Supplementary Material (ESI) for New Journal of Chemistry
This journal is (c) The Royal Society of Chemistry and
The Centre National de la Recherche Scientifique, 2008

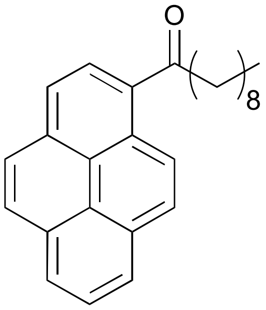
Binary low molecular weight functionalized organic gelators - characterization data

Pyrene derivatives

Shreedhar Bhat, Arno Hahma and Kimmo Leivo
Last updated: 20070920

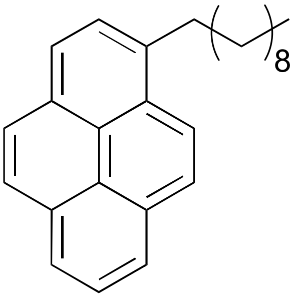
Spectral characterizations:
The solvent peak was adjusted to 77.23 for $CDCl_3$ and to 39.51 for DMSO-d6 at 30 ^{0}C. J values are given in Hz.

1-(pyren-1-yl)decan-1-one (1a), Hahma



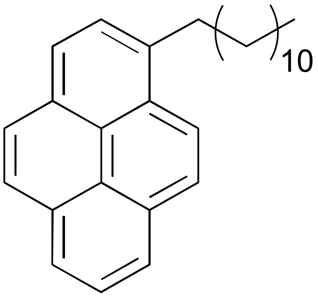
Decanoic acid (86 g, 0.5 mol) was first treated with excess of thionyl chloride (300 ml, 4.2 mol) and refluxed for 3-4 h. Excess of $SOCl_2$ was removed by distillation under reduced pressure. The decanoyl chloride (95 g, 0,5 mol) was mixed with pyrene (101 g, 0.5 mol) and DCE (1200 ml). To this mixture was added $TiCl_4$ (150 g, 0.75 mol) dropwise with stirring in ice bath below 5 ^{0}C during the addition. The brown complex formed was stirred for further 16 h at RT. The brown complex was cleaved by the addition of water and DCE was distilled off. The product was extracted into chloroform in a Soxhlet (1500 mL) and washed with water, saturated sodium bicarbonate (2 x 100 mL) and finally with water. The chloroform layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by recrystallization from hexane/chloroform 99/1. The pure product **1a** (156 g, 84 %) was isolated as yellow solid; mp. 59-61 ^{0}C (Found: C, 87.96; H, 7.86. Calc. for $C_{26}H_{38}O$: C, 87.60; H, 7.92%); ν_{max}(KBr)/cm^{-1} 3045, 2920, 1594, 1506, 1466, 1413, 1382, 1254, 1218, 1182, 1063, 958, 842 and 714; δ_H(500 MHz; $CDCl_3$) 0.88 (3 H, t, 7.0), 1.29 (10 H, m), 1.46 (2 H, m), 1.87 (2 H, q, 7.5), 3.20 (2 H, t, 7.5), 7.97-8.35 (8 H, m) and 8.86 (1 H, d, 9.5); δ_C(126 MHz; $CDCl_3$) 14.06, 22.64, 25.03, 29.26, 29.43, 29.46, 29.49, 31.86, 42.74, 123.99, 124.40, 124.84, 124.92, 125.05, 125.91, 125.92, 126.13, 126.34, 127.08, 127.37, 129.23, 129.33, 129.41, 130.61, 131.13, 133.08, 133.54 and 205.44; HRMS: *m/z* (TOF-ES+) 357.2237 (Calc. for : $C_{26}H_{28}O$+H 357.2216).

1-decylpyrene (1), Hahma



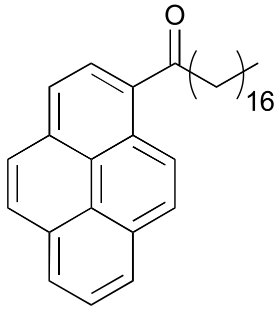
1-(pyren-1-yl)decan-1-one **1a** (148 g, 0.4 mol) and KOH (90 g, 1.6 mol) were mixed with digol (800 ml) and warmed to 180 ^{0}C. The solution turned brownish in color. To this solution hydrazine monohydrate (40 ml, 0.8 mol) was added slowly keeping temperature at 190-200 ^{0}C under nitrogen atmosphere for 12 h. Finally, the temperature was slowly raised to 220 ^{0}C. All the vapours were flushed out with nitrogen flow. The mixture was cooled to 50 ^{o}C. The product was extracted into 3 x 1000 ml hexane, which were filtered through 50 g of silica and dried over anhydrous $MgSO_4$. The combined extracts were evaporated to 1000 ml volume and left to crystallize over 3 days at RT. Additional crop was obtained by evaporating the hexane down to 400 ml and crystallizing overnight with seed crystals from the first batch. The pure product **1** (125 g, 88 %) was obtained as bright yellow solid; mp 69-71 ^{o}C (Found: C, 91.09; H, 8.92. Calc. for $C_{26}H_{30}$: C, 91.17; H, 8.83%); ν_{max}(KBr)/cm^{-1} 3039, 2954, 2917, 2850, 1463, 961, 841, 824, 760, 722, 707, 680 and 625; δ_H(500 MHz; $CDCl_3$) 0.88 (3 H, t), 1.2-1.35 (10 H, m), 1.38 (2 H, m), 1.50 (2 H, q), 1.85 (2 H, q), 3.33 (2 H, t), 7.87 (1 H, d, J 8.0), 7.97-8.20 (7 H, m) and 8.29 (1 H, d, J 9.0); δ_C(126 MHz; $CDCl_3$) 14.10, 22.68, 29.34, 29.60, 29.636, 29.644, 29.84, 31.91, 31.93, 33.60, 124.57, 124.73, 124.75, 125.107, 125.114, 125.70, 126.44, 127.04, 127.19, 127.52, 128.62, 129.70, 130.97, 131.48 and 137.35; HRMS: m/z (EI 70eV) 342.2355 (Calc. for C26H30: 342.2348).

1-dodecylpyrene (2), characterization data from Ref. 1



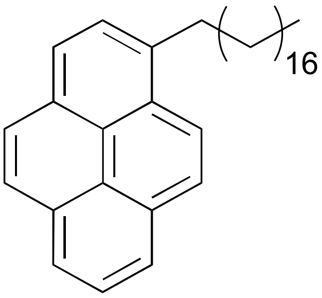
Synthesis procedure in Ref. 1; mp 72-73 °C (Found: C, 90.95; H, 9.33. Calc. for $C_{28}H_{34}$: C, 90.75; H, 9.25%); ν_{max}(thin film)/cm^{-1} 1465 and 840; δ_H(300 MHz; $CDCl_3$) 0.88 (3 H, t, J 6.8), 1.26-1.37 (16 H, m), 1.37 (2 H, q, J 7.5), 1.49 (2 H, m), 3.33 (2 H, t, J 7.7), 7.87 (1 H, d, J 7.8), 8.02 (2 H, m), 8.17 (5 H, m) and 8.29 (1 H, d, J 9.3); δ_C(75 MHz; $CDCl_3$) 22.07, 29.36, 29.61, 29.65, 29.68, 29.85, 31.93, 31.98, 33.64, 123.55, 124.59, 124.76, 124.77, 125.08, 125.74, 126.46, 127.07, 127.25, 127.54, 129.68, 130.96, 131.47 and 137.39; LRMS: *m/z* 384 (M^+).

1-(pyren-1-yl)octadecan-1-one (3a), Bhat and Leivo



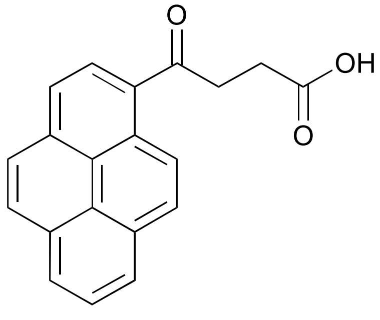
Stearic acid (4 g, 14.12 mmol) was first treated with excess of thionyl chloride (2.5 g, 21.2 mmol) and refluxed for 3-4 h. Excess of $SOCl_2$ was removed by distillation. The stearoyl chloride (3.6 g, 11.9 mmol) was mixed with pyrene (2 g, 9.9 mmol) and DCE (10 ml). To this mixture was added $TiCl_4$ (2.25 g, 11.9 mmol) dropwise with stirring over ice bath. The temperature was maintained below 5 ^{0}C during the addition. The brown complex formed was stirred for further 12 h. The brown complex was cleaved by the addition of water and dilute HCl. The product was extracted into DCM (20 mL) and washed with saturated sodium bicarbonate (2 x 85 mL), dil. HCl and finally with water. The DCM layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified further by chromatography over Merck 60 silica gel using DCM-hexane (1:9) as eluent. The pure product **3a** (3.25 g, 70 %) was isolated as yellow solid; mp 74-76 ^{o}C (Found: C, 87.09; H, 9.47. Calc. for $C_{34}H_{44}O$: C, 87.12; H, 9.46%); ν_{max}(KBr)/cm^{-1} 2953-2849, 1672, 1471, 843 and 716; δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, t, J 6.75), 1.25 (30 H, br s), 1.86 (2 H, m), 3.21 (2 H, t, J 7.5), 8.00-8.33 (8 H, m) and 8.87 (1 H, d, J 9.3); δ_C(63 MHz; $CDCl_3$) 14.11, 22.69, 25.03, 29.36, 29.44, 29.50, 29.62, 29.66, 29.70, 31.93, 42.73, 123.99, 124.40, 124.84, 125.04, 125.92, 126.13, 126.34, 127.08, 129.24, 129.33, 129.42, 130.60, 131.12, 133.05, 133.54 and 205.43; HRMS: *m/z* (EI 70eV) 469.3383 (Calc. for $C_{34}H_{44}O$: 469.3426).

1-octadecylpyrene (3), Bhat , Hahma and Leivo



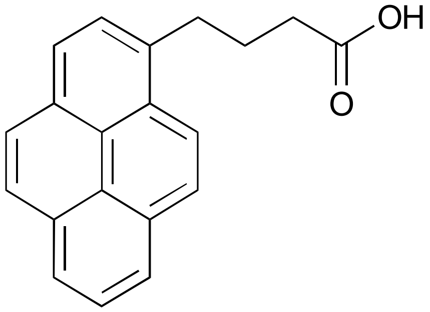
1-(pyren-1-yl)octadecan-1-one **3a** (0.5 g, 1.07 mmol) was mixed with KOH (0.36 g, 6.4 mmol) and digol (2 mL) and warmed to 110 ^{0}C. The hydrazine hydrate was then added dropwise to the above stirring mixture. This was stirred at 120 ^{0}C for 2-3 h. The temperature of the reaction was raised to 200 ^{0}C. After 1 h the reaction mixture was cooled to room temperature. The mixture was acidified with dil. HCl till neutral to litmus. The product was extracted in to chloroform and washed with saturated sodium bicarbonate (2 x 85 mL), dil. HCl and finally with water. The DCM layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified further by chromatography over Merck silica 60 using hexane as eluent. The pure product **3** (0.34 g, 70 %) was isolated as white solid; mp 83-84 ^{o}C (Found: C, 89.57; H, 10.27. Calc. for $C_{34}H_{46}$: C, 89.80, H, 10.19%); ν_{max}(KBr)/cm^{-1} 3039, 2965-2849, 1463 and 840; δ_H(250 MHz; $CDCl_3$) 0.89 (3 H, t, J 6.8), 1.26 (30 H, br s), 1.85 (2 H, m), 3.34 (2 H, t, J 7.5), 7.87 (1 H, d, J 7.8), 7.95-8.18 (7 H, m) and 8.29 (1 H, d, J 9.3); δ_C(63 MHz; $CDCl_3$) 14.11, 22.70, 29.37, 29.61, 29.71, 29.85, 31.94, 33.62, 123.54, 124.59, 124.75, 125.12, 125.73, 126.46, 127.06, 127.23, 127.54, 128.63, 129.70, 130.98, 131.49 and 137.38; HRMS: *m/z* (EI 70eV) 454.3595 (Calc. for $C_{34}H_{46}$: 454.3599).

4-oxo-4-(pyren-1-yl)butanoic acid (4a), Bhat



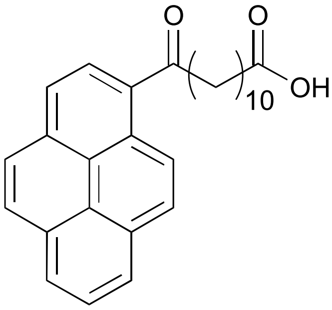
Succinic acid (0.4 g) was refluxed with excess of acetic anhydride (5 mL) for 10 h. After the reaction acetic anhydride and acetic acid were removed by distillation. A mixture containing pyrene (0.5 g, 2.5 mmol) and above succinic anhydride (about 0.39 g, 3 mmol) were dissolved in DCE (3 mL) and kept for stirring on ice bath. To this stirring solution $TiCl_4$ (0.56 g, 3 mmol) was added dropwise for 5 min and the stirring was continued for 24 h. The complex was hydrolyzed by the addition of water and dil. HCl. The product formed was extracted into EtOAc (15 mL) and washed with water (2 x 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The final product was further purified by chromatography over Merck silica 60 using acetone-DCM (1:9) as eluent. The pure product **4a** (0.51 g, 68 %) was obtained as pale yellow crystalline solid; mp 184-185°C (Found: C, 78.80; H, 4.52. Calc. for $C_{20}H_{13}O_3$ + ¼ H_2O: C, 78.55; H, 4.28%); ν_{max}(KBr)/cm^{-1} 3453, 1695, 1665 and 842; δ_H(250 MHz; DMSO-d6) 2.76 (2 H, t, J 6.0), 3.49 (2 H, t, J 6.0), 8.12-8.43 (7 H, m), 8.57 (1 H, d, J 8.3) and 8.77 (1 H, d, J 9.5); δ_C(63 MHz; DMSO-d6) 28.55, 36.92, 123.47, 123.96, 124.44, 125.97, 126.39, 126.44, 126.72, 127.15, 128.12, 129.14, 129.29, 129.94, 130.63, 132.48, 133.01, 173.89 and 203.18; HRMS: *m/z* (TOF-ES-) 301.0365 (Calc. for $C_{20}H_{14}O_3$ -H: 301.0865).

4-(pyren-1-yl)butanoic acid (4), Bhat



To a reaction mixture containing 4-oxo-4-(pyren-1-yl)butanoic acid **4a** (0.5 g, 1.65 mmol), digol (2.0 mL) and KOH (0.74 g, 13.2 mmol) at 110 ^{0}C was added hydrazine monohydrate (0.83 g, 16.5 mmol) slowly and stirred for 2 h at 120 ^{0}C. The temperature of the reaction was increased to 180 ^{0}C with continued stirring for at least 50 minutes. The reaction mixture was poured into ice bath and acidified till neutral to litmus and extracted with ethyl acetate (15 mL, 3 x 5 mL). Organic layer washed with water (2 x 5 mL) and dried over anhydrous Na_2SO_4. The crude product was further purified by column chromatography over Merck silica 60 using acetone-DCM (5:95) as eluent. The final product **4** (0.31 g, 65 %) was obtained as pale yellow solid; mp 182-183 °C (Found: C, 80.41; H, 5.42. Calc. for $C_{20}H_{16}O_2 + ½\ H_2O$: C, 80.84; H, 5.76%); ν_{max}(KBr)/cm^{-1} 3433, 2920, 2845, 1701 and 843; δ_H(250 MHz; $CDCl_3$) 2.22 (2 H, m), 2.52 (2 H, t, J 7.0), 3.43 (2 H, m), 7.87 (1 H, d, J 7.8), 7.95-8.20 (7 H, m) and 8.30 (1 H, d, J 9.3); δ_C(63 MHz; $CDCl_3$) 26.53, 32.68, 33.27, 123.25, 124.83, 124.86, 124.97, 125.03, 125.17, 125.88, 127.37, 127.50, 128.79, 130.09, 130.94, 131.46, 135.49 and 177.69; HRMS: *m/z* (EI 70eV) 288.1145 (Calc. for $C_{20}H_{16}O_2$: 288.1150).

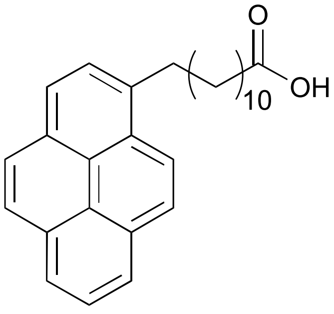
12-oxo-12-(pyren-1-yl)dodecanoic acid (5a), Bhat



Dodecanedioic acid (23 g, 0.1 mol) was first treated with excess of thionyl chloride (50 ml, 0.7 mol) and refluxed for 3-4 h. Excess of $SOCl_2$ was removed by distillation under reduced pressure. The dodecanedioic chloride was used without further purification.

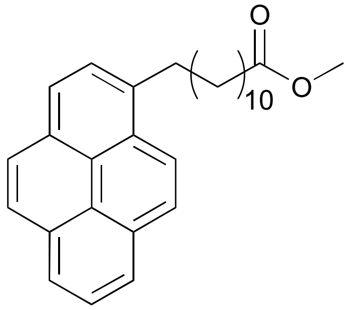
To a reaction mixture containing pyrene (10 g, 49.5 mmol) and dodecanedioic chloride (14 g, 52.4 mmol) in DCE (20 mL) was cooled in an ice bath for 15 min. To this stirring solution $TiCl_4$ (5.7 g, 52 mmol) was added dropwise for 20 min. The dark brown complex formed was allowed to warm to room temperature. The stirring was continued until the starting material disappeared by TLC. The complex was cleaved by the addition of water and the product was extracted into $CHCl_3$. Washed with water (2 x 5 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The product was further purified by chromatography over Merck silica 60 using acetone–DCM (1:9) as eluent. The pure product **5a** (5.0 g, 25 %) was obtained as pale yellow solid; mp 116-117 °C (Found: C, 50.27; H, 8.20. Calc. for $C_{28}H_{30}O_3$ + 14 H_2O: C, 50.43; H, 8.76%); ν_{max}(KBr)/cm^{-1} 3425, 3043, 2924, 2889, 2848, 1716, 1666 and 843; δ_H(250 MHz; DMSO-d6) 1.18 (10 H, br s), 1.26-1.45 (4 H, m), 1.71 (2 H, m), 2.14 (2 H, t, J 7.5), 3.22 (2 H, t, J 7.0), 8.09-8.39 (7 H, m), 8.50 (1 H, d, J 8.0) and 8.70 (1 H, d, J 9.3); δ_C(63 MHz; DMSO-d6) 24.38, 24.48, 28.52, 28.61, 28.68, 28.79, 28.83, 33.67, 42.00, 123.56, 124.06, 124.36, 124.47, 125.99, 126.43, 126.45, 126.77, 127.20, 128.15, 129.22, 129.27, 129.99, 130.68, 132.88, 132.96, 174.51 and 205.09; HRMS: *m/z* (TOF-ES-) 413.2171 (Calc. for $C_{28}H_{30}O_3$ - H: 413.2117).

12-(pyren-1-yl)dodecanoic acid (5), Bhat, Hahma and Leivo



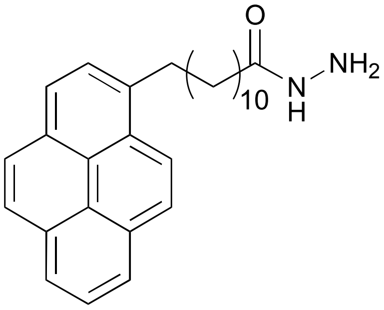
12-oxo-12-(pyren-1-yl)dodecanoic acid **5a** (0.3 g, 0.7 mmol) and KOH (0.3 g, 5.5 mmol) were mixed with digol (1 mL) and warmed to 110 ^{0}C the solution turned brownish in color. To this solution hydrazine monohydrate was added slowly and stirred at 120 ^{0}C for 2-3 h. Then the temperature was slowly raised to 200 ^{0}C. All the vapours were allowed to escape out under nitrogen flow. The mixture was cooled to room temperature and acidified with dil. HCl till neutral to litmus. The product was extracted into EtOAc, washed with water (2 x 5 mL) and dried over anhydrous Na_2SO_4. The crude product was concentrated to dryness under reduced pressure. The product was further purified by chromatography over Merck silica 60 using acetone-DCM (5:95) as eluent. The pure product **5** (0.19 g, 67 %) was obtained as pale yellow solid; mp 110-111 °C (Found: C, 80.52; H, 7.72. Batch 1: calc. for $C_{28}H_{32}O_2$+H_2O: C, 80.35; H, 8.18. Found: C, 82.58; H, 7.96. Batch 2: calc. for $C_{28}H_{32}O_2$+½ H_2O: C, 82.20; H, 8.12%); ν_{max}(KBr)/cm^{-1} 3435, 2921, 2846, 1705 and 844; δ_H(500 MHz; $CDCl_3$) 1.27 (10 H, br s), 1.38 (2 H, t, 7.5), 1.49 (2 H, q, 7.5), 1.63 (2 H, q, 7.5), 1.86 (2 H, q, 8.0), 2.34 (2 H, t, J 7.5), 3.34 (2 H, t, 8.0), 7.87 (1 H, d, J 8.0), 7.96-8.17 (7 H, m) and 8.29 (1 H, d, J 9.5); δ_C(126 MHz; $CDCl_3$) 24.67, 29.03, 29.19, 29.38, 29.54, 29.55, 29.56, 29.79, 31.92, 33.60, 33.88, 123.53, 124.59, 124.75, 124.76, 125.10, 125.11, 125.73, 126.45, 127.06, 127.23, 127.53, 128.62, 129.70, 130.97, 131.48, 137.35 and 179.21; HRMS: *m/z* (TOF-ES-) 399.2137 (Calc. for $C_{28}H_{32}O_2$-H: 399.2324).

Methyl-12-(pyren-1-yl)dodecanoate (6), Bhat, Hahma and Leivo



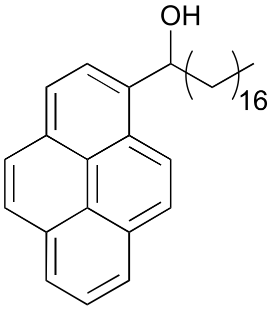
12-(pyren-1-yl)dodecanoic acid **5** (0.3 g, 0.75 mmol) was added to a solution containing 2 mL MeOH and 0.2 mL H_2SO_4 and refluxed for 4-5 h. After the completion, the reaction the mixture was neutralized with saturated $NaHCO_3$ and extracted into $CHCl_3$. The chloroform layer was washed with water (2 x 5 mL), dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purified further by column chromatography over Merck silica 60 using $CHCl_3$-hexane (2:8) as eluent. The pure product **6** (0.28 g, 90 %) was obtained as pale yellow solid; mp 57.5–58.0 °C (Found: C, 84.02; H, 8.31. Calc. for $C_{29}H_{34}O_2$ + ½ H_2O: C, 84.01; H, 8.27%); ν_{max}(KBr)/cm^{-1} 3455, 3040, 2928, 2852, 1741, 1155 and 841; δ_H(500 MHz; $CDCl_3$) 1.29 (10 H, br s), 1.39 (2 H, m), 1.50 (2 H, q, 7.5), 1.63 (2 H, m), 1.87 (2 H, q, 7.5), 2.31 (2 H, t, J 7.5), 3.34 (2 H, t, J 8.0), 3.68 (3 H, s), 7.87 (1 H, d, J 7.8), 7.97 – 8.17 (7 H, m) and 8.29 (1 H, d, J 9.0); δ_C(126 MHz; $CDCl_3$) 24.94, 29.12, 29.21, 29.40, 29.54, 29.55, 29.56, 29.79, 31.90, 33.57, 34.09, 51.36, 123.50, 124.56, 124.72, 124.74, 125.08, 125.09, 125.70, 126.43, 127.04, 127.19, 127.51, 128.60, 129.68, 130.95, 131.46, 137.31 and 174.26; HRMS: *m/z* (EI 70eV) 414.2551 (Calc. for $C_{29}H_{34}O_2$: 414.2558).

12-(pyren-1-yl)dodecanehydrazide (7), Bhat and Hahma



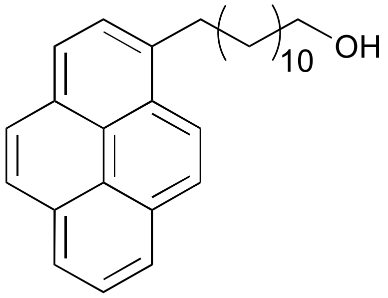
To a solution containing methyl-12-(pyren-1-yl)dodecanoate **6** (0.25 g, 0.6 mmol) in 3 mL methanol was added hydrazine hydrate (0.21 g, 4.2 mmol) and refluxed for 4 h. After the reaction the mixture was extracted into chloroform. The chloroform layer was washed with water (2 x 5 mL x 2) and dried over anhydrous Na_2SO_4. Chloroform was removed under reduced pressure. The crude material was purified further by column chromatography over Merck silica 60 using acetone-DCM (1:9) as the eluent. The pure product **7** (0.21 g, 80 %) was obtained as white solid; mp 122-123 °C (Found: C, 79.97; H, 8.113; N, 6.39. Calc. for $C_{28}H_{34}N_2O$ + ½ H_2O: C, 79.50; H, 8.33; N, 6.61%); ν_{max}(KBr)/cm^{-1} 3430, 3300, 2918, 2850, 1631, 1530 and 842; δ_H(500 MHz; $CDCl_3$) 1.27 (10 H, br s), 1.38 (2 H, m), 1.48 (2 H, m), 1.60 (2 H, m), 1.86 (2 H, q, 7.5), 2.12 (2 H, t, J 8.0), 3.34 (2 H, t, J 8.0), 3.88 (2 H, br s), 6.60 (1 H, br s), 7.87 (1 H, d, J 8.0), 7.96-8.17 (7 H, m) and 8.28 (1 H, d, J 9.5); δ_C(126 MHz; $CDCl_3$) 25.47, 29.25, 29.41, 29.54, 29.55, 29.79, 31.93, 33.60, 34.59, 123.54, 124.60, 124.77, 125.11, 125.13, 125.75, 126.47, 127.07, 127.24, 127.54, 128.64, 129.71, 130.98, 131.49 and 137.36; HRMS: *m/z* (TOF-ES+) 415.2757 (Calc. for $C_{28}H_{34}N_2O$+H: 415.2749).

1-(pyren-1-yl)octadecan-1-ol (8), Bhat



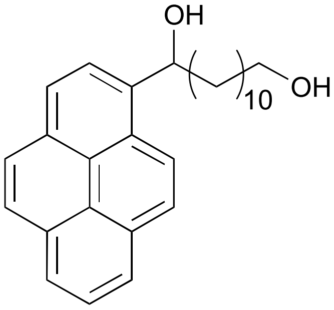
1-(pyren-1-yl)octadecan-1-one **3a** (0.1 g, 0.21 mmol) was dissolved in 1 mL of dry THF. This solution was added dropwise to a stirring suspension of LAH (0.08 g, 2.1 mmol) in 1 mL of dry THF. The resulting mixture was stirred for 3-4 h at RT. After the reaction, excess of LAH was neutralized by addition EtOAc and moist EtOH. The mixture was filtered and filtrate was concentrated and dried. The crude product was further purified by column chromatography over Merck silica 60 column using EtOAc-DCM (5:95) as eluent. The pure product **8** (0.072 g, 72 %) was isolated as a pale yellow powder; mp 85-87 °C (Found: C, 85.89; H, 9.90. Calc. for $C_{34}H_{46}O$ + ¼ H_2O: C, 85.93; H, 9.81%); ν_{max}(KBr)/cm^{-1} 3440, 2920, 2850, 1466, 1055 and 842; δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, t, 6.8), 1.24-1.61 (30 H, m), 2.00-2.13 (2 H, m), 5.79 (1 H, t, 6.5), 7.95-8.20 (8 H, m) and 8.36 (1 H, d, J 9.3); δ_C(63 MHz; $CDCl_3$) 14.33, 22.91, 26.49, 29.58, 29.92, 32.15, 39.42, 71.67, 122.79, 123.55, 125.14, 125.20, 125.21, 125.27, 125.43, 126.13, 127.40, 127.72, 127.77, 127.81, 130.84, 130.93, 131.66 and 138.68; HRMS: *m/z* (TOF-ES+) 493.2900 (Calc. for $C_{34}H_{46}ONa$: 493.3446).

12-(pyren-1-yl)dodecan-1-ol (9), Bhat



Methyl-12-(pyren-1-yl)dodecanoate **6** (0.1 g, 0.24 mmol) was dissolved in 1 mL of dry THF. This solution was added dropwise to a stirring suspension of LAH (0.092 g, 2.4 mmol) in 1 mL of dry THF. The resulting mixture was stirred for 3-4 h at RT. After the reaction, the excess of LAH was neutralized by addition EtOAc and moist EtOH. The mixture was filtered. Filtrate was concentrated and dried. The crude product was further purified by column chromatography over Merck silica 60 column using DCM-EtOAc (98:2) as the eluent. The pure product **9** (0.061 g, 66 %) was isolated as a white powder; mp 72-75 °C (Found: C, 86.54; H, 8.43. Calc. for $C_{28}H_{34}O$: C, 86.99; H, 8.86%); ν_{max}(KBr)/cm^{-1} 3411, 3038, 2920, 2849, 1465, 1057 and 843; δ_H(250 MHz; $CDCl_3$) 1.18 (1 H, br s), 1.28 (17 H, br s), 1.53 (2 H, m), 1.86 (2 H, q, 8.0), 3.34 (2 H, t, 7.8), 3.63 (2 H, t, 6.8), 7.87 (1 H, d, 7.8), 7.93-8.20 (7 H, m) and 8.29 (1 H, d, 9.3); δ_C(63 MHz; $CDCl_3$) 25.96, 29.64, 29.81, 30.05, 32.17, 33.05, 33.84, 63.33, 123.77, 124.82, 124.99, 125.33, 125.97, 126.69, 127.29, 127.47, 127.77, 128.85, 129.93, 131.20, 131.71 and 137.60; HRMS: *m/z* (TOF-ES+) 409.1206 (Calc. for $C_{28}H_{34}ONa$: 409.2507).

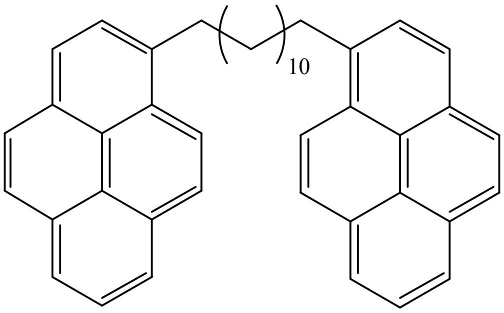
1-(pyren-1-yl)dodecane-1,12-diol (10), Bhat



12-oxo-12-(pyren-1-yl)dodecanoic acid **5a** (0.1 g, 0.24 mmol) was dissolved in 1 mL of dry THF. This solution was added dropwise to a stirring suspension of LAH (0.09 g, 2.4 mmol) in 1 mL of dry THF. The resulting mixture was stirred for 5-6 h at RT. After the reaction, excess of LAH was neutralized by addition EtOAc and moist EtOH. The mixture was filtered. Filtrate was concentrated and dried. The crude product was further purified by column chromatography over Merck silica 60 column using EtOAc/DCM (5:95) as eluent. The pure product **10** (0.068 g, 70 %) was isolated as a pale yellow powder; mp 111-112 °C (Found: C, 76.29; H, 8.93. Calc. for $C_{28}H_{34}O_2$ + 2 H_2O: C, 76.67; H, 8.73%); ν_{max}(KBr)/cm^{-1} 3415, 2920, 2850, 1465, 1057 and 843; δ_H(250 MHz; $CDCl_3$) 1.25 (14 H, br s), 1.54 (2 H, m), 2.05 (2 H, m), 3.62 (2 H, t, J 6.5), 5.80 (1 H, t, J 6.3), 7.97-8.21 (8 H, m) and 8.37 (1 H, d, J 9.5); δ_C(63 MHz; $CDCl_3$) 25.94, 26.47, 29.61, 29.73, 29.76, 29.81, 33.04, 39.42, 63.33, 71.68, 122.81, 123.57, 125.16, 125.22, 125.29, 125.46, 126.16, 127.42, 127.73, 127.79, 127.83, 130.86, 130.94, 131.67 and 138.69; HRMS: *m/z* (TOF-ES+) 425.2405 (Calc. for $C_{28}H_{34}O_2Na$: 425.2457).

Supplementary Material (ESI) for New Journal of Chemistry

1,1'-(dodecane-1,12-diyl)dipyrene (11), Hahma



To a reaction mixture containing pyrene (10.1 g, 0.05 mol) and dodecanedioic chloride (7 g, 0.026 mol; see **5a**) in dichloroethane (150 mL) was cooled in an ice bath for 15 minutes. To this stirred solution $TiCl_4$ (40 g, 0.2 mol) was added dropwise during 4 h at 5 °C or lower temperature. The dark brown complex formed was allowed to warm to room temperature. The stirring was continued until the pyrene disappeared by TLC. The complex was cleaved by the addition of water and the product was extracted into $CHCl_3$ in Soxhlet apparatus and washed with water (2 x 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure yielding a mixture of impure 1,12-di(pyren-1-yl)dodecane-1,12-dione and 12-oxo-12-(pyren-1-yl)dodecanoic acid **5a**, which were used as such in the next reaction.

200 ml of digol was added with KOH (25 g, 0.45 mol) and the mixture was heated to 180°C under nitrogen purge. Hydrazine hydrate (10 ml, 0.2 mol) was added dropwise keeping temperature above 180 °C under 20 h. After all hydrazine was added, temperature was raised to 220 °C for 4 h under nitrogen flush and the mixture was cooled to 50 °C. Hexane (5 x 500 ml) was added and refluxed for 20 minutes under vigorous stirring for each batch. The hexane phase was separated and mixed with 10 g of silica, filtered and evaporated under reduced pressure to 20 ml and then let evaporate to dryness slowly at normal pressure in a flask in a hood. Colorless crystalline powder of **11** (2.2 g, 15%) was obtained.

The digol phase was neutralized with 10 % HCl and extracted with chloroform (3 x 250 ml). The chloroform was washed with 2 x 100 ml of water and dried over $MgSO_4$. 75 g of silica was added to the chloroform and the solvent was evaporated to dryness under reduced pressure. The silica was eluted with THF-hexane-methanol (19:80:1) over 1.5 kg of Merck silica 60 in a preparative MPLC. The pure product **5** (3.5g, 18%) was recovered.

1,1'-(dodecane-1,12-diyl)dipyrene **11** (2.2 g, 15 %); mp 129-132 °C (Found: C, 92.57; H, 7.49. Calc. for $C_{44}H_{42}$: C, 92.58; H, 7.42%); ν_{max}(KBr)/cm^{-1} 3038, 2918, 2851, 1604, 1466, 1418, 1180, 963, 844, 758, 723, 706, 681 and 620; δ_H(500 MHz; $CDCl_3$) 1.28 (8 H, m), 1.37 (4 H, m), 1.48 (4 H, q), 1.82 (4 H, q), 3.33 (4 H, t), 7.86 (2 H, d, J 8.0), 7.96-8.03 (6 H, m), 8.08-8.16 (8 H, m) and 8.28 (2 H, d, J 9.5); δ_C(126 MHz; $CDCl_3$) 29.556, 29.580, 29.607, 29.802, 31.926, 33.602, 123.536, 124.583, 124.746, 124.758, 125.107, 125.120, 125.726, 126.455, 127.058, 127.226, 127.531, 128.631, 129.701, 130.974, 131.486 and 137.374; HRMS: *m/z* (EI 70eV) 570.3280 (Calc. for C44H42: 570.3287).

Chemicals

No.	Reagent	Company	Batch or Lot No.
1	Acetic anhydride	Riedel d.H.	33214
2	Acetone	BDH	20066.321/0601408
3	Benzene	Merck	1783
4	Capric acid (decanoic acid)	Fluka	21410
5	$CDCl_3$	Acros	AC16625
6	Chloroform	BDH	22711.324/0604759
7	1-Decanol	Fluka	30610
8	1,2-Dichloroethane (DCE)	J. T. Baker	46985
9	Dichloromethane (DCM)	Fluka	1141602-20105283
10	Diethyleneglycol (Digol)	Fluka	32160
11	DMSO-d6	Acros	17.489.29
12	1,12-Dodecanedioic acid	Fluka	44050
13	1-Dodecanol	Fluka	44100/254801
14	Ethyl acetate	Mallinckrodt	M9903/0019620002
15	n-Hexane	BDH	24577.460/07A230504
16	Hydrazine monohydrate	Fluka	433417/1 10503246
17	Hydrochloric acid	J. T. Baker	0531505004
18	Lithium aluminium hydride	Aldrich	S29494-185
19	Magnesium sulphate	Riedel d.H.	13143
20	Methanol	Merck	1.06009.2511
21	1-Octanol	Riedel d.H.	24134
22	Potassium hydroxide	BDH	B-400555- 409
23	Pyrene	Fluka	120266-19K
24	Silica gel 60(0.063-0.200 mm)	Merck	TA 1121734 -233
25	Sodium bicarbonate	J. T. Baker	0425110016
26	Sodium sulphate	Riedel d.H.	13462
27	Stearic acid	Fluka	NA
28	Succinic acid	Fluka	14080
29	Sulphuric acid	Fluka	41560
30	Tetrahydrofuran	LabScan	C20C11X/0527/6
31	2,4,5,7-Tetranitro-9-fluorenone	self-made	20070319/AH
32	Thionyl chloride	Merck	S36010-237
33	Titanium tetrachloride	Fluka	89541
34	Toluene	Baker	8077/0524107004
35	2,4,7-Trinitro-9-fluorenone	Aldrich	TP02128CE
36	1,3,5-Trinitrobenzene	self-made	20060828/AH

Reference

1 P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen and A. R. Raju, *Chem. Eur. J.*, 2003, **9**, 1922-1932.