

# Optical and electrical properties of 3-dimensional interlinked Au nanoparticle assemblies

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## SUPPORTING INFORMATION

### 1. Linker synthesis

<sup>1</sup>H/<sup>13</sup>C-NMR spectra were recorded on a Bruker AV400 instrument. Chemical shifts (δ) are quoted in parts per million (ppm), referenced to the appropriate residual solvent. Abbreviations used are: s, singlet; d, dublet; t, triplet; q, quartet; m, multiplet. All chemicals were used as received without any further purification.

#### Synthesis of dithiol derivatives:

*1,4-bis(mercaptoacetamide)phenylenediamine* (DMAAB). The compound was prepared according to the literature<sup>1</sup>. A suspension of thioglycolic acid (0.1 mol, 7 ml, 2 eq) and *p*-phenylenediamine (0.05 mol, 5.4 g, 1 eq) in 20 ml MeOH was refluxed for 14 h under CO<sub>2</sub> atmosphere at 120°C oil bath temperature. After slowly

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<sup>1</sup> Aswar, A.S.; Bhadange, S. G. *J. Indian Chem. Soc.* **1997**, 74, 679-682.

cooling down to RT the mixture was poured into 70 ml 1N chilled HCl solution. The precipitate formed is filtered off and suspended in 40 ml boiling H<sub>2</sub>O. The white solid is separated by filtration, dried in air and recrystallized in 250 ml ethanol twice (2.1%). <sup>1</sup>H (400.13 MHz, DMSO-d<sub>6</sub>) δ: 10.03 (s, 2H, -NH-), 7.52 (s, 4H, H<sub>arom</sub>), 3.28 (d, 4H, *J* 8, -CH<sub>2</sub>-), 2.92 (t, 2H, *J* 8, -SH); <sup>13</sup>C (100.62 MHz, DMF-d<sub>7</sub>) δ: 168.3 (-CO-), 135.1, 119.42 (2xC<sub>arom</sub>), 29.0 (-CH<sub>2</sub>-); Anal. calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 46.85; H, 4.72; N, 10.93; O, 12.48; S, 25.02. Found C, 47.03; H, 4.71; N, 10.9; O, 12.9; S, 24.7.

*1,4-Bis(mercaptoacetamido)cyclohexane (DMAAcH)*. 40 mmol (5.44 g, 1 eq) *trans*-1,4-diaminocyclohexane and 15.3 ml N-ethyl-diisopropylamine (11.38 g, 88 mol, 2.2 eq) were dissolved in 200 ml DCM and cooled with an ice bath. A solution of 17.8 g (7.67 ml, 88 mmol, 2.2 eq) bromoacetyl bromide in 20 ml DCM was added over 20 min from a dropping funnel. The mixture is stirred for additional two hours at RT and separated from the precipitate by filtration. The solid were thoroughly washed with 1N HCl, several times with water and finally with ethanol and dried in vacuum (80%). The intermediate was used without further purification. 3.8 g (10 mmol, 1 eq) *trans*-1,4-bis(bromoacetyl-amido)cyclohexane and 2.5 g potassium thioacetate were dissolved in 100 ml DMF. The solution was stirred for 2 h at RT. After removing the solvent the residual solid was intensely washed with water and ethanol. 1,4-bis(acetyl-mercaptoacetyl-amido)-cyclohexane was recrystallized twice from an ethanol/DMF mixture. <sup>1</sup>H (400.13 MHz, DMSO-d<sub>6</sub>) δ: 7.6 (s, 1H, -NH), 3.65 (s, 2H, -CH<sub>2</sub>-), 2.38 (s, 3H, -CH<sub>3</sub>), 1.95-1.75 (m, 2H), 1.4-1.2 (m, 2H); <sup>13</sup>C (100.62 MHz, DMF-d<sub>7</sub>, 393K) δ: 194.7 (CH<sub>3</sub>C=O), 167.1 (-NH-C=O), 49.1 (C<sub>tert</sub>), 34.0, 31.6, 29.9. 100 mg of the precursor 1,4-bis(acetylmercaptoacetyl-amido)cyclohexane were suspended in a mixture of 25 ml ethanol and 25 ml 6N HCl. The solution was stirred under nitrogen for 14 h at 50°C. The product was filtered off and dried under vacuum. <sup>1</sup>H (400.13

MHz, DMSO- $d_6$ )  $\delta$ : 7.88 (d, 1H,  $J$  8, -NH), 3.56-3.42 (m, 2H, HS-CH $_2$ ), 3.04 (d, 1H,  $J$  8, HN-CH), 1.9-1.7 (m, 2H, H $_{eq}$ ), 1.3-1.15 (m, 2H, H $_{ax}$ );  $^{13}\text{C}$  (100.62 MHz, DMF- $d_7$ )  $\delta$ : 169.4 (C=O), 48.3 (C $_{tert}$ ), 31.6, 27.9. MS (EI)  $m/z$  262.1 (10), 229.1 (44), 187.1 (28), 171.1 (59), 155.2 (7), 92.1 (100), 81.1 (68), 56.2 (27), 47.0 (20).

*1,4-Bis(mercaptomethyl)cyclohexane (cHDMT)*. To a stirred, cooled solution (0°C) of 15.18 g (104 mmol) cis/trans-1,4-bis(hydroxymethyl)cyclohexane and 59.63 (229 mmol) triphenylphosphine in 300 ml chloroform 38.89g N-bromosuccinimide were carefully added under a flow of nitrogen. After stirring over night most of the chloroform was removed and 600 ml hexane were added under vigorous stirring. The resulting waxy solid was filtered off and washed again with 200 ml hexane. After combining the organic fractions the solvent was evaporated. The remaining crude product was diluted with 50 ml hexane and the flask washed 4 times with portions of 50ml hexane. The organic fractions were combined and the solvent was evaporated. The crude product was recrystallized from ethanol in the freezer at -22°C. Yield: 4.84 g (18 mmol, 17.2%) of the pure *trans* isomer of 1,4-bis(bromomethyl)cyclohexane (leafy crystals).  $^1\text{H}$  (400.13 MHz, CDCl $_3$ )  $\delta$ : 3.31 (d,  $J$  6.4, 4H, R-CH $_2$ Br), 1.96 (m, 4H, R-H $_{eq}$ ), 1.63 (m, 2H, R $_2$ -CH-CH $_2$ Br), 1.09 (m, 4H, R-H $_{ax}$ );  $^{13}\text{C}$  (100.62 MHz, CDCl $_3$ )  $\delta$ : 41.34 (R $_2$ -CH-CH $_2$ Br), 40.17 (R-CH $_2$ Br), 31.42(C $_{ring}$ ).

*1,4-Bis(mercaptomethyl)cyclohexane (cHDMT)*. A mixture of 3.77g (14 mmol) trans-1,4-bis(bromomethyl)cyclohexane in 30 ml ethanol and 2.56g (37 mmol) thiourea dissolved in 25 ml water was refluxed for 24 h. After 16 h 5g NaOH in 50ml deionized water was added. The reaction mixture was cooled down, neutralized with H $_2$ SO $_4$  and extracted 3 times with 80ml tert.-butylether. After drying the combined organic phases with MgSO $_4$  the solvent was removed. The crude product was purified twice by column chromatography (1: 150ml AlO $_x$ , diameter: 5 cm, 1 ethylacetate : 9

n-hexane; 2: 175ml AlO<sub>x</sub>, diameter: 2 cm, 1 ethylacetate : 9 n-hexane). Yield: 525 mg (3 mmol, 21.3%) of a colorless oil. <sup>1</sup>H (400.13 MHz, CDCl<sub>3</sub>) δ: 2.44 (m, 4H, R-CH<sub>2</sub>SH), 1.94 (m, 4H, R-H<sub>eq</sub>), 1.63 (m, 2H, R<sub>2</sub>-CH-CH<sub>2</sub>SH), 1.32 (t, *J* 8.4, 2H, R-SH), 0.99 (m, 4H, R-H<sub>ax</sub>); <sup>13</sup>C (100.62 MHz, CDCl<sub>3</sub>) δ: 41.36(R<sub>2</sub>-CH-CH<sub>2</sub>SH), 31.98(C<sub>ring</sub>) 31.75(R-CH<sub>2</sub>SH).

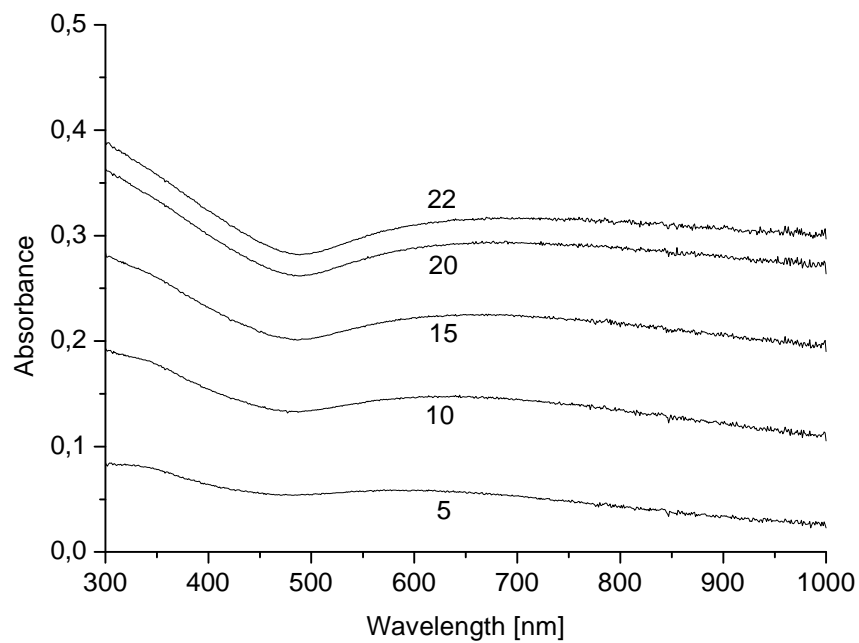
*Disodium 1,4-cyclohexanebisdithiocarbamate (cHBDT)*. The synthesis of cHBDT was carried out according to a procedure for disodium hexamethylenebisdithiocarbamate described elsewhere.<sup>2</sup>

*Disodium p-phenylenebisdithiocarbamate (PBDT)*. The compound was prepared according to a modified procedure of Lee et. al.<sup>3</sup> 5.4 g (50 mmol, 1 eq) *p*-phenylenediamine are suspended in a solution of 5 g NaOH in 100 ml H<sub>2</sub>O. The mixture is heated and stirred until the solution became homogeneous. After cooling down to RT 50 ml ethanol were added. To the solution was added dropwise 7.5 ml (9.52 g, 125 mmol, 2.5 eq) of carbondisulfide. The temperature of the mixture was maintained below 10 °C by external cooling. After addition was completed the solution was heated at 60 °C for 2 h, cooled down to RT and poured into about 2.5 l acetone. After 30 min a white crystal powder was filtered and washed thoroughly with acetone, dried under vacuum at RT (32%). <sup>1</sup>H (400.13 MHz, D<sub>2</sub>O) δ: 7.34 (s, H<sub>arom</sub>) ; <sup>13</sup>C (100.62 MHz, D<sub>2</sub>O) δ: 214.41 (-NH-C<sub>S</sub><sub>2</sub><sup>-</sup>), 139.3, 126.9 (2xC<sub>arom</sub>). Anal. calcd. for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>Na<sub>2</sub>S<sub>4</sub> · 4 H<sub>2</sub>O : C, 25.52; H, 3.75; N, 7.44; Na, 12.21; O, 17.00; S, 34.07. Found C, 25.31; H, 3.69; N, 7.68; Na, 11.94 O, 17.03; S, 34.2.

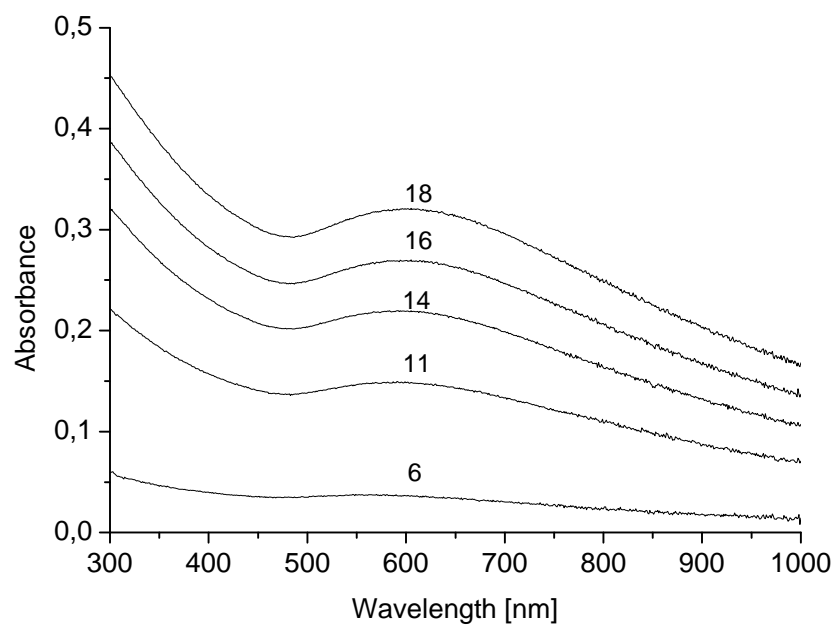
<sup>2</sup> Klöpping, H.L.; van der Kerk, G. J. M. *Recueil* **1951**, 70, 949-961.

<sup>3</sup> Lee, W. H.; Jung, O.-S.; Sohn, Y. S *Bull. Korean Chem. Soc.* **1986**, 7 (6), 421-425.

## 2. Absorption spectra of PBDT and cHBDT interlinked Au-NP films



**Figure S-1a.** Absorption spectra of 3-dimensional assemblies of Au-NPs interlinked with PBDT. The numbers refer to the assembly cycles.



**Figure S-1b.** Absorption spectra of 3-dimensional assemblies of Au-NPs interlinked with cHBDT. The numbers refer to the assembly cycles.