

Visible light responsive systems based on metastable-state photoacids

Yi Liao

Department of Chemistry, Florida Institute of Technology, Melbourne, Florida, USA 32901

ABSTRACT

Proton transfer is one of the most fundamental processes in nature. Metastable-state photoacids can reversibly generate a large proton concentration under visible light with moderate intensity, which provides a general approach to control various proton transfer processes. Several applications of mPAHs have been demonstrated recently including control of acid-catalyzed reactions, volume-change of hydrogels, polymer conductivity, bacteria killing, odorant release, and color change of materials. They have also been utilized to control supramolecular assemblies, molecular switches, microbial fuel cells and cationic sensors. In this talk, the mechanism, structure design, and applications of metastable-state photoacids are introduced. Recent development of different types of metastable-state photoacids is presented. Challenges and future work are also discussed.

Keywords: photoresponsive materials, visible light, proton transfer, photoacid

1. INTRODUCTION

Proton transfer is one of the most fundamental processes in nature and numerous chemical, material, and biological processes are driven by proton transfer. For example, biological systems use a proton gradient as an energy form to synthesize energetic chemicals for their biological functions; many organic reactions are catalyzed by Bronsted acids; and many materials have pH-sensitive properties. Our research focuses on development of a molecular tool, metastable-state photoacid, which can be generally used to control proton transfer processes with light. Metastable-state photoacids (mPAH) can produce a large proton concentration with high efficiency and good reversibility. The reversibility allows the processes to be stopped and/or reversed after they are initiated by light. In addition, visible light with moderate intensity, e.g. LED and sunlight, can be used to activate mPAHs. Therefore, mPAHs can be conveniently incorporated in different systems to control various proton transfer processes. This proceeding introduces the design and properties of mPAHs and reviews the applications we have demonstrated. Some applications explored by other groups are also mentioned.

2. MECHANISM AND DESIGN OF METASTABLE-STATE PHOTOACID

A photoacid is a molecule that transforms into a strong acid upon photo-irradiation. The strong acid can release a proton to induce a proton transfer process. A photoacid can be deemed as a molecular device that converts an input of light to an output of a proton. Metastable-state photoacid is different from the extensively studied photoacid generator (PAG) and excited-state photoacid in both mechanism and properties. Under irradiation, the excited mPAH undergoes an intramolecular photoreaction and transforms into a metastable structure, which is a strong acid. The proton dissociation occurs at the metastable state. The metastable state is not stable and thermally relaxes to the ground state, which is accompanied by recombination with the proton.

The first mPAH was designed based on protonation of a macrocyanine, which is related to the photochromic reaction of spiroopyran.¹ However, mPAHs can be generally designed by linking an electron-accepting moiety and a weakly acidic nucleophilic moiety with a double bond. Photo-induced trans-cis isomerization of the double bond allows a nucleophilic cyclization reaction to occur between the two moieties, which generates a highly-acidic metastable form (Figure 1). Based on this design, mPAHs with different structures and properties can be developed. The three types of mPAHs we have developed are shown in Figure 1.

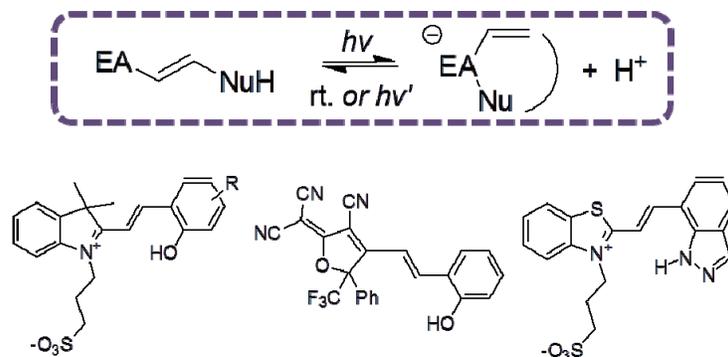


Figure 1. Design of mPAH and the three types of mPAHs with different electron accepting and nucleophilic moieties

3. PROPERTIES OF METASTABLE-STATE PHOTOACIDS

Properties of mPAHs are described using mPAH1 as an example. MPAH1 is the 1st MPAH reported in 2011.¹ It has been utilized in several applications, which are described in the following section. MPAH1 is an orange solid with a moderate solubility in water (~0.5 mM). Its maximum absorption wavelength is ~420 nm. A 470 nm LED was often used as the light source. The photoreaction quantum yield is above 0.3. When a ~0.5 mM aqueous solution of mPAH1 was irradiated, the pH drops more than 2 units from 5.5 to 3.3. When the light was turned off, the pH value returned to its original level in ~ 5 min. This cycle can be repeated many times (Figure 2). The reverse reaction is a 2nd order reaction and its rate can be tuned by modifying the molecular structure.²

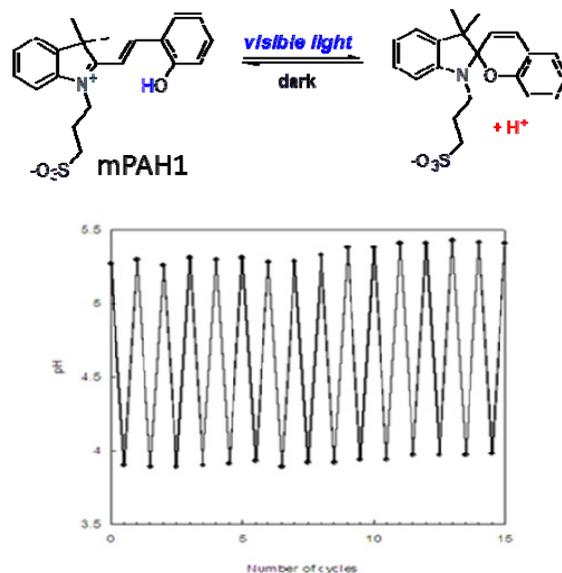


Figure 2. Photoreaction of mPAH1 and pH cycles produced by turning on and off irradiation.

4. APPLICATIONS OF METASTABLE STATE PHOTOACIDS

Metastable-state photoacids have many applications in chemical, biological and materials areas. Any system that is sensitive to acid, proton concentration (pH), or protonation could be controlled by mPAHs. We have demonstrated that a textbook reaction, Fisher esterification reaction, can be turned on and off using light when MPAH1 was used as a catalyst.¹ Hydrolysis reaction can also be catalyzed by acid and thus controlled by a MPAH. Based on this, we developed a polymeric material that can release fragrance under visible light and quickly stops releasing after the light is turned off (Figure 3).³ The material contains an mPAH with a fast reverse reaction rate and good stability. This material may find applications in digital scent technology.

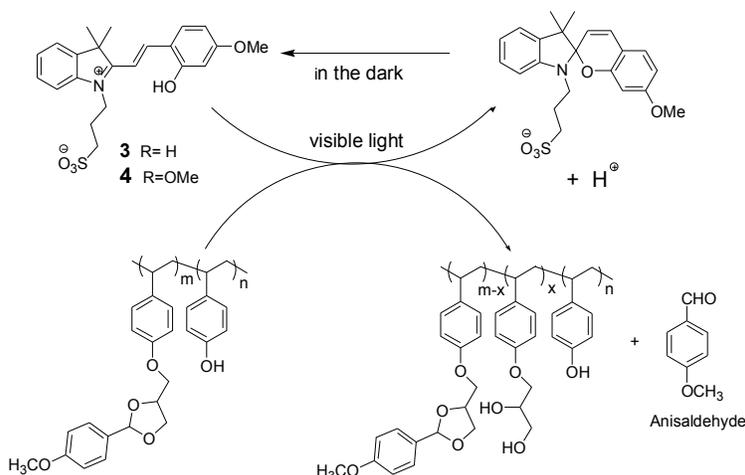


Figure 3. Photoinduced fragrance release

Protonation can change optical and electronic properties of a material. For example, polyaniline changes from an insulator to a conductor upon protonation. A composite of polyaniline and mPAH1 showed photoswitchable conductivity.⁴ However, the magnitude was only \sim one fold, which is because mPAH1 released most of its proton to the basic polyaniline before irradiation. The recently developed indazole type mPAH (Figure 1) may improve the magnitude of the conductivity change. Photochromic materials were also developed using mPAHs and pH dyes.⁵ Although photochromic compounds have been extensively studied for decades, it is very difficult to develop a photochromic material that changes from a specific color to another specific color. The color change of the photochromic material based on mPAH can be easily designed by choosing one or more pH dyes with desirable colors. Complicated visual effects, for example multiple color changes, can be developed as well.

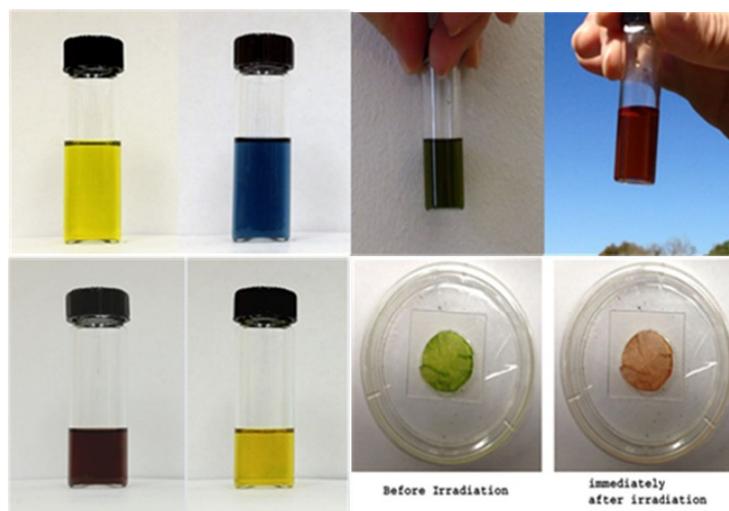


Figure 4. Photochromism based on proton transfer

A MPAH has also been used for killing bacteria. A strong bacterial inhibition of mPAH1 assisted by visible light has been reported.⁶ If combined the photoacid with colistin, the minimum inhibitory concentration of colistin on a multi-drug resistant bacteria can be improved \sim 32 times, significantly decrease the toxicity of the colistin in clinic (Figure 5).

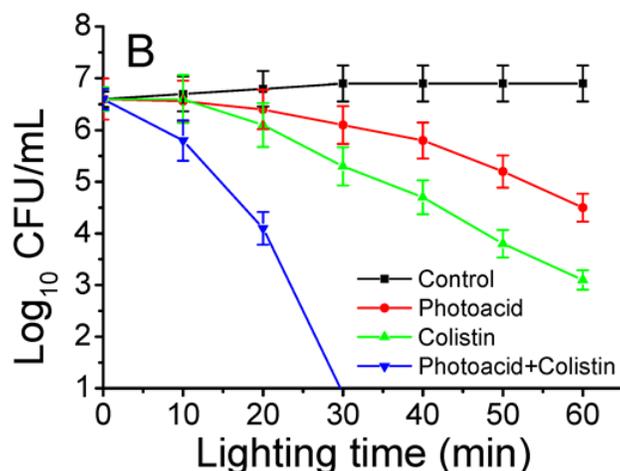


Figure 5. Visible light mediated killing of bacteria

Proton is a cation and can form hydrogen bond. Therefore, mPAHs can be used to control ionic interaction and hydrogen bonding, which has many applications in materials science. We showed that a hydrogel of poly(acrylic acid-co-acrylamide) in a solution of a mPAH shrank to $\sim 1/8$ of its original volume under irradiation (Figure 6), which is because photoinduced protonation of the carboxylic group reduce the repulsion between the carboxylic anions and the ionic strength in the hydrogel. Recently, we showed that hydrogen bond and ionic bond between a carboxylic acid and pyridine can be broken by the proton released from an mPAH.⁷ A mixture of a polymer of acrylic acid, poly(vinyl pyridine) and a mPAH in acetone/water changed from a cloudy suspension to a clear solution under irradiation. When the light was turned off the suspension reformed.

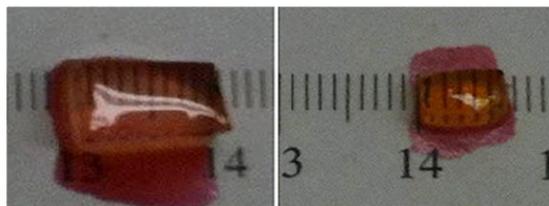


Figure 6. Photoinduced volume change of a hydrogel

Other groups have also used the mPAHs for different applications, for example, supramolecular assemblies,⁸ molecular switches,⁹ microbial fuel cells,¹⁰ and cationic sensors¹¹. The mPAH1 is the one that used most in these applications. Although mPAH1 are easy to synthesize and has good photoactivity and reversibility, it has several shortcomings. It does not function in relatively basic conditions including PBS buffer; it is not very stable in an aqueous solution with $\text{pH} > 4$; its reverse reaction is slow in organic media; and it does not absorb in near IR range. While mPAHs are utilized in more and more applications, fundamental research on mPAHs is necessary to understand their behavior and improve their properties. Modifying the structure of mPAH with electron donating groups can increase the reverse reaction rate and improve its stability in water. The indazole type mPAH functions in PBS buffer and thus could find applications in biomedical areas.

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