**Supplementary Material**

Surface Ligands in the Imprinting and Binding of Molecularly Imprinted Cross-Linked Micelles

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# General Method

Routine 1H and 13C 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. Fluorescence spectra were recorded at ambient temperature on a Varian Cary Eclipse Fluorescence spectrophotometer. Isothermal titration calorimetry (ITC) was performed using a MicroCal VP-ITC Microcalorimeter with Origin 7 software and VPViewer2000 (GE Healthcare, Northampton, MA).



Figure 1: 1H NMR spectra of MINP3(7). 1H NMR spectra of (a) **1** in CDCl3, (b) alkynyl-SCM in D2O, (c) MINP**3**(**7**) in D2O at 25 °C.

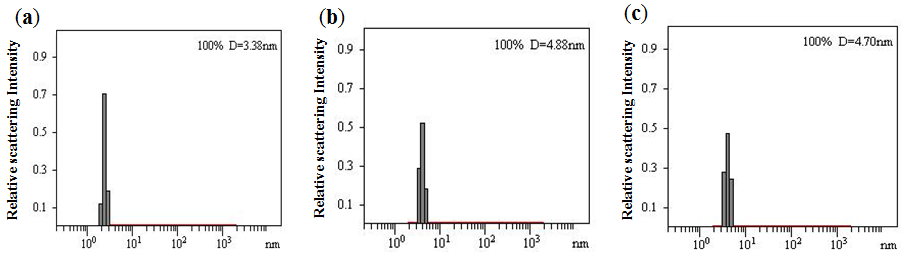


Figure 2S: DLS of MINP3(7). Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) alkynyl-SCM (b) surface-functionalized SCM and (c) MINP**3**(**7**) after purification

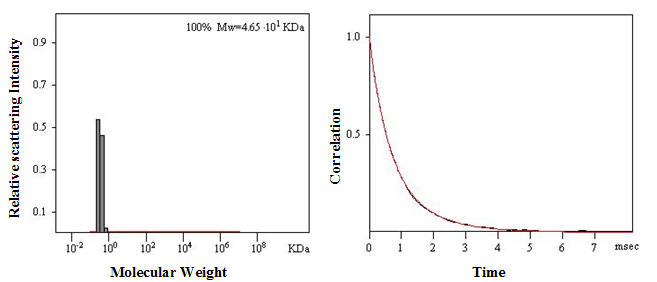


Figure 3S: Molecular Weight of MINP3(7). Distribution of the molecular weights of MINP**3**(**7**) and the correlation curves for DLS. The molecular weight distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP**3**(**7**) is assumed to contain one molecule of compound **1** (MW = 465 g/mol), 1.2 molecules of compound **2** (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of compound **3** (MW = 264 g/mol), the molecular weight of MINP**3**(**7**) translates to 46 [= 46500/(465+1.2×172+130+0.8×264)] of such units.



Figure 4S: 1H NMR spectra of MINP4(7). 1H NMR spectra of (a) **1** in CDCl3, (b) alkynyl-SCM in D2O, (c) MINP**4**(**7**) in D2O at 25 °C.

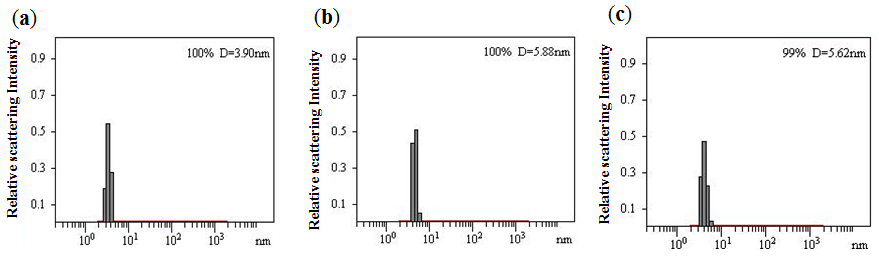


Figure 5S: DLS of MINP4(7). Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) alkynyl-SCM (b) surface-functionalized SCM and (c) MINP**4**(**7**) after purification

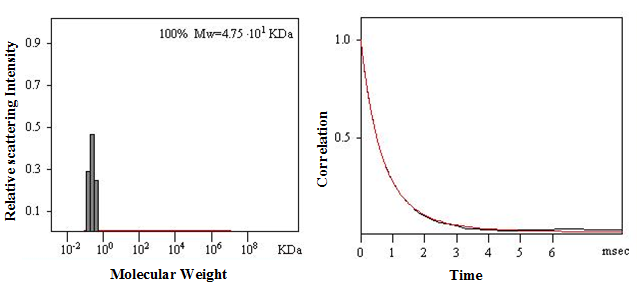


Figure 6S: Molecular Weight of MINP4(7). Distribution of the molecular weights MINP**4**(**7**)) and the correlation curves for DLS. The molecular weight distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP**4**(**7**) is assumed to contain one molecule of compound **1** (MW = 465 g/mol), 1.2 molecules of compound **2** (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of compound **4** (MW = 205 g/mol), the molecular weight of MINP**4**(**7**) translates to 49 [= 47500/(465+1.2×172+130+0.8×205)] of such units.



Figure 7S: 1H NMR spectra of MINP5(7). 1H NMR spectra of (a) **1** in CDCl3, (b) alkynyl-SCM in D2O, (c) MINP**5**(**7**) in D2O at 25 °C.

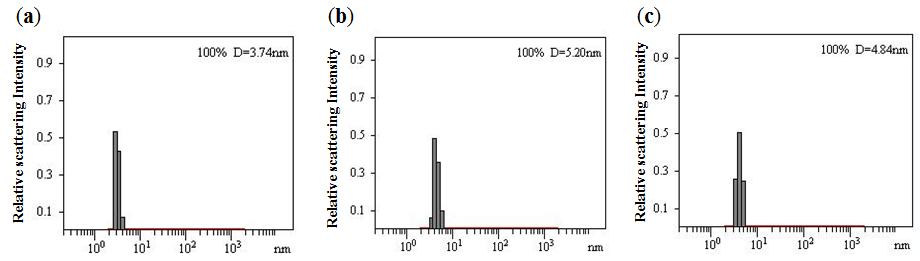


Figure 8S: DLS of MINP5(7). Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) alkynyl-SCM (b) surface-functionalized SCM, and (c) MINP**5**(**7**) after purification

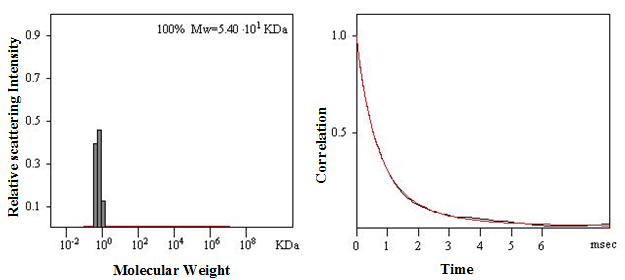


Figure 9S: Molecular Weight of MINP5(7). Distribution of the molecular weights of MINP**5**(**7**) and the correlation curves for DLS. The molecular weight distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP**5**(**7**) is assumed to contain one molecule of compound **1** (MW = 465 g/mol), 1.2 molecules of compound **2** (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of compound **5** (MW = 367 g/mol), the molecular weight of MINP**5**(**7**) translates to 49 [= 54000/(465+1.2×172+130+0.8×367)] of such units.



Figure 10S: 1H NMR spectra of MINP6(7). 1H NMR spectra of (a) **1** in CDCl3, (b) alkynyl-SCM in D2O (c) MINP**6**(**7**) in D2O at 25 °C.

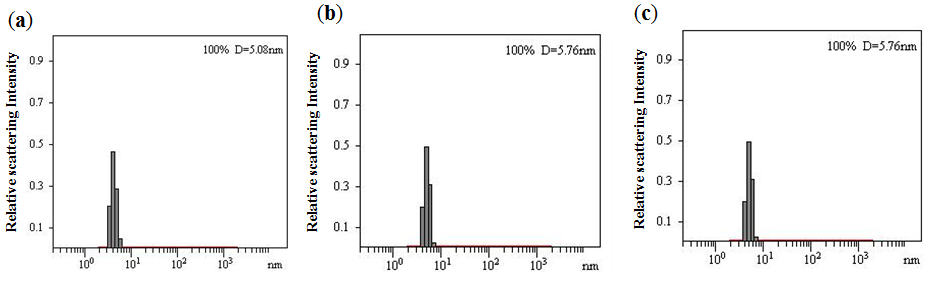


Figure 11S: DLS of MINP6(7). Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) alkynyl-SCM (b) surface-functionalized SCM, and (c) MINP**6**(**7**) after purification.

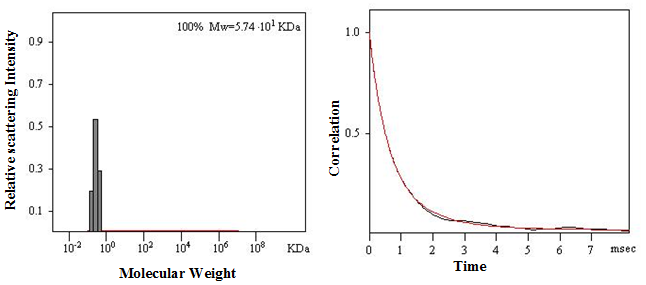


Figure 12S: Molecular Weight of MINP6(7). Distribution of the molecular weights of MINP**6**(**7**) and the correlation curves for DLS. The molecular weight distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP**6**(**7**) is assumed to contain one molecule of compound **1** (MW = 465 g/mol), 1.2 molecules of compound **3** (MW = 172 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of compound **6** (MW = 367 g/mol), the molecular weight of MINP**6**(**7**) translates to 52 [= 57400/(465+1.2×172+130+0.8×367)] of such units.

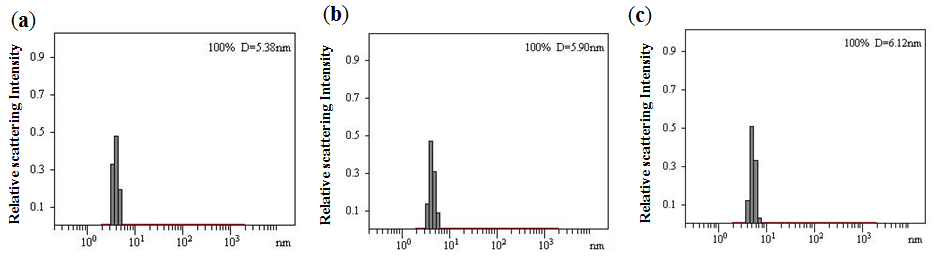


Figure 13S: DLS of MINP3,10(7). Distribution of the hydrodynamic diameters of the nanoparticles in water as determined by DLS for (a) alkynyl-SCM (b) surface-functionalized SCM, and (c) MINP**3,10**(**7**) after purification.

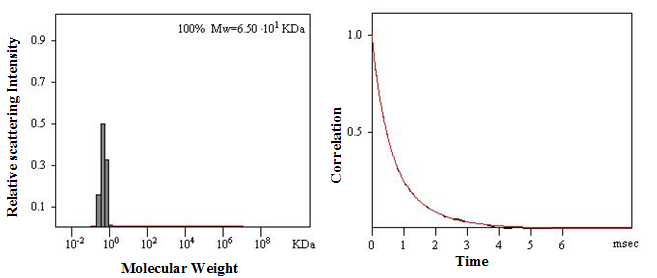
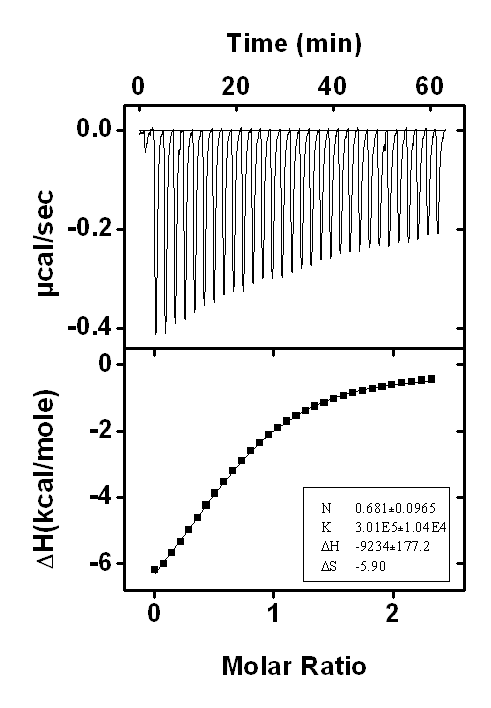
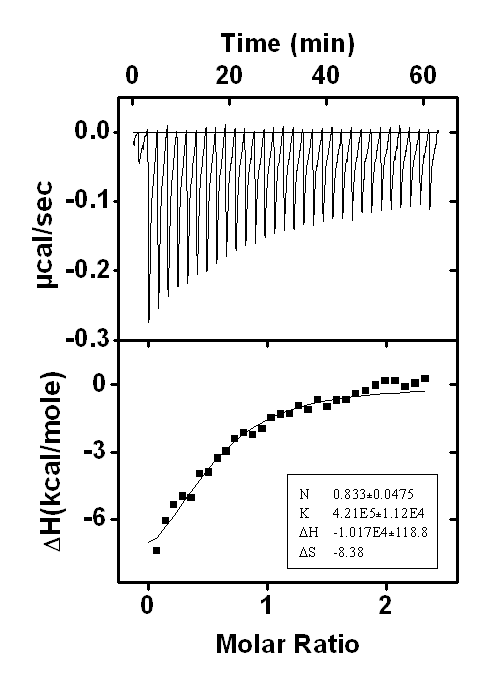
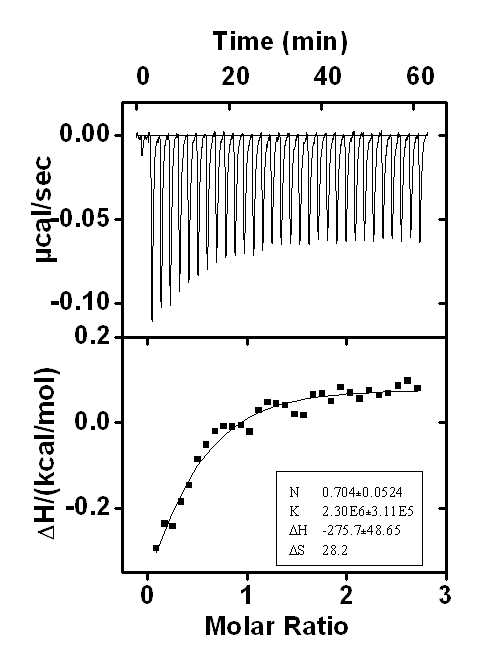


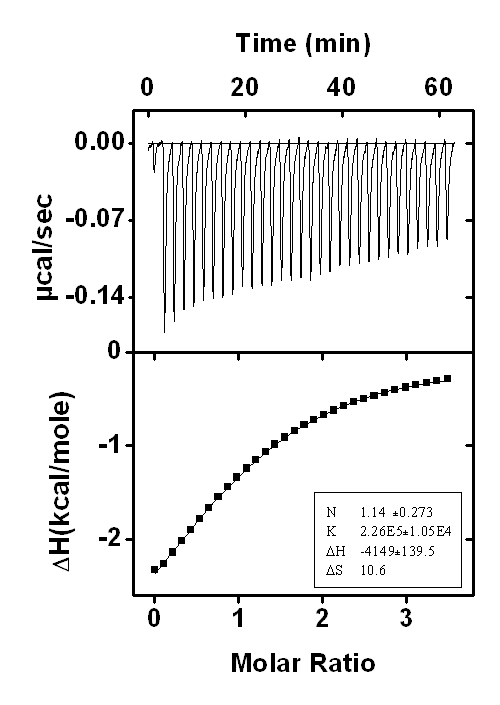
Figure 14S: Molecular Weight of MINP3,10(7). Distribution of the molecular weights of MINP**3,10**(**7**) and the correlation curves for DLS. The molecular weight distribution was calculated by the PRECISION DECONVOLVE program assuming the intensity of scattering is proportional to the mass of the particle squared. If each unit of building block for the MINP**3,10**(**7**) is assumed to contain one molecule of compound **1** (MW = 465 g/mol), 1.2 molecules of compound **10** (MW = 390 g/mol), one molecule of DVB (MW = 130 g/mol), and 0.8 molecules of compound **3** (MW = 264 g/mol), the molecular weight of MINP**3,10**(**7**) translates to 51 [= 65000/(465+1.2×390+130+0.8×264)] of such units.



**(c)**

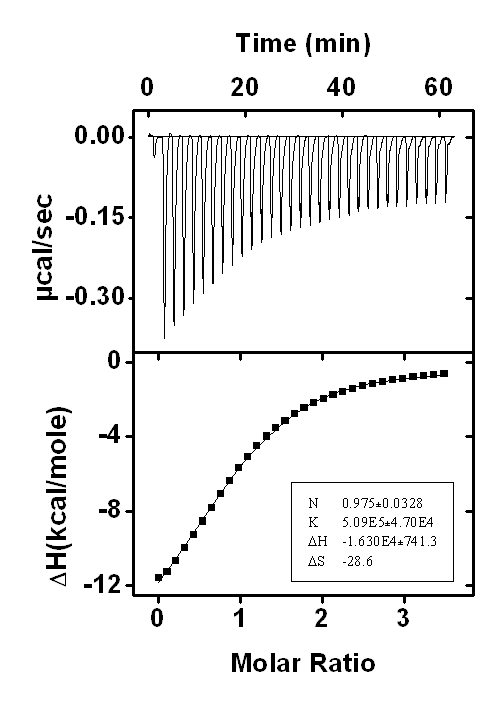
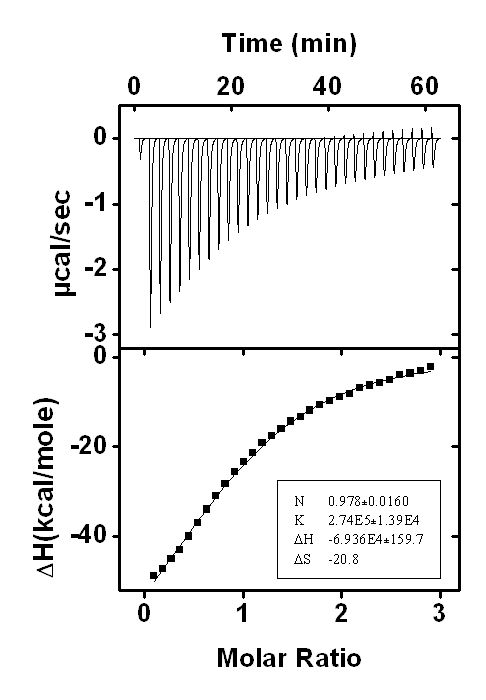
**(b)**

**(a)**



**(d)**

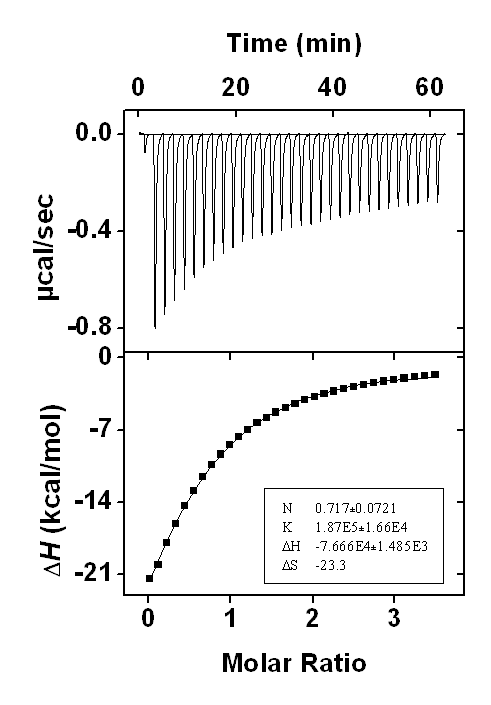
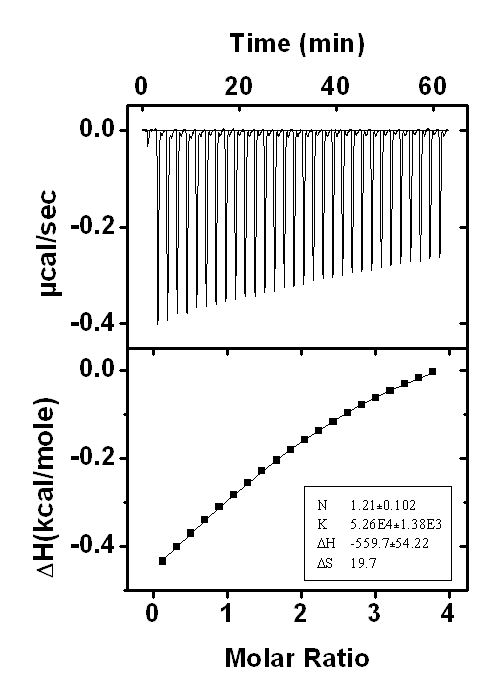
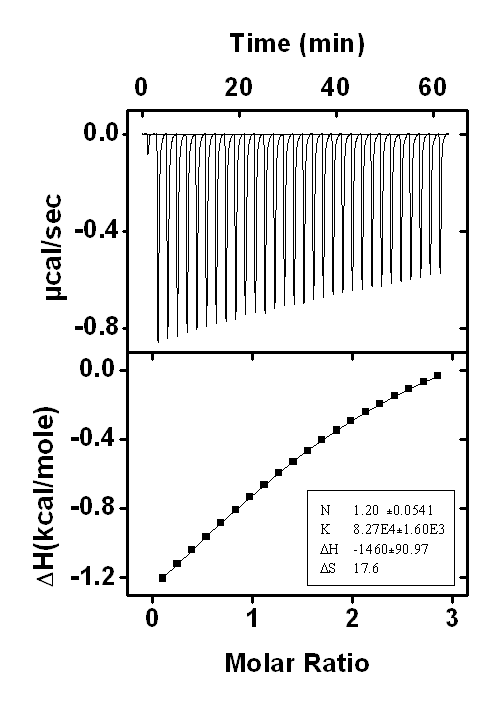
Figure 15S: ITC binding curves for guest 7. ITC titration curves obtained at 298 K for the binding of **7** by (a) MINP**3**(**7**), (b)MINP**4**(**7**), (c) MINP**5**(**7**), and (d)MINP**6**(**7**) prepared with 1 equiv of DVB. In general, an aqueous solution of an appropriate bile salt in Tris buffer (50 mM Tris, 150 mM NaCl, pH = 7.4) was injected in equal steps into 1.428 mL of the corresponding MINP solution (4.0 mg/mL) in the same buffer. The top panel shows the raw calorimetric data. The area under each peak represents the amount of heat generated at each ejection and is plotted against the molar ratio of the bile salt to the MINP. The smooth solid line is the best fit of the experimental data to the sequential binding of *N* equal and independent binding sites on the MINP. The heat of dilution for the bile salt, obtained by adding the bile salt to the buffer, was subtracted from the heat released during the binding. Binding parameters were auto-generated after curve fitting using Microcal Origin 7.

**(b)**

**(c)**

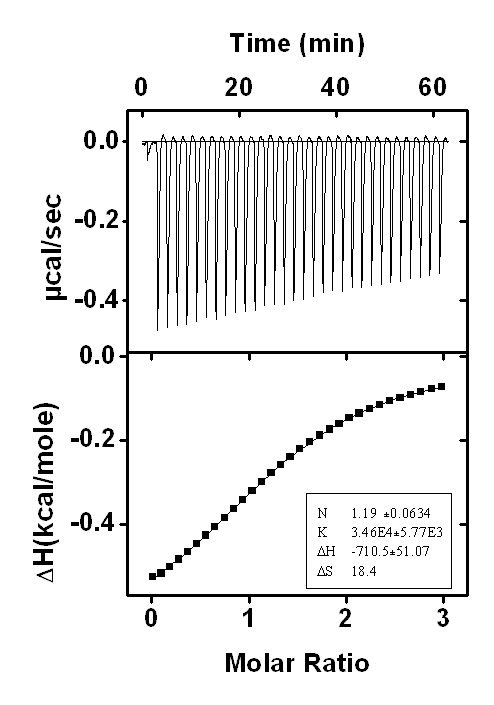
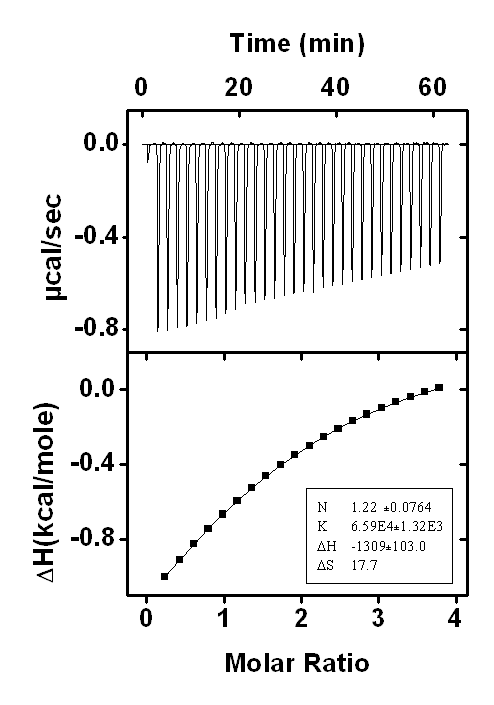
**(a)**

**(e)**

**(f)**

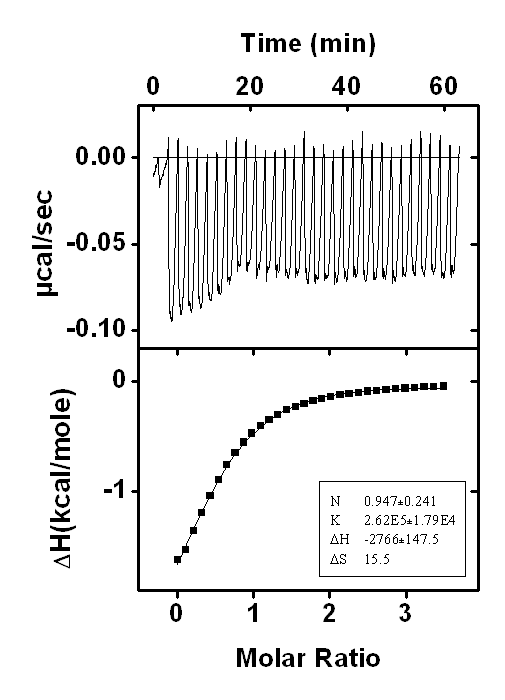
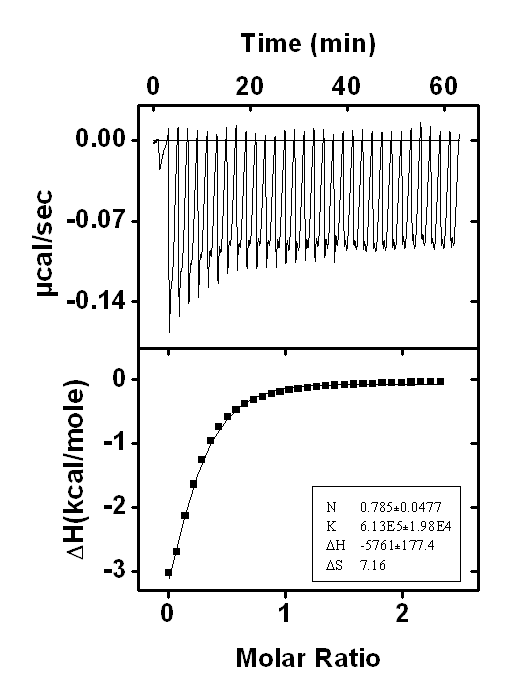
**(d)**

**(h)**

**(g)**

Figure 16S: ITC binding curves for guest 8 & 9. ITC titration curves obtained at 298 K for the binding of **8** by (a) MINP3(**8**),(b)MINP4(**8**),(c) MINP5(**8**),(d)MINP6(**8**),and **9** by (e) MINP3(**9),** (f)MINP4(**9**)**,** (g) MINP5(**9**),(h)MINP6(**9**) prepared with 1 equiv of DVB. In general, an aqueous solution of an appropriate bile salt in Tris buffer (50 mM Tris, 150 mM NaCl, pH = 7.4) was injected in equal steps into 1.428 mL of the corresponding MINP solution in the same buffer. The top panel shows the raw calorimetric data. The area under each peak represents the amount of heat generated at each ejection and is plotted against the molar ratio of the bile salt to the MINP. The smooth solid line is the best fit of the experimental data to the sequential binding of *N* equal and independent binding sites on the MINP. The heat of dilution for the bile salt, obtained by adding the bile salt to the buffer, was subtracted from the heat released during the binding. Binding parameters were auto-generated after curve fitting using Microcal Origin 7.

**(b)**

**(a)**

Figure 17S: ITC binding curves for guest 7 & 9. ITC titration curves obtained at 298 K for the binding of **7** by (a) MINP3,10(**7**),and **9** by(b)MINP3,10(**9**)prepared with 1 equiv of DVB. In general, an aqueous solution of an appropriate bile salt in Tris buffer (50 mM Tris, 150 mM NaCl, pH = 7.4) was injected in equal steps into 1.428 mL of the corresponding MINP solution in the same buffer. The top panel shows the raw calorimetric data. The area under each peak represents the amount of heat generated at each ejection and is plotted against the molar ratio of the bile salt to the MINP. The smooth solid line is the best fit of the experimental data to the sequential binding of *N* equal and independent binding sites on the MINP. The heat of dilution for the bile salt, obtained by adding the bile salt to the buffer, was subtracted from the heat released during the binding. Binding parameters were auto-generated after curve fitting using Microcal Origin 7.

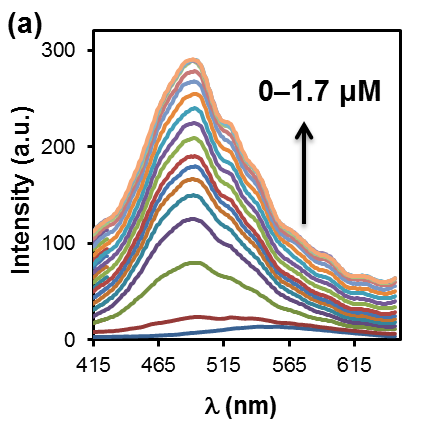
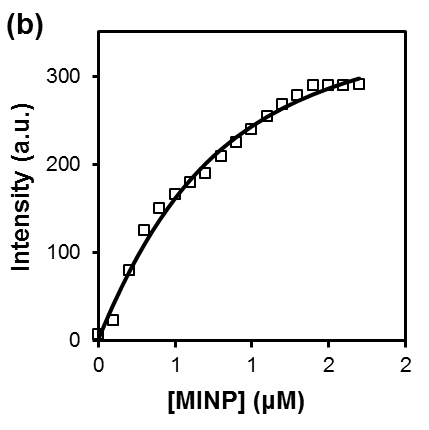
 

Figure 18S: Fluorescence binding curve for MINP3(7). (a) Emission spectra of compound **7** in the presence of 0-1.7 µM of MINP**3**(**7**) in Millipore water. [**7**] = 0.5 µM. λex = 340 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 491 nm to a 1:1 binding isotherm.

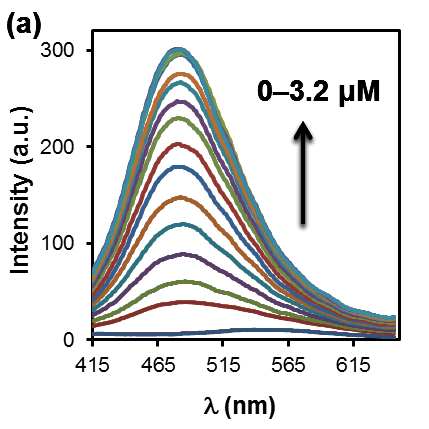
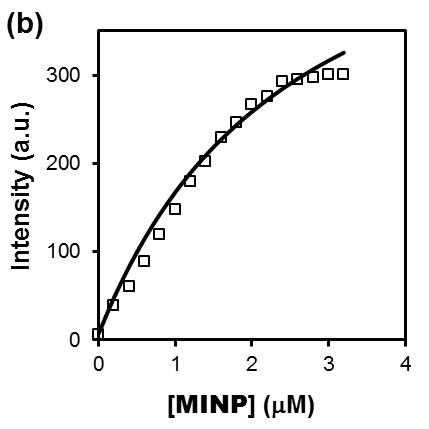
 

Figure 19S: Fluorescence binding curve for MINP4(7). (a) Emission spectra of compound **7** in the presence of 0-3.2 µM of MINP**4**(**7**) in Millipore water. [**7**] = 0.3 µM. λex = 340 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 483 nm to a 1:1 binding isotherm.

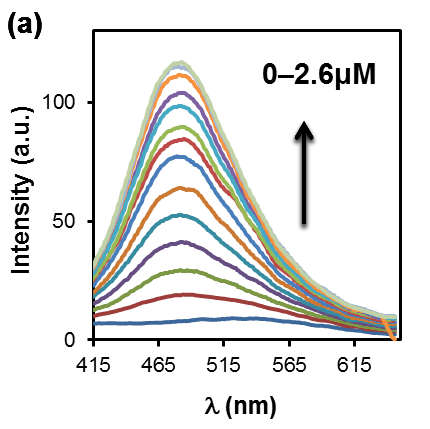
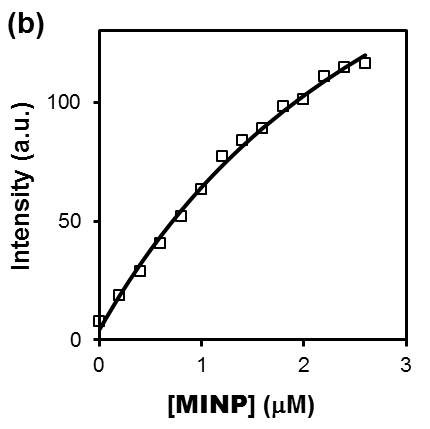
 

Figure 20S: Fluorescence binding curve for MINP5(7). (a) Emission spectra of compound **7** in the presence of 0-2.6 µM of MINP**5**(**7**) in Millipore water. [**7**] = 0.3 µM. λex = 340 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 478 nm to a 1:1 binding isotherm.

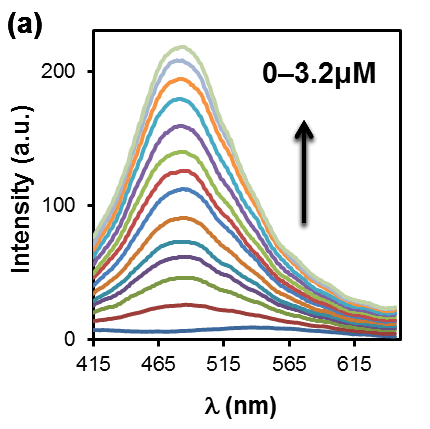
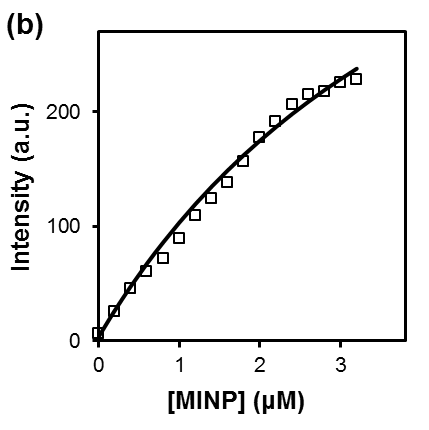
 

Figure 21S: Fluorescence binding curve for MINP6(7). (a) Emission spectra of compound **7** in the presence of 0-2.6 µM of MINP**6**(**7**) in Millipore water. [**7**] = 0.3 µM. λex = 340 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 475 nm to a 1:1 binding isotherm.

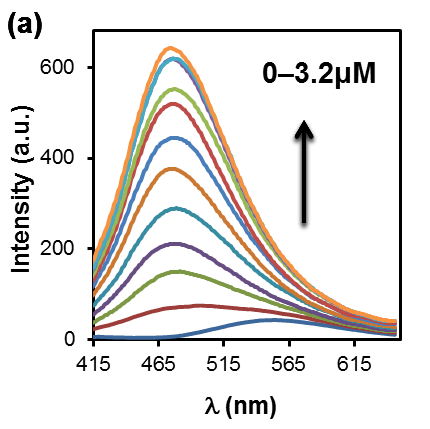
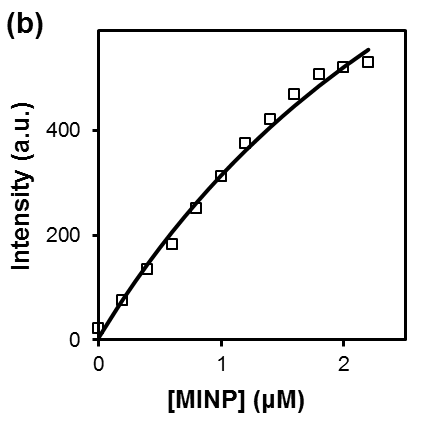
 

Figure 22S: Fluorescence binding curve for MINP3,10(7).(a) Emission spectra of compound **7** in the presence of 0-3.2 µM of MINP**3,10**(**7**)in Millipore water. [**7**] = 0.2 µM. λex = 340 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 503 nm to a 1:1 binding isotherm.

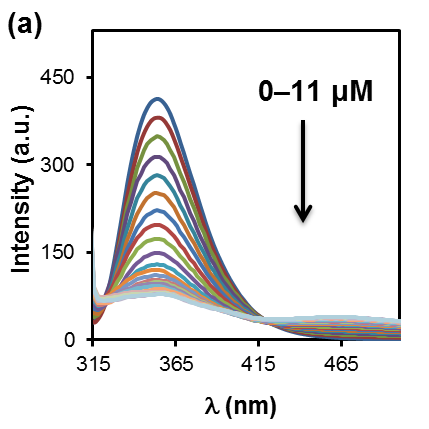
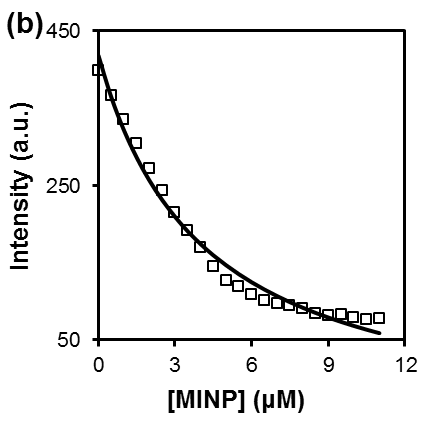
 

Figure 23S: Fluorescence binding curve for MINP3(7).(a) Emission spectra of compound **8** in the presence of 0-11 µM of MINP**3**(**7**)in Millipore water. [**8**] = 1.0 µM. λex = 295 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 348 nm to a 1:1 binding isotherm.

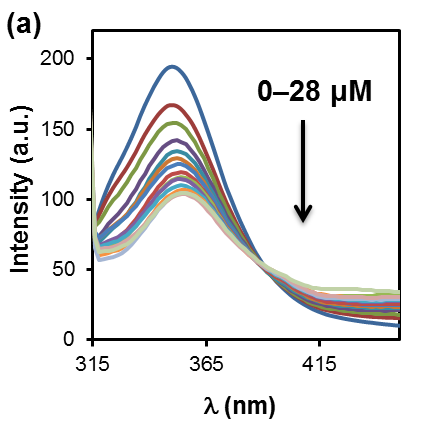
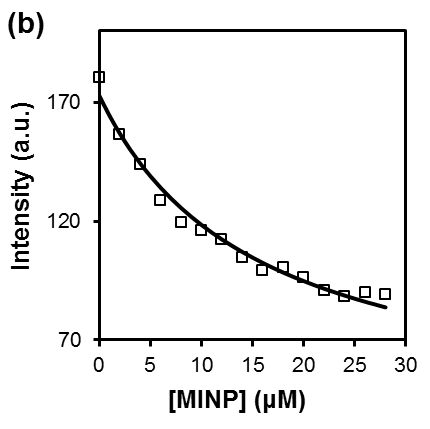
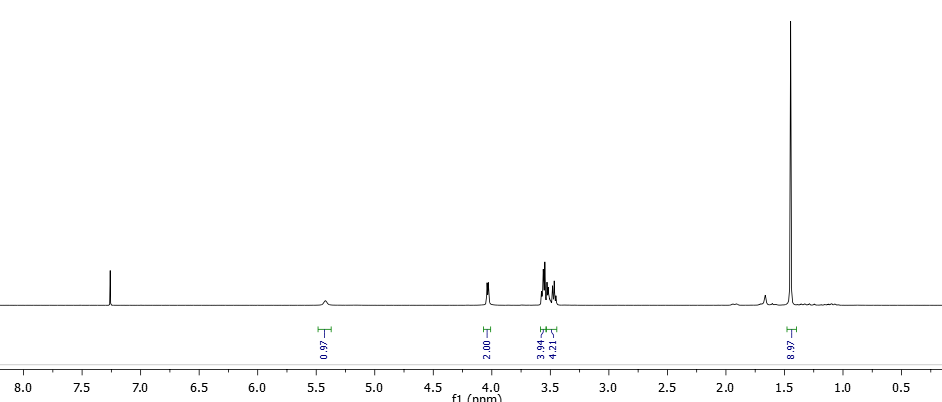
 

Figure 24S: Fluorescence binding curve for MINP3(7).(a) Emission spectra of compound **9** in the presence of 0-28 µM of MINP**3**(**7**)in Millipore water. [**9**] = 1.0 µM. λex = 295 nm. (b) Nonlinear least squares curve fitting of the fluorescence intensity at 342 nm to a 1:1 binding isotherm.

# 1H NMR spectra



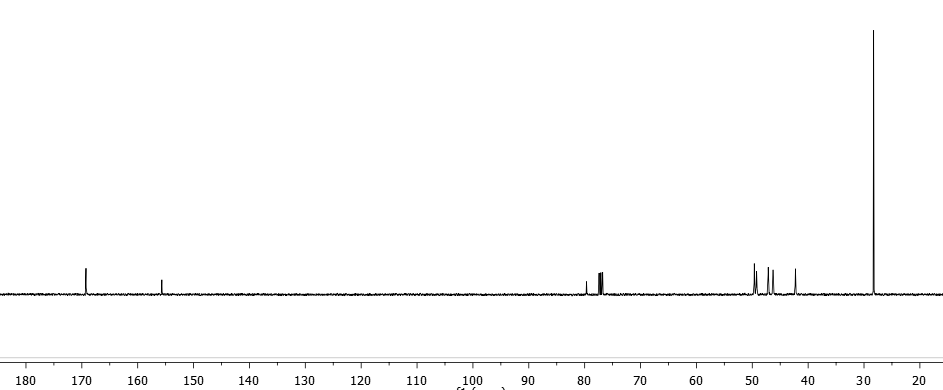
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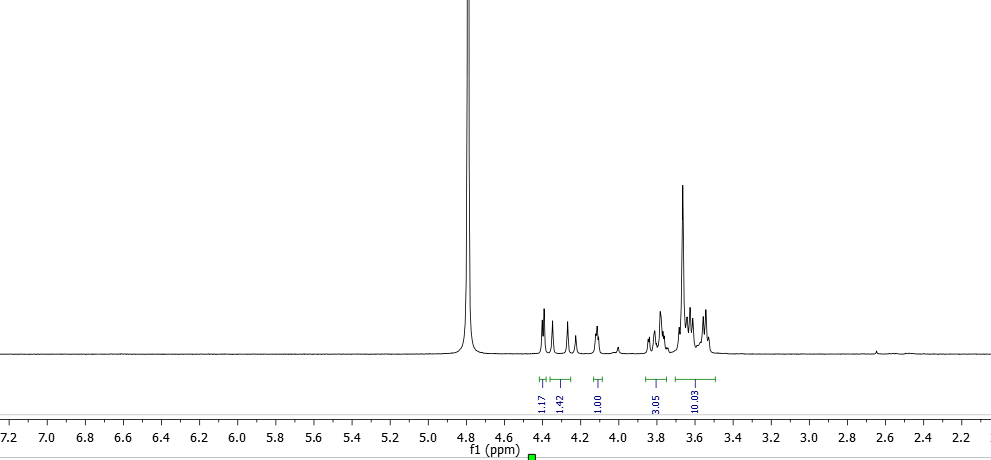
N-H

Ha

Hb







H**c ,**H**d ,**H**e ,**H**g**

H**b**

H**f**

H**a**



