca*. 80% solvent had been removed and a yellow-orange solid had formed. This solid was recovered by filtration and washed with water (3 × 10 mL) and dried. Concentration of the filtrate, followed by trituration with acetone afforded a further crop of solid. Recrystallisation from a methanol–acetone mixture gave bright yellow microcrystals (145 mg, 18%), mp 223–225 °C (Found: C, 55.31; H, 6.77; N, 14.86. $C_{13}H_{17}N_3O_3\cdot H_2O$ requires C, 55.51; H, 6.81; N, 14.93%) (Found: MH^+ *m/z* 264.13391; $C_{13}H_{17}N_3O_3$ requires 264.13427; Δ = 1.4 ppm). λ_{max} 378 (H_2O–methanol; 20 : 1); 390 (methanol) $\log_{10}\varepsilon$ 4.23; 408 (acetonitrile); 414 (DMSO) $\log_{10}\varepsilon$ 4.27; 412 (acetone), 422 (pyridine). ^{1}H NMR (d_6-DMSO) δ 7.97 (apparent s, 4H), 5.12 (br s, 2H, 2 × -CH_2O*H*), 4.11 (br s, -NCH_2), 3.67–3.72 (m, 4H, -NCH_2 and -CH_2OH), 3.54–3.58 (m, 2H, -CH_2OH), 2.25 (s, 3H, -CH_3). ^{13}C NMR (d_6-DMSO) δ 165.5 (C_Q), 149.0 (C_Q), 144.1 (C_Q), 140.8 (CH), 114.5 (CH), 97.1 (C_Q), 60.6 (CH_2), 59.6 (CH_2), 47.0 (CH), 18.2 (CH_3).

3,3′-Dinitrobenzil

This was prepared as previously described,[41] mp 130–131 °C (lit.[41] 132 °C). ^{1}H NMR ($CDCl_3$) δ 8.86 (s, 2H), 8.55–8.57 (m, 2H), 8.39 (d, *J* 7.8 Hz, 2H), 7.81 (dd, *J* 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 189.9 (C_Q), 149.0 (C_Q), 135.8 (CH), 134.1 (C_Q), 130.9 (CH), 129.7 (CH), 125.3 (CH).

1,1′-Bis(2-hydroxyethyl)-4,4′-trimethylenedipyridinium diiodide, 28

A mixture of 4,4′-trimethylenedipyridine (9.9 g, 0.05 mol) and 2-iodoethanol (21.5 g, 0.125 mol) in ethanol (50 mL) was refluxed for 16 h and then cooled. The solution was concentrated in vacuum to give a dark olive oil which was washed by successively shaking with ether, ethyl acetate and acetone and decanting off the supernatant liquid each time. The residual green-brown oil was allowed to stand in a stoppered flask for 48 h after which time the product had begun to solidify as small 'flowers'; the mixture was triturated to hasten solidification. Isopropanol was then added, and the product collected by filtration and washed with isopropanol to give a beige solid (25.9 g, 96%) that was suitable for use without further purification. The product could not be recrystallised from common alcohols. ^{1}H NMR (d_6-DMSO) δ 8.93 (d, *J* 6.4 Hz, 4H), 8.10 (d, *J* 6.4 Hz, 4H), 5.09 (br s, 2H, -CH_2O*H*), 4.63 (t, *J* 4.7 Hz, 4H), 3.85 (t, *J* 4.7 Hz, 4H), 3.14 (t, *J* 7.6 Hz, 4H), 2.12 (quintet, *J* 7.6 Hz, 2H). ^{13}C NMR (d_6-DMSO) δ 161.8 (C_Q), 144.8 (CH), 127.7 (CH), 62.7 (CH_2), 60.3 (CH_2), 34.3 (CH_2), 28.9 (CH_2).

General procedure for the preparation of bridged cyanine dyes 29a–d

To a stirred solution of 1,1′-bis(2-hydroxyethyl)-4,4′-trimethylenedipyridinium diiodide (5.42 g, 0.01 mol) and the appropriate α-diketone (0.01 mol) in hot methanol (50 mL) was added dropwise piperidine (1.70 g, 0.02 mol). The mixture was then refluxed for 16 h, cooled, and the crude product collected by filtration and washed with a little ethanol. The crude products, which were generally suitable for use after drying in a vacuum at 110 °C, were purified by a single recrystallisation.

1-(2-Hydroxyethyl)-4-{4,5,6,7-tetrahydro-1-[1-(2-hydroxyethyl)-pyridin-4(1*H*)-ylidene]-1*H*-inden-3-yl}pyridinium iodide, 29a. From cyclohexane-1,2-dione, green-black needles (MeOH) (3.50 g, 71%), mp 223–225 °C (Found: $M(-I)^+$ *m/z* 363.20557; $C_{23}H_{27}IN_2O_2$ requires $M(-I)^+$ *m/z* 363.20671; Δ = 3.1 ppm). λ_{max} 504 (H_2O); 534 (methanol) $\log_{10}\varepsilon$ 4.84; 528 (acetonitrile); 530 (DMSO) $\log_{10}\varepsilon$ 4.82; 534 (acetone); 542 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.10 (d, *J* 7.1 Hz, 4H), 7.61 (d, *J* 7.1 Hz, 4H), 7.53 (s, 1H), 5.13 (t, *J* 4.9 Hz, 2H, -CH_2O*H*), 4.20 (t, *J* 4.7 Hz, 4H, -NCH_2), 3.75–3.78 (m, 4H, -CH_2OH), 2.73 (s, 4H), 1.73 (s, 4H). ^{13}C NMR (d_6-DMSO) δ 151.0 (C_Q), 141.7 (CH), 127.6 (C_Q), 122.8 (C_Q), 120.5 (CH), 118.4 (CH), 60.5 (CH_2), 59.9 (CH_2), 27.1 (CH_2), 23.7 (CH_2).

1-(2-Hydroxyethyl)-4-{3-[1-(2-hydroxyethyl)pyridin-4(1*H*)-ylidene]-4,5-diphenylcyclopenta-1,4-dien-1-yl}pyridinium iodide, 29b. From benzil, bronze microcrystals (MeOH) (2.23 g, 38%), mp 281–289 °C (partial) (Found: C, 62.03; H, 5.03; N, 4.69. $C_{31}H_{29}IN_2O_2\cdot\frac{1}{2}H_2O$ requires C, 62.32; H, 5.06; N, 4.68%) (Found: $M(-I)^+$ *m/z* 461.22131; $C_{31}H_{29}IN_2O_2$ requires $M(-I)^+$ *m/z* 461.22236; Δ = 2.3 ppm). λ_{max} 484 (H_2O); 516 (methanol) $\log_{10}\varepsilon$ 4.85; 508 (acetonitrile); 510 (DMSO) $\log_{10}\varepsilon$ 4.86; 512 (5% aqueous acetone); 520 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.06 (d, *J* 7.0 Hz, 4H), 7.06–7.23 (m, 14H), 5.10 (t, *J* 5.0 Hz, 2H, -CH_2O*H*), 4.15 (t, *J* 4.60 Hz, 4H, -NCH_2), 3.70–3.75 (m, 4H, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 152.4 (C_Q), 141.8 (CH), 139.4 (C_Q), 132.0 (C_Q), 130.9 (CH), 128.3 (CH), 126.2 (CH), 122.3 (C_Q), 120.8 (CH), 119.0 (CH), 60.2 (2 × CH_2).

1-(2-Hydroxyethyl)-4-{3-[1-(2-hydroxyethyl)pyridin-4(1*H*)-ylidene]-4,5-bis(3-nitrophenyl)cyclopenta-1,4-dien-1-yl}pyridinium iodide, 29c. From 3,3′-dinitrobenzil, orange-brown microplates (H_2O–MeOH; 1 : 1) (4.27 g, 63%), mp > 300 °C (Found: C, 53.76; H, 4.06; N, 8.15. $C_{31}H_{27}IN_4O_6\cdot\frac{1}{2}H_2O$ requires C, 54.15; H, 4.10; N, 8.15%) (Found: $M(-I)^+$ *m/z* 551.19196; $C_{31}H_{27}IN_4O_6$ requires $M(-I)^+$ *m/z* 551.19251; Δ = 1.0 ppm). λ_{max} 472 (H_2O); 496 (methanol) $\log_{10}\varepsilon$ 4.85; 492 (acetonitrile); 494 (DMSO) $\log_{10}\varepsilon$ 4.87; 496 (acetone); 504 (pyridine). ^{1}H NMR (d_6-DMSO) δ 8.18 (d, *J* 6.8 Hz, 4H), 8.02–8.04 (m, 2H), 7.84 (s, 2H), 7.69 (s, 1H), 7.49–7.53 (m, 4H), 7.33 (d, *J* 6.8 Hz, 4H), 5.13 (br s, 2H, -CH_2O*H*), 4.22 (br s, 4H, -NCH_2), 3.74 (br s, 4H, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 152.3 (C_Q), 147.8 (C_Q), 142.4 (CH), 140.6 (C_Q), 137.8 (CH), 130.0 (CH), 129.6 (C_Q), 125.1 (CH), 121.8 (C_Q), 121.3 (2 × CH), 119.8 (CH), 60.6 (CH_2), 60.3 (CH_2).

1-(2-Hydroxyethyl)-4-{1-[1-(2-hydroxyethyl)pyridin-4(1*H*)-ylidene]-9*H*-cyclopenta[*l*]phenanthren-11-yl}pyridinium iodide, 29d. From 9,10-phenanthraquinone, bronze microcrystals (H_2O–*i*-PrOH; 1 : 1) (1.81 g, 31%), mp > 300 °C (Found: C, 61.07; H, 4.54; N, 4.63. $C_{31}H_{27}IN_2O_2 \cdot H_2O$ requires C, 61.60; H, 4.84; N, 4.63%). No parent ion was observed for this compound; instead an ion corresponding to $C_{31}H_{28}IN_2O_3$ was observed. λ_{max} 530 (H_2O); 554 (methanol) $\log_{10}\varepsilon$ 4.96; 562 (acetonitrile); 564 (DMSO) $\log_{10}\varepsilon$ 4.95; 566 (acetone); 576 (pyridine). ^{1}H NMR (d_6-DMSO) 9.56 (s, 1H), 8.20 (d, *J* 5.8 Hz, 2H), 8.15 (d, *J* 7.5 Hz, 4H), 7.95 (d, *J* 6.2 Hz, 2H), 7.42 (apparent t, *J* 7.3 Hz, 2H), 7.21 (apparent t, *J* 7.2 Hz, 2H), 7.01 (d, *J* 7.3 Hz, 2H), 6.74 (br s, 2H), 5.10 (br s, 1H, -CH_2OH), 5.00 (br s, 1H, -CH_2OH), 4.21 (br s, 2H, -NCH_2), 4.00 (br s, 2H, -NCH_2), 3.76 (br s, 2H, -CH_2OH), 3.62 (br s, 2H, -CH_2OH). ^{13}C NMR (d_6-DMSO) δ 152.1 (CH), 147.3 (C_Q), 146.9 (C_Q), 145.8 (C_Q), 142.1 (CH), 141.9 (CH), 128.1 (CH), 123.0 (CH), 121.2 (CH), 120.8 (C_Q), 116.5 (C_Q), 116.3 (CH), 112.0 (C_Q), 60.6 (CH_2), 60.3 (2 × CH_2), 60.1 (CH_2).

Polymer from reaction of tolylene 2,4-diisocyanate and 1-(2-hydroxyethyl)-4-{3-[1-(2-hydroxyethyl)pyridin-4(1*H*)-ylidene]-4,5-bis(3-nitrophenyl)cyclopenta-1,4-dien-1-yl}pyridinium iodide

To a stirred solution of dry **29c** (3.87 g, 5.71 mmol) in DMSO (15 mL) at 80 °C and under a nitrogen atmosphere was added dropwise toluene-2,4-diisocyanate (993 mg, 820 μL, 5.71 mmol). The mixture was then stirred at 80 °C for a further 16 h, cooled and the viscous liquid filtered through a plug of glass wool into a stirred volume of methanol (150 mL). The precipitate was collected by filtration and washed thoroughly with volumes of hot methanol, water and then methanol again to afford a brown powder (3.29 g). This was dissolved in a minimum volume of DMSO–cyclohexanone (1 : 1) and filtered through a glass frit into a stirred volume of methanol (300 mL) whereupon the solid rapidly reprecipitated. After collecting the solids, the dissolution–precipitation procedure was repeated and the final product collected by filtration, washed with 100 mL portions of boiling water, then boiling methanol, and dried in vacuum at 100 °C to give a chocolate-brown powder (1.77 g, 37%) (Found: C, 52.62; H, 3.92; N, 9.56; I 16.65. $C_{39}H_{33}IN_6O_8$ requires C, 55.72; H, 3.96; N, 10.00; I 15.10%). λ_{max} 494 (DMSO).

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