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Synthesis and application of some polycondensable fluorescent dyes

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Abstract

The preparation of some fluorescent polycondensable dyes derived from *N*-alkyl-4-alkylamino-1,8-naphthalimide and their application in the coloration of polyurethane foams is described. The degree of fluorescence of the resulting polymers is a function of the solubility of the dye within the monomeric solution. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Naphthalimide; Fluorescent dye; Polycondensable dyes; Polyurethane

1. Introduction

Derivatives of *N*-substituted-1,8-naphthalimides have found application in a number of areas including fluorescent dyes [1], light emitting diodes [2], liquid crystal displays [3] and ion probes [4]. In this paper we present the preparation of polycondensable *N*-alkyl-4-alkylamino-1,8-naphthalimide dyes and their application in the preparation of fluorescent polyurethane foams. Goods manufactured utilising such foams are found in a number of areas including; outdoor and water sports; bathroom accessories and the automobile industry.

The advantage of using polycondensable dyes over conventional dyes is that the dye becomes chemically bonded to the polymer. The dye, therefore, cannot be extracted from the polymer. The wet-fastness of a polymer coloured with a polycondensable dye when exposed to oil, surfactants or seawater is, as a consequence, much greater than polymers coloured with conventional dyes. In some cases the light fastness of the dye may also be increased when incorporated into the polymeric chain [5].

Provided that the quantity of dye used to colour the foam is reasonably low, which is normally the case, the mechanical and thermal properties of the foam remain unchanged and no alteration of the polymer production process is necessary [5]. Such dyes can, therefore, be used as a direct substitute for conventional dyes during the preparation of the coloured polymer.

2. Results and discussion

The initial target chosen was the bishydroxy moiety **2**. Two hydroxy groups were included in the target so that growth of the polymer chain would not be terminated. The resulting dye would, therefore, form

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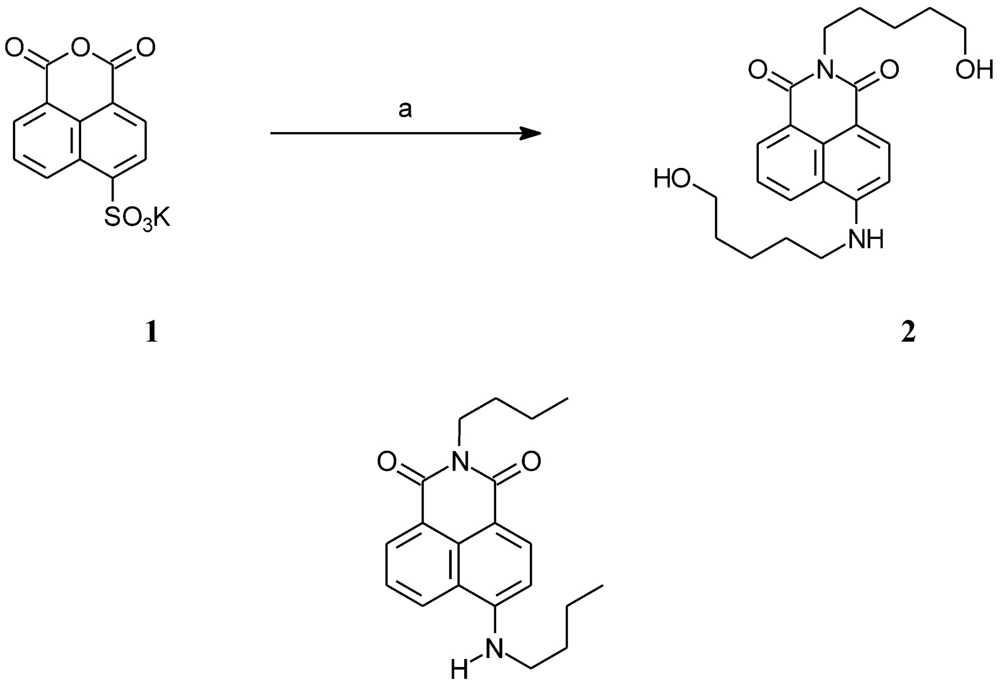
part of the polymer chain. Thus, compound **2** was prepared by the reaction of 5-amino-1-pentanol with 4-sulfo-1,8-naphthalic anhydride potassium salt **1** in aqueous solution at 120 °C (Scheme 1) in good yield (81%). As expected for a *N*-alkyl-4-alkylamino-1,8-naphthalimide, **2** was found to be yellow in colour with an intense green fluorescence.

Polyurethane foams containing ca. 0.1% w/w of dye **2** were intense yellow in color and exhibited no migration of the dye under the test conditions. However, the intensity of the emitted fluorescence was very weak. In contrast, foams prepared using 0.1% w/w of an analogous dye **3**, which did not contain functional groups capable of condensation, were intensely coloured and fluorescent but migration of the dye was found to occur. It was noted that **3** had a greater solubility than **2** in the solvent used to prepare the dye tincture. This suggests that the weak fluorescence exhibited by the foam containing **2** was caused by incomplete distribution of the dye within the monomeric solution. This would result in aggregation of the dye molecules within the polymer matrix and self-quenching of emitted fluorescence. Further support of this hypothesis was found by washing the non-fluorescent foams with ethanol to remove unreacted dye and low molecular weight polymer. This rendered foams containing dye **2** weakly fluorescent. The foams remained fluorescent after drying under vacuum to remove any bound solvent.

By changing the solvent used to prepare the dye tincture it was possible to alter the fluorescence of the resulting foams. The degree of fluorescence was found to correlate with the solubility of the dye in the solvent used to prepare the tincture, Table 1. Foams prepared using tinctures made up with dimethylsulfoxide (DMSO) were the most fluorescent. This was the only solvent that completely dissolved the dye used in the tincture. The remaining solvents partially dissolved the dye and showed varying degrees of fluorescence. Dye **2** was poorly soluble in both the polyol and 4,4′-methy-



1

2

3

Scheme 1. (a) 5-Amino-1-pentanol, water, 120 °C, 81% yield.

Table 1
The effects on solvent upon the fluorescence of polyurethane foam, 0 = non-fluorescent, 5 = extremely fluorescent

Solvent used for tincture	Empirical fluorescence
Diethylene glycol	1
Methanol	2
Ethanol	3
1-Propanol	3
1-Butanol	2
2-Propanol	2
Dimethylsulfoxide	4
Polyol	0
MDI	0

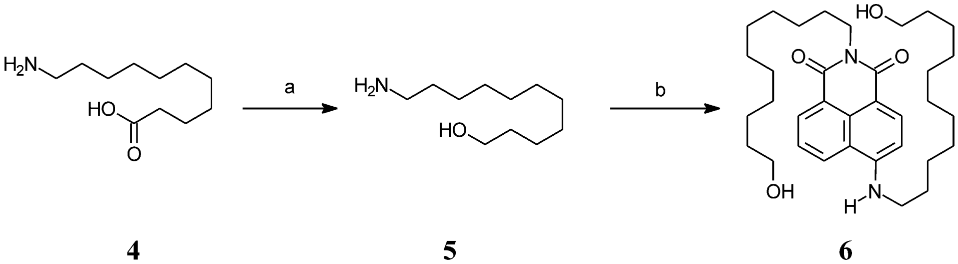
lenebis(phenylisocyanate). This was reflected in the foams produced, which exhibited no fluorescence. These results confirm that the degree of solubility of the dye in the monomeric solution has a direct influence on the fluorescent properties of the resultant foams.

In order to assess the effects of the alkyl groups attached to the fluorophore on the solubility of the dye in the monomeric solutions and, therefore, the fluorescent properties of the foams produced, two further dyes were prepared. Dye **6** which is analogous to **2** but with much longer hydroxyalkyl groups attached to the fluorophore; and dye **9** which contains an alkylamino group in the 4-position of the naphthalimide and the necessary dihydroxyalkyl group attached to the imido nitrogen.

Compound **6** was synthesised as indicated in Scheme 2. Thus, 11-amino-1-undecanol **5** was prepared by reducing 11-aminoundecanoic acid **4** with diborane (generated in situ by the reaction of sodium borohydride and iodine) in anhydrous tetrahydrofuran (THF). Reduction of 11-amino undecanoic acid with lithium aluminium hydride gave moderate yields (60% crude) of the corresponding alcohol and work-up of the reaction mixtures proved difficult and time consuming.

The preparation of *N*-(11-hydroxyundecyl)-4-(11-hydroxyundecyl)amino-1,8-naphthalimide **6** proved to be problematic and a number of reaction conditions were investigated before a satisfactory procedure was obtained. The range of conditions used and the results obtained are summarised in Table 2. Application of the conditions used to prepare **2** failed to produce any of the desired compound. This was due to the poor solubility of 11-amino-1-undecanol in water. The use of 1-propanol as a co-solvent did not significantly increase the yield of **6**. Attempts to catalyse the reaction by the addition of sodium hydroxide or acetic acid had little effect. Subsequent attempts were centred on methods found in the literature [6]. The use of 4-chloro-1,8-naphthalic anhydride produced only trace amounts of **6**. Increased yields were obtained by the use of the more reactive bromo derivative. The use of methoxyethanol and of *N*-methylpyrrolidinone gave moderate yields of **6**. The greatest yield of **6** (72%) was achieved by the reaction of 4-bromo-1,8-naphthalic anhydride with excess 11-amino-1-undecanol in DMSO at 130 °C in the presence of triethylamine.

Dye **9** was prepared as illustrated in Scheme 3. Reaction of 4-bromo-1,8-naphthalic anhydride **7** with serinol, in ethanol, afforded 4-bromo-*N*-(2-hydroxy-1-hydroxymethylethyl)-1,8-naphthalimide **8** in 84% yield. Subsequent reaction of **8** with 4-butylamine in DMSO at 80 °C afforded the desired 4-butylamino-*N*-(2-hydroxy-1-hydroxy methylethyl)-1,8-naphthalimide **9** in a yield of 65% from **7**. Reaction of **8** with 4-butylamine at higher

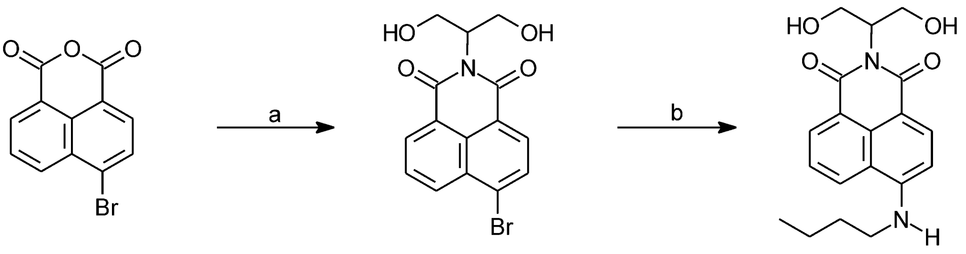


4 **5** **6**

Scheme 2. (a) $NaBH_4$, I_2, THF, R.T., 98% yield; (b) 4-bromo-1,8-naphthalic anhydride, Et_3N, DMSO, 130 °C, 72% yield.

Table 2
Conditions investigated for the preparation of *N*-(11-hydroxyundecyl)-4-(11-hydroxyundecylamino)-1,8-naphthalimide

4-Substituted-1,8-naphthalic anhydride	Base	Solvent	T (°C)	Time (h)	% Yield of **6**
K-sulfonate	–	H_2O	140	5	0
K-sulfonate	NaOH	1:1 H_2O:1-propanol	130	12	19
K-sulfonate	–	1:1 H_2O:1-propanol + 1% v/v acetic acid	140	48	0
K-sulfonate	–	1:1 H_2O:1-propanol	140	84	Trace
Chloride	Et_3N	MeOEtOH	125	4.5	Trace
Bromide	Et_3N	MeOEtOH	125	6.5	7
Bromide	Et_3N	MeOEtOH + catalytic $CuSO_4$	90	5	0
Bromide	Et_3N	MeOEtOH	125	20	25
Bromide	Et_3N	NMP	110	20	35
Bromide	Et_3N	DMSO	130	20	72



7 **8** **9**

Scheme 3. (a) $(HOCH_2)_2CHNH_2$, EtOH, 55 °C, 84% yield; (b) $CH_3(CH_2)_3NH_2$, DMSO, 80 °C, 65% yield from **7**.

temperatures produced mixtures of unidentifiable products.

Dye **6** was found to be poorly soluble in the monomeric solution used to prepare the polyurethane foams resulting in the formation of weakly coloured non-fluorescent foams. However, dye **9** was found to be significantly more soluble in organic solvents than **2** or **6**. Polyurethane foams incorporating **9** were slightly less fluorescent than the foams prepared using dye **3**. However, dye migration tests on the foams incorporating **9** exhibited no migration of dye. Washing of the foams in ethanol had no effect on the fluorescent properties of the foams produced, indicating that little association of the dye molecules occurred during the polymerisation process and that a very large percentage of the dye was incorporated into the polymer.

In this paper, the preparation of three fluorescent polycondensable dyes is presented. The successful application of such dyes for the coloration of polyurethane foams is dependent upon the degree of solubility of the dye in the tincture used to prepare such foams.

3. Experimental

4-Sulfo-1,8-naphthalic anhydride potassium salt was obtained as a ‘paste’ from Hollidays Dyes and Chemicals, Huddersfield, UK and was dried over P_2O_5 under reduced pressure (ca. 2 mm Hg). All other reagents were obtained from Aldrich, Acros, BDH, or Lancaster and were used without any further purification. Evaporations were carried out using a Büchi rotary evaporator followed by evaporation under high vacuum (typically ca. 2.0 mm Hg). Tetrahydrofuran was distilled from sodium wire and benzophenone and used directly.

All products were dried over P_2O_5 under reduced pressure (ca. 2 mmHg) before analysis.

Melting points were determined with a heated block and mercury in glass thermometer and are uncorrected. Combustion analyses were performed on Perkin-Elmer 240C or Carlo-Erba 1 106 elemental analysers. UV spectra were recorded on Perkin-Elmer Lambda 15 spectrometer. IR spectra were recorded using a Perkin-Elmer 783 spectrometer. ^1H NMR spectra were recorded at 200, 300 or 400 MHz on Bruker AC200, AC300 or A90 spectrometers, respectively, using residual incompletely deuterated solvent as internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 or 100 MHz on a Bruker AC300 or A90 spectrometers, respectively, using deuterated solvent as internal standard. Fast atom bombardment (FAB) mass spectra were obtained from a Kratos MS50 spectrometer, using a 2-nitrophenol matrix. Electron impact (EI) (70 eV) and chemical ionisation (CI) (using ammonia gas) mass spectra were obtained from Finnigan MAT 8430 or Kratos MS25 spectrometers. High resolution mass spectrometry was carried out using a Kratos Concept IS spectrometer.

3.1. N-(5-Hydroxypentyl)-4-(5-hydroxypentyl) amino-1,8-naphthalimide **2**

4-Sulfo-1,8-naphthalic anhydride potassium salt (10.0 g, 32 mmol) and 5-amino-1-pentanol (22.4 g; 216 mmol) were dissolved in water (300 ml) and stirred at 130 °C in an autoclave for 36 h. The reaction was then allowed to cool, precipitating the desired 4-alkylamino-*N*-alkyl-1,8-naphthalimide as a yellow solid (10.1 g, 81%). No further purification was necessary. M.p. 168–169 °C; (found C, 69.0; H, 7.4; N, 7.2; $C_{22}H_{28}O_4N_2$ requires C, 68.7; H, 7.3; N, 7.3%); λ_{max}(EtOH)/nm 204.9 (ϵ/dm^3 mol^{-1} cm^{-1} 40010), 230.1 (15860), 260.3 (19960) 284.2 (19880), 444.5 (16760); ν_{max}(KBr)/cm^{-1} inter alia 3380 *br* (O–H); 3330 (N–H); 1680, 1630 (C=O); δ_H(400 MHz, $[CD_3]_2SO$) 1.30–1.78 (12H, m, 2 × $HOCH_2(C\underline{H}_2)_2CH_2N$), 3.30–3.48 (6H, m, 2 × $C\underline{H}_2OH$ and $C\underline{H}_2NH$), 3.99 (2H, *t*, *J* 7.3, $CH_2C\underline{H}_2N[CO]_2$), 4.39 (1H, *t*, *J* 5.3, disappears upon addition of D_2O, $CH_2O\underline{H}$), 4.43 (1H, *t*, *J* 5.0, disappears upon addition of D_2O, $CH_2O\underline{H}$), 6.72 (1H, *d*, *J* 8.5, 3-H), 7.64 (1H, *t*, *J* 8.0, 6-H), 7.72 (1H, *t*, *J* 5.5, disappears upon addition of D_2O, $CH_2N\underline{H}$), 8.22 (1H, *d*, *J* 8.5, 2-H), 8.39 (1H, *d*, *J* 7.5, 7-H), 8.67 (1H, *d*, *J* 8.0, 5-H); δ_C(100 MHz, $[CD_3]_2SO$) 23.5 (*t*, $HO(CH_2)_2\underline{C}H_2(CH_2)_2$), 23.6 (*t*, $HO(CH_2)_2\underline{C}H_2\,(CH_2)_2$), 27.9 (*t*, $HOCH_2\underline{C}H_2$), 28.1 (*t*, $HOCH_2\ \underline{C}H_2$), 32.6 (2 *t*, $NCH_2\underline{C}H_2$), 39.6 (*t*, $CH_2\underline{C}H_2N\ [CO]_2$), 43.3 (*t*, $HN\underline{C}H_2$), 60.9 (*t*, $\underline{C}H_2OH$), 61.0 (*t*, $\underline{C}H_2OH$), 104.0 (*d*, C-3), 107.8 (*s*), 120.4 (*s*), 122.2 (s), 124.4 (*d*, C-6), 128.8 (d, C-5), 129.7 (*s*), 130.9 (d, C-7), 134.5 (*d*, C-2), 150.9 (*s*, C-4), 163.2 (*s*, C-11), 164.0 (*s*, C-12); *m/z* (FAB) inter alia 385 ($M^+ + H$, 100%).

3.2. 11-Aminoundecan-1-ol **5**

3.2.1. Procedure 1

Lithium aluminium hydride 1 M, (6.5 ml, 6.5 mmol) was added to a suspension of 11-aminoundecanoic acid (1.0g, 5 mmol) in dry tetrahydrofuran. The mixture was refluxed gently for ca. 20 h, allowed to cool to room temperature and aqueous potassium hydroxide was added (20 ml, 10% w/v). The mixture was then passed through a short alumina column and the residue extracted with refluxing tetrahydrofuran using a continuous solvent extractor for 3 days. The filtrate and extracts were combined, filtered and evaporated to afford the crude title compound **5** as a white solid (0.55 g, 61%).

3.2.2. Procedure 2

A solution of iodine (17.8 g, 70 mmol) in dry tetrahydrofuran (120 ml) was added dropwise over 1.5 h to a slurry of sodium borohydride (6.6 g, 175 mmol, in tetrahydrofuran 120 ml) at 0 °C under Ar. The resulting solution was then stirred until there was no further evolution of hydrogen. A suspension of 11-aminoundecanoic acid (70 mmol, 14.1 g in tetrahydrofuran 120 ml) was then added dropwise whilst allowing the solution to warm to room temperature. The solution was then stirred at room temperature for 48 h. Methanol (400 ml) was added and the solution was stirred at room temperature for 2 h. The solvent was evaporated to leave ca. 100 ml of the reaction liquor. Aqueous potassium hydroxide (4 M, 250 ml) was then added and the mixture was refluxed overnight.

After cooling, the reaction mixture was extracted with ethyl acetate (4×100 ml). The combined extracts were washed with aqueous sodium hydroxide (2×100 ml, 2 M), dried ($MgSO_4$) and evaporated to yield 11-amino-1-undecanol as a white solid (13.0 g, 98%). The title compound was used for subsequent reactions without further purification; m.p. 74–78 °C (Lit. [7] 71–73 °C); ν_{max}(nujol)/cm^{-1} inter alia 3490 (O–H), 3215 (N–H); δ_H(300 MHz, $CDCl_3$) 0.88–1.84 (21H, *m*, simplifies slightly upon addition of D_2O, NH_2 and OH, $9\times CH_2C\underline{H}_2CH_2$), 2.67 (2H, *t*, *J* 6.9, $C\underline{H}_2 NH_2$), 3.62 (2H, *t*, *J* 6.6, $C\underline{H}_2OH$); δ_C(75 MHz, $CDCl_3$) 25.9 (*t*), 26.8 (*t*), 29.4 (*t*), 29.5 (*t*), 32.8 (*t*), 33.5 (*t*), 42.0 (*t*, $\underline{C}H_2NH_2$), 62.5 (*t*, $\underline{C}H_2OH$); *m/z* (FAB) 188.2012 ($M^+ + H$, 100%, $C_{11}H_{26}NO$ requires 188.20142).

3.3. *N-(11-Hydroxyundecyl)-4-(11-hydroxyundecyl)amino-1,8-naphthalimide* **6**

4-Bromo-1,8-naphthalic anhydride (0.30 g, 1.1 mmol), 11-amino-1-undecanol (0.82 g, 4.4 mmol), triethylamine (0.16 ml, 1.1 mmol) and DMSO (7 ml) were placed in a sealed tube and heated to 130 °C overnight. The solution was then allowed to cool and water (20 ml) was added to precipitate a brown solid. The solid was recrystallised from ethanol/dichloromethane to yield the title compound **6** as a yellow solid (0.44 g, 72%). M.p. 132–134 °C; λ_{max}(EtOH)/nm 207.3 (ε/dm^3 mol^{-1} cm^{-1} 22300), 229.8 (13000), 259.9 (13780), 283.8 (13240), 325.0 (1930), 340.3 (1640), 443.4 (10450); ν_{max}(nujol)/cm^{-1} inter alia 3320 *br* (O–H/N–H); 1670, 1630 (C=O); δ_H(300 MHz, $[CD_3]_2SO$) 1.08–1.82 (36H, m, $2\times NCH_2(C\underline{H}_2)_9CH_2OH$), 4.00 (2H, *t*, *J* 6.9, $[CO]_2NC\underline{H}_2CH_2$), 4.33 (2H, t, *J* 5.0, disappears upon addition of D_2O, $CH_2O\underline{H}$), 6.78 (1H, *d*, *J* 8.7, 3-H), 7.68 (1H, *t*, *J* 7.8, 6-$\underline{H}$), 7.77 (1H, *br* s, disappears upon addition of D_2O, N–H), 8.27 (1H, *d*, *J* 8.7, 2-H), 8.44 (1H, *d*, *J* 6.9, 7-H), 8.72 (1H, *d*, *J* 8.5, 5-H); δ_C(75 MHz, $[CD_3]_2SO$) 26.7 (*t*), 26.8 (*t*), 27.8 (*t*), 28.0 (*t*), 29.0 (2 *t*), 29.1 (*t*), 29.2 (*t*), 29.3 (*t*), 32.7 (*t*), 39.4 (*t*, $[CO]_2N\underline{C}H_2CH_2$), 43.0 (*t*, $\underline{C}H_2NH$), 60.9 (2 *t*, $\underline{C}H_2OH$), 103.8 (*d*, C-3), 107.6 (*s*), 120.2 (*s*), 122.0 (*s*), 124.2 (*d*, C-6), 128.7 (*d*, C-5), 129.6 (*s*), 130.7 (*d*, C-7), 134.3 (*d*, C-2), 150.8 (*s*, C-4), 163.0 (*s*, C-11), 163.9 (*s*, C-12); *m/z* (CI) 553.3999 ($M^+ + H$, $C_{34}H_{53}N_2O_4$ requires 553.4005); (FAB) 553 ($M^+ + H$, 100%), 534 (34), 358 (42).

3.4. *4-Bromo-N-(2-hydroxy-1-hydroxymethylethyl) naphthalimide* **8**

4-Bromo-1,8-naphthalic anhydride (0.50 g, 1.8 mmol) and serinol (0. 18 g, 2.0 mmol) were added to ethanol (15 ml) and refluxed for ca. 6 h. The solution was then cooled to precipitate the desired compound **8** (0.529 g, 84%) as a white solid. M.p. 250–251 °C (Found C, 51.6; H, 3.3. N 4.2; Br 22.4; $C_{15}H_{12}NO_4Br$ requires C, 51.5; H, 3.5; N, 4.0; Br 22.8%); λ_{max}(EtOH)/nm 213.2 (ε/dm^3 mol^{-1} cm^{-1} 2320), 237.6 (3980), 341.2 (1750), 354.8 (1340); ν_{max}(nujol)/cm^{-1} inter alia 3420, 3360 (O–H); 1680, 1632 (C=O); δ_H(300 MHz, $[CD_3]_2SO$) 3.72–4.02 (4H, *m*, $CH[C\underline{H}_2OH]_2$), 4.8 (2H, *m*, disappears upon addition of D_2O, $CH_2O\underline{H}$), 5.15–5.27 (1H, *m*, $[CH_2]_2C\underline{H}N$), 8.01 (1H, dd, *J* 7.3 and 8.5, 6-H), 8.23 (1H, *d*, *J* 7.8, 3-H), 8.34 (1H, *d*, *J* 7.8, 2-H), 8.56 (2H, *m*, 5-H and 7-H); δ_C(75 MHz, $[CD_3]_2SO$) 58.5 (*d*, C-13), 59.1 (2 *t*, $\underline{C}H_2OH$), 122.7 (*s*), 123.4 (*s*), 128.5 (*s*), 128.9 (*d*), 129.7 (*s*), 131.0 (*d*), 131.4 (*d*), 131.6 (*d*), 132.3 (*d*), 163.8 (C=O), 163.9 (C=O); *m/z* (FAB) inter alia 350 (M^+, ^{79}Br, 92%), 332 (100).

3.5. *4-Butylamino-N-(2-hydroxy-1-hydroxymethylethyl)-1,8-naphthalimide* **9**

4-Bromo-*N*-(2-hydroxy-1-hydroxymethylethyl) naphthalimide **8** (0.198 g, 0.57 mmol) and butylamine (0.60 ml, 5.70 mmol) were dissolved in dimethylsulfoxide (5 ml) and stirred at 80 °C overnight. The resulting solution was then poured into water (ca. 20 ml) and the title compound was precipitated as an orange solid (0.15g, 77%); m.p. 146–147 °C; (found C, 66.88; H, 6.5; N, 8.1; $C_{19}H_{22}N_2O_4$ requires: C, 66.6; H, 6.5; N, 8.2%); λ_{max}(EtOH)/nm 204.2 (ε/dm ^{3} mol^{-1} cm^{-1} 36360), 229.6 (12760), 261.5 (17580), 283.9 (17420), 324.8 (1640), 340.0 (830), 442.6 (15300); ν_{max}(nujol)/cm^{-1} inter alia 3420, 3330, 3200 (N–H, O–H); 1650, 1625, 1600 (C=O), 1570, 1540; δ_H(300 MHz, $[CD_3]_2SO$) 0.95 (3H, *t*, *J* 7.3, $C\underline{H}_3CH_2$), 1.44 (2H, *s*, *J* 7.4, $CH_2C\underline{H}_2CH_3$), 1.67 (2H, *q*, *J* 7.3,

$CH_2C\underline{H}_2CH_2$), 3.25–3.48 (2H, *m*, collapses to triplet upon addition of D_2O, $NHC\underline{H}_2CH_2$), 3.75–4.00 (4H, *m*, $NCH[C\underline{H}_2OH]_2$), 4.73 (2H, *t*, *J* 5.9, disappears upon addition of D_2O, OH), 5.15–5.30 (1H, quintet, *J* 6.7, $NC\underline{H}[CH_2OH]_2$), 6.77 (1H, *d*, *J* 8.7, 3-H), 7.60–7.78 (2H, m, collapses to triplet integral 1 H upon addition of D_2O, 6-H and $\underline{H}NCH_2$), 8.25 (1H, *d*, *J* 8.5, 2-H), 8.41 (1H, *d*, *J* 7.3, 7-H), 8.70 (1H, *d*, *J* 8.3, 5-H); δ_C (75 MHz, $[CD_3]_2SO$) 14.0 (*q*, $\underline{C}H_3CH_2$), 20.1 (*t*, $CH_3C\underline{H}_2$), 30.2 (*t*, $CH_3CH_2\underline{C}H_2$), 42. 8 (*t*, $\underline{C}H_2NH$), 57.6 (*d*, $N\underline{C}H[CH_2OH]_2$), 59.6 (*t*, 2 × $\underline{C}H_2OH$), 103.9 (*d*, C-3), 108.4 (*s*), 120.2 (*s*), 122.7 (*s*), 124.3 (d, C-6), 128.4 (*d*, C-5), 129.9 (*s*), 130.7 (C-7), 134.4 (C-2), 150.5 (*s*), 164.1 (C-11), 164.9 (C-12); *m*/z (FAB) inter alia 343 ($M^+ + H$, 74%), 342 (M^+, 26), 325 (100), 269 (71).

3.6. Preparation and examination of the polyurethane fluorescent foams

Dye tinctures were prepared by mixing the appropriate dye (0.250 g) with a solvent (1 ml) until a homogenous mixture was obtained. See discussion for a list of the solvents used. An aliquot (0.250 g) of this tincture was then mixed with a proprietary polyol resin (25.0 g) until a homogenous mixture was obtained. A proprietary solution (12.5 g), containing 4,4′-methylenebis(phenyl isocyanate) (MDI) and a blowing agent, was then added and the mixture was stirred vigorously for 5 min. The foam was then allowed to set for 30 min.

Each of the foams was examined under normal and ultraviolet lighting conditions. The fluorescence of each of the foams was then rated on an empirical scale, were 0 indicates that the foam was non-fluorescent and a rating of 5 indicates a foam that was intensely fluorescent and comparable to a foam prepared from dye **3.**

Two migration tests were carried out on the foams. One entailed placing the foams in an oven at (50 °C) for 6 h, between a ca. 5 kg weight and a filter paper that had been soaked in coconut oil. Any migration of dye was indicated by staining of the filter paper. The second test involved placing the foams in a solution of detergent at 50 °C for 4 h. Migration of the dyes in this case was indicated by colouration of the solution.

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