**Research Proposal**

The main component of the proposed devices is a nanoscale *Metal/Mixed Self-Assembled Monolayer/Metal* heterostructure. The key issue is to create a monolayer whose conductance can be tuned by an external laser. The following mechanism is proposed to satisfy this requirement. The SAM consists of a mixture of molecules that have the same main structure but different substituents. The main structure has a π-electron system and contains a photoactive center. The photoactive center can undergo reversible isomerization upon photon adsorption, and thus change the conductivity of the molecules (ideally, the two isomers correspond to the ON and OFF states respectively). The substituents, having different electron affinity, shift the UV absorption band of the molecules accordingly. The total conductivity of the device will be determined by the number of molecules in the monolayer that are switched on or off. We will choose a mixture of these molecules with different components covering different but slightly overlapped absorption bands, so that when swept with a tunable laser, different components will be switched on or off sequentially. By controlling the frequency range of the laser sweep, we can switch on or off different number of molecules, and thus control the overall conductivity of the heterostructure. The device fabrication will employ a previous reported technique [3,6].

The rest of this proposal is divided into five sections. The first section will discuss the design and synthesis of candidate molecules for use in the devices. The second section will discuss the preparation of the mixed SAMs. The third and fourth sections

will describe the fabrication and characterization of the device. In the last section, some potential difficulties and experimental issues will be discussed, followed by a summary.

Preparation of Candidate Molecules

The first key issue is to design the desired molecular backbone, which should contain a π-electron system and a photoactive center. The photoactive center must be able to undergo photo-induced isomerization and change the conductivity of the whole molecule. At least in one of the isomer states, the organic backbone should be fully conjugated, which corresponds to the "ON" state, and the other state should be as insulating as possible. There are several such photoactive functional groups that are well studied in area of optoelectronics [20-24]. Three examples that contain fully conjugated backbones are given below.

Scheme 1.

1a   1b

Scheme 2.

2a   2b

Scheme 3.

3a   nitrospiropyran   3b
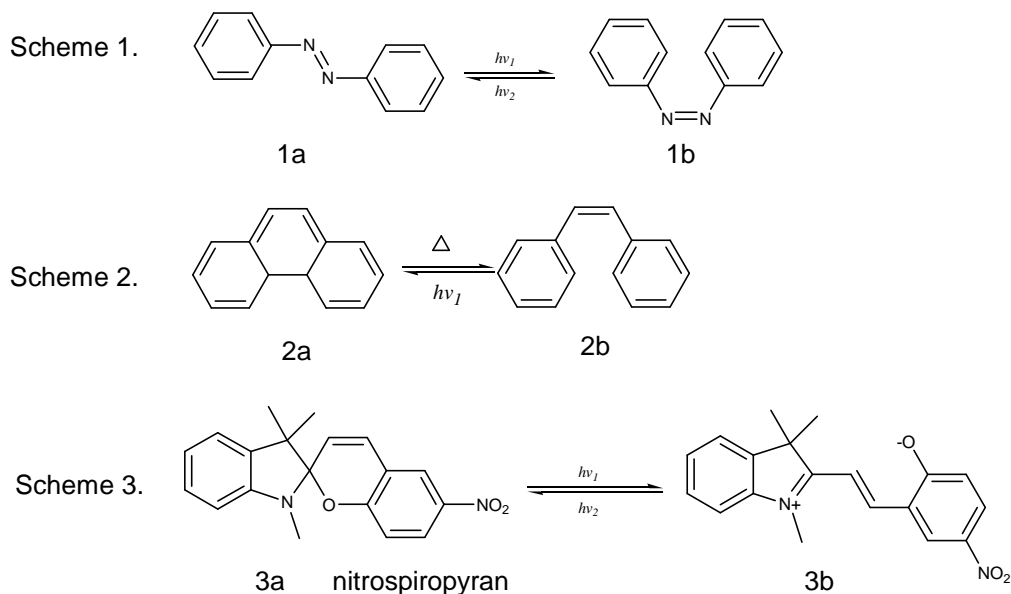
The molecules in Scheme 1 and 2 are simple and easy to manipulate or functionalize. Since these molecules (1a,1b,2a,2b) all have planar structures, they are expected to form more compact monolayers. However, in these two schemes, both left and right isomers have fully conjugated π electron systems. Thus they are not good molecular switches. In Scheme 3, isomer 3a does not have a fully conjugated backbone, while isomer 3b has a fully conjugated π electron system. When this molecule undergoes photo-isomerization, significant change in conductance can be expected. A less important reason that Scheme 3 is preferred is that the relative positions of two far ends of molecules do not change a lot during isomerization: when incorporated into the device, there will be some constraints on the movement. The isomerization will be difficult if the ends need to shift a lot relative to each other. In addition, during the synthesis of backbones in Scheme 3, a wide flexibility exists in adding different substituents to the benzene rings (details below).

The next step is to modify the backbone in Scheme 3 by adding a thiol group to the left end so that the molecules can form a self-assembled monolayer on the Au surface. Previous studies have shown that sulfur compounds have a strong affinity to transition metal surfaces (see Ref. 19 and references therein). In particular, many organosulfur compounds were found to form monolayers on gold surface, and can incorporate a wide range of substituents in the alkyl chain and at the chain terminals. The later property is particularly important to this proposal because we need to add different substituents to the backbone to shift the absorption band of the molecules. Because the thiol group is unstable and can be easily oxidized [25], disulfides, which are more stable, will be synthesized instead. Chemisorption of disulfide on a clean gold surface gives

indistinguishable monolayers compared to corresponding thiol [19]. The synthesis of di-

nitrospiropyran disulfide (compound **7**) is shown in Scheme 4. The first two steps were

already reported in literatures [26]. Reactions similar to the final synthesis step have been

reported (see examples in Appendix A). Therefore no particular difficulty is expected.

Scheme 4
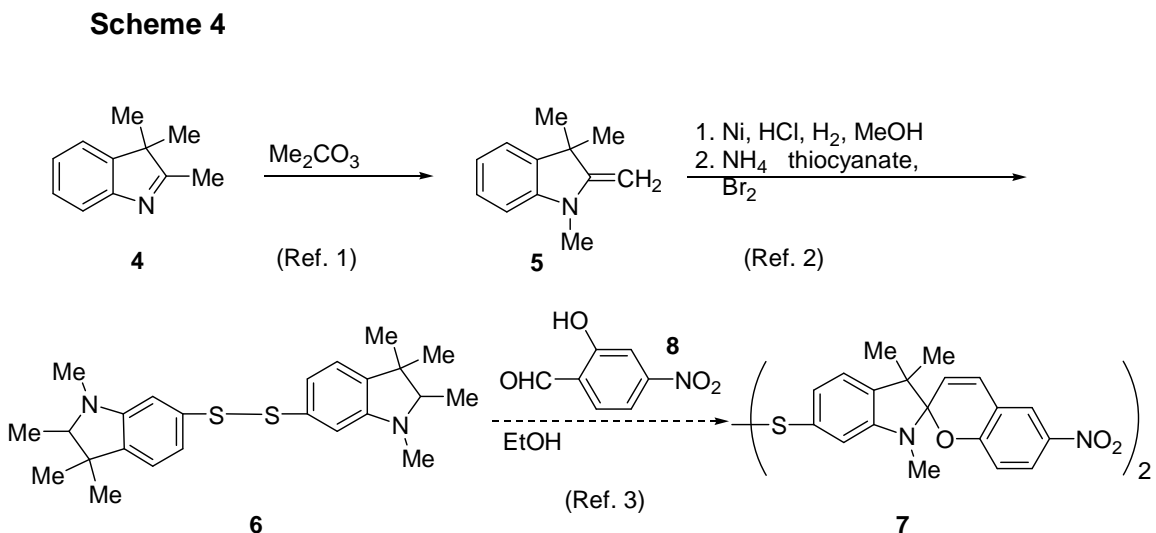
Ref. 1: Eur. Pat. Appl., 445643, 11 Sep 1991
Ref. 2: Khim. Geterotsikl. Soedin., (1), 104-9; 1988
Ref. 3: Sichuan Daxue Xuebao, Ziran Kexueban, 30(2), 283-7; 1993

The disulfide compound (**7**) has the desired properties for the proposed device. It

contains a photoactive center that can undergo photo-isomerization (Scheme 3) under

irradiations and switch between ON and OFF states. The next step is to add different

substituents to this backbone to create similar molecules that have slightly different

absorption bands. This can be done by replacing the starting compounds **4** or **8** with their

substituted derivatives. It has been shown that many derivatives of compound **8** can react

with indole moieties to form nitropiropyran units (see Appendix A). Following

Woodward's rule, the shift of absorption band can be estimated [25]. Some typical

substituents and corresponding shift in UV absorption band are shown in Table 1. For compound **7**, $\nu_1 \sim 340$ nm and $\nu_2 > 495$ nm (estimated from a very similar compound in Ref. [19, 20]; ν_1, ON $\Rightarrow$ OFF, ν_2, OFF$\Rightarrow$ ON; see Scheme 3).

Preparation of Mixed SAMs

SAMs are densely packed molecular monolayers adsorbed from solution onto solid substrates. Significant progress into understanding the formation process of SAMs has been made over the past few years. Studies of the formation of alkanethiol SAMs on the Au (111) surface showed a two-stage mechanism (see Fig. 2): an initial formation of a "striped" phase, which takes a few minutes, followed by nucleation and growth of islands in which molecules stand up and pack in self-organized patterns [19,27]. The first step, described well by diffusion-controlled Langmuir adsorption, was found to strongly depend upon thiol concentration. The second step can be described as a surface crystallization process, where alkyl chains get out of disordered state and into unit cells. The kinetics of the first step is determined by the mechanism of surface head group reaction, and activation energy may depend on the electron density of adsorbing sulfur. The kinetics of the second step is related to chain disorder, chain interactions and the surface mobility of chains (for more detail, see Ref. 19 and references therein).

The rates of formation of SAMs from disulfides or thiols are indistinguishable. A simple oxidative addition of S-S bond to the gold surface is possibly the mechanism in the formation of SAMs from sulfides:

$$RS\text{-}SR + Au_n^0 \implies RS^- Au^+ \cdot Au_n^0$$
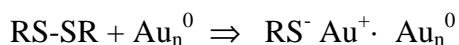
However, due to the disulfide bond cleavage mechanism, the rate of replacement of molecules in SAMs for disulfides is much slower than for thiols [19].

According to the mechanism given above, there should be no difficulty in growing SAMs of the molecules designed in previous section. The only concern is how to control the composition of the mixed SAMs. Formation of mixed SAMs could involve complicated competition mechanisms for thiols because replacement could occur in the second step. However, in our case, it is simpler because replacement more is less likely to occur for disulfides. Since in the first step adsorbing rate is strongly dependent upon the concentration of the solution, the final ratio of various components in the mixed SAM should be mainly determined by the composition of the solution. This assumption can be further justified since in our case all components have very similar structures.

Therefore, to prepare a mixed SAM of certain composition, we need a solution of the same composition. Typically, the solvent is tetra-hydrofuran (THF), and relatively dilute solutions (10^{-3} M) should be used. The entire growing procedure should be carried out in an inert atmosphere (e.g., Argon gas protected). It usually takes hours to days for the thickness and contact angles of monolayer to reach their final values. The optimal growing time, as well as suitable mixtures, where the conductance of the resulted mixed SAMs is tunable, needs to be found experimentally. These issues will be readdressed in the last section.

Device Fabrication

The device will be fabricated using a previously reported technique [3,6]. Two features essential to this proposal are included in the process. The first feature is the employment of a nanoscale device area. The area can be made smaller than the domain size of SAMs (about 1000 Å for alkanethiols on Au surface), thus the adsorbed organic layer is highly ordered and mostly defect free. The second feature is that during the

deposition of the top contact, several measures, namely low deposition temperature, very slow deposition rate and high vacuum, are taken to ensure that the deposited metal atoms accumulate at the SAM surface and do not penetrate into the organic layer. These measures also minimize damages to the SAM during deposition.

A schematic diagram of the fabrication of a similar device is shown in Fig. 3. The starting substrate for the device fabrication is a 250-µm-thick double-side polished Si (100) wafer, on which 50nm of Si_3N_4 is first deposited on by low-pressure chemical vapor deposition. The nitride on the back is then removed in a square of 400 µm by 400 µm by optical lithography and reactive ion etching (RIE). The exposed silicon is etched through to the top surface to leave a suspended silicon nitride membrane 40 µm by 40 µm. About 1000 Å thick of SiO_2 is then grown thermally on the sidewall to improve insulation. Electron beam lithography followed by reactive ion etching is used to open a pore in the suspended Si_3N_4 membrane. The RIE rates are substantially reduced so that the far side opening is much smaller than the actual pattern. The resulted pore has a bowl-shaped geometry cross section, with an opening of diameter of ~30 nm. A Au contact of 200 nm thickness is evaporated to fill the pore. The typical crystallite size for gold is approximately 50 nm, thus the lower surface in the nanopore is probably a single crystallite. The sample is then immediately immersed into a solution to self-assemble the active optoelectronic components. The sample is then rinsed, loaded into a high vacuum chamber, and mounted onto a liquid nitrogen cooled stage for bottom electrode evaporation. Approximately 200 nm of Au is evaporated at 77 K at a very slow rate (< 1 Å/s). The samples are then allowed to slowly warm up to room temperature (~ 24 h) for conductance measurements and demonstration of gating with a tunable laser.

Device Characterization

Two terminal current-voltage (*I-V*) characteristics are to be first measured at room temperature using standard semiconductor parameter analyzers. In the fabricated device, only one end of the molecules is chemically bonded to the gold electrode (S-Au) and the other end only has physical contact with the electrode. It has been suggested that the mechanisms, thus the barriers, for electrons ejected from the two electrodes are different [3]. Due to the asymmetry, prominent rectifying behavior is expected in the I-V characteristics (see an example shown in Fig. 4). To verify that the conductance of this device is controllable by a tunable laser, we need to fix the bias voltage to some positive value, and measure the conductance under different irradiations. The dye lasers will be the primary choice of light source due to its broad tenability and great operational flexibility [28]. In principle, first we need to verify that the conductance CHANGES under irradiations, and then we can proceed to demonstrate that the change is controllable.

Experimental Issues and Summary:

While the descriptions above suggest that the construction of the proposed device is feasible, there are still some experimental concerns and potential problems.

1). During the fabrication of the device, it is very important to ensure that the deposition of bottom Au electrode does not damage the monolayer and has no direct contact with the top Au electrode. We must also ensure that the monolayers themselves are mostly defect free within the domains. Thus, before proceeding to the device fabrication step, we may need to study the quality of the prepared monolayers carefully using standard tools such as X-ray Photon Spectroscopy (XPS), ellipsometry. In

principle, we need to determine the optimal growing time and corresponding solution concentration. Growing the SAMs at lower temperature and in different solvents is also in consideration.

2). Another important issue in realizing the proposed device is to find a mixture with slightly different absorption bands that in total cover some continuous range. Experimentally, we will need to first fabricate devices with different pure SAMs and measure their ν_1 and ν_2. Then we can try to make up suitable mixed SAMs. In addition, although, as discussed in the mixed SAM preparation section, the composition of mixed SAMs may be simply determined by the composition of the solutions, it is safe to verify it by using tools such as Fourier transform mass spectroscopy (FT-MS).

3). A potential problem: the photoisomerization of spiropyran actually consists of two steps. In the second step, the conformation of the carbon carbon double bond changes from *cis-* to *trans-* conformation. It is not clear how much the barrier will increase when one end is semi-fixed (one end of the molecules have physical contact with the Au electrode). Nevertheless, we can increase the flexibility of the molecules by adding to the nitro end a conjugated alkene chain.

In summary, a pseudo 3-terminal molecular device that uses a tunable laser as an external gate terminal has been described to experimentally study one possible way of gating in a molecular device.