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Bricks and mortar self-assembly of nanoparticles

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Abstract—The use of nanoparticles and polymers bearing complementary recognition elements provides a versatile method for the formation of nanoparticle aggregates. This assembly process is highly dependent upon the primary and secondary recognition elements attached to the polymer and nanoparticle; we have observed variations in aggregate morphology that are directly correlated to supramolecular events at the colloid–polymer interface. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Nanoparticle systems possess useful catalytic,[1] electronic,[2] magnetic,[3] optical,[4] and optoelectronic properties.[5] They also provide building blocks for more complex systems. Organization of functional nanoparticulate entities into spatially well-defined arrays provides a means to extend the desirable properties of these systems to the macroscopic level, allowing the eventual realization of complex devices.[6] Self-assembly methods provide a powerful tool to help achieve this goal of organizing nanoparticulate systems into well-defined constructs. Mirkin and Alivasatos demonstrated that DNA could be used to assemble small clusters of metallic nanoparticles.[7] These aggregates, however, were irregular in shape and size. Abbott have developed a bioanalytical method for rapid DNA sequence determination utilizing non-covalent interactions between recognition labeled gold colloids and a surface bound analyte.[8a,b] In more recent studies, Mirkin[8c] showed that DNA strands could be attached to surfaces and applied in the directed assembly of nanoparticles, while Kaifer and others have begun to use other recognition motifs[9] to explore nanoparticle assembly in solution. These aggregates, however, have again been rather small and/or irregular in size and shape.[10]

In recent research, we have explored the use of polymer-mediated 'bricks and mortar' strategies as a method for nanoparticle self-assembly. In one recent application of this method, we demonstrated that complementary three-point hydrogen bonded networks between a diaminotriazine-functionalized polymer **P1** and thymine-functionalized mixed-monolayer protected gold cluster (MMPC) **C2** lead to highly regular spherical composites (Fig. 1).[11] Using this bricks and mortar strategy, spheres of 100 ± 17 nm in diameter were obtained at room temperature. Lowering the temperature of the assembly process to $-20^{\circ}C$ resulted in larger constructs of up to 1 μm, comprised of $\sim 2.5\times10^{6}$ individual particles.

The ease of modification of both the MMPC and polymer components of our bricks and mortar system makes this methodology well suited to the creation of diverse systems. Starting with C_8-protected nanoparticles produced using the Schiffrin method[12] a diverse collection of MMPCs were obtained by application of Murray's place displacement methodology[13] using appropriate recognition element-bearing thiols (Fig. 2). The parent scaffold for the complementary series of polymeric 'mortars', is a 1:1 random co-polymer of styrene and *p*-chloromethyl styrene with a molecular weight of 5 kDa and a PDI of 1.4. The ease of functionalization of this polymer backbone allows for the

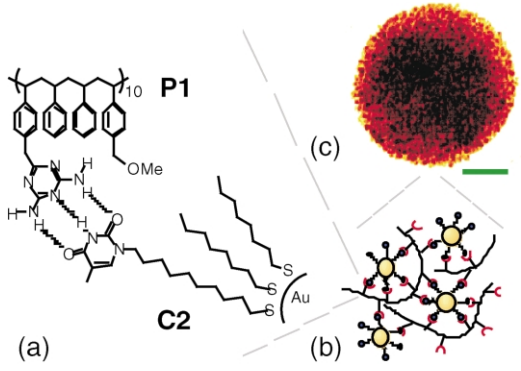

Figure 1. (a) Thymine colloid **C1** and triazine polymer **P1**; (b) schematic depiction of polymer-nanoparticle aggregation; (c) spherical aggregates produced from colloid **C1** and polymer **P1**.

Keywords: molecular recognition; nanoparticles; multi-scale order; hydrogen bonding; self-assembly.

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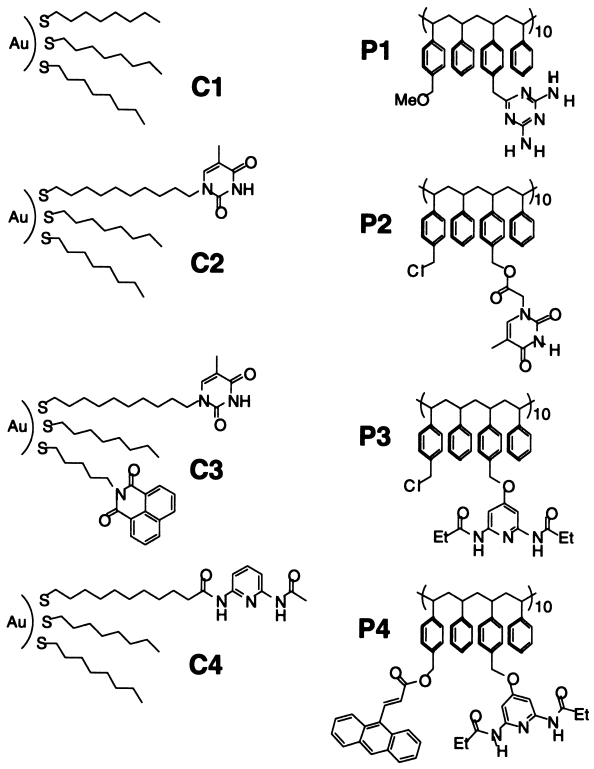
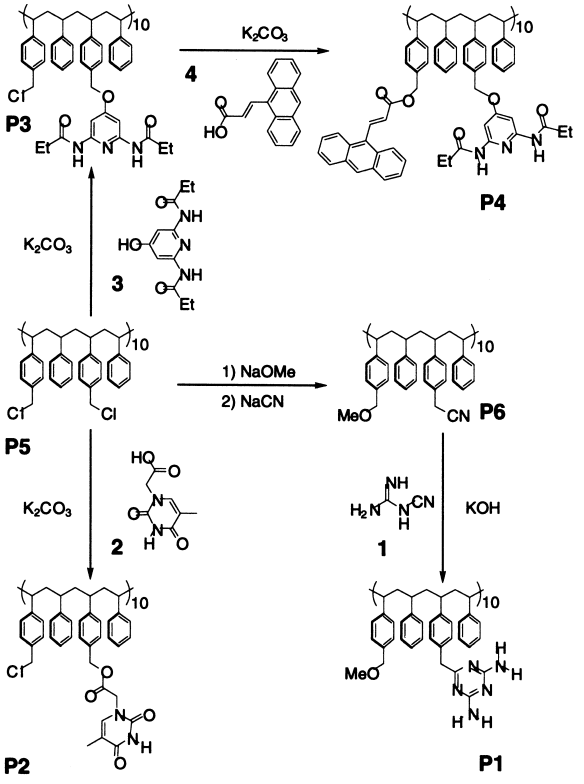
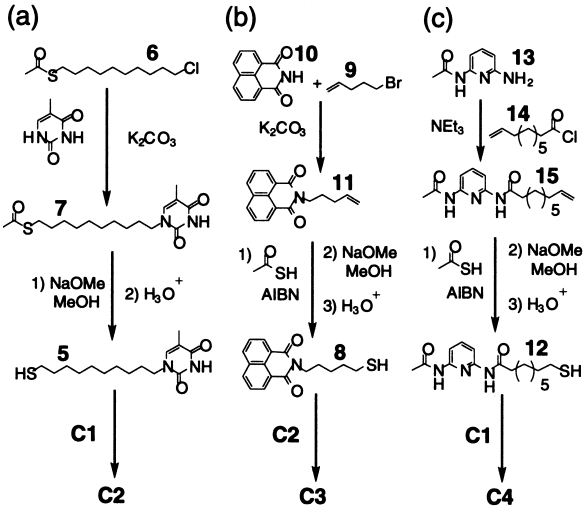


Figure 2. Structures of the MMPCs and polymers used in this study.

facile incorporation of a range of recognition elements (Fig. 2) via nucleophilic substitution under basic conditions.[14] We report here the use of these systems to explore the effects of varying the component functionality of polymer and MMPC on the aggregation process.



Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Polymer synthesis

The synthesis of all the polymers in this study (Scheme 1) begins with **P5**, a 1:1 ~40-mer copolymer of styrene and 4-chloromethylstyrene. Triazine polymer **P1** was formed by sequential displacement of the chloro sites with methoxide and cyanide to provide intermediate polymer **P6**. Reaction of the pendant cyano groups with dicyandiimide **1** in the presence of potassium hydroxide then gave **P1**.[15] Thymine polymer **P2** was obtained in one step from **P5** and thymine acetic acid **2** in the presence of mild base.[16] Diaminopyridine-functionalized polymer **P3** was produced in similar fashion using 4-hydroxy-2,6-dipropamidopyridine **3**.[16] Further substitution on **P3** with the anion of carboxylic acid **4** produced multitopic polymer **P4**. No side products were observed in any of the conversions.

2.2. MMPC synthesis

All MMPCs in this study were synthesized through Murray place displacement[13] of octanethiol-protected colloid **C1**.[12] Place exchange was performed under conditions that allowed for replacement of around 1 in every 8 of the approximately 100 ligands of **C1** with the appropriate thiol. Thymine substituted MMPC **C2** was formed via place exchange using thiol **5**, prepared in two steps from halothioacetate **6** (Scheme 2a). MMPC **C3** containing thymine and napthalimide moieties was prepared by place exchange of **C2** with napthalimide substituted pentanethiol **8**, synthesized starting from bromopent-4-ene (Scheme 2b) **9**. Diamidopyridine-functionalized MMPC **C4** was obtained using place displacement of **C1** with thiol **12**, synthesized from monoacyldiaminopyridine **13** in three steps (Fig. 2c).

2.3. Aggregation studies

To provide a screening technique for aggregation of polymer–MMPC systems, a simple colorimetric assay was developed.[17] In this procedure, solutions of the polymers were drop cast from chloroform into addressable portions

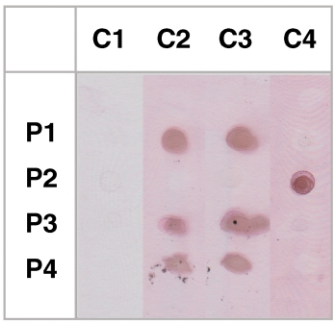


Figure 3. Image of surface-based screening method produced using a flatbed scanner. In this experiment, polymers were dropcast onto glass substrates, then dipped into solutions of the desired MMPC. Effective recognition between MMPC and polymer is readily apparent by the dark spot formed arising from nanoparticle binding.

of a series of glass slides. Upon drying, a slide was dipped into a given MMPC solution (1 mg mL^{-1}, 3:1 toluene/DCM) and subsequently rinsed with the same solvent.[†] In regions of the slide where recognition was effective, a stain corresponding to the color of the colloidal particles persisted after the rinsing step. Set side by side the slides produced a grid containing each permutation of MMPC brick and its potential polymer mortar (Fig. 3).

As expected, the only combinations that gave a positive stain were those featuring complementary three-point hydrogen bonding. Combinations where no recognition could take place (the simple octanethiol colloid) along with those lacking complementarity gave no stain. The combinations where aromatic stacking surfaces were present did not affect whether or not a stain persisted after rinsing.

To determine the stability and the structures of the polymer-nanoparticle aggregates, investigations into the architecture of each of the combinations of brick and mortar giving a positive stain test were carried out under a set of standard experimental conditions. In this procedure, dichloromethane solutions of MMPC (5 mg mL^{-1}) and polymer (0.5 mg mL^{-1}) were allowed to stand for 48 h. The resulting precipitates were washed with dichloromethane and redissolved in 1:1 THF/MeOH, a solvent that is expected to disrupt weakly aggregated species. The resulting solutions were examined immediately in duplicate using transmission electron microscopy (TEM), with representative structures shown.

The aggregates formed from the MMPC–polymer combinations (Fig. 4) were generally stable, although most show a far less densely packed morphology than the 100 nm aggregates displayed using thymine-decorated MMPC **C2** and diaminotriazine-substituted polymer **P1** (Fig. 1). For example, when thymine-based MMPC **C2** was combined with diaminopyridine-functionalized polymer **P3** little aggregation was observed (Fig. 4a). Likewise, diaminopyridine-substituted MMPC **C4** did not form a stable aggregate with thymine-functionalized polymer **P2**. There are two possible causes for these differences in behavior

[†] None of the polymers used show appreciable solubility in this solvent system.

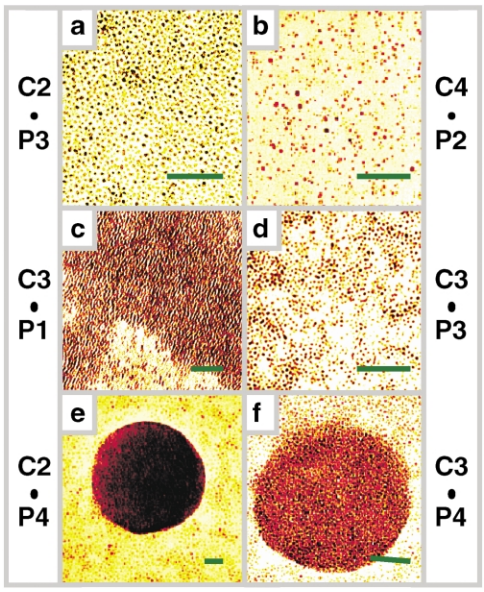


Figure 4. TEM images of the combinations of polymer and MMPC which displayed effective recognition behavior via the prescreening method (vide supra). The scale-bar indicates a distance of 25 nm.

between systems featuring diaminopyridine and diaminotriazine functionality. First, triazine polymer **P1** folds into a compact structure under the conditions employed for the assembly process, while **P3** is substantially more unfolded under the same conditions.[14] The more compact morphology displayed by **P1** should allow it to fill the interstitial voids between the spherical gold bricks with a smaller entropic penalty than that required for **P3**. A second possible origin for the difference in behavior between **P1** and **P3** is the larger number of hydrogen bond donor and acceptor groups featured by **P1** (Fig. 5). These additional binding sites should allow the formation of additional hydrogen bonding interactions between the colloid and polymer, as was observed intramolecularly for **P3**.[14]

The napthalimide/thymine MMPC **C3**–triazine polymer **P1** system provides loosely networked aggregates that are significantly smaller than the **C2**·**P1** parent (Fig. 4c). This result can be explained in terms of steric crowding around the binding sites that prevents efficient aggregation. As expected, there are no stable aggregates formed between **C3** and the analogous diamidopyridine polymer **P3** (Fig. 4d).

As anticipated, multivalent interactions play an important role in stabilizing polymer–MMPC aggregates. Large assemblies ~100 nm in diameter are obtained from the anthracene/diaminopyridine polymer **P4**–thymine-functionalized MMPC **C2** system that features both hydrogen

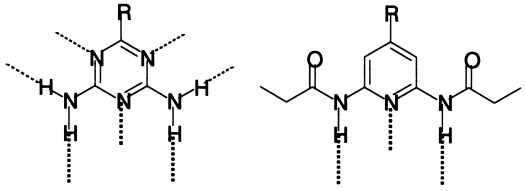


Figure 5. Potential hydrogen bond donor/acceptor sites for triazine polymer **P1** and diaminopyridine polymer **P3**.

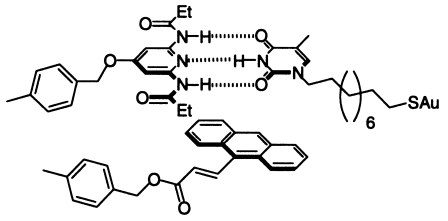


Figure 6. Proposed complementary π-stacking and hydrogen bonding between polymer **P4** and colloids **C2** and **C3**.

bonding and π–π interactions (Fig. 6). Due to its electron-rich character, anthracene is able to participate as an efficient partner in π–π interactions with the electron-poor heterocycles comprising the hydrogen bonded dyad. In contrast, napthalimide is itself strongly electron-poor therefore unsuitable for strong π–π interaction with the hydrogen bound pair. Similar size aggregates were obtained in the thymine/naphthalimide MMPC **C3**–**P4** system, but it is apparent that this system is packed less densely than either the **C2**·**P1** or **C2**·**P4** aggregates (Fig. 4e). This indicates that the naphthalimide moieties serve to disrupt polymer–MMPC interactions, consistent with the above experiments.

3. Conclusions

In summary, we have developed a methodology for the production of a diverse class of supramolecular constructs based upon incremental variations in the individual binding events. Combinatorial prescreening of effective recognition partners was afforded via the application of a simple assay. TEM showed that the morphology of the constructs varied with respect to the nature of the recognition partners and the degree of substitution, and that these effects could be rationalized in terms of steric and electronic effects on the level of the individual interacting moieties. Creation of large aggregates is promoted by the use of folded polymers as the mortar in the construction process, while bulky groups actively inhibit assembly.

A significant extra enthalpic contribution can be utilized for the creation of aggregates of this type by the complementary application of both hydrogen bonding and π–π interactions.

We are currently extending this approach exploring further control of aggregate morphology and also the application of this methodology in both catalytic and magnetic systems, the results of which will be reported in due course.

4. Experimental

4.1. General

All reagents were purchased from Aldrich and used as received, unless specified otherwise. All solvents were obtained from VWR and were reagent grade. Dichloromethane was distilled over CaH_2 prior to use. Thin layer chromatography (TLC) and flash column chromatography was carried out on glass pre-coated TLC plates with silica gel 60 and silica gel 60 (230–400 mesh), respectively. ^{1}H NMR was carried out on a Brüker 200 MHz spectrometer using tetramethylsilane as an internal standard in either $CDCl_3$ or DMSO-d_6. IR spectra were recorded as thin films on NaCl, using a MIDAC 1200 instrument. The melting points presented are uncorrected. TEM images were recorded on a JEOL 100CX electron microscope, on 300 mesh Cu grid with carbon film.

Full experimental details for the synthetic routes leading to polymers **P1**, **P2** and **P3** have been published previously.[14,17] Similarly, colloids **C1** and **C4** have also been reported.[2a] 10-Chlorodecanethiol-*S*-acetate **6** was prepared according to the literature procedure.[18]

4.1.1. N(1)-(10-acylmercaptodecyl)thymine (7). In a 250 mL round bottom flask, 10-chlorodecanethiol-*S*-acetate **6** (500 mg, 2.0 mmol), thymine (750 mg, 6.0 mmol), and K_2CO_3 (830 mg, 6.0 mmol) were suspended in 125 mL DMSO. The turbid yellow solution was then stirred at 60°C overnight, becoming dark brown. The reaction was then poured into EtOAc, extracted several times with H_2O to remove residual DMSO. Finally, the organic layer was washed once with a saturated aqueous NaCl solution and dried over $MgSO_4$. Solvent removal yielded a brown, oily solid, which was chromatographed (1:1 EtOAc/hexanes) to yield the product as an off white solid (310 mg, 46% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 8.11 (bs, 1H); 6.98 (s, 1H); 3.68 (t, 2H, J=7.4 Hz); 2.86 (t, 2H, J=7.4 Hz); 2.33 (s, 3H); 1.92 (s, 3H); ~1.6–1.2 (mm and bm, 16H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max} 3410, 3155, 3020, 2922, 2845, 1672, 1481, 1305, 1452, 1110 cm^{-1}. Anal. Calcd for $C_{17}H_{28}N_2O_2S$ (%): C, 59.98; H, 8.29; N, 8.23. Found (%): C, 60.12; H, 8.35; N, 7.98.

4.1.2. N(1)-(10-mercaptodecyl)thymine (5). In a 50 mL round bottom flask, **7** (220 mg, 0.65 mmol) was dissolved in 20 mL MeOH. Ar was bubbled through the clear solution for 30 min. NaOMe (1.2 mL of a 30 wt% solution in MeOH, 6.5 mmol) was added and the solution purged for another 15 min. After stirring overnight, the reaction solution was transferred to a 100 mL round bottom flask containing 50 mL saturated aqueous NH_4Cl. Solvents were removed, and the white paste was poured into H_2O and extracted with EtOAc. The organic layer was collected, washed once with a saturated aqueous NaCl solution and dried over $MgSO_4$. Solvent removal yielded a colorless viscous oil, which was chromatographed (1:1 EtOAc/hexanes) to yield the product as a white solid (175 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.98 (bs, 1H); 6.97 (s, 1H); 3.68 (t, 2H, J=7.6 Hz); 2.86 (a.q, 2H, J=6.88 Hz);1.93 (s, 3H); ~1.6–1.2 (mm and bm, 16H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max}: 3150, 3020, 2920, 2850, 2570, 1650, 1490 cm^{-1}. Anal. Calcd for $C_{15}H_{26}N_2O_2S$ (%): C, 60.38; H, 8.78; N, 9.38. Found (%): C, 60.62; H, 8.82; N, 9.06.

4.1.3. 1,8-Napthalimide-*N*-pent-4-ene (11). In a 250 mL round bottom flask, bromopent-4-ene (1.13 g, 7.6 mmol), 1,8-napthalimide (1.0 g, 5.1 mmol), and K_2CO_3 (1.5 g, 11 mmol) were suspended in 80 mL DMSO. The turbid yellow solution was then stirred at 60°C overnight, during

which time it became orange/brown. The reaction was then poured into water, extracted with EtOAc, and the organic layer washed several times with H_2O to remove residual DMSO. Finally, the organic layer was washed once with a saturated aqueous NaCl solution and dried over $MgSO_4$. Solvent removal yielded a brown solid which was chromatographed (1:1 EtOAc/hexanes) to yield the product as an off white solid (1.02 g, 76% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 8.62 (d, 2H, J=5.08 Hz); 8.22 (d, 2H, J=8.36 Hz); 7.77 (t, 2H, J=7.38 Hz); 5.87 (m, 1H); 5.02 (m, 2H); 4.20 (t, 2H, J=9.34 Hz); 2.21 (q, 2H, J=7.36 Hz); 1.85 (qu, 2H, J=7.38 Hz). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max}: 3090, 2910, 1590, 1660, 1690, 1320, 1210, 870 cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_2$ (%): C, 76.96; H, 5.70; N, 5.28. Found (%): C, 76.36; H, 5.68; N, 5.20.

4.1.4. 1,8-Napthalimide-*N*-(5-mercaptopentane) (8). In a 100 mL round bottom flask, **17** (1.10 g, 4.1 mmol) and thiol acetic acid (630 mg, 0.6 mL, 8.2 mmol) were dissolved in 25 mL toluene. Ar was then bubbled through the solution for 30 min. A catalytic amount of AIBN (ca. 30 mg) was then added, and the solution brought to reflux for three hours under argon. Once the brown solution had cooled to room temperature, the reaction was washed once each with saturated aqueous $NaHCO_3$ and NaCl solutions and dried over $MgSO_4$. Solvent removal yielded a brown, oily solid, which was filtered through a short SiO_2 column and used without further purification. 300 mg (0.88 mmol) of this material was then dissolved in 35 mL MeOH, and Ar was then bubbled through the clear solution for 30 min. NaOMe (0.5 mL of a 30 wt% solution in MeOH, 2.7 mmol) was added and the solution purged for another 15 min. After stirring overnight, the reaction solution was transferred to a 100 mL round bottom flask containing 50 mL saturated aqueous NH_4Cl. Solvents were removed, and the white paste was suspended in EtOAc and washed with H_2O. The organic layer was collected, washed once with a saturated aqueous NaCl solution and dried over $MgSO_4$. Solvent removal yielded a yellow solid, which was chromatographed (1:1 EtOAc/hexanes) to yield the product as a white solid (240 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 8.62 (d, 2H, J=6.88 Hz); 8.22 (d, 2H, J=8.38 Hz); 7.77 (t, 2H, J=7.88 Hz); 4.20 (t, 2H, J=7.38 Hz); 2.55 (a.q, 2H, J=7.40 Hz); ~1.8–1.4 (mm, 4H); 1.35 (t, 1H, J=7.38 Hz). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max}: 3075, 2910, 2830, 2525, 1690, 1650, 1595, 1550, 1350, 1220, 765 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_2S$ (%): C, 68.22; H, 5.73; N, 4.68. Found (%): C, 68.10; H, 5.79; N, 4.63.

4.1.5. MMPC C2 (thy-Au). In a 50 mL round bottom flask, MMPC **C1** (250 mg) and **5** (25 mg) were suspended in 30 mL CH_2Cl_2 to give a dark brown solution. Ar was bubbled through the solution for 0.5 h, and the reaction was then allowed to stir 48 h under Ar. The reaction solvent was then removed, and the resulting brown residue dissolved in the minimum amount of CH_2Cl_2 needed, and then precipitated by the addition of MeOH and placing the mixture in the freezer overnight. The product was collected by filtration and washed with MeOH (some product is soluble in MeOH and was discarded). This procedure was repeated until no free thiols were detected by NMR, and 175 mg of pure material was collected. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.02 (bs); 3.72(bs); 3.38 (bs); 1.91 (bs); 1.29 (bs); 0.88 (bs). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max}: 3190, 2985, 2915, 2875, 1790, 1480 cm^{-1}.

4.1.6. MMPC C3 (thy/nap-Au). In a 25 mL round bottom flask, MMPC **C2** (75 mg) and **8** (10 mg) were suspended in 10 mL CH_2Cl_2 to give a dark brown solution. Ar was bubbled through the solution for 0.5 h, and the reaction was then allowed to stir 48 h under Ar. The reaction solvent was then removed, and the resulting brown residue dissolved in the minimum amount of CH_2Cl_2 needed, then precipitated by addition of MeOH and placing the mixture in the freezer overnight. The product was collected by filtration and washed with MeOH. This procedure is repeated until no free thiols are detected by NMR, and 50 mg of pure material was collected. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 8.8 (bs); 8.2 (bs); 7.7 (bs); 7.05 (bs); 4.0 (bs); 3.4 (bs); 1.8–0.5 (mbs). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max}: 3195, 2980, 2915, 2880, 1690, 1595, 1550, 1410, 1280 cm^{-1}.

Acknowledgements

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