Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Fluorescent Nanoparticle Sensors with Tailor-Made Recognition Units and Proximate Fluorescent Reporter Groups

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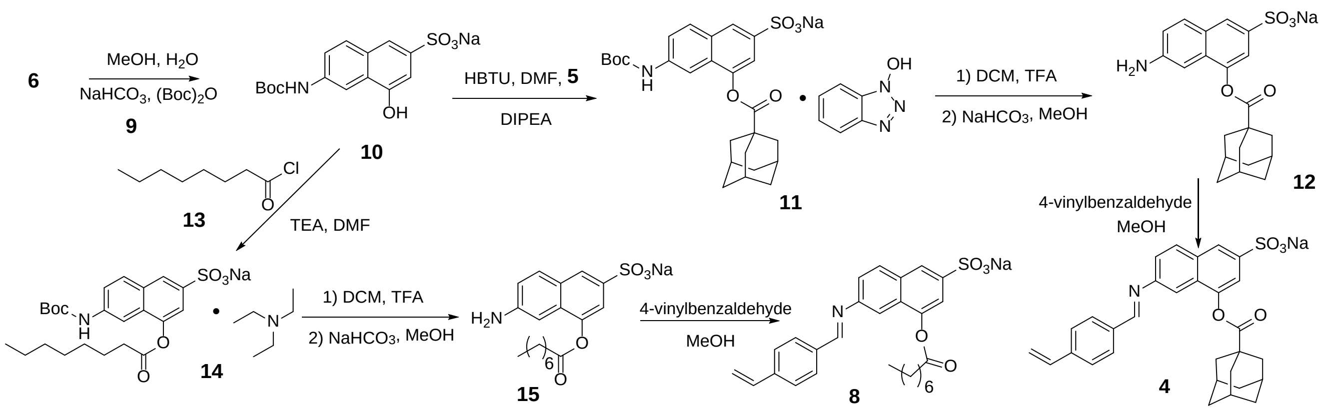
General Method

Routine ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400, on a Bruker AV II 600 or on a Varian VXR-400 spectrometer. ESI-MS mass was recorded on Shimadzu LCMS-2010 mass spectrometer. Dynamic light scattering (DLS) data were recorded at 25 °C using PDDLS/ CoolBatch 90T with PD2000DLS instrument. Isothermal titration calorimetry (ITC) was performed using a MicroCal VP-ITC Microcalorimeter with Origin 7 software and VPViewer2000 (GE Healthcare, Northampton, MA).

Scheme S1



Syntheses

4-vinylbenzaldehyde was synthesized following reported procedures.[1]

Compound 10. Compound **6** (500 mg, 2.09 mmol), di-*t*-butyl dicarbonate (912 mg, 4.18 mmol), and sodium bicarbonate (351 mg, 4.18 mmol) were dissolved in 50 mL of methanol and 2 mL of water. The reaction mixture was heated to 60 °C and stirred overnight. After the reaction mixture was concentrated by rotary evaporation, the residue was purified by flash column chromatography over silica gel with 15:1 ethyl acetate/methanol as the eluent to give a pink powder (539 mg, 71%). ^{1}H NMR (400 MHz, CD_3OD, δ) 8.29 (d, *J* = 2.2 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.55 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.22 (d, *J* = 1.5 Hz, 1H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, CD_3OD, δ) 154.0, 152.8, 140.4, 137.3, 129.9, 128.74, 126.4, 120.2,

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[1] D. Song, S. Cho, Y. Han, Y. You, W. Nam, *Org. Lett.* **2013**, *15*, 3582-3585.

116.1, 109.3, 104.8, 79.7, 27.4. ESI-MS (*m/z*): [M-Na] $^-$ cacld for $C_{15}H_{16}NO_6S$, 338.0704; found, 338.0706.

Compound 11. Compound **10** (27.4 mg, 0.152 mmol), HBTU (105 mg, 0.277 mmol), and DIPEA (89 mg, 0.689 mmol) were dissolved in 5 mL of DMF. After the mixture was stirred for 30 min, compound **5** (50 mg, 0.138 mmol) was added. The reaction mixture was stirred at room temperature overnight. After the solvent was removed by rotary evaporation, the residue was purified by flash column chromatography over silica gel with 20:1 dichloromethane/methanol as the eluent to give a light-yellow powder (61.1 mg, 61%). ^{1}H NMR (400 MHz, CD_3OD, δ) 8.18 (s, 1H), 8.15 (s, 1H), 7.89 – 7.86 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.44 (m, 4H), 2.26 (d, *J* = 2.9 Hz, 6H), 2.14 (s, 3H), 1.89 (s, 6H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, CD_3OD, δ) 177.53, 154.82, 147.72, 141.30, 140.57, 130.93, 130.65, 129.69, 127.95, 127.04, 124.00, 121.71, 118.51, 116.96, 111.59, 108.52, 81.03, 48.43, 42.58, 40.05, 37.52, 29.48, 28.65, 19.26. ESI-MS (*m/z*): [M-HOBt-Na] $^-$ cacld for $C_{26}H_{30}NO_7S$, 500.1743; found, 500.1759.

Compound 12. Compound **11** (61.1 mg, 0.093 mmol) was dissolved in 10 mL of trifluoroacetic acid. The reaction mixture was stirred at room temperature overnight. After trifluoroacetic acid was removed by rotary evaporation, the residue was redissolved in 25 mL of methanol with sodium bicarbonate (23.4 mg, 0.279 mmol). After stirred for 30 min, the reaction mixture was concentrated by rotary evaporation and the residue was purified by flash column chromatography over silica gel with 15:1 dichloromethane/methanol as the eluent to give a white powder (30.3 mg, 77%). ^{1}H NMR (400 MHz, CD_3OD, δ) 8.03 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.07 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 2.22 (d, *J* = 2.9 Hz, 6H), 2.14 (s, 3H), 1.87 (t, *J* = 3.2 Hz, 6H). ^{13}C NMR (151 MHz, CD_3OD, δ) 177.81, 149.60, 146.20, 131.16, 130.92, 128.52, 124.41, 120.91, 116.60, 101.60, 42.59, 40.12, 37.49, 29.43. ESI-MS (*m/z*): [M-Na] $^-$ cacld for $C_{21}H_{22}NO_5S$, 400.1219; found, 400.1218.

Compound 4. Compound **12** (0.020 mmol, 8.5 mg) and 4-vinylbenzaldehyde (13.2 mg, 0.100 mmol) were dissolved in10 mL of methanol. The reaction mixture was stirred overnight. Diethyl ether (40 mL) was added slowly. The precipitate formed was collected by filtration and washed with 5 mL of diethyl ether to yield a brown powder (9.8 mg, 85.4%). The product was used in the MINP preparation without further purification. ^{1}H NMR (400 MHz, DMSO-d_6, δ) 8.75 (s, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 8.09 (s, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 1H), 7.37 (s, 1H), 6.83 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.00 (d, *J* = 17.8 Hz, 1H), 5.41 (d, *J* = 10.9 Hz, 1H), 2.09-2.15 (m, 9H), 1.74-1.81 (m, 6H).

Compound 14. Compound **13** (44.9 mg, 0.276 mmol), **10** (50 mg, 0.138 mmol), and triethylamine (27.9 mg, 0.276 mmol) were dissolved in 10 mL of anhydrous DMF. The reaction mixture was stirred at room temperature overnight. After the solvent was removed by rotary evaporation, the residue was purified by flash column chromatography over silica gel with 20:1 dichloromethane/methanol as the eluent to give an off-white powder (42.2 mg, 52%). ^{1}H NMR (400 MHz, CD_3OD, δ) 8.16 (s, 2H), 7.90 (d, J = 8.9 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.50 (dd, J = 8.9, 2.2 Hz, 1H), 3.16 (q, J = 7.3 Hz, 6H), 2.79 (t, J = 7.5 Hz, 2H), 1.88 (m, 2H), 1.55 (s, 9H), 1.53 – 1.32 (m, 8H), 1.27 (t, J = 7.3 Hz, 9H), 0.93 (t, 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD, δ) 172.5, 153.5, 146.3, 140.2, 139.3, 129.6, 129.4, 128.3, 122.7, 120.5, 115.8, 107.0, 79.8, 46.5, 33.8, 31.5, 29.0, 28.8, 27.4, 24.9, 22.4, 13.2, 7.8. ESI-MS (*m/z*): $[M\text{-}Et_3N\text{-}Na]^-$ cacld for $C_{23}H_{30}NO_7S$, 464.1743; found, 464.1757.

Compound 15. Compound **14** (41.3 mg, 0.070 mmol) was dissolved in 5 mL of trifluoroacetic acid. The reaction mixture was stirred at room temperature overnight. After trifluoroacetic acid was removed by rotary evaporation, the residue was redissolved in 25 mL of methanol with sodium bicarbonate (27.6 mg, 0.328 mmol). After stirred for 30 min, the reaction mixture was concentrated by rotary evaporation and the residue was purified by flash column chromatography over silica gel with 15:1 dichloromethane/methanol as the eluent to give a brown powder (23.0 mg, 85%). ^{1}H NMR (400 MHz, CD_3OD, δ) 8.04 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.07 (dd, J = 8.8, 2.2 Hz, 1H), 6.89 (d, J = 2.3 Hz, 1H), 2.76 (t, J = 7.5 Hz, 2H), 1.82 (m, 2H), 1.55 – 1.27 (m, 8H), 0.93 (t, 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD, δ) 172.7, 148.3, 144.8, 136.4, 129.8, 129.5, 127.1, 123.2, 119.5, 115.3, 100.4, 33.6, 31.5, 28.9, 28.8, 24.7, 22.3, 13.1. ESI-MS (*m/z*): $[M\text{-}Na]^-$ cacld for $C_{18}H_{22}NO_5S$, 364.1219; found, 364.1224.

Compound 8. Compound **15** (0.020 mmol, 7.8 mg) and 4-vinylbenzaldehyde (13.2 mg, 0.100 mmol) were dissolved in 10 mL of methanol. The reaction mixture was stirred overnight. Diethyl ether (40 mL) was added slowly. The precipitate formed was collected by filtration and washed with 5 mL of diethyl ether to yield a brown powder (7.2 mg, 71.7%). The product was used in the MINP preparation without further purification. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 8.74 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.08 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.54 (s, 1H), 7.44 (s, 1H), 6.83 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.00 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.73 (m, 2H), 1.44 – 1.23 (m, 8H), 0.81 (d, *J* = 7.2 Hz, 3H).

Preparation of $MINP_4$, $MINP_7$, $MINP_8$.

MINPs were synthesized according to previously reported procedures.[2] To a micellar solution of **1** (10.2 mg, 0.02 mmol) in H_2O (2.0 mL), divinylbenzene (DVB, 2.8 μL, 0.02 mmol), the template–FM complex (**4**, **7** or **8**) in DMSO (0.0004 mmol), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) in DMSO (10 μL of a 12.8 mg/mL, 0.0005 mmol) were added. The mixture was sonicated for 10 min. Cross-linker **2** (4.1 mg, 0.024 mmol), $CuCl_2$ in H_2O (10 μL of 6.7 mg/mL, 0.0005 mmol), and sodium ascorbate in H_2O (10 μL of 99 mg/mL, 0.005 mmol) were then added and the reaction mixture was stirred slowly at room temperature for 12 h. Compound **3** (10.6 mg, 0.04 mmol), $CuCl_2$ (10 μL of a 6.7 mg/mL solution in H_2O, 0.0005 mmol), and sodium ascorbate (10 μL of a 99 mg/mL solution in H_2O, 0.005 mmol) were then added and the solution stirred for another 6 h at room temperature. The reaction mixture was transferred to a glass vial, purged with nitrogen for 15 min, sealed with a rubber stopper, and irradiated in a Rayonet reactor for 12 h. The reaction mixture was poured into acetone (8 mL). The precipitate was collected by centrifugation and washed with a mixture of methanol/acetic acid (5 mL/0.1 mL) three times. The off-white product was dried in air to afford the final MINPs (> 80%).

Preparation of MINP-CHO.

The appropriate MINP ($MINP_4$ or $MINP_8$) (15.2 mg) was sonicated in 2 mL of 6 M hydrochloric acid for 20 min. The resulting solution was stirred at 95 °C for 2 h. The mixture was poured into acetone (8 mL). The precipitate formed was collected by centrifugation and washed with a mixture of acetone/water (5 mL/1 mL) three times. The off-white product was dried in air to afford the corresponding MINP-CHO (12.0 mg, 79%). To monitor the hydrolysis yield, an aliquot (40 μL) of reaction mixture was taken and added to 1.5 mL of acetone. The precipitate formed was collected by centrifugation and washed by a mixture of acetone/water (1 mL/0.2 mL) three times. The dried precipitate was then dissolved in 2 mL of water to yield the MINP solution before the fluorescence spectrum was recorded. Fluorescence intensity at 405 nm was used to calculate the hydrolysis yield. The initial fluorescence intensity was used for 0% hydrolysis.

Preparation of MINP-Naph.

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[2] Arifuzzaman, M. D.; Zhao, Y. *J. Org. Chem.* **2017**, *81*, 7518.

The appropriate MINP-CHO (12.0 mg) was sonicated in 1 mL of anhydrous DMF for 20 min until it was fully dissolved. An aliquot (150 μL) of a stock solution of **6** (23.9 mg in 1 mL DMSO) was added. The reaction mixture was stirred for 2 h at room temperature. An aliquot of sodium borohydride stock solution (37.9 mg in 1 mL anhydrous DMF) was added. After stirred overnight, the reaction mixture was poured into acetone (8 mL). The precipitate formed was collected by centrifugation and washed with a mixture of acetone/water (5 mL/1 mL) three times and a mixture of methanol/acetic acid (5 mL/0.1 mL) three times. The off-white powdery product was dried in air. To remove the borate ions, the above product was re-dissolved in 2 mL of sodium chloride solution (5000 equiv to the concentration of MINP) overnight. The solution was transferred to a dialysis tube (MWCO 3.5K). The tube was placed in 2 L of deionized water with gentle stirring. The dialysis tube was sonicated and the water was changed after 2, 4, 6, and 20 h. After 48 h, the MINP solution was poured into 40 mL of acetone and the precipitate was collected by centrifugation. The precipitate was dried in air to yield MINP$_{\mathbf{4}}$-Naph or MINP$_{\mathbf{8}}$-Naph (8.6 mg, 72%).

Titration by Fluorescence Spectroscopy and Data Analysis Method

A stock solution of MINP (200 μM) was prepared in 10 mM HEPES buffer (pH 7.4) or water. Stock solutions (200 μM) of the guests were prepared in water. (For acids such as **5** that had low solubility in water, extensive sonication of the sample was used in the preparation of the stock solution.) For the titrations, a typical procedure is as follows. An aliquot (5–10 μL) of the guest stock solution was added to 2.00 mL of the appropriate solvent (HEPES buffer or water) in a quartz cuvette. The concentration of the guest was 1.0 μM. The sample was gently vortexed for 30 s before its fluorescence spectrum was recorded. Aliquots of the MINP solution was added and the spectrum was recorded after each addition. The titration was continued until saturation was reached and the total volume of the MINP solution added was kept below 100 μL. The binding constant was obtained by nonlinear least squares curving fitting of the emission intensity to the 1:1 binding isotherm.[3] All titrations were performed at room temperature.

Limit of Detection:

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[3] Schneider, H. J.; Yatsimirsky, A. K. *Principles and methods in supramolecular chemistry*; New York: J. Wiley, 2000; pp 137-146.

For adamantane carboxylic acid, blank fluorescence is 180.638 ± 3.834. Limit of detection, calculated by 3δ/slope, was 0.20 μM. δ was the standard deviation of six blank samples and the slope was from the fluorescence titration at low guest concentrations. For octanoic acid, blank fluorescence is 187.422 ± 2.584. Limit of detection, calculated by 3δ/slope, was 3.54 μM. δ is the standard deviation of six blank samples and the slope was from the fluorescence titration at low guest concentrations.

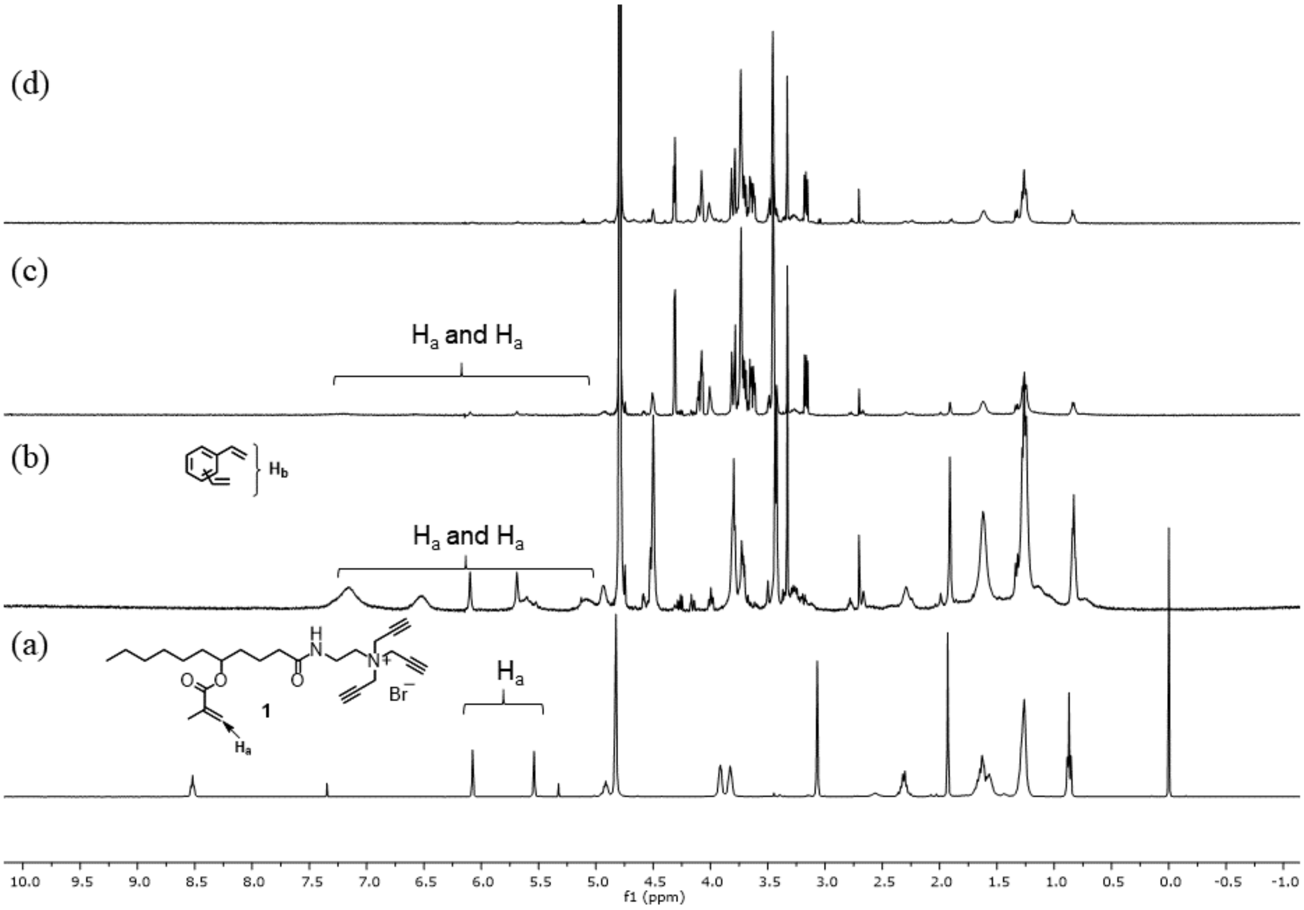


Figure S1. ^{1}H NMR spectra of (a) surfactant **1** in $CDCl_3$, (b) surface-cross-linked micelles (SCM) in D_2O, (c) surface-functionalized SCM in D_2O, and (d) core-cross-linked micelles in D_2O for MINP**4**.

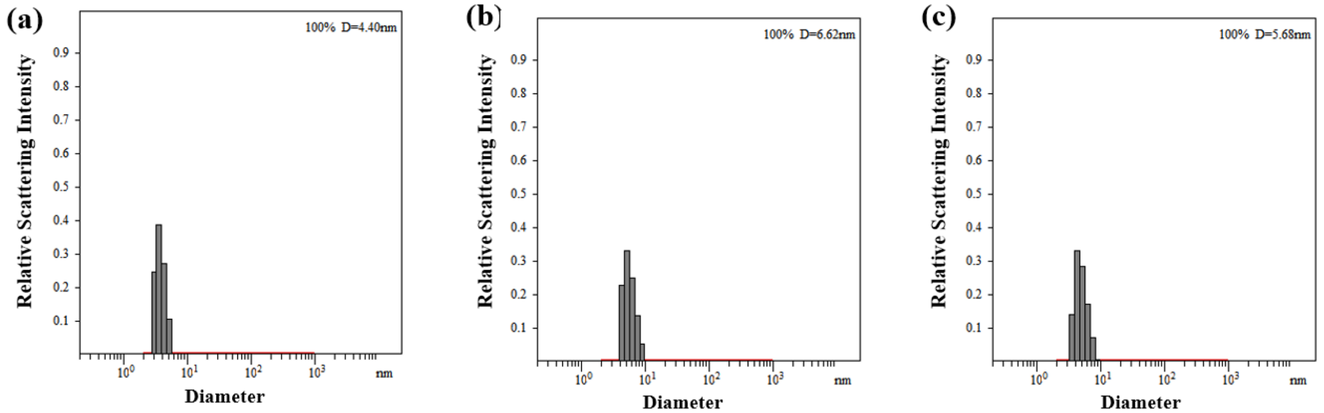


Figure S2. Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) surface-cross-linked micelles (SCM), (b) surface-functionalized SCM, and (c) purified MINP$_4$.

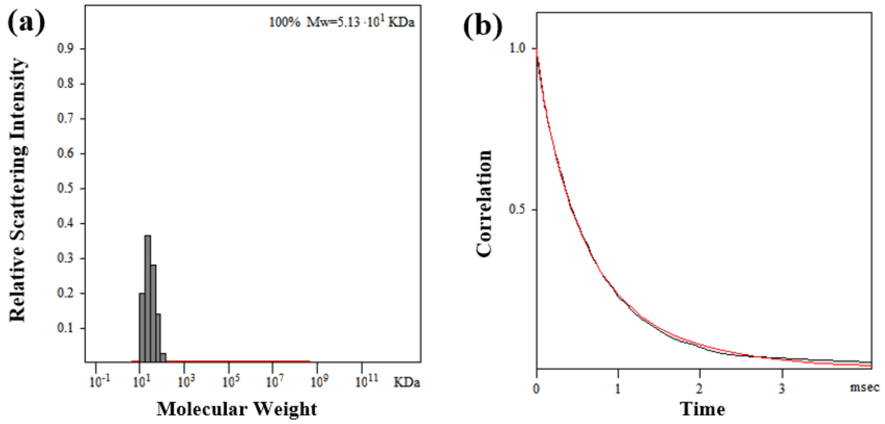


Figure S3. Distribution of the molecular weights and the correlation curve for MINP$_4$ from the DLS. The PRECISION DECONVOLVE program assumes the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP is assumed to contain one molecule of surfactant (MW = 465 g/mol), 1.2 molecules of cross linker (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of sugar derivative (MW = 264 g/mol), the molecular weight of MINP translates to 51 [= 51300 / (465 + 1.2×172 + 130 + 0.8×264)] of such units.

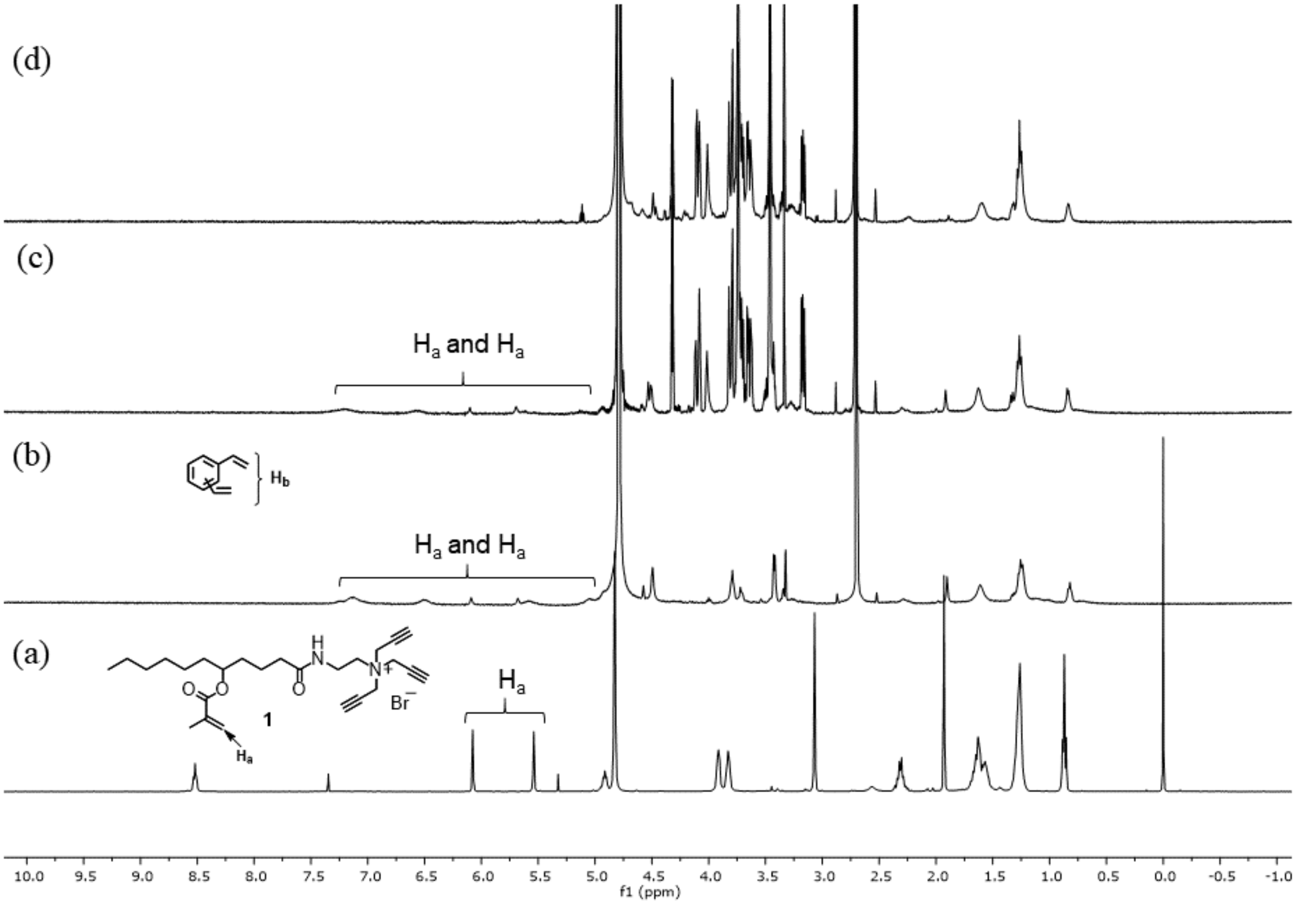


Figure S4. ^{1}H NMR spectra of (a) surfactant **1** in $CDCl_3$, (b) surface-cross-linked micelles (SCM) in D_2O, (c) surface-functionalized SCM in D_2O, and (d) core-cross-linked micelles in D_2O for $MINP_7$.

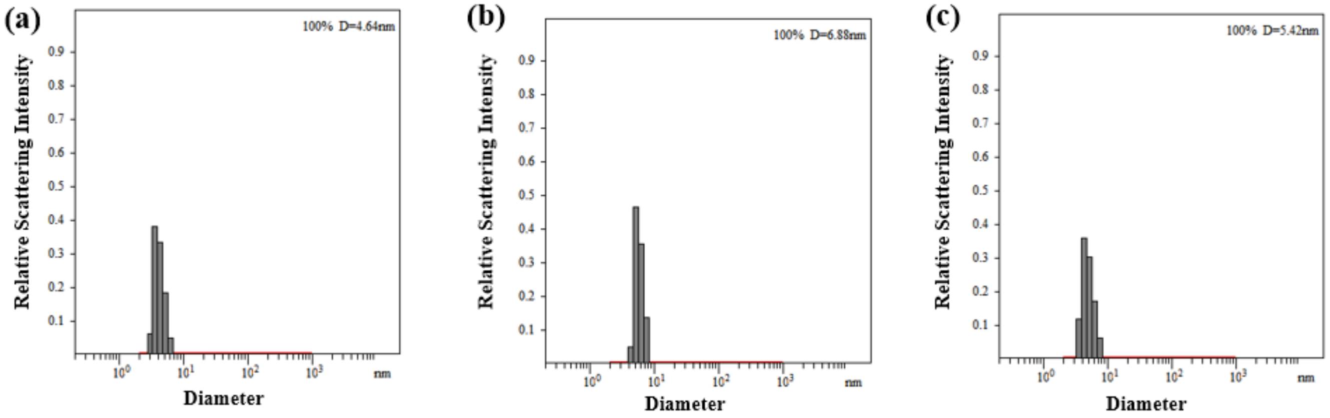


Figure S5. Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) surface-cross-linked micelles (SCM), (b) surface-functionalized SCM, and (c) purified $MINP_7$.

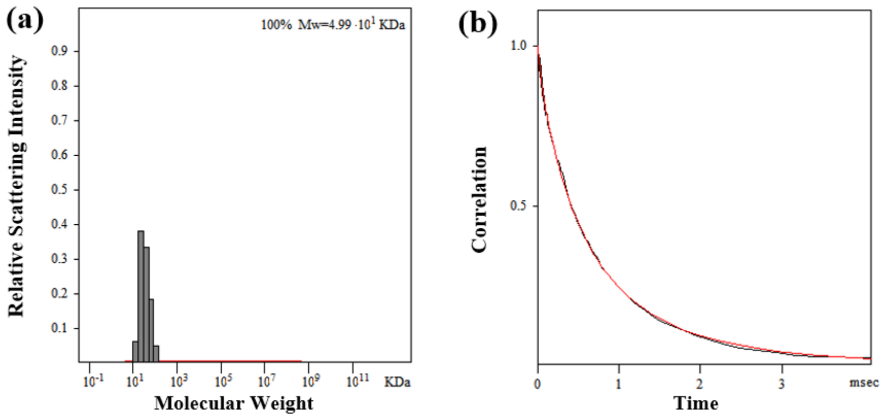


Figure S6. Distribution of the molecular weights and the correlation curve of $MINP_7$ from the DLS. The PRECISION DECONVOLVE program assumes the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP is assumed to contain one molecule of surfactant (MW = 465 g/mol), 1.2 molecules of cross linker (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of sugar derivative (MW = 264 g/mol), the molecular weight of MINP translates to 49 [= 49900 / (465 + 1.2×172 + 130 + 0.8×264)] of such units.

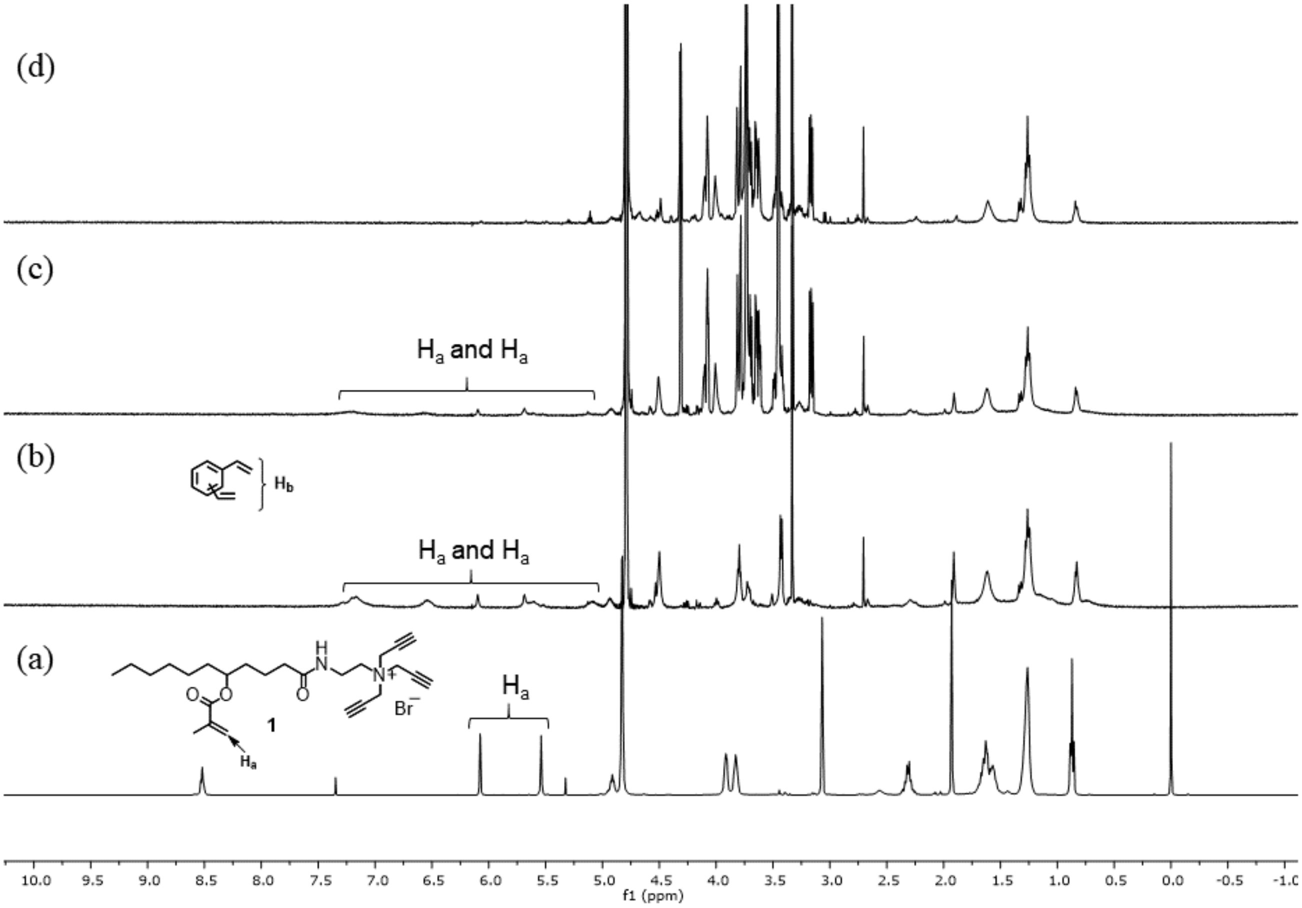


Figure S7. ^{1}H NMR spectra of (a) surfactant **1** in $CDCl_3$, (b) surface-cross-linked micelles (SCM) in D_2O, (c) surface-functionalized SCM in D_2O, and (d) core-cross-linked micelles in D_2O for MINP$_{\mathbf{8}}$.

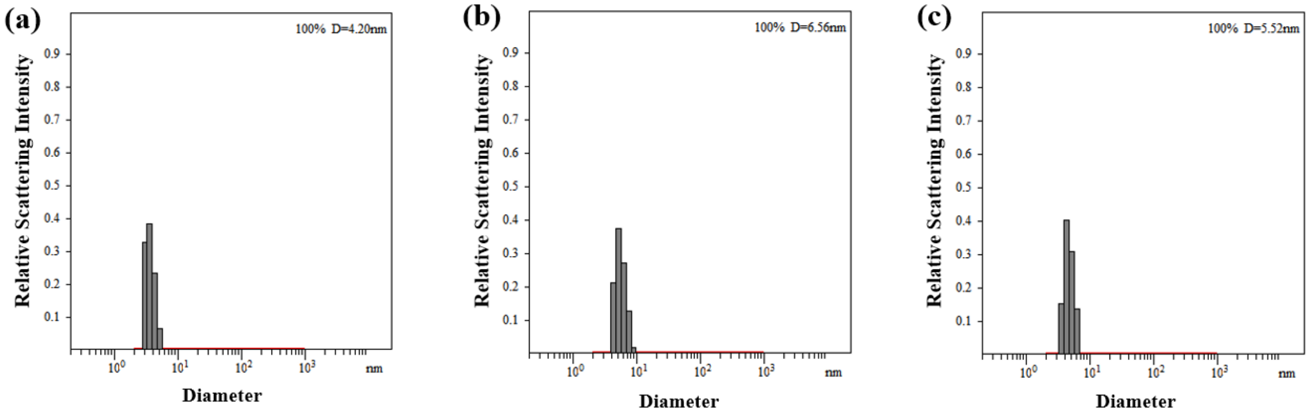


Figure S8. Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) surface-cross-linked micelles (SCM), (b) surface-functionalized SCM, and (c) purified MINP$_8$.

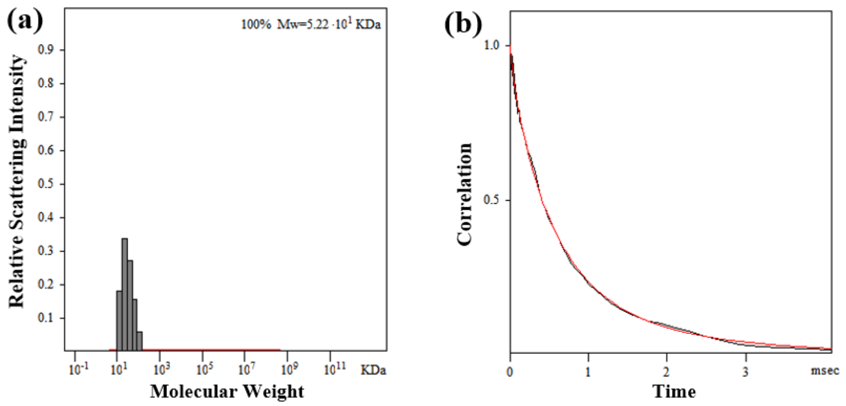


Figure S9. Distribution of the molecular weights and the correlation curve of MINP$_8$ from the DLS. The PRECISION DECONVOLVE program assumes the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP is assumed to contain one molecule of surfactant (MW = 465 g/mol), 1.2 molecules of cross linker (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of sugar derivative (MW = 264 g/mol), the molecular weight of MINP translates to 51 [= 52200 / (465 + 1.2×172 + 130 + 0.8×264)] of such units.

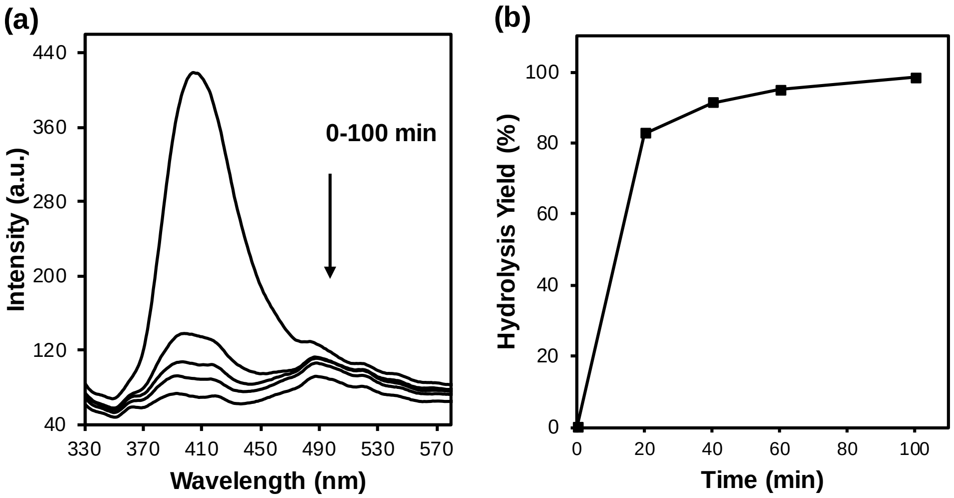


Figure S10. (a) Fluorescence spectra of MINP$_4$ hydrolysis. λ_{ex} = 307 nm. (b) Hydrolysis yield calculated based on fluorescence intensity at 405 nm. Fluorescence before heating was used for 0% hydrolysis.

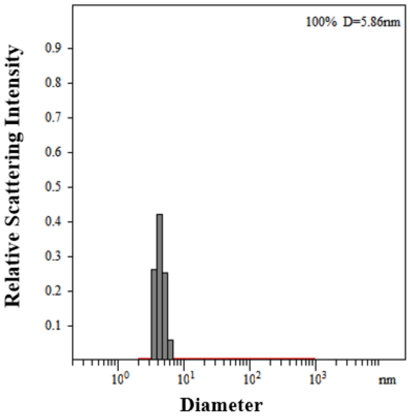


Figure S11. Distribution of the hydrodynamic diameters of the MINP$_4$-CHO in water as determined by DLS for MINP after HCl hydrolysis.

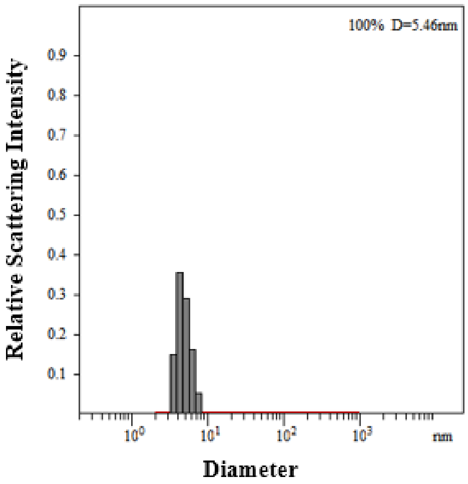


Figure S12. Distribution of the hydrodynamic diameters of the nanoparticles in 10 mM HEPES buffer (pH = 7.4) as determined by DLS for MINP$_4$-Naph after dialysis.

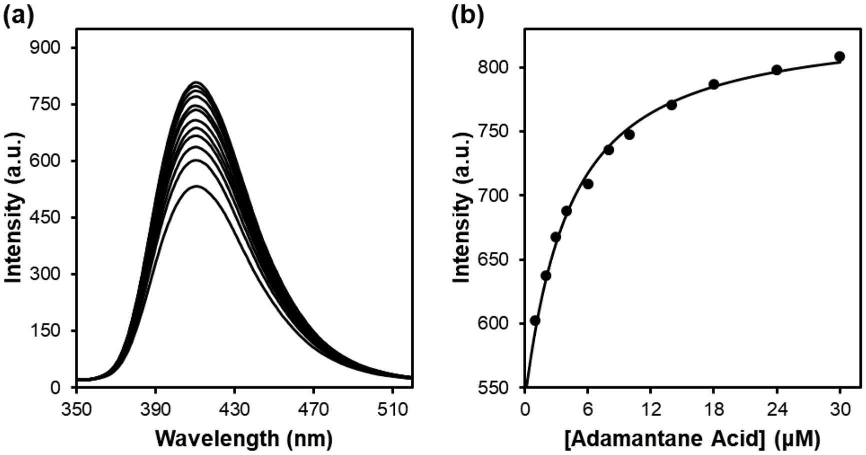


Figure S13. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of **5** in 10 mM HEPES buffer (pH = 7.4). [MINP$_4$-Naph] = 1.0 μM, The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm.

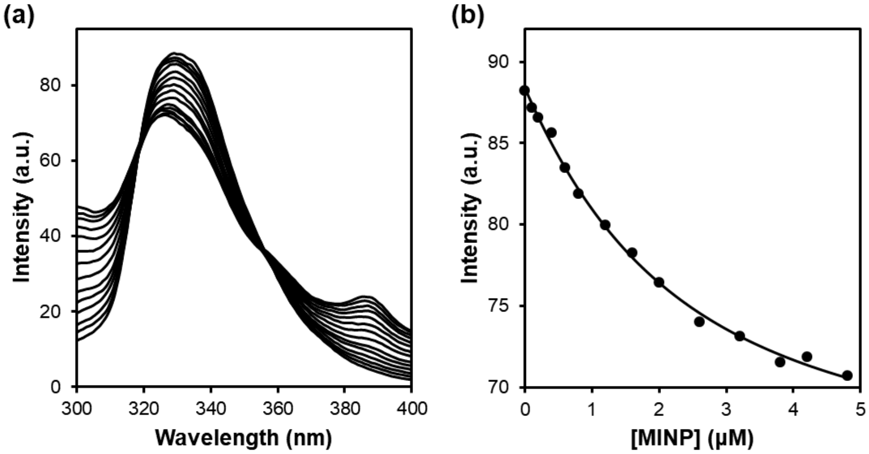


Figure S14. (a) Emission spectra of **7** upon the addition of different concentrations of MINP$_7$ unhydrolyzed in 1 M HCl solution. [**7**] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Plot of intensity at 330 nm with concentration of MINP and the nonlinear least squares fitting of the emission intensity at 330 nm to a 1:1 binding isotherm.

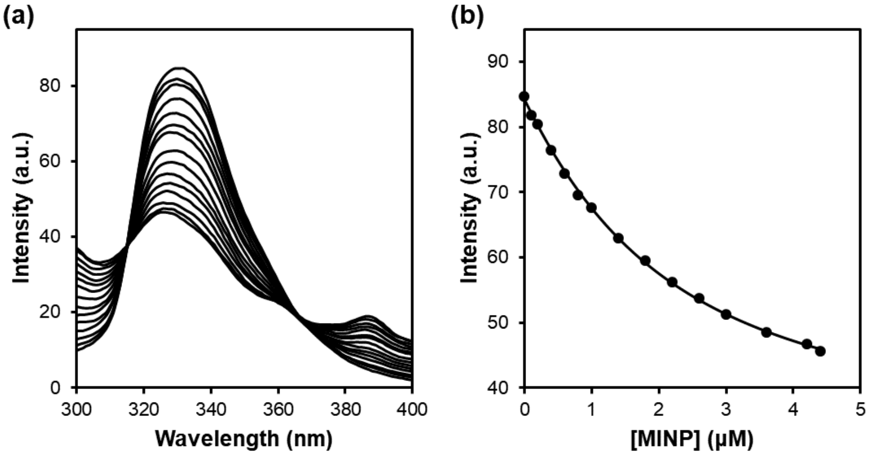


Figure S15. (a) Emission spectra of **7** upon the addition of different concentrations of MINP$_7$ after hydrolysis in 1 M HCl solution. [**7**] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Plot of intensity at 330 nm with concentration of MINP and nonlinear least squares fitting of the emission intensity at 330 nm to a 1:1 binding isotherm.

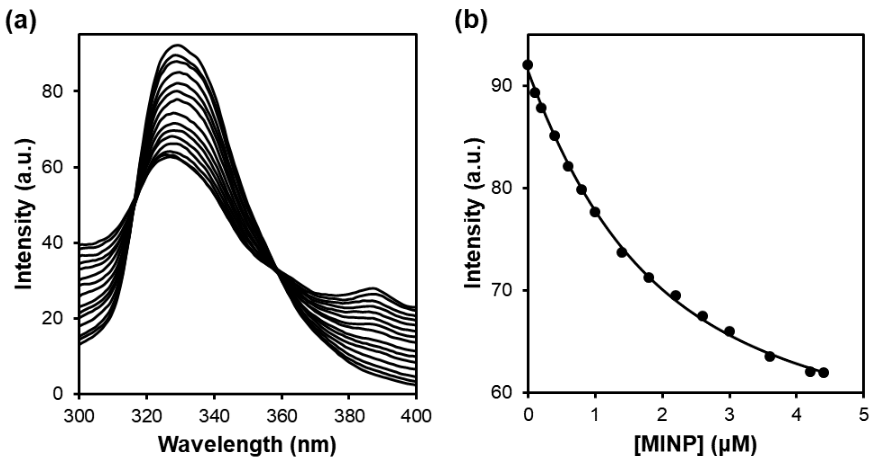


Figure S16. (a) Emission spectra of **7** upon the addition of different concentrations of MINP$_7$ after reductive amination in 1 M HCl solution, [**7**] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Plot of intensity at 330 nm with concentration of MINP and nonlinear least squares fitting of the emission intensity at 330 nm to a 1:1 binding isotherm.

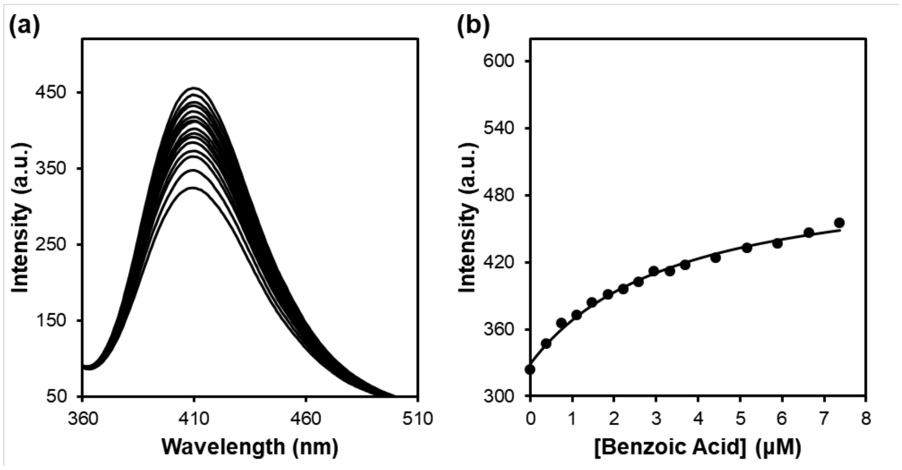


Figure S17. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of benzoic acid in H_2O. [MINP$_4$-Naph] = 0.2 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 2 of Table 1.

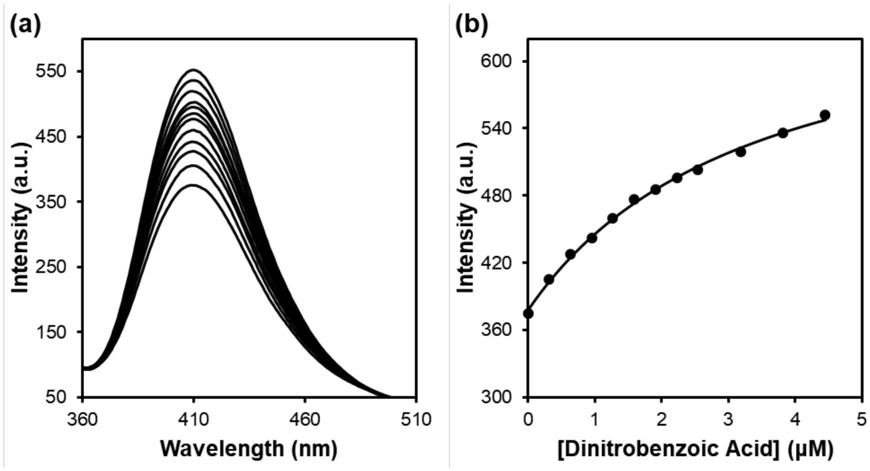


Figure S18. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of 3,5-dinitrobenzoic acid in H_2O. [MINP$_4$-Naph] = 0.2 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 3 of Table 1.

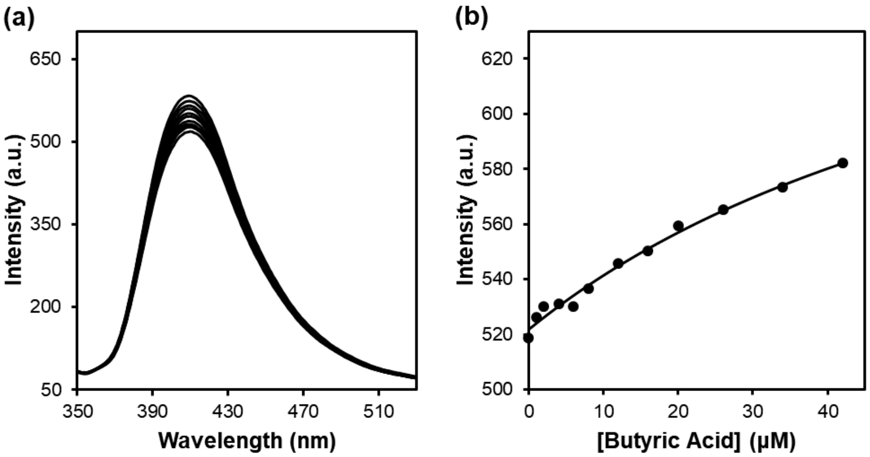


Figure S19. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of butyric acid in H_2O. [MINP$_4$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 4 of Table 1.

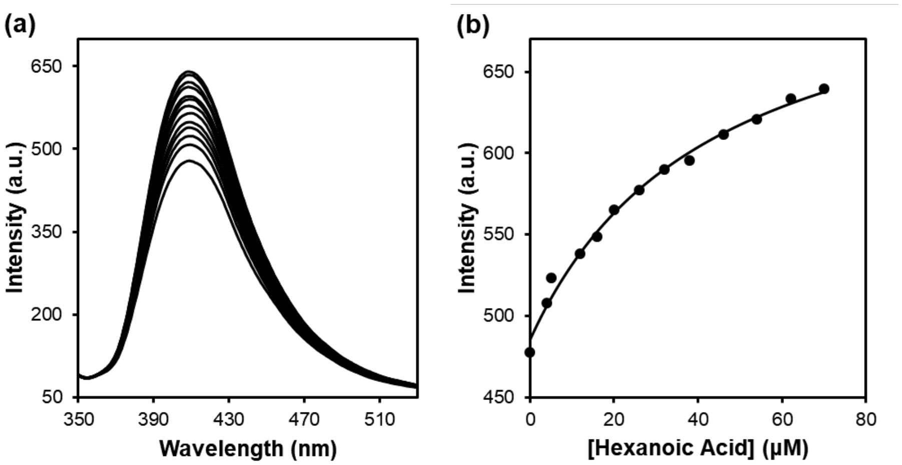


Figure S20. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of hexanoic acid in H_2O, [MINP$_4$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 5 of Table 1.

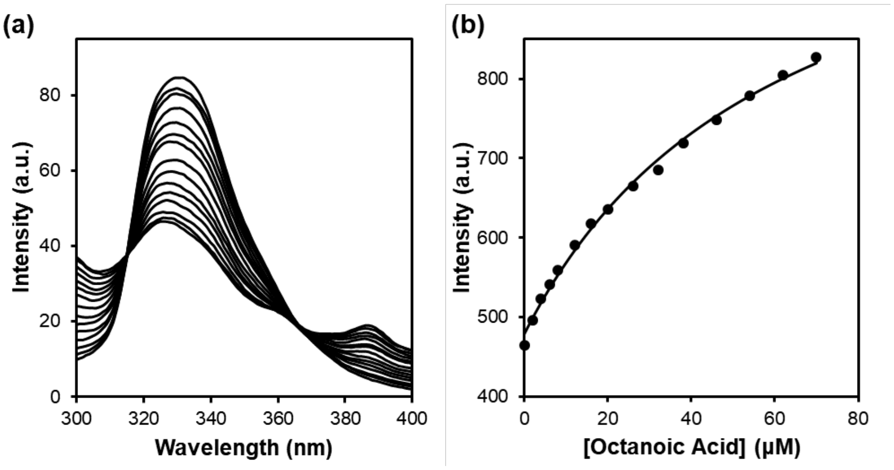


Figure S21. (a) Emission spectra of MINP$_4$-Naph upon the addition of different concentrations of octanoic acid in H_2O. [MINP$_4$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 6 of Table 1.

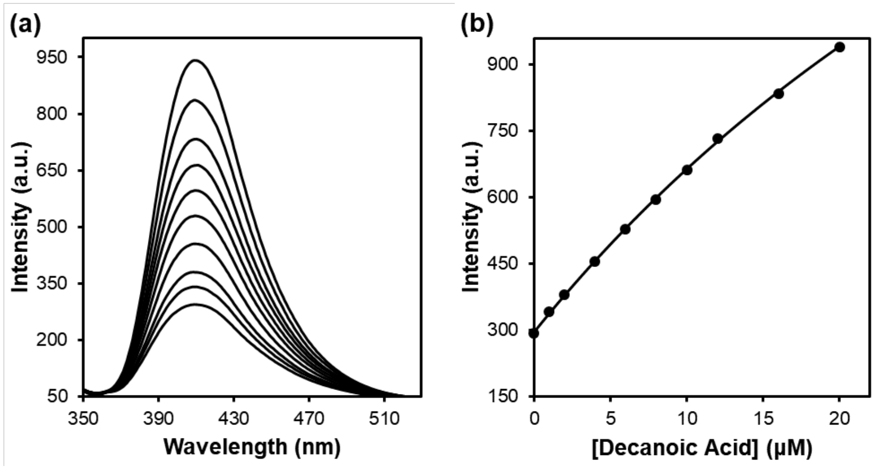


Figure S22. (a) Emission spectra of $MINP_4$-Naph upon the addition of different concentrations of decanoic acid in H_2O, [$MINP_4$-Naph] = 0.5 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 7 of Table 1.

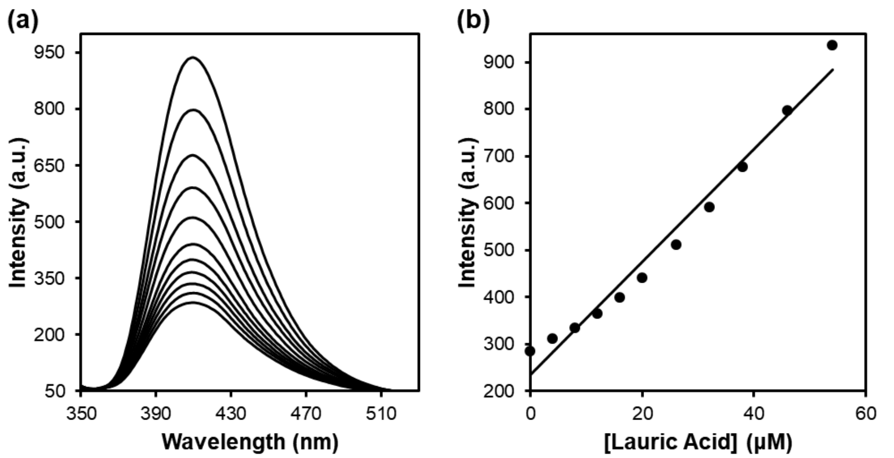


Figure S23. (a) Emission spectra of $MINP_4$-Naph upon the addition of different concentrations of lauric acid in H_2O, [$MINP_4$-Naph] = 0.5 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 8 of Table 1.

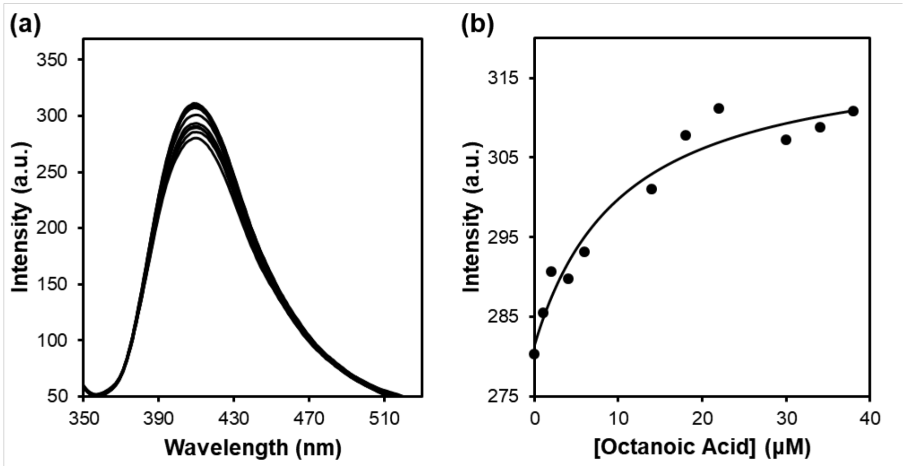


Figure S24. (a) Emission spectra of MINP$_8$-Naph upon the addition of different concentrations of octanoic acid in H_2O. [MINP$_8$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 9 of Table 1.

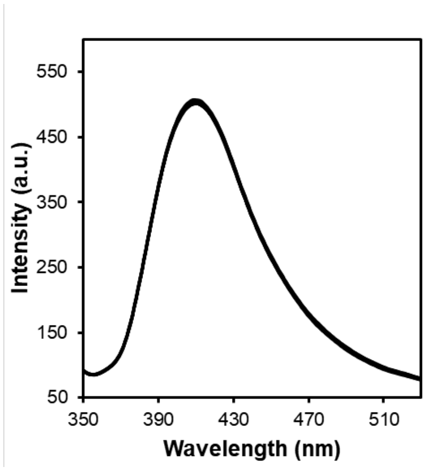


Figure S25. Emission spectra of MINP$_8$-Naph upon the addition of 0–50 μM of acetic acid in H_2O. [MINP$_8$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. The data correspond to entry 10 of Table 1.

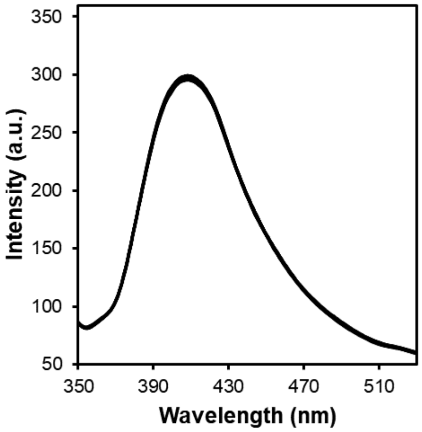


Figure S26. Emission spectra of MINP$_8$-Naph upon the addition of 0–50 μM of butyric acid in H_2O. [MINP$_8$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. The data correspond to entry 11 of Table 1.

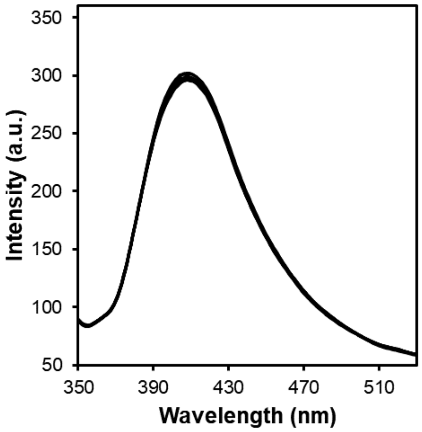


Figure S27. Emission spectra of MINP$_8$-Naph upon the addition of 0–50 μM of hexanoic acid in H_2O. [MINP$_8$-Naph] = 1.0 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. The data correspond to entry 12 of Table 1.

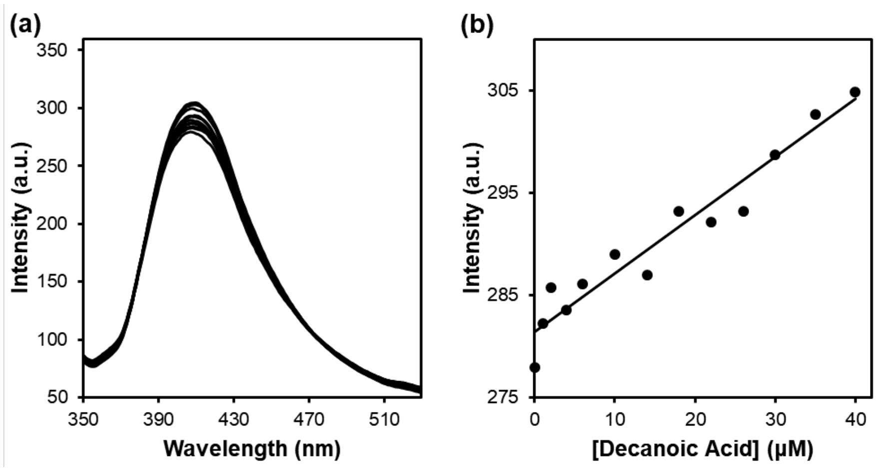


Figure S28. (a) Emission spectra of MINP$_8$-Naph upon the addition of different concentrations of decanoic acid at H_2O, [MINP$_8$-Naph] = 1.0 µM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 13 of Table 1.

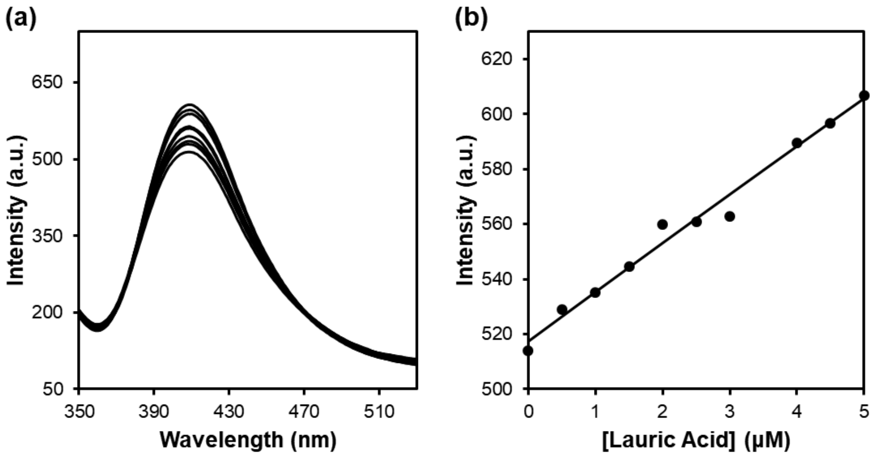


Figure S29. (a) Emission spectra of MINP$_8$-Naph upon the addition of different concentrations of lauric acid in H_2O, [MINP$_8$-Naph] = 0.5 µM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 14 of Table 1.

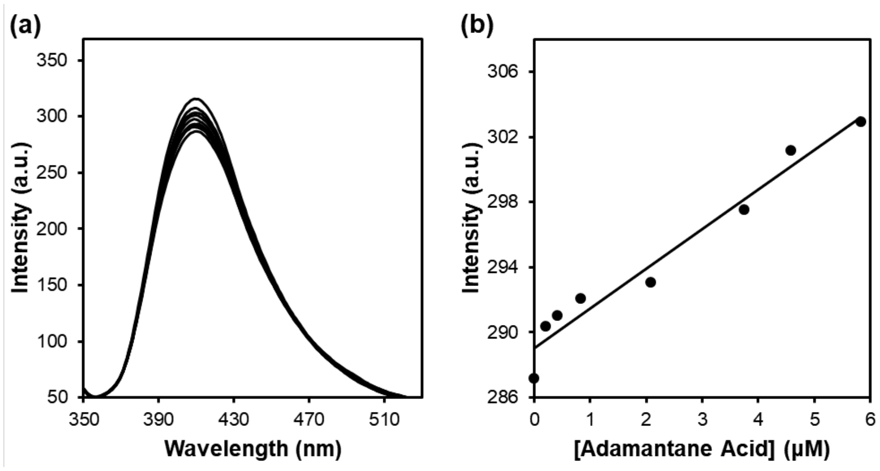


Figure S30. (a) Emission spectra of MINP$_8$-Naph upon the addition of different concentrations of **5** in H_2O. [MINP$_8$-Naph] = 0.5 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol. (b) Nonlinear least squares fitting of the emission intensity at 410 nm to a 1:1 binding isotherm. The data correspond to entry 15 of Table 1.

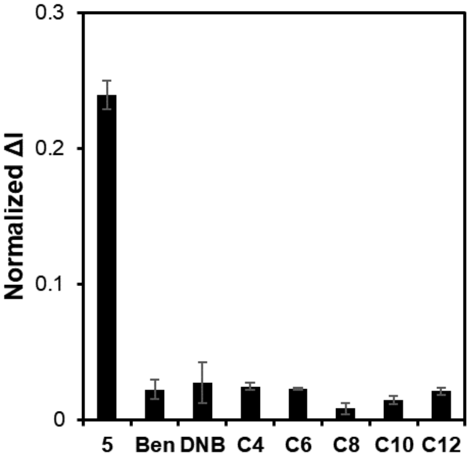


Figure S31. Normalized fluorescence change of MINP$_4$-Naph upon addition of 1 μM guests in H_2O. [MINP$_4$-Naph] = 0.5 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol.

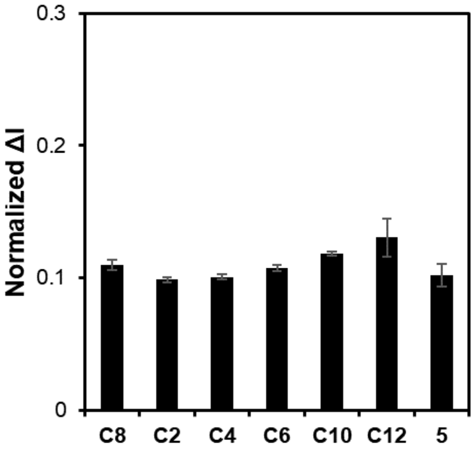
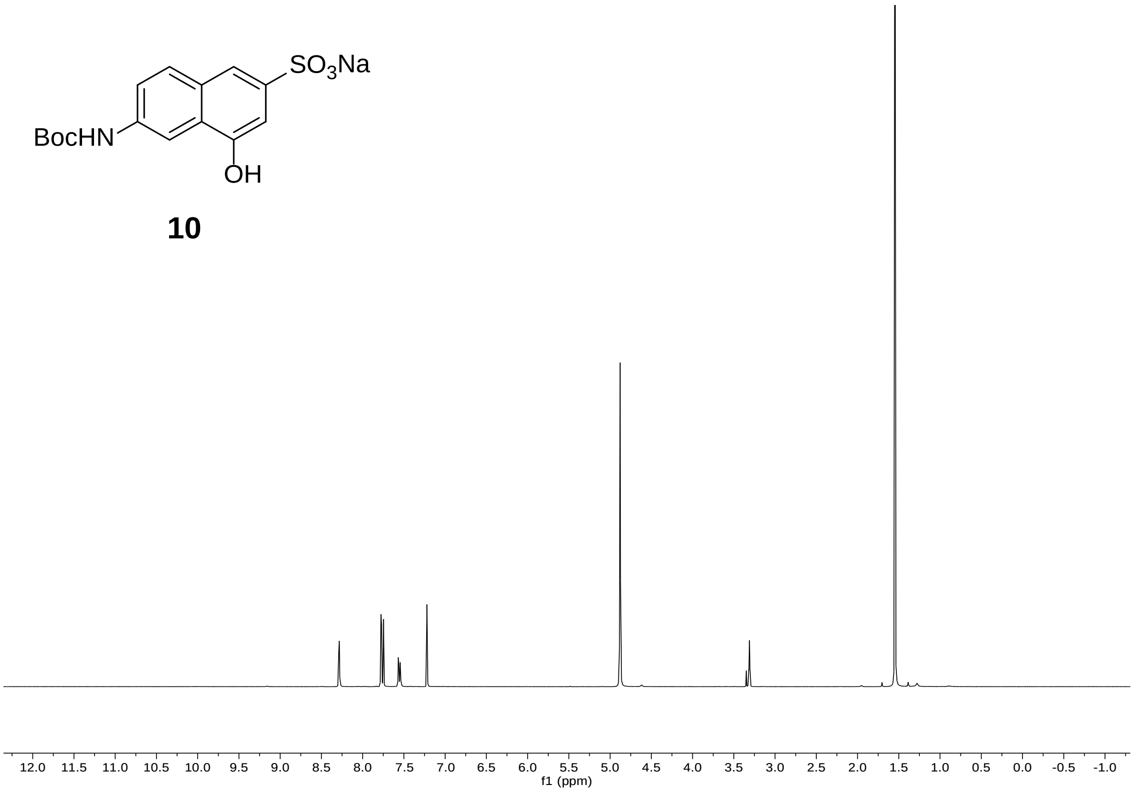
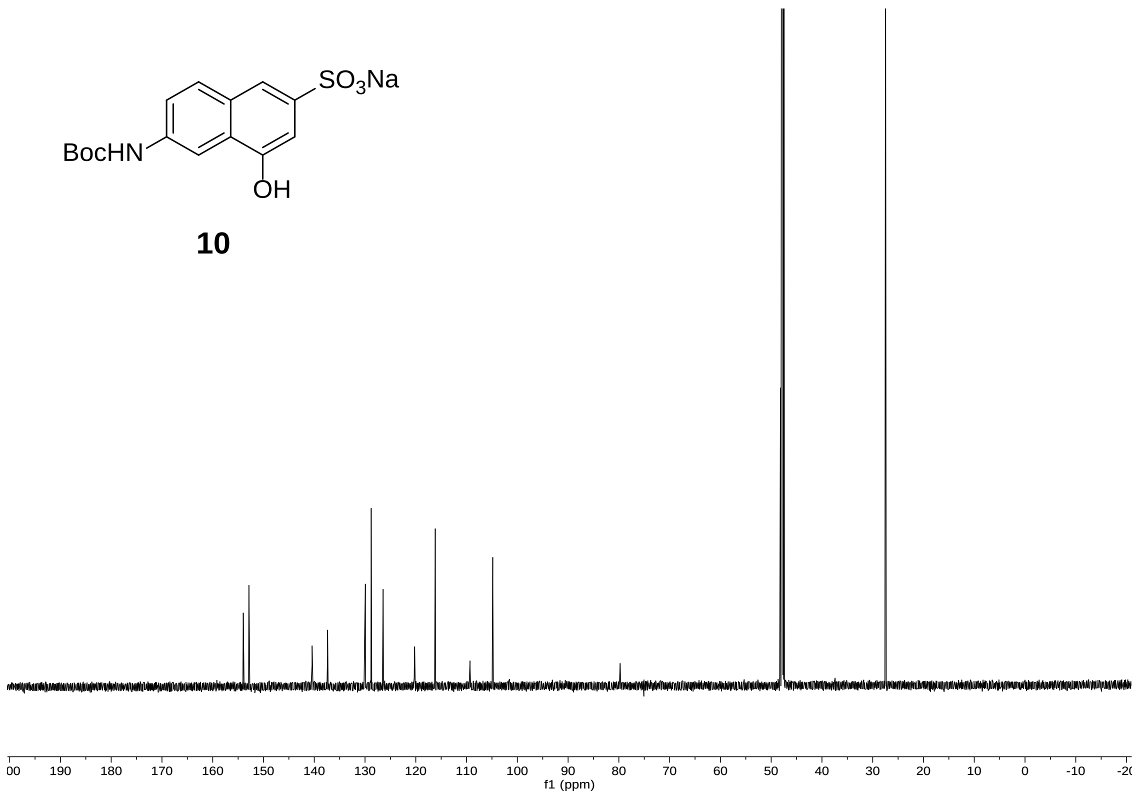


Figure S32. Normalized fluorescence change of MINP$_8$-Naph upon addition of 10 μM guests in H_2O. [MINP$_8$-Naph] = 1 μM. The concentration of MINP was calculated based on an approximate M.W. of 50000 g/mol.

^{1}H and ^{13}C NMR Spectra



10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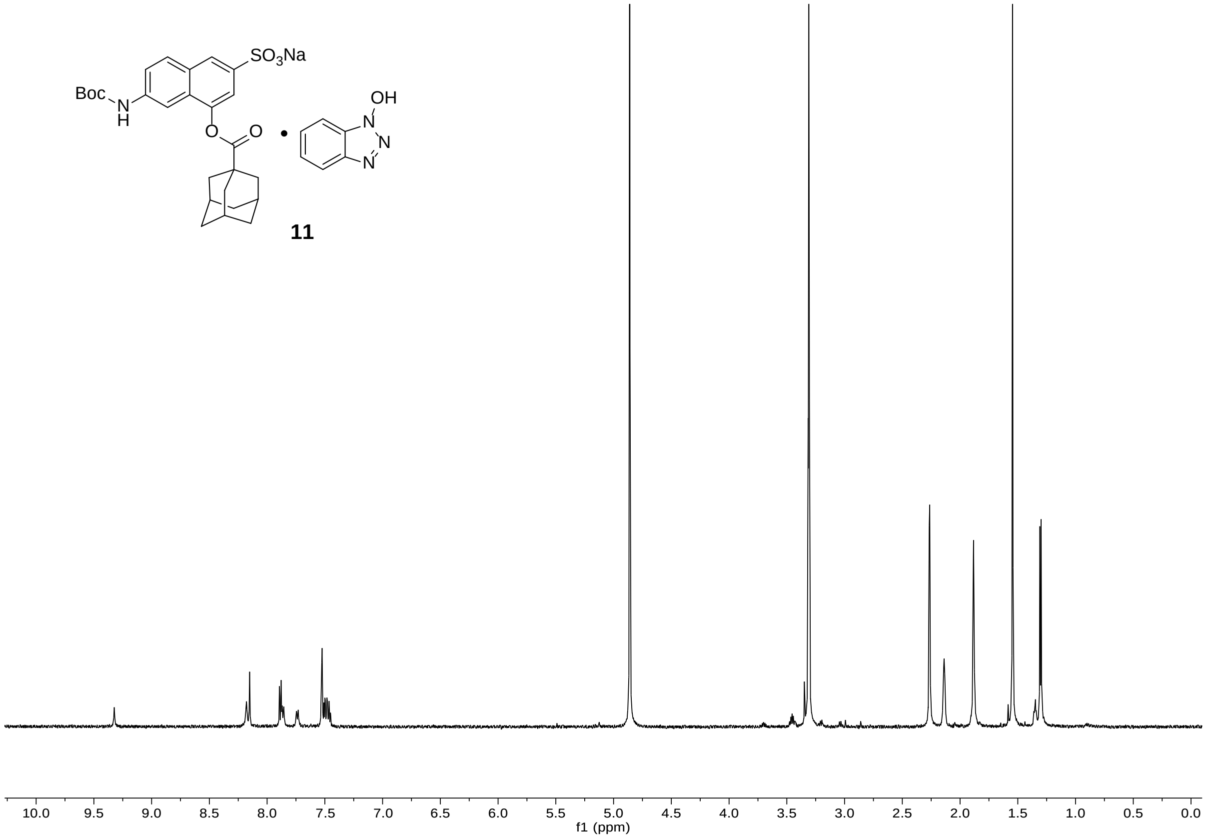
BocHN
OH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2(
f1 (ppm)

10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Boc
N
H
O
O
OH
N
N
N
10.0
9.5
9.0
8.5
8.0
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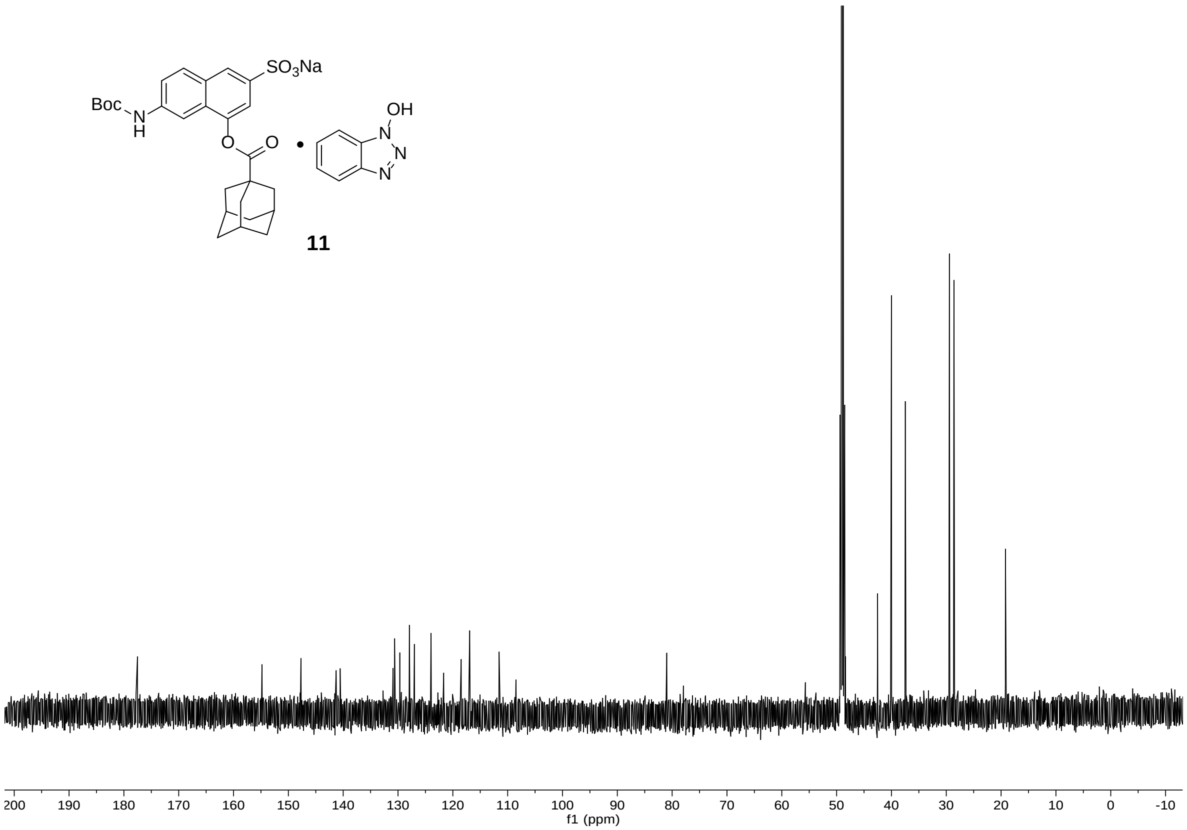
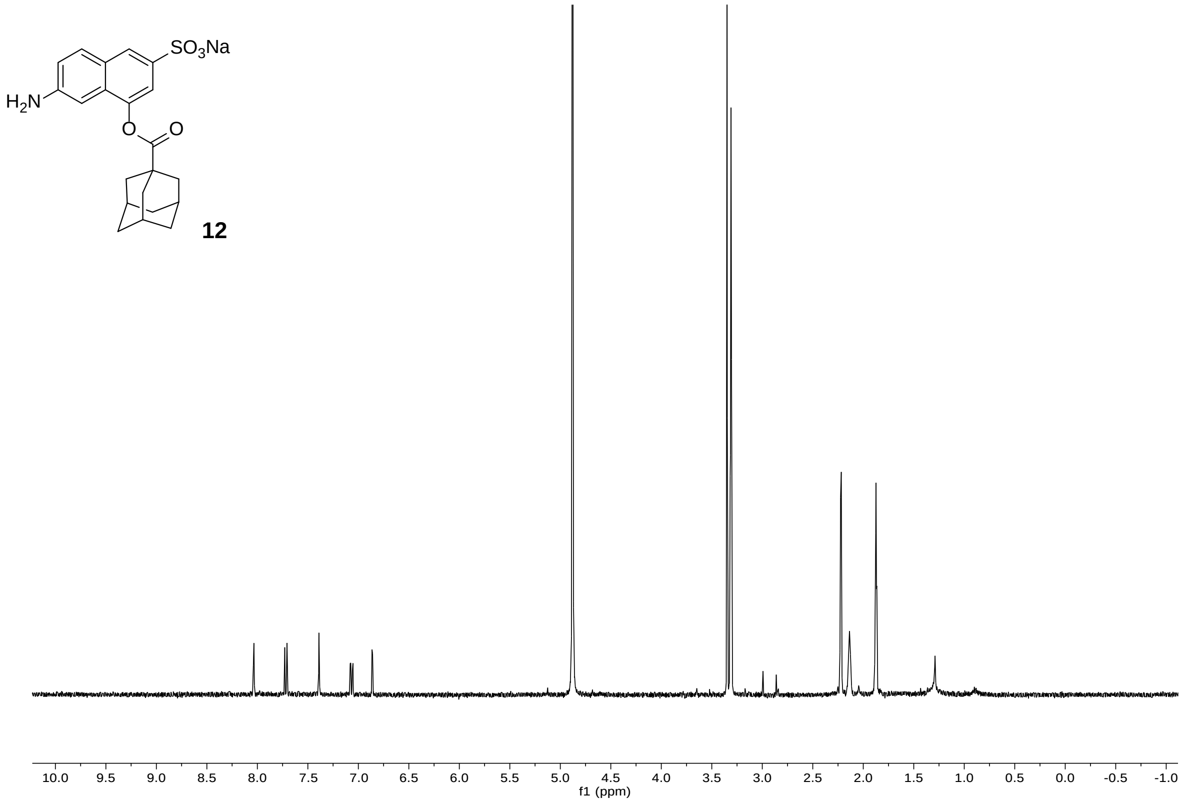
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

11


11

Boc
N
H
SO3Na
O
O
OH
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


12

H2N
SO3Na
O
O
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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0.0
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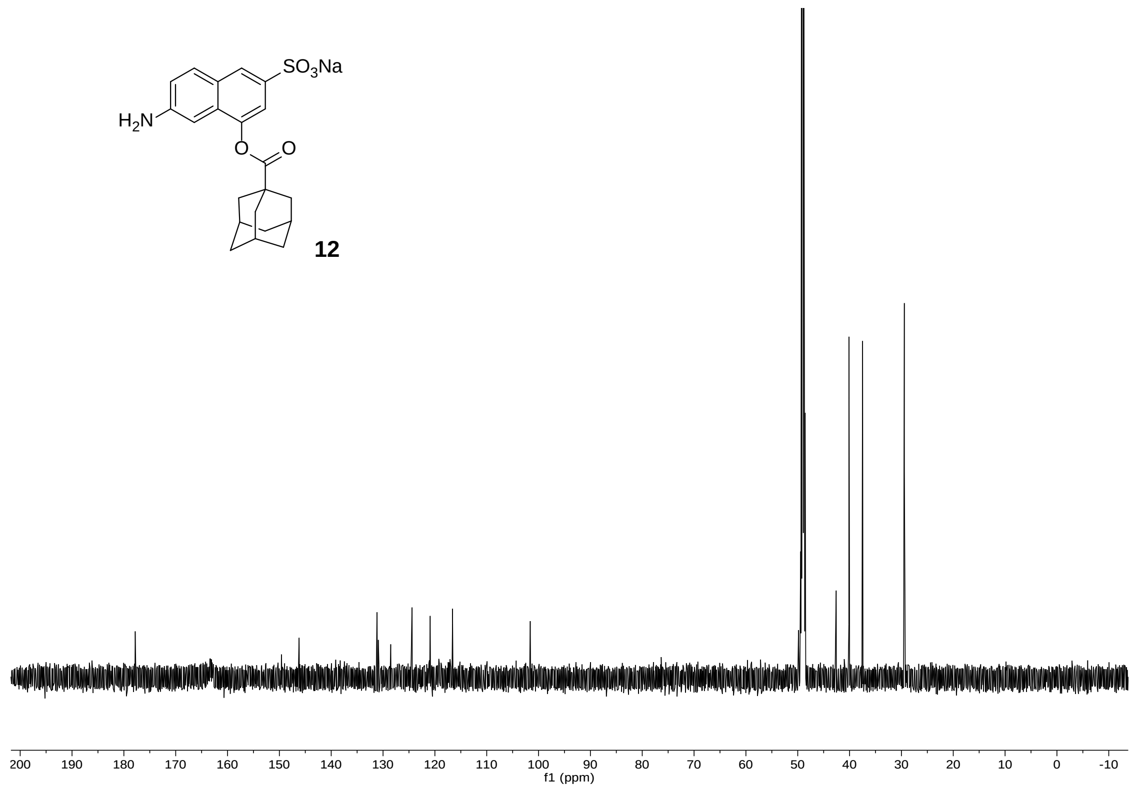
-1.0
f1 (ppm)


12

SO3Na
H2N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
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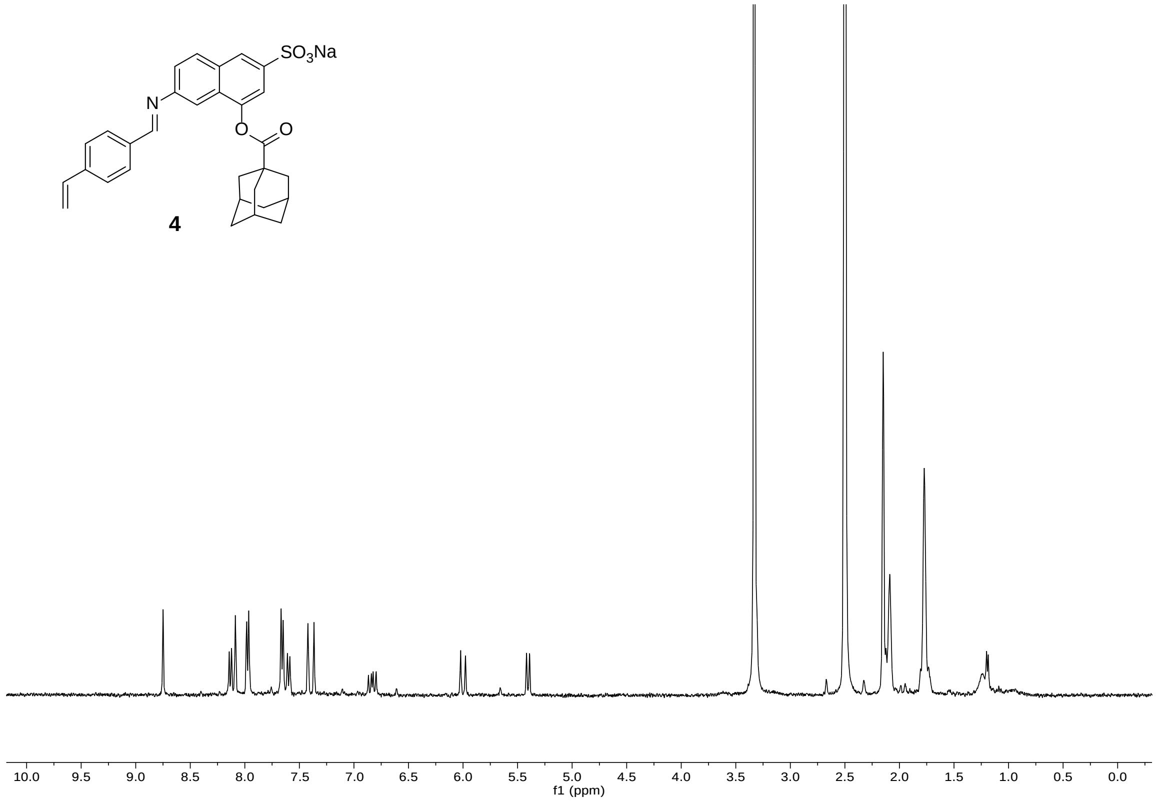
60
50
40
30
20
10
0
-10
f1 (ppm)


4

SO3Na
N
O
O
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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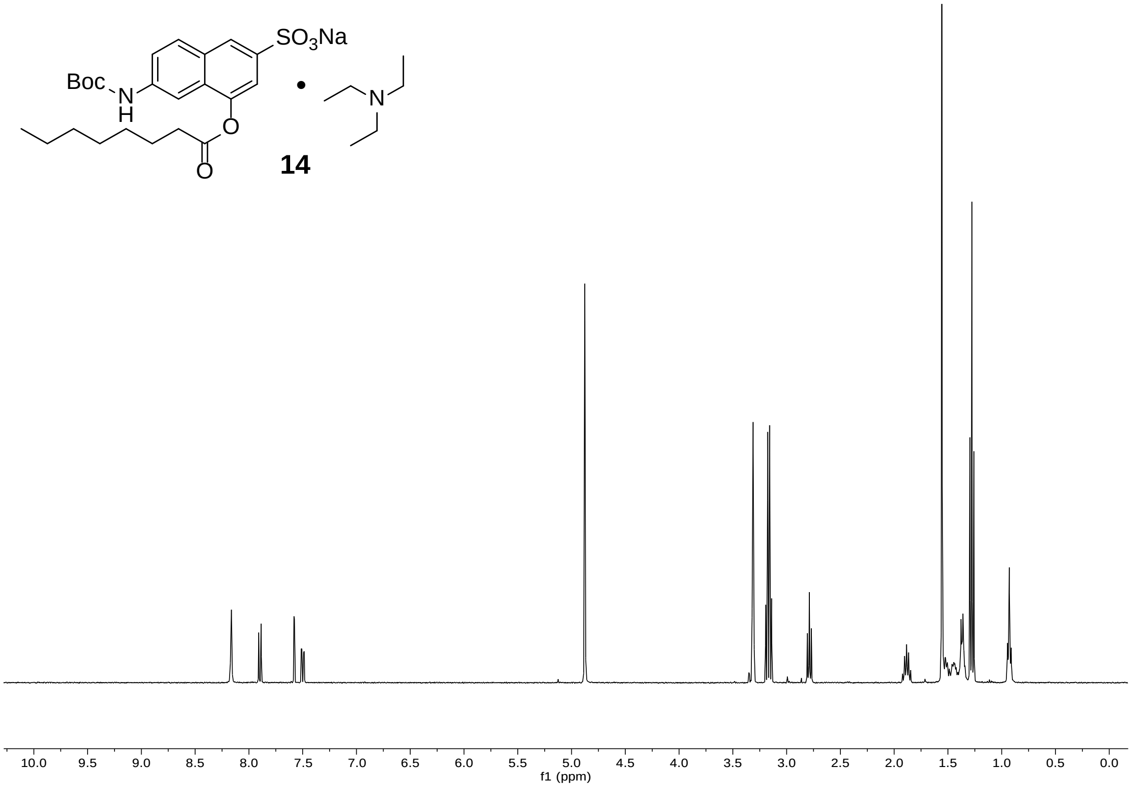
0.0
f1 (ppm)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Boc
N
H
O
O
N
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9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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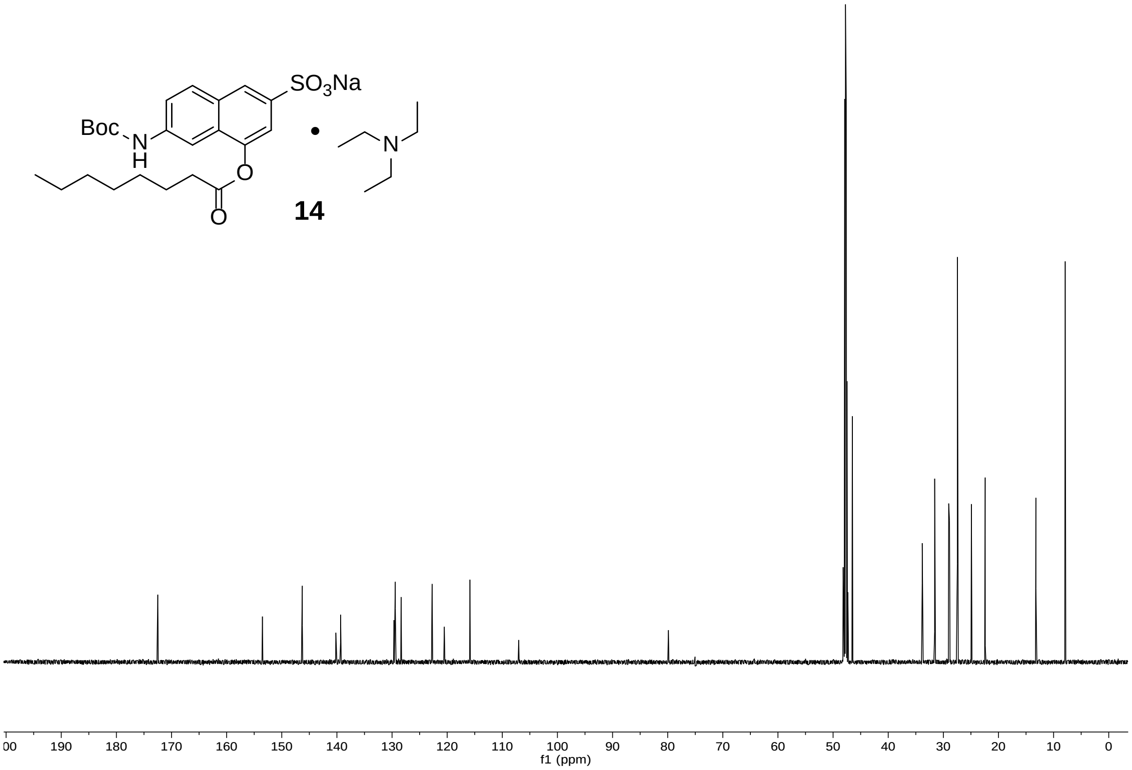
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

14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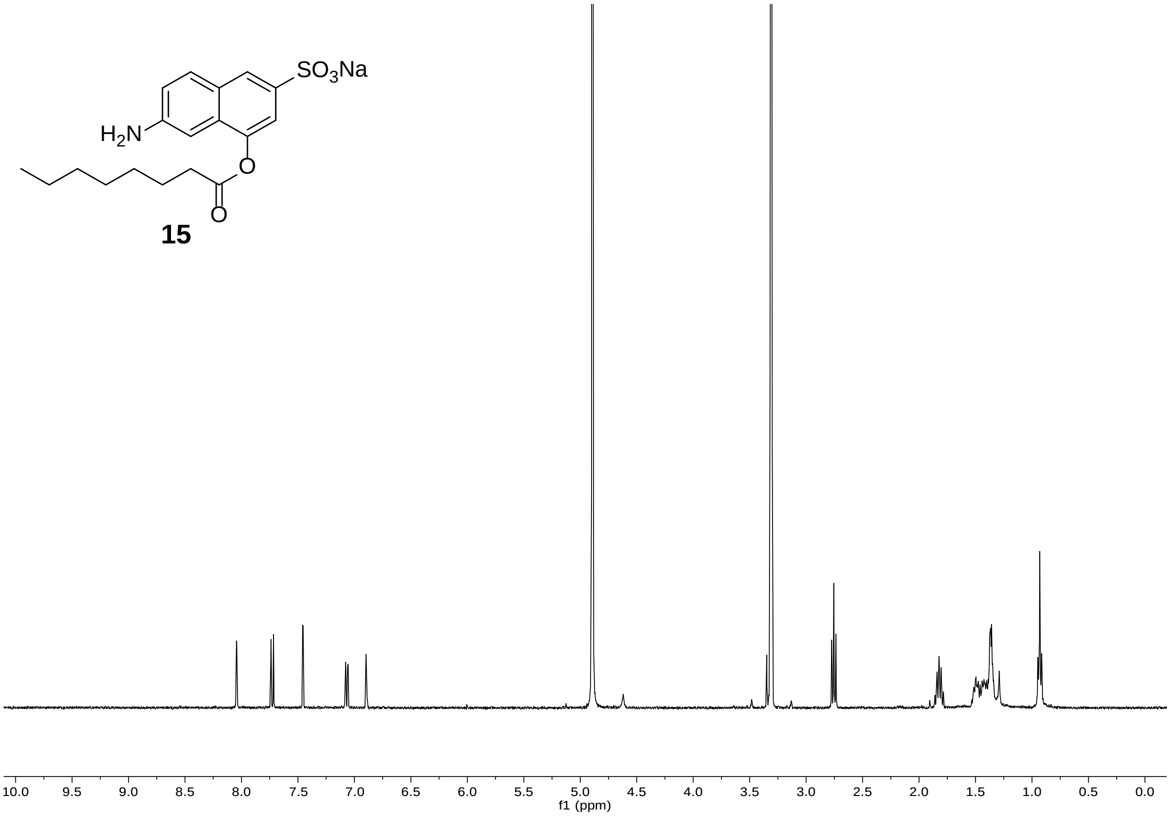
Boc
N
H
O
O
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

14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H2N
O
O
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9.5
9.0
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6.0
5.5
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3.5
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1.0
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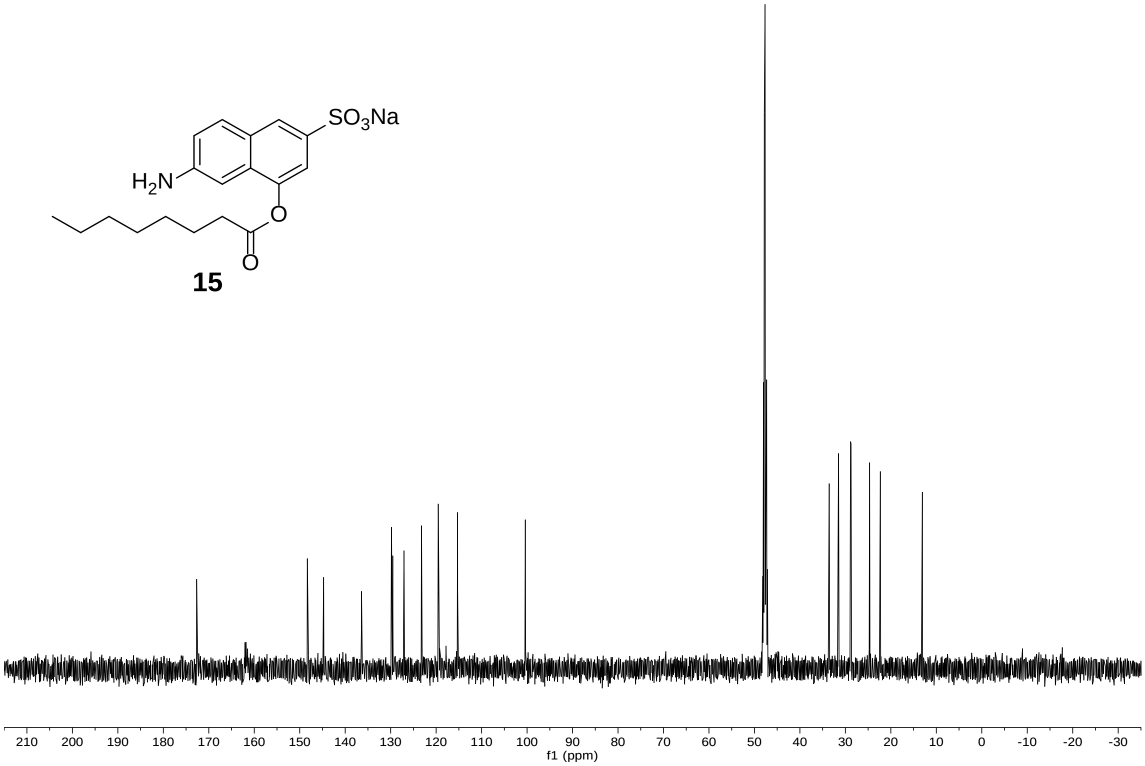
0.0
f1 (ppm)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H2N
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O
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140
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80
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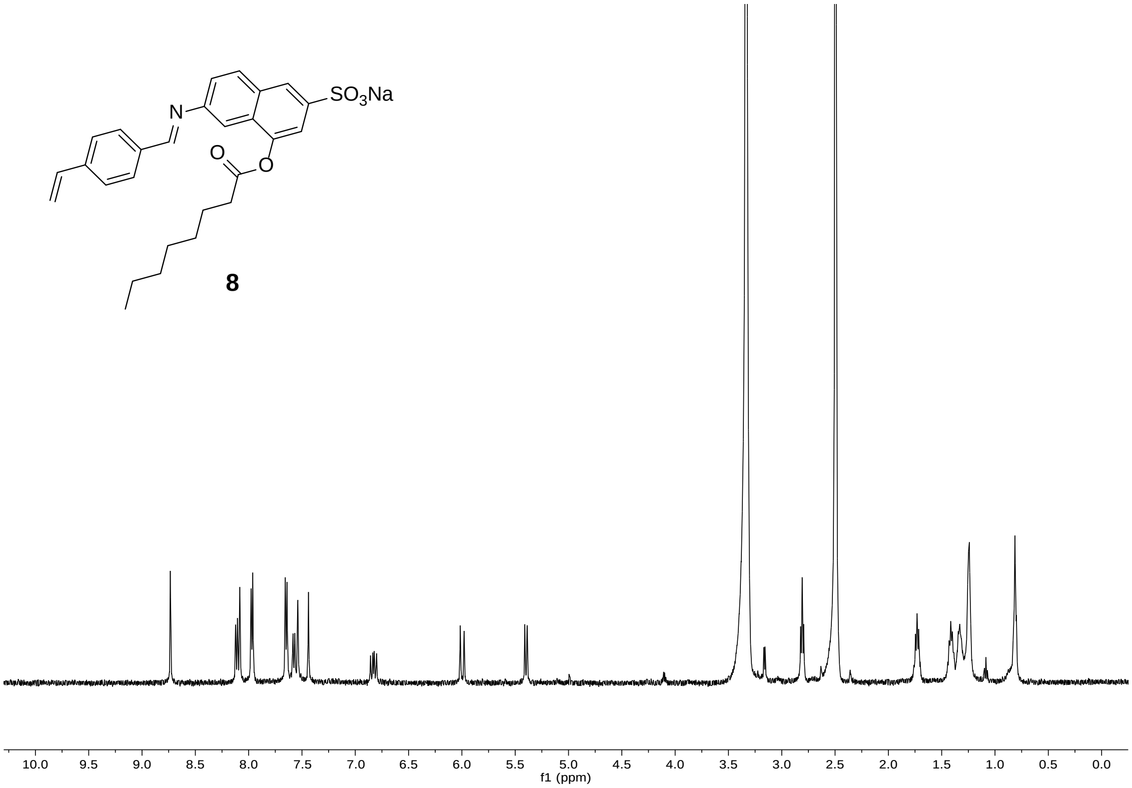
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


SO$_3$Na
N
O
O
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

8