

Self-Assembled Monolayers Based on Chelating Aromatic Dithiols on Gold

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Self-assembled monolayers (SAMs) were generated by the adsorption of xylene- α_1, α_2 -dithiol and 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene derivatives, $[\text{CH}_3(\text{CH}_2)_m]_2\text{C}_6\text{H}_2[\text{CH}_2\text{SH}]_2$ ($m = 0, 4, 12, 13, 14, 15$), on the surface of gold. These monolayers were characterized by optical ellipsometry and contact angle goniometry. Comparison of the thicknesses and wettabilities of the new SAMs to those generated from normal alkanethiols suggests that the new chelating dithiols generate densely packed and highly oriented monolayer films on gold. Furthermore, preliminary studies of film desorption in solution suggest that the new SAMs are more stable than normal SAMs on gold.

Introduction

Self-assembled monolayers (SAMs) hold great promise for the development of new molecular technologies.¹ In 1983, Nuzzo and Allara first reported the formation of oriented monolayers from the adsorption of dialkyl disulfides on gold.² Subsequent studies have focused predominantly on SAMs generated from the adsorption of alkanethiols on gold.^{3–6} These SAMs are the most thoroughly studied because of their facile generation, manipulation, and characterization. SAMs command much current interest because of their potential utility in various fields such as electrode modification,^{7–11} corrosion resistance,^{12,13} biomaterial coatings,^{14–16} and biosensor technology.^{17–19} SAMs on gold are particularly attractive for use in these technologies because (i) they form well-defined and well-ordered organic thin films, (ii) the interfacial properties can be tailored a priori using standard organic synthetic methods, (iii) the thickness of the films can be adjusted at the scale of angstroms, and (iv) the interaction between sulfur and the surface of gold is strong; the enthalpy of this interaction is estimated to be 40–45 kcal mol⁻¹.³

Despite these attractive features, SAMs generated from alkanethiols on gold possess a number of shortcomings. First, they are somewhat fragile,²⁰ decomposing upon exposure to moderate heat (e.g., 80 °C in hexadecane).²¹ Second, it is difficult to generate well-defined multicomponent interfaces by the adsorption of mixtures of two or more alkanethiols.^{22,23} In this approach, there is little or no control over the lateral structure and composition within the plane of the films.^{24–26} These shortcomings limit the use of SAMs in applications involving adhesion, lubrication, and optoelectronic device fabrication.²⁷

Although SAMs generated from normal alkanethiols have been studied extensively for over a decade, surprisingly little attention has been given to chelating thiol-based monolayers. The entropy-driven “chelate effect” is known to enhance the stabilities of ligand–metal complexes.²⁸ Literature studies show, for example, that the entropy change upon substituting two monodentate ligands with an analogous bis-chelating ligand is the primary thermodynamic driving force for the substitution.²⁹ Consequently, it is likely that SAMs formed from appropriately designed bis-chelating thiols on gold will exhibit stabilities greater than the sum of two sulfur–gold enthalpies and the van der Waals stabilization common to self-assembled organic thin films.³⁰ Ironically, one of the few studies to examine the use of discreet chelating moieties to generate SAMs on gold was the initial report of SAMs on gold by Nuzzo and Allara.² In this

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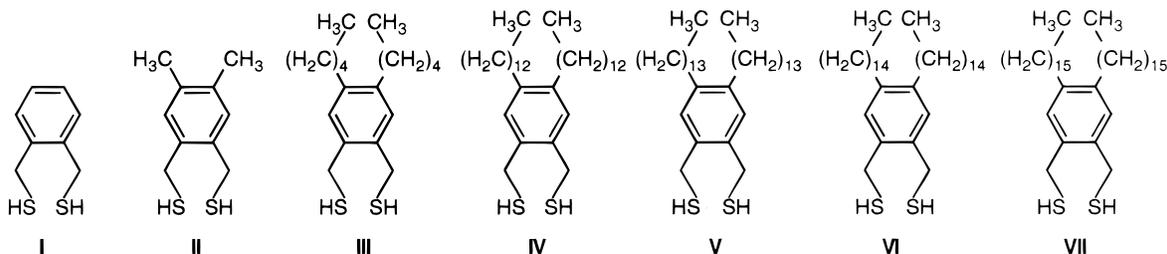


Figure 1. Structures of the chelating aromatic dithiols used for generating SAMs on gold.

study, various derivatives of oxidized dithiothreitol were found to generate monolayers on gold having reasonable thicknesses and wettabilities. Indeed, this work and subsequent work involving the generation of SAMs from multidentate ligands have established the viability of using discreet chelating moieties to generate well-defined SAMs on gold.^{31–33}

This paper describes the generation of SAMs on gold from a new class of chelating thiolate moiety that is specifically designed to provide films with enhanced stabilities and unprecedented structural and compositional flexibilities. The new chelating strategy is based on derivatives of 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene as shown in Figure 1. We chose a tetrasubstituted benzene to function as a connecting unit between two alkyl chains for five reasons. First, the geometry afforded by the 1,2,4,5-substituted benzene should provide a convenient bidentate chelating system that binds to the surface of gold and simultaneously directs long alkyl chains away from the surface of gold. Second, the small size of the benzene ring should add no steric bulk to the system; that is, the bulkiness should be no greater than that of two separate alkyl chains. Consequently, the new chelating moieties should be capable of generating ordered assemblies with packing arrays similar to those in normal SAMs. Third, molecular modeling of the targeted dithiols shows that the distance between the two sulfur atoms can span 5.0 Å without introducing any steric or torsional strain.³⁴ Since the sulfur atoms in normal SAMs on gold are believed to bind in the 3-fold hollow sites of Au(111) with a spacing of 4.99 Å,³ the modeling studies indicate that the targeted dithiols are capable of binding to gold in a fashion similar to that of normal alkanethiols. Fourth, it is possible that π -stacking of the aromatic rings will afford additional stability to the SAMs.^{35,36} Fifth, the aromatic ring can be used as a spectroscopic tag for structural and orientational characterization of the films.^{37–39}

Experimental Section

Materials. Single-crystal silicon (100) wafers, which were polished on one side, were obtained from Silicon Sense, Inc. Gold shot (99.99%) was obtained from Americana Precious Metals.

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The normal alkanethiols used to generate the SAMs were either commercially available or synthesized using unexceptional methods. The chelating aromatic dithiols were synthesized using an approach developed in our laboratories;⁴⁰ experimental details are included as Supporting Information. The purity of all thiols was >98% as judged by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. The liquids used for contact angle measurements were of the highest purity available from Aldrich Chemical Co. and were used without further purification.

Preparation of SAMs. Solutions of the thiols were prepared in weighing bottles that were cleaned by soaking overnight in "piranha solution" (7:3, concentrated H₂SO₄/30% H₂O₂); *caution: "piranha solution" reacts violently with organic materials and should be handled carefully.* The bottles were then thoroughly rinsed with deionized water and absolute ethanol, and dried overnight at 100 °C. Gold surfaces were prepared by the thermal evaporation of chromium (ca. 100 Å) onto silicon wafers, followed by the evaporation of gold (ca. 2000 Å). Chromium serves to promote the adhesion of gold to the surface of silicon.⁴¹ The gold-coated wafers were cut into slides (ca. 1 cm × 3 cm) with a diamond stylus. The slides were washed with absolute ethanol and blown dry with ultrapure nitrogen. The gold slides were then dipped in solutions of the respective thiols (1 mM in ethanol or isooctane) and allowed to equilibrate for 24 h. The resultant SAMs were thoroughly rinsed with absolute ethanol and blown dry with ultrapure nitrogen before characterization.

Measurements of Ellipsometric Thickness. The thicknesses of the monolayers were measured using a Rudolf Research Auto EL III ellipsometer equipped with a He–Ne laser operating at 632.8 nm and an incident angle of 70°. The optical constants for the bare gold were measured immediately after evaporation. The thicknesses of the monolayers were calculated assuming a refractive index of 1.45 for all monolayers. For each type of monolayer film, data were collected and averaged from measurements on four separate slides using three spots per slide. The thicknesses for all SAMs were reproducible within ±2 Å.

Contact Angle Measurements. Contact angles were measured with a Ramé-Hart model 100 contact angle goniometer at 293 K and ambient relative humidity. The contacting liquids, hexadecane (C₁₆H₃₄, HD) and water (H₂O, W), were dispensed and withdrawn using a Matrix Technologies micro-Electrapette 25 operated at the slowest possible speed (ca. 1 μL/s). For each type of monolayer film, contact angles were collected and averaged from measurements on four separate slides using at least 3 drops per slide. Data from both edges of each drop were utilized in the averaging.

Results and Discussion

For the purpose of comparison, we propose the following descriptive analogy: SAMs derived from chelating aromatic dithiols containing $2j$ carbon atoms should most readily correspond to SAMs derived from normal alkanethiols containing j carbon atoms. We count the chain length of the new SAMs by dividing the chelating dithiol in half along the chain axis and counting the number of carbon atoms per half (see Figure 2). For example, SAMs

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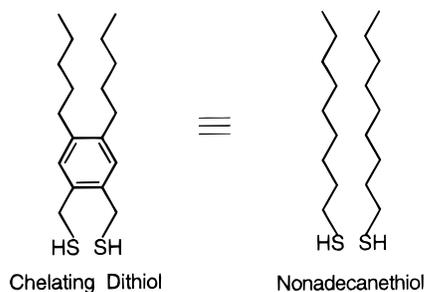


Figure 2. Structural comparison of chelating aromatic dithiols and normal alkanethiols. For both analogues shown, the number of carbon atoms per chain (j) equals nine.

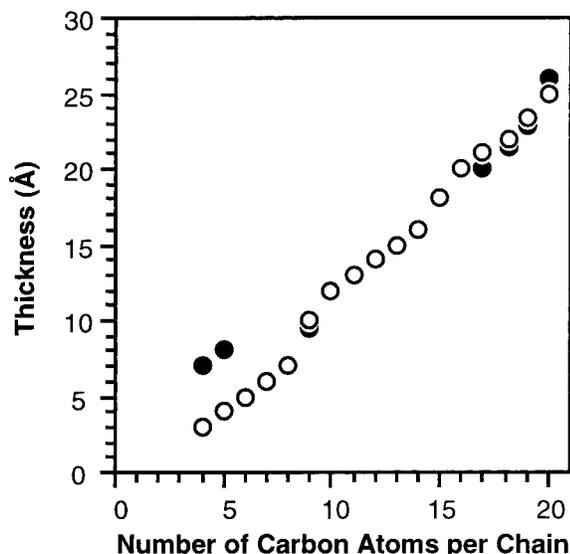


Figure 3. Ellipsometric thicknesses of films generated from the chelating aromatic dithiols (filled circles) and films generated from normal alkanethiols (hollow circles).

derived from $[\text{CH}_3(\text{CH}_2)_4]_2\text{C}_6\text{H}_2(\text{CH}_2\text{SH})_2$ should most readily correspond to SAMs derived from $\text{CH}_3(\text{CH}_2)_8\text{SH}$.

Thicknesses of the Films. One method of evaluating the quality of SAMs involves measuring their ellipsometric thicknesses.³ We compared the thicknesses of the films generated from the chelating aromatic dithiols to those generated from the corresponding normal alkanethiols (Figure 3).⁴² The thicknesses of the films derived from the chelating aromatic dithiols having chain lengths ≥ 9 carbon atoms (i.e., compounds **III–VII**) are within ± 1 Å of the films derived from the corresponding normal alkanethiols. These results are consistent with a model in which the long-chain chelating aromatic dithiols generate monolayer films with the alkyl chains oriented away from the surface.

The thicknesses of the films derived from the chelating aromatic dithiols having shorter chain lengths (i.e., compounds **I** and **II**) are, however, higher than those derived from the corresponding normal alkanethiols. Perhaps coincidentally, the measured thicknesses of the films derived from **I** and **II** are consistent with the

(42) Qualitatively, we observe little or no differences in the thicknesses and wettabilities of SAMs derived from normal alkanethiols regardless of whether the monolayers are adsorbed from ethanol or isooctane. Here we report the data for adsorption from ethanol to permit ready comparison to the literature where ethanol is the typical solvent of choice.³ We have found, however, that SAMs derived from the chelating aromatic dithiols exhibit consistent thicknesses and wettabilities when adsorbed from isooctane, but not from ethanol. The relatively poor solubilities of the chelating aromatic dithiols in ethanol might be at least partially responsible for this phenomenon.

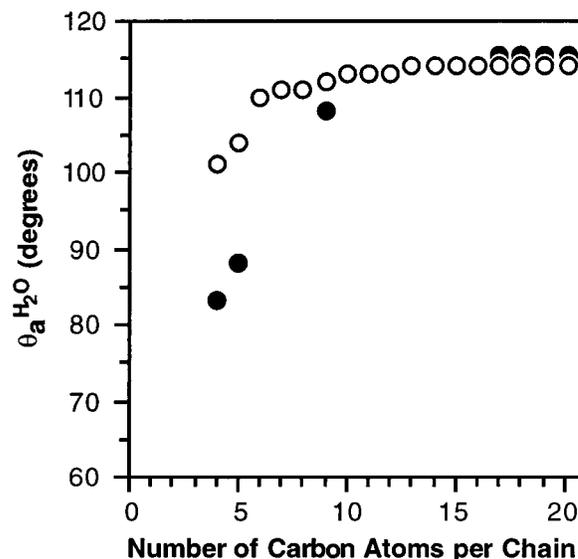


Figure 4. Contact angles of water on SAMs generated from the chelating aromatic dithiols (filled circles) and SAMs generated from normal alkanethiols (hollow circles).

calculated values of 7.5 and 8.5 Å for perpendicularly oriented **I** and **II**.³⁴ Since it is known that the alkyl chains of SAMs on gold derived from normal alkanethiols are tilted approximately 30° from the normal to the surface, the observed differences in thickness might correspond to differences in orientation for the shorter chelating SAMs. Due, however, to uncertainties involved in the ellipsometric measurements (e.g., use of the correct refractive indices,^{43,44} degree of coverage of the monolayer, cleanliness of the bare gold surfaces, etc.),³ this interpretation should be regarded with some degree of reservation until more evidence is available.

Wettabilities of the Films. Measurements of wettability are remarkably sensitive to the structure and quality of organic thin films.³ We compared the wettabilities of SAMs generated from the chelating aromatic dithiols to the wettabilities of SAMs generated from the corresponding normal alkanethiols (Figure 4). For the SAMs generated from the long-chain chelates (i.e., compounds **IV–VII**), the advancing contact angles of water ($\theta_a^{\text{H}_2\text{O}}$) were found to be $114 \pm 2^\circ$. The data for the normal SAMs with the four longest chain lengths (i.e., $j = 17–20$) were indistinguishable: values of $\theta_a^{\text{H}_2\text{O}}$ were found to be $115 \pm 2^\circ$. These data suggest that the interfaces formed by both types of SAMs are similarly hydrophobic.

Dispersive liquids such as hexadecane (HD) serve as particularly sensitive probes of the composition and orientation of the species that comprise low-energy surfaces.^{45,46} Consequently, we examined the contact angles of HD on the new SAMs and compared the values

(43) To explore this issue, we examined the ellipsometric thicknesses of SAMs generated from **I** and **II** as a function of the assumed refractive index. Since the refractive index for SAMs generated from normal alkanethiols is usually taken to be 1.45 or 1.50,³ and the refractive index of polystyrene is 1.57,⁴⁴ we varied the assumed refractive index from 1.40 to 1.60 in this study. The corresponding thicknesses decreased by approximately 1 Å. Since the observed thicknesses of the monolayers derived from **I** and **II** are greater than those generated from butanethiol and pentanethiol, respectively, by approximately 4 Å (see Figure 3), the influence of the assumed refractive index cannot account for the observed differences in thickness.

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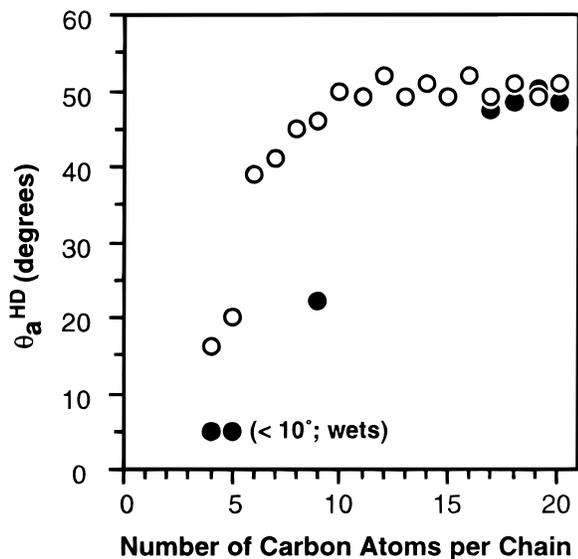


Figure 5. Contact angles of hexadecane on SAMs generated from the chelating aromatic dithiols (filled circles) and SAMs generated from normal alkanethiols (hollow circles).

Table 1. Average Advancing (θ_a) and Receding (θ_r) Contact Angles (deg) of Water and Hexadecane^a

long-chain SAMs	$\theta_a^{\text{H}_2\text{O}}$	$\theta_r^{\text{H}_2\text{O}}$	θ_a^{HD}	θ_r^{HD}
compounds IV–VII	114	103	48	36
$\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n = 16–19$)	115	103	51 ^b	40 ^b

^a The average contact angles of water are reproducible within $\pm 2^\circ$ of the reported value; the average contact angles of HD typically vary more widely ($\pm 3^\circ$) due to the “odd–even” effect (please see text). ^b The data reported are for alkanethiol adsorption from ethanol. For alkanethiol adsorption from isooctane, we observe $\theta_a^{\text{HD}} = 48^\circ$ and $\theta_r^{\text{HD}} = 36^\circ$.

to those observed on the normal SAMs (Figure 5). The SAMs generated from compounds **IV–VII** exhibited values of $\theta_a^{\text{HD}} = 48 \pm 2^\circ$, while the normal SAMs with the four longest chain lengths (i.e., $j = 17–20$) exhibited values of $\theta_a^{\text{HD}} = 51 \pm 3^\circ$ (adsorbed from ethanol) or $\theta_a^{\text{HD}} = 48 \pm 3^\circ$ (adsorbed from isooctane; see also Table 1).⁴⁷ The wettabilities of the normal SAMs appear to reflect the “odd–even” orientation of the terminal methyl group as a function of chain length for $j \geq 10$;⁴⁸ in contrast, the wettabilities of the chelating SAMs show no similar effect. As a whole, however, the wettability data suggest that the films formed from the long-chain chelating aromatic dithiols are densely packed and highly oriented, exposing terminal methyl rather than methylene groups.²¹

The absence of an “odd–even” effect for the chelating SAMs could result from a number of factors including (i) greater disorder of the chelating SAMs, (ii) conformational and/or electronic effects arising from the presence of the aromatic moiety, and (iii) different tilt angles for the two types of SAMs. Since values of contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$) can be used to probe the roughness or heterogeneity of a wetted surface,^{3,49} we examined the hystereses for both types of films (Table 1). The values are remarkably similar for the chelating SAMs ($\Delta\theta^{\text{H}_2\text{O}} = 11^\circ$; $\Delta\theta^{\text{HD}} = 12^\circ$) and the normal SAMs ($\Delta\theta^{\text{H}_2\text{O}} = 12^\circ$; $\Delta\theta^{\text{HD}} = 11^\circ$). These results suggest that there are no macroscopic differences in the roughness or heterogeneity (and

perhaps disorder)³ for these two types of films. Further characterization of the new chelating SAMs by infrared reflection–absorption spectroscopy (IRRAS) and atomic force microscopy (AFM) should provide more detailed insight into these issues.

The SAMs generated from shorter chain analogues (i.e., compounds **I–III**) exhibited lower contact angles (for both water and hexadecane) than their corresponding hydrocarbon analogues. Similarly, low contact angles have been observed for other short-chain thioaromatic monolayers on gold.^{50,51} Potential factors responsible for the low contact angles include (i) interactions between the test liquids and the surface of gold,^{21,52} (ii) interactions between the test liquids and the π -clouds of the benzene rings,⁵³ and (iii) disorder in the aromatic monolayer assembly.^{21,52}

Preliminary Evaluation of the Thermal Stabilities of the Films. Using ellipsometry,²¹ we probed the stability of the new chelating SAMs by comparing the solution-phase desorption of the SAM derived from **VI** to that of the analogous SAM derived from nonadecanethiol. At temperatures ranging from 80 to 110 °C in decahydronaphthalene (DHN), these studies showed that the chelating aromatic SAM was the more stable of the two. For example, after heating for 4 h at 80 °C in DHN, 50% of the SAM derived from **VI** remained on the surface, while only 30% of the SAM derived from nonadecanethiol remained. These preliminary studies suggest that the chelating aromatic SAMs can be used to generate films that are more thermally robust than those generated from their normal alkanethiol analogues.⁵⁴ A detailed investigation of the thermal stabilities of these and related films will be the subject of a future paper.

Comparison of New Chelating Aromatic SAMs with Previous Chelating SAMs.⁵⁵ In the initial report of chelating SAMs on gold, Nuzzo and Allara examined films formed from the adsorption of various derivatives of oxidized dithiothreitol.² Table 2 compares the thicknesses and wettabilities of methyl-terminated SAMs generated from an oxidized dithiothreitol and a chelating dithiol of equivalent molecular length. The comparison shows that the SAM derived from the chelating dithiol generates a thicker film and a more hydrophobic surface. There are at least two rationalizations for the observed differences. First, the asymmetric centers of the oxidized dithiothreitols require a large dihedral angle (ca. 67°)⁵⁶ between intramolecular alkyl chains. This relationship might introduce disorder into the resultant monolayers. The analogous dihedral angle in the chelating dithiols is approximately zero, allowing intramolecular chains to have the same orientation and thus the generation of more highly ordered SAMs. Second, the dithiothreitol-based molecules contain ester groups, which are known to cause disorder in monolayer assemblies.⁵⁷

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Table 2. Comparison of the Thicknesses and Wettabilities of Chelating SAMs on Gold²

chelating moiety	R	thickness (Å)	θ_a H ₂ O
	CH ₃ (CH ₂) ₁₄ CO	20.5 ± 1	96 ± 1°
	CH ₃ (CH ₂) ₁₄	25 ± 2	115 ± 2°

Comparison of New Chelating Aromatic SAMs with Previous Nonchelating Aromatic SAMs. Several studies have explored the effects of incorporating an aromatic ring into self-assembled monolayer films.^{35–39,50,51,58–60} In particular, Tao and co-workers have reported a series of studies examining the structures and other properties of SAMs generated from various aromatic-containing thiols on gold (as well as on silver and copper).^{36,51} These thiols generate densely packed and well-ordered films. Furthermore, it appears that the aromatic moiety introduces no unwanted steric influence upon the monolayer assemblies. These findings are consistent with the results present here, which demonstrate the feasibility of generating high-quality monolayer films from tetrasubstituted aromatic dithiols.

Conclusions

Several derivatives of 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene were synthesized and used to generate self-assembled monolayers on gold. The new SAMs were

characterized by optical ellipsometry and contact angle goniometry. On the basis of comparison of the observed thicknesses and wettabilities of the new SAMs to those derived from normal alkanethiols of similar chain length, we conclude that the chelating aromatic dithiols generate densely packed and highly oriented monolayer films with the sulfur atoms attached to and the alkyl chains directed away from the gold substrate. Preliminary studies of desorption in solution suggest that the chelating aromatic dithiols provide more robust SAMs than those derived from normal alkanethiols of similar chain length. Future studies will further explore the structure, stability, and utility of this new class of monolayer films.

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Supporting Information Available: Procedures for synthesis of the compounds **III** to **VII** (3 pages). Ordering information and Internet access instructions are given on any current masthead page.

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