Selective Formation of Benzo[c]cinnoline by Photocatalytic Reduction of 2,2′ Dinitrobiphenyl with TiO_2 and UV light irradiation

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Supporting Information

Content:

1. Materials

Degussa P25-TiO_2, iso-propanol, acetonitrile were purchased from Loba Chemicals. DNBP ($C_{12}H_8N_2O_4$) was purchased from sigma Aldrich, BC ($C_{12}H_8N_2$) was purchased from Alfa Aesar and used without further purification. Deionized water was obtained using an ultrafiltration system (Milli-Q, Millipore) with a measured conductivity 35 mho cm^{-1} at 25 $^{\circ}$C.

2. Product analysis methods

High Performance Liquid chromatography (HPLC): spectra were acquired by Agilent 1120 Compact LC equipped with a Qualisil BDS C-18 column (250 mm × 4.6 mm, 5 µm), at λ = 254 nm with flow rate 1 mL/min. The eluent consisted of: 70% methanol, 30% water aqueous solution. The reaction sample was centrifuged and filtered through cellulose filter (0.22 µm) and 20 µL of it was injected into the HPLC. The retention times of the compounds were compared with those of authentic samples.

Gas Chromatography-Mass Spectroscopy (GC-MS): spectra were measured by Shimadzu GC 2010 and MS QP 2010 Plus equipped with RTX-5 Sil MS column (30 m × 0.25 mm i.d.). Injection temperature was 270 °C, injection mode was split less, injection volume was 1 µL taken by using a 10 µL syringe, electron ionisation detector with temperature 310 °C, oven temperature was 100 °C, and carrier gas was helium with flow rate 1 mL/ min. The reaction solution (5 mL) obtained after photoreduction of DNBP was subjected to centrifugation, filteration (cellulose filter 0.22 µm), and then evaporated to dryness over rota-evaporator. Residue was dissolved in acetonitrile (5 mL) and injected (1 µL) for GC-MS analysis.

Calculations for DNBP reduced and BC produced done by GC chromatographs (Fig. 1 in the manuscript) in the reaction sample are as follows:

(i) Quantification of DNBP reduced after 8 h UV irradiation

5 mL DNBP (5 mM in acetonitrile) contains 25 µmol, peak height = 1.4 mAU (Fig. 1a)

After 8 h photoreduction of DNBP its peak height is 0.1 mAU (Fig. 1c)

$$\text{Amount of DNBP left or unreacted} = \frac{25\ \mu\text{mol} \times 0.1\ \text{mAU}}{1.4\ \text{mAU}} = 1.7\ \mu\text{mol}$$

Amount of DNBP reduced = 25- 1.7 = 23.3 µmol

(ii) Quantification of reaction product BC produced after 20 h UV irradiation

5 mL BC (1.5 mM) in acetonitrile contains 7.5 µmol, peak height is 0.88 mAU (Fig. 1b)

After 20 h photoreduction, BC peak height is 2.8 mAU (Fig. 1e)

$$\text{Amount of BC produced} = \frac{7.5\ \mu\text{mol} \times 2.8\ \text{mAU}}{0.88\ \text{mAU}} = 23.8\ \mu\text{mol}$$

Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR): spectra were recorded on Jeol-400 (^{1}H, 400 MHz) spectrometer at ambient temperature using $CDCl_3$ as solvent. Chemical shifts are reported in ppm from the solvent resonance. Data are reported as follows: chemical shift, multiplicity (d =doublet, dd =double doublet, m =multiplet, t =triplet, bs =broad spectrum), coupling constants and number of protons. Reaction solution from five test tubes was collected, centrifuged, filtered by cellulose filter (0.22 µm) and evaporated to dryness over rota evaporator. Residue was dissolved in $CDCl_3$ (0.5 mL) for NMR analysis. The NMR spectra of authentic

samples were taken by dissolving authentic DNBP (10 mg) and authentic BC (10 mg), separately in $CDCl_3$ (0.5 mL).

Gas chromatograph (GC):

The amount of acetone in the liquid phase was determined by Gas chromatograph [Bruker SCION 436-GC equipped with a fused-silica capillary column (BR-1, 10 m, 0.53 mm)] and flame ionization detector. The column oven temperature was kept at 50 °C for 1 min, temperature programmed at 10 °C/min up to 250 °C. The injection port was maintained at 230 °C, and the detector was maintained at 230 °C. All the samples were studied by injecting 0.1 μL (using 1 μL syringe) of the sample solution with nitrogen as a carrier gas at a constant flow rate of 1 mL/min. The reaction solution (1 cm^3) was added to a chloroform/water mixture (2:1 v/v, 3 cm^3). After the mixture had been stirred for 10-15 min, acetone in the chloroform phase was analysed.

The detection of CO_2 evolution during the photoreduction of DNBP was determined by injecting 1 mL of gaseous mixture from the reaction vessel (gas tight test tube) into GC (NUCON-5765) equipped with Thermal Conductivity Detector (TCD) and Porapak-Q column (2 m × 2 mm i.d.) having flow of nitrogen (30 mL/min) as carrier gas. Column oven was maintained at 40 ^oC while injector and detector were isothermally kept at 70 and 80 ^oC, respectively.

3. Figures

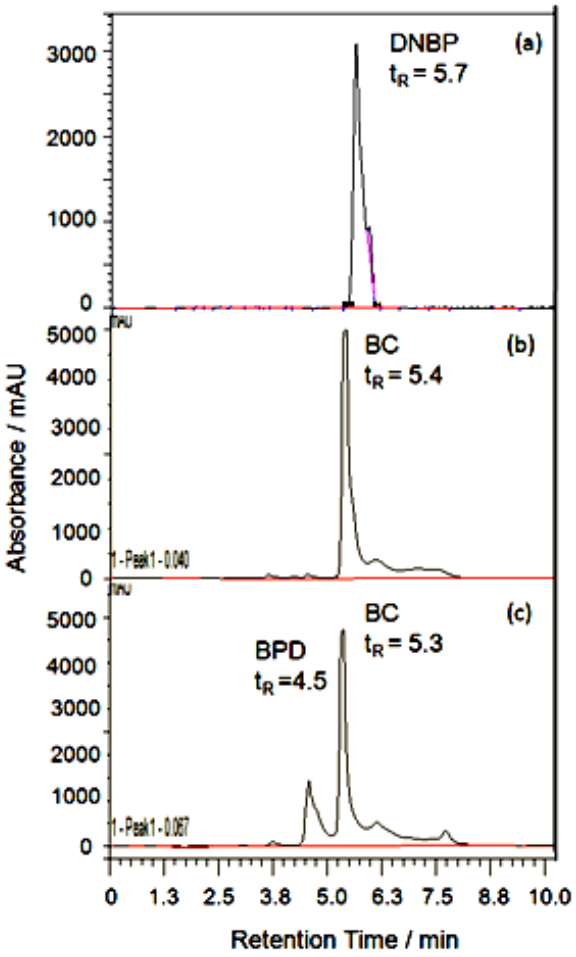

Fig. S1 HPLC Chromatograms of (a) DNBP authentic (25 µmol) (b) BC authentic (25 µmol) (c) reduction products of DNBP (25 µmol) with TiO_2 by 20 h light irradiation produced 23.7 µmol BC.

Calculations for the quantification of BC produced after the photoreduction of DNBP (25 µmol) under 20 h UV light irradiaton analysed by HPLC (Fig. S1) is as follows:

5 mL of BC (5 mM) in 50% IPA contains 25 µmol, peak height is 5150 mAU (**Fig. S1b, ESI)**

After 20 h photoreduction, BC peak height is 4900 mAU (**Fig. S1c, ESI)**

$$\text{Amount of BC produced} = \frac{25\ \mu\text{mol} \times 4900\ \text{mAU}}{5150\ \text{mAU}} = 23.7\ \mu\text{mol}$$

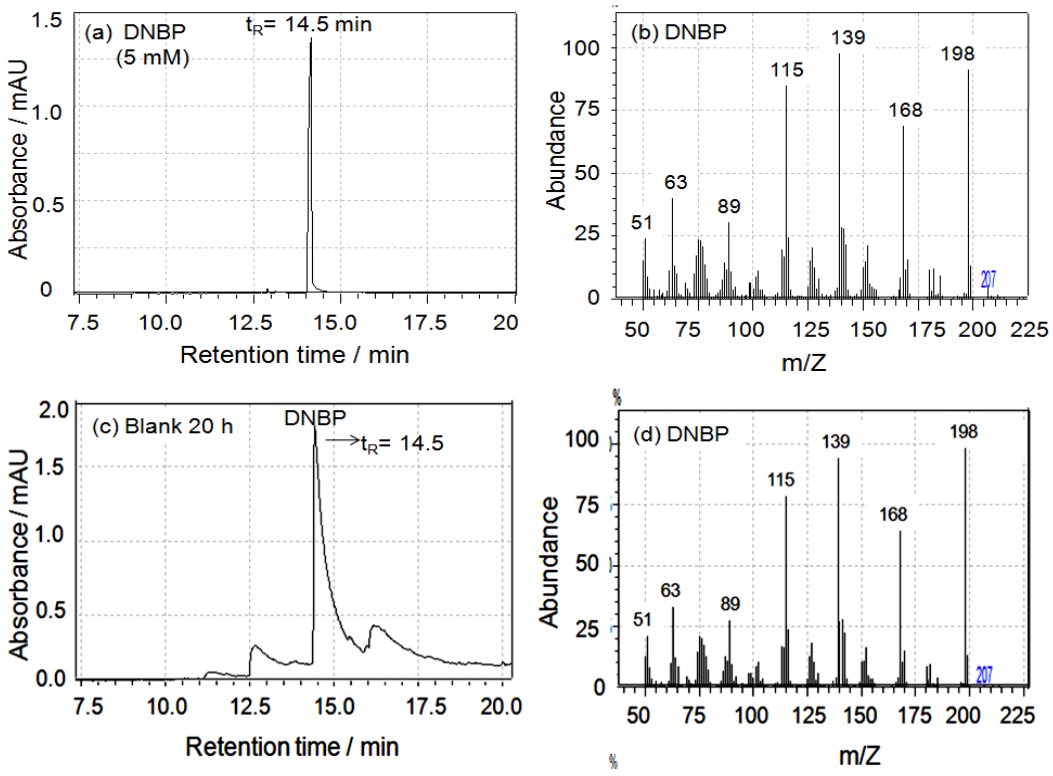

Fig. S2 (a) GC pattern of authentic DNBP (5 mM = 25 µmol) (b) its mass spectra (c) blank reaction after 20 h of UV irradiation and (d) its mass spectra showing mass of DNBP corresponding to peak at t_R = 14.5 min .

Reproducibility test:

HPLC chromatographs of a fresh reaction of DNBP (25 µmol) with 50 mg TiO_2 under 20 h UV irradiation was carried out recently on 19.3.2015

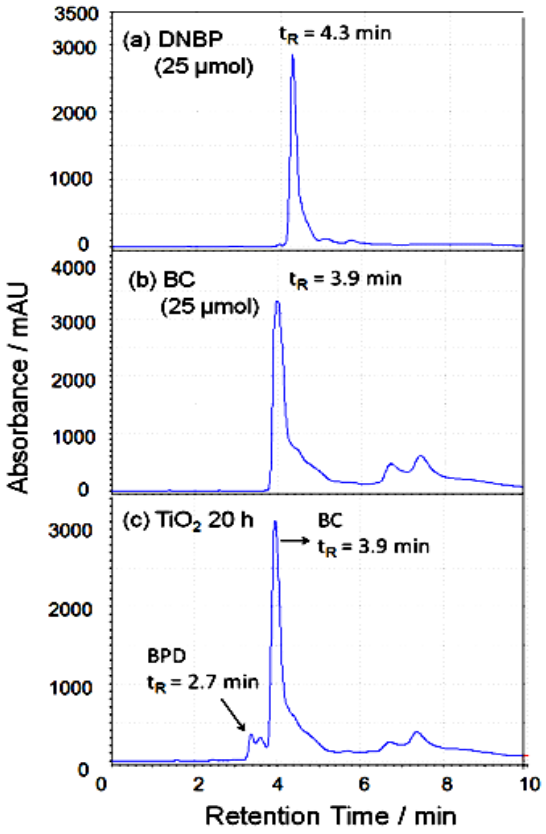

Fig. S3 HPLC pattern of (a) authentic DNBP (25 µmol) (b) authentic BC (25 µmol) (c) major products, BC (23.2 µmol) formed during DNBP (25 µmol) photoreduction by TiO_2 under 20 h of UV irradiation.

Calculations for quantification of BC in the fresh reaction analysed by HPLC (as shown above) as follows:

5 mL of 5 mM BC in 50% IPA contains 25 µmol, peak height is 3450 mAU (**Fig. S3b, ESI)**
After 20 h photoreduction, BC peak height is 3111 mAU (**Fig. S3c, ESI)**

$$\text{Amount of BC produced} = \frac{25\ \mu\text{mol} \times 3111\ \text{mAU}}{3450\ \text{mAU}} = 23.2\ \mu\text{mol}$$

Thus, obtained results confirm the reproducibility of BC formation during DNBP photoreduction.

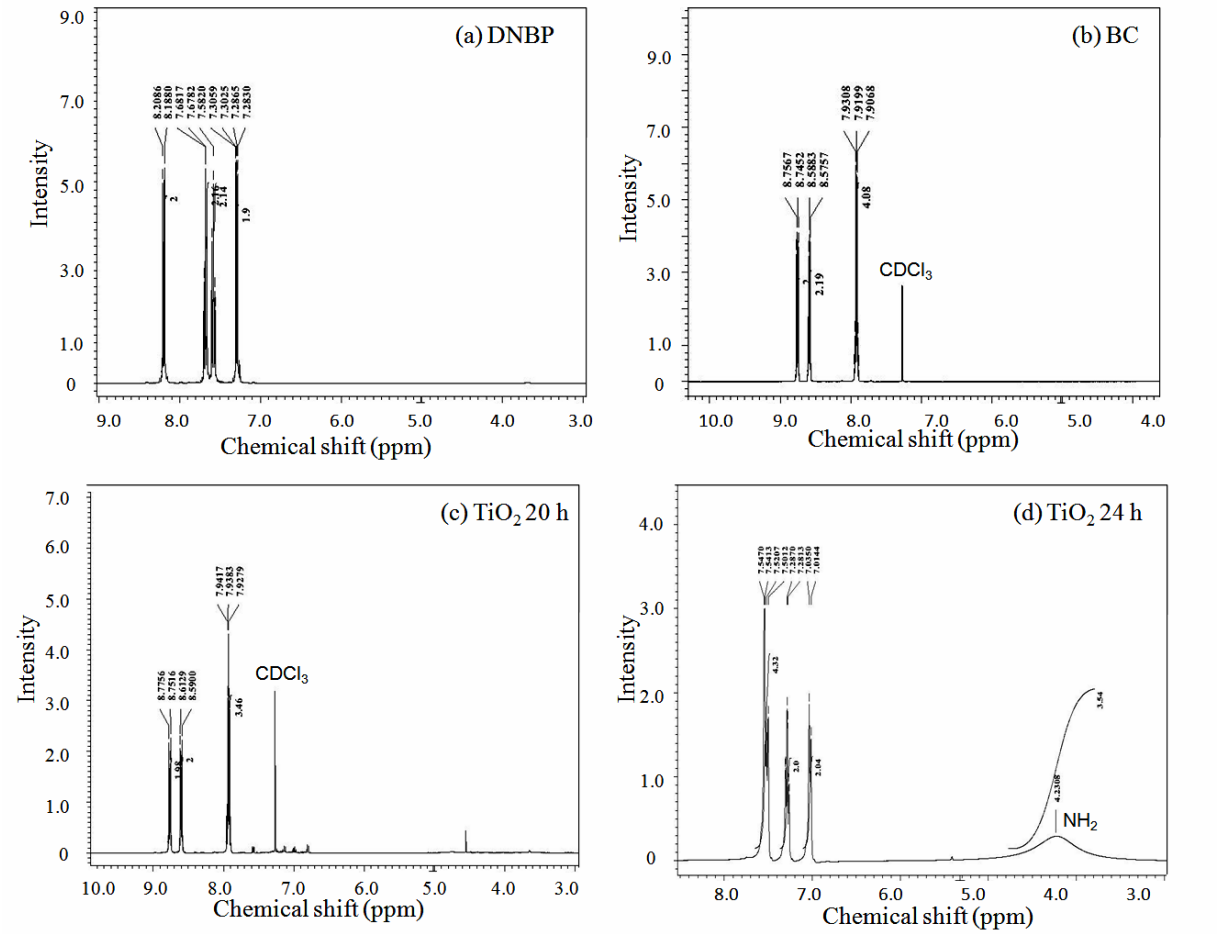

Fig. S4. NMR spectra of authentic (a) DNBP (b) BC and DNBP reduction product by TiO_2 after (c) 20 h and (d) 24 h UV irradiation.

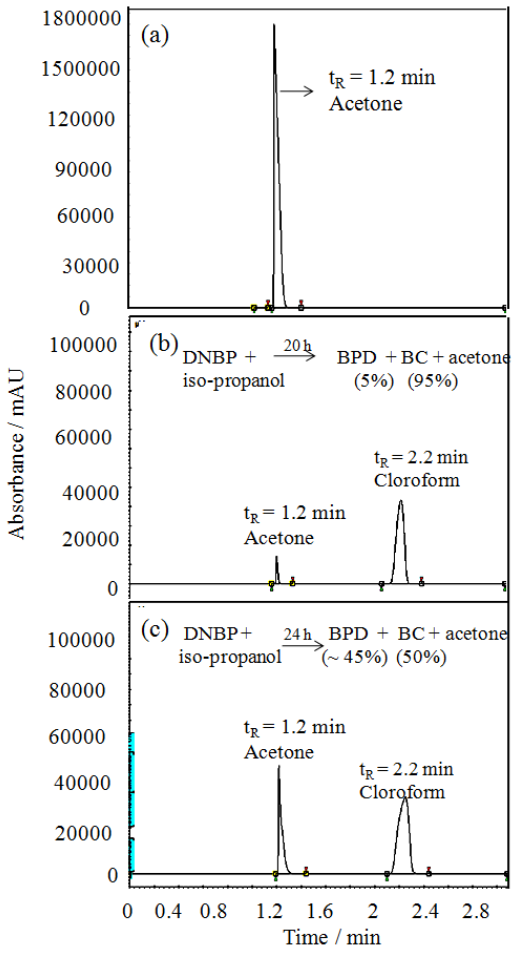

Fig. S5 GC pattern of (a) authentic acetone sample (b) acetone produced by the photoreduction of DNBP (25 µmol) by TiO_2 during 20 h and (c) 24 h UV irradiation.

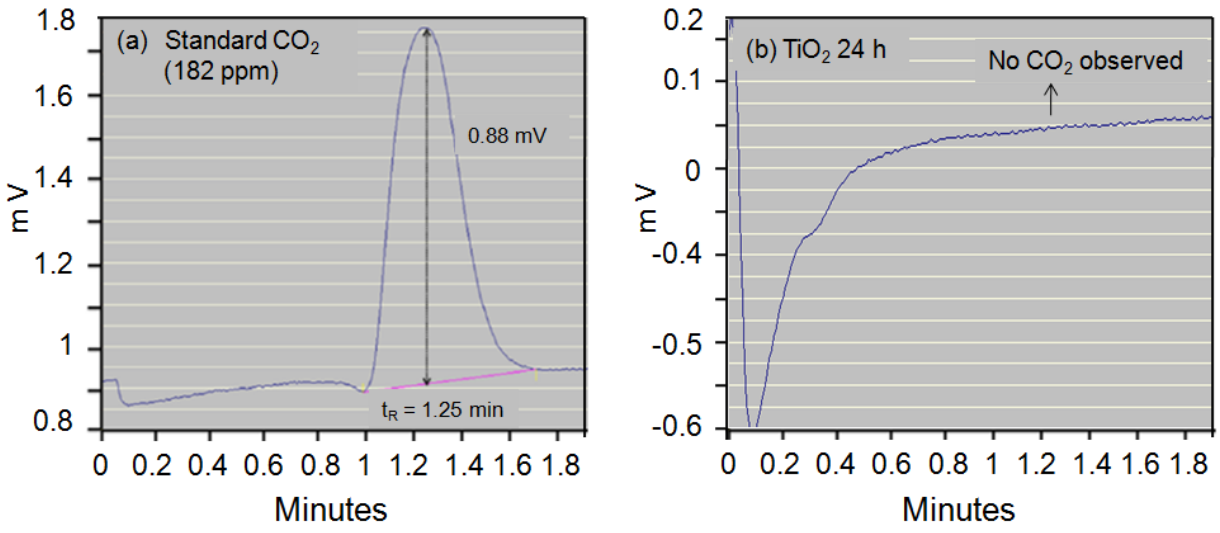

Fig. S6 GC chromatographs of (a) Standard CO_2 of 180 ppm (b) DNBP reaction with TiO_2 after 24 h of UV light irradiation (no peak for CO_2 at 1.25 min).