Electronic Supplementary Information

Water Detection in Organic Solvents Using a Copolymer Membrane Immobilised with a Fluorescent Intramolecular Charge Transfer-Type Dye: Effects of Intramolecular Hydrogen Bonds

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**Scheme 1.** Synthesis of pyridinium betaine dyes.

**General**

$^{1}$H NMR spectra (400 MHz) were obtained using a JEOL ECX-400 spectrometer with tetramethylsilane (0.00 ppm) as the internal standard. Low-resolution (LR) atmospheric solid analysis probe (ASAP) mass measurements were carried out with a Shimadzu LCMS-2020 and LabSolutions LCMS software. High-resolution (HR) electrospray ionization mass measurements were carried out with a Bruker microTOF system after calibration using a sodium formate solution. Elemental analyses were carried out on a J-Science Lab MICRO CORDER JM10 analyser. (E)-N,N-Diphenyl-4-(2-(pyridin-4-yl)vinyl)aniline (denoted as 4) was synthesised according to a previously reported protocol.$^{1}$

**Synthesis of 3a**

2,3-Dichloromaleic anhydride (0.4122 g, 2.469 mmol) and 2a (0.5620 g, 2.408 mmol) were dissolved in acetic acid (5.0 mL), and the mixture was refluxed for 3.5 h. After cooling, water (10.0 mL) was added to the mixture, and the resulting precipitate was filtrated. The residue was washed with water and methanol, yielding the target compound 3a as a white solid (0.8617 g, 2.254 mmol, 94% yield); $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.2$, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 1.66–1.58 (m, 2H), 1.31–1.26 (m, 14H), 0.88 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.3, 144.0, 133.7, 129.5, 128.1, 126.0, 35.8, 32.0, 31.4, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3; LR-ASAP-MS ($m$/z) calcd. For C$_{20}$H$_{26}$Cl$_2$NO$_2$ ([M + H]$^+$): 382.1; Found: 382.2; Anal. calcd. for C$_{20}$H$_{25}$Cl$_2$NO$_2$: C, 62.83; H, 6.59; N, 3.66. Found: C, 62.76; H, 6.54; N, 3.87.
Synthesis of 3b

2,3-Dichloromaleic anhydride (0.4593 g, 2.753 mmol) and 2b (0.322 mL, 2.748 mmol) were dissolved in acetic acid (5.0 mL), and the mixture was refluxed for 3.5 h. After cooling, water (10.0 mL) was added to the mixture, and the resulting precipitate was filtrated. The residue was washed with water and methanol yielding the target compound 3a as a white solid (0.6530 g, 2.436 mmol, 89 % yield); 

\[ \text{1H NMR (400 MHz, CDCl}_3 \delta 7.51 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 6.73 (dd, J = 17.4, 11.0 Hz, 1H), 5.79 (d, J = 17.4 Hz, 1H), 5.34 (d, J = 11.0 Hz, 1H); \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \delta 162.1, 138.1, 135.8, 133.8, 129.9, 127.2, 126.1, 115.7; LR-ASAP-MS (m/z) calcd. For C_{12}H_7Cl_2NO_2 ([M + H]^+): 268.0; Found: 268.0; Anal. calcd. for C_{12}H_7Cl_2NO_2: C, 53.76; H, 2.63; N, 5.22. Found: C, 53.63; H, 3.02; N, 5.19.} \]

Synthesis of PB-C10

The compounds 4 (98.0 mg, 0.2812 mmol), 3a (116.5 mg, 0.3047 mmol), and acetic anhydride (3.0 mL) were mixed, and the blend was refluxed for 15 min and then cooled in an ice bath. The obtained precipitate was filtrated and then washed with methanol and ethanol, yielding the target compound PB-C10 as a reddish-orange powder in 86% yield (0.1632 g, 0.2415 mmol);

\[ \text{1H NMR (400 MHz, CD}_2\text{Cl}_2 \delta 9.66 (d, J = 7.3 Hz, 2H), 7.71 (d, J = 7.3 Hz, 2H), 7.49–7.45 (m, 3H), 7.33–7.25 (m, 8H), 7.40–7.12 (m, 6H), 7.00 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 16.5 Hz, 1H), 2.63 (t, J = 7.8 Hz, 2H), 1.66–1.58 (m, 2H), 1.28–1.25 (m, 14H), 0.86 (t, J = 6.9 Hz, 3H); \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \delta 167.1, 165.0, 164.9, 163.3, 150.4, 147.5, 146.7, 142.4, 138.8, 136.5, 129.7, 129.3, 129.1, 129.0, 127.6, 126.4, 125.7, 124.5, 122.3, 121.4, 119.9, 100.2, 35.7, 32.0, 31.5, 29.7, 29.7, 29.6, 29.4, 22.8, 14.2; ESI-TOF MS (m/z) calcd. For C_{45}H_{45}N_3NaO_3 ([M + Na]^+): 698.3354; Found: 698.3345; Anal. calcd. for C_{45}H_{45}N_3O_3: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.79; H, 6.76; N, 6.12.} \]

Synthesis of PB1

The compounds 4 (26.0 mg, 74.6 μmol), 3b (22.5 mg, 83.9 μmol), and acetic anhydride (0.5 mL) were mixed, and the blend was refluxed for 15 min and then cooled in an ice bath. Hexane (10.0 mL) was added to the mixture, and the resulting precipitate was filtrated. The residue was washed with methanol and ethanol, yielding the target compound PB1 as a reddish-orange powder in 96.2% yield (40.3 mg, 71.8 μmol);

\[ \text{1H NMR (400 MHz, CD}_2\text{Cl}_2 \delta 9.65 (d, J = 6.9 Hz, 2H), 7.71 (d, J = 6.9 Hz, 2H), 7.50–7.44 (m, 5H), 7.14–7.12 (m, 6H), 7.00 (d, J = 9.2 Hz, 2H), 6.96 (d, J = 16.0 Hz, 1H), 6.74 (dd, J = 18.1, 11.0 Hz, 1H), 5.78 (d, J = 18.1 Hz, 1H), 5.28 (d, J = 11.0 Hz, 1H); \]

\[ \text{13C NMR (100 MHz, CDCl}_3 \delta 166.9, 164.9, 163.3, 150.4, 147.5, 146.7, 139.0, 136.7, 136.3, 131.2, 129.7, 129.3, 127.6, 126.8, 126.5, 125.8, 124.6, 122.3, 121.5, 119.9, 114.6, 100.3; ESI-TOF MS (m/z) calcd. For C_{37}H_{27}N_3NaO_3 ([M + Na]^+): 584.1945; Found: 584.1940; Anal. calcd. for C_{37}H_{27}N_3O_3: C, 79.13; H, 4.85; N, 7.48. Found: C, 79.01; H, 4.97; N, 7.36.} \]
Scheme 2. Synthesis of QP1.

**Synthesis of QP1**

QP1 was synthesised according to a previously reported method\(^2\). Briefly, the compound 5 (0.5940 g, 2.173 mmol) and 6 (0.4673 g, 2.182 mmol) were dissolved in dichloromethane (4.0 mL), and piperidine (20 µL, 0.20 mmol) was added to the mixture. The blend was refluxed for 24 h. After cooling, chloroform (30 mL) and water (30 mL) were added to the mixture, and the organic layer was washed with water (30 mL × 1) and sat. NaCl \(aq\) (30 mL × 2) and dried over Na\(_2\)SO\(_4\). Then, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: chloroform/methanol = 4/1 (v/v)). The target compound QP1 was obtained as a red solid (0.3110 g, 0.7318 mmol, 34% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.12 (d, \(J = 6.4\) Hz, 2H), 7.89 (d, \(J = 6.9\) Hz, 2H), 7.61 (d, \(J = 16.0\) Hz, 1H), 7.46 (d, \(J = 8.7\) Hz, 2H), 7.35–7.31 (m, 4H), 7.16–7.13 (m, 6H), 7.01 (d, \(J = 8.7\) Hz, 2H), 6.95 (d, \(J = 16.0\) Hz, 1H), 6.17–6.07 (m, 1H), 5.58–5.49 (m, 4H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.0, 150.7, 146.5, 144.1, 142.1, 130.8, 130.0, 129.7, 127.2, 125.9, 124.7, 123.5, 123.3, 121.0, 119.2, 62.1; ESI-TOF MS \((m/z)\) calcd. For C\(_{28}\)H\(_{25}\)N\(_2\) ([M]+): 389.2013; Found: 389.2003; Anal. calcd. for C\(_{28}\)H\(_{25}\)ClN\(_2\): C, 79.14; H, 5.93; N, 6.59. Found: C, 78.90; H, 5.99; N, 6.46.
Fig. S1. Preparation of the dye-immobilised copolymer membrane.

- DAAm/AAm = 8/2 (mol/mol)
- 0.5% Cross-linker

Fig. S2. (a) Response of the fluorescence intensity of PB1-mem to water in THF/water mixtures (from 0 vol% water in THF at 0 min to 40% water in THF). (b) Recovery of the fluorescence intensity of PB1-mem (from 40 vol% water in THF at 0 min to 0% water in THF).
Fig. S3. (a) Optimized structures and the distribution of frontier orbitals in the ground state and (b) optimized structures in the excited state of PB1 (left: SMD/THF, right: SMD/water at M06/6-31G(d,p) level).
Fig. S4. (a) Optimized structures in the ground state and frontier orbitals and (b) optimized structure in the excited state of QP1 (left: SMD/THF, right: SMD/water at M06/6-31G(d,p) level).
Fig. S5. Lippert–Mataga plots of the two synthesised dyes.

\[
\nu_g - \nu_e = \frac{2\hbar c}{\alpha}\varepsilon_0^{-2} - \Delta f + \text{constant}
\]
\[
\Delta f = \left(\frac{1}{2\epsilon + 1} - \frac{1}{2n^2 + 1}\right)
\]

\((\nu_g - \nu_e)\) : Stokes shifts (cm\(^{-1}\))
\(\hbar\) : Planck's constant (6.6256 \times 10\(^{-34}\) ergs)
\(c\) : speed of light (2.9979 \times 10\(^{10}\) cm/s)
\(\varepsilon\) : dielectric constant of solvent
\(n\) : refractive index of solvent
\(\mu_g, \mu_e\) : dipole moment in the ground and excited state
\(\alpha\) : radius of the cavity of the solute molecule

Fig. S6. Optimized structures in the ground state and excited states of PB1 with a water molecule (SMD/water at M06/6-31G(d,p) level).

Table S1. Total energy of PB1 and water in the ground state (SMD/water at M06/6-31G(d,p) level).

<table>
<thead>
<tr>
<th>Optimized structure</th>
<th>Total energy (a.u.)</th>
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<tr>
<td>PB1 (Fig. S3a)</td>
<td>-1776.837859</td>
</tr>
<tr>
<td>Water</td>
<td>-76.39901008</td>
</tr>
<tr>
<td>PB1 + water (Fig. S6)</td>
<td>-1853.244426</td>
</tr>
</tbody>
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\[\Delta E_{\text{total,g}} = 0.00755732 \text{ (4.742294 kcal/mol)}\]
Fig. S7. Rotational energy barrier $\Delta E_g$ plotted against the dihedral angle $\phi_{\text{bet.g}}$ between the maleimide and pyridinium rings (C–C–N–C) in the ground state.

Fig. S8. Predicted IR spectra of PB1 (SMD/water).
Fig. S9. $^1$H NMR (above) and $^{13}$C NMR (below) spectra of 3a in CDCl$_3$. 
Fig. S10. $^1$H NMR (above) and $^{13}$C NMR (below) spectra of 3b in CDCl$_3$. 
Fig. S11. $^1$H NMR spectrum in CD$_2$Cl$_2$ (above) and $^{13}$C NMR spectrum in CDCl$_3$ (below) of PB-C10.
Fig. S12. $^1$H NMR spectrum in CD$_2$Cl$_2$ (above) and $^{13}$C NMR spectrum in CDCl$_3$ (below) of PB1.
**Fig. S13.** $^1$H NMR (above) and $^{13}$C NMR (below) spectra of QP1 in CDCl$_3$. 
Fig. S14. $^1$H NMR spectra of $\alpha$-hydrogens of the pyridinium ring (brown line: PB1, green line: QP1, in CDCl$_3$).

Fig. S15. Fluorescence spectra of PB1-mem with each ratio of DMAA/AAm (mol/mol) in anhydrous THF ($\lambda_{ex} = 490$ nm).
Fig. S16. Effects of acid (1M HCl aq.) and base (1M NaOH aq.) as impurities in THF, DMSO, and N,N-dimethylformamide (DMF). (a) PB1-mem ($\lambda_{ex} = 490$ nm) and (b) QP1-mem ($\lambda_{ex} = 460$ nm) in each solution. Each impurity was 0.5 vol% added to each organic solvents, and the membranes were soaked in each solution for 5 minutes. Then, fluorescence spectra were measured, and relative fluorescence intensity to that in an anhydrous organic solvent was investigated.

References