Photocatalytic Activation of Pyridine for Addition Reactions: An Unconventional Reaction Feature between a Photo-Induced Hole and Electron on TiO₂

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S1. General Experimental Section

All reagents and solvents were purchased from Alfa Aesar, Dikma, Acros and Beijing Chemical Reagent without further purification. Column chromatography was carried out using P9-058 (particle size, 200-300 mesh, Yantai chemical industry institute, China) as the stationary phase, and TLC was performed on precoated silica gel plates (0.2 mm thick, HSG F254, China) and observed under UV light. One dimensional $^1$H and $^{13}$C NMR spectrum were recorded on Bruker AVANCE-600 600MHz spectrometer. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s=singlet, d=doublet, t=triplet, b=broad. Two dimensional NMR spectra were recorded on Bruker AVANCE-600 600MHz spectrometer. Mass Spectra were recorded by a Thermo-Finnigan Trace DSQ GC-MS and Agilent 5975C GC-MS, and high resolution MS spectra were recorded by Waters GCT. GC spectra were recorded on a Hitachi G3900 spectrometer. P25 Titania was purchased from Degussa (Germany).

General Procedure:
The preparation of a large amount of objective products by TiO$_2$ photocatalysis-hydroheteroarylation

To a known amount of diphenylethlyene in pyrex glass bottle, 2.71 g P25-TiO$_2$ was added into 11 ml pyridine or picoline solution, and the bottle was sealed with a rubber cap. The resulting mixture was degassed with argon for 30 minutes and then filled in 10 psi pressure argon gas for 7 minutes. Then, the bottle was put in glovebox for 24 hours to let the rubber heal. Then the mixture was irradiated by a 300W Xenon light (HXUV-300, Aulight) for a certain time with magnet stirring. After irradiation, 30 ml dichloromethane was added in four times to the clay-like mixture to extract the product from TiO$_2$ suspension. Every time, 30 ml dichloromethane was added, then the dispersion was ultrasonified for 1 hour, and then after high-speed centrifugation, titania was separated with the organic phase. After every centrifugation, the solution was transferred into 25 ml flask, the solid residue was re-added another 30 ml dichloromethane. After 3 times ultrasonification extraction, almost 99% products were collected from TiO$_2$ suspension which could be affirmed by residue solution GC spectrum. The solvent was removed under reduced pressure and the crude reaction mixture was purified by column chromatography to isolate the product which could be used as a standard GC substance to measure the yield of other reaction with a FID detector according to the effective carbon number rule or directly mixed with internal standard solution to obtain a GC yield. The GC yield was taken when the reaction is in a small amount micro-mole level where the isolated yield was gotten when we use mille-mole level amount of reactants.
**Scheme S1.** General procedure for the P25 TiO\(_2\) photocatalyzed pyridine alkylation with diphenylethlylene

**S2 Control experiments under different conditions**

**Table S1** Blank experiments

<table>
<thead>
<tr>
<th>condition</th>
<th>Conversion %</th>
<th>Yield%</th>
</tr>
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<tbody>
<tr>
<td>TiO(_2)/ dark</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SiO(_2)/ UV</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>TiO(_2)/dark/333K</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>UV</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>UV/TiO(_2)/DBU(100eq)</td>
<td>2</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Experimental conditions: 1,1-diphenylethlyene (0.9mg, 5.0µmol), P-25 TiO\(_2\) (0.2g, 2.5mmol) was added into 4 ml picolines solution under irradiation for 8 hours. Conversion and selectivity is based on GC analysis (standard compounds by commercial resources and products after column chromatography purification). Yield detected by GC.

**S3.** Photo-induced electrons accumulation experiments when 4-methyl-pyridine and N,N-dimethyl-analine, N-methylpyroidine and benzyltrimethylsilane as a hole scavenger under anaerobic CH\(_3\)CN TiO\(_2\) solutions

For every substrate as hole scavenger, electron accumulation experiments was carried out in acetonitrile suspension of TiO\(_2\) with a certain amount of target substrate using a PLX-SXE 300 W Xe lamp (Beijing Trusttech Co. Ltd). In a typical procedure of photochemical reduction, 100 mg TiO\(_2\) was dispersed in 50 mL acetonitrile solution with 200 µL target substrate and purged by Argon for 30 min to produce an anaerobic atmosphere. The resulting suspension was then irradiated for 5 h by a PLX-SXE 300 W Xe lamp.
Fe$^{3+}$-1,10-Phenanthroline photometric measurement

The measurement of electron concentration of samples contains two steps, the titration of electrons by Fe(NO$_3$)$_3$ solution and then formation color Fe(II)-o-Phenanthroline for a photometric measurement. The titration of electrons was conducted in the Argon glove box. The concentration of Fe(NO$_3$)$_3$ solutions employed in this measurement is $4 \times 10^{-3}$ M. Before the titration, the Fe(NO$_3$)$_3$ solution is purged by Argon for 30 min to remove oxygen. In a typical procedure, 2.5 mL electron-trapped TiO$_2$ suspending solution was taken in the Argon glove box and mixed with 2.5 mL Fe(NO$_3$)$_3$ solution. 5 min later, the resulting mixed solution was taken out to conduct the modified 1,10-Phenanthroline photometric measurement.

1,10-Phenanthroline photometric measurement is a very popular method for the measurement of Fe ions. In this study, we uses the modified 1,10-Phenanthroline photometric method to measure the concentration Fe$^{2+}$ ions, which were produced by the reaction of electrons and Fe$^{3+}$ ions in the mixed solution mentioned above, and thus to measure the concentration of charged electrons. The modified 1,10-Phenanthroline photometric measurement was conducted in air atmosphere. 0.2% 1,10-phenanthroline water solution and pH = 4.6 HAc-NaAc buffer solution were previously prepared for use. The pH = 4.6 HAc-NaAc buffer solution was prepared by dissolving 135 g sodium acetate and 120 mL acetic acid into 500 mL water solution. In a typical procedure, 1.5 mL mixed solution taken from the Argon glove box was mixed with 1.5 mL pH = 4.6 HAc-NaAc buffer solution, and then added with 1 mL 0.2% 1, 10-phenanthroline water solution. The solution suddenly turned red color. 5 minutes later, the resulting suspending solution was carried in centrifugation for separation of TiO$_2$ powders, and the clear fluid was transferred in a quartz cuvette and measured on a Hitachi U3900 spectroscopy. Obtained absorbance value was compared with the standard fitting line (Fig S1) to obtain a specific Fe$^{2+}$ concentration. Since charged TiO$_2$ solution was double diluted by Fe$^{3+}$ solution, the electron concentration of charged TiO$_2$ solutions is twice the obtained Fe$^{2+}$ concentration. The standard fitting line as shown in Fig S1 was obtained in the same method with certain concentration (10$^{-5}$ M, 10$^{-4}$ M, 2$\times$10$^{-4}$ M, 5$\times$10$^{-4}$ M and 10$^{-3}$ M) FeCl$_3$ solutions as samples to be measured.

S4. Low temperature EPR measurement of electron-trapped TiO$_2$ sample for different substrate as hole scavenger

Low temperature (80 K) EPR measurement was employed to observe Ti$^{3+}$ signals of electron-trapped samples. Liquid Nitrogen was employed as the cooling agency. Before the measurement, electron-trapped TiO$_2$ suspending solution sample (in acetonitrile) with different target substrate after 5 h UV irradiation under room temperature as above described, were collected and filled into a special cavity in the Argon glove box and sealed. The obtained sample was then cooled to 80 K by liquid Nitrogen and transferred into a vacuum cryostat for EPR measurement. EPR spectra were obtained in dark. The settings for the EPR spectrometer at low temperature (80 K) were as follows: center field, 3400 G; sweep width, 400 G; microwave frequency, 9.52 GHz; field modulation frequency, 100 kHz.
S5. TEMPO-trapping experiments

0.2 g P25 was added into small Pyrex glass reaction tube with rubber septum. 5 μmol benzyltrimethylsilane, 300 μmol maleic anhydride and 5 ml dry CH₃CN were added into the tube. After Ar purging, the tube was irradiated by 300W Xe lamp for 2 h. In the paralleling reaction, 50 μmol TEMPO was added and all the other reagents and procedure were kept the same. For the pyridine addition experiments, 5 μmol 1,1-diphenylethlyene and 5 ml 4-picoline was added into the reaction tube. After Ar purging, the tube was exposed to 300W Xe lamp irradiation for 4h. To examine the effect of radical trapping reagent, 50 μmol TEMPO was added while keeping other condition unchanged.

After irradiation, to detect the products of the 1,1-diphenylethlyene and 4-picoline, the products were separated with photocatalyst by centrifugation and were characterized by Agilent 7890B GC-MS. Before GC-MS determination 2.5 μmol bromobenzene was added into the sample solution and used as internal standard. In addition, for the reaction between maleic anhydride and benzyltrimethylsilane, 2.5 μmol 2-octanol was introduced and used as internal standard before GC-MS.

Table S2. TEMPO effect on the TiO₂-photocatalytic adduction reaction

<table>
<thead>
<tr>
<th>reaction</th>
<th>conditions</th>
<th>conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic anhydride+benzyltrimethylsilane&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Without TEMPO</td>
<td>benzyltrimethylsilane conversion 98%</td>
</tr>
<tr>
<td></td>
<td>With TEMPO</td>
<td>80%</td>
</tr>
<tr>
<td>4-picoline+1,1-diphenylethlyene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Without TEMPO</td>
<td>Addition product yield 53%</td>
</tr>
<tr>
<td></td>
<td>With TEMPO</td>
<td>51%</td>
</tr>
</tbody>
</table>

<sup>a</sup> 5 μmol benzyltrimethylsilane, 300 μmol maleic anhydride in 5 ml dry CH₃CN; <sup>b</sup> 5 μmol 1,1-diphenylethlyene and 5 ml 4-picoline
**Figure S1.** (a) and (b): GC-MS spectra for the reaction between benzytrimethylsilane and maleic anhydride before and after 2h UV light irradiation without TEMPO, respectively, in which bromobenzene was used as internal standard; (c) and (d): as (a) and (b) but with TEMPO, in which 2-octanolas another internal standard was introduced before GC-MS determination because the peak of bromobenzene seriously overlapped with a product from TEMPO reaction (see panel d). (e) and (f): GC-MS spectra for the reaction between 4-picoline and 1,1-diphenylethylene without and with TEMPO after 4h UV light irradiation, respectively, in which n-butyl ortho-phthalate was used as internal standard.

**S6. Photoelectrochemical experiments**

TiO₂-film electrode preparation: 1 g P25 TiO₂ was suspended in n-butanol (13% w/w) and stirred with a magnetic stir bar overnight, and then was coated on the indium tin oxide (FTO) surface. The TiO₂-loaded films were calcined at 450 °C for 3 h in air. Photoelectrochemical measurement was carried out in a three-electrode electrochemical cell. TiO₂ film was employed as working electrode, and a Pt sheet
and Ag/AgCl/saturated KCl were used as the counter and reference electrode respectively. The supporting electrolyte was a 0.15 M \( \text{TBABF}_4 \) in CH\(_3\)CN solution (50 ml). The TiO\(_2\) working electrodes (2.5×2.5 cm\(^2\)) were irradiated by a 300W Xe lamp. The photocurrent in the presence of 4-picoline and benzyltrimethylsilane were compared under otherwise identical conditions.

Figure S2. The influence of 4-picoline (a) and benzyltrimethylsilane (b) on the photocurrent of TiO\(_2\) electrode under UV irradiation. Experimental conditions: 0.15 M \( \text{TBABF}_4 \) electrolyte in CH\(_3\)CN solution (50 ml), irradiated by a 300W Xe lamp.

S7. Photoluminescence experiments
All samples for PL determination were prepared into slurry of 0.05 ml CH\(_3\)CN and 100 mg P25-TiO\(_2\) photocatalyst, then 0.01 mmol 4-picoline, N,N-dimethylaniline, M-methylpyrrolidine and benzyltrimethylsilanewere were added separately to the P25-TiO\(_2\)/CH\(_3\)CN slurry samples and then thoroughly mixed. After that, the samples were pressed tightly under two quartz matrix, and fixed on the PL instrument with pulse laser-induced florescence performance. Spectra-Physics Ti-sapphire pulse-laser with a wavelength of 390 nm was employed as excitation light source. The parameters were 150 fs, 1000Hz pulse, light intensity 5.7 mW.

Figure S3. The difference photoluminescence spectra of PL in the presence of the different substrate, relative to those on the blank TiO\(_2\).

S8. Synthesis and characterization of 2a-e and 3a
2a 1-(2,2-diphenyl)-ethylpyridine
1,1-diphenylethylene (20mg, 0.11mmol), and TiO₂ (2.71g, 34mmol) were reacted in pyridine solution (11ml) in accordance with the general procedure. After 8 days irradiation reaction and column chromatography purification, 2a was obtained as white needle crystal (25.3mg, 0.1mmol, 89% yield) ¹H NMR (600MHz, d⁶-acetone, 298K) : δ=3.56 (d, 2H, J=7.9Hz) 4.74 (t, 1H, J=7.9Hz) 7.09(m, 2H) 7.14( t, 2H, J=8.1Hz) 7.25( t, 4H, J=7.62Hz) 7.35( d, 4H, J=7.3Hz) 7.51 (t, 1H, 7.7Hz) 8.49 (d, 1H, J=4.8Hz) ¹³CNMR δ= 28.94, 43.71, 50.81, 12.98, 123.52, 125.99, 127.97, 135.68, 144.84, 149.08, 160.00 LR-EIMS: m/z=259 [M⁺]; HR-EIMS: m/z=259.1364(calcd. for C₂₀H₁₉N, 259.1361)

2b 4-methyl-2-(2,2-diphenyl)-ethylpyridine

1,1-diphenylethylene (20mg, 0.11mmol), and TiO₂ (2.71g, 34mmol) were reacted in 4-picoline solution in accordance with the general procedure. After 8 days irradiation reaction and column chromatography purification, 2b was obtained as white needle crystal (27mg, 0.1mmol, 90% yield) ¹H NMR (600MHz, d⁶-acetone, 298K) : δ=2.19(s,3H) 3.51(d,2H, J=8.1Hz) 4.75 (t, 1H, J=7.7Hz) 6.91 (d, 1H, J=5.0Hz) 6.95 (s, 1H) 7.14 (t, 2H, J=7.3Hz) 7.25 (t, 4H J=7.9Hz). 7.35 (d, 4H, J=7.5Hz) 8.33 (d, 1H, J=4.9Hz). ¹³CNMR δ=19.83, 43.55, 50.63, 121.91, 124.34, 125.96, 127.97, 128.22, 144.93, 146.55, 148.81, 159.72. LR-EIMS: m/z=273 [M⁺]; HR-EIMS: m/z=273.1522(calcd. for C₂₀H₁₉N, 273.1517).

We also take a gram-scale reaction with 4-picoline. We put 0.2g 1,1-diphenylethlyene to react in 11 ml 4-picoline in the presence of 2.2g TiO₂(P25) into a pyrex glass bottle. And the reactants and catalyst was irradiated for 9 days. And we got 0.1g 2b after column chromatography purification. The isolated yield of this gram-scale reaction was 53%.

2c 2-Methyl-5-(2,2-diphenyl)-ethylpyridine
After 8 days of irradiation, (20mg 1,1-diphenylethylene, 11 ml 3-picoline and 0.44g TiO₂) reacted and yielded two region isomers. 2c:2d=1.2:1, and after column chromatography purification, we got 10.5mg yellow solid. ¹H NMR (600MHz, d⁶-acetone, 298K) :δ=2.22 (s, 3H) 3.51 (d, 2H, J=7.2Hz) 4.71 (t, 1H, J=7.9) 6.99 (d, 1H, J=7.5Hz) 7.13 (t, 2H, J=7.5Hz) 7.25 (t, 4H, J=8.0Hz) 7.35 (m, 5H) 8.32 (s, 1H). ¹³C NMR (150MHz, d⁶-acetone, 298K) δ=16.84, 43.04, 50.89, 122.90, 125.96, 127.96, 128.21, 130.03, 136.13, 144.94, 149.40, 156.93, LR-EIMS: m/z=273 [M⁺]; HR-EIMS: m/z=273.1521 (calcd. for C₂₀H₁₉N, 273.1517). HMBC recognized

2d 2-Methyl-1-(2,2-diphenyl)-ethylpyridine

After purification, we got 8.7mg 2e’s region isomer 2d as a light-yellow solid. ¹H NMR (600MHz, d⁶-acetone, 298K) :δ=2.14 (s, 3H), 3.54 (d, 2H, J=8.6Hz), 4.86 (t, 1H, J=7.7Hz), 7.02 (q, 1H, J=3.7Hz), 7.14 (t, 2H, J=7.3Hz), 7.24 (t, 4H, J=8.0Hz), 7.31 (d, 4H, J=7.3Hz), 8.32 (s, 1H), 7.38 (d, 1H, J=7.7Hz) 8.33 (d, 1H, J=4.4Hz) ¹³C NMR (150MHz, d⁶-acetone, 298K) δ=17.91, 40.16, 44.99, 120.97, 125.92, 128.04, 128.10, 131.43, 137.03, 145.14, 146.43, 158.17 LR-EIMS: m/z=273 [M⁺]; HR-EIMS: m/z=273.1521 (calcd. for C₂₀H₁₉N, 273.1517)

2e 1-Methyl-5-(2,2-diphenyl)-ethylpyridine

1,1-diphenylethylene (20mg, 0.11mmol), 2-picoline (11ml,121mmol) and TiO₂ (2.71g, 34mmol) were reacted in accordance with the general procedure. Following irradiation for 8 days 2e was obtained as a light-yellow solid (2.7mg, 0.02mmol, 9% yield) after column chromatography.(Isolated yield) ¹H NMR (600MHz, d⁶-acetone, 298K) :δ=2.43 (s, 3H) 3.50 (d, 2H, J=21Hz) 4.72 (t, 1H, J=8Hz) 6.86 (d, 1H, J=7.6Hz) 6.95 (d, 1H, J=7.6Hz) 7.14 (t, 2H, J=3Hz) 7.15 (t, 4H, J=7.7Hz) 7.34 (d, 4H, J=7.3Hz) 7.39 (t, 1H, J=7.7Hz). ¹³C NMR (150MHz, d⁶-acetone, 298K) : δ=23.62, 43.62, 50.75, 120.18, 120.40, 125.94, 127.96, 128.21, 135.95, 144.95, 157.43, 159.12
LR-EIMS: \textit{m/z}=273 \text{ [M$^+$]; HR-EIMS: m/z=273.1522 (calcd. for C$_{19}$H$_{17}$N, 273.1517).}

Another experiment with small amount of substrate was taken (5mmol 1,1-diphenylethylene (0.91mg), was reacted with 2-picoline and TiO$_2$ in accordance with the general procedure. After 24 hours irradiation and extraction, the GC yield was obtained with the correspondence of the purified standard products. We get a 25% yield of 2e.

3a  2-(1,2-diphenylethyl)-4-methylpyridine

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\begin{array}{c}
\text{苯} \\
\text{苯} \\
\text{吡啶} \\
\text{苯}
\end{array}
\]

Trans-stilbene 20mg (0.11mmol) and TiO$_2$ (2.71g, 34mmol) were reacted in 4-picoline solution (11 ml) in accordance with the general procedure. After 8 days irradiation reaction and column chromatography purification, 3a was obtained as yellow needle crystal. (7.5mg, 25% yield) $^1$H NMR (600MHz, d$_6$-acetone, 298K) δ=2.25 (s, 3H), 3.33 ( q, 1H, J=10.39Hz) 3.69 (q, 1H, J=13.69Hz) 4.41 (t, 1H, J=8.38Hz) 7.00 (d,1H,J=4.86Hz) 7.09(m,1H) 7.10 (s,1H) 7.14-7.16(m,5H) 7.25(t,2H,J=7.4Hz) 7.42(d, 2H, J=7.4Hz) 8.43(d, 1H,J=5Hz) $^{13}$CNMR δ=19.90,41.01, 55.03,122.30, 124.02, 125.63,126.15, 127.87, 128.12,129.05,140.80,144.04, 162.61
LR-EIMS: m/z=273 [M$^+$], HR-EIMS: m/z= 273.1513, calc. Mass=273.1517

3b

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\begin{array}{c}
\text{苯} \\
\text{吡啶} \\
\text{苯}
\end{array}
\]

4-methyl-2-(2-phenylpropyl)pyridine

$\alpha$-methylstyrene 20mg (0.17mmol) and TiO$_2$ (2.71g, 34mmol) were reacted in 4-picoline solution (11 ml) in accordance with the general procedure. After 8 days
irradiation reaction and column chromatography purification, 3b was obtained as yellow oil. (15mg, 42% yield) $^1$H NMR (400MHz, $d^6$-acetone, 298K) $\delta=1.87$ (s, 3H), 2.63 (s, 3H) 3.76 (b, 3H) 7.20, 7.79 (m, 5H) 7.80 (d, 2H, J=22.78Hz) 8.66 (s, 1H) LR-EIMS: m/z=211 [M$^+$], HR-ESI MS: m/z=212.1434, [M+1]$^+$ calc. Mass=212.14338

S9. NMR spectrum of products

2a

![NMR spectrum of product 2a](image-url)
$^1$HNMR spectrum of 2a

$^{13}$CNMR spectrum of 2a
H-H COSY spectrum of 2a

HMBC spectrum of 2a
HSQC spectrum of 2a

2b
$^1$HNMR spectrum of 2b

$^{13}$CNMR spectrum of 2b
H-H COSY spectrum of 2b

HMBC spectrum of 2b
HSQC spectrum of 2b

2c
\textbf{1H NMR of 2c}

\textbf{13C NMR of 2c}

NMR spectrum of 2c
H-H COSY spectrum of 2c

HMBC of 2c
HSQC spectrum of 2e

2d

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\begin{align*}
\text{HSQC spectrum of 2e} \\
\text{2d}
\end{align*}
\]
$^1$HNMR of 2d

$^{13}$CNMR spectrum of 2d
H-H COSY spectrum of 2d

HMBC spectrum of 2d
HSQC spectrum of 2d

2e

![Chemical structure image]
$^1$H NMR spectrum of 2e

$^{13}$C NMR of 2e
H-H COSY spectrum of 2e

HMBC spectrum of 2e
HSQC spectrum of 2e

3a

$^1$H NMR spectrum of 3a
$^{13}$C NMR of 3a
H-H COSY spectrum of 3a

3b

4-methyl-2-(2-phenylpropyl)pyridine

1H NMR
3b HR-ESI MS: m/z = 212.14342, [M+1]^+ calc. Mass = 212.14338