

Cu (II) Vitamin C-complex Catalyzed Photo-Induced homocoupling reaction of aryl boronic acid in base-free and visible light conditions

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General Remarks

All chemicals were purchased from Chemical Companies. The FT-IR spectra were recorded on NICOLET system. The TGA measurements were obtained by a TGA-50 (Shimadzu) at the heating rate of 10 °C min⁻¹ flowing air atmosphere. TEM images were obtained by TEM instrumentation (Philips CM 10). Inductively coupled plasma (ICP) atomic emission spectroscopy was conducted with an OPTIMA 7300DV. Diffuse reflectance UV–Vis spectra were recorded using an Avantes spectrometer (Avaspec-2048-TEC model). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a PHI 1600 ESCA XPS system. Progresses of the reactions were monitored by TLC using silica-gel SIL G/UV 254 plates and also by GC-FID on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 µm coating) capillary column. NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument.

Preparation of TiO₂

To a solution of TiCl₃ (0.05 mol) in a mixture of double-distilled water and absolute ethanol (1:1) was added citric acid (0.15 mol) and ethylene glycol (0.15 mol) subsequently. The resulting mixture was dissolved at 45 °C under ultrasound for 15 min to give a clear violet solution. The solution was refluxed at 120 °C for 8 h which turned into a metal–citrate homogeneous complex with a little color change from clear violet to black-violet. After cooling down, in order to bring about the required chemical reactions for the development of polymerization and evaporation of the solvent, the sol was further slowly heated at 90 °C for 6 h in an open bath until a beige wet gel was obtained. During continuous heating at this temperature, the polymerization between citric acid, ethylene glycol, and complexes is developed and ultimately sol became more viscous as a wet gel. In the final step of the sol-gel process, the wet gel was fully dried by direct

heating on the hot plate at 150 °C for 6 h. The resultant production was black powder. Then it was calcined in a furnace at 600 °C for 3 h at a rate of 5 °C min⁻¹.

TiO₂ nanoparticles of approximately 18-20 nm diameters were prepared by the PC sol-gel method.

Preparation of TiO₂-AA nanohybrid

To 1.0 gr TiO₂ particles were gradually added 10.0 mL of 0.01 M ascorbic acid in water over a period of 20 min at room temperature under ultrasonic agitation. Then, the reaction mixture was stirred at room temperature for 8 h. Afterwards, the product was centrifuged and washed with distilled water. Finally, TiO₂-AA nanohybrid was obtained after drying for 4 h at 100 °C.

Preparation of TiO₂-AA-Cu nanohybrid

For fabrication of TiO₂-AA-Cu nanohybrid, 1.0 mmol Cu(OAc)₂ dissolved in ethanol was gradually added to 0.2 gr of TiO₂-AA over a period of 20 min at room temperature under ultrasonic agitation. Then, the as-obtained mixture was refluxed for 12 h. Afterward, the product was centrifuged and washed with ethanol. Finally, TiO₂-AA-Cu nanohybrid was obtained after drying for 12 h at 100 °C.⁴⁶

GC program condition

The quantification of biphenyls was carried out by using a Shimadzu-16A gas chromatograph equipped with a flame ionization detector and a Rtx®-1 fused-silica capillary column with a 30 m × 0.25 mm I.D. In a typical procedure for biphenyl, 3 µl of the reaction mixture containing acetophenone as internal standard was injected. The injection port and detector were operated at 275 and 285°C, respectively. The Ar was used as carrier gas. The column was held at 100°C for 1 min, increased to a final temperature of 260°C at a ramp of 10°C·min⁻¹ and then held for 5 min in this temperature.

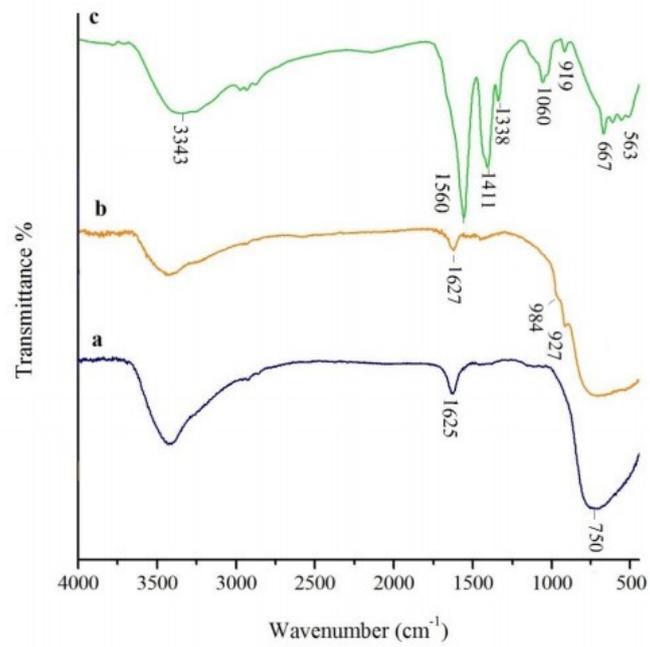


Fig S1. FTIR spectra of (a) TiO₂, (b) TiO₂-AA, (c) TiO₂-AA-Cu (II) nanohybrid

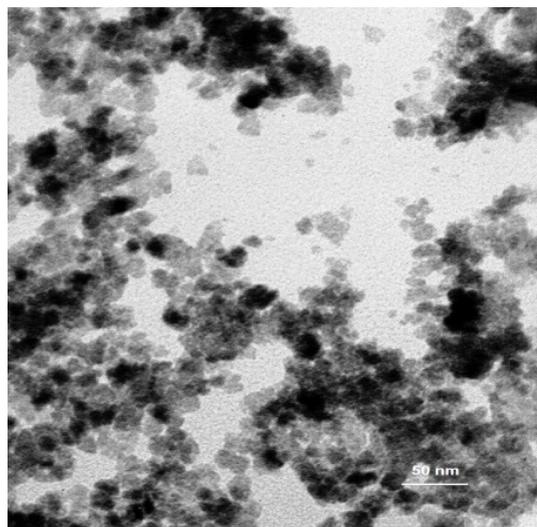


Fig S2. TEM image of TiO₂-AA-Cu (II) nanohybrid

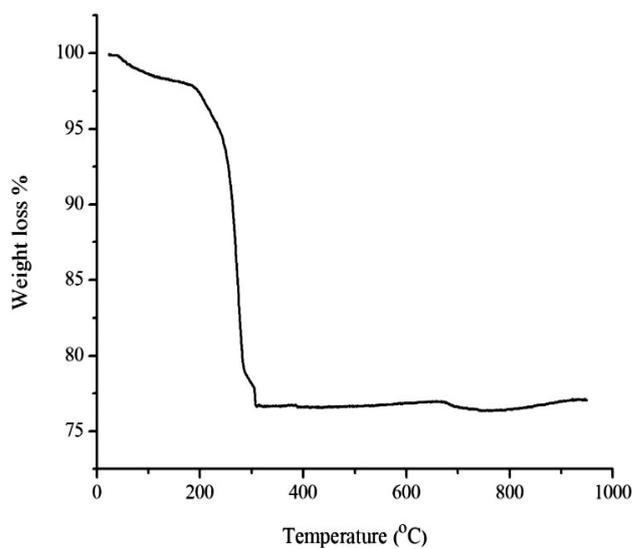


Fig S3. TGA curve of $\text{TiO}_2\text{-AA-Cu (II)}$ nano hybrid

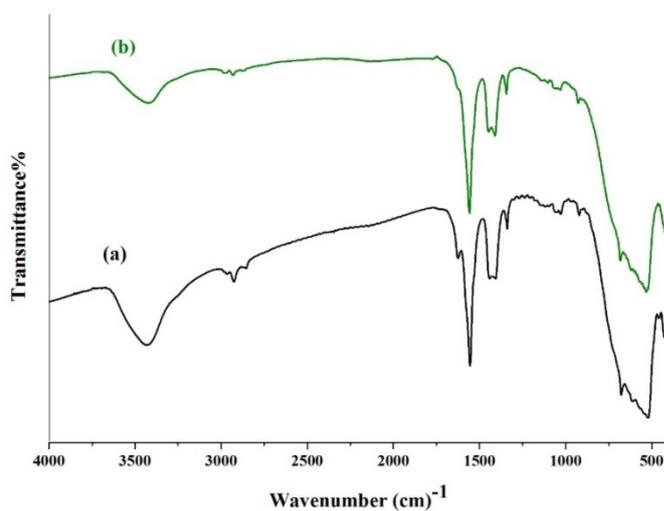
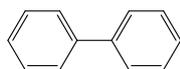


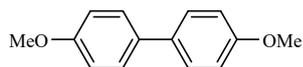
Fig. S4. Comparison of FTIR spectra of fresh $\text{TiO}_2\text{-AA-Cu (II)}$ (a) with a used one (b) in homocoupling of phenylboronic acid after six runs

Spectral Data:



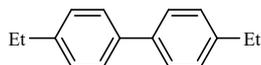
Biphenyl

$^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 7.53\text{-}7.65$ (m, 4H), 7.45 (t, $J = 7.4$ Hz, 4H), 7.29-7.37 (m, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): $\delta = 141.3, 128.6, 127.3, 127.2$.



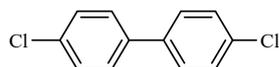
4,4'-Dimethoxy-1,1'-biphenyl

^1H NMR (300 MHz, CDCl_3): δ = 7.46 (d, J =8.6 Hz, 4H), 6.93 (d, J =8.6 Hz, 4H), 3.85 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ = 158.2, 134.3, 127.6, 114.3, 55.4.



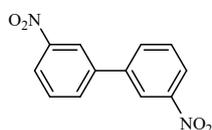
4,4'-diethyl-1,1'-biphenyl

^1H NMR (300MHz, DMSO-d_6 , ppm) δ 7.54 (d, J = 5.6 Hz, 4H), 7.26 (d, J = 5.6 Hz, 4H), 2.64 (s, 4H), 1.23 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6 , ppm) δ 142.80, 137.70, 128.40, 126.50, 27.92, 15.73.



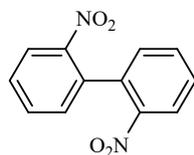
4,4'-dichloro-1,1'-biphenyl

^1H NMR (300 MHz, CDCl_3): δ = 7.37-7.52 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3): δ = 138.5, 133.6, 129.1, 128.3.



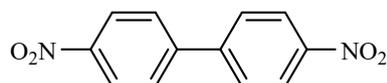
3,3'-Dinitrobiphenyl

^1H NMR (300 MHz, CDCl_3): δ = 8.52 (br s, 2H), 8.31 (d, J =8.1 Hz, 2H), 7.98 (d, J =7.7 Hz, 2H), 7.72 (t, J =7.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 148.91, 140.42, 133.10, 130.31, 123.32, 122.12.



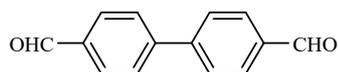
2,2'-dinitro-1,1'-biphenyl

^1H NMR (300 MHz, CDCl_3): δ = 8.23 (d, J =8.1 Hz, 2H), 7.69 (t, J =7.3 Hz, 2H), 7.61 (t, J =7.3 Hz, 2H), 7.32 (d, J =7.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 147.21, 134.20, 133.42, 130.90, 129.13, 124.80.



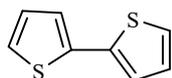
4,4'-dinitro-1,1'-biphenyl

^1H NMR (300 MHz, DMSO- d_6 , ppm) δ 8.04 (d, 4H, J = 8.2 Hz), 8.02–7.95 (d, 4H, J = 8.2 Hz). ^{13}C NMR (75 MHz, DMSO d_6 , ppm) δ 147.78, 139.16, 125.41, 104.93.



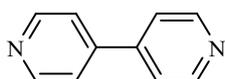
[1,1'-biphenyl]-4,4'-dicarbaldehyde

^1H NMR (300 MHz, CDCl_3): δ = 10.10 (s, 2H), 8.03 (d, J =8.2 Hz, 4H), 7.82 (d, J =8.2 Hz, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ = 191.72, 145.63, 135.91, 130.40, 128.0.



2,2'-bithiophene

^1H NMR (300MHz, CDCl_3): δ = 7.23 (dd, J = 5.2 Hz, J = 1.2 Hz, 2 H), 7.17 (dd, J = 3.6 Hz, J = 1.2 Hz, 2 H), 7.05–7.02 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 137.41, 127.79, 124.40, 123.81.



4,4'-bipyridine

^1H NMR (300 MHz, DMSO- d_6 , ppm) δ 8.74 (d, 4H, J = 5 Hz), 7.83 (d, 4H, J = 5 Hz). ^{13}C NMR (75 MHz, DMSO- d_6 , ppm) δ 150.81, 144.54, 121.55.