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Author/s:

Franzese, S;Saker Neto, N;Wong, WWH

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# Extended Reichardt's Dye—Synthesis and Solvatochromic Properties

Stephen Franzese,<sup>[a]</sup> Nicolau Saker Neto,<sup>[a]</sup> and Wallace W. H. Wong<sup>\*[a]</sup>

Three new pyridinium-phenolate dyes based on the benchmark solvatochromic dye Betaine 30 were synthesised. The dyes contained phenylene spacers between the donor and acceptor groups. Their UV-Vis absorption spectra were measured, with the dyes showing strong negative solvatochromic behaviour comparable to that of Betaine 30. These results stood in contrast to the behaviour of the  $\pi$ -extended dye Betaine 21, originally reported in 1963. This dye was synthesised and found

to be significantly more solvatochromic than previously reported but prone to degrade. All  $\pi$ -extended dyes synthesised were found to be unstable in certain solvents. Although the increased distance between donor and acceptor did not enhance solvatochromism to the extent predicted, it was still determined that the reduced planarity caused by a phenylene spacer is not as detrimental as believed.

## Introduction

The electronic absorption spectra of compounds are subject to changes in position, intensity and shape due to changes in the surrounding medium.<sup>[1]</sup> This behaviour is termed solvatochromism. A compound can be either negatively solvatochromic (where the species absorbs at shorter wavelength as solvent polarity increases) or positively solvatochromic (where the reverse occurs).<sup>[2]</sup> This shift is caused by differential solvation of the ground and excited states of the solvatochromic molecule (Figure 1).<sup>[2,3]</sup> In negative solvatochromism, the ground state of the molecule is better stabilised by a more polar solvent, with only a relatively small stabilisation of its excited state, causing the energy required to reach the excited state to be larger compared to when dissolved in a non-polar solvent. In the case of positive solvatochromism, it is the excited state which is better stabilised in polar solvents, leading to the opposite effect.<sup>[1,2]</sup>

In 1963, Reichardt and co-workers synthesised **1B** (Betaine 30, also known as Reichardt's Dye, Figure 2),<sup>[4]</sup> one of the most solvatochromic dyes known.<sup>[5,6]</sup> **1B** has a large permanent dipole moment and a large conjugated  $\pi$  system that can be polarised.<sup>[3]</sup> As a result, it is negatively solvatochromic.<sup>[7]</sup> The large red-shift in the wavelength of its absorption maximum – increasing from polar solvents (438 nm in 1,1,1,3,3,3-hexafluoro-2-propanol) to non-polar solvents (881 nm in  $\text{CCl}_4$ )<sup>[8]</sup> – has

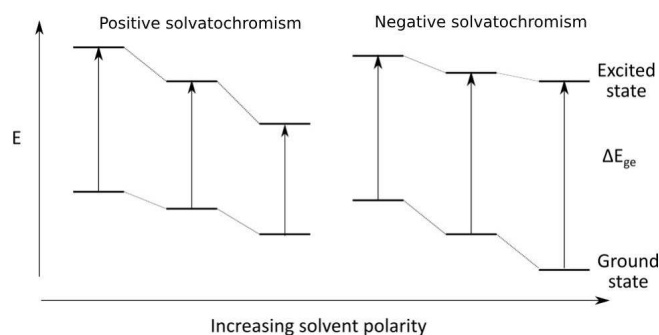


Figure 1. Schematic diagram of solvent effects on the electronic transition energy of dipolar species in polar medium (adapted from Nigam and Rutan).

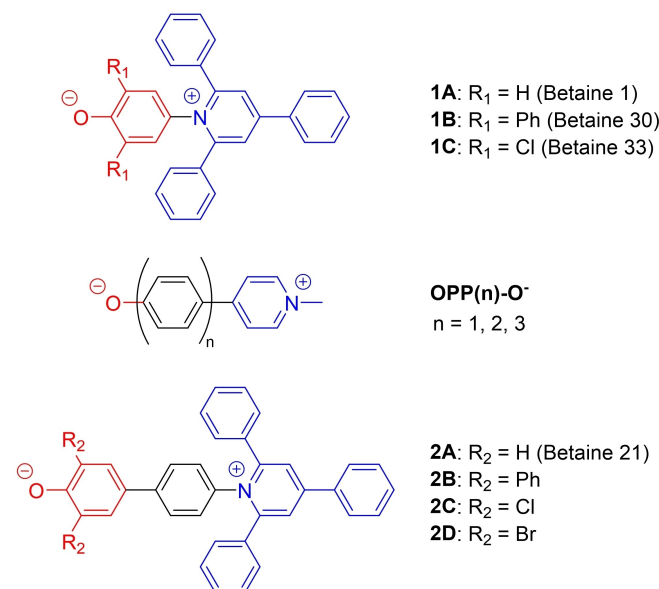


Figure 2. Structures of pyridinium phenolate dyes.

enabled the dye to act as an effective polarity indicator. It is the basis of the widely-used  $E_T(30)$  polarity scale, where  $E_T$  stands

[a] S. Franzese, Dr. N. Saker Neto, Dr. W. W. H. Wong  
 ARC Centre of Excellence in Exciton Science, School of Chemistry  
 Bio21 Institute, University of Melbourne  
 Parkville, Victoria 3010, Australia  
 E-mail: wwhwong@unimelb.edu.au

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for electronic transition energy.<sup>[9]</sup> It is calculated by taking the frequency of the maximum of the dye's longest wavelength absorption band which is then used to determine the energy associated with that transition following Equation 1.<sup>[10]</sup>

$$E_T \text{ (kcal mol}^{-1}\text{)} = hcN_A\tilde{\nu}_{max} \text{ (cm}^{-1}\text{)} \quad (1)$$

In addition, **1B** is noted for the simplicity of its synthesis,<sup>[11]</sup> its solubility in a wide range of solvents<sup>[11]</sup> and the ease with which it can be used to determine a solvent's polarity by eye.<sup>[5]</sup>

**1B** is an example of a pyridinium phenolate dye which is a subset of the broader category of donor-acceptor (D-A) dyes. D-A dyes contain an electron-rich donor unit connected to an electron-poor acceptor unit by a  $\pi$ -conjugated bridge, typically an aromatic spacer (phenylene, phenylenevinylene, thienylene units, etc.).<sup>[6]</sup> In the case of **1B**, the donor is the phenolate (Figure 2, highlighted in red) and the acceptor is the pyridinium (shown in blue).<sup>[3]</sup> Both the donor-bridge-acceptor topology and the substituents' donor/acceptor strengths can affect the energetics of these molecules, with the latter having a particularly strong influence.<sup>[6]</sup> Another type of pyridinium phenolate dyes are oligo-*para*-phenylenes (OPPs).<sup>[12]</sup> Our group has synthesised and examined the properties of pyridinium phenolates with OPP bridges (Figure 2).<sup>[6]</sup> It was found that by increasing the distance between the donor and acceptor using phenylene spacers, the dye could be made more sensitive to polarity changes, with **OPP(2)-O<sup>-</sup>**'s solvatochromism being comparable to that of **1B**.<sup>[6]</sup> However, increasing the bridge did not appear to improve the solvatochromism of **OPP(3)-O<sup>-</sup>**, which was attributed to a loss of conjugation caused by the molecule twisting.<sup>[6]</sup> We recently expanded this series to include fluorene and ethylene  $\pi$ -bridges which showed increased the solvatochromic effect due to increased  $\pi$ -conjugation.<sup>[13]</sup>

While many derivatives of **1B** have been synthesised<sup>[1,3,14,15]</sup> – adding solubilising groups, varying the substituents ortho to the phenolate (see **1C**, Figure 2), replacing the phenolate with other electron-donating groups – there has been little exploration on effect of  $\pi$ -extension. Given the aforementioned results for the  $\pi$ -extended OPP dye series, we decided to investigate the effect an addition of a phenylene spacer would have on **1B**. We aimed to synthesise **2B** (Figure 2) which has a phenylene bridge between the donor and acceptor groups. We also planned to explore the effect of different substituents ortho to the phenolate by synthesising derivatives of **2B** with chloro and bromo groups in place of the flanking phenyl groups (**2C** and **2D**, respectively, Figure 2). **1C** (Betaine 33, figure 2) is a derivative of **1B** with chloro substituents ortho to the phenolate. It is used to determine  $E_T(30)$  values of more acidic solvents as its  $pK_a$  is lower than that of **1B**, and its  $E_T$  values can be correlated to the  $E_T(30)$  scale.<sup>[3,14]</sup> There is no previously reported derivative of **1B** with bromo substituents.

Reichardt et al. in their 1963 paper reported the synthesis of **2A** (Betaine 21, Figure 2) which contains a phenylene bridge but differs from **2B** in that it lacks the phenyl groups ortho to the phenolate.<sup>[4]</sup> They noted its solvatochromism was poor, shifting from 422.5 nm in methanol to 452 nm in chloroform.<sup>[4]</sup> They attributed this observation to the higher energy require-

ment of the electron transfer from the phenolate anion to the pyridinium cation due to the non-planar nature of the biphenyl moiety.<sup>[4]</sup> Nonetheless, **OPP(3)-O<sup>-</sup>**, which is longer than **2A** and contains more biphenyl twisting, still showed notable solvatochromism,<sup>[6]</sup> suggesting this lack of planarity may not affect solvatochromism as significantly as suggested in Reichardt's report.

## Results and Discussion

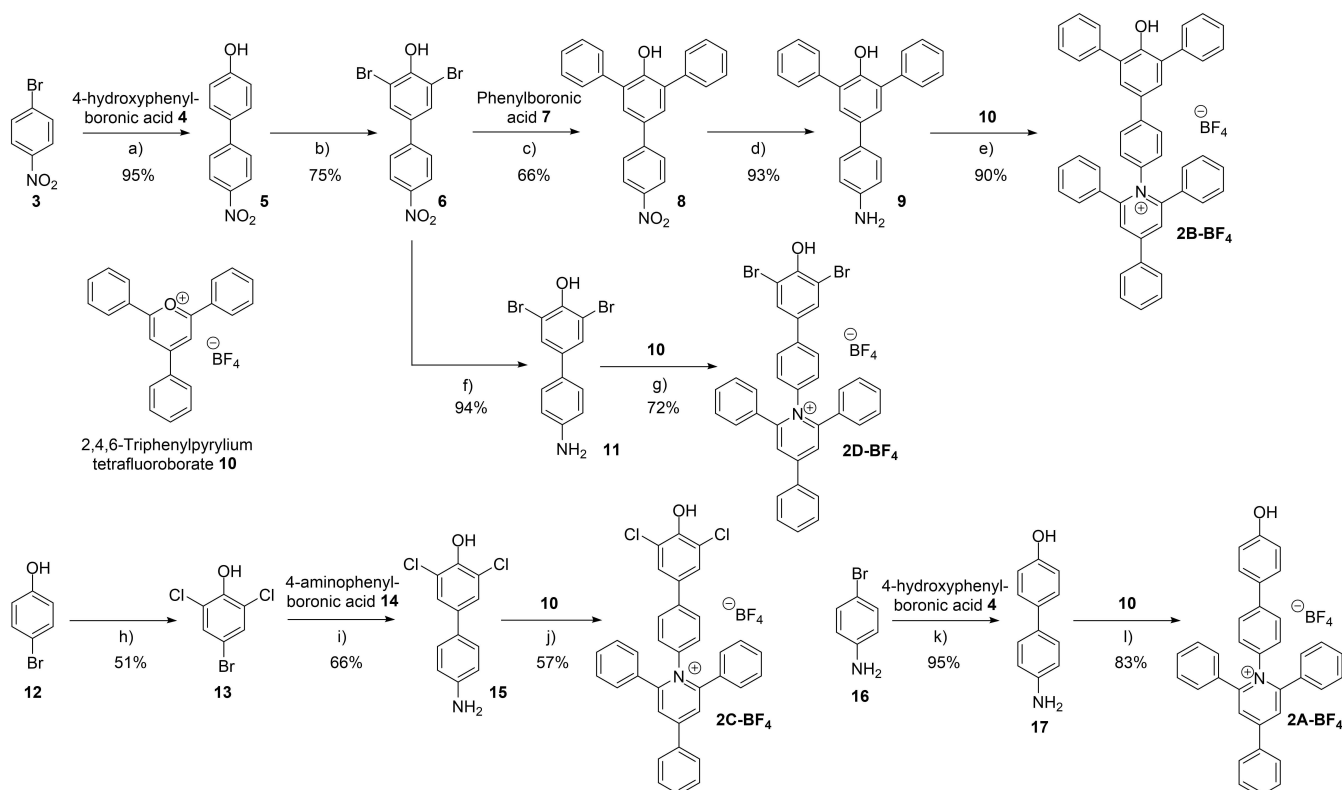
### Synthesis

Compounds **2A**, **2B**, **2C** and **2D** were synthesised following the procedures outlined in Scheme 1 below. All steps were achieved in good to excellent yields producing products in 100 mg to gram scale. Some of the key reactions and optimizations are discussed in the following paragraphs.

The Suzuki-Miyaura coupling of 4-bromonitrobenzene **3** and 4-hydroxyphenylboronic acid **4** was initially performed using  $K_3PO_4$  (2 eq.) as the base, which resulted in unsatisfactory yields. This was believed to be due to the base deprotonating the phenol with the resultant negative charge on the phenolate delocalising into the empty p orbital of the boron, suppressing its ability to transmetalate. KF (4 eq.), a weaker base, was tested and an excellent isolated yield of 95 % was achieved.

For **2C**, the chlorination of the biphenyl **5** was initially attempted, but yielded a mixture of mono-, di- and tri-chlorinated products. Instead, 4-bromophenol **12** was chlorinated to give 4-bromo-2,6-dichlorophenol **13** in 51 % yield. Suzuki-Miyaura cross coupling was performed using  $tBu_3P$  as the ligand and  $K_3PO_4$  as the base to produce aniline **15**. The coupling was selective and occurred first on the bromo group. Some further coupling on the chloro groups were observed, but the desired product was isolated by column chromatography in 66 % yield.

Originally, we planned to isolate the zwitterionic form of the dyes by treating the  $BF_4^-$  salts with aqueous triethylamine and collecting the precipitated product as has been done with **1B** previously.<sup>[11]</sup> Although the zwitterions are sufficiently soluble for spectroscopy in most solvents, they tend to precipitate even at low concentrations (**2B** precipitates in methanol, DMSO and acetonitrile at 6.0 mM, **2D** precipitates in pyridine at 0.3 mM). Decomposition of the dyes were also observed in certain solvents, making it difficult to purify. We will discuss the decomposition issue in more detail later in this report. To resolve this, excess 2,6,4-triphenylpyrylium tetrafluoroborate **10** was used in the condensation reaction with the various aniline intermediates. The resulting  $BF_4^-$  salts were isolated by filtration. **2A-BF<sub>4</sub>** was purified by washing with ethanol while **2B-BF<sub>4</sub>** and **2D-BF<sub>4</sub>** were washed with both ethanol and isopropyl alcohol. **2C** was washed with isopropyl alcohol followed by a small amount of methanol.



**Scheme 1.** Syntheses of **2B-BF<sub>4</sub>**, **2C-BF<sub>4</sub>**, **2D-BF<sub>4</sub>** and **2A-BF<sub>4</sub>**: a) Pd<sub>2</sub>dba<sub>3</sub> (2.5 mol%), tBu<sub>3</sub>P-HBF<sub>4</sub> (6.0 mol%), KF<sub>(aq)</sub> (2 M, 4 eq.), THF, 65 °C, 20 h; b) TsOH·H<sub>2</sub>O (2.0 eq.), NBS (3.0 eq.), MeOH, r.t., 20 h; c) Pd<sub>2</sub>dba<sub>3</sub> (5.0 mol%), tBu<sub>3</sub>P-HBF<sub>4</sub> (12.0 mol%), KF<sub>(aq)</sub> (2 M, 8.0 eq.), THF, 65 °C, 20 h; d) SnCl<sub>2</sub>·H<sub>2</sub>O (6.0 eq.), 32% HCl<sub>(aq)</sub> (~7 eq.), EtOH, 80 °C, 46 h; e) EtOH, 90 °C, 20 h; f) SnCl<sub>2</sub>·H<sub>2</sub>O (6.0 eq.), 32% HCl<sub>(aq)</sub> (~7 eq.), EtOH, 90 °C, 26 h; g) EtOH, 90 °C, 21 h; h) NCS (2.5 eq.), TsOH·H<sub>2</sub>O (2 eq.), MeOH, r.t., 20 h; i) Pd<sub>2</sub>dba<sub>3</sub> (2.5 mol%), tBu<sub>3</sub>P-HBF<sub>4</sub> (6.0 mol%), K<sub>3</sub>PO<sub>4(aq)</sub> (2 M, 2 eq.), THF, 65 °C, 24 h; j) EtOH, 90 °C, 24 h; k) Pd<sub>2</sub>dba<sub>3</sub> (2.5 mol%), tBu<sub>3</sub>P-HBF<sub>4</sub> (6.0 mol%), KF<sub>(aq)</sub> (2 M, 4 eq.), THF, 65 °C, 24 h; l) EtOH, 90 °C, 3 h.

## UV-Vis Spectroscopy

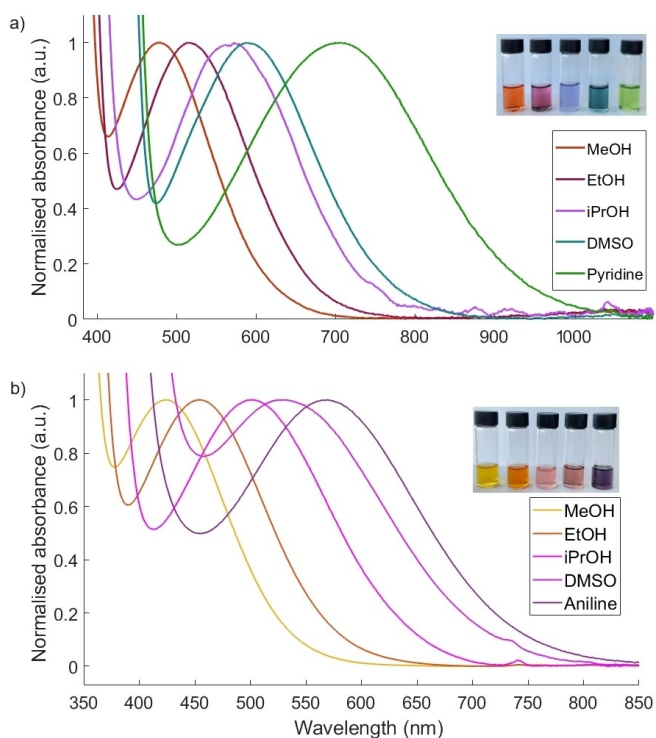
When preparing samples for spectroscopy, the BF<sub>4</sub><sup>-</sup> salts were suspended in the desired solvent and deprotonated *in situ* by adding *N,N,N',N'*-tetramethylguanidine (TMG) as a base. TMG was chosen for its miscibility with organic solvents and as it is a strong, non-aqueous base. Blanks containing TMG did not show any absorbance peaks in the range analysed in this work. By this method, the dye could dissolve sufficiently for spectroscopy in more solvents than had been accessible using the zwitterion, noting that precipitation was still observed in some solvents over time. In certain solvents, such as isopropyl alcohol and long-chain alcohols, dissolution of the dye took a short amount of time (approximately a minute) before the solution became visibly coloured. A result of this method is that the values obtained deviate slightly from those obtained in the pure solvents. Measurements using the pure zwitterion and with TMG added (Table S1) showed slight variations in certain solvents compared to those using the protonated salt. Absorptivity increased in all solvents when TMG was added and some solvents (e.g. sulfolane, trimethyl phosphate) did not show absorption bands without TMG.

The molar absorption coefficients of the dyes (using 5 mmol dye and 5 μL of TMG dissolved in methanol to get a volume of 50 mL) were calculated to be  $2.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ,

$3.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for **2B**, **2C** and **2D**, respectively. Using the same method, the absorption coefficient of **1B** was determined to be  $2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ , similar to that reported in the literature<sup>[4]</sup> ( $3510 \text{ M}^{-1} \text{ cm}^{-1}$ ), although this was measured without TMG.

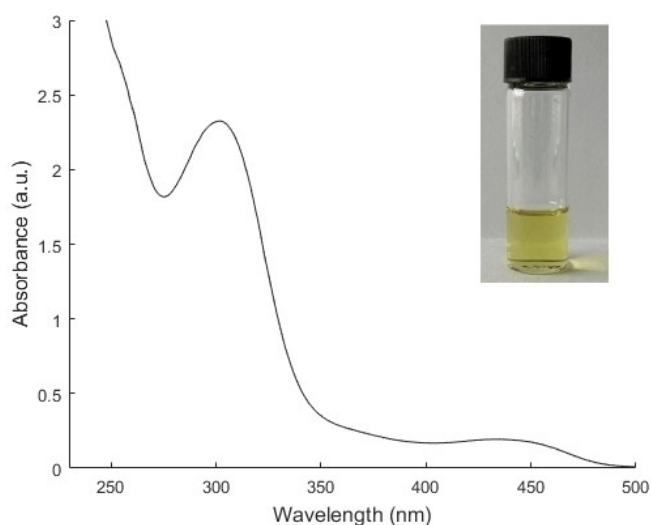
The prepared dye solutions all show a charge-transfer (CT) peak at long wavelengths and a more intense peak at shorter wavelengths (Figure S1). The normalised absorption spectra, normalised at the CT peak, for **2B** in a selected set of solvents are shown in Figure 3. The CT peak moved to longer wavelengths with decreasing solvent polarity, becoming broader and less intense. The spectra of **2C** and **2D** (Figure S2) were almost identical, absorbing at very similar wavelengths for most solvents. The wavelength maxima of the solvatochromic absorbance bands of the dyes were measured in 20 different solvents and the results are reported in Table 1.

The three new dyes **2B**, **2C**, and **2D** all showed pronounced negative solvatochromism, contrary to the results reported by Reichardt et al. for **2A**.<sup>[4]</sup> However, these extended dyes showed a tendency to degrade in some solvents. This contrasts with Reichardt's dye **1B** which shows good stability.<sup>[1]</sup> Solutions of the three dyes in a range of less polar aprotic solvents (THF, diethyl ether, ethyl acetate, chloroform and DCM, along with the relatively polar acetone and nitromethane) turn irreversibly yellow with the absorption spectra showing a non-solvatochromic



**Figure 3.** a) Normalised absorbance spectra of **2B**, (inset) **2B** in solution (left to right: methanol, ethanol, isopropyl alcohol, DMSO, pyridine); b) Normalised absorbance spectra of **2A**, (inset) **2A** in solution (left to right: methanol, ethanol, isopropyl alcohol, DMSO, aniline).

mic absorption peak at 430–450 nm (Figure 4). The electrospray mass spectrometry analysis of **2B** dissolved in THF in air showed a mass peak corresponding to the protonated parent ion with addition of an oxygen atom (see Figures S4 and S5). When the dye was kept under an inert atmosphere and dissolved in degassed THF, the degradation was reduced, likely only occurring when the vial was opened to air to prepare the sample for mass spectrometry. Other unidentified degradation



**Figure 4.** Absorbance spectrum of **2B** in THF, (inset) degraded **2B** in THF.

Solvent	<b>1A</b> <sup>[a]</sup>	<b>2A</b>	<b>1B</b>	<b>2B</b>	<b>1C</b> <sup>[b]</sup>	<b>2C</b>	<b>2D</b>
Ethylene glycol	437	–	505	469	–	410	413
Formamide	–	–	512	476	–	421	424
Methanol	442	425	515	478	442	414	420
Ethanol	467	454	552	515	470	450	449
1-Propanol	477	–	568	535	–	458	462
Benzyl alcohol	–	–	548	553	–	472	*
1-Butanol	484	–	575	551	–	466	472
1-Pentanol	–	–	579	555	–	469	473
Isopropyl alcohol	501	501	590	573	–	486	485
1-Octanol	–	–	590	560	–	477	485
Propylene carbonate	–	–	607	548	–	468	468
Acetonitrile	–	*	625	563	516	485	484
DMSO	–	532	633	588	530	495	492
Aniline	–	569	643	641	–	535	535
Sulfolane	–	–	618	552	–	476	479
Trimethyl phosphate	–	–	650	588	–	497	494
DMF	–	*	660	620	–	511	509
DMAc	–	*	669	627	–	521	516
Benzonitrile	–	–	652	593	–	507	513
Pyridine	–	*	702	705	586	566	538
$E_{T(\text{MeOH})}^-$ $E_{T(\text{Pyridine})}^-$ (kcal mol <sup>-1</sup> )	–	–	14.8	19.3	15.9	18.5	14.9

[a] Data obtained from [4]; [b] Data obtained from [14]; – Not reported/measured; \* No CT band observed due to degradation.

products formed in different solvents (see Figure S7). The <sup>1</sup>H NMR spectrum of **2B** after degradation in THF (Figure S6) suggests multiple degradation products. The degradation generally occurs rapidly; spectra with clear, solvatochromic CT peaks could not be obtained in these solvents.

The dyes also cannot be used in acidic solvents using the method outlined above as the TMG will react with the solvent and the dyes are easily reprotonated. The solutions of protonated dyes are also yellow in colour and so it can at times be difficult to distinguish degradation from reprotonation. This observed dye degradation offered a potential explanation for the poor solvatochromic behaviour of **2A** reported by Reichardt et al. In that work, the absorption wavelengths of **2A** were only reported for methanol and chloroform.<sup>[4]</sup> Since **2B** degraded in chloroform, showing a peak at ~450 nm, it was possible that the poor solvatochromism observed was simply degradation. To confirm, **2A** was synthesised (Scheme 1) to measure its absorption spectra in a broader range of solvents. As can be seen by both its colour changes and absorbance band maxima (Figure 3 and Table 1), **2A** was found to be significantly more solvatochromic than previously reported. However, it is even

less stable in solution than **2B**, degrading in acetonitrile, DMF and pyridine, giving shoulder-like peaks in the range of 400–500 nm. As with the other dyes, the solutions of degraded **2A** are yellow, incidentally the same colour it is in methanol. Like **2B**, ESI-MS spectrum showed a peak corresponding to addition of an oxygen atom (Figure S8).

The ground state of these zwitterionic dyes is more stable in polar solvents compared to non-polar solvents which is the underlying reason for the negative solvatochromic effect, as discussed in the introduction. We hypothesise that the decrease stability in less polar solvents is also the reason for the reduced chemical stability. With **1B** this effect is likely less noticeable as the steric bulk of the flanking phenyl rings hinders reaction, while with **2B** the phenyl bridge is more open to attack. The behaviour of **2A**, degrading more easily than **2B**, lends credence to this theory as it is less protected than **2B**.

In the following section, we will discuss the electronic transition energies of the extended dyes compared to Betaine 30. We will attempt to rationalise the differences in relation to the  $\pi$ -extension and the electronic effects of the substituents.

### Comparison of Electronic Transition Energies

Electronic transition energies ( $E_T$ , kcal mol<sup>-1</sup>) were estimated for the dyes using the most red-shifted absorbance maxima ( $E_T = 28591/\lambda_{max}$  (nm)). Using  $E_T(30)$  values reported in the literature,<sup>[1]</sup> the  $E_T$  values of **2B** showed poor correlation with the  $E_T(30)$  scale for non-hydrogen bond donating (non-HBD) solvents, particularly with benzonitrile and sulfolane. To account for this, **1B** was thus prepared following the literature<sup>[11]</sup> and this sample – dissolved in its zwitterionic form, but with TMG added to avoid reprotonation – gave values that better fit the data obtained for the synthesised dyes.

Smaller  $E_T$  values result from smaller energy gaps between the ground and excited state. All the dyes synthesised, including **2A**, gave  $E_T$  values greater than **1B** for most solvents. This is attributed to the reduced conjugation introduced by the bridge's propensity to twist. This reduced conjugation would also cause the charges at the donor and acceptor groups to be more localised, thereby increasing the ground state dipole compared to **1B**. Since dipole moments increase proportionally with distance,<sup>[16]</sup> the dipole moments of the extended dyes are also likely to be larger than that of **1B** due to the greater separation between the two charges.

For **2C** and **2D**, the addition of the electronegative chlorine atoms to the donor reduces its electron density. This makes it a weaker donor and thereby lowers the energy of the highest unoccupied molecular orbital – and thus the ground state energy – of the dye which in turn causes a larger energy gap between the ground and excited states. Hence the dyes **2C** and **2D** absorb at shorter wavelengths than **2B**.

While collecting the UV-vis absorbance spectra of the dyes, it was noted that the peak in DMSO was at a lower wavelength than expected based on **1B**'s behaviour. It was initially assumed to be caused by traces of water in the solvent, but drying had no effect. As the spectra were measured in more solvents, the

trend was found to continue, with the overall order of polarity differing slightly from that given by the  $E_T(30)$  scale: aniline ( $E_T(30) = 44.3$ ) appears to be less polar than DMF ( $E_T(30) = 43.2$ ), and isopropyl alcohol ( $E_T(30) = 48.4$ ) less polar than acetonitrile ( $E_T(30) = 45.6$ ). That is, for solvents with similar  $E_T(30)$  values, if one were hydrogen-bond donating (HBD) and the other non-HBD, the HBD solvent would give a lower  $E_T$  value. Using the dye as a pure zwitterion did not change this effect, suggesting it is not the result of the  $BF_4^-$  or TMG in solution.

By plotting the calculated  $E_T$  values of the dyes and comparing them to those determined from **1B**, one can construct a line of best fit for each dye (Figure 5). The slopes of these lines offer an indication of the separation between the values with respect to the  $E_T(30)$  scale: **1B** will have a gradient of unity by definition and dyes with a slope greater than 1 have a larger separation between their  $E_T$  values. The calculated slopes are also shown in Figure 5.

The slopes for **2B**, **2C** and **2D** are 1.09, 1.04 and 0.947, respectively. This suggests that they have solvatochromism comparable to that of **1B**. **2A** gives a slope of 1.47, suggesting greater sensitivity to changes in solvent polarity than **1B**, although this value was obtained using a much smaller set of solvents, most of which were alcohols. Prompted by the observed poor agreement in the order of  $E_T$  values for HBD and non-HBD solvents, lines of best fit were constructed for the two categories separately. The correlation between  $E_T$  and  $E_T(30)$  was found to be stronger when comparing only HBD or non-HBD solvents (Figure S3); for all dyes these slopes are greater than 1 and larger than those obtained using the full data set (Table S2).

For **2B** and **2C**, the sensitivity to polarity changes appears to be greater in non-HBD solvents than HBD solvents, particularly in the case of **2B** (it gives a slope of 1.79 for non-HBD solvents compared to 1.34 for HBD solvents). For **2D** the two slopes are approximately the same, with the lines only differing by their intercepts. Such differential behaviour has been previously observed in derivatives of **1B** and other D–A dyes.<sup>[4,10,15,17,18]</sup> It is typically attributed to differences in the dyes' abilities to form

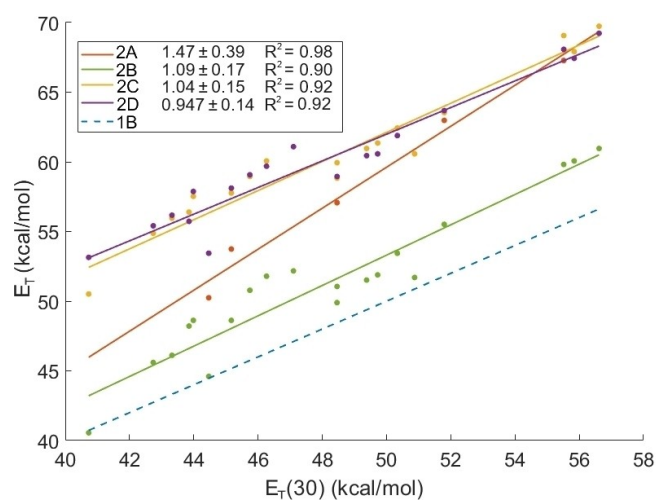


Figure 5. Transition energies of **1B**, **2A**, **2B**, **2C** and **2D** versus the empirical parameter of polarity  $E_T(30)$  with lines of best fit and slopes.

hydrogen bonds compared to the **1B** reference, which is dependent on the donor phenolate moiety.<sup>[4,15]</sup> In this case, the more localised charge of the phenolate increases its ability to form hydrogen bonds. **2D** has the steric bulk of the electron-withdrawing bromo substituents that could both hinder hydrogen bonding and reduce the phenolate's charge density compared to **2B**. This may account for why it is similarly sensitive to HBD and non-HBD solvents. The poor solubility and tendency to degrade of these  $\pi$ -extended dyes makes it difficult to investigate their behaviour and confirm these theories.

A longer bridge allows for greater twisting, decreasing conjugation. This, along with the increased distance, produces a larger dipole and increases the sensitivity of the ground state's energy to polarity changes, but it also inhibits the transfer of electrons which can negate this effect. Nonetheless, even if increasing the length between donor and acceptor reduces conjugation and does not significantly enhance solvatochromism, it is still evident that the decreased planarity is not as detrimental as previously believed. Although the  $\pi$ -extended D–A dyes still show impressive solvatochromic behaviour, it is expected that, as with **OPP(3)-O<sup>-</sup>**, increasing the bridge length further would lead to insufficient orbital overlap and diminished solvatochromism.

## Conclusions

Three new pyridinium-phenolate dyes with phenylene spacers between the donor and acceptor groups were synthesised and their UV-Vis absorption spectra measured. All three dyes show strong negative solvatochromic behaviour comparable to that of the benchmark dye **1B**. These results stood in contrast to the reported behaviour of the  $\pi$ -extended dye **2A**. **2A** was synthesised and found to be significantly more solvatochromic than previously reported, with its alleged poor solvatochromism determined to be the result of degradation. All  $\pi$ -extended dyes synthesised were found to be unstable in certain solvents which was attributed to their bridge being less protected compared to **1B**.

Previous studies showed that **OPP(2)-O<sup>-</sup>** with a donor and acceptor separated by two phenylene spacers was the most solvatochromic of the OPP series.<sup>[6]</sup> Our group had planned to determine if this idea could be extended to **1B** and produce a significantly more solvatochromic dye. The results, however, showed that the magnitude of the absorbance maxima shifts was similar to that of **1B**, but with the range of values being higher in energy.

These higher energy values relative to **1B** suggest that these extended dyes are less conjugated. Our recent studies on the behaviour of the more conjugated OPP dyes with fluorene bridges showed improved solvatochromism compared to the phenylene analogues.<sup>[13]</sup> Given the solvatochromism of the  $\pi$ -extended betaine dyes reported in this paper, it is proposed that the sensitivity to solvent polarity could be increased by replacing the biphenyl bridge with a fluorene unit.

## Experimental

### Materials and Methods

Commercial reagents were used as received except in the case of aniline used for UV-vis absorption measurements which was purified by chromatography using basic Brockman I alumina (40–300  $\mu\text{m}$ , 60 Å). For air-sensitive reactions, standard Schlenk techniques were used. Solvents were sparged with dry nitrogen gas for 30 min prior to addition, and the systems were closed with a rubber septum or Teflon cap and maintained under a positive nitrogen pressure. Merck-Millipore silica gel Keisegel 60 was used for chromatographic purification via flash chromatography (40–63  $\mu\text{m}$ , 230–400 mesh) or dry column vacuum chromatography<sup>[19]</sup> (15–40  $\mu\text{m}$ , >400 mesh). Thin layer chromatography was performed on Merck-Millipore Silica gel 60G F<sub>254</sub> glass plates, and spots were revealed under 254 nm and 365 nm light from a mercury lamp. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on a 500 MHz Bruker spectrometer, and shifts were referenced to the NMR solvent signals. Mass spectra were obtained on a Thermo Exactive Plus Orbitrap ESI-MS spectrometer operating in positive or negative mode. UV-vis absorption spectra were obtained with an Agilent 8453 UV-visible spectrometer. Infrared absorption spectra were obtained with a Perkin-Elmer SpectrumOne ATR FT-IR spectrometer in the region of 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ .

### Synthesis Procedures

#### 4-Hydroxy-4'-Nitrobiphenyl 5

4-Bromonitrobenzene (2.00 g, 9.9 mmol, 1.0 eq.), 4-hydroxyphenylboronic acid (1.78 g, 13 mmol, 1.3 eq.), Pd<sub>2</sub>dba<sub>3</sub> (138 mg, 2.5 mol %) and <sup>t</sup>Bu<sub>3</sub>P-HBF<sub>4</sub> (181 mg, 6 mol %) were added to a flask followed by vacuum/N<sub>2</sub> cycles. The solids were dissolved in 30 mL of THF and to the solution 20 mL (100 mmol, 4 eq.) of 2 M aqueous KF was added. The solution was stirred at room temperature for 0.5 h and then stirred at 65 °C for 20 h. The water layer was removed and Mg<sub>2</sub>SO<sub>4</sub> was added. The solids were filtered off by a short silica plug and the product washed out with THF. 1 M NaOH(aq) was added to THF solution, causing precipitation of a red solid. This was filtered through a glass frit, washed with THF and small amount of water. The solid was collected from the filter by dissolution with methanol. The methanol solution was concentrated by rotary evaporation. 1 M HCl(aq) was added, and the solution diluted with water to approximately 10 times the volume. The yellow precipitate that formed was then filtered and washed with water. The product was collected with THF and the solvent was then evaporated, yielding 2.02 g (95 %) of a yellow solid.

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  6.90 (d,  $J$  = 7.3 Hz, 2H), 7.64 (d,  $J$  = 7.3 Hz, 2H), 7.86 (d,  $J$  = 7.5 Hz, 2H), 8.24 (d,  $J$  = 7.5 Hz, 2H), 9.89 (s, 1H).

<sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  158.7, 146.7, 145.7, 128.6, 128.3, 126.7, 124.1, 116.1.

ESI-HRMS:  $m/z$  [M–H]<sup>-</sup> calculated for C<sub>12</sub>H<sub>8</sub>NO<sub>3</sub>: 214.05097; found: 214.04980 (+5 ppm error).

#### 2,6-Dibromo-4-Hydroxy-4'-Nitrobiphenyl 6

Compound **5** (2.93 g, 14 mmol, 1.0 eq.) and *p*-toluenesulfonic acid (5.18 g, 27 mmol, 2.0 eq.) were dissolved in 20 mL of methanol and placed in an ice bath. 6.06 g (34 mmol, 2.5 eq.) of *N*-bromosuccinimide was slowly added with stirring. The reaction was then left stirring at room temperature for 20 h. A yellow precipitate

formed. 30 mL of water was added to further precipitate the product, which was then collected by vacuum filtration, washed with water and then with a MeOH/water (1:1) mixture. The product was then recrystallised in hot ethyl acetate. After filtration, the product was dried over vacuum to yield 3.82 g (75%) of a pale orange solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  7.96 (d,  $J=7.4$  Hz, 2H), 8 (s, 2H), 8.24 (d,  $J=7.4$  Hz, 2H), 10.38 (br s, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  151.8, 146.7, 143.7, 132.0, 135.1, 127.7, 124.2, 112.7.

ESI-HRMS:  $m/z$   $[\text{M}-\text{H}]^-$  calculated for  $\text{C}_{12}\text{H}_6\text{Br}_2\text{NO}_3$ : 369.87199; found: 369.87146 (+1 ppm error).

#### 4-Hydroxy-2,6-Diphenyl-4'-Nitrophenyl 8

Compound **6** (1.30 g, 3.5 mmol, 1.0 eq.), phenylboronic acid (1.11 g, 9.1 mmol, 2.6 eq.),  $\text{Pd}_2\text{dba}_3$  (97.1 mg, 5 mol%) and  $^t\text{Bu}_3\text{P}\cdot\text{HBF}_4$  (127 mg, 12 mol%) were added to a flask followed by vacuum/ $\text{N}_2$  cycles. The solids were dissolved in 40 mL of THF and 7 mL (14 mmol, 4.0 eq.) of 2 M aqueous  $\text{K}_3\text{PO}_4$  was added to the solution. The solution was stirred at 65 °C for 22 h. The water layer was removed and  $\text{Mg}_2\text{SO}_4$  was added. The solids were filtered off by a short silica plug and the product washed out with THF. The solvent was evaporated, and the product was purified by redissolving it in hot DCM and precipitating it with petroleum spirits, yielding 846 mg (66%) of a fine, needle-like, yellow crystalline solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.59 (s, 1H), 7.74 (tt,  $J=7.4$ , 1.3 Hz, 2H), 7.53 (t,  $J=7.61$  Hz, 4H), 7.57 (s, 2H), 7.61 (dd,  $J=8.4$ , 1.3 Hz, 4H), 7.77 (d,  $J=8.9$  Hz, 2H), 8.28 (d,  $J=8.9$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 147.1, 146.8, 137.0, 131.33, 129.8, 129.4, 129.2, 129.0, 128.3, 127.3, 124.3.

ESI-HRMS:  $m/z$   $[\text{M}-\text{H}]^-$  calculated for  $\text{C}_{24}\text{H}_{16}\text{NO}_3$ : 366.11357; found: 366.11359 (−0.05 ppm error).

#### 4-Amino-4'-Hydroxy-2',6'-Diphenylbiphenyl 9

Compound **8** (800 mg, 2.2 mmol, 1.0 eq.) and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  (2.95 g, 13 mmol, 6 eq.) were dissolved in 25 mL of ethanol and stirred at 80 °C for 46 h. The solution was then neutralised with  $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  pH 7 buffer. A white precipitate formed. The suspension was washed thrice with DCM and the organic layers collected. The solvent was removed by rotary evaporation and the solid product was dried under high vacuum to yield 683 mg (93%) of a white, crystalline solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.69 (s, 2H), 5.41 (s, 1H), 6.75 (d,  $J=8.5$  Hz, 2H), 7.42 (tt,  $J=6.2$ , 1.6 Hz, 2H), 7.44 (d,  $J=8.6$  Hz, 2H), 7.48 (s, 2H), 7.51 (t,  $J=7.7$  Hz, 4H), 7.62 (dd,  $J=8.3$ , 1.3 Hz, 4H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 145.6, 137.9, 134.0, 131.1, 129.5, 129.1, 129.0, 128.1, 127.8, 127.8, 115.6.

ESI-HRMS:  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{20}\text{NO}$ : 338.15394; found: 338.15412 (−0.5 ppm error).

#### Compound 2B-BF<sub>4</sub>

Compound **9** (675 mg, 2.0 mmol, 1.0 eq.) and 2,4,6-triphenyl-pyrylium tetrafluoroborate (840 mg, 2.1 mmol, 1.1 eq.) were dissolved in 30 mL of ethanol. The solution was then heated to 80 °C and stirred for 19 h. The solvent was then removed by rotary evaporation. The product was washed with isopropyl alcohol and dried over vacuum to yield 1.29 g (90%) of a pale yellow solid.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.68 (s, 2H), 8.60 (s, 1H), 8.37 (d,  $J=7.3$  Hz, 2H), 7.68 (m, 3H), 7.60 (d,  $J=8.7$  Hz, 2H), 7.58 (d,  $J=7.1$  Hz, 4H), 7.49 (m, 6H), 7.44 (t,  $J=7.6$  Hz), 7.37 (m, 10H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  156.4, 155.5, 151.0, 140.53, 138.3, 137.7, 133.4, 133.2, 132.6, 131.5, 130.0, 130.0, 129.8, 129.5, 129.1, 128.8, 128.2, 128.1, 128.1, 127.1, 125.9, 125.1.

ESI-HRMS:  $m/z$   $[\text{M}]^+$  calculated for  $\text{C}_{47}\text{H}_{34}\text{NO}$ : 628.26349; found: 628.26434 (−1 ppm error).

#### 4-Amino-2',6'-Dibromo-4'-Hydroxybiphenyl 11

Compound **6** (500 mg, 1.3 mmol, 1 eq.) and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  (1.815 g, 8.04 mmol, 6 eq.) were dissolved in 25 mL of ethanol and stirred at 90 °C for 23 h. The solution was then neutralised with  $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  pH 7 buffer. An orange precipitate formed. The suspension was washed thrice with DCM and the organic layers collected. The solvent was removed by rotary evaporation and the solid product was dried under high vacuum to yield 430 mg (94%) of a yellow, crystalline solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  9.73 (br s, 1H), 7.66 (s, 2H), 7.31 (d,  $J=8.5$  Hz, 2H), 6.60 (d,  $J=8.5$  Hz, 2H), 5.26 (br s, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  148.6, 135.5, 128.7, 127.0, 124.4, 114.2, 112.6.

ESI-HRMS:  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{NO}$ : 341.91237; found: 341.91253 (−0.5 ppm error).

#### Compound 2D-BF<sub>4</sub>

Compound **11** (430 mg, 2.0 mmol, 1.0 eq.) and 2,4,6-triphenylpyrylium tetrafluoroborate (436.5 mg, 2.1 mmol, 1.0 eq.) were dissolved in 20 mL of ethanol. The solution was then heated to 90 °C and stirred for 21 h. A yellow precipitate formed upon cooling to room temperature. The product was filtered and washed with isopropyl alcohol and dried over vacuum to yield 665 mg (72%) of a pale yellow solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  7.38 (d,  $J=1.8$  Hz, 2H), 7.39 (d,  $J=2.1$  Hz, 4H), 7.47 (m, 4H), 7.51 (d,  $J=8.9$  Hz, 2H), 7.55 (d,  $J=8.7$  Hz, 2H), 7.75 (s, 2H), 7.68 (m, 3H), 8.37 (d,  $J=7.2$  Hz, 2H), 8.69 (s, 2H), 10.20 (br s, 1H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  156.4, 155.5, 151.0, 138.4, 137.9, 133.4, 133.1, 132.6, 131.9, 130.2, 130.0, 129.8, 129.7, 129.3, 128.8, 128.2, 126.0, 125.1, 112.5.

ESI-HRMS:  $m/z$   $[\text{M}]^+$  calculated for  $\text{C}_{35}\text{H}_{24}\text{Br}_2\text{NO}$ : 632.02192; found: 632.02277 (−1 ppm error).

#### 4-Bromo-2,6-Dichlorophenol 13

4-Bromophenol **12** (1.00 g, 5.8 mmol, 1.0 eq.) and *p*-toluenesulfonic acid (2.21 g, 11.6 mmol, 2.0 eq.) were dissolved in 25 mL of methanol and placed in an ice bath. 1.94 g (14.6 mmol, 2.5 eq.) of *N*-chlorosuccinimide was slowly added with stirring. The reaction was then left stirring at room temperature for 20 h. 8.5 mL of 32%  $\text{HCl}_{(\text{aq})}$  diluted with 8.9 mL of water was then added. 3.324 mg of  $\text{Na}_2\text{S}_2\text{O}_5$  dissolved in 50 mL of water was then added slowly to the solution which was subsequently neutralised with  $\text{NaHCO}_3$  followed by  $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  pH 7 buffer. The product was then collected by vacuum filtration, washed with water and dried under high vacuum to yield 0.72 g (51%) of a white, crystalline solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.95 (s, 1H), 7.41 (s, 2H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 131.0, 122.1, 111.8.

ESI-HRMS:  $m/z$   $[\text{M}-\text{H}]^-$  calculated for  $\text{C}_6\text{H}_2\text{BrCl}_2\text{O}$ : 238.86716; found: 238.86681 (+1 ppm error).

#### 4-Amino-2',6'-Dichloro-4'-Hydroxybiphenyl 15

Compound **13** (450 mg, 1.9 mmol, 1 eq.), 4-aminophenylboronic acid pinacol ester (367 mg, 1.67 mmol, 0.9 eq.),  $\text{Pd}_2\text{dba}_3$  (34.1 mg, 2.5 mol%) and  $^t\text{Bu}_3\text{P}\cdot\text{HBF}_4$  (25.9 mg, 6 mol%) were added to a flask followed by vacuum/ $\text{N}_2$  cycles. The solids were dissolved in 25 mL of THF and 2 mL (4 mmol, 2.2 eq.) of 2 M aqueous  $\text{K}_3\text{PO}_4$  was added to the solution. The solution was stirred at 65 °C for 24 h. The water layer was removed and  $\text{Mg}_2\text{SO}_4$  was added. The solids were filtered off by a short silica plug and the product washed out with THF. The solvent was evaporated, and the product was purified by flash chromatography (EtOAc/petroleum spirits, 1:1). The earliest fractions contained starting material and were discarded. The first major band to elute contained the product ( $R_f=0.5$  EtOAc/Petroleum spirits 1:1). This fraction was collected, and the solvent evaporated, yielding 282 mg (66%) of a yellow crystalline solid.

$^1\text{H}$  NMR (500 MHz, MeOD)  $\delta$  7.40 (s, 2H), 7.28 (d,  $J=8.5$  Hz, 2H), 6.76 (d,  $J=8.5$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, MeOD)  $\delta$  148.8, 148.6, 135.9, 129.4, 128.2, 126.8, 123.6, 116.8.

ESI-HRMS:  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{NO}$ : 254.01340; found: 254.01351 (−0.4 ppm error).

#### Compound 2C-BF<sub>4</sub>

Compound **15** (282 mg, 1.1 mmol, 1.0 eq.) and 2,4,6-triphenylpyrylium tetrafluoroborate (440 mg, 1.1 mmol, 1 eq.) were dissolved in 30 mL of ethanol. The solution was then heated to 90 °C and stirred for 24 h. The solvent was then removed by rotary evaporation. The product was washed with isopropyl alcohol followed by a small amount of methanol. It was then dried over vacuum to yield 402 mg (57%) of a pale yellow solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  10.31 (br s, 1H), 8.68 (s, 2H), 8.37 (d,  $J=7.4$  Hz, 2H), 7.68 (m, 3H), 7.59 (s, 2H), 7.55 (d,  $J=8.6$  Hz, 2H), 7.51 (d,  $J=8.9$  Hz, 2H), 7.48 (m, 4H), 7.38 (d,  $J=1.9$  Hz, 4H), 7.37 (d,  $J=1.9$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  156.4, 155.6, 149.3, 138.4, 138.1, 133.4, 133.1, 132.6, 130.4, 130.1, 129.8, 129.8, 129.3, 128.9, 128.2, 126.6, 125.9, 125.2, 122.9.

ESI-HRMS:  $m/z$   $[\text{M}]^+$  calculated for  $\text{C}_{35}\text{H}_{24}\text{Cl}_2\text{NO}$ : 544.12295; found: 544.12347 (−1 ppm error).

#### 4-Amino-4'-Hydroxybiphenyl 17

4-Bromoaniline (2.00 g, 11.6 mmol, 1.0 eq.), 4-hydroxyphenylboronic acid (2.085 g, 15.11 mmol, 1.3 eq.),  $\text{Pd}_2\text{dba}_3$  (212.9 mg, 2.5 mol%) and  $^t\text{Bu}_3\text{P}\cdot\text{HBF}_4$  (161.9 mg, 6 mol%) were added to a flask followed by vacuum/ $\text{N}_2$  cycles. The solids were dissolved in 30 mL of THF and to the solution 24 mL (48 mmol, 4.1 eq.) of 2 M aqueous KF was added. The solution was stirred at room temperature for 0.5 h and then stirred at 65 °C for 20 h. The water layer was removed and  $\text{Mg}_2\text{SO}_4$  was added. The solids were filtered off by a short silica plug, the product washed out with THF and the solvent removed by rotary evaporation. The crude product was suspended in diethyl ether, centrifuged and the supernatant discarded. The remaining diethyl ether was removed by rotary evaporation. The solid was dissolved in a minimum amount of THF to which diethyl

ether was added to precipitate the product. The product was filtered off, collected by vacuum filtration and washed with diethyl ether. The product was dried over vacuum to yield 1.63 g (76%) of a light brown, powdery solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  9.28 (s, 1H), 7.32 (d,  $J=8.5$  Hz, 2H), 7.23 (d,  $J=8.5$  Hz, 2H), 6.76 (d,  $J=8.5$  Hz, 2H), 6.60 (d,  $J=8.5$  Hz, 2H), 5.05 (s, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  155.7, 147.4, 131.8, 127.9, 126.5, 126.5, 115.5, 114.3.

ESI-HRMS:  $m/z$   $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{12}\text{H}_{12}\text{NO}$ : 186.09134; found: 186.09135 (−0.05 ppm error).

#### Compound 2A-BF<sub>4</sub>

Compound **17** (57 mg, 0.31 mmol, 1.0 eq.) and 2,4,6-triphenylpyrylium tetrafluoroborate (121.9 mg, 0.31 mmol, 1 eq.) were dissolved in 4 mL of ethanol. The solution was then heated to 90 °C and stirred for 3 h. A yellow precipitate formed which was collected by vacuum filtration and was washed with ethanol. It was then dried under high vacuum to yield 121.6 mg (83%) of a pale yellow solid.

$^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  9.69 (s, 1H), 8.67 (s, 2H), 8.37 (d,  $J=6.9$  Hz, 2H), 7.68 (m, 3H), 7.48 (m, 4H), 7.45 (d,  $J=1.8$  Hz, 4H), 7.40 (d,  $J=8.7$  Hz, 2H), 7.38 (m, 6H), 6.77 (d,  $J=8.7$  Hz, 2H).

$^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  157.9, 156.5, 155.4, 140.7, 137.3, 133.4, 133.2, 132.6, 130.0, 129.8, 129.7, 129.1, 128.8, 128.2, 128.1, 127.8, 125.2, 115.8.

ESI-HRMS:  $m/z$   $[\text{M}]^+$  calculated for  $\text{C}_{35}\text{H}_{26}\text{NO}$ : 476.20089; found: 476.20134 (−0.9 ppm error).

## Supporting Information

The supporting information file includes NMR spectra and photophysical data.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** pyridinium phenolate · betaine ·  $\pi$ -extension · solvatochromism

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## RESEARCH ARTICLE

Three new pyridinium phenolate dyes with phenylene  $\pi$ -extension were synthesised and all exhibited strong negative solvatochromism similar to the well-known Betaine 30 dye. This contrasts with the  $\pi$ -extended Betaine 21 previously reported to show poor solvatochromism. We found Betaine 21 to be significantly more solvatochromic than reported, with its alleged insensitivity attributed to degradation in certain solvents.



*S. Franzese, Dr. N. Saker Neto,  
Dr. W. W. H. Wong\**

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**Extended Reichardt's Dye—Synthesis  
and Solvatochromic Properties**

