Photogeneration of a diene template for surface Diels–Alder reactions: Photoenolization of an *ortho*-methyl-benzophenone-modified Au cluster

Arnold J. Kell, Christopher C. Montcalm, and Mark S. Workentin

Abstract: A series of monolayer-protected clusters (MPCs) modified with a photoreactive [4-(11-mercaptoundecyl)-phenyl](2-methylphenyl)methanone (**1**) moiety have been prepared where **1** is co-absorbed to the MPC surface with dodecanethiol, octadecanethiol, or 11-mercaptoundecanoic acid methyl ester. Upon irradiation the MPC-anchored **1** reacts efficiently through its triplet excited states, yielding 1,4-biradicals that collapse to synthetically useful, long-lived photodienol intermediates, which can be efficiently trapped in Diels–Alder type chemistry by dienophiles — namely, dimethyl acetylenedicarboxylate (DMAD). In all cases the Diels–Alder trapping of the dienol occurred efficiently resulting in >60% conversion to the Diels–Alder adduct. This indicates that the local environment surrounding **1** did not influence its ability to react via the Diels–Alder reaction; however, the reaction could not be taken to completion. The inability to react completely is attributed to **1** binding to distinct sites on the MPC core; there are edge, vertice, and terrace sites. Selective population of these specific sites and the subsequent irradiations show that MPCs with **1** anchored predominantly at edge and vertice sites results in an extent of reaction of 85 ± 3%, whereas selectively populating the terrace sites results in an extent of reaction of 36 ± 2%. These results suggest that **1** anchored to edge and vertice sites is more reactive to the Diels–Alder reaction than that involving terrace sites.

Key words: monolayer protected cluster, site selective reactivity, Diels–Alder, photochemistry.

Resume : On a préparé une série d'agrégats protégés en monocouches (« MPC »), modifiés par une portion photoréactive de [4-(11-mercaptoundécyl)phényl](2-méthylphéyl)méthanone (**1**) cooabsorbée sur la surface des « MPC » avec du dodécanethiol, de l'octadécanethiol ou du 11-mercaptoundécanoate de méthyle. Par irradiation, le composé **1** attaché au « MPC » réagit de façon efficace, par le biais de ses états excités, pour donner des 1,4-biradicaux qui se décomposent en intermédiaires photodiénoliques utiles d'un point de vue synthétique et qui peuvent être piégés d'une façon efficace par des diénophiles tel l'acétylènedicarboxylate de diméthyle (ADCM), dans des réactions de type Diels–Alder. Dans tous les cas, le piégeage de type Diels–Alder du diénol se fait d'une façon efficace conduisant à plus de 60 % de conversion en adduit de Diels–Alder. Ce résultat indique que l'environnement local autour du composé **1** n'influence pas sa facilité à réagir par le biais de la réaction de Diels–Alder; toutefois, il n'a pas été possible d'obtenir une réaction complète. On attribue cette inhabilité du composé **1** à réagir complètement à la nature des sites auxquels il est attaché sur les « MPC » qui comportent des sites en bordures, aux sommets et sur des terrasses. Une population sélective de chacun de ces sites spécifiques suivie d'irradiations montrent que le degré de réaction s'élève à 85 ± 3 % lorsque le composé **1** s'est fixé sur des sites en bordures ou aux sommets des « MPC » mais qu'il n'est que de 36 ± 2 % lorsque le composé **1** s'est fixé sur des sites des terrasses des « MPC ». Ces résultats suggèrent que le composé **1** fixé sur des sites en bordure ou aux sommets sont plus réactifs vis-à-vis de la réaction de Diels–Alder que ceux des terrasses.

Mots clés : agrégat protégé en monocouche, réactivité sélective d'un site, Diels–Alder, photochimie.

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Introduction

The irradiation of *ortho*-alkylated benzophenones generates synthetically useful *ortho*-quinodimethane enol intermediates (1, 2). This reaction, first described by Yang and Rivas (3), involves an intramolecular γ-hydrogen atom abstraction from the *ortho*-alkyl substituent by the n,π* excited state of the carbonyl group, which generates a 1,4-biradical that subsequently collapses to the respective *E* and *Z*-dienols (Scheme 1). The lifetime of the *Z*-dienol is very short (0.03–1 μs) whereas that of the *E*-dienol is significantly longer (3 s). The *Z*-dienol has a short lifetime because its orienta-

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Dedicated to Professor Don Arnold for his many contributions to chemistry in Canada.

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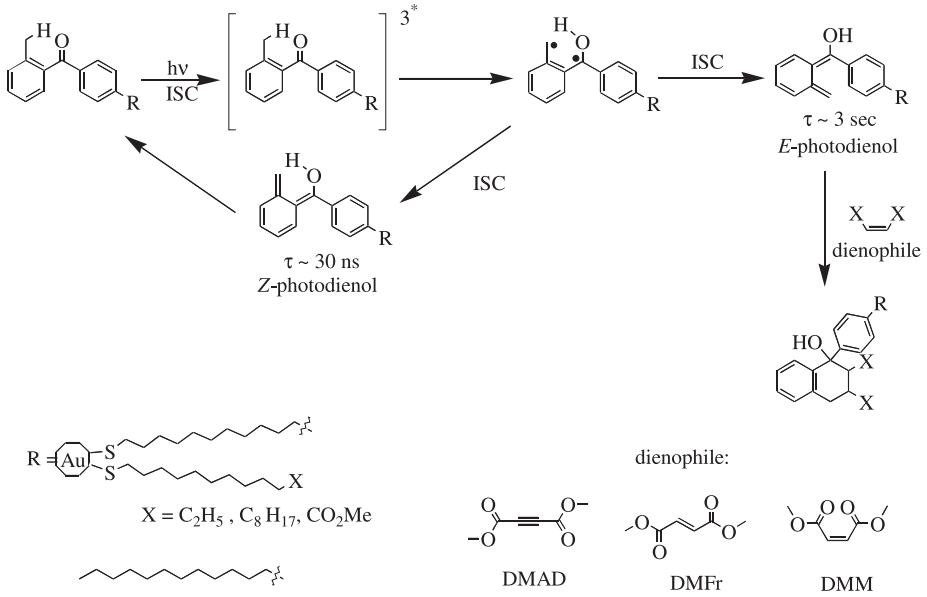
Scheme 1. The generation of the photodienol and its subsequent Diels–Alder reaction.



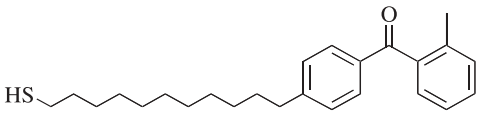
tion allows reketonization and re-aromatization to occur easily through a 1,5-hydrogen shift; the reketonization process for the *E*-dienol requires acid or base catalysis. The long-lived *E*-dienol provides an intermediate that can be efficiently trapped by Diels–Alder dienophiles to yield, exclusively, the endo products, with excellent regioselectivity (1, 2). In this report we extend this photoinitiated Diels–Alder reaction to monolayer-protected gold clusters or MPCs. While there are a variety of reported photoinduced reactions on planar metal surfaces (4–15), there are surprisingly few reports of photochemical reactions (16, 17) or photophysical properties (18–20) of organic molecules anchored to MPCs even though these substrates are emerging as important new materials (21, 22). In recent studies we reported the intramolecular Norrish–Yang Type II photoreaction of an aryl ketone in this type of MPC environment (23, 24); those studies illustrated, among other things, that unimolecular carbonyl photoreactions can be efficient in MPCs and can lead to surface modifications. Here we report the photodienolization of an *ortho*-methyl-benzophenone-modified gold MPC and the subsequent trapping of the dienol by a model dienophile (Scheme 1). To the best of our knowledge, this study represents the first example of a bimolecular photochemical reaction on an MPC. Mrksich and co-workers recently reported elegant studies of an electrochemically generated quinone-immobilized dienophile on planar gold using Diels–Alder chemistry and showed that the reaction can be used for selective modification with proteins (25–28).

Little has been done to elucidate the dynamics (29) and reactivity associated with substrates anchored to MPC surfaces, considering that the MPC core is well known to be inhomogeneous (21, 30): there are edge, vertice, and terrace sites on each MPC. These distinct sites may display different reactivity; we have found evidence for this in our earlier studies (23). It is of interest to observe how efficiently a photo-induced bimolecular reaction, such as the Diels–Alder trapping of the *E*-dienol, can occur on the MPC surface and what factors associated with the MPC environment influence its reactivity. The Diels–Alder reaction between the photodienol and a dienophile is a versatile probe of the MPC environment. This reaction allows for the study of (*i*) the ability of the ketone to be excited to the dienol in the MPC environment, (*ii*) the ability to trap the dienol, and (*iii*) the effects that co-absorbed substrates on the MPC surface have on the ability of the photodienol to react with a dienophile (will the photodienol in the monolayer environment be too sterically hindered to allow the subsequent Diels–Alder reaction?). Additionally, because the MPC core contains a number of distinct sites, selectively populating the different sites with **1** will help elucidate where these bimolecular reactions occur most efficiently on the MPC surface.

To address our interests in MPC reactivity we have prepared a series of MPCs designed to probe a variety of properties within the MPC environment (Fig. 1). A [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone (**1**) (Scheme 2) substrate was "place-exchanged" onto the surface of previously prepared dodecanethiolate (C_{12}MPC), octadecanethiolate (C_{18}MPC), and 11-mercaptoundecanoic acid methyl ester (MeO_2CC_{10}MPC) MPCs. The corresponding MPCs, defined as **1**-C_{12}MPC, **1**-C_{18}MPC, and **1**-MeO_2CC_{10}MPC, respectively, where, for example, **1**-C_{12}MPC represents the place-exchange of **1** onto an original C_{12}MPC, were then irradiated in the presence of a dienophile, namely dimethyl acetylenedicarboxylate (DMAD). The majority of this report makes use of DMAD as the dienophile, but the reaction was also shown to occur efficiently with other dienophiles such as dimethyl fumarate (DMFr) and dimethyl maleate (DMM). The dienophiles were selected because they were symmetric, making product identification more straightforward, and because the solution photochemistry involving *ortho*-methyl benzophenone with these dienophiles is well known to occur efficiently and regioselectively (i.e., where possible, only the endo product is generated) (3, 31–33).

The base MPCs were chosen so that a variety of effects associated with the Diels–Alder reaction between the photodienol and a dienophile could be studied. If we assume that

Scheme 2. The probe molecule incorporated into the MPC.



1

the methylene chains of both **1** and the dilutant chain (or the substrate on the original MPC, namely C_{12}, C_{18}, or MeO_2CC_{10}) pack similarly, then the mixed **1**-C_{12}MPC will allow for the photochemical generation of the dienol directly at the interface. In the case of **1**-C_{18}MPC, the resulting photodienol is expected to be embedded within the monolayer. This is of interest because embedding the dienol may hinder its ability to react with a dienophile. Both of these mixed MPCs bear nonpolar terminal methyl groups on the dilutant chain. Because the terminal groups on MPCs are known to influence some of their physical properties (21) — MPCs containing terminal carboxylic acid groups are soluble in methanol and water, whereas MPCs containing terminal methyl groups are soluble only in nonpolar solvents such as chloroform, dichloromethane, benzene, and hexanes — we were also interested in employing a dilutant chain containing a terminal ester. The terminal ester would serve to change the local polarity at the interface and may allow the polar dienophile to be incorporated into the interface (because both are polar), possibly allowing the Diels–Alder reaction to occur more efficiently. We were also interested in determining if the reactivity of **1** is influenced by its location on the MPC surface. As mentioned earlier, MPCs have distinct sites. Selective population of the different sites of the MPC surface with **1** will allow for the determination of differences in the efficiency of the Diels–Alder reaction when it occurs at edge and vertice sites, as compared with terrace sites. The extent of this bimolecular reaction within the MPC environment will be a valuable tool, employed in determining how steric and environmental effects introduced by the monolayer affect the ability of the dienophile to react with the surface-bound dienol.

Results and discussion

The **1**-MPCs were prepared from a [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone (**1**) precursor (Scheme 2). The synthesis of **1** started from (11-bromoundecyl)benzene, prepared by the addition of phenyl lithium to a large excess of 1,11-dibromoundecane. A Friedel–Crafts acylation reaction between (11-bromoundecyl)benzene generated in the mixture and *o*-toluoyl chloride in the presence of $AlCl_3$ generated 4-(11-bromoundecyl)phenyl(2-methylphenyl)methanone. The bromide was then converted to thiol through the reaction of potassium thioacetate and the hydrolysis of the resulting thioester with ethanolic K_2CO_3. The resulting thiol (**1**) was purified via column chromatography using 3:1 dichloromethane:hexanes as eluant and characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and mass spectrometry. Details of the synthetic transformations are provided in the experimental section.

Generally MPCs are prepared by the reduction of hydrogen tetrachloroaurate in the presence of a thiol (34, 35). This protocol is incompatible with **1** because the presence of a reducing agent will convert the carbonyl functionality to an alcohol. So, to prepare the desired **1**-MPC, we employ the place-exchange reaction (36, 37) developed by Murray and co-workers starting from well-defined base MPCs (35). The place-exchange reaction is an equilibrium-based reaction involving the replacement of free thiol from solution onto the MPC surface (36, 37). It is accomplished by stirring an excess of a thiol that is to be exchanged onto the MPC surface in the presence of an already prepared base MPC for 4–5 days. As mentioned earlier, the MPC core consists of different sites. It has been suggested that the place-exchange reaction populates the edge and vertice sites quickly (within 1 h) and population of the terrace occurs over a much longer timescale (36). This means that depending on the timescale of the place-exchange reaction, **1** can populate predominantly the edge and vertice sites (1 h), or all sites (the terrace, edge, and vertice sites) can be populated over much longer exchange times (4–5 days). This is an important property of the place-exchange reaction that was exploited and will be addressed later. The base MPCs were prepared according to procedures outlined by Murray and co-workers, as they are known to produce relatively monodisperse MPCs with a core diameter of 2.0 nm and general stoichiometry of $Au_{314}(X)_{108}$, where there are 314 gold atoms comprising the MPC core and X is the thiolate surrounding the MPC core (35).

Proton NMR spectroscopy was used to determine the purity and the extent of exchange (stoichiometry) of the resulting mixed MPCs (**1**-C_{12}MPC, **1**-C_{18}MPC, and **1**-MeO_2CC_{10}MPC, respectively). The purity of the MPC is judged by the amount of free thiol or disulfide remaining in solution after work-up and isolation of the MPC. Any free thiol or disulfide would appear as sharp resonances in the ^{1}H NMR spectrum. Figures 2*a* and 3*a* are typical ^{1}H NMR spectra, recorded in benzene-d_6, of the **1**-C_{12}MPC and **1**-MeO_2CC_{10}MPC, respectively, isolated after place-exchange; of particular note is the absence of sharp resonances assignable to free thiol (or disulphide in solution). The ^{1}H NMR spectrum of **1**-C_{18}MPC is not shown, but is similar to these (see supplemental information).[2] All of the spectra exhibit distinctive broad resonances (38, 39) at the chemical shifts measured for pure **1** in benzene-d_6 solution, confirming that the place-exchange has occurred. These resonances include those of the aromatic protons on the phenyl rings *ortho* to the carbonyl at 7.85 (2H) and 7.22 (1H) ppm, the protons on the methyl function *ortho* to the carbonyl at 2.29 ppm, and the CH_2 protons of the alkyl spacer α to the benzophenone function at 2.57 ppm (Figs. 2*a* and 3*a*). The remaining methylene protons of the alkyl chain for **1** appear between 1.15 and 1.90 ppm along with those of the dilutant chain, either C_{12}, C_{18}, or MeO_2CC_{10}. The resonance signal at 0.9 ppm in Fig. 2*a* is due to the terminal methyl protons of the remaining dodecanethiolate present on the MPC after the place-

[2] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

Fig. 1. Cartoon depictions of the various MPCs studied, showing that the photodienol will be (*a*) at the interface, (*b*) embedded within the monolayer, or (*c*) near a more polar co-absorbed substrate.

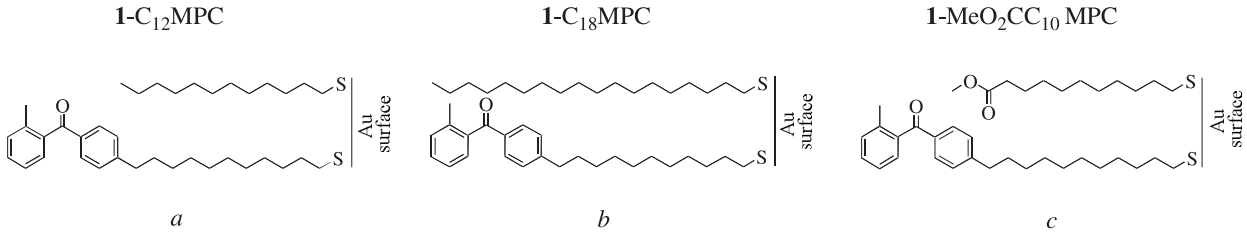


Fig. 2. The irradiation of $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$ in benzene-d_6 (*) before irradiation (*a*) and after an irradiation period of 80 h in the presence of a 3-times molar excess of DMAD (*b*). The filled arrows indicate the decrease in intensity for the resonances associated with $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$ while the hollow arrows indicate an increase in the resonances associated with the product, namely $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{26}(\mathbf{1}\text{-DMAD})_{32}$. Note: the DMAD has been washed away before the final ^{1}H NMR spectra was acquired. The ^{1}H NMR spectrum of an authentic sample of the model compound (2-DMAD) in benzene-d_6 is shown in (*c*) (actual molecule pictured).

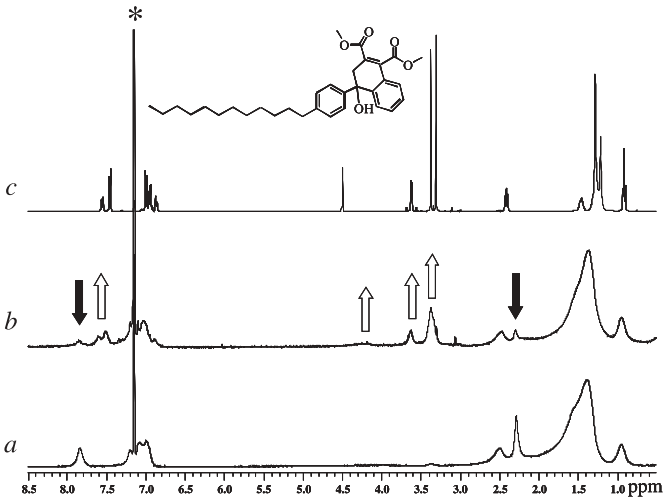
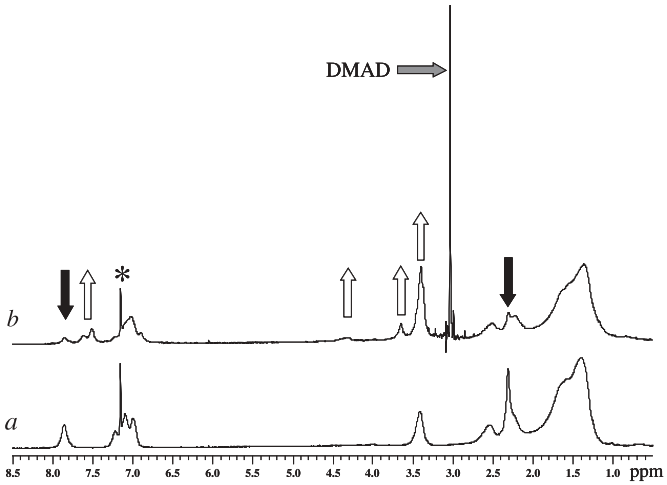


Fig. 3. The irradiation of $Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{49}$ in benzene-d_6 (*) before irradiation (*a*) and after an irradiation period of ~96 h in the presence of a 3-times molar excess of DMAD (*b*). The filled arrows indicate the decrease in intensity for the resonances associated with $Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{49}$ while the hollow arrows indicate an increase in the resonances associated with the product, namely $Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{15}(\mathbf{1}\text{-DMAD})_{34}$.



exchange reaction (or in the case of **1**-C_{18}MPC, the resonance at 0.9 ppm is due to the terminal methyl group of octadecanethiolate). As expected, the resonances associated with the protons α, β, and γ to the thiolate moiety are not observed: because the substrates are anchored to the MPC surface they are unable to rotate freely, and the signal broadens into the baseline. There is some overlap of the broad resonances attributed to the terminal methyl group of the dilutant chain and those of the methylene groups of both **1** and the dilutant chain in the **1**-C_{12} and **1**-C_{18}MPCs. This necessitates the use of an I_2 decomposition reaction that quantitatively liberates any thiolate bound to the MPC surface as disulfide and reduces the MPC core to elemental gold, allowing accurate integration to determine their stoichiometries (40). As mentioned above, the MPCs employed in the study have a general stoichiometry of $Au_{314}(X)_{108}$, where X is either $C_{12}S$, $C_{18}S$, or $MeO_2CC_{10}S$. The total number of substrates bound to the MPC surface is expected to remain constant after place-exchange, so the stoichiometry is based on the **1**:X ratio. The stoichiometries of the MPCs were $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$ and $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$ for the **1**-C_{12}MPC and the **1**-C_{18}MPC, respectively. These stoichiometries were determined in deuteriochloroform solution by comparison of the integrations for the resonance signal at 7.72 ppm attributed to the aromatic protons α to the carbonyl in **1** and the resonance signal at 0.86 ppm attributed to the terminal methyl group of either C_{12} or C_{18} after I_2 decomposition of the appropriate MPC.

In Fig. 3*a*, the resonance signal at 3.35 ppm and the shoulder at 2.28 ppm are due to the terminal methyl protons of the ester and the methylene protons α to the ester, respectively, on the MeO_2CC_{10} moiety. The stoichiometry of the mixed **1**-MeO_2CC_{10}MPC was determined directly from the ^{1}H NMR spectrum of the MPC in benzene-d_6 by taking the ratio of the integrations for the resonance at 3.35 ppm (from MeO_2CC_{10}) and 7.85 ppm (from **1**) and was found to be $Au_{314}(MeCO_2C_{10}S)_{59}(\mathbf{1})_{49}$. This was possible because there was no overlap in these resonance signals, allowing accurate integration directly from the MPC.

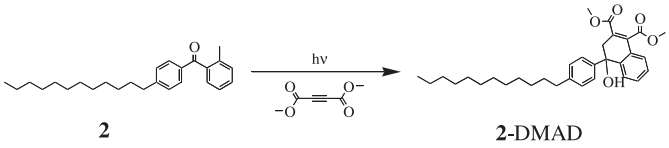
Irradiations were carried out in argon- or N_2-purged benzene-d_6 solutions in Pyrex NMR tubes using a Rayonet photochemical reactor fitted with 350 nm bulbs and a merry-go-round apparatus. Generally, the solutions contained ~15–20 mg of **1**-C_{12}MPC, **1**-C_{18}MPC, or **1**-MeO_2CC_{10}MPC dis-

solved in 0.5 mL benzene-d_6 (~0.008–0.012 M with respect to **1**), with a three-times molar excess of the dienophile, namely dimethyl acetylenedicarboxylate (DMAD). Irradiation under these conditions produced MPCs consistent with the trapping of the photodienol (Scheme 1). The reaction can be monitored directly by NMR spectroscopy; this is illustrated in Figs. 2 and 3 for **1**-C_{12}MPC and **1**-MeO_2CC_{10}MPC, respectively, where the MPCs were irradiated in the presence of DMAD as the dienophile. The ^{1}H NMR and IR spectra of the MPCs irradiated in the presence of DMAD can be compared with those of an authentic sample of the Diels–Alder products made from irradiation of [4-(dodecyl)phenyl](2-methylphenyl)methanone (**2**), with DMAD as dienophile (Scheme 3). The irradiation product of **2** with DMAD was characterized via ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, as well as mass spectrometry. The ^{1}H NMR spectrum of **2**-DMAD is shown in Fig. 2*c*. The key spectral changes that occur upon irradiation of **1**-C_{12}MPC, **1**-C_{18}MPC, and **1**-MeO_2CC_{10}MPC with DMAD are consistent with the formation of the Diels–Alder product. These include the appearance of two overlapping, broad aromatic peaks at 7.6 and 7.5 ppm and another aromatic resonance signal at 6.87 ppm, as well as broad peaks at 4.15 (the hydroxyl H), 3.62 (the methylene H's), and 3.35 ppm (the methyl ester H's), concomitant with a decrease in the intensity of broad aromatic peaks at 7.85, 7.22, and 7.05, along with the broad resonance at 2.39 ppm (the *ortho* methyl group of **1**) (Figs. 2 and 3). The ^{1}H NMR spectra comparing **1**-C_{12}MPC, **1**-DMADC_{12}MPC, and the model compound **2**-DMAD are shown in Figs. 2*a*–*c*, respectively. The IR spectra of the irradiated MPCs are consistent with the product as well, evidenced by the growth of peaks between 1715–1730 cm^{-1} (consistent with an ester functionality) and between 3434–3468 cm^{-1} (consistent with a hydroxyl moiety). Product formation was generally complete after 48–60 h with no sign of further reaction on extended irradiation. The success of these trapping experiments allows us to formulate some ideas about the reactivity and steric constraints of substrates confined to the MPC surface.

We begin our analysis of the Diels–Alder trapping of the photodienol by comparing the extents of reaction for the cases where the photodienol is directly at the interface (**1**-C_{12}MPC), when it is embedded within the monolayer (**1**-C_{18}MPC), and when the local polarity of the interface is varied (**1**-MeO_2CC_{10}MPC). The reaction proceeds efficiently, generating only one product on extensive irradiation on all of the MPCs studied. Irradiation of $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$, $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$, and $Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{49}$ produces MPCs with final stoichiometries of $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{26}$(**1**-DMAD)$_{32}$ (64 ± 2% conversion to the Diels–Alder adduct), $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{13}$(**1**-DMAD)$_{21}$ (60 ± 2%), and Au_{314}-$(MeO_2CC_{10}S)_{59}(\mathbf{1})_{15}$(**1**-DMAD)$_{34}$ (69%), respectively. The irradiations were carried out at least twice for $Au_{314}(C_{12}S)_{50}$-$(\mathbf{1})_{58}$ and $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$, whereas $Au_{314}(MeO_2CC_{10}S)_{59}$-$(\mathbf{1})_{49}$ was irradiated only once in parallel with $Au_{314}(C_{12}S)_{50}$-$(\mathbf{1})_{58}$ (Table 1).

These conversions are essentially identical, suggesting that the ability of the reaction to proceed is not affected by the length or the polarity of the dilutant chain co-absorbed to the MPC with **1**. The extent of reaction was also not affected by the relative concentration of DMAD: the concentration was varied from 1 to 10 times the molar excess of **1**. Though the physical environment of the MPC was different in each of these MPCs studied, the reaction only proceeds to ~65% conversion in all cases. Assuming that the substrates bound to the MPC are distributed over the entire MPC surface because the place-exchange reaction employed was carried out over 5 days, the extent of reaction may be related to the number of **1** bound at the edge and vertice positions of the MPC as compared with the number bound to the terrace. That is, there may be a site-dependent reactivity associated with the substrates bound to the MPC surfaces.

Scheme 3. The photochemical generation of **2**-DMAD from **2**, which serves as the model for this reaction on the MPC surface.



2 **2**-DMAD

As mentioned above, in the MPCs studied **1** should be positioned in each of the three distinct sites (i.e., on the edge, vertice, or terrace) (Fig. 4). It is assumed that every **1** bound to the MPC is capable of forming the photodienol. If this is the case, there must be certain sites on the MPC surface where the photodienol can be more efficiently trapped as the Diels–Alder adduct and others where the reaction is less efficient. It is intriguing to propose that there is a correlation between the position of substrates on the MPC core and the extent of reaction. To investigate this, the place-exchange reaction was exploited to selectively populate either the edge and vertice sites or the terrace sites with **1**.

Selective population of the edge and vertice sites occurs if short (~1 h) place-exchange reactions are carried out (36). Using this strategy, C_{12}MPC was stirred in the presence of **1** in toluene for 1 h under a nitrogen atmosphere, generating **1**(edge)-C_{12}MPC, where **1**(edge) implies that the **1** is positioned predominantly at the edge and vertice sites of a C_{12}MPC, as suggested by Murray and co-workers.[3] The MPC was purified and I_2 decomposition was utilized to determine the stoichiometry of this MPC, which was $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{37}$. The MPC was then weighed out (~15 mg), dissolved in benzene-d_6, and irradiated in the presence of DMAD (three-times excess) until there were no further change in the ^{1}H NMR spectrum (Fig. 5). The spectral changes were similar to those explained for the above MPCs. Upon purification to remove the excess DMAD, the stoichiometry of the irradiated MPC was found to be $Au_{314}(C_{12}S)_{71}(\mathbf{1})_5$(**1**-DMAD)$_{32}$, which translates to an 85 ± 3% conversion to Diels–Alder adduct based on two irradiations. This is a significant increase in the conversion of **1** to the Diels–Alder adduct, suggesting that **1** positioned at the edge and vertice more readily undergo the reaction. However, this result does not indicate if **1** bound to the terrace is less reactive towards the Diels–Alder reaction. This can only be determined by preparing an MPC where **1** has been selectively positioned on the terrace.

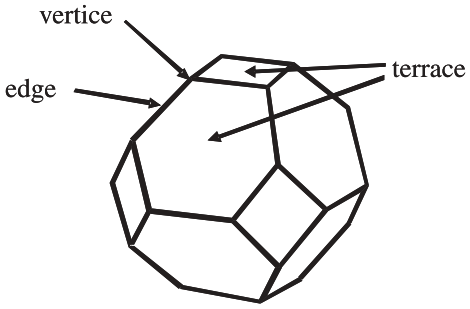
[3] This is known to populate some of the terrace as well; see ref. 36.

Table 1. Stoichiometries of the original MPCs and the extents of reaction for their irradiations in the presence of DMAD.

MPC[a]	Stoichiometry (before irradiation)	Stoichiometry (after irradiation in presence of DMAD)[b]	Conversion (%)[c]
1-C_{12}MPC	$Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$[d]	$Au_{314}(C_{12}S)_{50}(\mathbf{1})_{26}(\mathbf{1}\text{-DMAD})_{32}$	64 ± 2
1-C_{18}MPC	$Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$[d]	$Au_{314}(C_{18}S)_{74}(\mathbf{1})_{13}(\mathbf{1}\text{-DMAD})_{21}$	60 ± 2
1-$C_{10}CO_2$MeMPC	$Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{49}$[e]	$Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{15}(\mathbf{1}\text{-DMAD})_{34}$	69
1(edge)-C_{12}MPC	$Au_{314}(C_{12}S)_{71}(\mathbf{1})_{37}$[d]	$Au_{314}(C_{12}S)_{71}(\mathbf{1})_{5}(\mathbf{1}\text{-DMAD})_{32}$	85 ± 3
1(terrace)-C_{12}MPC	$Au_{314}(C_{12}S)_{90}(\mathbf{1})_{18}$[d]	$Au_{314}(C_{12}S)_{90}(\mathbf{1})_{11}(\mathbf{1}\text{-DMAD})_{7}$	36 ± 2

[a]For example, **1**-C_{12}MPC represents **1** place exchanged onto an original dodecanethiolate MPC.
[b]Determined via ratio integrations for of resonances attributed to **1** (7.85 ppm) and **1**-DMAD (7.6–7.5 ppm) in the ^{1}H NMR spectrum, uncertainty is ±5%.
[c]Conversion determined as (the number of **1**-DMAD ligands generated)/(number of **1** ligands on starting MPC).
[d]Determined via ratio of integrations for the mixed disulfides generated upon I_2 decomposition of the MPC; uncertainty is ±5%.
[e]Determined via ratio of integrations for the substrates on the actual MPC in solution; uncertainty is ±5%.

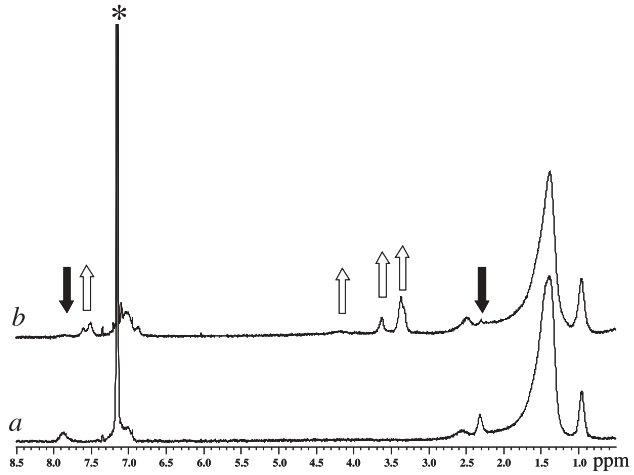
Fig. 4. A cartoon representation of the MPC core and the assignments of the edge, vertice, and terrace sites.



Selectively populating the terrace with **1** is not as straightforward as populating the edge and vertice sites. The procedure involves initial preparation **1**-C_{12}MPC in a place-exchange reaction carried out over 5 days. This should populate the terrace, edge, and vertice sites with **1**. The resulting MPC (with a stoichiometry of $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$) is then subjected to a subsequent place-exchange reaction in the presence of an excess of dodecanethiol ($C_{12}SH$) for 1 h, which should populate predominantly the edge and vertice sites with dodecanethiol and displace any **1** positioned there. Conveniently, any **1** on the terrace should be trapped, allowing for the study of the reaction between its photodienol and DMAD. The stoichiometry of the resulting MPC was determined as for the other MPCs and found to be $Au_{314}(C_{12}S)_{90}(\mathbf{1})_{18}$ and will be referred to as **1**(terrace)-C_{12}MPC, where **1**(terrace) implies that **1** is predominantly at the terrace and the dilutant chain is $C_{12}S$. Upon irradiation of **1**(terrace)-C_{12}MPC in the presence of a three-times molar excess of DMAD, similar spectral changes were observed as for the previous MPCs, and the final stoichiometry of the MPC was $Au_{314}(C_{12}S)_{90}(\mathbf{1})_{11}(\mathbf{1}\text{-DMAD})_{7}$, which translates to a 36 ± 2% conversion to the Diels–Alder adduct based on two irradiations (Fig. 6). This conversion is much lower than that for the MPCs containing **1** at the edge and vertice positions, suggesting that the reactivity on the MPC surface is position dependent.

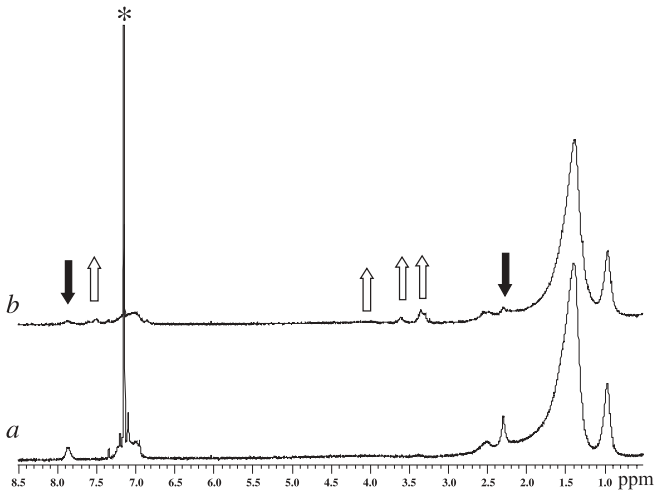
It is reasonable to assume that the edge and vertice sites, which may provide more room for a bimolecular reaction to occur based on the highly faceted shape of the MPC core (Fig. 4), are the positions on the MPC surface where the Diels–Alder reaction is occurring more efficiently. The idea of the edge and vertice sites anchoring substrates with less

Fig. 5. The irradiation of $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{37}$ (where **1** is positioned predominantly at the edge and vertice sites on the MPC surface) in benzene-d_6 (*) before irradiation (*a*) and after an irradiation period fo 96 h in the presence of a 3-times molar excess of DMAD (*b*). The filled arrows indicate the decrease in intensity for the resonances associated with $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{37}$ while the hollow arrows indicate an increase in the resonances associated with the product, namely $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{5}(\mathbf{1}\text{-DMAD})_{32}$. Note: the DMAD was washed away before the ^{1}H NMR spectrum was acquired for (*b*).



order has been reported recently through an investigation that described how intracluster hydrogen bonding decreases the rate of cyanide-induced MPC decomposition (41), presumably because the highly faceted gold core prohibits effective intracluster chain interactions directly at the edge and vertice sites in the absence of substrates capable of hydrogen bonding. Our own work also suggests that mobility constraints imposed by aryl ketones anchored to terrace sites on MPCs prevent the unimolecular Norrish–Yang Type II reaction from occurring, whereas the reaction occurs more readily at the edge and vertice sites (23, 24). Also of note is a study involving the S_N2 reaction of amines and MPC-bound terminal bromides (40). The authors found the S_N2 reaction proceeds quite efficiently (at least 80% completion) regardless of the bulkiness of the amine. Though the product conversions for this simple reaction are higher than we report, the authors employed MPCs smaller (~140 gold atoms in the MPC core) than those we used. The smaller MPC

Fig. 6. The irradiation of $Au_{314}(C_{12}S)_{90}(\mathbf{1})_{18}$ (where **1** is positioned predominantly at terrace sites on the MPC surface) in benzene-d_6 (*) before irradiation (*a*) and after an irradiation period fo 96 h in the presence of a 3-times molar excess of DMAD (*b*). The filled arrows indicate the decrease in intensity for the resonances associated with $Au_{314}(C_{12}S)_{90}(\mathbf{1})_{18}$ while the hollow arrows indicate an increase in the resonances associated with the product, namely $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{11}(\mathbf{1}\text{-DMAD})_7$. Note: the DMAD was washed away before the ^{1}H NMR spectrum was acquired for (*b*).



cores may result in more disordered monolayers. There have also been studies carried out on 2-D self-assembled monolayers (SAMs) suggesting that if edge sites are produced within the monolayer, the substrates at the edge sites are much more mobile and floppy, as evidenced by their ability to "trap" embedded groups (42, 43).

If the conversion were related to the number of edge and vertice sites on an MPC one may assume that it would be directly related to the percentage of edge and vertice sites on the MPC itself. Our results indicate that the conversion to Diels–Alder adduct is ~65%. A rough calculation[4] indicates that, assuming equal distribution over all sites on the MPC, 41% of **1** should reside at the edge and vertice sites. If the substrates at the edge and vertice sites and one atom row adjacent to the edge and vertice sites were able to undergo the reaction, this would account for 86% of the sites on the MPC surface. Because the conversion lies somewhere between these numbers, we offer the following explanation: there is the possibility that there is not an equal distribution of **1** over the entire surface of the MPC and slightly more **1** is concentrated at the edge and vertice sites. If this were true, it could explain why the conversion to Diels–Alder adduct is higher than the percentage of edge and vertice sites on the MPC surface. It is also possible that some of the **1** directly adjacent to the edge and vertice is capable of reacting, which would increase the conversion as well. We prefer the former explanation, based on the mechanism of place-exchange. At the beginning of the place-exchange reaction there is much more **1** than dodecanethiol in solution. The edge and vertice sites are populated with **1** quickly, resulting in the displacement of dodecanethiol into solution. Consequently, both dodecanethiol and **1** will be in solution, but excess **1** is employed in the place-exchange reaction, so there will always be a higher concentration of **1** in solution. Because population of the MPC during the place-exchange reaction is dependent on the concentration of thiol in solution, and because the edge and vertice sites are populated most easily, they may be populated to a greater extent with **1**. This could account for the conversion of the $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$, $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$, and $Au_{314}(MeO_2CC_{10})_{59}(\mathbf{1})_{49}$ to $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{26}(\text{DMAD-}\mathbf{1})_{32}$ (64 ± 2% conversion to Diels–Alder adduct), $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{13}(\text{DMAD-}\mathbf{1})_{21}$ (62 ± 2%), and $Au_{314}(MeO_2CC_{10})_{59}(\mathbf{1})_{15}(\mathbf{1}\text{-DMAD})_{34}$ (69%), respectively, being slightly higher than expected.

Also of note are the results of irradiations of **1**-C_{12} and **1**-C_{18} MPCs in the presence of DMFr and DMM. The spectral changes observed in the ^{1}H NMR spectra are consistent with the generation of the Diels–Alder adducts, with the final stoichiometry of the photolysed MPCs being $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{21}(\mathbf{1}\text{-DMFr})_{37}$ (64% conversion), $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{13}(\mathbf{1}\text{-DMFr})_{21}$ (63% conversion), $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{22}(\mathbf{1}\text{- DMM})_{36}$ (61% conversion), and $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{15}(\mathbf{1}\text{-DMM})_{19}$ (58% conversion), respectively. The average conversion for these reactions is 62 ± 4%, which is, within experimental error, what we would expect based on the results of the analogous reaction with DMAD. These reactions show a variety of dienophiles can be employed in this reaction, and we are working on exploiting this aspect of the chemistry. The spectral data for the DMFr- and DMM-modified MPCs are provided in the supplemental information.

Experimental

Commercial solvents and reagents used

The compounds dodecanethiol, octadecanethiol, hydrogen tetrachloroaurate(III), tetraoctylammonium bromide, sodium borohydride, 1,11-dibromoundecane, 1.8 M phenyl lithium in cyclohexane-ether, *o*-toluoyl chloride, potassium thioacetate, dimethyl acetylenedicarboxylate, dimethyl maleate, and dimethyl fumarate were all purchased from Aldrich and used as received. Potassium carbonate (Caledon), aluminum chloride (BHD), benzene-d_6 (Cambridge Isotope Laboratories), and iodine (BDH) were also used as received. Acetone, dichloromethane, benzene, toluene, methanol, diethyl ether, and hexanes were purchased from either Caledon or EM Science and used as received. Tetrahydrofuran was dried by distillation from sodium/benzophenone. Ethanol (both anhydrous and 95%) was purchased from Commercial Alcohols Inc. Silica gel was purchased from EM Science.

General instrumentation

^{1}H NMR spectra were recorded on a Varian Mercury 400 (400.087 MHz) spectrometer in either deuteriochloroform or benzene-d_6 solutions and are reported in parts per million (ppm) with respect to chloroform or benzene peaks at 7.26 ppm or 7.15 ppm, respectively. ^{13}C NMR spectra were

[4] Our calculation assumes equal distribution of the substrate over the entire surface and involves dividing the number of atoms directly at edge and vertice sites and by the total number of surface atoms (41%) or dividing the number of atoms at the edge and vertice sites and those directly adjacent to the edge and vertice sites by the total number of surface atoms (86%).

recorded on a Varian Mercury 400 (100.602 MHz) spectrometer in either deuteriochloroform or benzene-d_6 solution and are reported in parts per million with respect to chloroform or benzene peaks at 77.0 or 128.02 ppm. UV–vis absorption spectra were recorded on a Cary 100Bio spectrometer in spectrometry-grade benzene. Mass spectra and exact masses were recorded on a MAT 8200 Finnigan high resolution mass spectrometer; the latter employed a mass of 12.0000 for carbon. IR spectra were recorded on a Bomem MB-Series or a Bruker Vector 33 spectrometer using a dropcasting technique on NaCl plates and are reported in wavenumbers (cm^{-1}).

Steady-state photolysis experiments

Steady-state irradiation experiments were carried out in septa-sealed Pyrex NMR tubes using benzene-d_6 as solvent or 5 mL Pyrex photolysis cells using reagent-grade benzene as solvent. The light source was a Rayonet photochemical reactor fitted with bulbs that emitted UV light in the 300–400 nm range, with a maximum at 350 nm and a merry-go-round apparatus to ensure an equal amount of radiation was received. In a typical procedure, ~15–20 mg of MPC was weighed out and placed under vacuum to ensure all solvent was removed. The MPC was then dissolved in ~0.5 mL benzene-d_6, degassed for 15 min with either argon or nitrogen gas, and sealed with a rubber septum and Parafilm. An ^{1}H NMR spectrum was recorded prior to the addition of dienophile and at intermittent reaction times until the reaction was complete. The temperature of the solutions was typically 38 ± 2°C.

[4-(11-Mercaptoundecyl)phenyl](2-methylphenyl)methanone (1)

To a solution of 1,11-dibromoundecane (5.2 g, 16.5 mmol) in dry THF (25 mL) was added phenyl lithium (3.7 mL of a 1.8 M solution, 6.7 mmol) dropwise, generating 11-phenyl-1-bromoundecane in situ. After aqueous workup and drying, the 11-phenylbromoundecane – 1,11-dibromoundecane mixture was redissolved with 25 mL dichloromethane and cooled in a salted ice bath. When the flask was cooled, *o*-toluoyl chloride (1.12 g, 7.26 mmol) and aluminum chloride (1.01 g, 7.59 mmol) were added, and the mixture was stirred for 4 h, maintaining a temperature of 0°C. Upon aqueous workup and drying with $MgSO_4$, the resulting [4-(11-bromoundecyl)phenyl](2-methylphenyl)methanone was purified via gradient column chromatography on silica gel, beginning with 10:1 hexanes:dichloromethane to elute the unreacted dibromoundecane and ending with 2:1 hexanes:dichloromethane which eluted [4-(11-bromoundecyl)phenyl](2-methylphenyl)methanone (0.90 g) as a clear colorless oil. The bromide was converted to the thioacetate through a reaction with potassium thioacetate in acetone, quantitatively generating [4-(11-acetylsulfanylundecyl)phenyl](2-methylphenyl)methanone. The thioacetate (0.72 g, 1.7 mmol) was then transferred to a 100-mL round-bottom flask fitted with a reflux condenser, dissolved in absolute ethanol, and the solution degassed with argon for 15 min after which time the solution was charged with potassium carbonate (0.24 g, 2.07 mmol) and heated to reflux for 3 h. The ethanol was removed via rotary evaporation, and the resulting liquid was redissolved in dichloromethane and washed with saturated ammonium chloride (30 mL), washed with 3 × 30 mL of distilled water, and dried over $MgSO_4$ for 20 min. Concentration yielded a yellowish oil that was purified by column chromatography using silica gel and 3:1 dichloromethane:hexanes as eluant; a colorless oil (0.5 g, 1.30 mmol) was produced in 76% yield. UV–vis (benzene) (nm) (ε ($M^{-1}cm^{-1}$)): 339 (9.790 × 10), 277 (7.832 × 10^3). IR (cm^{-1}) (dropcast on NaCl): 2925, 2853, 1661, 1604, 1267. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ: 7.73 (d, J = 7.8 Hz, 2H), 7.38 (m, H), 7.28 (m, 5H), 2.67 (t, J = 7.8 Hz, 2H), 2.52 (quartet, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.61 (m, 4H), 1.44–1.19 (m, 15H (includes SH proton)). ^{13}C NMR (400 MHz, $CDCl_3$) (ppm) δ: 198.36, 148.99, 138.90, 136.45, 135.24, 130.82, 130.29, 129.94, 128.51, 128.28, 125.08, 36.06, 34.05, 31.16, 29.51, 29.48, 29.45, 29.40, 29.25, 29.02, 28.34, 24.63, 19.91. EI-MS *m*/*z* (%): 382 (20), 364 (6), 223 (8), 195 (100), 119 (23), 84 (20), 49 (33). Exact mass calcd.: 382.2330; found: 382.2329.

[4-(11-Dodecyl)phenyl](2-methylphenyl)methanone (2)

To a flame-dried, 10-mL round-bottom flask fitted with an argon inlet and condenser was added aluminum chloride (1.8 g, 13.5 mmol), dichloromethane (7 mL), and phenyldodecane (2.5 g, 10.0 mmol), and the mixture was cooled in a salted ice bath. A solution containing *o*-toluoyl chloride (1.7 g, 11.0 mmol) in 2 mL of dichloromethane was then added to the mixture over 1 min. This mixture was left stirring for 3 h while warming to room temperature. The reaction was then quenched by pouring the entire contents of the flask into a beaker containing 40 mL of distilled water cooled in an ice bath. The organic layer was diluted with 20 mL dichloromethane, washed with 4 × 50 mL of distilled water, and dried over $MgSO_4$ for 30 min. Concentration of the dried organic phase yielded a yellow oil, which was purified by column chromatography using silica gel and 1:1 hexanes:dichloromethane as eluant, generating a clear, colorless liquid (1.83 g, 5.02 mmol) in 50% yield. IR (cm^{-1}) (dropcast on NaCl): 2926, 2853, 1662, 1605, 1264. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ: 7.72 (d, J = 7.8 Hz, 2H), 7.37 (t, H), 7.30–7.21 (m, 5H), 2.65 (t, J = 2H), 2.31 (s, 3H), 1.62 (quintet, 2H), 1.37–1.21 (m, 18H), 0.86 (t, 3H). ^{1}H NMR (400 MHz, C_6D_6) (ppm) δ: 7.84 (d, 2H J = 8.6 Hz), 7.20 (t, J = 7.8 Hz, H), 7.07 (m, H), 7.01–6.89 (m, 4H), 2.40 (t, J = 7.8 Hz, 2H), 2.28 (s, 3H), 1.45 (broad quintet, 2H), 1.36–1.16 (m, 18H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) (ppm) δ: 198.36, 149.04, 138.95, 136.48, 135.26, 130.85, 130.30, 129.95, 128.49, 128.25, 125.09, 36.04, 31.90, 31.11, 29.64, 29.61, 29.54, 29.45, 29.33, 29.28, 22.67, 14.11. EI-MS *m*/*z* (%): 364 (3.5), 195 (100), 119 (9), 91 (8). Exact mass calcd.: 364.2766; found: 364.2765.

Dodecanethiolate MPC (C_{12}MPC)

Following the procedures of Brust et al. (34) and Murray and co-workers (35): to a 250-mL round-bottom flask was added hydrogen tetrachloroaurate(III) trihydrate (0.30 g, 0.768 mmol) dissolved in 28 mL distilled water (resulting in a bright yellow solution) and tetraoctylammonium bromide (2.01 g, 0.369 mmol) dissolved in 70 mL toluene (a clear and colorless solution). The contents were rapidly stirred for 30 min at room temperature to facilitate the phase transfer of

the hydrogen tetrachloroaurate(III) trihydrate into the toluene layer, which resulted in the organic layer turning a dark orange color and the aqueous layer becoming clear and colorless. After phase transfer, the aqueous layer was removed and dodecanethiol (0.15 g, 0.18 mL, 0.762 mmol) was added via a volumetric pipet to the solution, which was allowed to stir at room temperature while a fresh solution of sodium borohydride (0.33 g, 8.68 mmol) in 18 mL water was prepared. The aqueous sodium borohydride was added to the toluene solution over ~5 s and the mixture was allowed to stir at room temperature overnight (~18 h). The organic layer was washed with 3 × 20 mL distilled water, dried with $MgSO_4$, and concentrated. The concentrated MPC was then suspended in 200 mL of 95% ethanol and placed in the freezer overnight, during which time the C_{12}MPC precipitated from solution. The ethanol was then decanted and the MPC was dissolved in benzene and concentrated, resulting in the formation of a film in the round-bottom flask. This film was washed repeatedly with 10 × 15 mL of 95% ethanol warmed to 40°C. The MPC was pure, according to the ^{1}H NMR spectrum, which showed no signs of dodecanethiol, dodecyldisulfide, or tetraoctylammonium bromide.

Octadecanethiolate MPC (C_{18}MPC)

The octadecanethiolate MPC was synthesized as described above for the dodecanethiolate MPC. The procedure involved 0.20 g (0.51 mmol) hydrogen tetrachloroaurate, 1.32 g (2.41 mmol) tetraoctylammonium bromide, 0.20 g (5.59 mmol) sodium borohydride, and 0.146 g (0.51 mmol) octadecanethiol.

11-Mercaptoundecanoic acid methyl ester MPC (MeO_2CC_{10}MPC)

The MPC was synthesized as described above for the dodecanethiolate MPC. The procedure involved 0.30 g (0.76 mmol) hydrogen tetrachloroaurate, 2.04 g (3.42 mmol) tetraoctylammonium bromide, 0.32 g (8.36 mmol) sodium borohydride, and 0.177 g (0.76 mmol) 11-mercaptoundecanoic acid methyl ester. The MPC was purified by washing with hexanes.

[4-(11-Mercaptoundecyl)phenyl](2-methylphenyl)methanone – dodecanethiolate MPC (1-C_{12}MPC)

Following the procedure outlined by Murray and co-workers (36, 37), C_{12}MPC (0.11 g, 0.136 mmol of dodecanethiol) was dissolved in 34 mL toluene in a 100-mL round-bottom flask fitted with an argon inlet. Excess [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone (0.0629 g, 0.163 mmol) was then added to the flask and the mixture was stirred for 4–5 days under argon. After 4–5 days the solution was concentrated and the mixed MPC was washed with warm (35–40°C) 95% ethanol to remove excess [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)-methanone and dodecanethiol. The ^{1}H NMR (400 MHz, C_6D_6) spectra indicated that the [4-(11-mercaptoundecyl)-phenyl](2-methylphenyl)methanone was incorporated onto the MPC, and iodine-induced decomposition indicated that the MPC had a composition of $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$. Population of the edge and vertice sites with **1** was accomplished using the same conditions but with a decreased time period over which the exchange reaction took place (1 h) (36). The resulting MPC had a stoichiometry of $Au_{314}(C_{12}S)_{71}(\mathbf{1})_{37}$. Population of the terrace with **1** was accomplished by stirring the $Au_{314}(C_{12}S)_{50}(\mathbf{1})_{58}$ (0.050 g) (prepared via the 5 day place-exchange reaction described above) dissolved in 10 mL toluene with an excess of dodecanethiol (0.10 g) under a nitrogen atmosphere for 1 h. The resulting MPC had a stoichiometry of $Au_{314}(C_{12}S)_{90}(\mathbf{1})_{18}$.

[4-(11-Mercaptoundecyl)phenyl](2-methylphenyl)methanone – octadecanethiolate MPC (1-C_{18}MPC)

Following the procedure outlined above for $Au_{314}(SC_{12})_{50}(\mathbf{1})_{58}$, C_{18}MPC (0.05 g, 0.044 mmol octadecanethiolate) was dissolved in 15 mL toluene in a 100-mL round-bottom flask fitted with an argon inlet, to which [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)-methanone (0.0226 g, 0.059 mmol) dissolved in ~3 mL toluene was added. After stirring for 4 days, the toluene was removed by rotary evaporation, and the mixed MPC was washed with a warmed (35–40°C) 6:1 ethanol:toluene solution to remove excess [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone and octadecanethiol. The resulting MPC had a composition of $Au_{314}(C_{18}S)_{74}(\mathbf{1})_{34}$, as determined via iodine decomposition.

[4-(11-Mercaptoundecyl)phenyl](2-methylphenyl)methanone – 11-mercaptoundecanoic acid methyl ester MPC (1-MeO_2CC_{10}MPC)

Following the procedure outlined above for $Au_{314}(SC_{12})_{50}(\mathbf{1})_{58}$, MeO_2CC_{10}MPC (0.15 g, 0.16 mmol 11-mercaptoundecanoic acid methyl ester) was dissolved in 40 mL toluene in a 100-mL round-bottom flask fitted with an argon inlet, to which [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone (0.073 g, 0.19 mmol) was added. After stirring for 4 days, the toluene was removed by rotary evaporation, and the mixed MPC was washed with ethanol to remove excess [4-(11-mercaptoundecyl)phenyl](2-methylphenyl)methanone and 11-mercaptoundecanoic acid methyl ester. The resulting MPC had a composition of $Au_{314}(MeO_2CC_{10}S)_{59}(\mathbf{1})_{49}$, as determined by direct integration of the aromatic resonances at 7.85 ppm (resonances from protons α to carbonyl) and 3.42 ppm (resonances from protons of the terminal ester) in benzene-d_6 solution.

MPC decomposition procedure

As reported by Murray and co-workers (40), approximately 10 mg of mixed MPC was placed in a 10-mL round-bottom flask and dissolved in 2 mL dichloromethane. A small crystal of iodine (~1 mg) was added, and the solution was stirred until the originally brown, opaque solution became clear and a light purple colour with a black precipitate (20 min). The dichloromethane was rotary evaporated, and 0.5 mL deuteriochloroform was added to redissolve the resulting mixed disulfide. This was placed in an NMR tube by first passing it through a pipette equipped with a Kimwipe filter to remove the precipitate. The sample was then analyzed by ^{1}H NMR spectroscopy, where the integrations for the appropriate resonance signals were compared.

Generation of 2-methyl-4′-(dodecyl)benzophenone Diels–Alder adducts

In a typical procedure, [4-(11-dodecyl)phenyl](2-methylphenyl)methanone (**2**) (0.1 g, 0.41 mmol) was dissolved in

5 mL of benzene, transferred to a 5 mL Pyrex photolysis cell sealed with a septum, and the solution was degassed with argon for 20 min. The dienophile (namely dimethyl acetylenedicarboxylate, dimethyl fumarate, or dimethyl maleate) (0.41 mmol) was then added to the degassed solution via syringe, and the mixture was irradiated for 12 h. The product was purified via column chromatography, employing 1% methanol in dichloromethane as eluant.

2-DMAD Diels–Alder adduct

IR (cm^{-1}) (dropcast on NaCl): 3474, 2924, 2853, 1732. ^1H NMR (400 MHz, C_6D_6) (ppm) δ: 7.55 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 8.6 Hz, 2H), 6.9–7.05 (m, 4H), 6.82 (d, J = 7.8 Hz, 1H), 4.26 (s, 1H), 2.61 (s, 2H), 3.34 (s, 3H), 3.28 (s, 3H), 2.95 (t, J = 5.5 Hz, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.38–1.60 (m, 4H), 1.0–1.3 (br, 14H) 0.85 (t, J = 7.0 Hz, 3H). ^{13}C NMR (400 MHz, C_6D_6) (ppm) δ: 168.06, 166.66, 143.40, 142.09, 141.84, 140.41, 130.78, 128.51, 127.50, 127.36, 126.13, 74.67, 52.17, 36.12, 32.59, 32.01, 31.20, 30.39, 30.36, 30.28, 30.19, 30.09, 30.00, 23.40, 14.69. EI-MS *m/z* (%): 554 (45), 552 (42), 303 (6), 223 (8), 195 (100), 119 (23), 84 (20), 49 (33). Exact mass calcd.: 506.3032; found: 506.3028.

Conclusions

The Diels–Alder reaction of the photodienol generated from **1** in the MPC environment is shown to proceed efficiently, with similar extents of reaction regardless of the local environment surrounding the reactive group. In addition, this reaction exhibited evidence suggesting site-dependant reactivity. It appears as though there are properties inherent to substrates bound at specific sites on the MPC core that render them more or less reactive toward the Diels–Alder reaction. This is evidenced by the general trend observed with respect to the reactivity of **1** on the MPC surface: in the comparison of the reactivity of the multi-site-populated MPC — where all of the sites on the MPC are populated (**1**-C_{12}MPC) — placing **1** predominantly at terrace sites (**1**(terrace)-C_{12}MPC) results in significantly lower conversions, while placing **1** predominantly at edge and vertice sites (**1**(edge)-C_{12}MPC) results in significantly higher conversions. In fact, quantitatively speaking, the same amount of **1** reacts efficiently when the entire MPC is populated (**1**-C_{12}MPC) as when the majority of **1** is at the edge and vertice sites (**1**(edge)-C_{12}MPC); the number of **1** converted to **1**-DMAD is 32 in each case. Qualitatively, we attribute a more hindered environment within the terrace of the MPC as the main cause of the lowered extent of conversion. The most accessible sites — those at the edge and vertice — on the MPCs can undergo this rather complex bimolecular reaction more efficiently. Those within the terrace (where the monolayer is very well packed and more accurately mimics that of a 2-D SAM) are more hindered and less likely to undergo the rather complex bimolecular reaction. It is difficult to predict if the decreased ability for the terrace-bound dienol to react is due to steric constraints that do not allow the dienophile to reach the photodienol or if the dienophile is able to reach the dienol but cannot achieve the geometry required for the reaction to occur. The inability for these bimolecular reactions to reach completion is similar to what we have found for unimolecular reactions carried out on identical MPC cores (23, 24). However, the reasons for the lowered extents of reaction are not expected to be the same. Mobility constraints play a definitive role in the efficiency of unimolecular reactions carried out on MPCs, but in this investigation, which involves bimolecular reactivity, sterics and the ability to adopt specific orientations play key roles in the efficiency of the reaction.

It is intriguing to propose that there are differences in reactivity and dynamics associated with the distinct sites on the MPC surface. We are currently investigating the effect that increasing and decreasing the size of the MPC core has on the extent of reaction, because the size of the terrace can be easily manipulated by increasing or decreasing the size of the metal core. This study will provide more insight on the physical properties inherent to substrates when they are anchored to specific sites on these highly faceted gold cores.

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