Supplementary Information

Smart Amphiphiles: Hydro/Organogelators for *In Situ* Reduction of Gold

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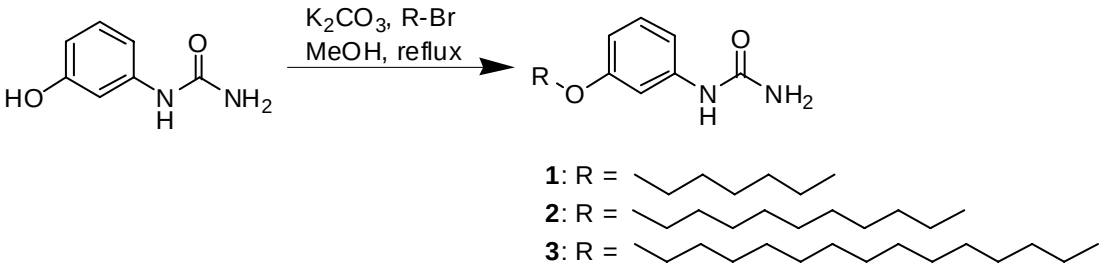
Scheme S1.



Experimental.

General Procedure for the synthesis of urea based amphiphiles, 1-3. *N*-carbamyl-*m*-aminophenol (0.456g, 3 mmol) was dissolved in 30 ml of dry methanol to that 1-alkylbromide (3.6 mmol) and K_2CO_3 (2.07 g, 15 mmol) was added, the resulting mixture was refluxed for 48 hrs. The reaction mixture was filtered to collect the intended product and separate it from the K_2CO_3. After evaporation of the solvent, upon addition of water white precipitate was formed, solid was filtered and washed with the water (3 × 25 mL) and $CHCl_3$ (3 × 25 mL). **1**, **2** and **3** were obtained as pure solids in 85, 70 and 79% yields respectively.

***N*-carbamyl-*m*-aminohexyloxybenzene, 1.** ^{1}H-NMR, (Acetone-d_6, 300MHz) δ 8.0 (*s*, 1H), 7.36 (*s*, 1H), 7.15 (*t*, 1H), 6.98 (*d*, 1H), 6.55 (*d*, 1H), 5.4 (*s*, 2H), 4.05 (*t*, 2H), 1.85 (*m*, 2H), 1.45 (*br s*, 2H), 1.35 (m, 4H), 0.95 (*m*, 3H). FT-IR, 3454 cm^{-1}, 2952 cm^{-1}, 1670 cm^{-1}. Anal. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.06; H, 8.52; N, 11.86. Found: C, 66.01; H, 8.56; N. 11.88.

***N*-carbamyl-*m*-aminodecyloxybenzene, 2.** ^{1}H-NMR, (Acetone-d_6, 300MHz) δ 8.05 (*s*, 1H), 7.34 (*s*, 1H), 7.15 (*t*, 1H), 6.98 (*d*, 1H), 6.5 (*d*, 1H), 5.4 (*s*, 2H), 4.0 (*t*, 2H), 1.85 (*m*, 2H), 1.45 (*br s*, 2H), 1.35 (m, 12H), 0.95 (*m*, 3H). FT-IR, 3454 cm^{-1}, 2952 cm^{-1}, 1670 cm^{-1}. Anal. Calcd. for $C_{17}H_{28}N_2O_2$: C, 69.81; H, 9.64; N, 9.58. Found: C, 69.78; H, 9.66; N. 9.57.

***N*-carbamyl-*m*-aminotetradecyloxybenezene, 3.** ^{1}H-NMR, (Acetone-d_6, 300MHz) δ 8.05 (*s*, 1H), 7.38 (*s*, 1H), 7.15 (*t*, 1H), 6.98 (*d*, 1H), 6.55 (*d*, 1H), 5.45 (*s*, 2H), 3.98 (*t*, 2H), 1.85 (*m*, 2H), 1.45 (*br s*, 2H), 1.35 (m, 20H), 0.95 (*m*, 3H). FT-IR, 3454 cm^{-1}, 2952 cm^{-1}, 1670 cm^{-1}. Anal. Calcd. for $C_{21}H_{36}N_2O_2$: C, 72.37; H, 10.4; N, 8.03. Found: C, 72.35; H, 10.37; N. 8.09.

Typical hydrogel and gold nanoparticle preparation. $HAuCl_4$ stock solution was made in acetone and water separately. Required amount (1-10 mg) of gelator was weighed and taken in 2 mL screw capped vial, to that appropriate amount of solvent (1-2 mL) and $HAuCl_4$ solution were added and closed tightly. The vial was heated to 40-50 ºC with shaking until the solid was completely dissolved. The solution was set aside and allowed to cool to room temperature. Within 2 to 30 mins GNPs embedded pink coloured gels were formed. Gelation was considered to be occurred when we observed no gravitational flow in inverted tube.

Table S1. The gelation ability of **1-3** in water and various organic solvents.[a]

solvent	3	2	1
water	G (0.1)[b][92][c]	G (0.4) [84]	G (0.4) [70]
cyclohexane	G (0.2) [78]	G (0.5) [75]	G (0.6) [81]
benzene	G (0.5) [68]	G (1.0) [62]	G (1.0) [60]
toluene	G (0.5) [68]	G (1.0) [60]	G (1.0) [64]
CCl_4	G (0.4) [75]	G (1.2) [66]	G (1.25) [68]
$CHCl_3$	G (0.6) [57]	G (1.5) [49]	Sol
CH_3CN	G (0.4) [73]	G (1.0) [67]	Sol
acetone	G (0.6) [73]	Sol	Sol
1,4-dioxane	G (1.0) [78]	Sol	Sol
methonol	G (1.0) [70]	Sol	Sol
DMF	Sol	Sol	Sol
DMSO	Sol	Sol	Sol

[a]G = stable gel at room temperature. [b]Minimum gelation concentrations showed in ( ). [c]Gel melting temperatures, T_{gel} showed in [ ]. Sol = soluble.

Table S2. FT-IR absorbance bands of urea carbonyl group in various states of **2** and **3**.[a]

Compound	acetone solution	solid from	xerogel
2	1667	1649	1641
3	1659	1636	1630

[a]Xerogels were prepared by freeze drying of D_2O gels.

(Explanation: The observed carbonyl stretching values of xerogel and solid phase are lower than solution phase which suggesting that these amphiphiles are indeed participating in extensive hydrogen bonding in solid state as well as gel state.)

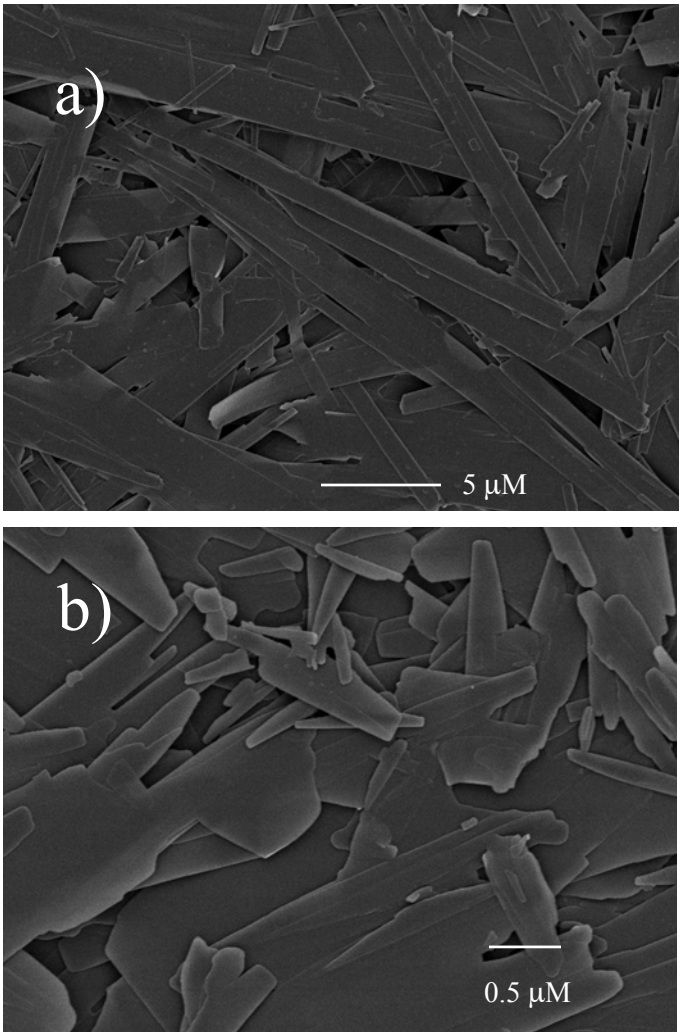


Figure S1. SEM image of xerogels prepared from gels of a) **2** in CH_3CN, b) **2** in water.

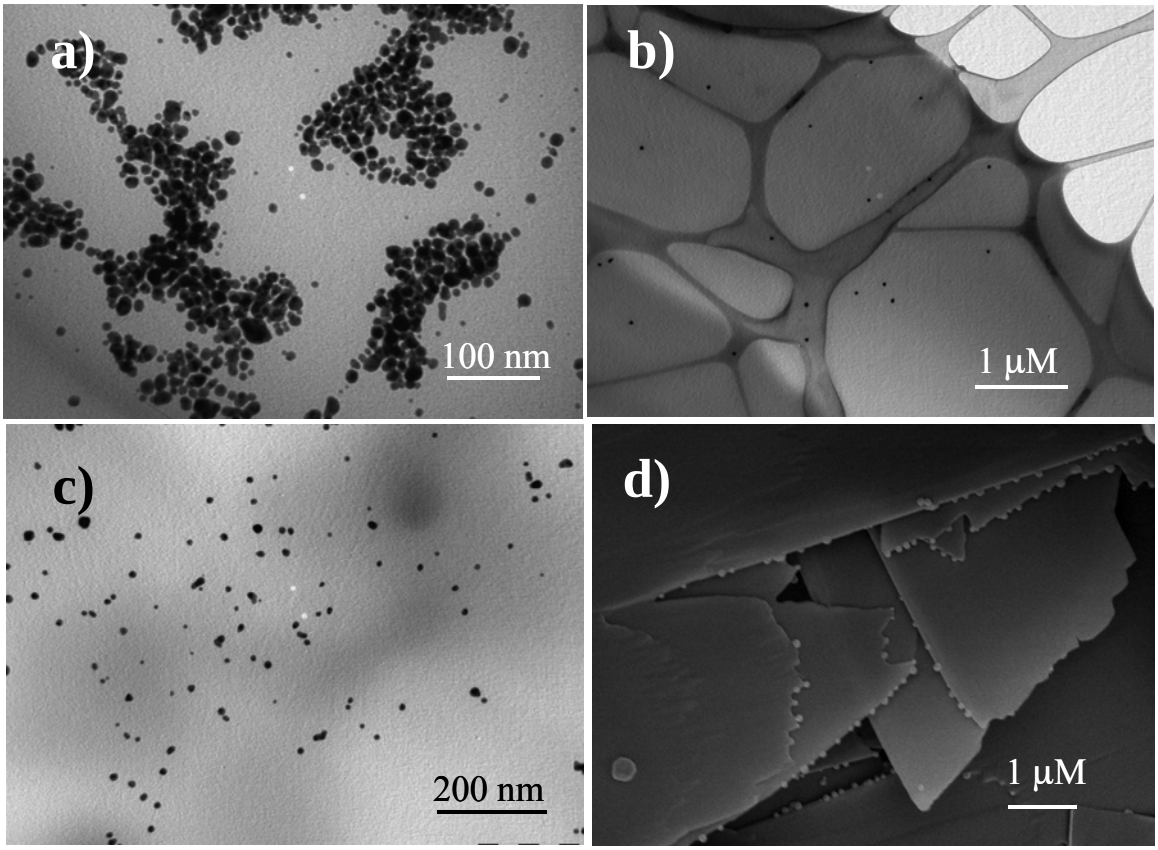


Figure S2. TEM image of a) **1** capped gold nanoparticles in acetone solution. b, c) acetone gel of **3** with gold nanoparticles. SEM image of xerogels prepared from gel of d) **2** in water with gold nanoparticles.

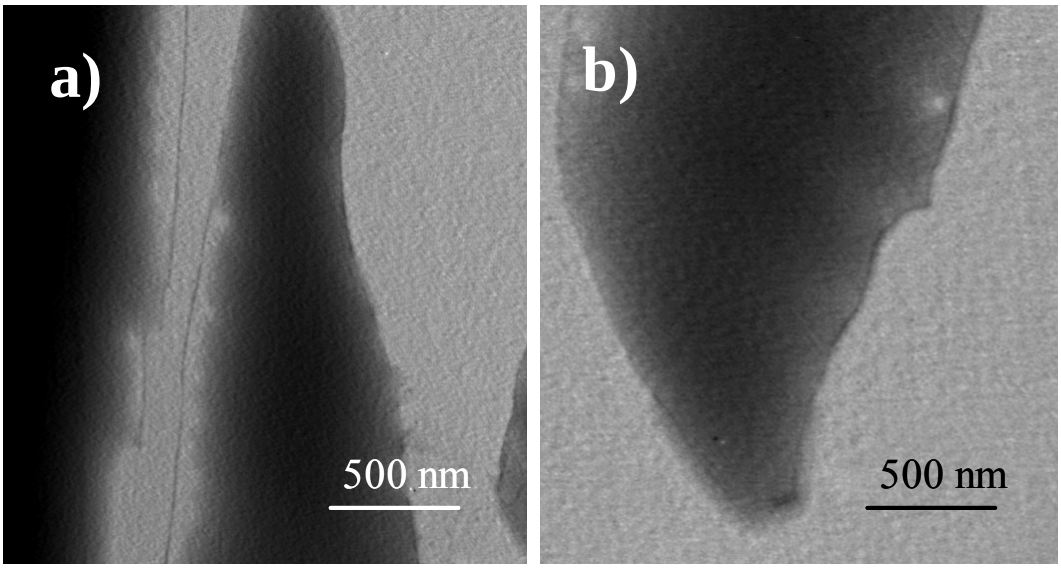


Figure S3. TEM image of a) acetone gel of **3**, b) hydrogel of **2** without gold nanoparticles.

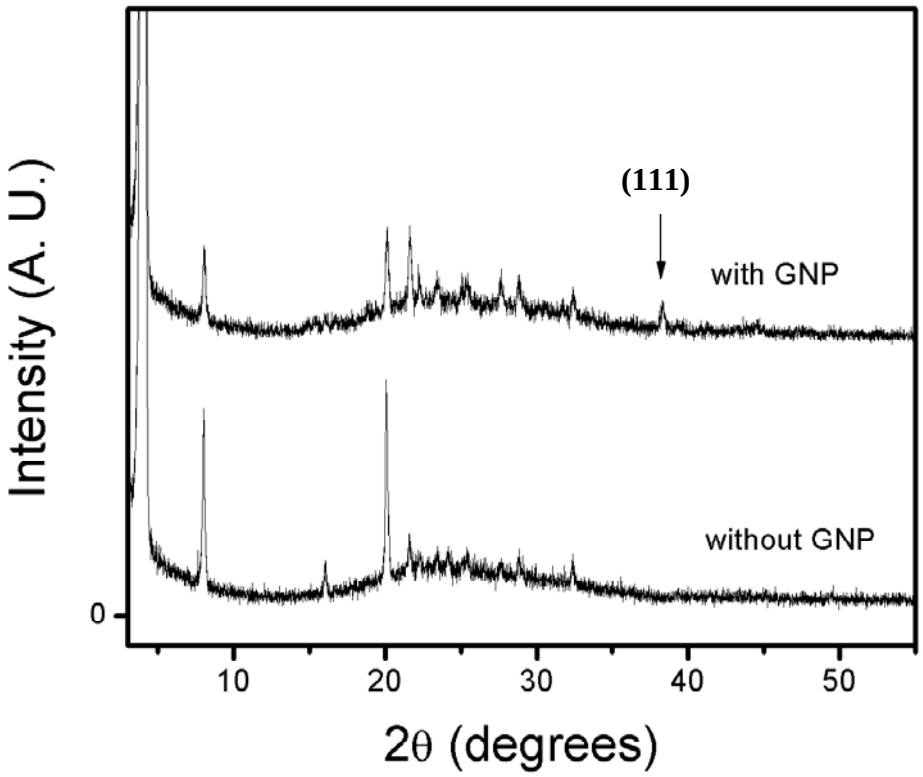


Figure S4. XRD diagrams of the hydrogels of **1** with and without gold nanoparticles (arrow shows peak corresponding to typical gold (111) plane).

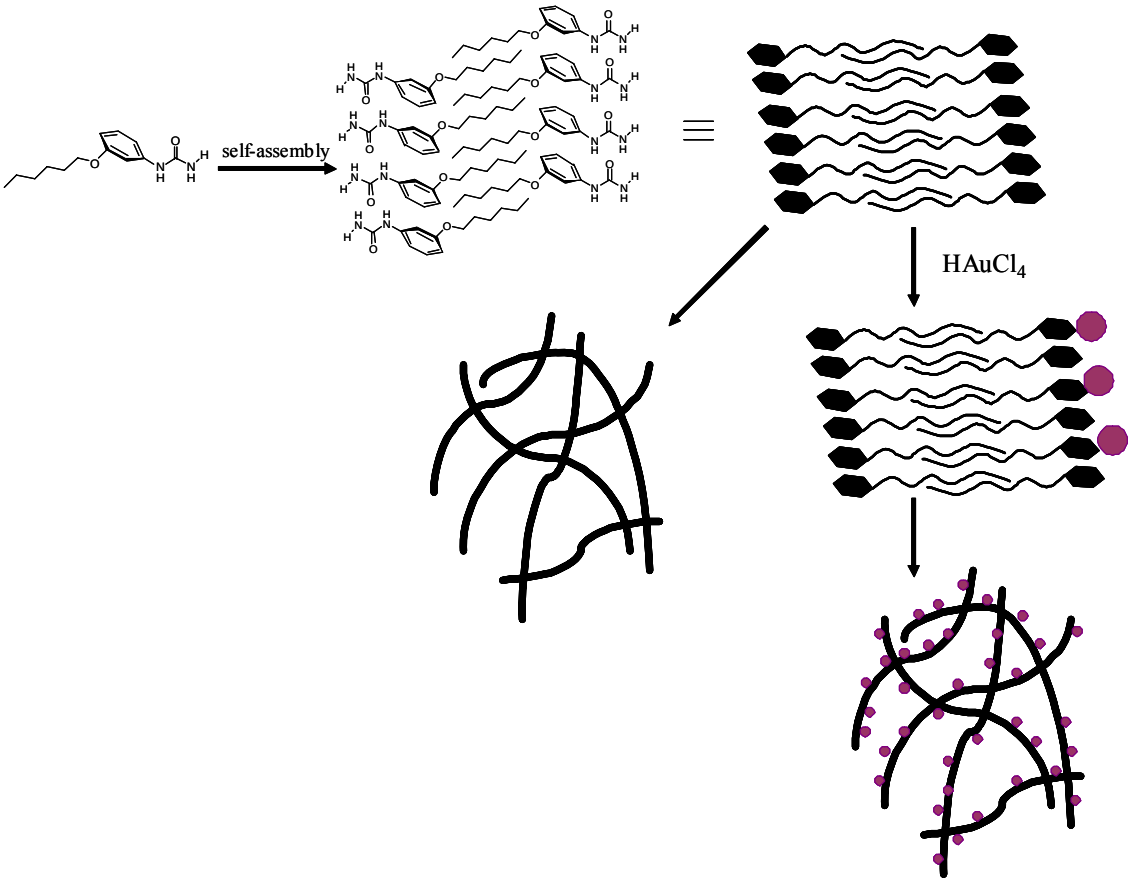


Figure S5. Schematic illustration for self-assembly of urea amphiphiles in hydrogels and arrangement for gold nanoparticles around hydrogel fibers.