Supporting Information

for

A novel metastable-state photoacid for reversible protonation of strong bases

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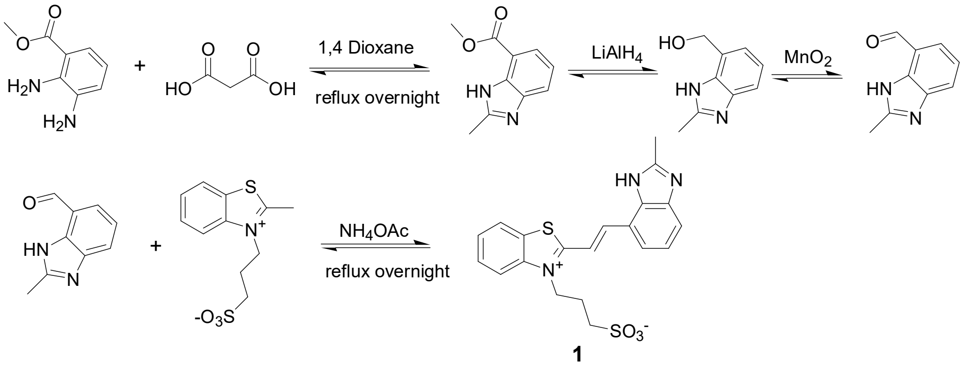
Experimental

1. General information

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz spectrometer using deuterated dimethylsulfoxide (DMSO-d6) with tetramethyl silane (TMS) as an internal standard unless otherwise stated. All chemical shifts are quoted in δ (ppm) and coupling constants in Hertz (Hz) using the high-frequency positive convention. Reagents and solvents were commercially available and used as received without any further purification. UV-vis spectra were obtained from a Varian Cary 60 Scan UV-Vis spectrophotometer. The LED array was purchased from www.elixa.com

2. Synthesis of mPAH 1

Photoacid **1** was synthesized according to the route in Scheme 1 in the main article, which is also shown below.



2.1 *Synthesis of methyl-2methyl-1H-benzo[d]imidazole-7-carboxylate*

Methyl-2,3-diaminobenzoate (1.65g, 9.9 mmol) and malonic acid (5.6g, 55.7 mmol) were dissolved in 7 mL dry 1,4 dioxane and refluxed overnight at ~120 °C. Then 50 mL of ethyl acetate was added, followed by 20 mL of saturated sodium bicarbonate, and the solution was stirred for 30 min. After the organic layer containing the product was separated. The product in the aqueous layer was extracted by EtOAc (3 x 150 mL). The combined organic layers were dried by anhydrous sodium sulfate, and concentrated by rotary evaporation. Then ~1 mL THF was added, and 200 mL of hexane was added dropwise to precipitate the product, which was collected by filtration (1.13 g, 60% yield). In case a small amount of side product stays, the product can be further purified using column chromatography with 1:1 ethyl acetate and hexanes. ^{1}H NMR (400 MHz, DMSO) δ 12.22 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 3.94 (s, 3H), 2.55 (s, 3H).

2.2 *Synthesis of (2-methyl-1H-benzo[d]imidazol-7-yl)methanol*

$LiAlH_4$ (0.54g, 13.88 mmol) was dissolved in 30 mL of dry THF under N_2 gas. In a sealed test tube methyl-2methyl-1H-benzo[d]imidazole-7-carboxylate (0.42 g, 2.21 mmol) was dissolved in 10 mL of dry THF, and then transferred to the $LiAlH_4$ solution in an ice bath. The reaction solution was stirred at room temperature overnight. Then 10% H_2SO_4 (2 mL) was added dropwise until bubbling stopped. The mixture was added about 40 mL of dichloromethane (DCM), and some anhydrous sodium sulfate. The mixture was filtered and the filtrate was collected. The remaining solid was rinsed with methanol and DCM. The combined organic solutions were dried by rotary evaporation to get the product. (0.24g Yield 67%) ^{1}H NMR (400 MHz, DMSO) δ 12.11 (s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.01 (m, 2H), 4.78 (s, 2H), 2.47 (s, 3H).

2.3 *Synthesis of 2-methyl-1H-benzo[d]imidazol-7-carbaldehyde*

(2-methyl-1H-benzo[d]imidazol-7-yl)methanol (0.229g,1.41mmol) was dissolved in 10 mL of dry THF, and activated MnO_2 (1.36g, 15.64 mmol) was added. The reaction mixture was stirred overnight at room temperature. The solution was filtered and the solid was washed with DCM multiple times. Multiple filtration sometimes was needed to remove all the MnO_2 powder. The filtrate was dried by rotary evaporation to yield the product. (0.14g, Yield 64%.) ^{1}H NMR (400 MHz, DMSO) δ 12.68 (s, 1H), 10.37 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 5.5 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 1H), 2.45 (s, 3H).

2.4 *Synthesis of the photoacid mPAH 1*

2-methyl-1H-benzo[d]imidazol-7-carbaldehyde (0.12g, 0.75mmol) and 2-methyl-1-(3-sulfonatepropyl)-benzothiazolium (0.22g, 0.82mmol) was dissolved in 3 mL of MeOH and trace amount of NH_4OAc was added as the catalyst. The mixture was refluxed at 90 °C overnight in the dark. The precipitate was filtered and rinsed with cold ethanol to yield the yellow-orange product. (0.17g, yield 54%) ^1H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 8.87 (d, J = 13.5 Hz, 1H), 8.52 (d, J = 15.6 Hz, 1H), 8.42 (t, J = 8.7 Hz, 2H), 7.94 – 7.84 (m, J = 12.8, 8.0 Hz, 2H), 7.79 (t, J = 7.7 Hz, 1H), 7.69 (d, J = 4.4 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 5.06 (d, J = 3.3 Hz, 2H), 2.72 (t, J = 6.1 Hz, 2H), 2.64 (s, 3H), 2.33 – 2.23 (m, J = 13.9, 6.7 Hz, 2H).

3. Determining the photoacidity (pK_a_MS)

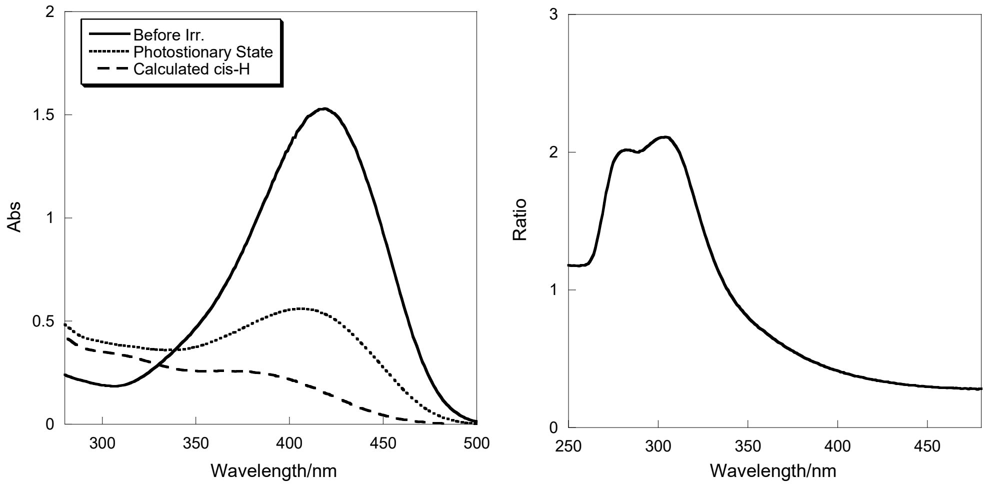
MPAH **1** was dissolved in a 1 mM (or 10 mM) morpholine solution in methanol. The solution in a 4-side 1-cm quartz cuvette was placed in a UV-Vis absorption spectrometer. A 470 nm LED lamp was placed on the side of the cuvette. The irradiation direction is perpendicular to the detection beam of the spectrometer. The solution was continuously irradiated by the LED and scanned by the spectrometer at the same time. The photostationary state was achieved when the spectrum of the solution stopped changing. The spectrum of the photostationary state is shown in Fig. 2b of the main text. The photostationary state is mainly composed of trans-H, cis-H, and SP. The absorbance at 287 nm (Abs1) and at 419 nm (Abs2) were recorded. The two wavelengths were chosen because they are the λ_{max} of SP and trans-H, respectively. Three equations of [SP], [trans-H] and [cis-H] can be written as below:

$$T = [SP] + [cisH] + [transH] \qquad \text{Eq.1}$$

$$Abs_1 = \varepsilon_{SP_1} l[SP] + \varepsilon_{cisH_1} l[cisH] + \varepsilon_{transH_1} l[transH] \qquad \text{Eq.2}$$

$$Abs_2 = \varepsilon_{cisH_2} l[cisH] + \varepsilon_{transH_2} l[transH] \qquad \text{Eq.3}$$

T is the total concentration, which is the concentration of **1**. ε is the molar absorptivity of the corresponding species at the two wavelengths and l is the path length of light (1 cm). Since SP does not absorb 419 nm light, there is no [SP] term in Eq 3. The molar absorptivity of [SP] and [trans-H] can be obtained from the spectra of pure [SP] and pure trans-H (Fig 1 in the main text). It is difficult to directly take the spectrum of pure cis-H because it forms an equilibrium with [trans-H] and [SP]. As shown in Fig 1a in the main text, little SP forms when trans-H is irradiated in a solution without base. When a small amount of acid is added, essentially no SP forms. In this case, only trans-H and cis-H exist in the photostationary state. Therefore a solution of **1** in ~1mM acetic acid solution in methanol was irradiated to achieve a photostationary state. (It is worth mentioning that a high concentration of strong acid must be avoided since **1** could be protonated.) The spectra of the unirradiated solution and the photostationary state are shown in Fig.S1. Since the twisted conformation of cis-H reduces the conjugation, it does not absorb the wavelength as long as that of the trans-H. Above a certain wavelength, the absorption of the photostationary state is solely due to the trans-H. This wavelength can be determined by checking the ratio between the absorption of the photostationary state and that of the unirradiated solution (all trans-H). The ratio above this wavelength becomes a constant, which is the ratio of the [trans-H] in the photostationary state and the total concentration. As shown in Fig. 1b, the curve of the ratio starts to flatten out when the wavelength is above 450 nm. The ratio at 480 nm (0.25) was used for the calculation. The spectrum of cis-H can be obtained by subtracting the spectrum of the photostationary state by the spectrum of trans-H in the photostationary state, which is calculated by multiplying the spectrum of the unirradiated sample by the ratio. (Fig S1) The molar absorptivity of cis-H at the two wavelengths can be calculated from the spectrum of cis-H. Since T, Abs_1, Abs_2, and all the molar absorptivity are known, Equation 1-3 can be solved to yield [SP], [cisH], and [transH], which are 3.3×10^{-5} M, 9.6×10^{-6} M, and 6.0×10^{-6}, respectively for the sample with the spectra shown in Fig. 2b in the main text. The proton dissociation constant of the acidic metastable state is defined as $K_a=[SP][H^+]/[cis\text{-}H]$. Since the concentration of morpholine is much larger than that of **1**. The solution can be deemed as a buffer with constant $[H^+]$, which can be calculated from the pK_a of morpholine, which is 8.5 adjusted from the pK_a in water (8.3). The pK_{a}_MS calculated from the spectrum of the 1 mM morpholine solution was 9.7, and that from the 10 mM solution was 9.8, showing good consistency of this method.



(a) (b)

Fig. S1 (a) Absorption spectra of **1** in 1 mM acetic acid solution before and under irradiation, and the calculated spectrum of cis-H. (b) The absorbance ratio of the sample under irradiation to that before irradiation.