**Supporting Information (11 pages)**

**General.** $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian VXR 500 or Varian Unity 300 spectrometer and were referenced to TMS, residual C*H*$Cl_3$ ($^{1}H$), C*H*$D_2OD$ ($^{1}H$) or *CH*$D_2COOD$ ($^{1}H$) and *C*$DCl_3$ ($^{13}C$), *C*$D_3OD$ ($^{13}C$) or *C*$D_3COOD$ ($^{13}C$). Mass spectrometric data were obtained on a JEOL SX 102A mass spectrometer. UV-Vis data were obtained using a Hewlett-Packard 8453 spectrophotometer. Fluorescence data were also obtained using a Perkin-Elmer LS-50B fluorometer. THF was dried over Na°/benzophenone, and $CH_2Cl_2$ was dried over $CaH_2$ prior to use. Other reagents and solvents were obtained commercially and were used as received unless otherwise noted. Differential Scanning Calorimetric experiments were conducted on a Calorimetry Sciences Corporation M4100 DCDSC. pH measurements were performed with a Lab Craft 101 pH meter.

**Compound 5:** To a round-bottom flask were added **4** (3.2 g, 4.26 mmol), *p*-toluenesulfonic acid (74 mg, 0.42 mmol), MeOH (15 mL) and $CH_2Cl_2$ (100 mL). The solution was stirred at room temperature for 3 h followed by addition of saturated aqueous $NaHCO_3$ (15 mL). The mixture was washed with brine then extracted with EtOAc (3 x 40 mL). The combined extracts were dried over anhydrous $Na_2SO_4$. The desired product (2.02 g, 92% yield) was isolated as a light yellow oil after flash chromatography (silica gel, EtOAc/hexanes 1:4). $^{1}H$ NMR ($CDCl_3$, 300 MHz) δ 6.01-5.83 (m, 3 H), 5.34-5.05 (series of multiplets, 6 H), 4.12-3.97 (m, 4 H), 3.82-3.66 (series of multiplets, 2 H), 3.60 (bs, 2 H), 3.54 (t, $J$ = 2.6 Hz, 1 H), 3.32 (d, $J$ = 1.5 Hz, 1 H),

3.20-3.08 (m, 1 H), 2.33-2.18 (m, 3 H), 2.16-1.95 (q, *J* = 9.8 Hz, 1 H), 1.91-0.97 (series of multiplets, 21 H), 0.90 (d, *J* = 6.7 Hz, 3 H), 0.89 (s, 3 H), 0.66 (s, 3 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 136.20, 136.01, 116.42, 115.65, 80.94, 79.27, 75.01, 69.54, 69.42, 68.88, 63.80, 46.56, 46.49, 42.76, 42.18, 39.96, 35.74, 35.56, 35.18, 31.96, 29.64, 29.04, 28.17, 27.80, 27.62, 23.38, 23.16, 17.96, 12.74; HRFAB-MS (thioglycerol+$Na^+$ matrix) *m/e*: ($[M+Na]^+$) 537.3908 (100%), cacld. 537.3920.

**Compound 6:** NaH (0.994g, 24.8 mmol) was added to a solution of compound **5** (1.28g, 2.48 mmol) in dry DMF (20 mL). The solution was then stirred for 30 min under $N_2$. Methyl iodide (1.54 mL, 24.8 mmol) was added, and the solution was stirred at r.t. under $N_2$ for an additional 8 h. The mixture was washed with water (15 mL) and extracted with $Et_2O$ (3 x 30 mL). The combined extracts were washed with brine and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified by chromatography (silica gel, 10% EtOAc in hexanes) to give the desired product (1.18 g, 90% yield) as a clear glass. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.96-5.88 (m, 3 H), 5.32-5.18 (m, 3 H), 5.16-5.05 (m, 3 H), 4.10-4.04 (m, 2 H), 4.02-3.98 (ddd, *J* = 12.3, 5.5, 1.5 Hz, 1 H), 3.54 (t, *J* = 2.4 Hz, 1 H), 3.36-3.28 (m, 6 H), 3.18-3.0 (m, 1 H), 2.31-2.18 (m, 3 H), 2.04-1.97 (q, *J* = 9.8 Hz, 1 H), 1.88-0.94 (series of multiplets, 21 H), 0.94-0.87 (m, 7 H), 0.66 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 125 MHZ) δ136.21, 136.01, 116.36, 115.62, 80.94, 79.30, 75.06, 73.76, 69.53, 69.43, 68.87, 58.69, 46.59, 46.51, 42.75, 42.22,

40.00, 35.80, 35.59, 35.21, 32.37, 29.09, 28.18, 27.79, 37.65, 26.48, 23.41, 23.18, 17.98, 12.75; HRFAB-MS (thioglycerol+Na matrix) *m/e*: ($[M+Na]^+$) 529.4249 (45.1 %); cacld. 529.4257.

**Compound 2a:** Compound **5** (0.402 g, 0.78 mmol) was dissolved in a 2:3:2 solution of $CH_3CN/H_2O/CCl_4$. $RuCl_3 \cdot H_2O$ (9 mg, .039 mmol) and $NaIO_4$ (2.15 g, 10.01 mmol) were added to the mixture and the solution was stirred at r.t. for 3 h. The precipitate was filtered off and washed with EtOAc (3 x 30 mL). The combined filtrate was washed with brine and dried over anhydrous $Na_2SO_4$. Chromatography (silica gel, $CH_2Cl_2$/MeOH/$NH_4OH$ 10:5:1.5) afforded the desired product (0.142 g, 30% yield) as a white solid. $^1H$ NMR ($CD_3COOD$/ $CDCl_3$, 500 MHz) 4.13 (s, 2 H), 4.09 (d, *J* = 6.5 Hz, 1H), 4.03 (m, 2H), 3.85 (s, 2H), 3.82 (s, 2H), 3.62 (t, 2H *J* = 4.5 Hz), 3.61 (s, 1H), 3.17 (s, 1H), 2.24-1.92 (series of multiplets, 6 H), 1.82-1.28 (series of multiplets, 16 H), 0.98 (d, *J* = 10.5 Hz, 3 H), 0.94 (s, 3 H), 0.71 (s, 3 H); $^{13}C$ NMR ($CD_3COOD/CDCl_3$, 125 MHz) δ 171.64, 171.34, 171.23, 166.85, 76.42, 70.71, 70.38, 66.86. 66.06, 65.46, 55.92, 54.02, 51.98, 50.08, 47.85, 46.17, 42.50, 42.22, 41.39, 39.91, 35.55, 34.52, 31.75, 30.33, 29.87, 29.68, 23.43, 22.92, 17.62, 12.64; HRFAB-MS (thioglycerol+Na matrix) *m/e*: ($[M+Na]^+$); 605.2920 (85.7%) cacld. 605.2938.

**Compound 3a:** Compound **6** (1.28 g, 2.42 mmol) was dissolved in a 2:3:2 solution of $CH_3CN/H_2O/CCl_4$. $RuCl_3 \cdot H_2O$ (27 mg, 0.121 mmol) and $NaIO_4$ (6.70 g, 31.3 mmol) were added to the mixture, and the solution was stirred at r.t. for 3 h. The precipitate was filtered off and washed with EtOAc (3 x 50 mL). The combined extracts were washed with brine and dried

over anhydrous $Na_2SO_4$. Chromatography (silica gel, $CH_2Cl_2$/MeOH/$NH_4OH$ 10:5:1.5) afforded the desired product (0.466 g, 33% yield) as a white solid. $^1H$ NMR ($CD_3COOD$/ $CDCl_3$, 500 MHz) δ 4.38 (d, *J* = 15.63 Hz, 1 H), 4.09 (s, 2 H), 4.07 (d, *J* = 16.2 Hz, 1 H), 3.92 (d, *J* = 16.12 Hz, 1 H), 3.90 (d, *J* = 15.62 Hz, 1 H), 3.58 (s, 1 H), 3.44 (d, *J* = 2.93 Hz, 1 H), 3.30 (t, *J* = 6.84 Hz, 2 H), 3.29 (s, 3 H), 3.21-3.14 (m, 1 H), 2.26-2.01 (series of multiplets, 4 H), 1.90-1.60 (series of multiplets, 9 H), 1.52-0.92 (series of multiplets, 11 H), 0.90 (d, *J* = 6.83 Hz, 3 H), 0.85 (s, 3 H), 0.63 (s, 3 H); $^{13}C$ NMR ($CD_3COOD/CDCl_3$, 125 MHz) δ 171.58, 171.27, 167.23, 74.02, 67.89, 66.89, 66.09, 58.07, 49.57, 47.30, 46.92, 43.09, 42.21, 40.26, 36.27, 35.50, 35.06, 30.16, 28.58, 28.16, 27.07, 26.26, 24.09, 23.78, 22.74, 18.17, 12.55; HRFAB-MS (thioglycerol+Na matrix) *m/e*: ($[M+4Na]^+$) 671.2778 (100 %); cacld. 671.2670.

**Dye solubilization aggregation studies.** Orange OT was purified by water precipitation of an acetone solution then recrystallized from ethanol. Sodium dodecyl sulfate (SDS) solutions were prepared by dilution of a 100 mM stock solution using Millipore water. Incrementally varied concentrations of the sodium salts **2b** and **3b** were prepared by dilution of a 100 m*M* solution using Millipore water. To ensure that all carboxylic acids were deprotonated, the pH value of each solution was adjusted to between 11-12 by addition of NaOH solution (this was necessary with only the most dilute solutions of amphiphiles). An aliquot of 1.5 mL of each sample was mixed (gently rocked) in the presence of excess solid orange OT for 3 days. Following

agitation, the excess orange OT was removed via filtration. An aliquot of 300 μL of each sample was then diluted with 1.2 mL of absolute ethanol to give a total of 1.5 mL. The absorbance of each sample was measured at 486 nm, through a 1 cm path-length cell. Each experiment was repeated at least 5 times with separately prepared solutions.

**Prodan fluorescence aggregation studies.** Prodan was purchased from Molecular Probes and was used as received. Incrementally varied concentrations of **2b** and **3b** were prepared by dilution of a stock solution as described above. An aliquot of 200 μL of a 5 μM solution of Prodan in Millipore water was added to 2 mL of each solution while gently stirring with a small magnetic stir bar in a cuvette for 20 seconds followed by sonication for an additional 20 seconds before measurements were made. Prodan fluorescence spectra were measured over a range of 350 - 600 nm ($\lambda_{ex}$ = 351 nm, slit width = 5 nm).

**Determination of p*K*a values.** Acid **3a** was dissolved in millipore water at concentration of 0.01 *M*. This solution was titrated with 0.01 *M* NaOH. The pH vs. the amount of NaOH added was plotted (Figure S1). The first derivative reached a maximum at ca. pH 5.7.

**Differential Scanning Calorimetry.**

DSC experiments were performed on 0.5 mL of solutions of **2a** and **3b** at concentrations incrementally varied between 0.001 to 0.010 *M* with a temperature range of 25 to 95 °C. No heats of aggregate dissociation were measured.

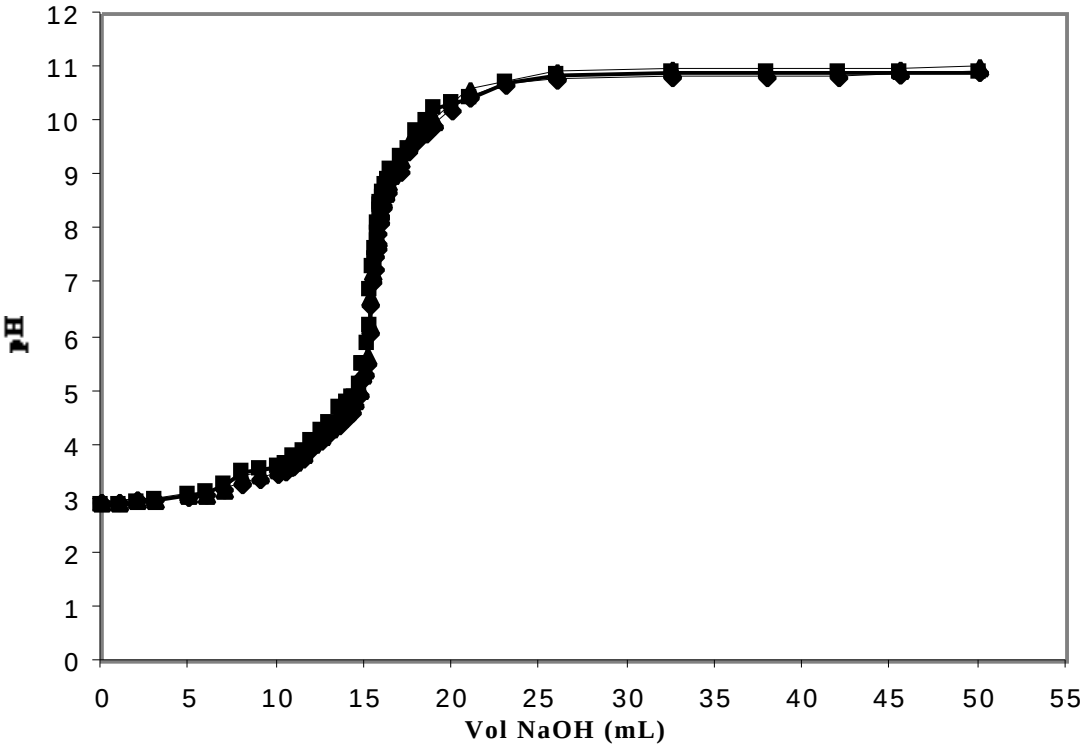


**Figure S1.** pH titration of **3b** (0.010 *M*) with NaOH (0.010 *M*). ▼,◆ and ■: experiments 1, 2 and 3, respectively.

**$^{1}$H NMR spectra of compounds 2a, 3a, 5 and 6.**