Directional self-assembly of gold nanorods into 1D and 2D arrays by quadruple hydrogen bonding

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Materials and methods

General information

Chemicals were obtained from TCI, Energy Chemical or Adamas-beta® and used as received. All moisture sensitive reactions were carried out under N\textsubscript{2} using oven-dried glassware. Flash column chromatography was performed using Merck silica gel 60. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded using a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm using the residual solvent peaks at $\delta = 7.26$ (\textsuperscript{1}H NMR) ppm and 77.16 (\textsuperscript{13}C NMR) ppm in CDCl\textsubscript{3} and $\delta = 2.50$ (\textsuperscript{1}H NMR) ppm and 39.52 (\textsuperscript{13}C NMR) ppm in DMSO-d\textsubscript{6}. HRMS were recorded on a Xevo G2-XS QTof (Waters Comportaion). Transmission electron microscope (TEM) samples were examined by using a JEM-ARM200F operating at 200 kV. Atomic force microscopy (AFM) analysis was executed on a Bruker dimension icon.

Synthesis

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.8]
\node at (0,0) {5};
\node at (2,1) {6};
\node at (4,2) {7};
\node at (0,-1) {8};
\node at (2,-2) {1};
\draw (-1,0.5) -- (0,0) -- (1,0.5) node[midway, above] {EtOH, reflux, 72.6\%};
\draw (0,0) -- (1,1) node[midway, above] {BuNCO, Pyridine, reflux, 56.2\%};
\draw (1,1) -- (2,2) node[midway, above] {HCl in MeOH, MeOH, reflux, 66.2\%};
\draw (-1,-0.5) -- (0,0) -- (1,-0.5) node[midway, above] {Iscou, reflux, 95.2\%};
\end{scope}
\end{tikzpicture}
\end{center}

Scheme S1 Synthesis of thiol-functionalized UPy derivative 1.

Figure S1 (a) Structure of crosslinker 2 and the formation of the dimers by double hydrogen bonding; (b) structure of crosslinker 3 and 4 and the formation of the dimers by triple hydrogen bonding.
Scheme S2 Synthesis of crosslinker 4.

Compound 3\textsuperscript{1,2}, 5\textsuperscript{3} and 9\textsuperscript{4} were synthesized according to the literature.

**2-amino-6-(hex-5-en-1-yl)pyrimidin-4(3H)-one (6):** A solution of guanidinium carbonate (2.7 g, 15.0 mmol) and 3-oxo-8-nonenoic acid ethyl ester (5, 4.1 g, 20.7 mmol) in EtOH (50 mL) was refluxed overnight. After removing the solvent, the residue was purified by flash chromatography (CH\textsubscript{2}Cl\textsubscript{2}/MeOH 10/1, 5/1, 3/1) to give 6 as white solid (2.9 g, 72.6%). \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}) \( \delta \) 10.57 (s, 1H), 6.44 (br. s, 2H), 5.73-5.82 (m, 1H), 5.37 (s, 1H), 4.92-5.02 (m, 2H), 2.23 (t, \( J = 7.6 \) Hz, 2H), 1.99-2.05 (m, 2H), 1.49-1.57 (m, 2H), 1.30-1.38 (m, 2H); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}) \( \delta \) 169.7, 162.9, 155.6, 138.7, 114.8, 99.6, 36.9, 33.0, 27.9, 27.0; HRMS (ESI) calcd. for ([M+H]\textsuperscript{+}): C\textsubscript{10}H\textsubscript{16}N\textsubscript{3}O 194.1293; Found: 194.1295;

**1-butyl-3-(6-(hex-5-en-1-yl)-4-oxo-1,4-dihydropyrimidin-2-yl) urea (7):** To a stirred suspension of 2-amino-6-(hex-5-en-1-yl)pyrimidin-4(3H)-one (6, 0.2 g, 1.0 mmol) in dry pyridine (5 mL) was added n-butyl isocyanate (1.0 g, 10.1 mmol) under N\textsubscript{2}. The resulting mixture was refluxed for 16h. Then the solvent was evaporated and the reside was purified by flash chromatography (pure CH\textsubscript{2}Cl\textsubscript{2} to CH\textsubscript{2}Cl\textsubscript{2}/MeOH 40/1, 20/1), yielding 0.17 g (56.2%) of 7 as white solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 13.20 (s, 1H), 11.88 (s, 1H), 10.15 (s, 1H), 5.83 (s, 1H), 5.72-5.81 (m, 1H), 4.96-5.04 (m, 2H), 3.23-3.28 (m, 2H), 2.47 (t, \( J = 8.0 \) Hz, 2H), 2.09 (q, \( J = 8.0 \) Hz, 2H), 1.59-1.71 (m, 4H), 1.34-1.50 (m, 4H), 0.93 (t, \( J = 8.0 \) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 173.3, 156.8, 154.9, 152.3, 138.0, 115.3, 106.0, 40.0, 33.3, 32.7, 31.7, 28.1, 26.5, 20.3, 13.9; HRMS (ESI) calcd. for ([M+H]\textsuperscript{+}): C\textsubscript{15}H\textsubscript{25}N\textsubscript{4}O\textsubscript{2} 293.1978; Found: 293.1981;

**S-(6-(2-(3-butylureido)-6-oxo-3,6-dihydropyrimidin-4-yl)hexyl) ethanethioate (8):** To a mixture of 1-butyl-3-(6-(hex-5-en-1-yl)-4-oxo-1,4-dihydropyrimidin-2-yl) urea (7, 1.0 g, 3.4 mmol) and 2,2'-Azobis(2-methylpropionitrile) (0.3 g, 1.8 mmol) was added 66 mL of dry toluene. The suspension was bubbled with N\textsubscript{2} for 20 min. Then the thiolacetic acid (1.3 g, 17.1 mmol) was added under N\textsubscript{2} and the resulting mixture was refluxed for 14 h. After cooling down to rt, the solvent was evaporated and the
residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 50/1, 30/1, 20/1) to give 8 as white solid (1.2 g, 95.2%). $^1$H NMR (400MHz, CDCl$_3$): δ 13.20 (s, 1H), 11.88 (s, 1H), 10.14 (s, 1H), 5.82 (s, 1H), 3.22-3.28 (m, 2H), 2.86 (t, $J = 8.0$ Hz, 2H), 2.46 (t, $J = 8.0$ Hz, 2H), 2.33 (s, 3H), 1.59-1.61 (m, 4H), 1.34-1.41 (m, 8H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.1, 173.3, 156.7, 154.9, 152.3, 106.0, 39.9, 32.7, 31.7, 30.8, 29.4, 29.0, 28.44, 28.35, 26.9, 20.3, 13.91; HRMS (ESI) calcd. for ([M+H$^+$]+): C$_{17}$H$_{29}$N$_4$O$_3$S 369.1960; Found: 369.1962;

1-butyl-3-(6-(6-mercaptohexyl)-4-oxo-1,4-diarylmimidazin-2-yl)urea (1): S-(6-(2-(3-butyleno)-6-oxo-3,6-diarylmimidazin-4-yl)hexyl) ethanethioate (8, 0.35 g, 1.0 mmol) was dissolved in methanol (15 mL) at 60°C. Then HCl in methanol (4 M, 2.5 mL) was added and the reaction mixture was refluxed for 6 h. After removing the solvent, the residue was subjected to flash chromatography. Elution with CH$_2$Cl$_2$/MeOH 50/1, 30/1, 20/1 afforded 0.21 g (65.2%) of 1 as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 13.20 (s, 1H), 11.88 (s, 1H), 10.14 (s, 1H), 5.82 (s, 1H), 3.23-3.28 (m, 2H), 2.50-2.55 (m, 2H), 2.47 (t, $J = 8.0$ Hz, 2H), 1.57-1.68 (m, 6H), 1.25-1.43 (m, 6H), 0.94 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 173.3, 156.8, 154.9, 152.3, 106.0, 40.0, 33.9, 32.8, 31.7, 28.4, 28.0, 27.0, 24.6, 20.3, 13.9; HRMS (ESI) calcd. for ([M+H$^+$]+): C$_{15}$H$_{27}$N$_4$O$_2$S 327.1855; Found: 327.1851;

6,6'(((disulfanediylbis(hexane-6,1-diyl))bis(oxy))bis(4,1-phenylene))bis(1,3,5-triazine-2,4-diamine) (10): A mixture of 4-((6-mercaptohexyl)oxy)benzonitrile (9, 0.2 g, 0.85 mmol), dicyandiamide (0.286 g, 3.4 mmol) and KOH (0.095 g, 1.7 mmol) in dry 2-methoxyethanol (7 mL) was refluxed overnight. Then the solvent was concentrated and the residue was added cold water. The precipitate was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 20/1) to give compound 10 as white solid (0.14 g, 51.8%). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.18 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.66 (br. s, 4H), 4.01 (t, $J = 8.0$ Hz, 2H), 2.71 (t, $J = 8.0$ Hz, 2H), 1.63-1.74 (m, 4H), 1.41-1.43 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 169.8, 167.4, 161.1, 129.4, 129.3, 113.9, 67.5, 37.8, 28.53, 28.50, 27.5, 25.1; HRMS (ESI) calcd. for ([M+H$^+$]+): C$_{30}$H$_{41}$N$_{10}$O$_2$S$_2$ 637.2855; Found: 637.2856;

6-(4-(4,6-diamino-1,3,5-triazin-2-yl)phenoxy)hexane-1-thiol (4): A solution of 6,6'(((disulfanediylbis(hexane-6,1-diyl))bis(oxy))bis(4,1-phenylene))bis(1,3,5-triazine-2,4-diamine) (10, 0.1 g, 0.16 mmol), DL-dithiothreitol (DTT, 0.072 g, 0.47 mmol)
and triethylamine (TEA, 0.09 mL, 0.64 mmol) in dry THF (6 mL) was stirred at rt for 48 h. Then the solvent was evaporated and the residue was purified by flash chromatography (CH$_2$Cl$_2$/MeOH 50/1), yielding 0.09 g (89.7%) of 4 as white solid. 

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.18 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 8.0 Hz, 2H), 6.65 (br. s, 4H), 4.02 (t, $J$ = 8.0 Hz, 2H), 2.50 (q, $J$ = 8.0 Hz, 2H), 2.25 (t, $J$ = 8.0 Hz, 1H), 1.71-1.75 (m, 2H), 1.55-1.58 (m, 2H), 1.39-1.43 (m, 4H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 169.8, 167.3, 161.1, 129.4, 129.3, 113.9, 67.5, 33.3, 28.6, 27.5, 25.0, 23.7; HRMS (ESI) calcd. for ([M+H]$^+$): C$_{15}$H$_{22}$N$_5$OS 320.1545; Found: 320.1540;

**Preparation of gold nanorods (GNRs):** All glassware were cleaned in a bath of freshly prepared 1:3 HNO$_3$/HCl and rinsed with ultrapure water for 15 minutes prior to use. Briefly, the seed solution was firstly prepared by mixing 0.125 mL of 0.01 M hydrogen tetrachloroaurate(III) trihydrate (HAuCl$_4$·3H$_2$O) solution and 3.75 mL of 0.1 M aqueous solution of hexadecyltrimethylammonium bromide (CTAB), and then rapidly adding 0.3 mL of 0.01 M fresh NaBH$_4$ solution. After stirring vigorously for 2 min, 3-5 nm seed solution can be obtained. Next, a growth solution was prepared by adding 1.8 mL of 0.01 M HAuCl$_4$·3H$_2$O to 42.75 mL of 0.1 M CTAB solution, followed by 0.27 mL of 0.01 M AgNO$_3$, 0.288 mL of 0.1 M ascorbic acid and 0.2 mL of seed solution in order. The seed solution was thoroughly mixed and allowed to stand overnight to obtain GNRs. After the reaction was completed, an aqueous solution of GNRs was centrifuged at 10,000 r/min for 10 min, and washed with pure water for three times to remove excess CTAB from the solution. Samples for TEM studies were prepared by drop-casting the GNRs solution onto carbon-coated copper grids and air-drying for one day.

**General procedure of assembly linkage of GNRs:** The assembly process was initiated by the addition of crosslinker to the purified CTAB-GNRs. For this, calculated amounts of crosslinker dissolved in methanol with a range of concentrations (2.3-15.3 mM) were added to the purified GNRs solution. Then the mixture was gently stirred for 10 min and subsequently stood for 2 h. After that, one drop taken from the above solution was directly casted on a copper mesh for TEM measurement.
Representative TEM images

**Figure S2** Representative TEM image of as synthesized GNRs.

**Figure S3** Representative low magnification TEM images depicting the alignment of GNRs at 2.3 mM of crosslinker 1.
Figure S4 (a) AFM image of 2D ordered structures formed at 12.3 mM of crosslinker I; (b) the height profile of the 2D array; (c) packing model showing stacking of GNRs with a lateral displacement; (d) the overlap of GNRs is clearly shown in the TEM image of 2D ordered structures. The height of assembled superstructure is observed about 33.6 nm, which is approximately 3.4 times the diameter of individual GNRs, indicating this 2D array assembly structure consists of 4 layers of GNRs. In the model presented here, the second layer can stack onto the first layer, but with a lateral displacement so that the nanorods in the second layer are located halfway between the nanorods in the first layer, which was proven to be the most stable configuration for self-assembly.
**Figure S5** Representative TEM image. No obvious alignment is observed in the absence of crosslinker 1 at a high concentration of GNRs.

**Figure S6** Representative TEM images of GNR assemblies at different concentrations of crosslinker 2 with double hydrogen bonding. (a) 2.3 mM, (b) 4.6 mM, (c and d) 9.2 mM, (e) 12.3 mM, (f) 15.3 mM.
Figure S7 Representative TEM images of GNR assemblies at different concentrations of crosslinker 3 and 4 with triple hydrogen bonding. (a) 2.3 mM, (b) 4.6 mM, (c and d) 9.2 mM, (e) 12.3 mM, (f) 15.3 mM.

Figure S8 Histogram of distribution of the pairwise spacing between the attached ends of GNRs functionalized with crosslinking 1 measured in TEM images.

Reference