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A convenient preparation of long chain 4-(4-*n*-alkylphenylazo)phenols and their 4-pentylbenzoate esters

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A homologous series of 4-(4-alkylphenylazo)phenols **1[n]** *(n* = 2–22, even) was prepared in yields of 40–70% by Negishi coupling of alkylzinc chlorides with 4-(4-iodophenylazo)phenol (**3**). The phenols were converted to the corresponding 4-pentylbenzoates **2[n]**, which exhibit enantiotropic nematic phases even for **2[22]**.

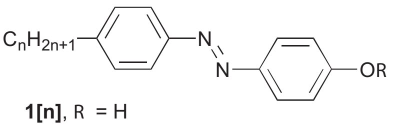
Keywords: azobenzene; homologous series; synthesis

1. Introduction

Functionalised azobenzenes were among the first successful nematic liquid crystals used in the display industry (*1–5*), constitute an important class of materials for information processing and storage (*6–9*), and are being explored as molecular photoswitches (*10*, *11*). One of the key intermediates is 4-(4-alkylphenylazo)phenol (**1[n]**), which typically is alkylated (*12–14*) or acylated (*12*, *15–18*) to give azobenzene liquid crystals. Most of these materials are nematogenic and smectic phases are seldom observed, even for higher homologues (*14*). Therefore, azobenzenes are attractive for studying trends in the N-I transition in a long homologous series.

The reported 4-(4-alkylphenylazo)phenols (**1[2]**–**1[10]**) were prepared by diazotisation of the corresponding 4-alkylaniline followed by coupling with phenol (*12*, *13*, *17*, *19–22*). The reactions are typically run in aqueous solutions, which make the preparation of higher analogues difficult. An additional impediment for the preparation of higher homologues of **1[n]** is the relatively high cost of the appropriate 4-alkylanilines.

An alternative synthetic approach to phenols **1[n]** is the introduction of the alkyl group to a suitable azobenzene precursor. An efficient Pd-catalysed coupling of an alkylmagnesium halide with appropriate iodoarenes was demonstrated for the preparation of 4-alkylanilines, 4-alkylphenols and 4-alkylbenzoic acids (*23*). However, Grignard reagents are incompatible with azobenzenes and the reaction leads to the reduction of the azo functionality (*24*, *25*). Therefore, we envisioned using the organozinc reagent as a coupling partner, as it is known to tolerate many functional groups such as the carbonyl (*26*).



1[n], R = H
2[n], R = 4-$C_5H_{11}C_6H_4CO$

Here we describe the preparation of phenols **1[n]** with *n* = 2–22 (even) using a Pd-catalysed coupling reaction of a suitable azobenzene precursor with alkylzinc chlorides. Subsequently, the phenols were esterified giving a series of 4-pentylbenzoates **2[n]**, for which the mesogenic properties were investigated.

2. Results and discussion

2.1 *Synthesis*

Phenols **1[n]** were obtained by reaction of alkylzinc chloride with 4-(4-iodophenylazo)phenol (**3**) in tetrahydrofuran (THF) in the presence of N-methylpyrrolidone (NMP), LiCl, NaH (sodium hydride deprotonates phenol **3**, which minimises the amount of organozinc reagent necessary for the complete transformation) and catalyst PEPPSI-IPr (Scheme 1). This catalyst was chosen because it is user-friendly and has been shown to promote effective coupling of a variety of aryl chlorides, bromides, iodides, triflates, tosylates and mesylates to alkyl centres under Negishi conditions (*27*).

The reaction was conducted at elevated temperatures, and the products were isolated by column chromatography followed by recrystallisation giving phenols **1[n]** in 40–70% yield. The alkylzinc chlorides were prepared by treatment of the corresponding alkylmagnesium bromides with anhydrous $ZnCl_2$. The concentration of the Grignard reagents was estimated via titration with molecular iodine (I_2) (*28*). For

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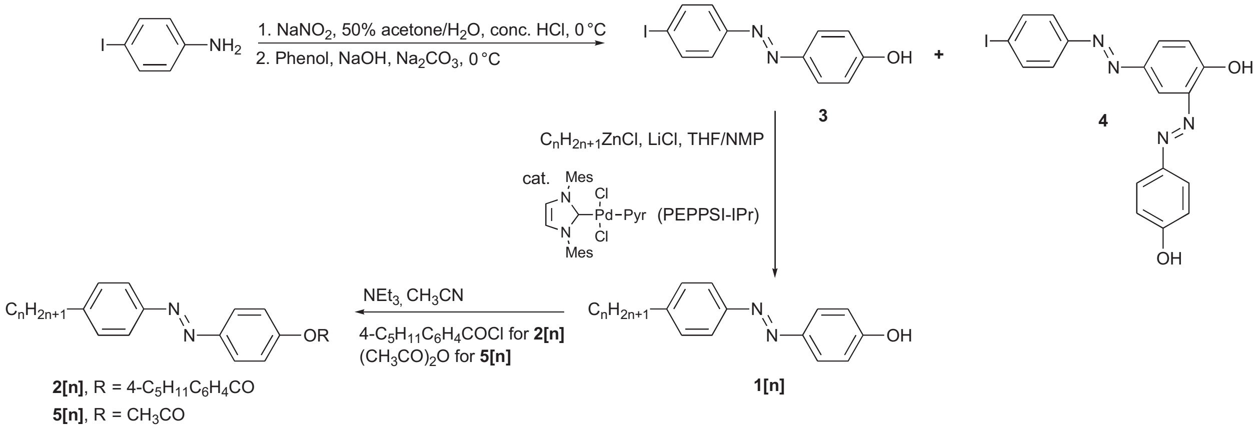


Scheme 1. Synthesis of 4-(4-alkylphenylazo)phenols **1[n]** and their esters **2[n]** and **5[n]**.

comparison purposes phenols **1[4]** and **1[6]** were prepared by diazocoupling of the corresponding 4-alkylanilines and phenol and isolated in about 70% yield. The yields for **1[1]**–**1[6]** were reported in a range of 87–92% (*12*) and for higher homologues (**1[6]**, **1[7]** and **1[10]**) in a range of 30–50% (*22*).

The iodide **3** (*29*) was prepared in 77% yield by diazocoupling of 4-iodoaniline with phenol following a general literature procedure (*20*) (Scheme 1). Analysis of the crude product revealed the presence of about 5% of bis-coupling product **4** which was separated as an insoluble fraction during recrystallisation and independently characterised.

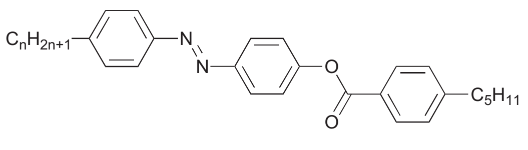
Benzoates **2[n]** were prepared by treatment of phenols **1[n]** with 4-pentylbenzoyl chloride in the presence of NEt_3 (Scheme 1). Similarly, two acetates, **5[16]** and **5[18]**, were prepared by treatment of the appropriate phenol **1[n]** with acetic anhydride.

2.2 Mesogenic properties

Transition temperatures and enthalpies for series **2[n]** were determined by differential scanning calorimetry (DSC) and results are shown in Table 1. Phase types were assigned by comparison of microscopic textures observed in polarised light with those published for reference compounds and established trends in thermodynamic stability (*30–32*).

All benzoates exhibit enantiotropic nematic phases with the clearing temperatures decreasing from 207°C for **2[2]** to 130.5°C for **2[22]**. An enantiotropic smectic C (SmC) phase appears in the homologous series beginning with the tetradecyl derivative **2[14]** (Figure 1). Compounds **2[18]** and **2[20]** exhibit the unusual melting-crystallisation-melting sequence in thermal analysis, arising from the different stability of two crystalline polymorphs. Such behaviour has been observed in several other mesogens (*33*, *34*).

Table 1. Transition temperatures (°C) and transition enthalpies (ΔH, kJ mol^{-1}) for **2[n]**.[a]



2[n]

2[2]	Cr 120 N 207.4 I (24.2) (1.1)	**2[14]**	Cr_1 76 Cr_2 80 SmC 84.7 N 153.1 I (46.0)[c] (0.5) (1.4)
2[4]	Cr 84 (24.3) N 200.1 (1.4) I [b]	**2[16]**	Cr 84 SmC 89.2 N 146.4 I (57.6) (0.4) (1.4)
2[6]	Cr 76 (25.5) N 187.7 (1.5) I	**2[18]**	Cr_1 79 Cr_2 86 SmC 93.3 N 140.7 I [d] (0.3) (1.5)
2[8]	Cr 80 (21.9) N 177.6 (1.5) I	**2[20]**	Cr_1 83 Cr_2 90 SmC 96.5 N 135.5 I [d] (0.2) (1.3)
2[10]	Cr_1 52 (21.7) Cr_2 86 (23.3) N 169.1 (1.2) I	**2[22]**	Cr 86 SmC 100.9 N 130.5 I (91.7) (0.1) (1.7)
2[12]	Cr_1 69 (29.3) Cr_2 79 (22.3) N 159.8 (1.4) I		

[a] Cr, crystal; Sm, smectic; N, nematic; I, isotropic.

[b] Lit. (*16*) Cr 83 N 200 I.

[c] Combined enthalpy for Cr–Cr and Cr–Sm transitions.

[d] Sequence: melting–crystallisation–melting.

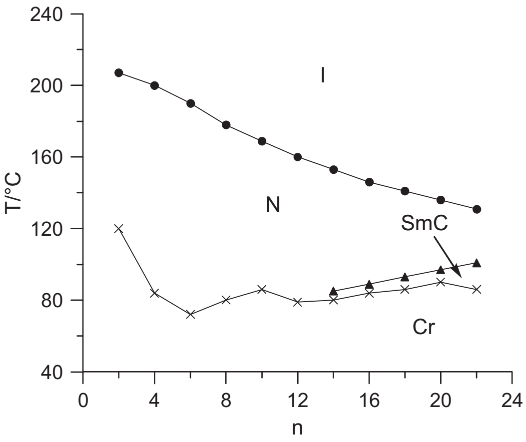


Figure 1. Transition temperatures versus the terminal chain length for **2[n]**.

Our studies confirmed the transition temperatures reported previously for benzoate **2[4]**, which together with **2[5]**, are the only known members of the series **2[n]** (*16*).

Two acetates, **5[16]** and **5[18]**, showed no liquid crystalline behaviour even upon supercooling by 30 K, and the series was not investigated further.

Inspection of data for series **2[n]** in Figure 1 demonstrated that the trend in the N-I transition temperatures does not follow that observed for alkoxyphenyl derivatives, which typically conform to a simple exponential decay (*35–38*). Instead the observed trend in T_{NI} for **2[n]** is similar to that found for alkylbenzene and alkylcyclohexane homologous series (*35*, *39*).

3. Summary and conclusions

The Negishi C-C coupling method allows for convenient preparation of alkylazobenzenes even with long alkyl chains. This method can, in principle, be used for the preparation of more complex azobenzenes, such as those suitable for advanced photonic materials, using functionalised organozinc reagents available through modern synthetic methods (*40–44*).

4. Experimental

4.1 General methods

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was obtained at 300 MHz in $CDCl_3$. Elemental analysis was provided by Atlantic Microlab (Norcross, GA, US). Optical microscopy and phase identification were performed using a PZO ‘Biolar’ polarised microscope equipped with an HCS 402 Instec hot stage. Thermal analysis was obtained using a 2920 DSC (TA Instruments, New Castle, DE, US). Transition temperatures (onset) and enthalpies were obtained using small samples (0.3–0.6 mg) and a heating rate of 5 K minute^{-1} under a flow of nitrogen gas. The clearing transition was less than 0.3 K wide. THF was distilled over potassium in the presence of benzophenone. CH_3CN was distilled over CaH_2, and NEt_3 was distilled over KOH. Anhydrous NMP was obtained commercially.

$ZnCl_2$ and LiCl were dried at 100°C under vacuum for 1 hour before use. Alkylmagnesium reagents were prepared in refluxing anhydrous THF (20 ml) from the corresponding alkyl bromides (around 6 mmol) in the presence of magnesium activated by I_2 vapour. The concentration of the Grignard reagent (0.1–0.2 M) was determined using I_2 in the presence of LiCl following a literature procedure (*28*).

4.2 Synthesis

*4.2.1 4-(4-n-Alkylphenylazo)phenols (**1[n]**) general procedure*

Under nitrogen atmosphere, a THF solution of alkylmagnesium bromide (RMgBr) (2.3 mmol) was added slowly to anhydrous $ZnCl_2$ (0.347 g, 2.62 mmol), resulting in an exothermic reaction. After cooling to room temperature, a solution of LiCl (0.085 g, 2.00 mmol) in anhydrous THF (3 ml) was added, giving a nearly homogeneous organozinc reagent. In a separate three-necked flask under nitrogen atmosphere, equipped with stir bar, condenser, septa and stopcock, NaH (0.053 g, 1.33 mmol) was added to a solution of iodide **3** (0.500 g, 1.54 mmol) in anhydrous THF (5 ml), followed by anhydrous NMP (2 ml), PEPPSI-IPr (0.020 g, 2 mol%) and the organozinc reagent. The resulting reaction mixture was gently refluxed until no more starting **3** was detected by ^{1}H NMR (around 2 hours). The reaction was cooled and quenched by addition of NH_4Cl (25 ml). The resulting mixture was extracted with CH_2Cl_2 (3×10 ml), the organic layers were combined, dried (Na_2SO_4), and evaporated to dryness. Phenol **1[n]** was isolated using column chromatography (CH_2Cl_2, $R_f = 0.35$). Analytical samples were obtained by recrystallisation from iso-octane, and also for **1[2]**, **1[4]**, **1[6]** and **1[14]** from CH_3CN containing toluene.

^{1}H NMR data for phenols **1[2]** (*5*). **1[4]** (*11*) and **1[6]** (*9*, *12*) are consistent with those reported in the literature.

*4.2.1.1 4-(4-n-Octylphenylazo)phenol (**1[8]**)* Yield 71%; mp 76°C; ^{1}H NMR δ 0.86 (t, J = 6.8 Hz, 3H), 1.20–1.37 (m, 10H), 1.59–1.69 (m, 2H), 2.65 (t, J = 7.8 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H). Elemental analysis: calculated for $C_{20}H_{26}N_2O\bullet0.5\ H_2O$: C, 75.20; H, 8.52; N, 8.77. Found: C, 75.62; H, 8.29; N, 8.74.

*4.2.1.2 4-(4-n-Decylphenylazo)phenol (**1[10]**)* Yield 53%; mp 77°C; ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.17–1.37 (m, 14H), 1.59–1.69 (m, 2H), 2.65 (t, J = 7.7 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.9 Hz, 2H). Elemental analysis: calculated for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.03; H, 8.97; N, 8.22.

*4.2.1.3 4-(4-n-Dodecylphenylazo)phenol (**1[12]**)* Mp 87°C; ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3H), 1.17–1.38 (m, 18H), 1.58–1.69 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 5.2 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 7.9 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). Elemental analysis: calculated for $C_{24}H_{34}N_2O$: C, 78.64; H, 9.35; N, 7.64. Found: C, 78.73; H, 9.34; N, 7.64.

*4.2.1.4 4-(4-n-Tetradecylphenylazo)phenol (**1[14]**)* Yield 40%; mp 91°C; ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.17–1.38 (m, 22H), 1.58–1.69 (m, 2H), 2.65 (t, J = 7.7 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H). Elemental analysis: calculated for $C_{26}H_{38}N_2O$: C, 79.14; H, 9.71; N, 7.10. Found: C, 78.66; H, 9.81; N, 6.94.

*4.2.1.5 4-(4-n-Hexadecylphenylazo)phenol (**1[16]**)* Yield 60%; mp 98°C; ^{1}H NMR δ 0.86 (t, J = 6.8 Hz, 3H), 1.17–1.37 (m, 26H), 1.58–1.68 (m, 2H), 2.65 (t, J = 7.7 Hz, 2H) 5.1 (s, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H). Elemental analysis: calculated for $C_{28}H_{42}N_2O$: C, 79.57; H, 10.02; N, 6.63. Found: C, 79.33; H, 10.22; N, 6.37.

*4.2.1.6 4-(4-n-Octadecylphenylazo)phenol (**1[18]**)* Yield 34%; mp 100°C; ^{1}H NMR δ 0.86 (t, J = 6.9 Hz, 3H), 1.17–1.38 (m, 30H), 1.57–1.69 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H). Elemental analysis: calculated for $C_{30}H_{46}N_2O$: C, 79.95; H, 10.29; N, 6.22. Found: C, 78.75; H, 10.19; N, 6.22.

*4.2.1.7 4-(4-n-Eicosylphenylazo)phenol (**1[20]**)* Yield 38%; 104°C ^{1}H NMR δ 0.86 (t, J = 7.0 Hz, 3H), 1.17–1.38 (m, 34H), 1.57–1.69 (m, 2H), 2.65 (t, J = 7.7 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.9 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.9 Hz, 2H). Elemental analysis: calculated for $C_{32}H_{50}N_2O$: C, 80.28; H, 10.53; N, 5.85. Found: C, 80.00; H, 10.74; N, 5.57.

*4.2.1.8 4-(4-n-Docosylphenylazo)phenol (**1[22]**)* Yield 38%; ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.17–1.39 (m, 38H), 1.59–1.69 (m, 2H), 2.65 (t, J = 7.8 Hz, 2H), 5.1 (s, 1H), 6.92 (d, J = 8.9 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H).

*4.2.2 4-(4-n-Alkylphenylazo)phenyl 4-pentylbenzoate (**2[n]**) general procedure*

Under nitrogen atmosphere, an orange solution of the appropriate phenol **1[n]** (0.075 g), anhydrous NEt_3 (2 molar equivalents), and anhydrous CH_3CN (3 ml) was stirred for 5 minutes at room temperature. 4-Pentylbenzoyl chloride (1.1 molar equivalents) was added dropwise. Solvent was evaporated, the residue was washed with hexane, and the solution was filtered to remove insoluble material. Evaporation gave the crude product, which was purified using a silica gel plug (CH_2Cl_2/hexane, 1:9). Repeated recrystallisation from iso-octane then from CH_3CN gave analytically pure benzoate **2[n]**.

*4.2.2.1 4-(4-n-Ethylphenylazo)phenyl 4-pentylbenzoate (**2[2]**)* 37% yield: ^{1}H NMR δ 0.89 (t, J = 6.7 Hz, 3H), 1.27 (t, J = 7.6 Hz, 3H), 1.28–1.35 (m, 4H), 1.65 (quint, J = 7.3 Hz, 2H), 2.69 (t, J = 7.7 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 7.28–7.36 (m, 6H), 7.84 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H). Elemental analysis: calculated for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.67; H, 7.00; N, 6.99.

*4.2.2.2 4-(4-n-Butylphenylazo)phenyl 4-pentylbenzoate (**2[4]**)* Yield 64%; ^{1}H NMR δ 0.89 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H), 1.29–1.41 (m, 6H), 1.58–1.70 (m, 4H), 2.63-2.72 (m, 4H), 7.28–7.36 (m, 6H), 7.83 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H). Elemental analysis: calculated for $C_{28}H_{32}N_2O_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.22; H, 7.50; N, 6.66.

*4.2.2.3 4-(4-n-Hexylphenylazo)phenyl 4-pentylbenzoate (**2[6]**)* Yield 24%: ^{1}H NMR δ 0.82–0.91 (m, 6H), 1.25–1.37 (m, 10H), 1.60–1.70 (m, 4H), 2.67 (t, J = 7.3 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 7.28–7.36 (m, 6H), 7.83 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.1 Hz, 2H). Elemental analysis: calculated for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95; N, 6.13. Found: C, 78.99; H, 8.05; N, 6.19.

*4.2.2.4 4-(4-n-Octylphenylazo)phenyl 4-pentylbenzoate (**2[8]**)* Yield 40%; ^{1}H NMR δ 0.86 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H), 1.23–1.37 (m, 14H), 1.60–1.70 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H). Elemental analysis: calculated for $C_{32}H_{40}N_2O_2$: C, 79.30; H, 8.32; N, 5.78. Found: C, 78.16; H, 8.16; N, 5.82.

*4.2.2.5 4-(4-n-Decylphenylazo)phenyl 4-pentylbenzoate (**2[10]**)* Yield 50%; ^{1}H NMR δ 0.82–0.92 (m, 6H), 1.21–1.37 (m, 18H), 1.59–1.67 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.69 (7.8 Hz, 2H), 7.28–7.36 (m, 6H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H). Elemental analysis: calculated for $C_{34}H_{44}N_2O_2$: C, 79.65; H, 8.65; N, 5.46. Found: C, 79.39; H, 8.66; N, 5.46.

*4.2.2.6 4-(4-n-Dodecylphenylazo)phenyl 4-pentylbenzoate (**2[12]**)* Yield 37%; ^{1}H NMR δ 0.87 (t, *J* = 7.8 Hz, 3H), 0.89 (t, *J* = 7.6 Hz, 3H), 1.21–1.37 (m, 22H), 1.59–1.67 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H). Elemental analysis: calculated for $C_{36}H_{48}N_2O_2$: C, 79.96; H, 8.95; N, 5.18. Found: C, 79.36; H, 8.96; N, 5.09.

*4.2.2.7 4-(4-n-Tetradecylphenylazo)phenyl 4-pentylbenzoate (**2[14]**)* Yield 56%; ^{1}HNMR δ 0.86 (t, *J* = 7.8 Hz, 3H), 0.89 (t, *J* = 7.6 Hz, 3H), 1.20–1.38 (m, 26H), 1.57–1.70 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.7, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 9.2 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H). Elemental analysis: calculated for $C_{38}H_{52}N_2O_2$: C, 80.24; H, 9.21; N, 4.92. Found: C, 80.06; H, 9.34; N, 4.93.

*4.2.2.8 4-(4-n-Hexadecylphenylazo)phenyl 4-pentylbenzoate (**2[16]**)* Yield 36%; ^{1}H NMR δ 0.86 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.3 Hz, 3H), 1.17–1.38 (m, 30H), 1.60–1.70 (m, 4H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 8.11 (d, *J* = 7.9 Hz, 2H). Elemental analysis: calculated for $C_{40}H_{56}N_2O_2$: C, 80.49; H, 9.46; N, 4.69. Found: C, 80.25; H, 9.53; N, 4.73.

*4.2.2.9 4-(4-n-Octadecylphenylazo)phenyl 4-pentylbenzoate (**2[18]**)* Yield 33%; ^{1}H NMR δ 0.86 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 1.18–1.39 (m, 34H), 1.60–1.70 (m, 4H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 7.4 Hz, 2H). Elemental analysis: calculated for $C_{42}H_{60}N_2O_2$: C, 80.72; H, 9.68; N, 4.48. Found: C, 80.61; H, 9.74; N, 4.51.

*4.2.2.10 4-(4-n-Eicosylphenylazo)phenyl 4-pentylbenzoate (**2[20]**)* Yield 69%; ^{1}H NMR δ 0.86 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H), 1.18–1.38 (m, 38 H), 1.58–1.70 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 9.4 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 2H). Elemental analysis: calculated for $C_{44}H_{64}N_2O_2$: C, 80.93; H, 9.88; N, 4.29. Found: C, 80.79; H, 10.02; N, 4.32.

*4.2.2.11 4-(4-n-Docosylphenylazo)phenyl 4-pentylbenzoate (**2[22]**)* Yield 44%; NMR δ 0.86 (t, *J* = 8.0 Hz, 3H), 0.89 (t, *J* = 7.7 Hz, 3H), 1.19–1.38 (m, 42 H), 1.57–1.70 (m, 4H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H). Elemental analysis: calculated for $C_{46}H_{68}N_2O_2$: C, 81.12; H, 10.06; N, 4.11. Found: C, 80.69; H, 10.12; N, 4.13.

*4.2.3 4-Iodophenylazophenol(21) (**3**)*

Concentrated HCl (10 ml) was added to a solution of 4-iodoaniline (8.66 g, 39.5 mmol), dissolved in acetone/H_2O (1:1, 100 ml), and cooled to 0°C. A cold solution of $NaNO_2$ in H_2O (50 ml) was added slowly. In a separate flask, phenol (4.02 g, 42.8 mmol), NaOH (1.68 g, 48.1 mmol) and Na_2CO_3 (6.97 g, 84.0 mmol) were dissolved in cold H_2O (100 ml). The diazonium salt solution was added slowly, forming a brown/orange precipitate, which was filtered and dried. The crude product was dissolved in hot aq. EtOH, insoluble material was filtered off, and upon cooling azophenol **3** crystallised out giving 9.85 g (77% yield) of orange crystals: mp 167°C (lit. (*29*) mp 172°C); ^{1}H NMR δ 5.3 (br s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.61

(d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H).

*2.2.4 2,4-bis-(4-Iodophenylazo)phenol (**4**)*

The fraction insoluble in hot EtOH obtained in the preparation of **3** (0.50 g) was recrystallised from toluene giving brown crystals: mp 235–238°C dec.; ^{1}H NMR δ 4.9 (br s, 1H), 7.15 (d, J = 8.9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 4H), 7.88 (d, J = 9.3 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 8.03 (dd, J_1 = 8.6 Hz, J_2 = 2.3 Hz, 1H), 8.56 (d, J = 1.7 Hz, 1H).

*2.2.5 4-(4-n-Alkylphenylazo)phenyl acetate (**5[n]**) general procedure*

Under nitrogen atmosphere, an orange solution of the corresponding phenol **1[n]** (0.10 g), anhydrous NEt_3 (1.1 molar equivalents) and CH_3CN (8 ml) was stirred for 5 minutes at rt. Acetic anhydride (1.1 molar equivalents) was added dropwise, immediately forming a yellow precipitate. Solvent was evaporated, the reaction mixture was quenched with $NaHCO_3/H_2O$ (10 ml, 1:1) and the product extracted into CH_2Cl_2 (3 × 10 ml). The organic layers were combined, dried (Na_2SO_4), and evaporated to dryness. Double recrystallisation from cold iso-octane and single recrystallisation from CH_3CN gave pure acetate **5[n]**.

*2.2.5.1 4-(4-n-Hexadecylphenylazo)phenyl acetate (**5[16]**)* Yield 69%; mp 76°C; ^{1}H NMR δ 0.86 (t, J = 7.5 Hz, 3H), 1.20–1.36 (m, 26H), 1.58–1.67 (m, 2H), 2.32 (s, 3H), 2.66 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H). Elemental analysis: calculated for $C_{30}H_{44}N_2O_2$: C, 77.54; H, 9.54; N, 6.03. Found: C, 77.65; H, 9.59; N, 6.02.

*2.2.5.2 4-(4-n-Octadecylphenylazo)phenyl acetate (**5[18]**)* Yield 88%; mp 79°C; ^{1}H NMR δ 0.86 (t, J = 6.7 Hz, 3H), 1.19–1.38 (m, 30H), 1.60–1.67 (m, 2H), 2.32 (s, 3H), 2.66 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H). Elemental analysis: calculated for $C_{32}H_{48}N_2O_2$: C, 78.00; H, 9.82; N, 5.69. Found: C, 78.00; H, 9.89; N, 5.70.

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