Supporting Information

An Ambipolar Azaacene as a Stable Photocathode for Metal-Free Light-Driven Water Reduction

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Contents

Experimental Section

Materials

1,4-bis((triisopropylsilyl)ethynyl)phenazine-2,3-diamine and cyclopenta[*fg*]acenaphthylene-1,2,5,6-tetraone were synthesized according to the reported procedure.[1] Other chemicals and solvents were used directly without further purification.

Characterization

Using $CDCl_3$and CF_3COOD (TFA) as solvents and tetramethylsilane (TMS) as the internal standard, ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Advance 300 NMR spectrometer at ambient temperature. High resolution mass spectrum (HRMS) was performed on a Waters Q-Tof premier mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 ^oC/min. The solid-state UV-Vis diffuse-reflectance spectrum was recorded at room temperature on powder samples with a Model UV-2501 PC. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption data were calculated from the reflectance spectrum using the Kubelka–Munkfunction: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient and R is the reflectance.

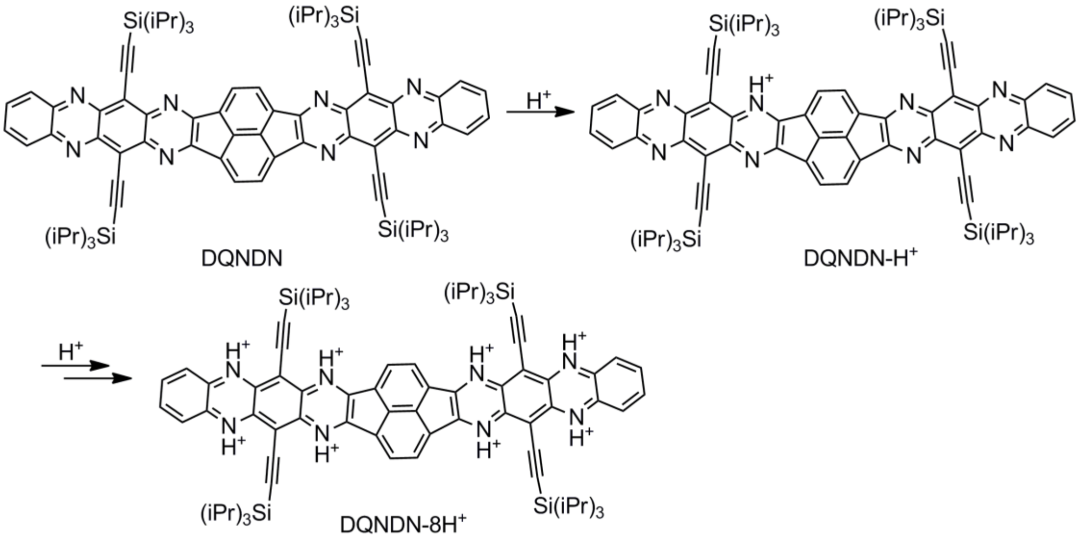
Electrode Preparation

To fabricate the photoelectrode, a well-dispersed 5 mg/mL suspension for DQNDN with pure ethanol as solvent was prepared by brief sonication in a water bath. Fluorine-doped tin oxide (FTO) coated glasses (1.0 × 2.0 cm^2) were used as the substrate. The substrates were cleaned thoroughly by sonication in 5% detergent (Decon ® 90) for 30 minutes first and then rinsed with de-ionized water (DI water) for several times, which were followed by sonication in DI water, acetone, 2-propanol for each 15 minutes. After that, 25 μL of different sample suspensions were dropped onto the surface of FTO substrates, which were masked using Ti foil with an effective area of 0.283 cm^2. The samples were first dried naturally in the dark to avoid the photochemical formation of phosgene, and then placed in a 60˚C oven for 30 minutes.

Photoelectrochemical Measurements

The photoelectrochemical tests were performed using an electrochemical workstation (CHI760E). The PEC property of **DQNDN** nanofibers was measured in a three-electrode electrochemical system with Ag/AgCl electrode in a saturated KCl solution, Pt plate, **DQNDN** nanofiber film, and 0.5 M Na_2SO_4 as reference, counter, working electrodes, and electrolyte under a 300 W xenon lamp (Newport) coupled to an AM 1.5G filter. When **DQNDN** was used as a photoanode in PEC cells, the following reactions were presented:

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+$$



As a result, the performance and stability decreased. However, when **DQNDN** was used as a photocathode, the only following reaction was presented:

$$2H_2O + 4e^- \longrightarrow H_2 + 4OH^-$$

which did not affect the performance and stability of PEC cells.

Mott-Schottky Plot

The Mott-Schottky plot of the **DQNDN** photoelectrode was obtained using impedance-potential technique. The capacitance of the semiconductor-electrolyte interface was collected at 1000 Hz, with 10mV AC voltage amplitude, in the same electrolyte (0.5 M Na_2SO_4) and setup for photoelectrochemical measurements. To convert the measured voltage into the voltage vs. the reversible hydrogen electrode (RHE), the following calculation was performed: $V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059 \times pH$.

Synthesis of DQNDN

A mixture of 1,4-bis((triisopropylsilyl)ethynyl)phenazine-2,3-diamine (285 mg, 0.5 mmol) and cyclopenta[*fg*]acenaphthylene-1,2,5,6-tetraone (47 mg, 0.2 mmol) in acetic acid/chloroform (150 mL, v:v = 1:1) was stirred and refluxed under nitrogen for 72 h. After cooling to room temperature, the mixture was poured into methanol and the obtained precipitate was isolated by filtration and washed with methanol. The crude product was dispersed into chloroform and stirred for 1 h. The obtained precipitate (177, 0.136 mmol, 68%) was isolated by filtration and washed with chloroform, THF, DMF, methanol.

^{1}H NMR (300 MHz, TFA) δ 8.98 (s, 4H), 8.68 (s, 4H), 8.55 (s, 4H), 1.66 – 1.35 (m, 84H).

^{13}C NMR (75 MHz, TFA) δ 155.32, 139.09, 134.82, 134.52, 133.79, 132.30, 129.08, 123.00, 121.36, 117.49, 92.64, 13.19, 7.03.

HR-MS, formula, $C_{82}H_{96}N_8Si_4$, calc. mass, 1305.6913, found, 1305.6953.

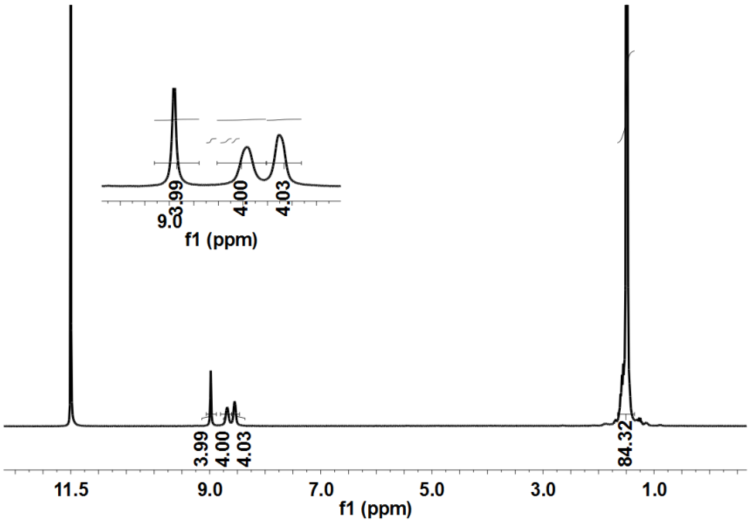


Figure S1 ^{1}H NMR spectrum of **DQNDN** in CF_3COOD (TFA).

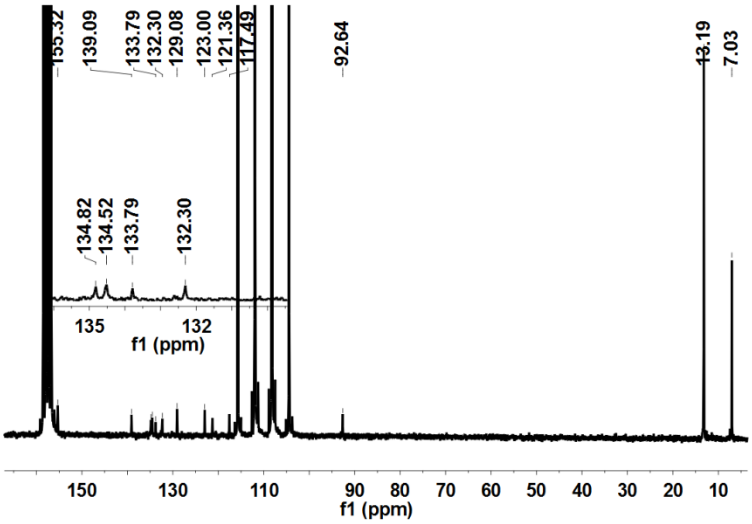
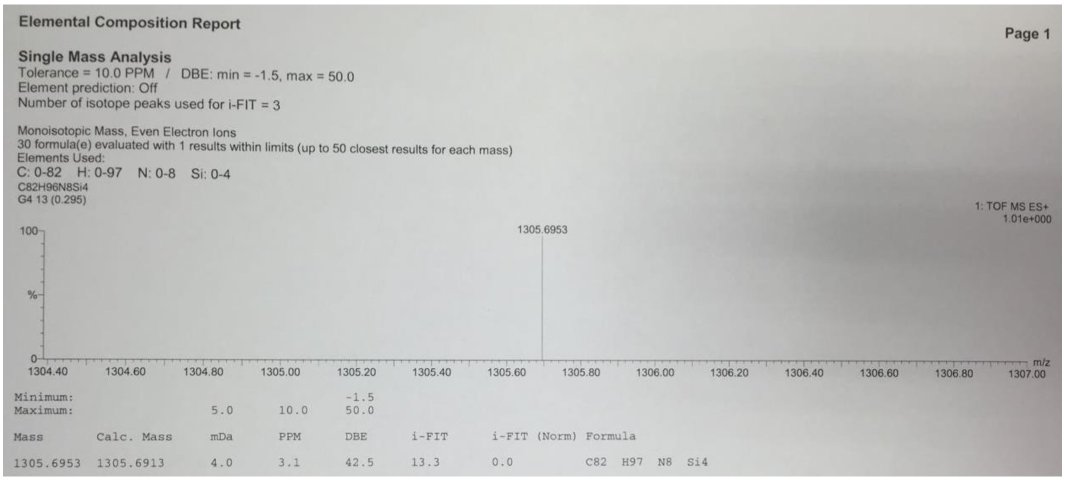


Figure S2 ^{13}C NMR spectrum of **DQNDN** in TFA.



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-82 H: 0-97 N: 0-8 Si: 0-4
C82H96N8Si4
G4 13 (0.295)

1: TOF MS ES+
1.01e+000

```
Minimum:                                   -1.5
Maximum:                   5.0      10.0   50.0

Mass       Calc. Mass      mDa      PPM    DBE      i-FIT      i-FIT (Norm) Formula

1305.6953  1305.6913       4.0      3.1    42.5     13.3       0.0          C82  H97  N8  Si4
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Figure S3 HR-MS of **DQNDN**.

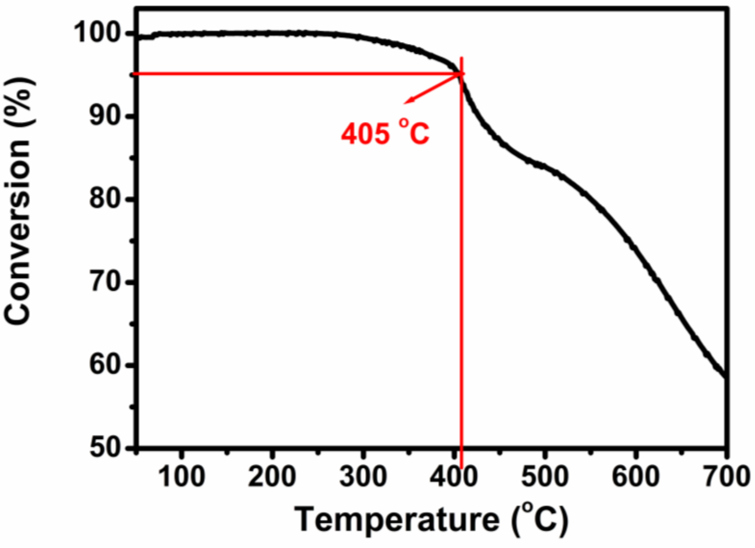

Figure S4 TGA curve of **DQNDN**.

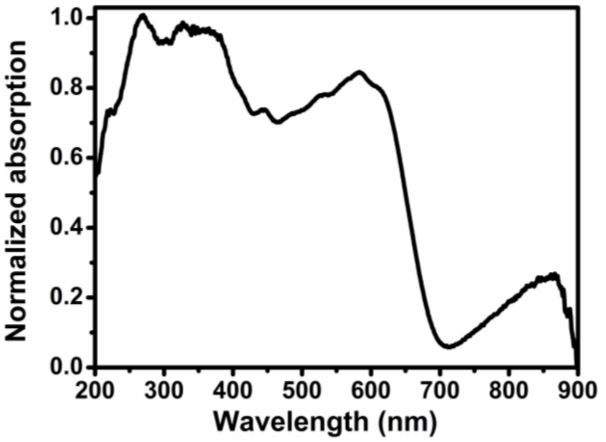

Figure S5 Solid-state absorption spectrum of **DQNDN** nanofibers.

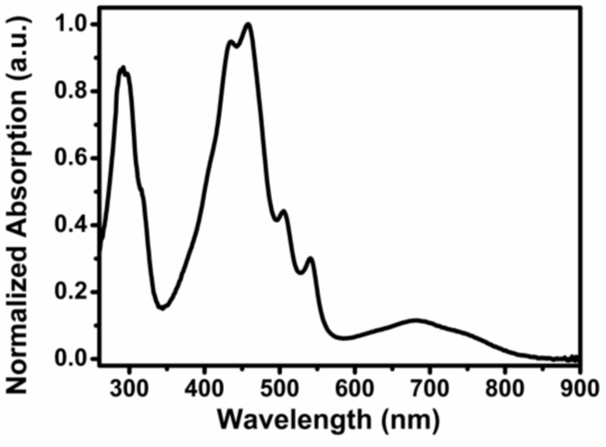

Figure S6 Normalized absorption spectrum of **DQNDN** in TFA.

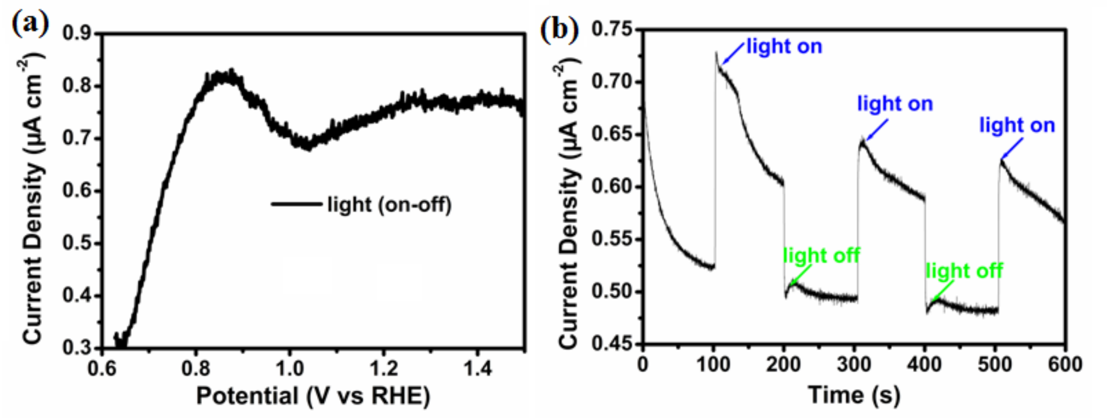

Figure S7 (a) The current density-potential curve of **DQNDN** nanofibers; (b) the transient photocurrent density of **DQNDN** nanofibers under 1.23 V versus RHE.

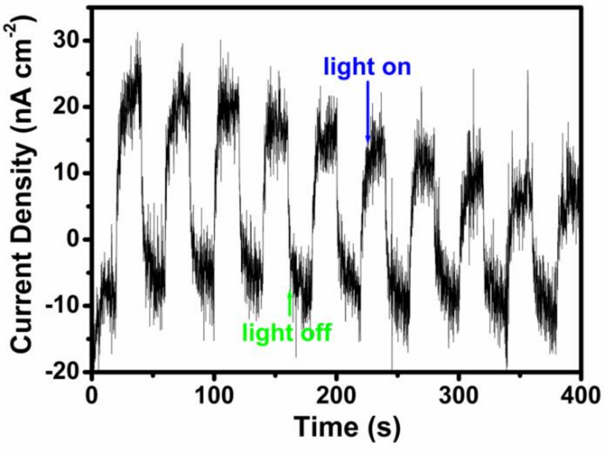

Figure S8 The transient photocurrent density of **DQNDN** nanofibers under 0.61 V versus RHE.

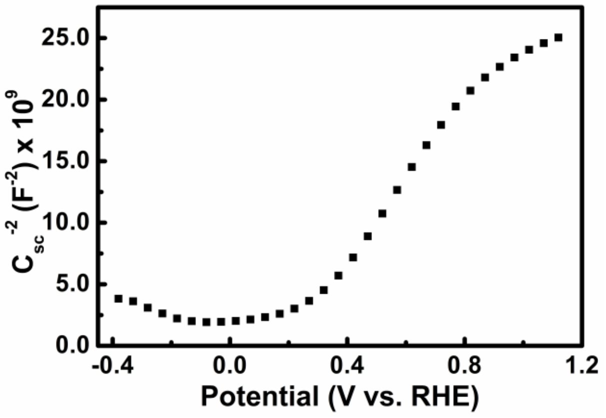

Figure S9 Mott-Schottky plot of **DQNDN** nanofibers.

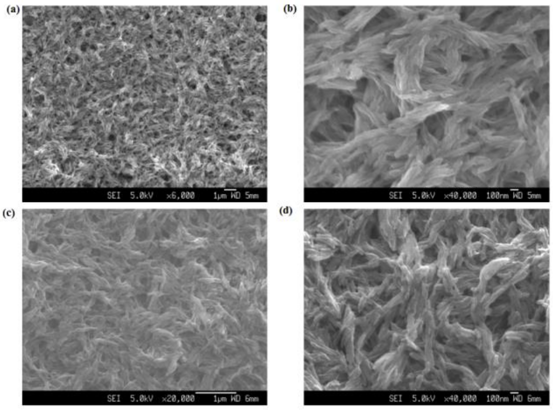

Figure S10 SEM images of nanostructured **DQNDN** nanofibers before (a, b) and after i-t measurement (c, d). (a,c) Low resolution and (b,d) high resolution.

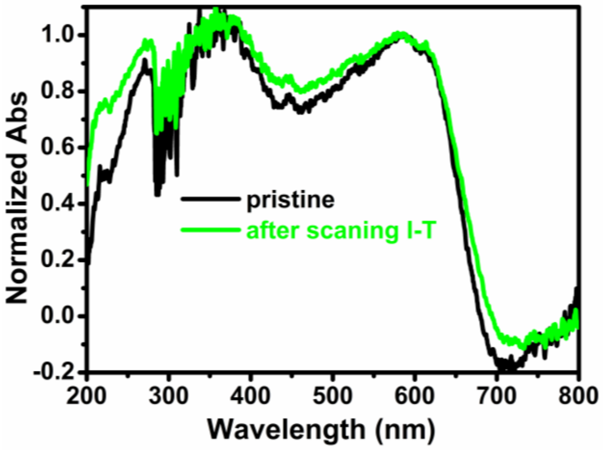

Figure S11 Solid-state absorption spectrum of **DQNDN** before and after i-t measurement.

References

1 B. D. Lindner, J. U. Engelhart, O. Tverskoy, A. L. Appleton, F. Rominger, A. Peters, H. J. Himmel and U. H. Bunz, *Angew. Chem. Int. Ed.*, 2011, **50**, 8588-8591.

2 L. Zhu, Z.-S. Fu, H.-J. Pan, W. Feng, C. Chen and Z.-Q. Fan, *Dalton Trans.*, 2014, **43**, 2900-2906.