

Supporting Information

Artificial Photosynthesis of Methanol from Carbon Dioxide with Water via Nile Reds-embedded TiO₂ Photocathode

Yongjian Jia¹, Yanjie Xu¹, Rong Nie¹, Fengjuan Chen¹, Zhenping Zhu², Jianguo Wang² and Huanwang Jing^{1,2}*

¹State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

²State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

Table of Contents

1. General.....	S2
2. Synthesis of NRx dye.....	S3
3. Characterization of NRx dyes.....	S7
4. Normalized UV-vis absorption & photoluminescence spectra of NRx dyes.....	S17
5. Molecular orbitals of NRx dyes.....	S19
6. Preparation of electrodes.....	S20
7. X-ray photoelectron spectroscopy (XPS) of Pd/NR2@TiO ₂	S22
8. X-ray diffraction (XRD).....	S23
9. Cyclic voltammetry and Electrochemical impedance spectroscopy of trielectrode system.....	S24
10. TEM images of Pd/NR2@TiO ₂ Photocathode.....	S26
11. SEM images of Pd/NR2@TiO ₂ Photocathode.....	S27
12. Mott-Schottky curves.....	S28
13. Artificial photosynthetic experiments.....	S31
14. Selected copies of ¹ H NMR spectra of electrolyte.....	S32
15. References.....	S35

General:

All reagents and solvents were purchased from commercial sources. THF, toluene and triethylamine were dried over sodium/benzophenone and freshly distilled before use. CH₂Cl₂ was dried over CaH₂ and freshly distilled prior to use. All other chemicals were of analytical grade.

FTO glass was purchased from Nippon Sheet Glass Co. Ltd. The FTO conducting glass (F: SnO₂, 15Ω/square) was washed with a detergent solution, deionized water, absolute ethanol, and acetone successively under ultrasonication for 30 min before use.

Characterization of NRx dyes

The ¹H NMR and ¹³C NMR spectra of organic compounds were obtained by using Varian 300 MHz spectrometer. Chemical shifts are reported as δ values relative to internal deuterium chloroform (δ 77.27 for ¹H NMR and 77.36 for ¹³C NMR) and DMSO-*d*₆ (δ 2.50 for ¹H NMR and 39.00 for ¹³C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

The high resolution mass spectra were acquired on by using an Orbitrap spectrometer.

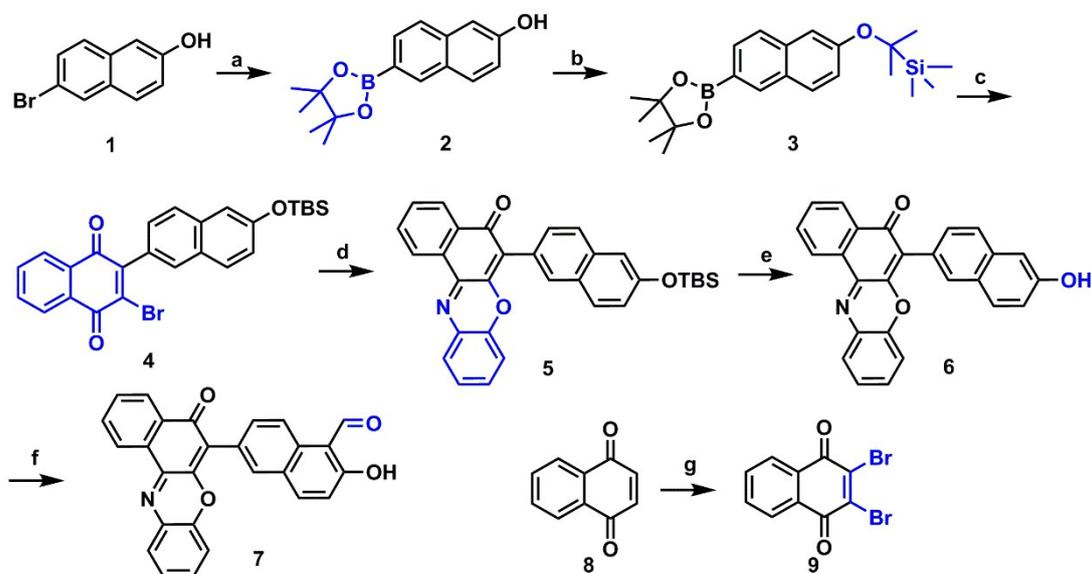
The UV-vis absorption spectra were determined by an UV-3600 spectrophotometer in *N,N*-dimethylformamide (DMF) at room temperature. The photoluminescence spectra were obtained by an F-7000 fluorescence spectrophotometer.

All the electrochemical experiments were performed on an electrochemical workstation (CHI660D, CHINA). Electrochemical redox potentials were obtained by cyclic voltammetry using a traditional three-electrode system. The counter electrode was a Pt wire, Ag/AgCl (sat. KCl) was used as a reference electrode. The electrolyte of tetrabutylammoniumhexafluorophosphate (TBAPF₆, 0.1M) was used for cyclic voltammetry determination.

Facilities for Characterization of Photocathode

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) characterization were performed on a Tecnai-G20-F30 electron microscope under accelerating voltage of 300 kV. The X-ray photoelectron spectroscopy (XPS) was recorded on a VG Scientific ESCALB210-XPS photoelectron spectrometer with an Mg Kα X-ray resource. The spectra of various elements were calibrated according to C1s = 284.6 eV. Thermogravimetric analyses (TGA) were carried out with a STA PT1600 thermogravimetric analyzer at a heating rate of 10 °C/min from room temperature to 700°C. The Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets in the range of 4000-400 cm⁻¹ on a NEXUS 670 spectrometer. X-ray diffraction (XRD) patterns were collected on an X'Pert PRO diffractometer using Cu-Kα radiation (λ = 0.1541 nm) with 2θ ranging from 25° to 80°. EPR spin-trapping experiments were carried out with a Bruker ER200DSRC10/12 spectrometer equipped with a TE 201 resonator (microwave frequency of 9.4 GHz). The electrochemical impedance spectroscopy (EIS) experiments were conducted with amplitude of 5 mV and frequency ranging from 100 kHz to 0.1 Hz in 0.1M KHCO₃ solution (CO₂ saturation). Mott-Schottky analysis was carried out with electrodes of Pd/NRx@TiO₂, a platinum electrode, an Ag/AgCl (Sat. KCl) electrode and non-CO₂ pumped 0.1 M KHCO₃ solution used as a working electrode, counter electrode, reference electrode and electrolyte, respectively.

Synthesis of NRx dyes



a, Pd(dppf)₂Cl₂, KOAc, 1,4-dioxane, 90%; b, TBSCl, Imidazole, CH₂Cl₂, 99%; c, Pd(PPh₃)₄, K₂CO₃, THF, H₂O, 57%, Suzuki Cross-Coupling; d, 2-aminophenol, K₂CO₃, 95% Ethanol, Reflux 70%, Michael addition reaction; e, n-Bu₄NF, Dry THF, 99%; f, CF₃COOH, HMTA, Reflux, 80%, g, CH₃COOH, Br₂, 98%.

The preparation of intermediates and NR2 dye:

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-ol (2) [S1]

The 6-bromonaphthalen-2-ol (2.02g, 9.1mmol, 1 eq.), potassium acetate (2.7g, 27mmol, 3 eq.), and bis(pinacolato)diboron (2.5g, 10mmol, 1.1 eq.) were dissolved in dry dioxane, and the resulting mixtures were degassed with a stream of Ar. After 10 min, Pd(dppf)₂Cl₂ (0.3g, 0.05 eq.) was added. The resulting mixture was heated to 90°C, and stirred under Ar for 24h until the reaction is complete, which was monitored by TLC. Then the solution was cooled to room temperature and then evaporated to dryness under reduced pressure. The residue was purified by chromatography using petroleum ether/ ethyl acetate 10:1 as eluant and yielded the product as a white solid (90%).

¹H NMR (300 MHz, CDCl₃) δ 8.29 (s, 1H, phenyl), 7.81-7.75 (m, 3H, phenyl), 7.64 (d, *J* = 8.3 Hz, 1H, phenyl), 7.12 (d, *J* = 2.5 Hz, 1H, phenyl), 7.10 (d, *J* = 2.5 Hz, 1H, phenyl), 7.07 (d, *J* = 2.5 Hz, 1H, phenyl), 5.34 (s, 1H, OH), 1.39(s, 12H, CH₃);

¹³C NMR (75 MHz, CDCl₃) δ 136.16, 131.12, 130.75, 125.52, 117.73, 109.37, 83.88, 77.42, 77.00, 76.58, 24.88.

Trimethyl(2-((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene-2-yl)oxy)propan-2-yl)silane (3) [S2]

Compound 2(2.95g, 11 mmol) were dissolved in dry CH₂Cl₂ and cooled to 0 °C. *tert*-Butyldimethylsilyl chloride (2g, 13.2 mmol, 1.2 eq.) and imidazole (2.2g, 33mmol, 3 eq.) were added under Ar atmosphere. The solution was allowed to warm to room temperature for 12 hours. Water was added to quench the reaction and the mixture extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. A white solid was gained quantitatively and could be used without further purification.

¹H NMR (300 MHz, CDCl₃) δ 8.31 (s, 1H, phenyl), 7.82-7.76 (m, 2H 8.2 Hz, 1H, phenyl), 7.19 (d, *J* = 2.2 Hz, 1H, phenyl), 7.15-7.04 (m, 1H, phenyl), 1.39 (s, 12H, CH₃), 1.03 (d, *J* = 1.0 Hz, 9H, Si-CH₃), 0.26 (d, *J* = 1.0 Hz, 6H, SiC-CH₃).

^{13}C NMR (75 MHz, CDCl_3) δ 136.15, 130.89, 130.34, 125.95, 122.17, 114.86, 83.90, 77.58, 77.16, 76.74, 25.84, 25.03, -4.17.

HRMS (m/z , FAB+) calcd for $\text{C}_{22}\text{H}_{33}\text{BO}_3\text{Si}$, [M+H]: 385.2365; found, 385.2351.

3-Bromo-6'-((*tert*-butyldimethylsilyloxy)-[2,2'-binaphthalene]-1,4-dione, (4). [S3]

In a 100ml Schlenk tube, 2,3-dibromonaphthalene-1,4-dione (Compound **9**, 2.6g, 8.34mmol, 1 eq.) and Compound **3** (1.6g, 4.17mmol, 2.2 eq.) were dissolved in 20 ml of Toluene. $\text{Pd}(\text{PPh}_3)_4$ (0.34g, 0.05 eq.), 2 M aqueous solution of K_2CO_3 (5 eq.) was added and the reaction mixture was freeze-dried by liquid nitrogen for 3 times, and then the reaction was heated at 90 °C for 48h. The solution was then diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by chromatography using petroleum ether/ ethyl acetate 250:1 as eluent. The target product was obtained as a red solid in 57% yield after evaporation of solvent and dry in a vacuum desiccator.

^1H NMR (300 MHz, CDCl_3) δ 8.29-8.25 (m, 1H, phenyl), 8.21 – 8.17 (m, 1H, phenyl), 7.85-7.78 (m, 6H, naphthyl), 7.40 (d, J = 8.7 Hz, 1H, phenyl), 7.15 (d, J = 8.7 Hz, 1H, phenyl), 1.05 (s, 9H, Si- CH_3), 0.29 (s, 6H, SiC- CH_3).

^{13}C NMR (75 MHz, CDCl_3) δ 181.89, 178.43, 154.86, 149.83, 139.10, 134.95, 134.50, 134.21, 131.71, 131.27, 130.22, 129.41, 129.34, 128.47, 127.67, 127.55, 126.90, 126.52, 122.88, 115.07, 25.85, 18.44, 1.17, -4.16.

ESI-HRMS (m/z), Calcd for $\text{C}_{26}\text{H}_{25}\text{BrO}_3\text{Si}$, [M+H]:493.0829; found: 493.0809.

6-(6-((*tert*-Butyldimethylsilyloxy)naphthalen-2-yl)-5*H*-benzo[a]phenoxazin-5-one (5) [S4]

Compound **4** (3.54, 7.2mmol, 1eq) was added to the solution in 2-amino phenol (0.78 g, 7.2mmol, 1eq) in 95 % of ethanol (50mL). A catalytic amount of anhydrous potassium carbonate was added to the reaction mixture and it was refluxed for 2 h under argon. The reaction mixture was cooled to room temperature, and filtered by vacuum filtration, and the precipitate was washed with 95 % of ethanol, dried in vacuum. A red solid was gained in 70% yield.

^1H NMR (300 MHz, CDCl_3) δ 8.79 (d, J = 7.5 Hz, 1H, phenyl), 8.39 (d, J = 7.5 Hz, 1H, phenyl), 7.98 (s, 1H), 7.81 (dd, J = 14.8, 7.2 Hz, 5H, naphthyl), 7.57 (d, J = 8.2 Hz, 1H, phenyl), 7.36 (dd, J = 16.2, 7.6 Hz, 2H, phenyl), 7.18-7.08 (m, 2H, phenyl), 1.04 (s, 9H, Si- CH_3), 0.28 (s, 6H, SiC- CH_3);

^{13}C NMR (75 MHz, CDCl_3) δ 182.77, 154.17, 147.54, 147.08, 147.04, 144.22, 134.45, 132.99, 132.17, 132.12, 132.00, 131.42, 131.16, 130.19, 130.01, 129.69, 129.12, 128.70, 126.63, 126.27, 125.30, 124.65, 122.29, 119.48, 116.19, 115.02, 28.02, 25.91, 18.48, 1.18, -4.13.

ESI-HRMS (m/z), Calcd for $\text{C}_{32}\text{H}_{29}\text{NO}_3\text{Si}$, [M+H]: 504.1989; found: 504.1974.

6-(6-Hydroxynaphthalen-2-yl)-5*H*-benzo[a]phenoxazin-5-one, (6).

Compound **5** (0.31g, 0.62g, 1 eq.) was dissolved in dry THF and cooled to 0 °C. Tetrabutylammonium fluoride (0.46g, 1.73mmol, 2.5eq. of 1M in THF) were added under Ar atmosphere and the reaction was then warmed to room temperature for 5h. Saturated ammonium chloride was added. The mixture was extracted with ethyl acetate. The organic layer was washed with brine, then dried with MgSO_4 , filtered and concentrated under reduced pressure. The dark red solid was obtained in 97% yield by recrystallization with THF/*n*-hexane (1:1, v/v).

^1H NMR (300 MHz, d_6 -DMSO) δ 9.85 (s, 1H, OH), 8.73 (d, J = 7.3 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 7.93 (dd, J = 16.9, 10.7 Hz, 4H, naphthyl), 7.79 (dd, J = 15.0, 8.8 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.13 (d, J = 8.8 Hz, 1H).

^{13}C NMR (101 MHz, d_6 -DMSO) δ 181.44, 155.84, 146.67, 146.65, 143.54, 134.08, 132.17, 132.10, 131.84, 131.63, 131.26, 130.43, 129.81, 129.70, 129.08, 128.66, 127.26, 125.61, 125.21,

125.06, 125.00, 124.04, 118.60, 118.24, 115.72, 108.55.

ESI-HRMS (m/z), Calcd for $C_{26}H_{15}NO_3$, $[M+H]^+$: 390.1125; found: 390.1111.

2-Hydroxy-6-(5-oxo-5H-benzo[a]phenoxazin-6-yl)-1-naphth-aldehyde; (7, NR2).

To a solution of compound 15 (2.23g, 13.4 mmol) in trifluoroacetic acid (TFA, 30 mL), hexamethylenetetramine (HTMA, 1.88g, 13.4mmol, 1eq) was added at room temperature. The mixture was then heated to 90 °C and kept for 24h. After cooling to the room temperature, diluted hydrochloric acid was added, stirred for 30min. The precipitate was filtered, washed with water and dried in vacuum to give a dark-red solid in 80% yield.

1H NMR (300 MHz, d_6 -DMSO) δ 12.11 (s, 1H, CHO), 10.85 (s, 1H, OH), 8.99 (s, 1H), 8.66 (s, 1H), 8.00 (s, 1H, naphthyl), 7.43 (m, 3H), 7.25 (s, 1H), 7.18 (s, 2H), 6.99 (m, 1H).

^{13}C NMR (d_6 -DMSO, 101 MHz) δ 194.25, 181.83, 159.03, 158.66, 147.37, 144.46, 132.85, 132.59, 132.28, 131.91, 131.50, 131.14, 130.98, 129.80, 126.19, 125.96, 124.74, 124.60, 121.67, 117.70, 114.71, 107.80, 105.49.

ESI-HRMS (m/z), Calcd for $C_{27}H_{15}NO_4$, $[M+H]^+$: 418.1074; found: 418.1059.

2,3-Dibromonaphthalene-1,4-dione, (9) [S5]

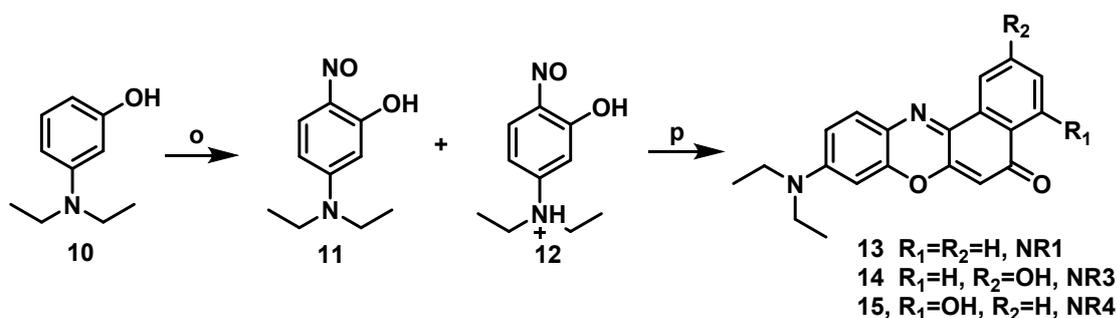
To a solution of naphthalene-1,4-dione (compound 8, 10 g, 63 mmol) in glacial acetic acid, liquid bromine (6.50 mL, 126 mmol, 2eq) was added dropwise. The resulting solution was stirred at room temperature for 30 min and then heated to 110 °C. After 8 h reaction at this temperature, the mixture was poured into 250 mL ice-water, the precipitate was formed, filtered and washed with water and dried under vacuum. The pure product was gained as yellow solid in 98% yield.

1H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, $J = 5.7, 3.3$ Hz, 1H), 7.78 (dd, $J = 5.7, 3.2$ Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.96, 142.70, 134.67, 130.88, 128.36, 109.91.

Preparation of NR1, NR3 & NR4 Dyes.

The dyes were prepared referring to a literature procedure [S6].



o, $NaNO_2$, HCl, Ethanol, H_2O , 90%; p, 1-Naphthol/naphthalene-1,6-diol/ 1,8-naphthalenediol, DMF, 80°C, 23%.

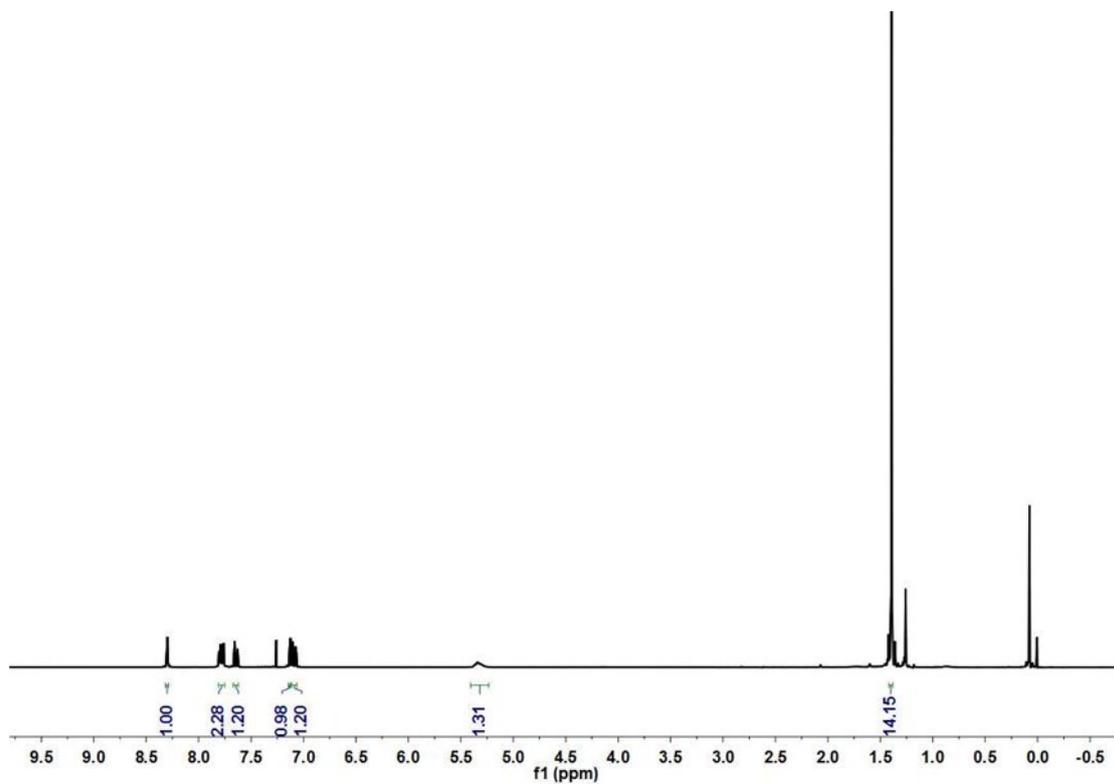
5-(Diethylamino)-2-nitrosophenol (11)

3-Diethylaminophenol (12.02 g, 72.6 mmol) was dissolved in a mixture of 26 mL of conc. HCl and 16 mL of distilled water. An aqueous solution of $NaNO_2$ (5.01 g, 72.6mmol) was added to the obtained solution in a bath of ice-water. The reaction mixture was then stirred for 4 h at 0–5 °C. The precipitate was filtered, dried in vacuum. The residue was recrystallized with a mixture of ethanol and diethylether (1:1, V/V), a mixture of 11 and 12 was obtained as a yellow powder.

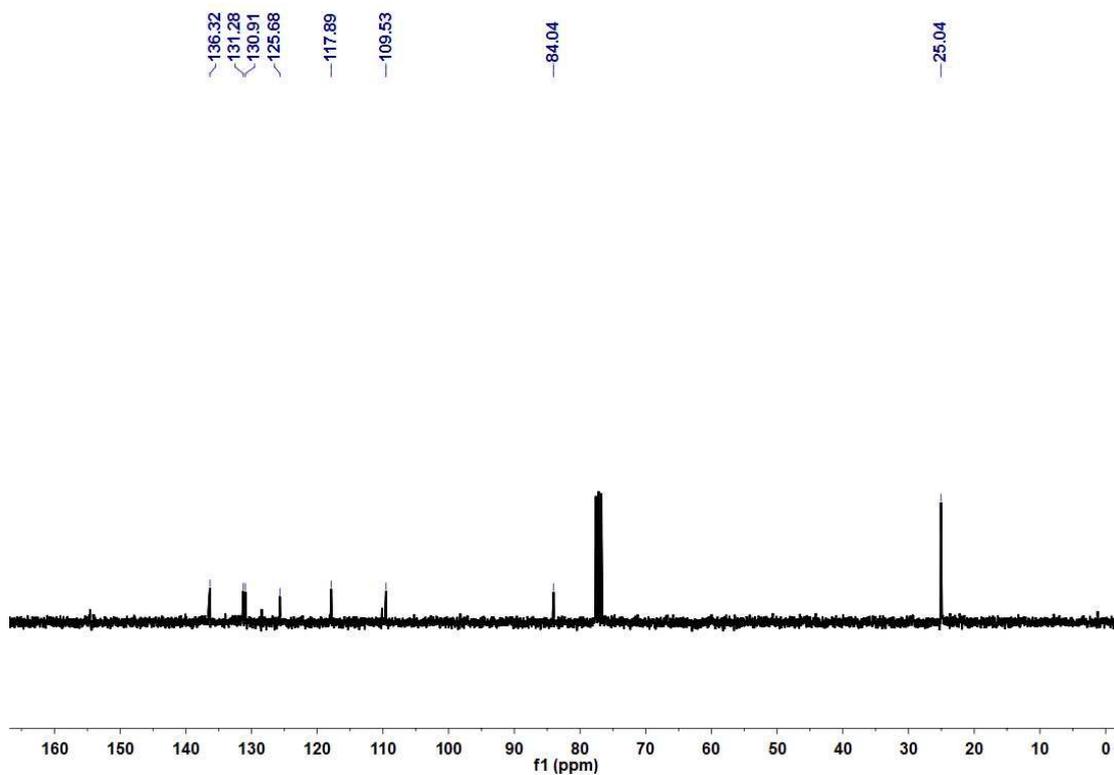
A DMF solution of 5-diethylamino-2-nitrosophenol hydrochloride (1.14 g, 4.94mmol) and 1,6-dihydroxynaphthalene (0.19 g, 4.94 mmol) were merged into an oil bath at 80°C for 4 h. The DMF

was then removed under reduced pressure. The target product was gained after further purification by chromatography using petroleum ether/ ethyl acetate 1:2.

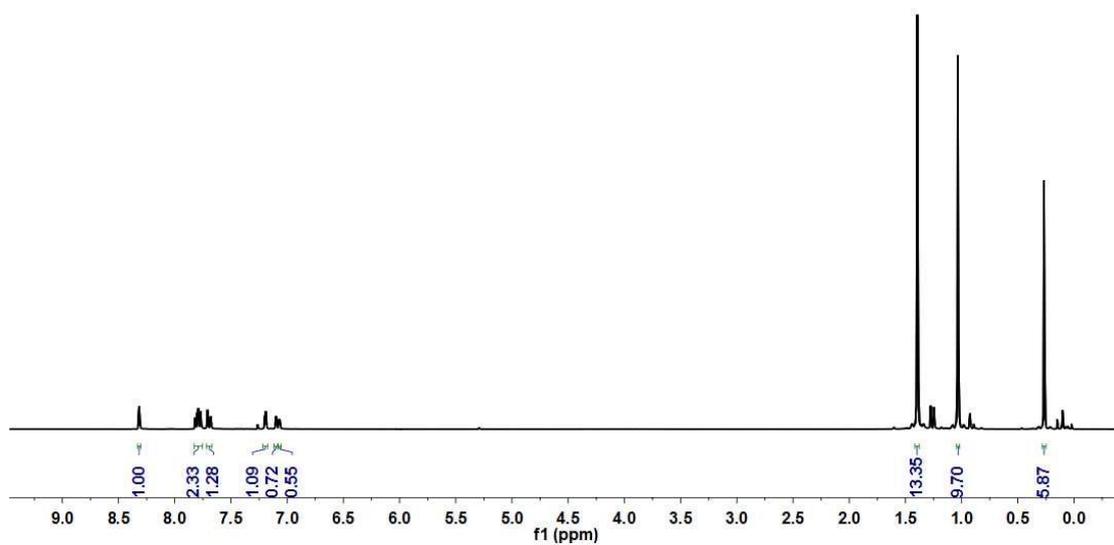
Copy ^1H NMR of Compound 2



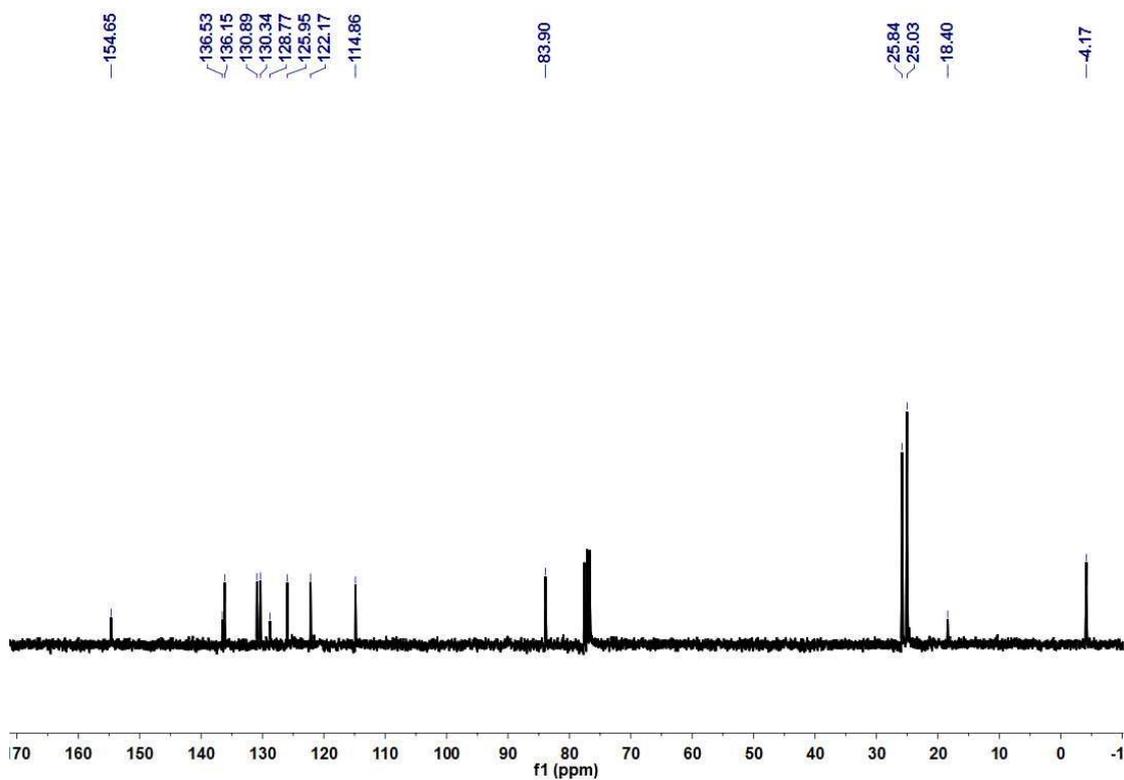
Copy ^{13}C NMR of Compound 2



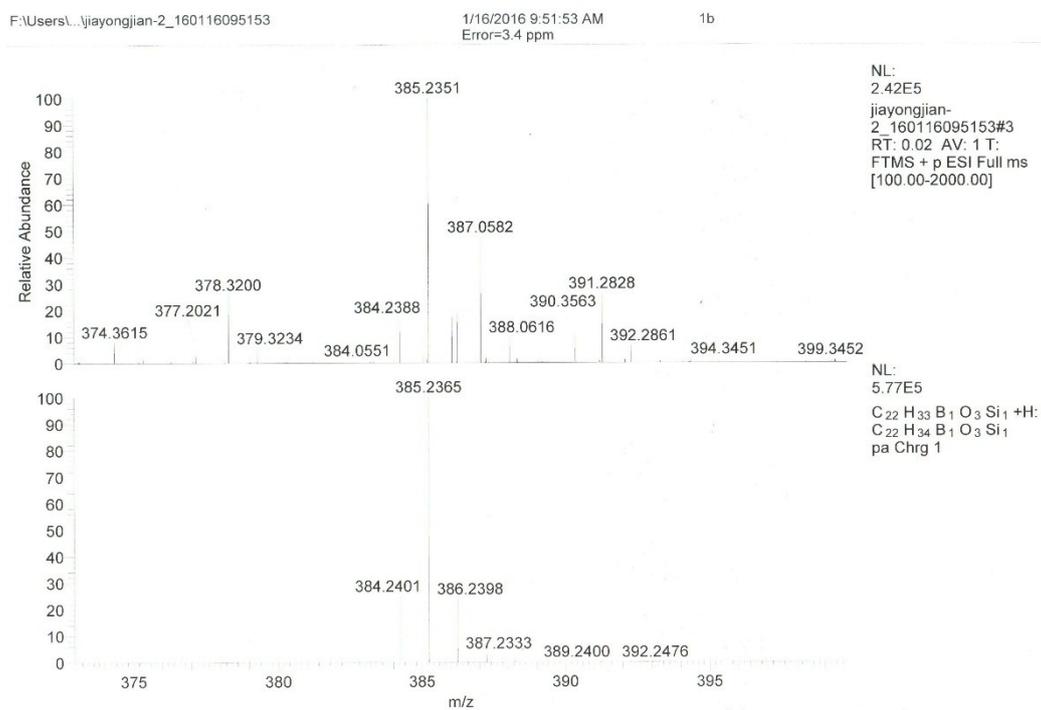
Copy ¹H NMR of Compound 3



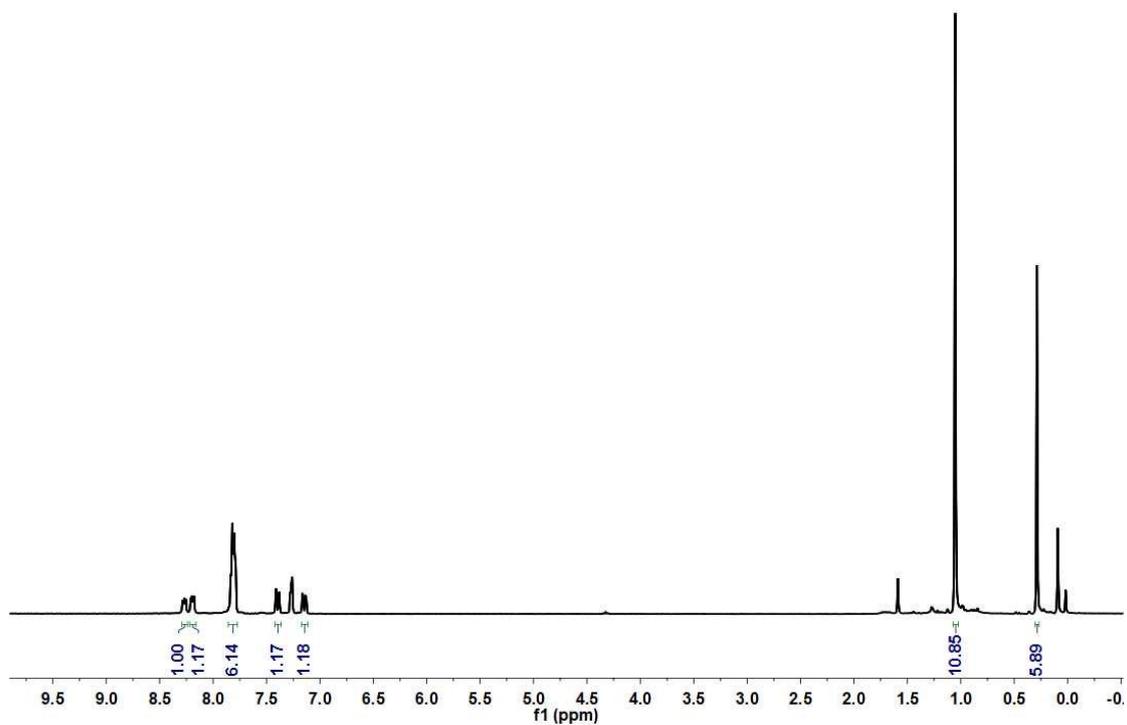
Copy ¹³C NMR of Compound 3



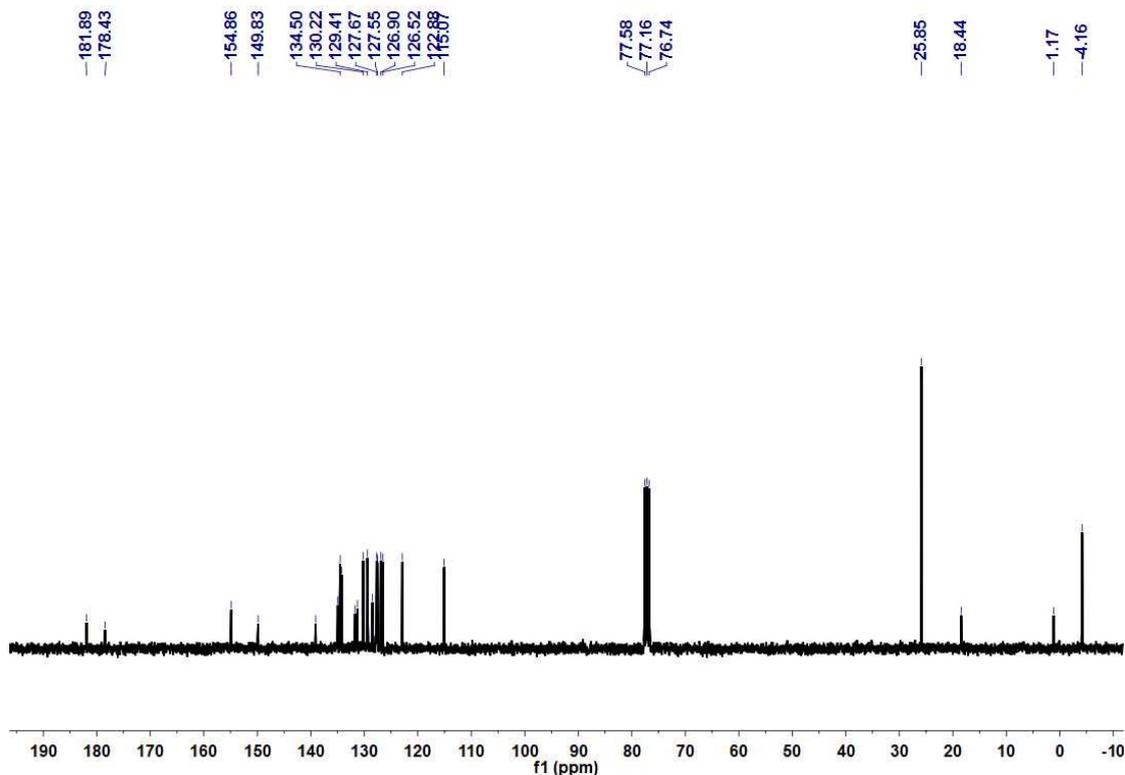
Copy HRMS of Compound 3



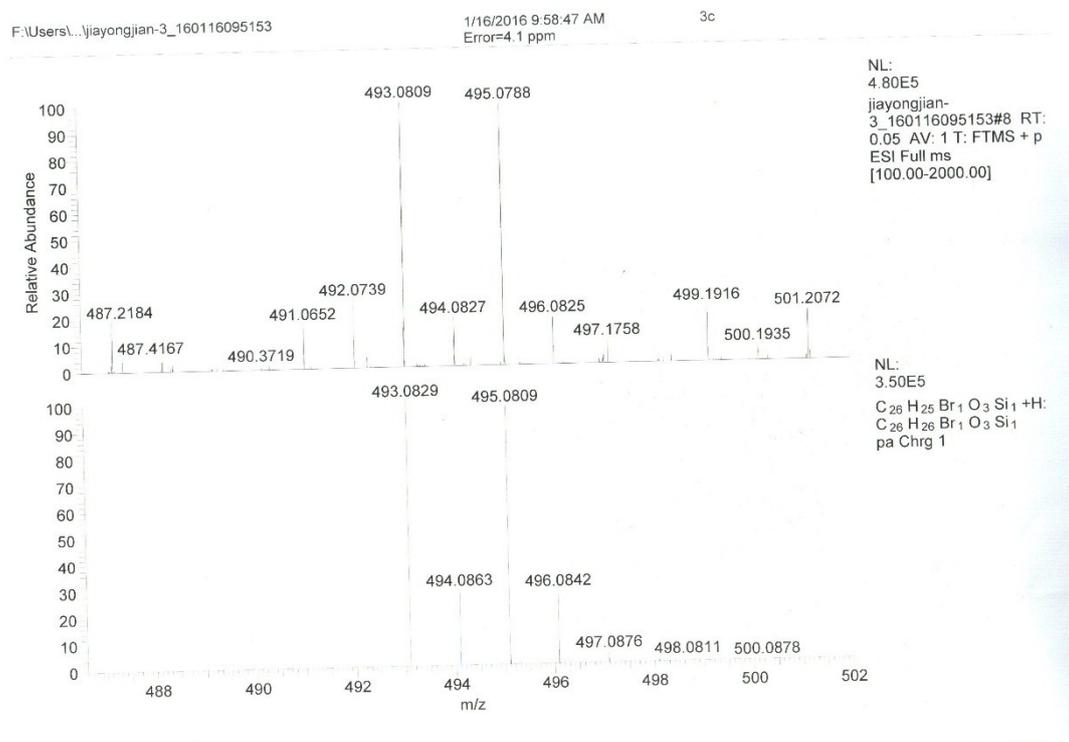
Copy ¹H NMR of Compound 4



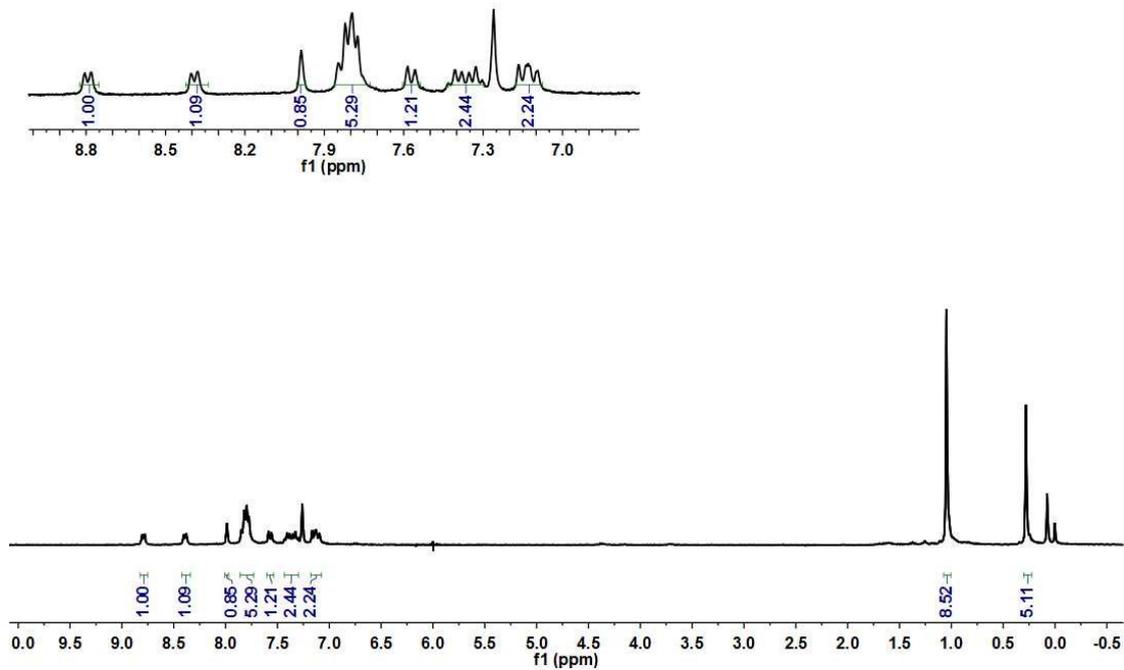
Copy ¹³C NMR of Compound 4



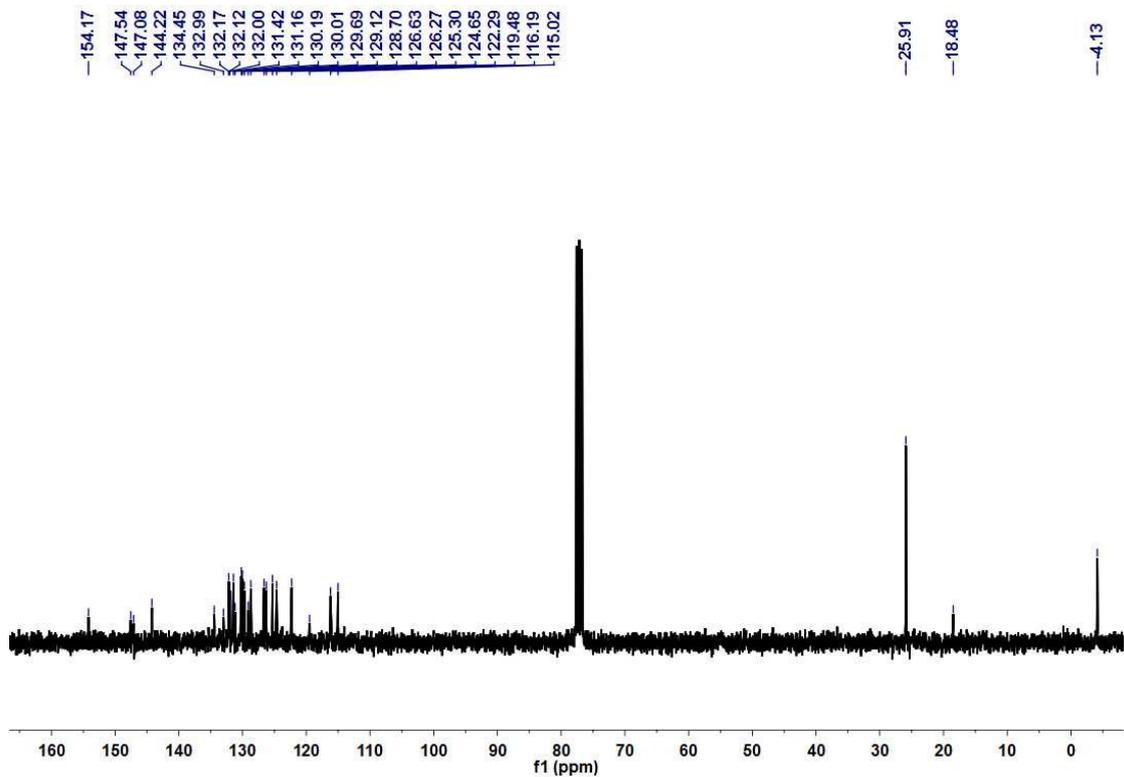
Copy HRMS of Compound 4



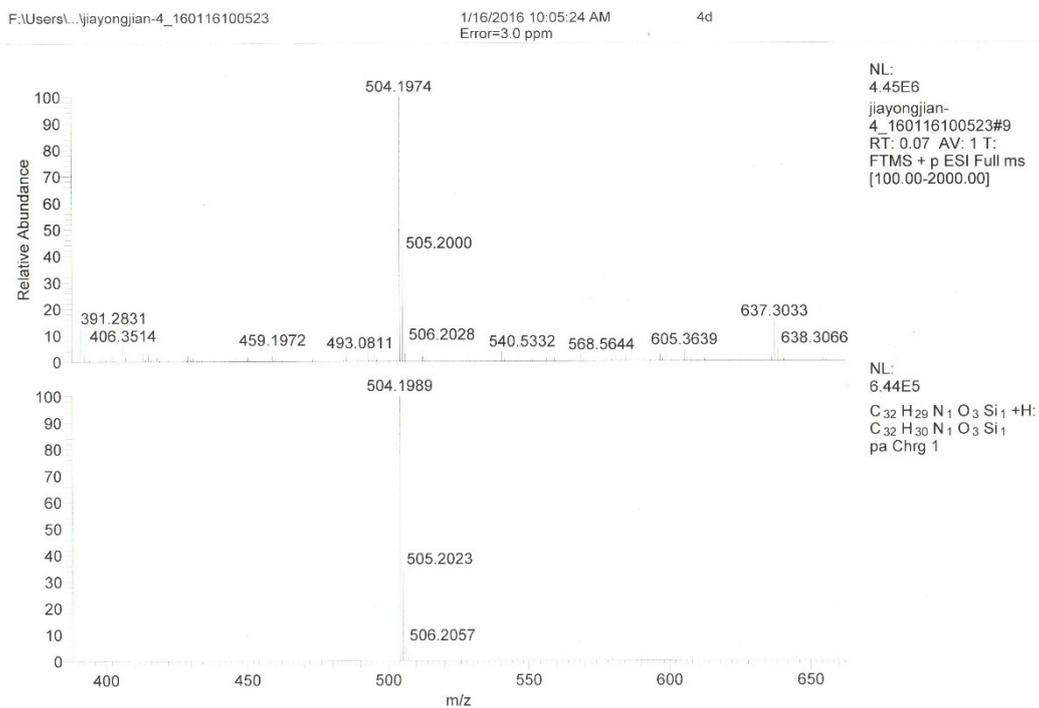
Copy of ^1H NMR Compound 5



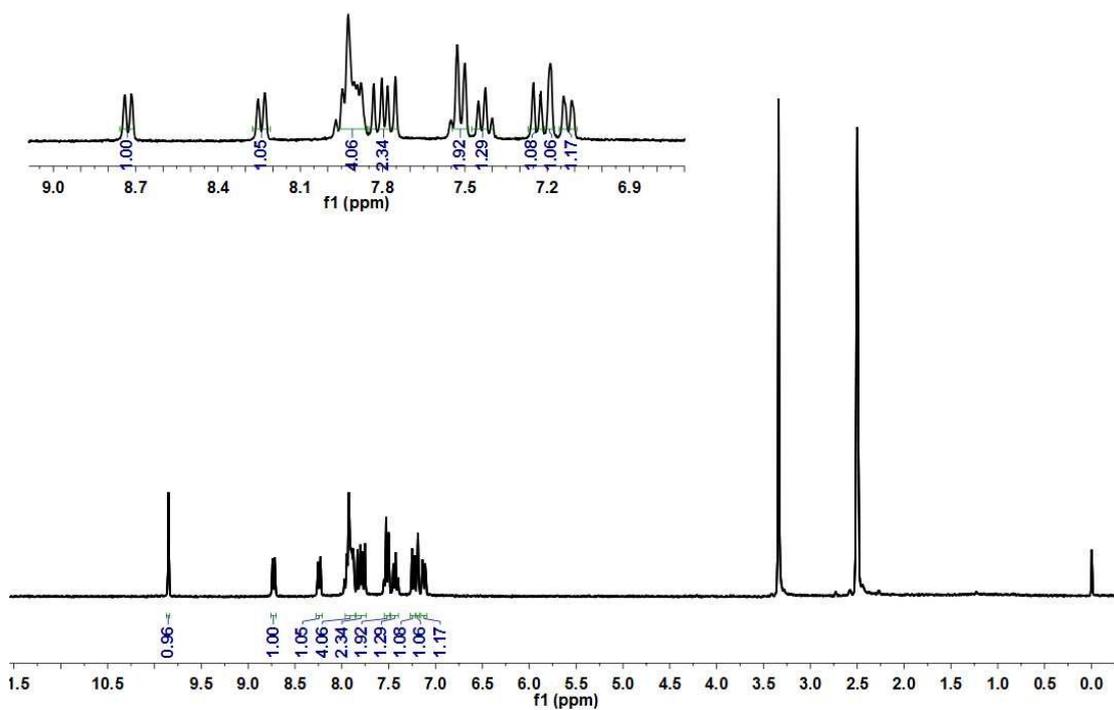
Copy of ^{13}C NMR Compound 5



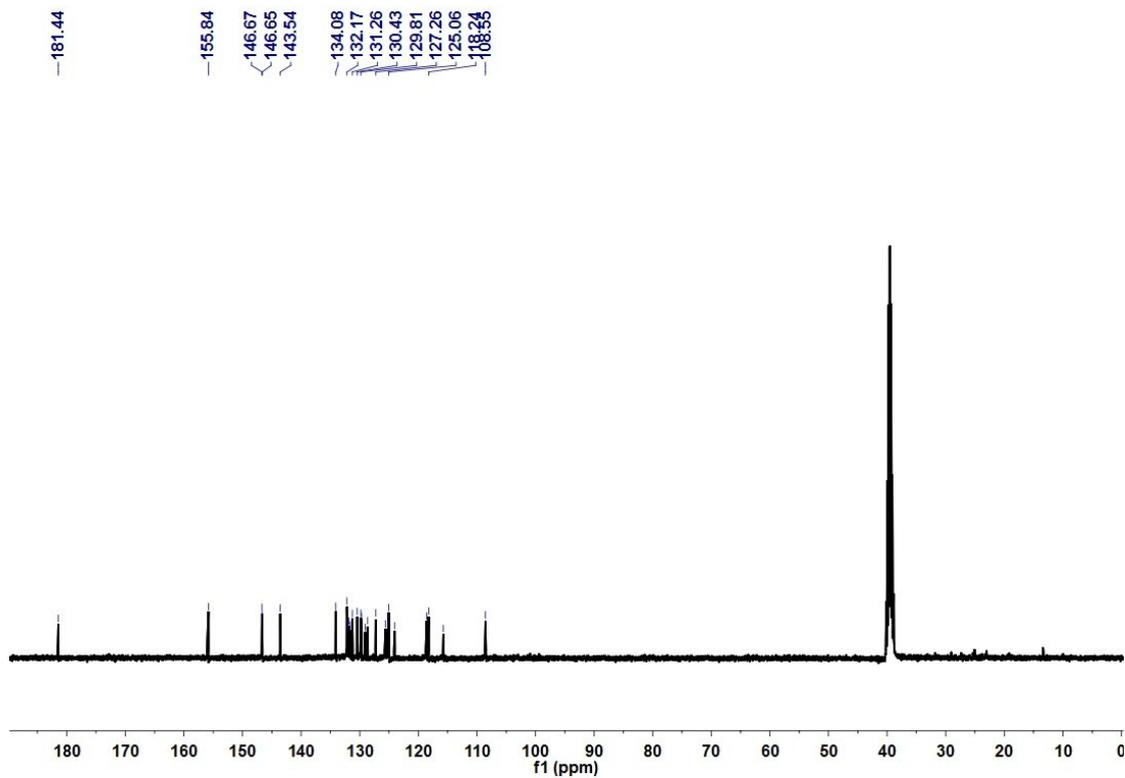
Copy HRMS of Compound 5



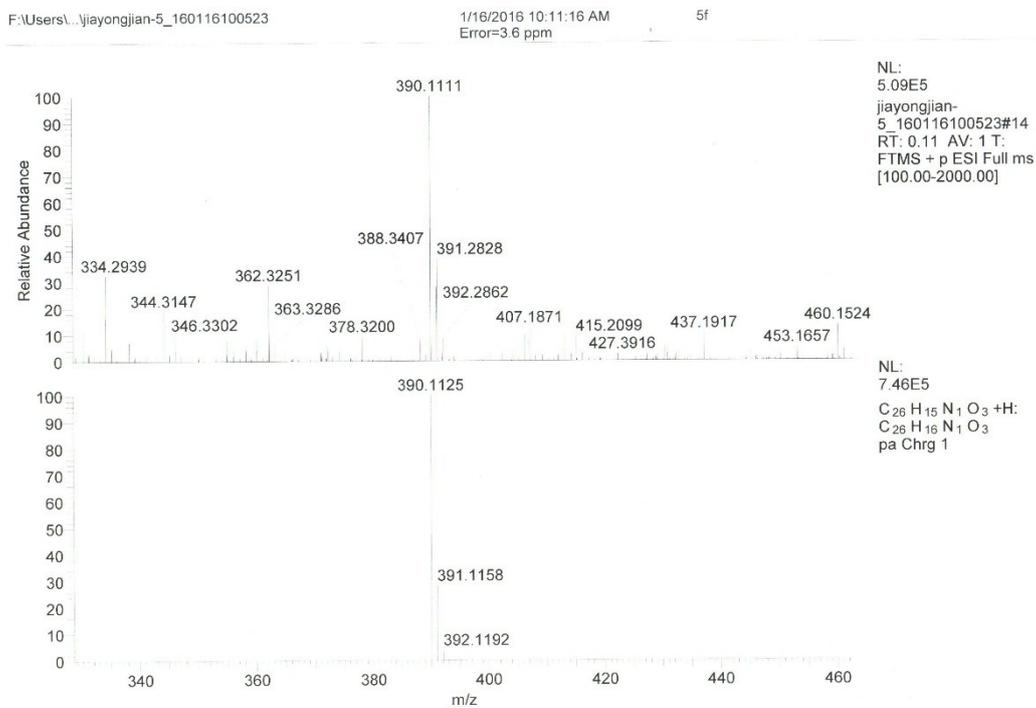
Copy ¹H NMR of Compound 6



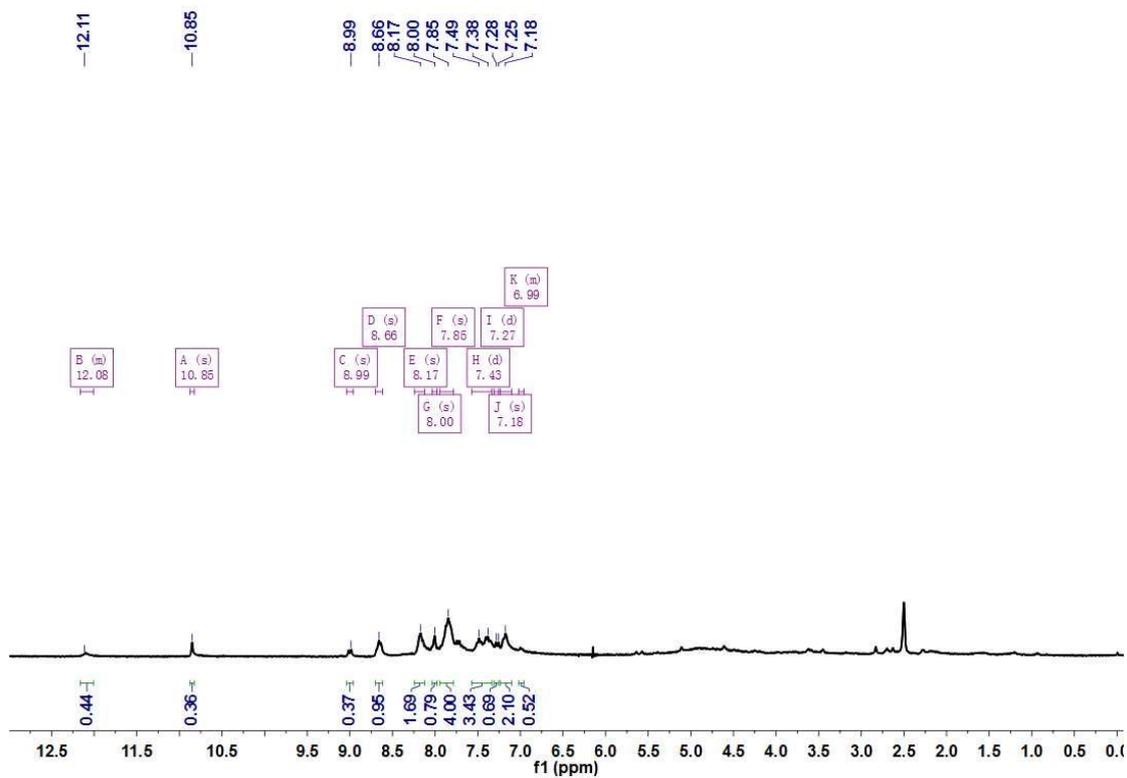
Copy ¹³C NMR of Compound 6



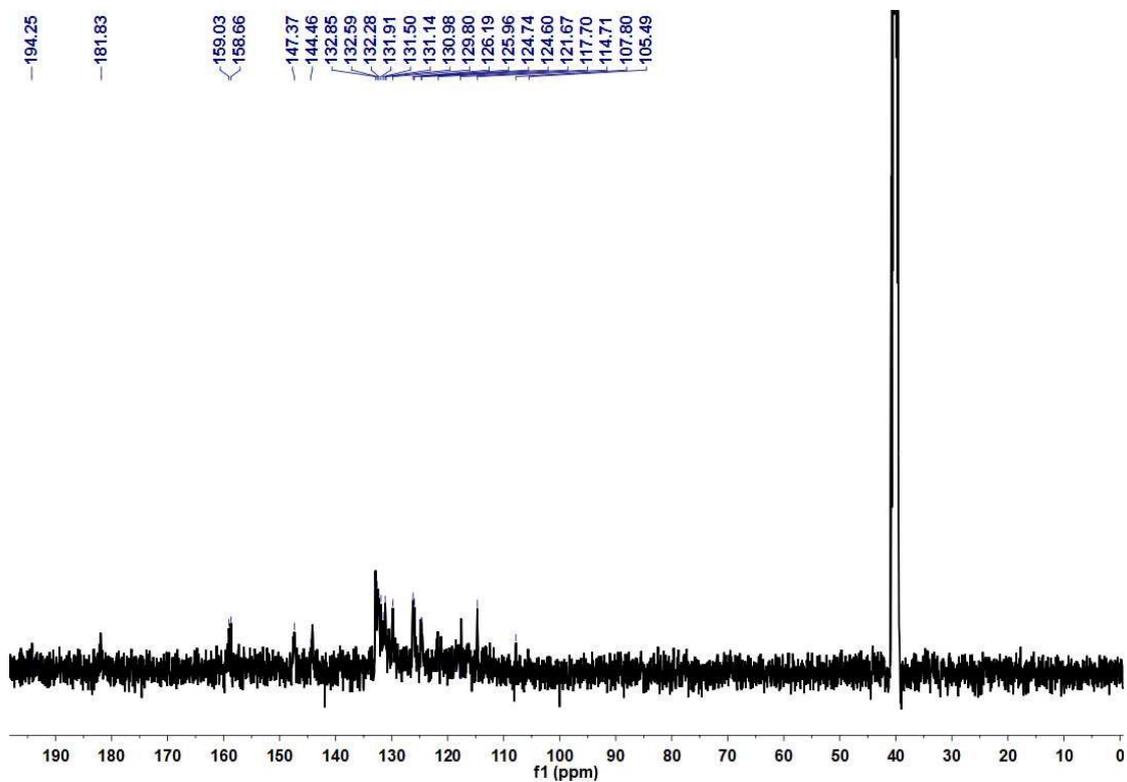
Copy HRMS of Compound 6



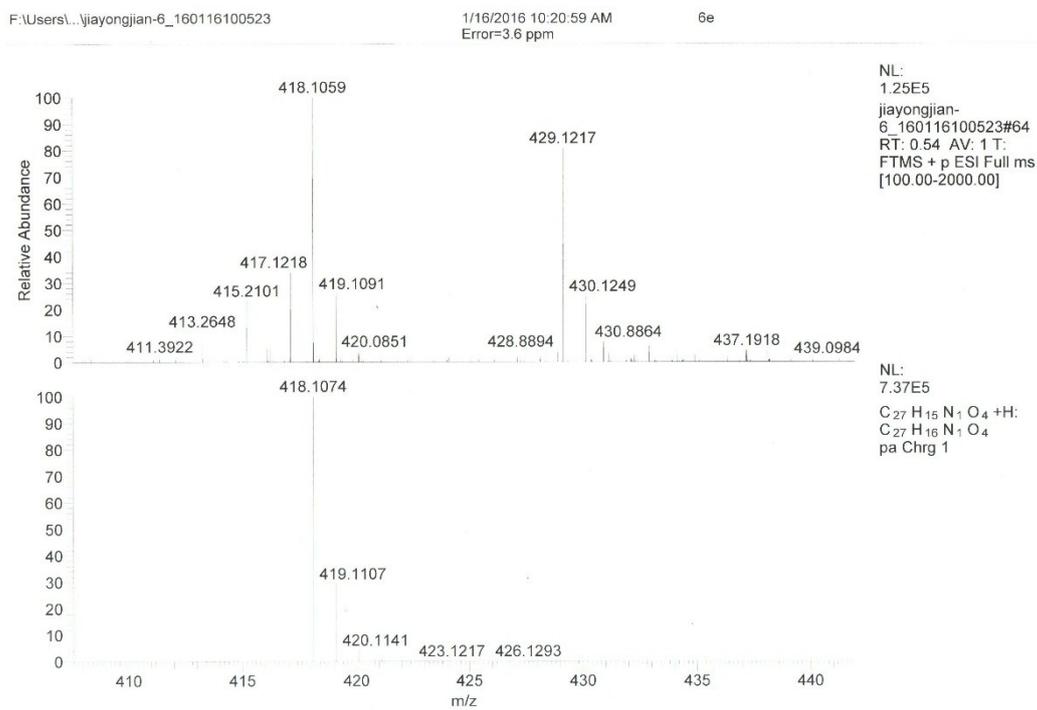
Copy ¹H NMR of Compound 7



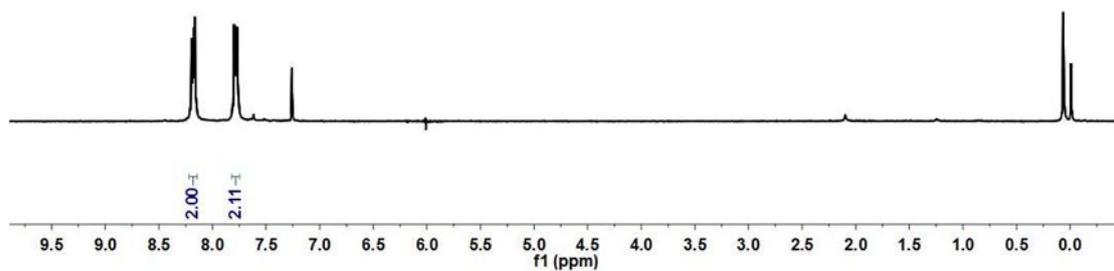
Copy ¹³C NMR of Compound 7



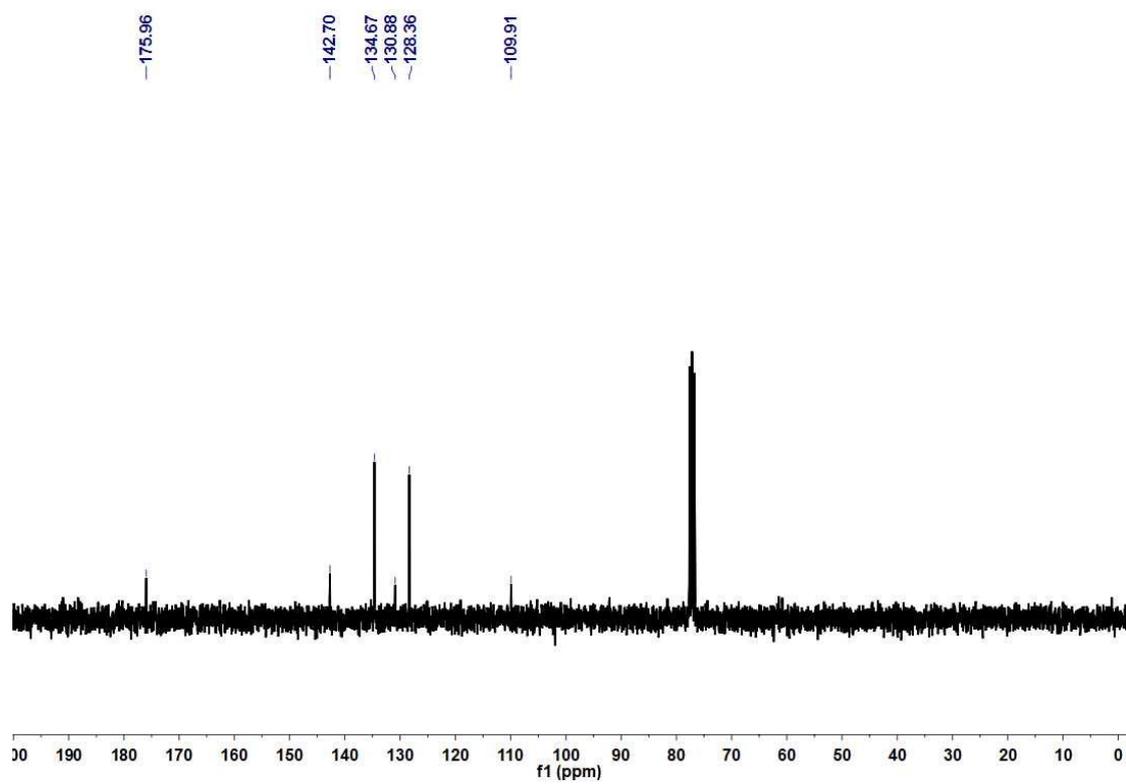
Copy HRMS of Compound 7



Copy ¹H NMR of Compound 9



Copy ^{13}C NMR of Compound 9



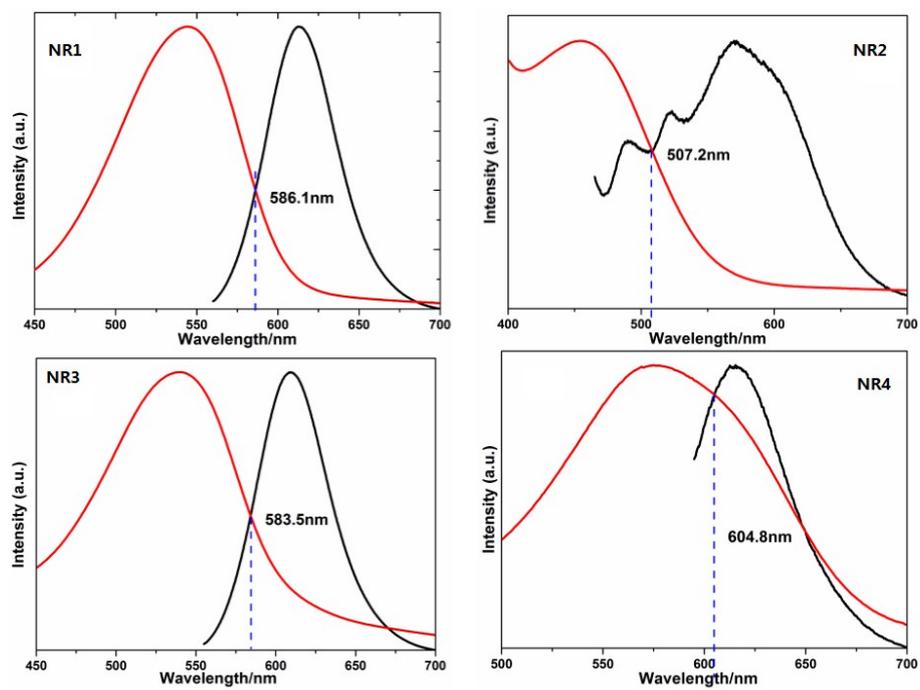


Fig. S1 Normalized UV-vis absorption (red) & photoluminescence spectra (black) of NR_x dyes in DMF at 25 °C

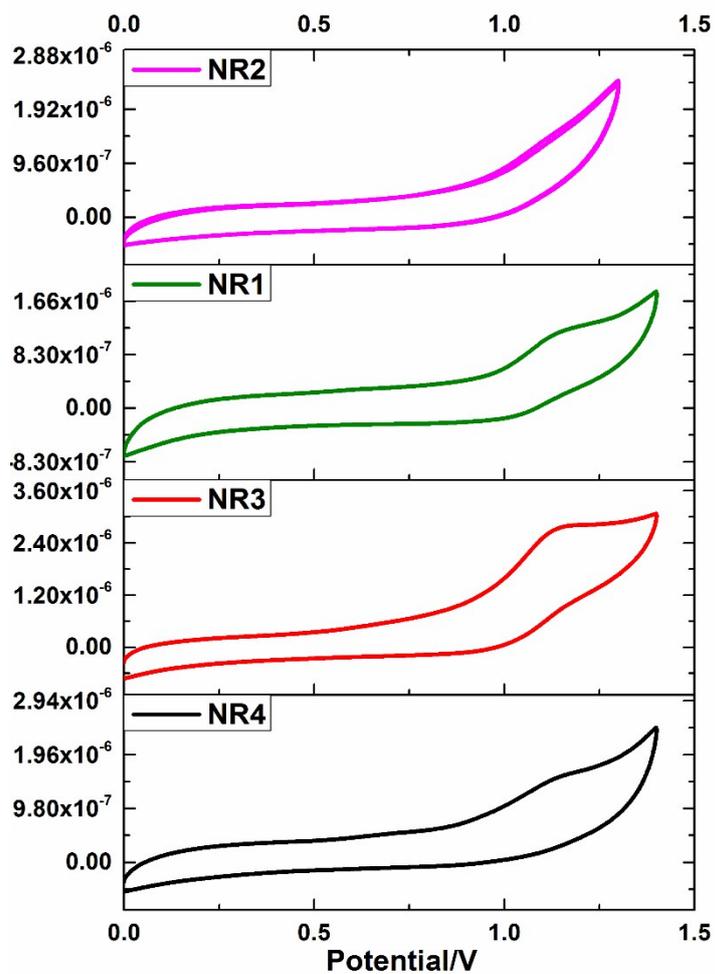


Fig. S2 Cyclic voltammograms of NRx dyes

DFT calculation

DFT calculations are performed using Gaussian 03 package. All the electronic structures for the optimized geometry are calculated at B3LYP/6-31G**/B3LYP/6-31+G* level.

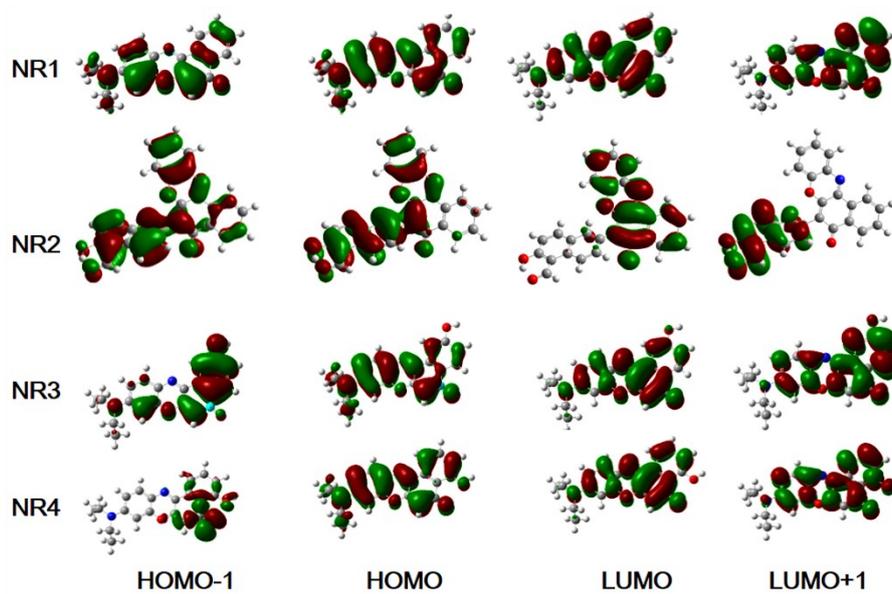


Fig. S3 Electron distribution of frontier orbitals using DFT of NR_x dyes

Preparation of BiVO₆ (photoanode)

The preparation of anode, as a water oxidation electrode, were according to the literature [S7, S8].

Preparation of Photocathodes

a) Preparation of TiO₂@FTO

The TiO₂ /FTO plates were fabricated by following our previous report [S9]

b) Preparation of APTES@TiO₂

The TiO₂ film was immersed in the ethanol solution containing 3-aminopropyltriethoxysilane (APTES), and then heated at 70°C for 12 hours. After cooling to room temperature, the film was washed with deionized water, dried and used in the next step.

c) Preparation of NR_x@TiO₂

The plates of APTES@TiO₂ were dropped in the THF solution of NR_x dyes, and refluxed for 24 hours. The dye molecules were reacted with amine groups of APTES@TiO₂ leading to the colored photocathodes of NR_x@TiO₂ that were washed with THF and dried in air at 50 °C.

d) Preparation of Pd/NR_x@TiO₂

The Pd nano-particles were sunken onto the surface of NR_x@TiO₂ by pulse electron deposition technique. The electrolyte was PdCl₂ aqueous solution (2g L⁻¹, pH = 1.5). The reference and auxiliary electrodes were a Pt wire.

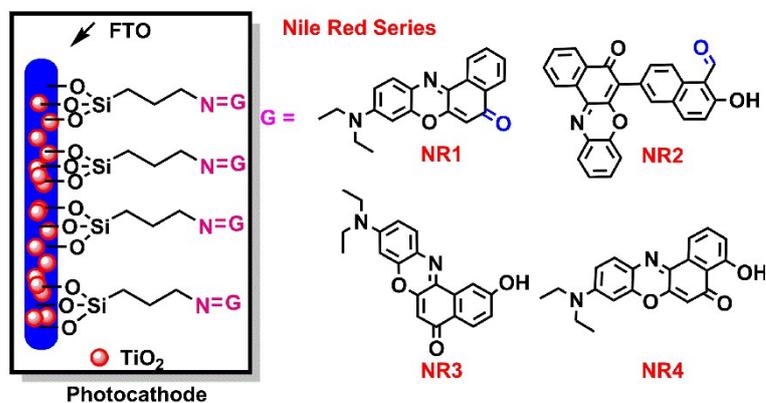


Fig. S4 the structure of photocathodes

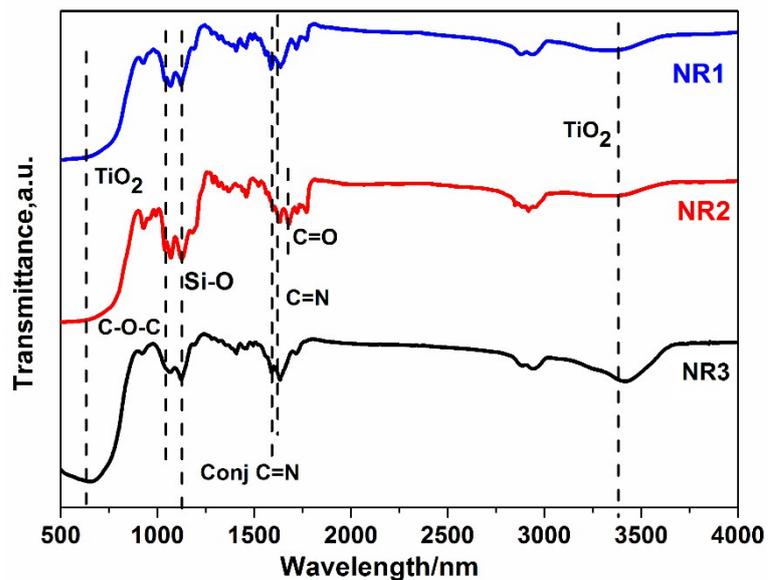


Fig. S5 FTIR of organic and inorganic composites

1068 cm^{-1} : Si-O stretching vibration; 1680 cm^{-1} : C=N stretching vibration of Schiff base. 500 cm^{-1} and 3200 cm^{-1} : vibrations of TiO_2 .

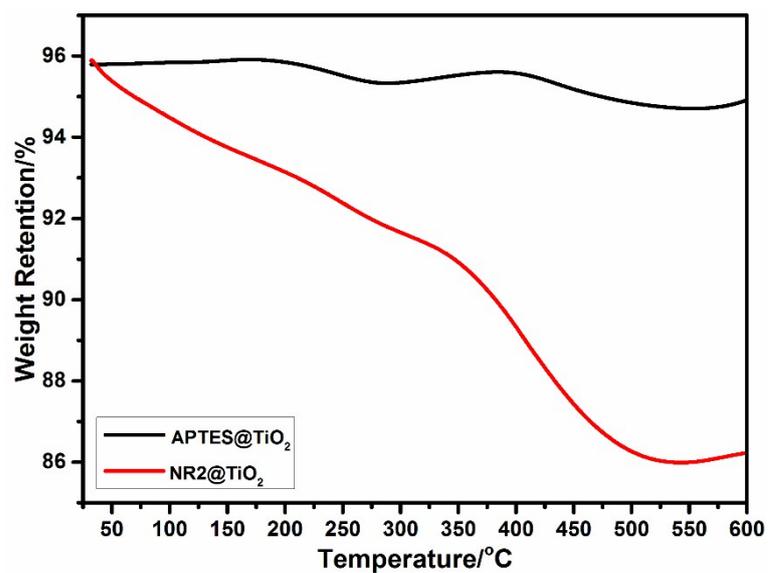
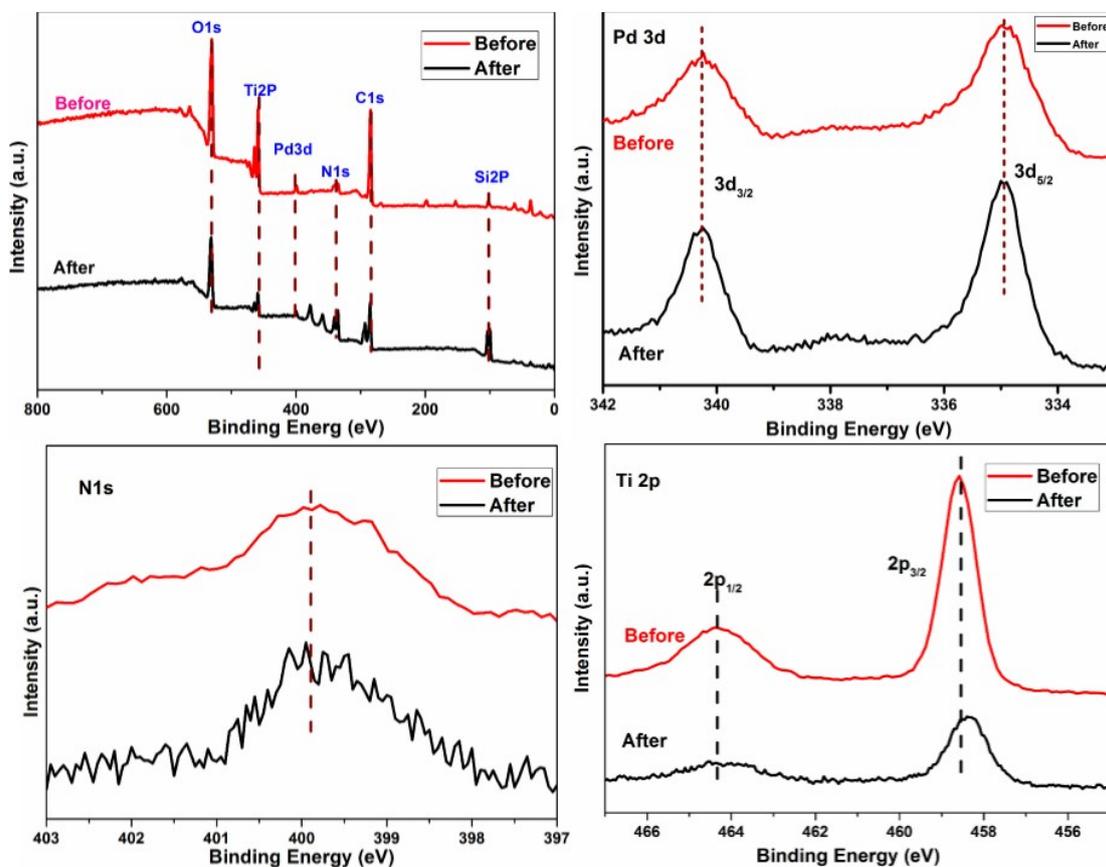


Fig. S6 TGA of APTES@TiO₂ (Black) and NR2@TiO₂ (Red) Photocathodes

Characterization of Photocathode (Pd/NR2@TiO₂)



The binding energies of N 1s (397.2 eV), Ti 2p_{3/2} (458.5 eV), Ti 2p_{1/2} (464.3 eV), Pd 3d_{5/2} (334.4 eV) and Pd 3d_{3/2} (339.7 eV) are assigned to the C=N-C, Ti (IV) and Pd⁰ respectively.

Fig. S7 X-ray photoelectron spectroscopy (XPS) of Pd/NR2@TiO₂ photocathode before (red) and after (Black) artificial photosynthetic reaction

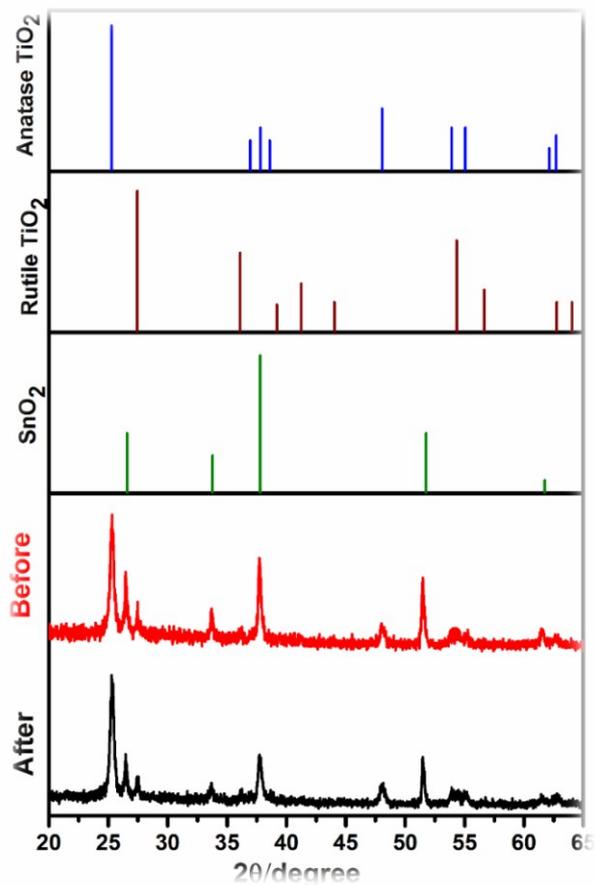


Fig. S8 XRD patterns and analysis of Pd/NR2@TiO₂ photocathode before (Red) and after (Black) artificial photosynthetic reaction

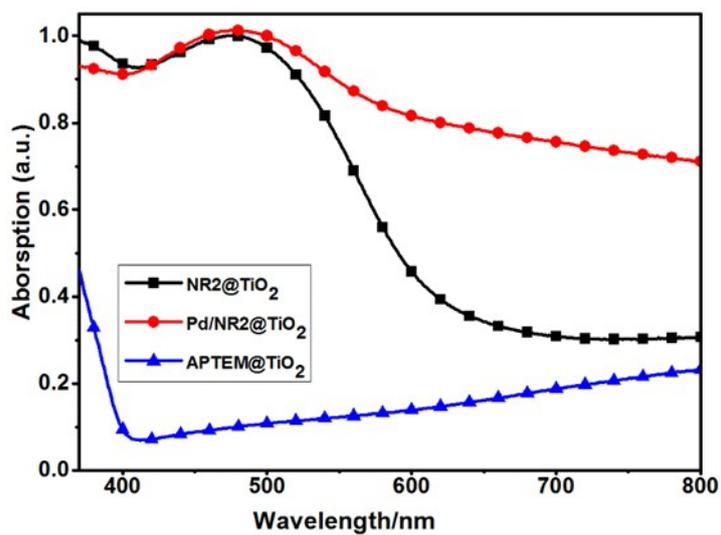


Fig. S9 The UV-*vis* absorption of various reformative TiO₂ films

Cyclic voltammetry and Electrochemical impedance spectra of trielectrode system

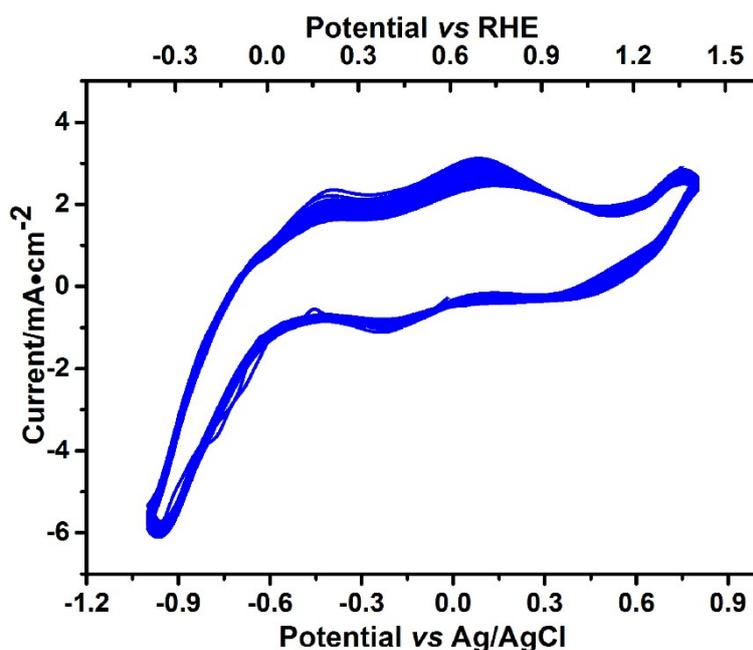


Fig. S10 100 continuous cyclic voltammograms of Pd/NR2@TiO₂ photocathode obtained at a scan rate of 50 mV s⁻¹ in CO₂ saturated KHCO₃ (0.1 M)

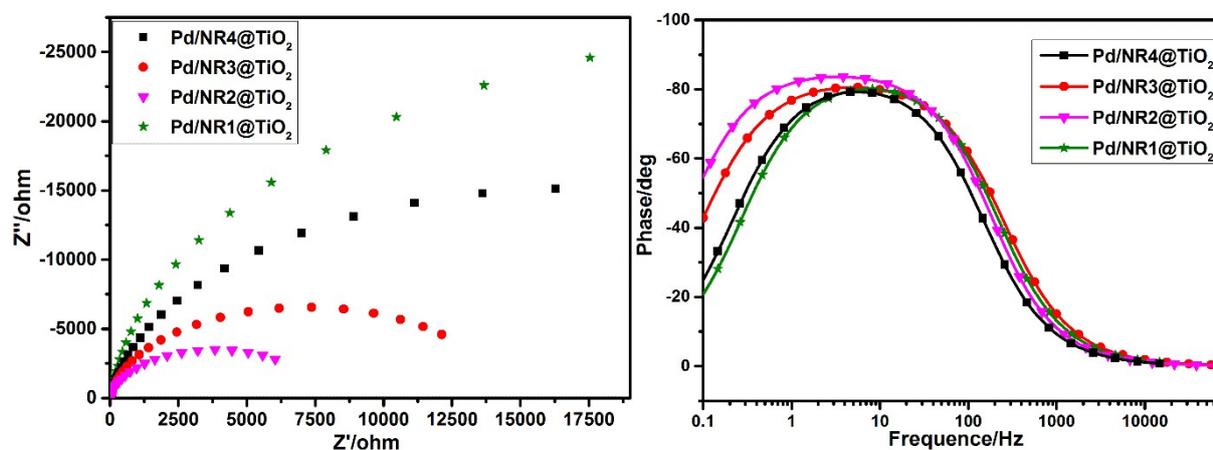


Fig. S11 Nyquist and Bode plots of electrodes in a CO₂ sat 0.1 M. KHCO₃ solution (Ag/AgCl)

Electron life (τ_n) was calculated by the equation:

$$\tau_n = \frac{1}{2\pi f_m}$$

f_m was locked at the peak value of frequency in Bode plots.

Table S1 Electrochemical impedance results of Pd/NR_x@TiO₂.

Photocathode	R_{ct}/Ω	τ_n/ms
Pd/NR1@TiO ₂	57513	19
Pd/NR2@TiO ₂	7672	42
Pd/NR3@TiO ₂	14321	39
Pd/NR4@TiO ₂	33900	28

High resolution transmission electron microscopy (HRTEM) and TEM pictures

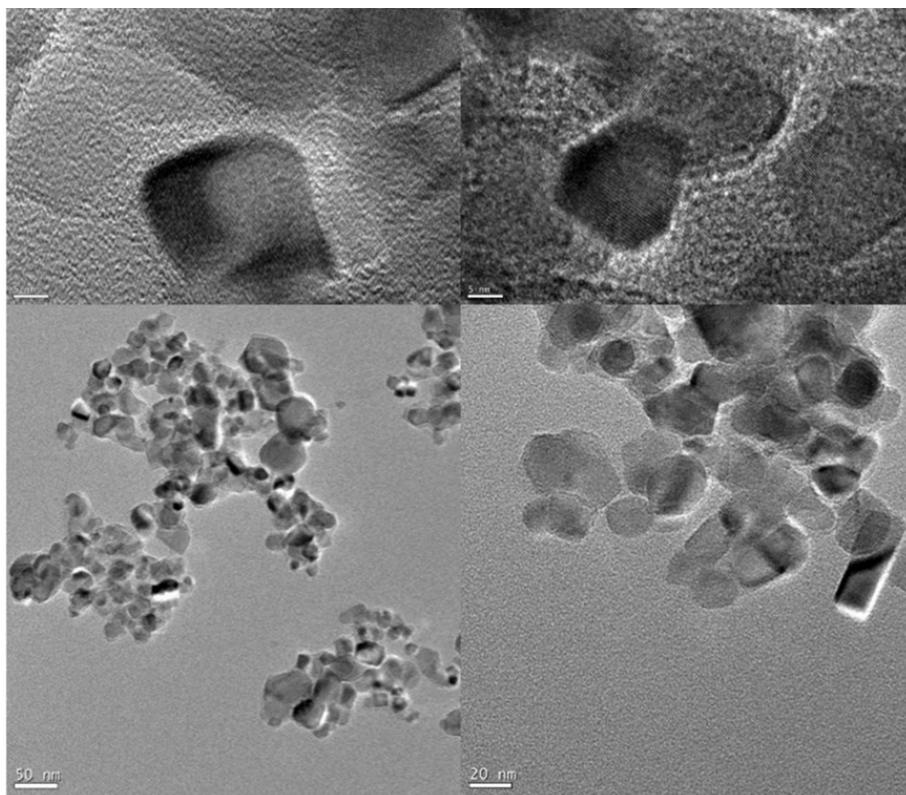


Fig. S12 HRTEM and TEM images of Pd/NR2@TiO₂ Photocathode

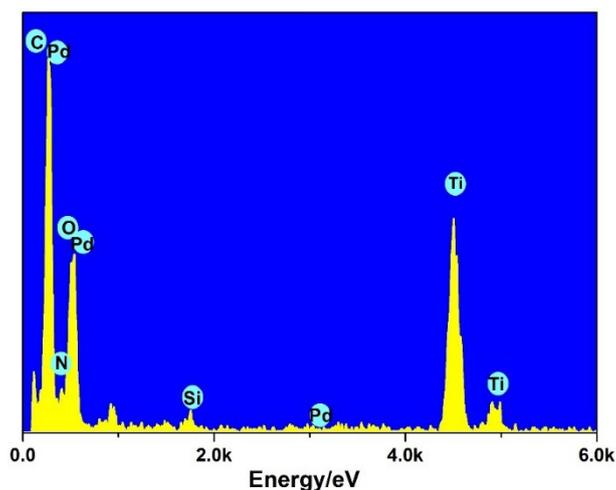


Fig. S13 The element test of Pd/NR2@TiO₂ Photocathode by EDS

Scanning electron microscopy Characterization

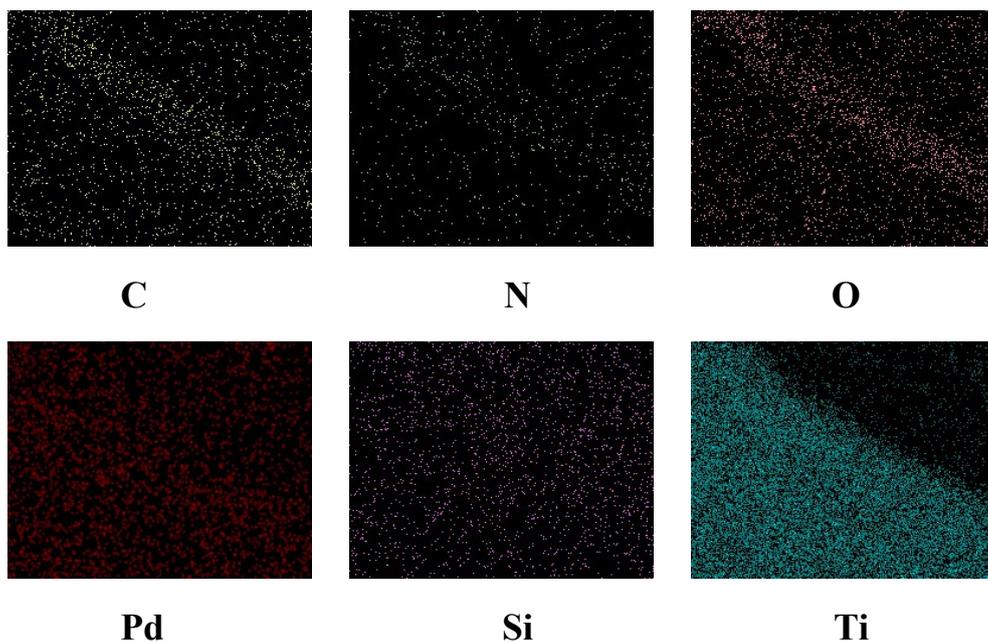


Fig. S14. Surface elements distribution of Pd/NR₂@TiO₂ Photocathode

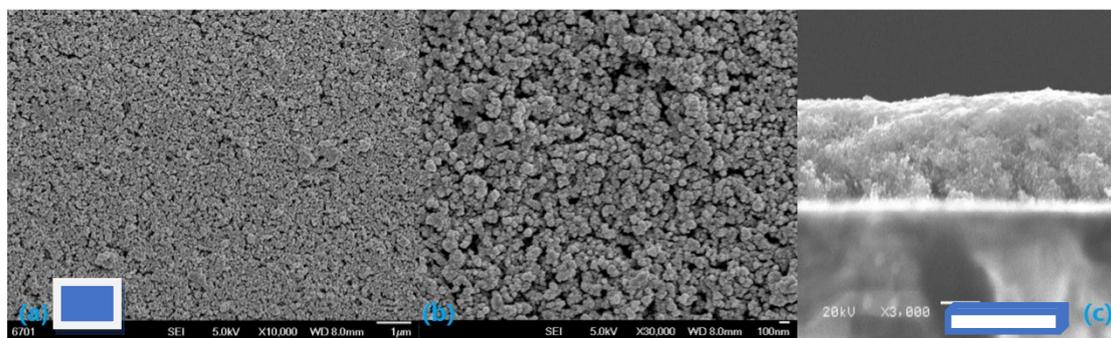


Fig. S15. SEM images (a, b, Top; c, Side) Pd/NR₂@TiO₂ Photocathode

Table S2 Average E_{fb} values and slopes obtained from Mott-Schottky plots

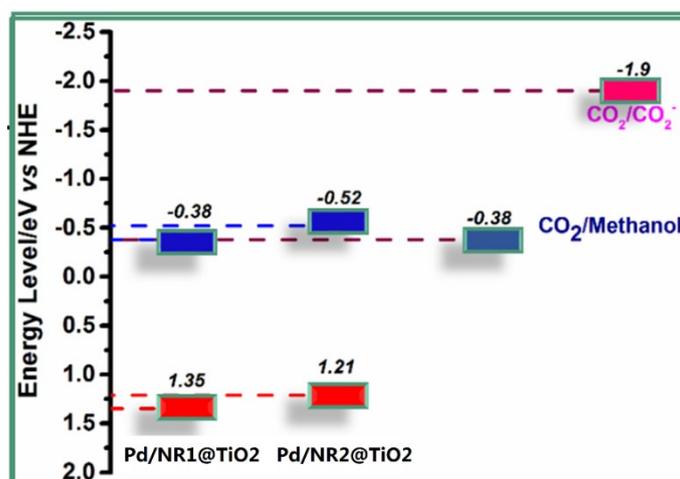
Photocathode	E_{fb} (vs Ag/AgCl)	E_{fb} (vs NHE)	Carrier Concentration(N_D)
<i>Pd/NR1@TiO₂</i>	-0.58 V	-0.38V	$0.94 \times 10^{19} \text{cm}^{-3}$
<i>Pd/NR2@TiO₂</i>	-0.72 V	-0.52V	$1.098 \times 10^{19} \text{cm}^{-3}$

$$E \text{ (vs. NHE)} = E_{fb} \text{ (vs. Ag/AgCl)} + 0.197\text{V}$$

$$E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + E_{Ag/AgCl}(\text{ref}) + 0.0596\text{pH}$$

$$ND = \frac{2}{r\epsilon_0\epsilon_r e}$$

The flat band potential was obtained by the Mott–Schottky analysis method at a scanning rate $10 \text{ mV} \cdot \text{s}^{-1}$ with the potential range from -1 to 0 V at 0.5 kHz under dark condition.

**Fig. S16** A diagram showing approximate band edge positions for Pd/NR_x@TiO₂ together with the thermodynamic potentials of CO₂ reduction to various reduction products vs. NHE at pH7.

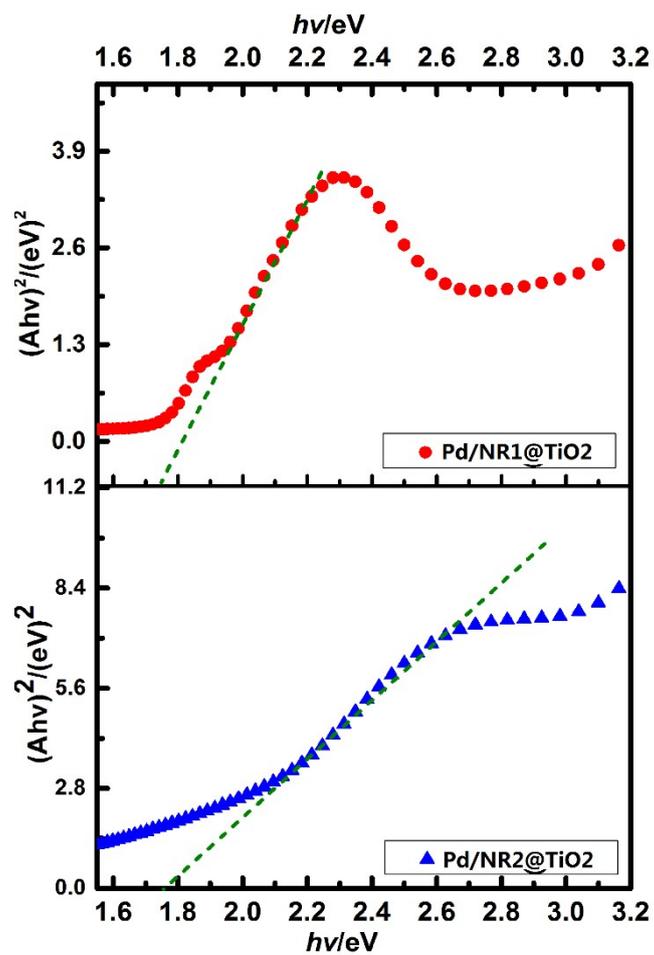


Fig. S17 $(Ah\nu)^2$ vs. $h\nu$ curves of Pd/NR_x@TiO₂ photocathode

Table S3 CB and VB of Pd/NR_x@TiO₂

Photocathode	CB(eV) vs. <i>NHE</i>	VB(eV) vs. <i>NHE</i>
Pd/NR1@TiO ₂	-0.38	1.35
Pd/NR2@TiO ₂	-0.52	1.21

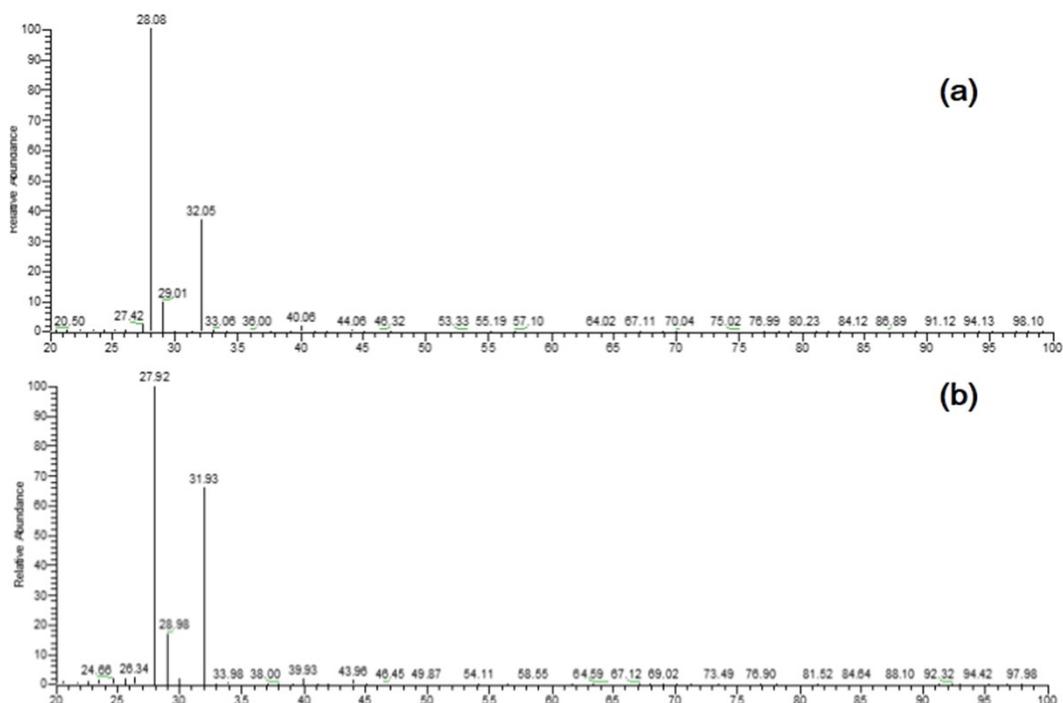


Fig. S18 Trace Oxygen Evolution utilizing Pd/NR2@TiO₂ for 48h. (a) GC-MS of Background and (b) GC-MS of the upper gas in APE system.

According to mass spectrum, N/O ratio of the instrument background was locked at 2.7, while that of sample was 14.28. It manifest the photosystem II of PC system using the energy in sunlight to oxidize water work to liberate oxygen.

Artificial photosynthetic experiments

Artificial photosynthetic experiments were performed as follows: an airtight reactor equipped with a multi-modificatory TiO₂ as photocathode, Co/Pi/W:BiVO₄ as photoanode was charged with KHCO₃ aqueous solution (0.1M.). The mixture was bubbled and saturated with a stream of high-purity Carbon Dioxide (99.999%) (pH = 6.96). The reactor was irradiated by a 300W Xenon lamp (PLS-SXE300C, Perfect Light, China), meanwhile, the tiny voltage (~0.6V) was actuated between the photoanode and photocathode by a silicon cell. The liquid products were quantified by NMR (JOEL 400 MHz) spectroscopy, in which appropriate electrolyte was mixed with 35 μl standard liquid (1ml D₂O+ 10mM dimethyl sulfoxide + 50mM phloroglucinol). The one-dimensional ¹H spectrum was measured with water suppression using a pre-saturation method.

$$\text{Rate} = \frac{C_{\text{DMSO}} (\text{mM}) \times \text{Area}_{\text{product}}}{\text{Time}(\text{h}) \times 1.96(\text{cm}^{-2})}$$

$$\Phi_{\text{cell}} = \frac{6 \times \text{moles of methanol yeilds}}{\text{moles of photon absorbed by catalyst}}$$

Total photon absorbed by catalysis

$$\begin{aligned} & \text{absorbed light flux} \left(\frac{\text{mW}}{\text{cm}^2} \right) \times \text{surface area}(\text{cm}^2) \times \text{radiation time}(\text{s}) \\ & \hline = & \text{each photon energy}(\text{J}) \times 6.02 \times 10^{23} \end{aligned}$$

Each photon energy: $E = \frac{hc}{\lambda}$

Planck's constant $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$, $c = 3 \times 10^8 \text{ m/s}$, $\lambda \cong 500 \text{ nm}$.

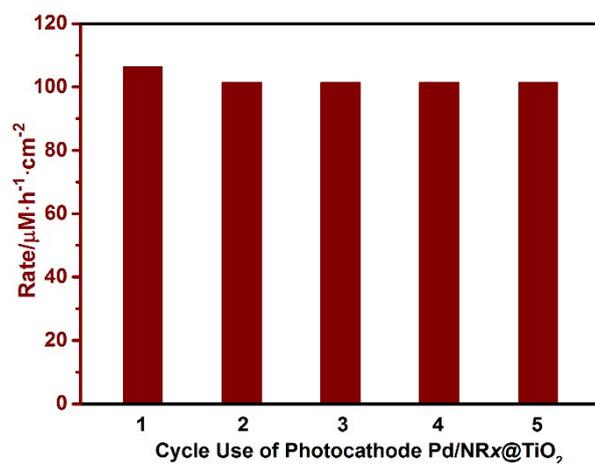
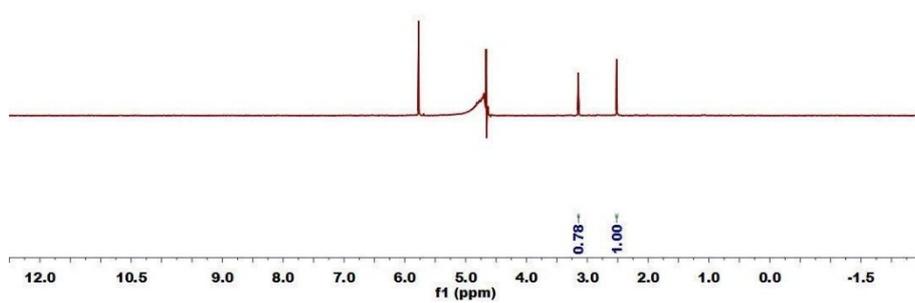


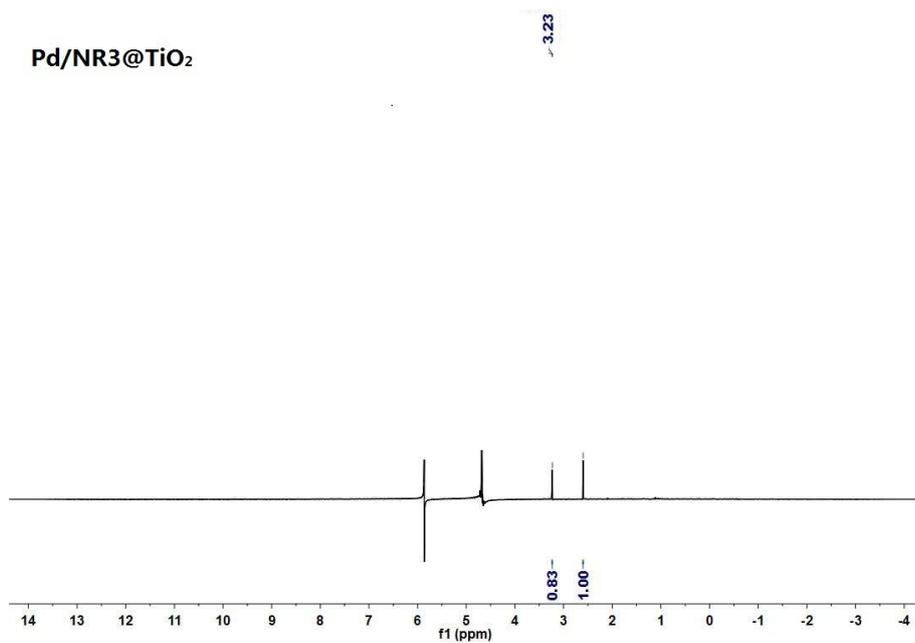
Fig S19 Stability of photocathode Pd/NR₂@TiO₂ in APE

Selected copies of ^1H NMR spectra of Artificial Photoelectric experiments

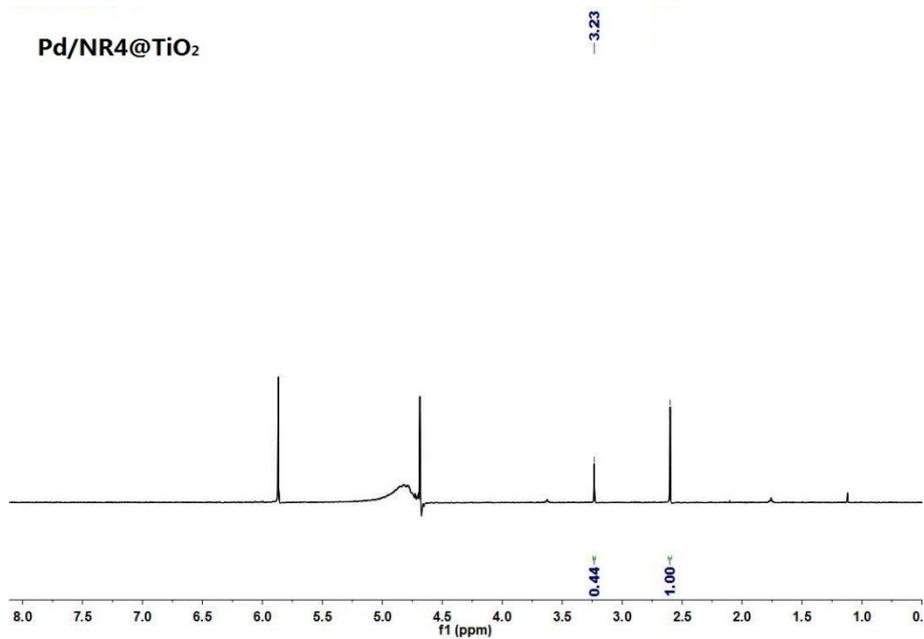
Pd/NR2@TiO₂-4h



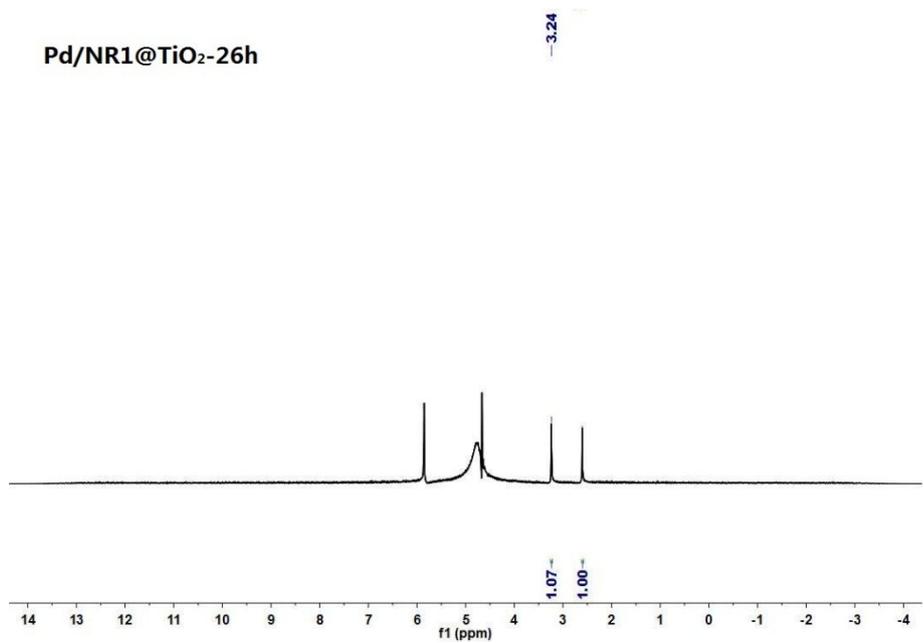
Pd/NR3@TiO₂



Pd/NR4@TiO₂



Pd/NR1@TiO₂-26h



References:

- [S1] Chen, W.; Shen, Y.; Li, Z. Y.; Zhang, M. R.; Lu, C. H. and Shen Y. M. Design and synthesis of 2-phenylnaphthalenoids as inhibitors of DNA topoisomerase II α and antitumor agents. *European J of Medicinal Chem* 2014, 86, 782-796.
- [S2] Pan, J; Chen, M. F.; Warner, W.; He, M. Q.; Dalton, L.; and Hogen-Esch, T. E. Synthesis and Self-Assembly of Diblock Copolymers through Hydrogen Bonding. Semiquantitative Determination of Binding Constants. *Macromolecules*, 2000, 33, 7835–7841.
- [S3] Khrystyna B., Omar K., Svyatoslav P., Volodymyr N., Thierry T. and Patrice V.; Novel Synthesis of 5-Substituted 5H-Benzo[b]carbazole-6, 11-diones via Double Buchwald–Hartwig Reaction. *Synlett* 2014, 25, 2765-2768.
- [S4] Ravichandiran, P.; Jegan, A.; Premnath, D.; Periasamy, V. S. and Vasanthkumar, S. Design, synthesis, molecular docking as histone deacetylase (HDAC8) inhibitors, cytotoxicity and antibacterial evaluation of novel 6-(4-(4-aminophenylsulfonyl)phenylamino)-5Hbenzo[a]phenoxazin-5-one derivatives. *Med Chem Res* 2015, 24, 197–208.
- [S5] Anuratha, M.; Jawahar, A.; Umadevi, M.; Sathe, V. G.; Vanelle, P.; Terme, T.; Meenakumari, V.; Milton Franklin Benial, A. SERS investigations of 2,3-dibromo-1,4-naphthoquinone on silver nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2013, 105, 218–222.
- [S6] Liu, S. L.; Sheng, R.; O'Connor, M. J.; Cui, Y.; Yoon, Y.; Kurilova, S.; Lee, D. and Cho, W. Simultaneous In Situ Quantification of Two Cellular Lipid Pools Using Orthogonal Fluorescent Sensors. *Angew. Chem. Int. Ed.* 2014, 53, 14387-14391.
- [S7] (a), Seabold, J. A.; Choi, K. S. Efficient and Stable Photo-Oxidation of Water by a Bismuth Vanadate Photoanode Coupled with an Iron Oxyhydroxide Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* 2012, 134, 2186–2192; (b), Kim, T. W.; Choi, K. S. Nanoporous BiVO₄ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science*, 2014, 343, 990-994; (c), Cho, S. K.; Park, H. S.; Lee, H. C.; Nam, K. M.; Bard, A. J. Metal Doping of BiVO₄ by Composite Electrodeposition with Improved Photoelectrochemical Water Oxidation. *J. Phy. Chem. C.* 2013, 117, 23048-23056.
- [S8] Kanan, M. W., Nocera, D. G. In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co²⁺. *Science* 2008, 321, 1072–1075.
- [S9] Gou, F. L.; Jiang X.; Fang, R.; Jing, H. W. and Zhu Z. P.; Strategy to Improve Photovoltaic Performance of DSSC Sensitized by Zinc Porphyrin Using Salicylic Acid as a Tridentate Anchoring Group. *ACS Appl. Mater. Interfaces* 2014, 6, 6697–6703.