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Surface charge inversion of Self-assembled monolayers by visible light: cargo loading and release by photoreactions

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1. The synthesis of 1 and 2

1 and 2 was synthesized according to the literature[1]. Briefly, 4-pyridinemethanol (8.7 g, 0.08 mol) was dissolved in 400 mL of dried dichloromethane, and then triethylamine (25.2 g, 0.25 mol) was added in the solution. After cooling the solution to about 0 °C, a 50 mL solution of acryloyl chloride (15.5 g, 0.17 mol) in dried dichloromethane was added dropwise in 1 h. The reaction mixture was stirred at room temperature for 19 h and checked by TLC for disappearance of starting material. The precipitate was filtered off, and the filtrate was concentrated in vacuum. Then the concentrated solution was re-dissolved in ethyl acetate (EA) and washed with NaCO₃ and H₂O. The organic layers were collected and dried by MgSO₄, and the solvent was evaporated. The compound 1 was obtained. The crude product was purified by silica gel column chromatography with the eluent, a mixture of ethyl acetate and petroleum ether (v/v = 7:3).

Next, 1 (2.7 g, 16.6 mmol) was dissolved in 50 mL of dried acetonitrile, and methyl trifluoromethanesulfonate (3.6 g, 21.95 mmol) was added. The reaction mixture was stirred at room temperature for 4 h and checked by TLC for disappearance of 1. Then the solution was concentrated in vacuum and re-dissolved in ethanol. Finally, the solvent was evaporated and NAP ester 2 was obtained.

In the ¹H-NMR spectra of the two esters (Fig. S1), several signals are observed in the range of 5.8 - 6.6 ppm (d, e and f), which are attributed to the H-atoms from acrylic group. Comparing with 1, the pyridine proton b in the N-methylated product 2 exhibits a pronounced downfield shift, and a new signal (g) from the
methyl group appears at 4.3 ppm (Fig. S1), indicating the formation of 2. This result is also supported by other data from $^{13}$C-NMR, UV, IR and MS (Fig S2-S5).

Compound 1: $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 8.61 (d, $J = 3.2$ Hz, 2H, ArH), 7.28 (d, $J = 3.0$ Hz, 2H, ArH), 6.51 (dd, $J = 17.3$ Hz, $J = 1.2$ Hz, 1H, $CH_2=CH$), 6.22 (m, 1H, $CH_2=CH$), 5.93 (dd, $J = 10.4$ Hz, $J = 1.2$ Hz, 1H, $CH_2=CH$), 5.22 (s, 2H, OCH$_2$). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 165.75, 150.18, 144.98, 132.06, 127.85, 121.99, 64.40; UV-vis (nm, ethanol) $\lambda_{\text{max}}$ 257, 208; FT-IR (cm$^{-1}$) 3432, 3031, 1736, 1608, 1408, 1274, 1177, 1057, 980, 812; TOF-MS-ES calculated for [M+H]$^+$: C$_9$H$_{10}$O$_2$N: 164.176. Found: 164.071.

Compound 2: $^1$H-NMR (400 MHz, MeCN-d$_3$) $\delta$: 8.58 (d, $J = 4.4$ Hz, 2H, ArH), 7.96 (d, $J = 4.0$ Hz, 2H, ArH), 6.51 (dd, $J = 11.6$ Hz, $J = 0.8$ Hz, 1H, $CH_2=CH$), 6.31 (m, 1H, $CH_2=CH$), 6.03 (dd, $J = 7.0$ Hz, $J = 0.7$ Hz, 1H, $CH_2=CH$), 5.45 (s, 2H, OCH$_2$), 4.28 (s, 3H, CH$_3$). $^{13}$C-NMR (100MHz, MeCN-d$_3$) $\delta$: 164.79, 156.05, 144.87, 132.03, 126.95, 124.78, 62.84, 47.57; UV-vis (nm, H$_2$O) $\lambda_{\text{max}}$ 256, 221; FT-IR (cm$^{-1}$) 3432, 3070, 1728, 1650, 1470, 1411, 1275, 1160, 1034, 642; TOF-MS-ES calculated for [M]$^+$: C$_{10}$H$_{12}$O$_2$N: 178.211. Found: 178.094; for [M]$^-$: CF$_3$SO$_3$: 149.070. Found: 148.952.

![Fig. S1 $^1$H-NMR spectra of 1 in CDCl$_3$ (bottom) and 2 in MeCN-d3 (top).](image-url)
**Fig. S2** $^{13}$C-NMR spectra of 1 in CDCl$_3$ (top) and 2 in MeCN-d$_3$ (bottom). The stars show the chemical shift of the solvents, respectively.

**Fig. S3** The UV-vis spectra of 1 in ethanol and 2 in deionized water, respectively.
Fig. S4 The FT-IR spectra of 1 and 2, respectively.

Fig. S5 The TOF-MS-ES mass spectra of 1 (top) and 2 (middle and bottom), respectively.

2. The loading and release of NAP ester 2

The substrate I was immersed into a mixture of NAP ester 2 and eosin for 1 min, and then was exposed...
to green LED light (3 W, λ= 515 nm) at a distance of 1 cm. After that, the NAP ester 2 was loaded and the substrate (II) was rinsed by extensive deionized (DI) water to remove the free eosin and NAP ester 2. As to the release of NAP ester 2, the NAP-loaded substrate (II) was immersed into a mixture of Ru(II) and Vc for 1 min, and then exposed to blue LED light (12 W, λ= 452 nm) at a distance of 1 cm. Finally, the NAP ester 2 was released from the substrates.

To the best of our knowledge, it is difficult to precisely determine the yields of the reactions within a monolayer. However, it is known that thiol-ene chemistry is a fast and efficient method to realize the coupling reactions. (Craig J. Hawker et al. Nat. Chem. 2, 138; Kristi S. Anseth et al., Nat. Chem., 3, 925). Furthermore, we can observe that the absorbance at 260 nm (from NAP ester 2) are rapidly increased in the first 10 min (Fig. 3a). On the other hand, Falvey et al. reported that NAP groups can be efficiently removed from the NAP esters (yield ~ 94%, J. Org. Chem., 2009, 74, 3894). Moreover, we can also observe that the absorbance at 260 nm is almost disappeared after irradiation (~40 min) (Fig. 3c). Therefore, it is reasonable to expect that the two reactions are realized with high yields.

**Fig. S6** The static contact angles (CA) of the three substrates (I, II and III). CA were measured with a constant volume drop of the DI water (5 μL) and recorded by a drop shape analysis system (DSA 100, Kruss) at room temperature (n=6).

3. The cyclic voltammetry measurements

The cyclic voltammetry was performed at room temperature by using a BAS 100 B electrochemical workstation. A carbon electrode was applied as the working electrode. A Pt wire constituted the counter electrode, and an Ag-AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M lithium perchlorate in dry acetonitrile. The solution was deoxygenated by bubbling argon gas through the solution for 15 min. The potential was swept from -1.6 to 1.6 V with the sweep rate of 100 mV/s to record
the current-voltage curve, see Fig S3.

![Cyclic voltammogram of NAP ester 2 in 0.1 M dried acetonitrile solution of lithium perchlorate.](image)

**Fig. S7** Cyclic voltammogram of NAP ester 2 in 0.1 M dried acetonitrile solution of lithium perchlorate.

### 4. The driving force calculation (ΔG) of NAP ester 2

The driving forces (ΔG) for the possible routes of direct and mediate electron transfer (DET and MET) can be estimated from the equations below:

\[
\Delta G_{\text{DET}} = 23.06(E_{\text{ox1}} - E_{\text{red}}) - E_{\text{oo}}
\]

\[
\Delta G_{\text{MET}} = 23.06(E_{\text{ox2}} - E_{\text{red}})
\]

$E_{\text{ox1}}$ is the oxidation potential of Ru(II)$^{2+/3+}$ couple, $E_{\text{ox2}}$ is the ground-state oxidation potential of Ru(II)$^{2+/+}$ couple, $E_{\text{oo}}$ is the energy of triplet metal-ligand charge transfer excited state of Ru(II) ($^3$MLTC), $E_{\text{red}}$ is the reduction potential of NAP ester 2. The values of $E_{\text{ox1}}$, $E_{\text{ox2}}$, $E_{\text{oo}}$ and $E_{\text{red}}$ are 1.29 V, -1.33 V, 48.9 kcal/mol and -1.25 V, respectively. Thus, the driving forces (i.e., $\Delta G_{\text{DET}}$ and $\Delta G_{\text{MET}}$) are 9.7 kcal/mol and -1.8 kcal/mol, respectively.

### 5. The preparation of thiolated quartz substrates

The thiolated quartz substrates (I) were prepared by silanization treatments with 3-mercaptopropyl triethoxysilane. The cleaned quartz substrates were immersed into a 3-mercaptopropyl triethoxysilane solution in dichloromethane (v/v= 1/500) for about 4 h at room temperature, and were sequentially rinsed with dichloromethane, ethanol, respectively, and dried by air flow.
The UV-vis spectra of control systems for the loading (a), release (b, c and d) of NAP ester 2. The concentrations of NAP ester 2, eosin, Ru(II) and Vc were 10 mM, 72 μM, 44 μM and 100 mM, respectively. The irradiation time were 15 min (a) and 40 min (b, c and d), respectively.

**Fig. S8** The UV-vis spectra of control systems for the loading (a), release (b, c and d) of NAP ester 2. The concentrations of NAP ester 2, eosin, Ru(II) and Vc were 10 mM, 72 μM, 44 μM and 100 mM, respectively. The irradiation time were 15 min (a) and 40 min (b, c and d), respectively.

**Fig. S9** The UV-vis spectrum of aqueous solution of Ru(II) complex.

6. The absorption and remove of eosin and Ru(II)
**Fig. S10** The UV-vis spectra of eosin (a) and Ru(II) (b) in DI water, and the substrates II (a) and III (b) before and after the acid-wash (dialysis) treatments.

References