Supporting Information for

Synthesis and Hepatic Transport of Strongly Fluorescent Cholephilic Dipyrinones

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Supporting Information Available

The syntheses of **1c**, **2c**, **3c**; **1d**, **2d**, **3d**, **4d**, **6d**, **7d**, **8d**, **9d**, **10d**; and **1e**, **2e**, **3e**, **4e**, **6e**, **7e**, **8e**,
9e, **10e** are described. UV-visible spectral data from compounds **1–3** are available in Table S-1.

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Contents

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The spectral data were obtained in spectral grade solvents which were distilled under Ar stream just prior to use. Before the distillation CHCl_3 was passed through a basic alumina column. Distillation of $(\text{CH}_3)_2\text{SO}$ solvent was carried out at 0.5 mm Hg vacuum collecting the solvent at 0 °C and thawing it under Ar.

General procedure for sulfonation to 1b–1e. Finely powdered solid bridged dipyrinone **2b–2e** (0.40 mmol) was placed in a flask immersed in a cooling bath at 0 °C, and 5 mL of conc. H_2SO_4 (precooled to 0 °C) was added. The solid slowly dissolved to give a magenta colored solution, which was stirred for 2 h at 0 °C. Then the temperature was lowered to -5 to -10 °C, and the solution was slowly neutralized with sat. aq. Na_2CO_3 while introducing a stream of air in order to reduce foaming. After dilution with water to ~150 mL, extraction with CH_2Cl_2 resulted in removal of the starting material in the case of **1b** and **1c**. In the case of **1d** and **1e**, the product was also extracted. The latter two, after evaporation of CH_2Cl_2 , were purified by radial chromatography. In the case of **1b** and **1c**, the yellow alkaline aqueous solution was evaporated to dryness and the pigment was removed from the solid mixture with Na_2SO_4 by extraction with abs. EtOH. After evaporation of the ethanol, the residue was purified by radial chromatography.

General Procedure for Inserting Bridging Carbonyl. Dipyrinone **3a–3e** (0.50 mmol) was dissolved in 35 mL of dry CH_2Cl_2 . To this solution was added 0.41 g (2.50 mmol, 5 eq.) of 1,1'-carbonyldiimidazole, 0.38 g (2.50 mmol, 5 eq.) of DBU and 0.50 g of 4Å molecular sieve. The solution was allowed to reflux with magnetic stirring for 19 h before being cooled and filtered to remove the molecular sieve debris. The filtered solution was then washed sequentially with water (2 × 50 mL) and brine (50 mL) then dried over anh. MgSO_4 . The organic solvent was removed

(rotovap) to give a crude brownish oil, which was purified by radial chromatography (using 1% MeOH in CH₂Cl₂ as eluent) to give bright yellow crystals of the pure product.

General Procedure for Condensation to Dipyrinone. A solution of 2.0 mmol pyrrolinone **4a–4e** and 2.5 mmol of 3,5-dimethyl-2-formyl-1*H*-pyrrole (**5**)¹¹ in 8 mL of ethanol and 2.5 mL of 4 M KOH was heated at reflux for 1–2 days. The mixture was cooled and poured into 200 mL of ice water. The precipitated yellow product was collected by filtration, washed with water (3 × 50 mL) and dried under vacuum (P₂O₅) to give crude dipyrinones **3**. Alternatively, **3d–3e** were extracted into CH₂Cl₂. The extracts were washed with H₂O and, after removal of solvent, the residue was purified by radial chromatography. The products **3a–3e** were recrystallized from CH₃OH or CH₂Cl₂-hexane to give pure dipyrinones.

Sodium 2-*n*-Butyl-3,7,9-trimethyl-*N,N'*-carbonyl-(10*H*)-dipyrin-1-one-8-sulfonate (1c). Sulfonation according to the general procedure of 100 mg (0.35 mmol) of **2c** afforded 105 mg (77%) of **1c** with m.p. >300 °C; IR (thin film) ν 2928, 2360, 1751, 1379, 1214 cm⁻¹; ¹H-NMR (d₆-DMSO) δ 0.85 (3H, t, *J* = 7.3 Hz), 1.15–1.52 (4H, m), 2.13 (3H, s), 2.21 (3H, s), 2.26 (2H, t, *J* = 7.3 Hz), 2.77 (3H, s), 6.97 (1H, s) ppm; ¹³C-NMR (d₆-DMSO) δ 9.8, 10.5, 13.9, 14.1, 22.3, 23.0, 30.5, 98.8, 120.4, 126.2, 130.3, 131.7, 132.0, 134.9, 142.3, 143.3, 167.0 ppm; HRMS (FAB, 3-NBA): calcd.: 387.0991 (C₁₇H₂₀N₂O₅S, M+Na⁺); found: 387.0992, Δ = 0.1 mDa, error: 0.3 ppm.

2-*n*-Butyl-3,7,9-trimethyl-*N,N'*-carbonyl-(10*H*)-dipyrin-1-one (2c). Using the general procedure for inserting a bridging carbonyl, 0.30 g (1.16 mmol) of **3c** gave 0.22 g (0.77 mmol) of **2c** (66%) with m.p. 130–132 °C; IR (thin film) ν 2927, 1758, 1684, 1522, 1309 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.91 (3H, t, *J* = 7.3 Hz), 1.40 (2H, m), 1.50 (2H, m), 2.12, (3H, s), 2.14 (3H, s), 2.38

(2H, t, $J = 7.3$ Hz), 2.67 (3H, s), 6.00 (1H, s), 6.38 (1H, s) ppm; ^{13}C -NMR (CDCl_3) δ 9.6, 10.6, 13.8, 15.6, 22.4, 23.2, 30.6, 97.2, 117.1, 120.7, 126.7, 131.2, 131.3, 134.9, 140.6, 143.4, 167.2 ppm; Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2$ (284.4): C, 71.81; H, 7.10; N, 9.85. Found: C, 71.46; H, 7.22; N, 9.66.

2-*n*-Butyl-3,7,9-trimethyl-(10*H*)-dipyrroin-1-one (3c). The general procedure for dipyrroinone synthesis, using 0.25 g (1.63 mmol) of 3-*n*-butyl-4-methylpyrrolin-2-one (**4c**), gave a 44% yield of the desired dipyrroinone (0.19 g, 0.72 mmol), with m.p. 232–233 °C; IR (thin film) ν 3349, 2913, 1677, 1637, 1466, 1376, 1264 cm^{-1} ; ^1H -NMR (CDCl_3) δ 0.90 (3H, t, $J = 7.5$ Hz), 1.34 (2H, m), 1.49 (2H, m), 2.13 (3H, s), 2.19 (3H, s), 2.38 (2H, t, $J = 7.5$ Hz), 2.43 (3H, s), 5.82 (1H, s), 6.11 (1H, s), 10.41 (1H, br.s), 11.24 (1H, br.s) ppm; ^{13}C -NMR (CDCl_3) δ 9.8, 11.4, 13.2, 13.9, 22.6, 23.4, 31.4, 101.1, 110.0, 126.1, 127.9, 128.2, 129.1, 134.0, 142.1, 173.7 ppm; Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}$ (258.4): C, 74.38; H, 8.56; N, 10.84. Found: C, 74.25; H, 8.44; N, 10.37.

Sodium 3-*n*-Heptyl-2,7,9-trimethyl-N,N'-carbonyl-(10*H*)-dipyrroin-1-one-8-sulfonate (1d). According to the general procedure for sulfonation, 101 mg (0.31 mmol) of **2d** gave 109 mg (83%) of **1d**. It had IR (thin film) ν : 2925, 1768, 1686, 1361, 1318 cm^{-1} ; ^1H -NMR (d_6 -DMSO) δ 0.85 (3H, t, $J = 7.5$ Hz), 1.24–1.60 (10H, m), 1.84 (3H, s), 2.25 (3H, s), 2.57 (2H, t, $J = 7.5$ Hz), 2.80 (3H, s), 6.98 (1H, s); ^{13}C -NMR (d_6 -DMSO) δ 8.3, 10.1, 13.5, 13.9, 22.0, 23.7, 28.4, 28.7, 28.9, 31.2, 98.3, 120.0, 125.5, 125.7, 130.7, 131.4, 134.4, 142.8, 145.9, 166.9 ppm; HRMS (FAB, 3-NBA): calcd.: 451.1280 ($\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_5\text{Na}_2\text{S}$, $\text{M}+\text{Na}^+$); found, 451.1291, $\Delta = 1.1$ mDa, error: 2.5 ppm.

3-*n*-Heptyl-2,7,9-trimethyl-N,N'-carbonyl-(10*H*)-dipyrroin-1-one (2d). The general procedure for inserting bridging carbonyl on **3d** (0.30 g, 1.00 mmol) gave 0.25 g (0.75 mmol) of

2d (75%) with m.p. 102–104 °C; IR (thin film) ν 2926, 1762, 1689, 1637, 1522, 1309 cm^{-1} ; ^1H -NMR (CDCl_3) δ 0.89 (3H, t, $J = 7.3$ Hz), 1.16-1.56 (10H, m), 1.95 (3H, s), 2.15 (3H, s), 2.51 (2H, t, $J = 7.3$ Hz), 2.68 (3H, s), 6.02 (1H, s), 6.37 (1H, s) ppm; ^{13}C -NMR (CDCl_3) δ 8.6, 10.6, 13.9, 15.5, 22.6, 24.6, 28.9, 29.3, 29.4, 31.7, 97.1, 117.2, 120.7, 126.8, 126.9, 130.9, 135.0, 143.4, 145.3, 167.5 ppm; Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ (326.4): C, 73.59; H, 8.03; N, 8.58. Found: C, 73.15; H, 8.49; N, 8.43.

3-*n*-Heptyl-2,7,9-trimethyl-(10*H*)-dipyrroin-1-one (3d). The general procedure for dipyrroinone synthesis gave a 42% yield (0.30 g, 1.00 mmol) of the target dipyrroinone from 0.46 g (2.38 mmol) of 4-*n*-heptyl-3-methylpyrrolin-2-one (**4d**). Dipyrroinone **3d** had m.p. 232–233 °C; IR (thin film) ν 3347, 2926, 1671, 1637, 1581, 1475, 1378, 1261 cm^{-1} ; ^1H -NMR (CDCl_3) δ 0.88 (3H, t, $J = 7.0$ Hz), 1.25-1.75 (10H, m), 1.94 (3H, s), 2.18 (3H, s), 2.44 (3H, s), 2.52 (2H, t, $J = 7.3$ Hz), 5.82 (1H, s), 6.12 (1H, s), 10.33 (1H, br.s), 11.11 (1H, br.s) ppm; ^{13}C -NMR (CDCl_3) δ 8.7, 11.4, 13.4, 14.0, 22.6, 24.5, 29.0, 29.3, 30.4, 31.4, 101.3, 110.0, 122.9, 123.1, 126.2, 127.4, 134.2, 147.0, 173.9 ppm; Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}$ (300.4): C, 75.96; H, 8.72; N, 9.32. Found: C, 75.78; H, 8.92, N, 9.00.

4-*n*-Heptyl-3-methyl-3-pyrrolin-2-one (4d). To a solution of **6d** (2.0 g, 5.7 mmol) in absol. ethanol (100 mL) was added sodium borohydride (0.22 g, 5.7 mmol, 1.0 mol equiv.) in small portions over 5 min, with stirring. The mixture was stirred an additional 20 min before another portion of sodium borohydride (0.22 g, 5.7 mmol, 1.0 mol equiv.) was added. After stirring another 60 min, the solvent was removed (rotovap) to dryness. The oily brown residue was dried for 4 h under vacuum (1 mm Hg) then taken up into CH_2Cl_2 (100 mL). Inorganic solids were removed by suction filtration and washed with CH_2Cl_2 (3 x 30 mL). The combined organic

solution was passed through a short column of anh. NaHCO₃. Evaporation of the solvent (rotovap) yielded **4d** as a colorless solid (0.74 g, 66%). It had: m.p. 41-42 °C; IR (KBr, film) ν 3169, 3069, 2953, 2930, 2855, 1694, 1655, 1467, 1390, 1363, 1343, 1303, 1196 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.88 (3H, t, J = 7.3 Hz), 1.29-1.45 (8H, m), 1.47 (2H, m), 1.80 (3H, s), 2.35 (2H, t, J = 7.3 Hz), 3.81 (2H, d, J = 1.5 Hz), 7.26 (1H, brs) ppm; ¹³C-NMR (CDCl₃) δ 8.1, 13.8, 22.4, 27.7, 28.2, 28.8, 29.2, 31.5, 48.3, 128.0, 153.3, 176.4 ppm; GC-MS (R_t: 15 min) m/z (%) = 196[M⁺ + 1](4), 195[M⁺](1.3), 152(1.5), 138(1.6), 124(8), 111(13), 110(100), 96(45), 82(16).

Anal. Calcd for C₁₂H₂₁NO (195.3): C, 73.80; H, 10.84; N, 7.14;

Found: C, 72.48; H, 10.32; N, 7.17.

4-*n*-Heptyl-3-methyl-5-*p*-toluenesulfonyl-3-pyrrolin-2-one (6d). To a solution of **7d** (17.5 g, 42.4 mmol) in TFA (50 mL) was added H₂O (10 mL) dropwise over 2 min. After stirring at room temperature for 4 h, the solution was diluted with CH₂Cl₂ (200 mL); then, water (100 mL) was added. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic phase was washed with aq. NaHCO₃ (2 x 100 mL), water (100 mL) and brine (100 mL). After drying over anh. Na₂SO₄, and removing the solvent, the crude brown product was crystallized from CH₂Cl₂-hexane to yield colorless **6d** (7.4 g, 50%) suitable for carrying on to the next step. It had m.p. 196-198 °C: IR (KBr, film) ν 3377, 3183, 3072, 2956, 2927, 2857, 1701, 1597, 1594, 1462, 1404, 1386, 1357, 1339, 1316, 1304, 1290, 1215 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.87 (3H, t, J = 7.3 Hz), 1.30-1.51 (10H, m), 1.56 (3H, s), 2.40 (3H, s), 2.75 (2H, m), 5.13 (1H, s), 7.08 (1H, s), 7.29 (2H, d, J = 7.8 Hz), 7.63 (2H, d, J = 7.8 Hz) ppm; ¹³C-NMR (CDCl₃) δ 8.4, 13.8, 21.5, 22.4, 26.8, 28.4, 28.7, 29.2, 31.5, 76.4, 129.3, 129.5,

130.3, 133.5, 145.7, 147.7, 173.1 ppm; GC-MS (R_t : 14 min) m/z (%) = 348[$M^+ - 1$](3), 377(9), 331(35), 281(8), 269(12), 253(89), 209(18), 166(8), 138(14), 126(24), 125(100), 113(17).

5-Bromo-3-*n*-heptyl-4-methyl-2-*p*-toluenesulfonyl-1*H*-pyrrole (7d). In a 500-mL round-bottomed flask, fitted with a magnetic stirring bar and a dropping funnel, was added 3-*n*-heptyl-4-methyl-2-*p*-toluenesulfonyl-1*H*-pyrrole (**8d**, 16.3 g, 0.05 mol) and CH_2Cl_2 (100 mL), and the solution was chilled to $-5\text{ }^\circ\text{C}$ using an ice-salt bath. To this mixture was added a solution of bromine (8.4 g, 0.053 mol, 1.05 mol equiv.) in dichloromethane (100 mL) dropwise over 40 min. After the addition was complete, the mixture was stirred for a further 10 min at the same temperature. Dilute aq. ammonia (10%, 200 mL) was added dropwise to neutralize any acid in the solution. The organic layer was then separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 100). The combined organic phase was washed with aq. NaHCO_3 (2 x 100 mL), H_2O (100 mL) and brine (100 mL). After drying over anhyd. Na_2SO_4 , and removing the solvent, the crude brown product was crystallized from CH_2Cl_2 -hexane to yield colorless product **7d** (19.6 g, 95%). It had m.p. $90\text{--}92\text{ }^\circ\text{C}$; IR (KBr, film) ν 3259, 2932, 2856, 1719, 1654, 1594, 1550, 1534, 1436, 1371, 1295 cm^{-1} ; ^1H -NMR (CDCl_3) δ 0.86 (3H, t, $J = 7.3\text{ Hz}$), 1.27-1.29 (10H, m), 1.89 (3H, s), 2.38 (3H, s), 2.39 (2H, t, $J = 7.3\text{ Hz}$), 7.27 (2H, d, $J = 7.8\text{ Hz}$), 7.77 (2H, d, $J = 7.8\text{ Hz}$), 9.46 (1H, s) ppm; ^{13}C -NMR (CDCl_3) δ 10.0, 13.9, 21.3, 22.5, 24.8, 28.9, 29.5, 29.9, 31.6, 104.9, 126.7, 129.4, 129.6, 130.3, 130.6, 143.6, 146.4 ppm; GC-MS (R_t : 23 min): m/z (%) = 415[$M^+ + 3$](0.3), 414[$M^+ + 2$](0.9), 413[$M^+ + 1$](4.1), 412[M^+](0.9), 329(1.8), 257(13), 229(31.5), 199(40), 187(36), 177(33), 174(97), 172(100), 139(12), 134(38), 91(19).

Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{BrNO}_2\text{S}$ (412.4): C, 55.34; H, 6.35; N, 3.40;

Found: C, 55.34; H, 6.28; N, 3.26.

3-*n*-Heptyl-4-methyl-2-*p*-toluenesulfonyl-1*H*-pyrrole (8d). In a 250-mL round-bottom flask, fitted with a magnetic stirring bar and a dropping funnel, was added *p*-toluenesulfonylmethyl isocyanide (TosMIC, 18.9 g, 0.097 mol, 1.1 mol equiv.) and 1,1,3,3-tetramethylguanidine (22 mL, 20 g, 0.18 mol, 2.0 mol equiv.). To the stirred mixture was added a solution of 2-nitro-3-acetoxy-*n*-decane (**9d**, 21.5 g, 0.088 mol) in dry THF (80 mL) and 2-propanol (80 mL) dropwise over 2 h. The reaction mixture was allowed to stir at room temperature for 8 h before removing all solvent (rotovap). The resulting dark-brown oil was taken up into CH₂Cl₂ (200 mL), washed with H₂O (2 x 100 mL), 10% aq. HCl (2 x 50 mL), sat. aq. NaHCO₃ (100 mL) and brine (100 mL). After drying over anh. Na₂SO₄, the solution was passed through a short silica gel column (4 cm x 10 cm) and washed with CH₂Cl₂. After removing the solvent, the residue was crystallized from CH₂Cl₂-hexane to yield the pure title compound (**8d**, 43 g, 45%). It had m.p. 66-68 °C; IR (KBr, film): ν 3335, 2932, 2855, 1720, 1632, 1539, 1556, 1459, 1376, 1305 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.86 (3H, t, J = 7.3 Hz), 1.28-1.30 (10H, m), 1.92 (3H, s), 2.33 (3H, s), 2.53 (2H, t, J = 7.3 Hz), 6.66 (1H, s), 7.21 (2H, d, J = 7.8 Hz), 7.72 (2H, d, J = 7.8 Hz), 9.41 (1H, s) ppm; ¹³C-NMR (CDCl₃) δ 9.8, 13.8, 21.2, 22.5, 24.2, 29.0, 29.6, 30.1, 31.6, 120.4, 121.2, 126.5, 129.1, 129.5, 129.6, 140.4, 143.2 ppm; GC-MS (R_t: 22 min) *m/z* (%) = 335[M⁺ + 2](0.2), 334[M⁺ + 1](0.5), 333[M⁺](2.4), 249(1.3), 229(3.3), 199(2.1), 184(3.7), 178(92), 139(5), 94(100).

Anal. Calcd for C₁₉H₂₇NO₂S (333.5): C, 68.43; H, 8.16; N, 4.20;

Calcd for C₁₉H₂₇NO₂S · 1/4H₂O (338.5): C, 67.45; H, 8.13; N, 4.14;

Found: C, 67.33; H, 8.02; N, 4.03.

2-Nitrodecan-3-ol acetate (9d). 2-Nitrodecan-3-ol from **10d** (24 g, 0.12 mol) was added dropwise over 10 min to a solution of acetic anhydride (19 mL, 0.19 mol, 1.5 mol equiv.) and 4-dimethylaminopyrriidine (DMAP, 0.5 g) in CH₂Cl₂ (50 mL). Due to the exothermic reaction, the temperature of the solution can quickly reach 40 °C. The mixture was allowed to stir at room temperature overnight. Methanol (30 mL) was added to destroy excess of acetic anhydride. After stirring for a further 30 min, the solution was poured into dilute sodium bicarbonate (90 g in 500 mL of water) and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and filtered through a short column of silica. Evaporation of the solvent gave the desired product as a clear liquid (26.6 g, 92%) which is a mixture of two diastereomers and is sufficiently pure to be used in the next step. It had: IR (KBr, film): ν 2932, 2867, 1748, 1556, 1534, 1485, 1376, 1381, 1218 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.80 (3H, t, J = 6.8 Hz), 1.19 (10H, m), 1.47 (3H, 2xd, J = 6.8 Hz, J = 6.8 Hz), 1.54 (2H, m), 2.00 (3H, s), 4.64 (1H, m), 5.26 (1H, m) ppm; ¹³C-NMR (CDCl₃) δ 13.2, 13.7, 15.3, 20.3, 20.3, 22.3, 24.4, 25.1, 28.7, 28.9, 29.0, 30.1, 30.2, 31.4, 73.0, 73.2, 83.7, 84.3, 169.5 ppm; GC-MS (R_t: 12.2 and 12.4 min, two isomers). For the isomer at 12.2: m/z (%) = 200[M⁺ – NO₂] 228(0.2), 168(0.5), 138(7.7), 127(5.6), 111(6.9), 97(28), 83(77), 67(19), 55(100). For the isomer at 12.4 min: m/z (%) = 228(0.5), 199(0.7), 168(0.3), 156(20.9), 138(6.2), 127(5.3), 111(5.2), 97(29), 83(7.8), 67(18.70), 55(100).

2-Nitrodecan-3-ol (10d). To a mixture of *n*-octyl aldehyde (20 mL, 16.42 g, 0.13 mol), 2-propanol (50 mL) and potassium fluoride (0.37 g, 6.3 mmol 0.05 mol equiv.), nitroethane (9.1 mL, 9.7 g, 0.13 mol, 1.0 mole equiv.) was added at once under stirring. The mixture was warmed to 40 °C and kept 12 h under continuous stirring before removing the solvent (rotovap). The resulting oily crude product was filtered to remove solid inorganic waste and washed with

dichloromethane. After removing all solvent (rotovap), a colorless oily product was obtained (24 g, 94%), which is a mixture of two diastereomers and is sufficiently pure to be used directly for the next step. It had: IR (KBr, film): ν 3421, 2955, 3855, 1730, 1555, 1432, 1373, 1288 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ 0.82 (3H, t, J = 7.3 Hz), 1.21 (10H, m), 1.38 (2H, m), 1.45 (3H, s), 2.98 (1H, brs), 3.84, 4.10 (1H, m), 4.47 (1H, m) ppm (a mixture of two isomers); $^{13}\text{C-NMR}$ (CDCl_3) δ 12.1, 13.8, 15.8, 22.4, 24.9, 25.5, 28.9, 29.1, 29.1, 31.5, 32.7, 33.7, 72.1, 72.8, 86.3, 87.7 ppm.

Sodium 3-*n*-Decyl-2,7,9-trimethyl-N,N'-carbonyl-(10*H*)-dipyrrin-1-one-8-sulfonate (1e).

By the general procedure for sulfonation, pigment **2e** (184 mg, 0.50 mmol) was sulfonated to give, after chromatography, 186 mg (79%) of **1e** with m.p. decomp. >227–233 °C; IR (thin film) ν 2928, 1770, 1685, 1374, 1224, 1185 cm^{-1} ; $^1\text{H-NMR}$ (d_6 -DMSO) δ 0.83 (3H, t, J = 7.0 Hz), 1.22 (12H, m), 1.24 (2H, m), 1.50 (2H, m), 1.83 (3H, s), 2.25 (3H, s), 2.56 (2H, t, J = 7.4 Hz), 2.81 (3H, s), 6.98 (1H, s) ppm; $^{13}\text{C-NMR}$ (d_6 -DMSO) δ 8.3, 10.1, 13.5, 13.9, 22.0, 23.7, 28.6, 28.72, 28.74, 28.8, 28.9, 28.9, 31.2, 98.3, 120.0, 125.6, 125.7, 130.8, 131.5, 134.3, 142.8, 145.9, 166.8 ppm; HRMS (FAB, 3-NBA): calcd.: 493.1749 ($\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_5\text{Na}_2\text{S}$, $\text{M}+\text{Na}^+$); found 493.1739, Δ = 1.0 mDa, error: 2.1 ppm.

3-*n*-Decyl-2,7,9-trimethyl-N,N'-carbonyl-(10*H*)-dipyrrin-1-one (2e). Following the general procedure for introducing the carbonyl bridge, 0.68 g (2.00 mmol) of **3e** was cyclized to 0.69 g (93%) of **2e** with m.p. 82–83 °C; IR (thin film) ν 2928, 1767, 1687, 1638, 1527, 1434, 1360, 1190 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ 0.87 (3H, t, J = 7.0 Hz), 1.26 (10H, m), 1.34 (4H, m), 1.57 (2H, m), 1.95 (3H, s), 2.15 (3H, s), 2.50 (2H, t, J = 7.7 Hz), 2.67 (3H, s), 6.01 (1H, s), 6.36 (1H, s) ppm; $^{13}\text{C-NMR}$ (CDCl_3) δ 8.7, 10.7, 14.1, 15.6, 22.6, 24.7, 29.3, 29.35, 29.40, 29.5, 29.6, 31.8,

97.3, 117.2, 120.8, 126.7, 126.8, 130.8, 135.0, 143.5, 145.4, 167.7 ppm; Anal. Calcd. for $C_{23}H_{32}N_2O_2$ (368.5): C, 74.96; H, 8.75; N, 7.60. Found: C, 74.79; H, 8.74; N, 7.61.

3-*n*-Decyl-2,7,9-trimethyl-(10*H*)-dipyrroin-1-one (3e). Following the general procedure for dipyrroinone synthesis, 0.95 g (4.00 mmol) of 4-*n*-decyl-3-methylpyrrolin-2-one (**4e**) was condensed with **5** to afford after chromatography and recrystallization 0.93 g (68%) of **3e** with m.p. 174–175 °C; IR (thin film) ν 3349, 2927, 1672, 1637, 1579, 1471, 1377, 1262 cm^{-1} ; ^1H -NMR ($CDCl_3$) δ 0.88 (3H, t, $J = 6.8$ Hz), 1.30 (14H, m), 1.56 (2H, m), 1.94 (3H, s), 2.18 (3H, s), 2.45 (3H, s), 2.53 (2H, t, $J = 7.7$ Hz), 5.83 (1H, d, $^4J = 1.7$ Hz), 6.13 (1H, s), 10.49 (1H, br.s), 11.37 (1H, br.s) ppm; ^{13}C -NMR ($CDCl_3$) δ 8.7, 11.5, 13.4, 14.1, 22.7, 24.6, 29.3, 29.4, 29.48, 29.54, 29.6, 30.5, 31.9, 101.4, 110.1, 123.0, 123.2, 126.3, 127.5, 134.3, 147.1, 174.1 ppm; Anal. Calcd. for $C_{22}H_{34}N_2O$ (342.5): C, 77.14; H, 10.01; N, 8.18. Found: C, 76.83; H, 9.75; N, 8.01.

4-*n*-Decyl-3-methyl-3-pyrrolin-2-one (4e). To a solution of 1.57 g (4.00 mmol) of tosylpyrrolinone **6e** in 40 mL of abs. EtOH was added sodium borohydride (182 mg, 4.80 mmol) during 5 min and after 10 min—another 182 mg (4.80 mmol) portion. After 10 min the solvent was evaporated under vacuum and the residue was partitioned between 100 mL of CH_2Cl_2 and 30 mL of 1% aq. HCl. The organic layer was washed with H_2O (2 x 30 mL), dried (Na_2SO_4), filtered and the solvent was evaporated under vacuum. The residue was purified by radial chromatography and recrystallization from CH_3OH-H_2O to give 0.86 g (91%) of pyrrolinone **4e** with m.p. 63-64 °C; IR (thin film) ν 3200, 3076, 2955, 2853, 1700, 1678, 1477, 1383, 1354, 1200, 1140; ^1H -NMR ($CDCl_3$) δ 0.87 (3H, t, $J = 6.8$ Hz), 1.26 (14H, m), 1.47 (2H, m), 1.79 (3H, br.t, $^5J = 1.3$ Hz), 2.35 (2H, t, $J = 7.7$ Hz), 3.82 (2H, br.q, $^5J = 1.3$ Hz), 7.08 (1H, br.s) ppm;

^{13}C -NMR (CDCl_3) δ 8.3, 14.0, 22.6, 27.8, 28.3, 29.2, 29.3, 29.4, 29.47, 29.50, 31.8, 48.5, 128.0, 153.6, 176.7 ppm.

Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{NO}$: C, 75.89; H, 11.47; N, 5.90.

Found: C, 76.18; H, 11.85; N, 5.95

4-*n*-Decyl-3-methyl-5-*p*-toluenesulfonyl-3-pyrrolin-2-one (6e). Bromopyrrole **7e** (2.27 g, 5.00 mmol) was treated with a mixture of TFA (80 mL) and H_2O (16 mL) for 17 h at room temperature. The solution was diluted with 300 mL of H_2O and the product was extracted with CH_2Cl_2 (5 x 50 mL). The combined extracts were washed with 5% aq. NaHCO_3 (100 mL), then with H_2O (2 x 100 mL) and after drying over Na_2SO_4 and filtration, the solvent was evaporated under vacuum. The residue was purified by radial chromatography and recrystallization from hexane to afford 1.78 g (91%) of pyrrolinone **6e** with m.p. 124-125 °C; IR (thin film) ν 3369, 3179, 2955, 2853, 1704, 1597, 1407, 1383, 1354, 1290, 1140; ^1H -NMR (CDCl_3) δ 0.88 (3H, t, J = 6.7 Hz), 1.28 (14H, m), 1.47 (1H, m), 1.57 (3H, s), 1.66 (1H, m), 2.42 (3H, s), 2.46 (1H, m), 2.72 (1H, m), 5.11 (1H, s), 6.50 (1H, br.s), 7.29 (2H, m, ^3J = 8.1 Hz), 7.64 (2H, m, ^3J = 8.1 Hz) ppm; ^{13}C -NMR (CDCl_3) δ 8.5, 14.1, 21.7, 22.6, 26.9, 28.5, 29.234, 29.237, 29.4, 29.47, 29.50, 31.8, 77.1, 129.4, 129.6, 130.5, 133.6, 145.8, 147.7, 173.5 ppm.

Anal. Calcd. for $\text{C}_{22}\text{H}_{33}\text{NO}_3\text{S}$ (391.6): C, 67.48; H, 8.50; N, 3.58.

Found: C, 67.80; H, 8.54; N, 3.51.

5-Bromo-3-*n*-decyl-4-methyl-2-*p*-toluenesulfonyl-1*H*-pyrrole (7e). To a cooled to 0 °C solution of 3.76 g (10.00 mmol) of pyrrole **8e** in 80 mL of anh. CH_2Cl_2 was added a solution of 7.50 g (20.00 mmol) of phenyltrimethylammonium tribromide in 70 mL of CH_2Cl_2 during 15

min. After the addition was complete, the mixture was stirred for 15 min at 0 °C, then diluted with 200 mL of CH₂Cl₂ and washed with 5% aq. Na₂S₂O₃ (2 x 100 mL) and with H₂O (2 x 100 mL). After drying over MgSO₄, filtration and evaporation of the solvent, the residue was purified by radial chromatography and recrystallization from hexane to give 4.06 g (89%) of bromopyrrole **7e** with m.p. 89-90 °C; IR (thin film) ν 3271, 2935, 1719, 1637, 1531, 1448, 1372, 1289 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.89 (3H, t, J = 7.0 Hz), 1.26 (16H, m), 1.90 (3H, s), 2.40 (3H, s), 2.55 (2H, t, J = 7.6 Hz), 7.27 (2H, m, ³J = 8.3 Hz), 7.77 (2H, m, ³J = 8.3 Hz), 9.10 (1H, br.s) ppm; ¹³C-NMR (CDCl₃) δ 9.9, 14.1, 21.5, 22.7, 24.9, 29.3, 29.4, 29.55, 29.62, 29.7, 30.0, 31.9, 105.0, 120.7, 124.3, 126.8, 129.8, 130.7, 139.7, 143.8 ppm.

Anal. Calcd for C₂₂H₃₂BrNO₂S (454.5): C, 58.14; H, 7.10; N, 3.08.

Found: C, 58.49; H, 7.23; N, 3.09.

3-*n*-Decyl-4-methyl-2-*p*-toluenesulfonyl-1*H*-pyrrole (8e). To a solution of 9.76 g (50.00 mmol) of TosMIC and 12.4 mL (100.00 mmol) of tetramethylguanidine in 50 mL of *i*-propanol:THF = 1:1 was added a solution of nitroacetate **9e** (14.30 g, 50.00 mmol) in 12 mL of *i*-propanol:THF = 1:1 during 45 min and the mixture was stirred for 20 h. After dilution with 200 mL of CH₂Cl₂, it was washed with 5% aq. HCl (100 mL), then with 5% aq. NaHCO₃ (100 mL) and H₂O (3 x 100 mL). The solution was dried over MgSO₄, filtered, and the solvents evaporated under vacuum. The residue was purified by radial chromatography and recrystallization from hexane to afford 11.45 g (61%) of pyrrole **8e** with m.p. 63-64 °C; IR (thin film) ν 3340, 2936, 1719, 1634, 1531, 1456, 1373, 1285 cm⁻¹; ¹H-NMR (CDCl₃) δ 0.89 (3H, t, J = 7.1 Hz), 1.26 (16H, m), 1.96 (3H, d, ⁴J = 0.9 Hz), 2.39 (3H, s), 2.54 (2H, t, J = 7.6 Hz), 6.69 (1H, dq, ³J = 2.8, ⁴J = 0.9 Hz), 7.26 (2H, m, ³J = 8.4 Hz), 7.75 (2H, m, ³J = 8.4 Hz), 8.92 (1H,

br.s) ppm; ^{13}C -NMR (CDCl_3) δ 10.0, 14.1, 21.4, 22.6, 24.3, 29.3, 29.5, 29.55, 29.61, 29.8, 30.2, 31.9, 120.7, 121.1, 123.1, 126.6, 129.6, 129.8, 140.3, 143.3 ppm.

Anal. Calcd. for $\text{C}_{22}\text{H}_{33}\text{NO}_2\text{S}$ (375.6): C, 70.35; H, 8.86; N, 3.73.

Found: C, 70.14; H, 9.11; N, 3.72.

3-Acetoxy-2-nitrotridecane (9e). Crude alcohol **10e** was acetylated with 18.8 mL (0.20 mol) of acetic anhydride in 60 mL of anh. CH_2Cl_2 in the presence of 50 mg of DMAP for 18 h at room temperature. Excess of acetic anhydride was destroyed with methanol (15 mL) added during 20 min, and after 1 h the mixture was diluted with 100 mL of CH_2Cl_2 . The solution was poured carefully into 150 mL of sat. aq. NaHCO_3 , then washed with H_2O (3 x 100 mL), dried (MgSO_4), filtered and the solvents were evaporated under vacuum. The residue was kept under 0.5 mm Hg vacuum at 40 °C for 3 h to give 27.5 g (96% from aldehyde) acetate **9e** as a mixture of erythro and threo diastereomers (1:1 ratio) which was used without further purification in the next step. ^1H -NMR (CDCl_3) δ 0.88 (3H, t, J = 7.0 Hz), 1.25 (16H, m), 1.52, 1.54 (2 x 1.5H, 2 x d, J = 6.7, 6.8 Hz), 1.55, 1.63 (2 x 1H, 2 x m), 2.05, 2.07 (2 x 1.5H, 2 x s), 4.65 (0.5H, qd, J = 6.9, 4.0 Hz), 4.70 (0.5H, qd, J = 6.9, 6.9 Hz), 5.28, 5.31 (2 x 0.5H, 2 x m) ppm; ^{13}C -NMR (CDCl_3) δ 13.4, 14.0, 15.6, 20.6, 20.7, 22.6, 24.5, 25.3, 29.1, 29.2, 29.27, 29.30, 29.4, 29.5, 30.2, 30.3, 31.8, 73.2, 73.4, 83.8, 84.5, 169.8, 170.0 ppm.

2-Nitrotridecan-3-ol (10e). To a solution of 17.0 g (0.10 mol) of 1-undecylic aldehyde and 9.0 g (0.12 mol) of nitroethane in 10 mL of anh. CH_3CN was added slowly 1.5 mL (10 mmol) of DBU and the mixture was stirred for 24 h. The mixture was diluted with 200 mL of EtOAc - Et_2O (1:1) and washed with 5% aq. HCl (100 mL) and H_2O (3 x 100 mL). After drying (MgSO_4) and filtration, the solvents were evaporated under vacuum and the residue was kept

under 0.5 mm Hg vacuum at 40 °C for 3 h to afford an almost quantitative yield of nitroalcohol **10e** as a mixture of erythro and threo diastereomers (1:1 ratio) with sufficient purity to be used in the next step. $^1\text{H-NMR}$ (CDCl_3) δ 0.88 (3H, t, $J = 7.0$ Hz), 1.26 (16H, m), 1.43, 1.51 (2 x 1H, 2 x m), 1.55, 1.56 (2 x 1.5H, 2 x d, $J = 6.9, 6.9$ Hz), 2.26 (1H, br.s), 3.90, 4.17 (2 x 0.5H, 2 x m), 4.50 (0.5H, dq, $J = 6.9, 2.9$ Hz), 4.54 (0.5H, dq, $J = 6.9, 6.9$ Hz) ppm; $^{13}\text{C-NMR}$ (CDCl_3) δ : 12.3, 14.1, 16.2, 22.6, 25.1, 25.7, 29.28, 29.31, 29.4, 29.425, 29.426, 29.51, 29.54, 31.9, 32.99, 33.02, 72.1, 72.9, 86.3, 87.7 ppm; HRMS (FAB, 3-NBA) calcd. for $\text{C}_{13}\text{H}_{27}\text{NO}_3 + ^7\text{Li}$ 252.2151; found 252.2147, $\Delta = 0.4$ mDa, error 1.6 ppm.

Table S-1. UV-vis Data for N,N'-Carbonyl-bridged Dipyrinones **1** and **2**, and their Dipyrinone Precursors (**3**).^a

Dipyrinone Pigment	$\epsilon_{\max}$ ($\lambda_{\max}$, nm)						
	Benzene	CHCl ₃	(CH ₃) ₂ CO	CH ₃ OH	CH ₃ CN	(CH ₃) ₂ SO	H ₂ O
1a	15,300 (417)	14,500 (418)	16,200 (419)	16,200 (412)	14,500 (415)	16,200 (421)	8,500 (412)
1b	9,600 (408)	9,600 (406)	10,600 (411)	9,600 (403)	10,600 (407)	9,600 (414)	6,700 (404)
1c	9,800 (414)	9,800 (415)	11,100 (417)	11,100 (410)	11,100 (415)	10,500 (419)	9,800 (411)
1d	14,900 (409)	14,900 (409)	16,700 (414)	16,700 (408)	15,800 (411)	15,800 (418)	14,900 (409)
1e	16,600 (407)	17,800 (411)	16,900 (411)	18,400 (412)	17,900 (414)	18,300 (421)	16,000 (413)
2a	17,500 (423)	17,200 (420)	16,800 (412)	17,400 (420)	14,100 (409)	17,900 (420)	<i>b</i>
2b	14,500 (413)	15,900 (423)	13,900 (413)	13,900 (421)	15,200 (416)	13,900 (418)	<i>b</i>
2c	18,000 (414)	18,600 (421)	18,600 (413)	18,600 (420)	18,000 (416)	18,600 (420)	<i>b</i>
2d	14,800 (413)	15,500 (424)	14,800 (413)	14,800 (421)	15,500 (416)	15,500 (420)	<i>b</i>
2e	18,500 (425)	18,300 (421)	18,300 (415)	18,300 (421)	18,500 (416)	18,800 (421)	<i>b</i>
3a	33,200 (402)	26,400 (400)	24,300 (347)	26,900 (408)	24,900 (396)	29,000 (406)	<i>b</i>
3b	32,100 (402)	28,200 (400)	22,400 (396)	25,000 (409)	23,700 (396)	24,400 (405)	<i>b</i>
3c	38,200 (402)	33,000 (400)	33,000 (396)	36,700 (407)	32,000 (395)	34,000 (405)	<i>b</i>
3d	34,800 (402)	30,500 (401)	29,000 (398)	32,000 (408)	29,000 (396)	28,300 (407)	<i>b</i>
3e	39,800 (403)	33,800 (399)	32,100 (397)	36,600 (408)	31,700 (395)	34,600 (407)	<i>b</i>

^a ϵ in L mol⁻¹ cm⁻¹ at 22 °C and concentrations $\sim 1.5 \times 10^{-5}$ M. ^b Insoluble.