Supporting information

β-Cyclodextrin/TiO₂: Green Nest for Reduction of Nitroaromatic Compounds

Mazaher Abdollahi Kakroudi^a, Foad Kazemi^{a,b} *, Babak Kaboudin^a

^a Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), 49195-1159, Zanjan, Iran ^bCenter for Climate and Global Warming(CCGW), Institute for Advanced Studies in Basic

Sciences (IASBS), Gava Zang, Zanjan, Iran *e-mail: kazemi_f@iasbs.ac.ir

Table of Contents:

- 1. Materials and Apparatuses
- 2. General experimental procedure for photocatalytic reduction of nitroaromatic compounds
- 3. General procedure for one-pot photo-reductive *N*-formylation and *N*-acylation of nitroaromatic compounds
- 4. UV-Vis analysis of *o*-amino phenol and *o*-nitro phenol with addition of β -CD solution
- 5. TGA curve for the β -CD-TiO₂
- 6. DRS (Diffuse reflectance spectra) of the β -CD-TiO₂
- 7. Nitrogen adsorption-desorption isotherm of the β -CD-TiO₂
- 8. TEM images of TiO₂ P25 and β -CD-TiO₂
- 9. Raman spectroscopy of β -CD-TiO₂ and TiO₂ P25
- 10. FT-IR spectroscopy of β -CD-TiO₂ and TiO₂ P25
- 11. ¹³C NMR and ¹H NMR of the amide products

1. Materials and Apparatuses

All the reagents purchased from Merck, Aldrich and used without further purification. TiO_2 p25 was purchased from Degussa.

N₂ adsorption-desorption isotherms were obtained at 77 K using BELSORP max apparatus.

UV-Visible diffusive reflectance spectra (DRS) were measured on Varian Cary 100 UV-Vis spectrophotometer with diffuse reflectance accessory, samples were mixed in BaSO₄ (1:20 sample BaSO₄) and pressed into a tablet, a BaSO₄ tablet made under the same conditions was used as a reference. The photoluminescence (PL) spectra were measured at 25 °C with a fluorospectrophotometer (Varian) using Xe lamp as an excitation source. Photocatalytic reduction test was also carried out under daily sunlight irradiation (9 am– 3pm, sunlight intensity between $10-80 \times 10^3$ Lux).

2 General experimental procedures for photocatalytic reduction of nitro compounds under sunlight irradiations

 β -CD (0.1 mmol) was dissolved in water (15 ml) by warming to 60 °C until a clear solution was formed. Nitro compounds (0.1mmol) were added to this solution and were sonicated for 10 min. Then, commercial TiO₂ (P25) (30 mg) and oxalic acid (15 mg) was added into a round bottom Pyrex flask (25 ml). The reaction mixture was degassed by Ar gas (20 min) and sealed with a septum. Afterwards, the flask was irradiated under stirring with sunlight according to the data in Table1. After the completion of the reaction, a suitable amount of NaHCO₃ were added *p*H to control the around 7 and the mixture was stirred at room temperature. The organic material was extracted with ethyl acetate. The organic phase was then dried using anhydrous MgSO₄. The reaction mixture was analyzed with Gas Chromatograph.



Fig S1. Reduction of nitro compounds using β -CD-P25 TiO₂ under sunlight irradiations in water.

The mole ratio of nitro to ammonium formate is 1 to 3.2 and nitro to oxalic acid is 1 to 1.7. The ammonium formate and oxalic acid convert to ammonia, carbon dioxide or carbon dioxide during photocatalytic reaction respectively. We found that, in experimental control test, when the reaction carried out in the presence of excess amount of ammonium formate, amine product was obtained in quantitative yield after separation by extraction with EtOAc. The aqueous phase including excess of ammonium formate can be used for next reduction cycle without loss of the conversion yield.



Scheme S1. Two cycles reduction of 3-nitroacetophenone in the presence of excess amount of ammonium formate.

3. General procedure for one-pot *N*-formylation and *N*-acylation of nitro compounds under sunlight irradiations

 β -CD (0.1 mmol) was dissolved in water (15 ml) by warming to 60 °C until a clear solution was formed. Nitro compounds (0.1mmol) were added to this solution and were sonicated for 10 min. Commercial TiO₂ (P25) (30 mg), ammonium formate (25 mg) and triethy orthoformate (0.2 ml) for formylation or anhydride (0.12 mmol) were added into a round bottom Pyrex flask (25 ml). The reaction mixture was degassed by Ar gas (20 min) and sealed with a septum. Afterwards, the flask was irradiated under stirring with sunlight according to the data in Table 3. The organic material was extracted with ethyl acetate. The organic phase was then dried (anhydrous MgSO₄), filtered, and the solvent was removed under vacuum. Pure products were obtained after recrystallization or by column chromatography on silica using the n-hexane and ethyl acetate mixture as an eluent (SiO₂; n-Hexane, EtOAc 5:1).



Fig S2. One-pot photo-reductive *N*-formylation and *N*-acylation of nitro compounds using β -CD-P25 TiO₂ under sunlight irradiations in water.

4. UV-Vis spectra data



Fig S3. UV-Vis titration of 2-Amino phenol with β -CD solution



Fig S4. UV-Vis titration of 2-Nitro phenol with β -CD solution





Fig S5. TG/DTG analysis of β -CD-P25 TiO₂

6. DRS (Diffuse reflectance spectra) of β -CD-TiO₂



Fig S6: UV–vis absorption spectra (a) plot of the transformed Kubelka–Munk function versus the energy of light absorbed by the TiO₂ (b) and (c) CD-TiO₂

7. Nitrogen adsorption-desorption isotherm of the β -CD-TiO₂ and TiO₂ P25

Table S1: Physical Properties of the Catalysts

Catalyst	BET (m²/g)	Pore volume (cm ³ /g)
TiO ₂ P25	70	0.6
β -CD-TiO ₂ P25	48	0.48



FigS7: N₂ Adsorption / desorption isotherm of TiO₂ P25 (left) and β -CD-TiO₂ P25 (right).



8. TEM images of β -CD-TiO₂ and TiO₂ P25

Figure S8: TEM images of β -CD-TiO₂(a) and TiO₂ P25 (b)



9- Raman spectroscopy β -CD-TiO₂ and TiO₂ P25

Fig S9. Raman spectra of β -CD-TiO₂ and TiO₂ P25



10- FT-IR Spectra of β -CD-TiO₂ and P25 TiO₂

Fig. S10: FT-IR Spectra of β -CD-TiO₂



Fig S11. FT-IR Spectra of P25 TiO₂

11.13C NMR, 1H NMR and FT-IR data of the amide compounds



N-phenylbenzamide

Melting point: 159–161 °C, (162 °C); IR (KBr): v3340, 1655, 1593, 1526, 1434, 1316, 1255, 1025, 803, 751, 686, 646, 503 cm⁻¹; ¹H-NMR (250 MHz; CDCl₃; TMS): $\delta_{\rm H} = 7.87$ (d, J = 6.75 Hz, 3H), 7.65 (d, J = 7.75 Hz, 2H), 7.58-7.46 (m, 3H), 7.38 (t, J = 7.5 Hz, 2H), 7.16 (t, J = 7.25 Hz, 1H); 13C-NMR (62.9 MHz, CDCl₃; TMS): $\delta_{\rm C} = 209$, 165.0, 157.0, 131.9, 129.1, 128.8, 127.0, 124.6, 120.1.



N-phenylacetamide

Melting point: 112–114 °C, (114–115 °C); ¹H-NMR (250 MHz; CDCl₃; TMS): δ H = 7. (d, *J*=7.75 Hz, 2H), 7.32 (t, *J*=7.5 Hz, 2H), 7.11 (t, *J*=7.25 Hz, 1H), 2.19 (s, 3H); ¹³C-NMR (62.9 MHz, CDCl₃; TMS): δ C = 168.5, 137.9, 129.0, 124.3, 119.9, 24.5.

N-(p-tolyl) acetamide

Melting point: 151–154 °C, (151 °C); ¹H-NMR (250 MHz; CDCl₃; TMS): δH = 7.37 (d, *J*=8 Hz, 2H), 7.11 (d, *J*=8 Hz, 2H), 2.31 (s, 3H), 2.15 (s, 3H); ¹³C-NMR (62.9 MHz, CDCl₃; TMS): δC = 168.3, 135.3, 133.9, 129.4, 120.0, 24.5, 20.8.



N-(4-benzoylphenyl) acetamide

Boiling Point: 459 °C; ¹H-NMR (250 MHz; CDCl₃; TMS): δH = 10.04 (s, 1H), 7.21-7.66 (m, 9H), 1.73 (s, 3H); ¹³C-NMR (62.9 MHz, CDCl₃; TMS): δC = 195.5, 168.5, 137.6, 136.7, 132.9, 132.1, 131.3, 130.2, 129.9, 128.5, 124.5, 124.0, 23.5.



N-(2-acetylphenyl) benzamide

Boiling Point: 367.4 °C; ¹H-NMR (250 MHz; CDCl₃; TMS): δH = 10.04 (s, 1H), 7.21-7.66 (m, 9H), 1.73 (s, 3H); ¹³C-NMR (62.9 MHz, CDCl₃; TMS): δC = 195.5, 168.5, 137.6, 136.7, 132.9, 132.1, 131.3, 130.2, 129.9, 128.5, 124.5, 124.0, 23.5.



2-Methylbenzimidazole

¹H NMR (400 MHz, CDCl₃): δ 2.67 (s, 3 H), 7.26 (m, 2H), 7.57 (m, 2H), 8.42 (b, s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.8, 114.4, 122.3, 138.4, and 151.0.

All N-formamide products gave satisfactory spectroscopic data according to the literature [1-6].

N-p-tolylformamide

Melting point: 52-54°C

N-phenylformamide Melting point: 48-50 °C

HC

N-(4-Hydroxyphenylformamide)

Melting point: 140-143 °C

Reference

- [1] M. Hosseini-Sarvari, J. Sharghi. J. Org. Chem., 2006, 71, 6652.
- [2] A. Khazaei, E. Mehdipour, Iran Polym. J., 1999, 8, 257.
- [3] K. Bao, W. Zhang, X. Bu, Z. Song, L. Zhang, M. Cheng. Chem. Commun., 2008, 5428.
- [4] H. Tumma, N. K. Nagaraju, V. Reddy. J. Mol. Catal. A: Chem. 2009, 310, 121.
- [5] G. Brahmachari, S. Laskar., Tetrahedron Lett. 2010, 51, 2319.
- [6] T. V. Pratap, S. Baskaran. Tetrahedron Lett., 2001, 42, 1983.