

Instrumental Technique

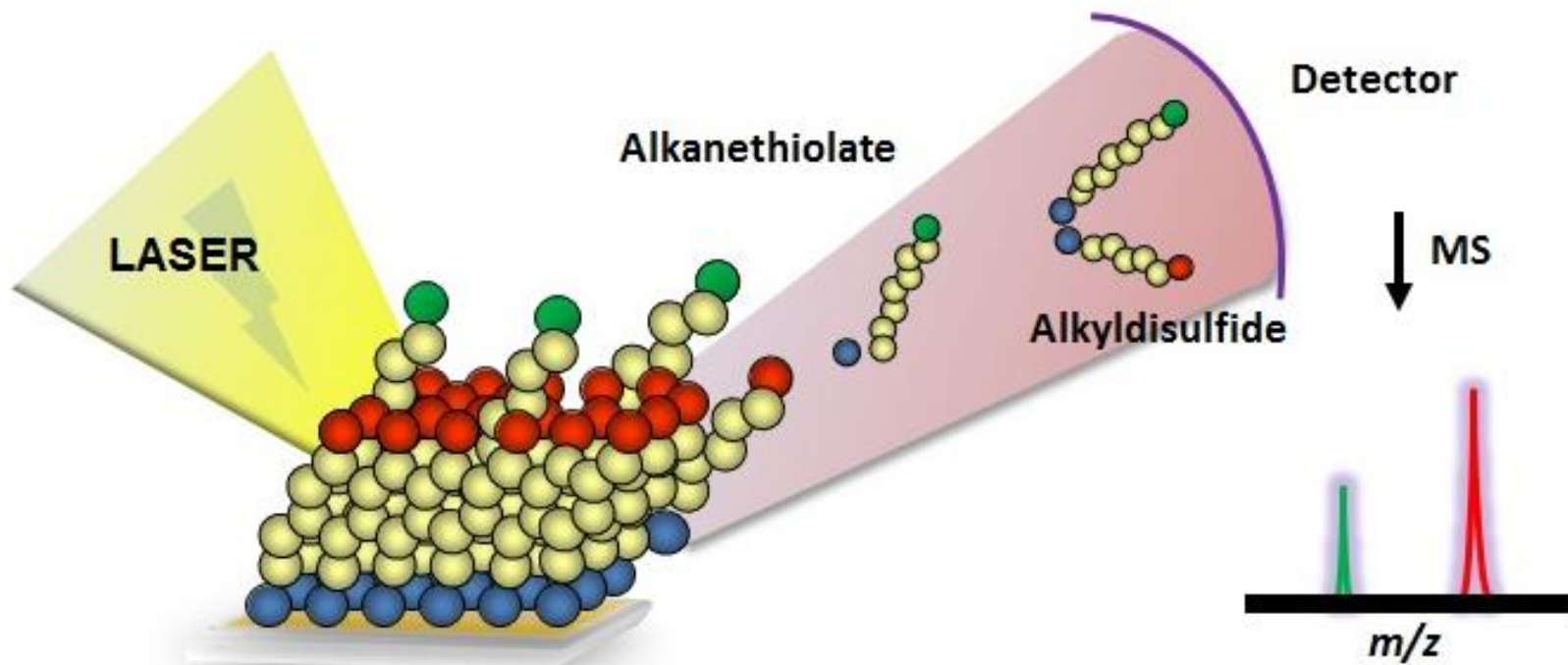
SAMDI-MS

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Introduction

- ❖ For reactions performed in solution, the products are easily isolated, purified and characterized using NMR, IR and other spectroscopic methods.
- ❖ The small amount of product present when these same reactions are performed at a two dimensional interface makes these analytical tools useless and instead requires the use of several methods that are sensitive but limited in the structural information they provide.
- ❖ This presentation will describe the combination of self-assembled monolayers with matrix-assisted laser desorption-ionization mass spectrometry - a technique termed as SAMDI MS - that permits a rapid characterization of products resulting from interfacial reactions.
- ❖ It has gone from a proof-of concept strategy to a powerful tool for chemical and biochemical discovery.

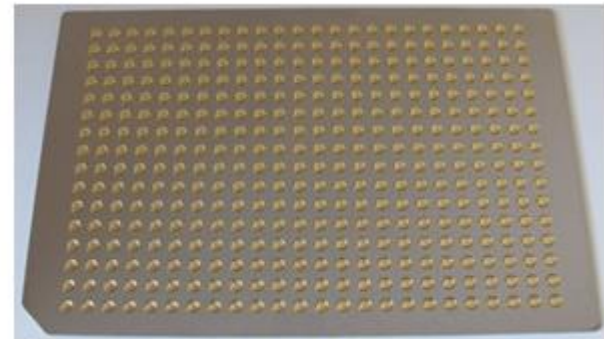
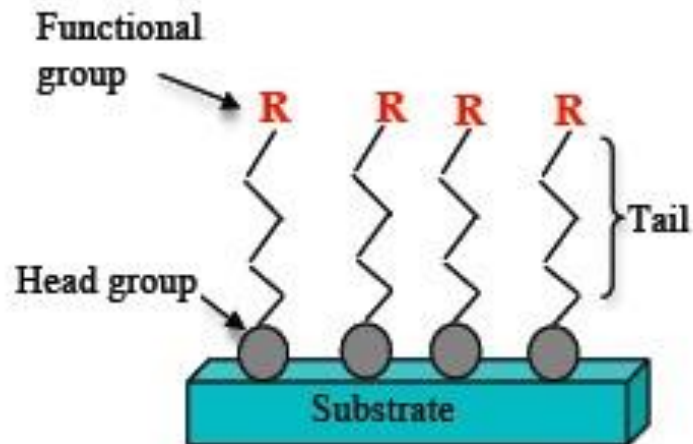
Mechanism



Self-assembled monolayers can be characterized using matrix assisted laser desorption-ionization mass spectrometry in a technique termed SAMDI MS. A nitrogen laser is used to desorb the monolayer to give alkanethiolate and the corresponding disulfide molecules. The mass spectrometer reports the mass-to-charge ratio for these molecules and can provide information on the products, yields and rates of interfacial reactions.

SAMs

- ❖ The self-assembled monolayers are an attractive platform for surface chemistry because they are easily prepared by immersing a gold-coated substrate in a solution of terminally-substituted alkanethiols under normal laboratory environments and because they are synthetically flexible.
- ❖ The chemisorption of thiol for gold is quite specific and because the resulting monolayers are thermally stable and compatible with a wide range of solvents and reagents.



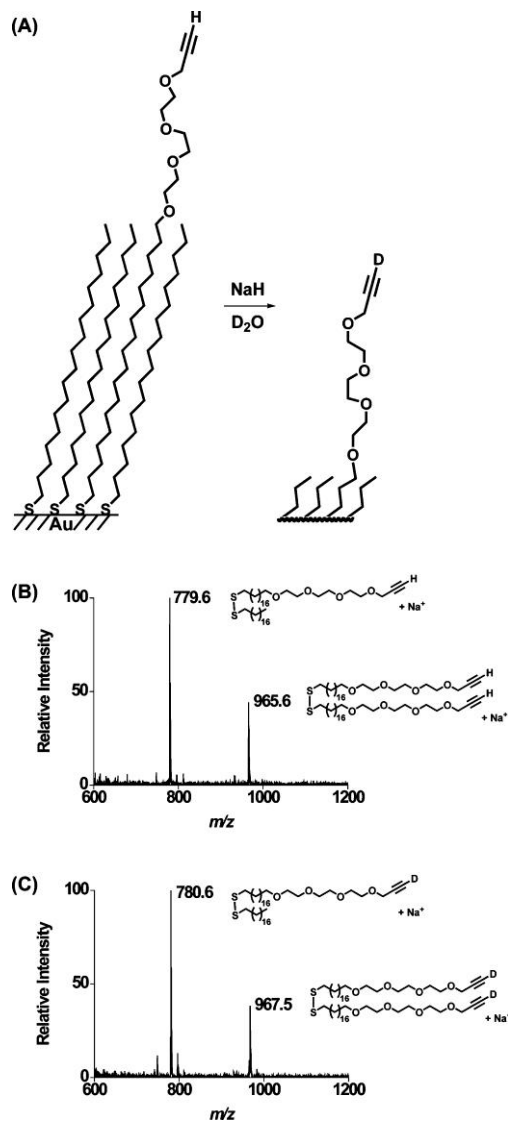


Figure 3 (A) A monolayer presenting a terminal acetylene group was treated with D₂O and base to promote the deuteration reaction. SAMDI mass spectra before (B) and after (C) the reaction show the high yield conversion and good mass resolution of SAMDI.

Entry	SAM	Reactant	Condition	Product
1			NaH D ₂ O	
2			Pd(PPh ₃) ₄ , CuI TBAF, THF	
3			AgNO ₃ Acetone	
4		H ₂ O	Au(PPh ₃)Cl, AgOTf Toluene	
5		Br-C≡C-TIPS	CuI, HO-NH ₂ ·HCl n-BuNH ₂ , H ₂ O, THF	
6			TBAF THF, 0 °C	
7			Pd ₂ (dba) ₃ , P(t-Bu) ₃ KF, THF	
8		MeI	NaH THF	
9			BF ₃ ·Et ₂ O Et ₂ O	
10			PPh ₃ , DEAD THF	
11		PPh ₃	THF	
12		TsCl	NaH THF	
13		EtO ⁻ Na ⁺	EtOD	
14			MeOH	
15			DMF	
16			DMSO	

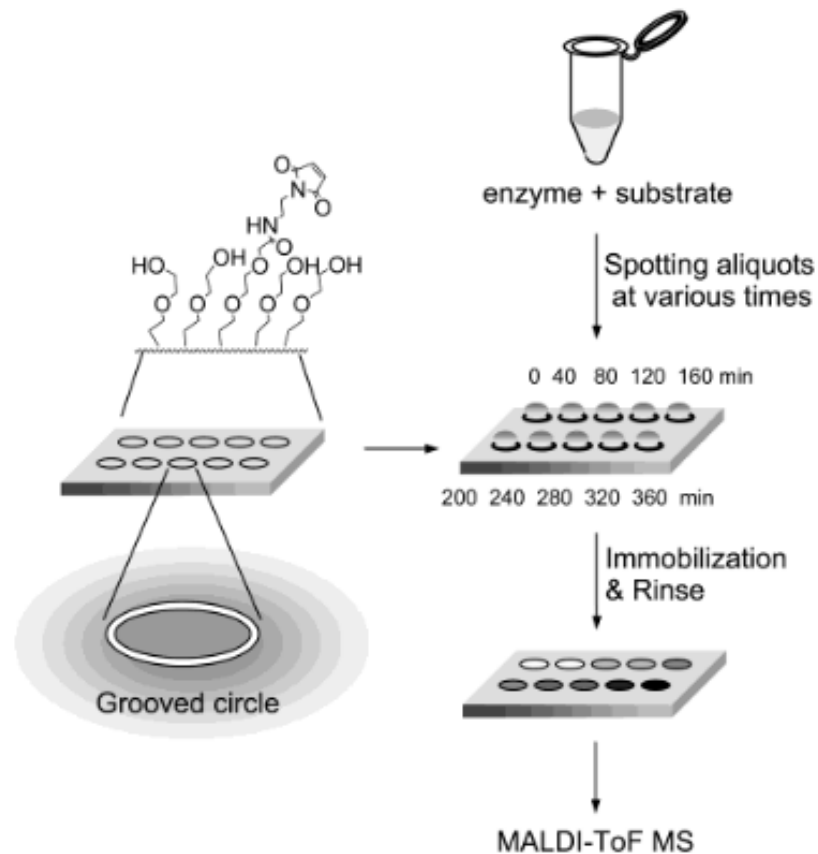
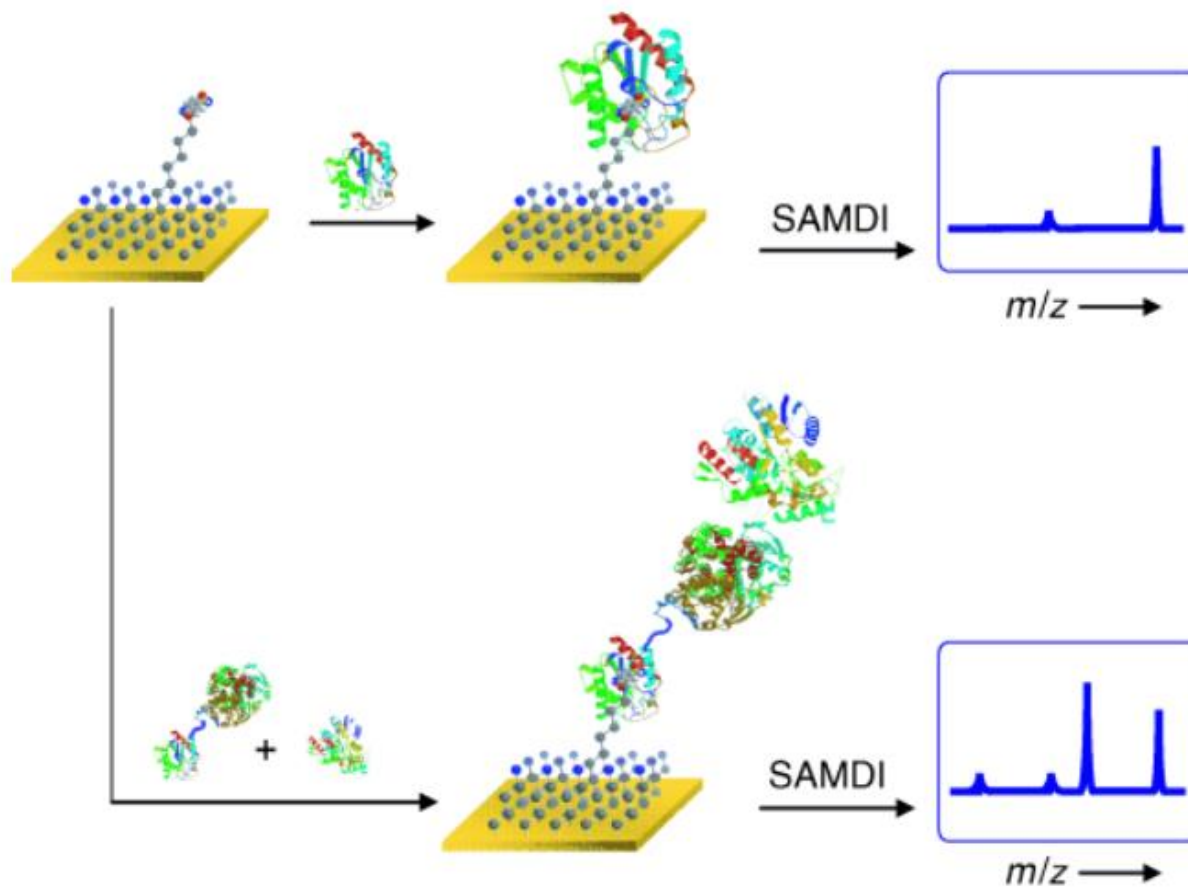


Figure 3. Scheme for obtaining kinetic information of the RMT1 assays using a "pull down" method. The enzymatic reaction was carried out in a homogeneous solution by mixing all the required components in a reaction vessel. Aliquots of the reaction mixture were then transferred to designated areas on a maleimide-presenting monolayer at various times to give selective immobilization of the peptide. The monolayer was rinsed, treated with matrix, and analyzed by MALDI-TOFMS directly.



W. S. Yeo, D. H. Min , R. W. Hsieh, G. L. Greene and M. Mrksich, *Angew. Chem. Int. Ed.* **2005**, *44*(34), 5480-5483

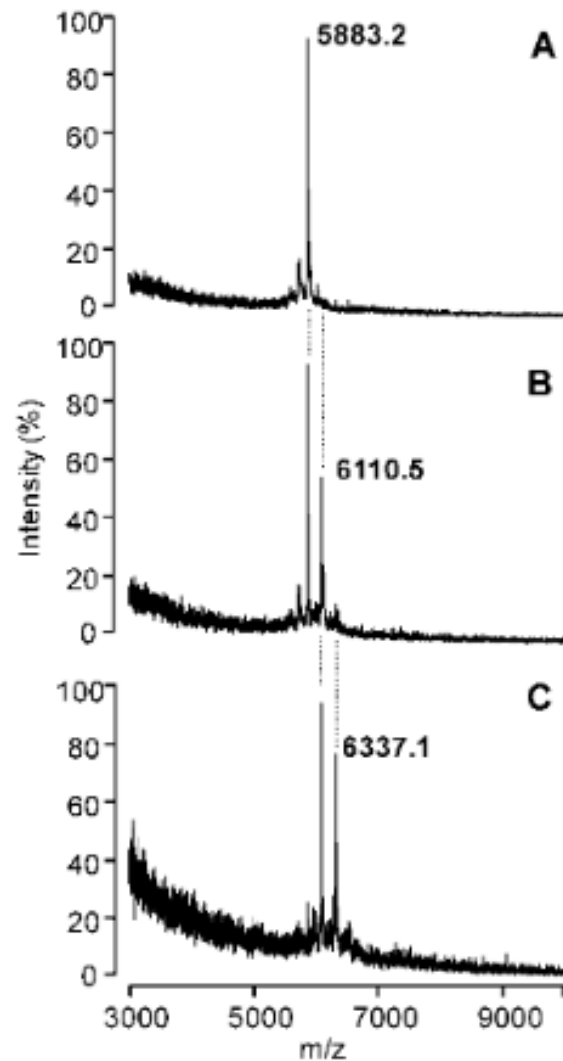


Figure 4. SAMDI MS was used to characterize the products resulting from reaction of a biotinylated duplex DNA (5'-biotin-TTT TAT ATA CGT ATA TCG) with *cis*-[Pt(NH₂)₂Cl₂]. Spectra are shown for reaction times of 0, 4 and 21 hr (A, B and C, respectively).

Conclusion

- ❖ Studies in surface chemistry instead use several methods to assemble an understanding (often times incomplete) of interfacial structure, including infrared spectroscopy to identify functional groups, x-ray photoelectron spectroscopy to determine the elemental composition and ellipsometry to measure the thickness of a monolayer.
- ❖ By providing the molecular weight of the alkanethiols, SAMDI complements these methods and provides molecular information that is not available with other methods.
- ❖ Most significantly, this method is straightforward to use and provides the synthetic chemist with information that can be used to develop and implement a wide range of chemistries on monolayers.

THANK YOU