Electronic Supplementary Information

Visible light induced hydrogen production over thiophenothiazine-based dye sensitized TiO_2 photocatalyst in neutral water

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Characterization details

^{1}H NMR spectra were measured on a Bruker Spectrometer operating at 300 MHz and chemical shifts were reported in ppm ($CDCl_3$ as solvent and TMS as the internal standard). Mass spectra (MS) were measured on a Micro mass Q-Tof Micro spectrometer instrument. UV-visible absorption spectra (UV) and UV-vis diffuse reflectance spectra (DRS) were determined on a recorded at ambient temperature using Cary-500 UV-vis spectrophotometer along with the usage of different compartment for DRS. Fluorescence spectra were measured on Agilent technologies Cary eclipse fluorescence spectrometer with a slit width of both excitation and emission. The time-resolved measurements were performed on a Horiba−Jobin−Yvon Fluoro Cube fluorescence lifetime system using Nano LED at 450 nm (IBH UK) as the excitation source and TBX photon detection module as the detector. The decays were analyzed using IBH DAS-6 decay analysis software. Cyclic voltammetry (CV) measurement was carried out on a CH electrochemical workstation CHI600E, in a three-electrode cell with a Pt disk counter electrode, a Ag/AgCl reference electrode and a glassy carbon working electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile (AcCN) at a scan rate of 50 mVs^{-1} using ferrocene (4.80 eV vs. vacuum) as standard. The highest occupied molecular orbital (HOMO) energy levels were obtained using the onsets oxidation potentials from the CV curves. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps (Eg) for the compounds were estimated from the onsets absorption of UV-vis absorption spectra in methanol. Perkin–Elmer, USA; FTIR spectra of the samples were recorded in the range of 400–4000 cm^{-1} on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Powder X-ray diffraction (PXRD) was performed with a Bruker AXS diffractometer (D8 advance) at a generator voltage of 40 kV and current 30 mA using Cu-Kα radiation (λ= 1.5406 Å). The sample was scanned in the range of 2θ= 5-100° with the scan rate 1s/step. Field emission scanning electron microscopy (FESEM) was performed on a Carl Zeiss microscopy introduces SIGMA HD field-emission scanning electron microscope. High resolution transmission electron microscopy (HRTEM) micrograph of the sample was prepared by taking acetone dispersion of Pt-TiO_2 on the carbon coated copper grid and drying at room temperature in air followed by vacuum. HRTEM was carried by JEOL 2010EX operated at an accelerating voltage of 200 KV fitted with a CCD camera. The photocatalytic experiments were carried out under external light source using a 450 W Oriel Research Arc lamp Source (New Port, USA, model no: 66924; working at 400 W) equipped with xenon (Xe) lamp, and cutoff filter (λ > 400 nm). GC analysis was performed by Perkin-Elmer gas chromatograph Clarus-580 instrument with a thermal conductivity detector and a 5Å molecular sieve column (2 mm × 2 mm) using Argon as carrier gas.

Calculation: All theoretical calculations were carried out using the density functional theory (DFT) and geometry optimization for UP-series dyes were performed at the B3LYP/DND (dmol3) level. Then, the frontier molecular orbitals were analyzed.

Experimental Section

Materials and reagents

In the present work, all chemicals used were analytical grade, and were purchased from commercial sources. Importantly, commercial TiO_2 anatase (nanopowder, <25 nm particle size, assay 99.7%, specific surface area 45-55 m^2/g), 2-methylthiophenothiazine and 1-bromoalkane were purchased from the Sigma-Aldrich, USA and used without further purification. Solvents used as reaction media were purchased from local sources and used after distillation. Used hexane (Hex) refers to the fraction boiling in the range of 60–70 ºC. Reactions were monitored using analytical TLC plates (Merck, silica gel 60 F254, 0.25 mm) and compounds were resolved with ultraviolet light. Silica gel (100–120 mesh) was used for column chromatography.

Synthesis of UP1 dye

10-butyl-2-(methylthio)-10H-phenothiazine (1a). 10-Butyl-2-(methylthio)-10H-phenothiazine was prepared by the alkyl substitution on nitrogen atom of phenothiazine group. 1-Bromobutane (47.7 mg, 3.04 mmol) and potassium iodide (catalytic) was added in a prepared 2-methylthiophenothiazine (500 mg, 2.03 mmol) 25 ml dimethyl sulfoxide (DMSO) solution under inert atmosphere. The mixture solution was kept on stirring after 10 min potassium hydroxide (404 mg, 4.04 mmol) added in reaction mixture. The reaction mixture was stirred for 5 h at room temperature (rt) and then 50 ml of water was added in mixture solution. The crude product was extracted with diethyl ether (3 x 20 ml). The organic layer was separated and washed with water and saturated aqueous solution of ammonium chloride then dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Hex: EA, 98: 2) on silica gel to obtained pure compound as obtained colourless oil (700 mg, 90% yield). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.96 (t, 3H, CH_3), 1.46 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 3.82 (t, 2H, CH_2), 6.80–6.98 (m, 4H, ar), 7.04 (d, 1H, ar), 7.13–7.26 (m, 2H, ar). MS (ESI), m/z [M^+]: 301.11, calcd: 301.09, $C_{17}H_{19}NS_2$, calcd: C, 67.73, H, 6.35, N, 4.65, S, 21.27 found: C, 67.71, H, 6.32, N, 4.62, S, 21.25.

10-butyl-8-(methylthio)-10H-phenothiazine-3-carbaldehyde (1b). 10-Butyl-8-(methylthio)-10H-phenothiazine-3-carbaldehyde (**3**) was prepared by the Vilsmeier–Haack formylation reaction. $POCl_3$ (0.025 ml, 0.25 mmol) was added dropwise to (0.25 ml 3.25 mmol) of freshly distilled DMF at 0 ºC under inert atmosphere. 250 mg (1.7 mmol) of 10-butyl-2-(methylthio)-10H-phenothiazine (**2)** dissolved in DMF was added dropwise to the above-mentioned $POCl_3$/DMF complex at rt. The reaction mixture was stirred at 80 ºC for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled at rt. The reaction mixture was quenched with saturated aqueous sodium bicarbonate and poured into ice water. The crude product was extracted into ethyl acetate (3 x 20 ml) and the organic layer washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Hex: EA, 95: 5) on silica gel to obtained pure compound as obtained of the yellow solid (**3)** (445 mg, 83% yield). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.96 (t, 3H, CH_3), 1.52 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 2.49 (s, 3H, CH_3), 3.93 (t, 2H, CH_2), 6.70 (s, 1H, ar), 6.87–7.09 (m, 2H, ar), 7.09–7.21 (m, 2H, ar), 7.50 (s, 1H, ar), 10.06 (s, 1H, CHO). MS (ESI), m/z [M^+]: 329.13, calcd: 329.09, $C_{18}H_{19}NOS_2$, C: 65.62; H, 5.81; N, 4.25; O, 4.86; S, 19.46, found: C, 65.59; H, 5.78; N, 4.22; O, 4.84; S, 19.44.

(E)-3-(10-Butyl-8-(methylthio)-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (1c). 0.03 ml (0.33 mmol) of piperidine was added to a solution of 10-butyl-8-(methylthio)-10H-phenothiazine-3-carbaldehyde (**3)** (110 mg, 0.33 mmol) and cyanoacetic acid (28 mg, 0.33 mmol) in toluene (15 ml). The reaction mixture was refluxed for 7 h under inert atmosphere. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2: CH_3OH, 98: 2) on

silica gel to afford compound **UP1** (**4)** as a red solid (120 mg, 91% yield). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.97 (s, 3H, CH_3), 1.49 (s, 2H, CH_2), 1.81 (s, 2H, CH_2), 2.50 (s, 3H, CH_3), 3.92 (s, 2H, CH_2), 6.83 (s, 1H, ar), 6.95 (d, 2H, ar), 7.14 (d, 2H, ar), 7.93 (s, 1H, ar), 8.62 (s, 1H, ar). MS (ESI), m/z [M^+]: 396.13, calcd: 396.53; $C_{21}H_{20}N_2O_2S_2$: calcd: C, 63.61; H, 5.08; N, 7.06; O, 8.07; S, 16.17; found: C, 63.59; H, 5.05; N, 7.05; O, 8.04; S, 16.15.

Synthesis of UP2 dye

10-Pentyl-2-(methylthio)-10H-phenothiazine (2a). This compound was prepared by a procedure similar to that used for **1a**, using 1-bromopentane instead of 1-bromobutane. Colourless oil product was obtained (750 mg, 90 % yield). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.96 (t, 3H, CH_3), 1.45 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 2.47 (s, 3H, CH_3), 3.94 (t, 2H, CH_2), 6.82 – 6.92 (m, 4H, ar), 7.26 (d, 1H, ar), 7.11 – 7.16 (m, 2H, ar). MS (ESI), m/z [M^+]: 315.09, calcd: 315.11, $C_{18}H_{21}NS_2$, calcd: C, 68.52, H, 6.71, N, 4.44, S, 20.33, found: C, 68.55, H, 6.73, N, 4.45, S, 20.29.

10-Pentyl-8-(methylthio)-10H-phenothiazine-3-carbaldehyde (2b). This compound was prepared by a procedure similar to that used for **1b**. The product **2b** was obtained as yellow oil. Yield: 500 mg (85 %). 0.93 (t, 3H, CH_3), 1.44 (m, 2H, CH_2) 1.47 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 2.47 (s, 3H, CH_3), 3.9 (t, 2H, CH_2), 6.86 – 6.99 (m, 4H, ar), 7.28 (d, 1H, ar), 7.12–7.28 (m, 2H, ar) 10.07 (s, 1H, CHO). MS (ESI), m/z [M^+]: 343.13, calcd: 343.10, $C_{19}H_{21}NOS_2$: calcd: C, 66.43; H, 6.16; N, 4.08; O, 4.66; S, 18.67; found: C, 66.46; H, 6.16; N, 4.10; O, 4.64; S, 18.69.

(E)-3-(10-Pentyl-8-(methylthio)-10H phenothiazin-3-yl)-2-cyanoacrylic acid (2c). This compound was prepared by a procedure similar to that used for **1c**. The product **2c** was obtained as a red solid. labelled as **UP2 (5)**, Yield: 150 mg (90 %). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.91 (s, 3H, CH_3), 1.43 (s, 2H, CH_2), 1.86 (s, 2H, CH_2), 2.09 (s, 2H, CH_2), 2.48 (s, 3H, CH_3), 3.87 (s, 2H, CH_2), 6.82 (s, 1H, ar), 6.96 (d, 2H, ar), 7.12 (d, 2H, ar), 7.28 (s, 1H, ar), 8.43 (s, 1H, ar). MS (ESI), m/z [M^+]: 409.11, calcd: 410.11; $C_{21}H_{20}N_2O_2S_2$: calcd: C, 64.36; H, 5.40; N, 6.82; O, 7.79; S, 15.62; found: C, 64.34; H, 5.39; N, 6.80; O, 7.77; S, 15.58.

Synthesis of UP3 dye

10-Hexyl-2-(methylthio)-10H-phenothiazine (3a). This compound was prepared by a procedure similar to that used for **1a**, using 1-bromohexane instead of 1-bromobutane. Colourless oil product was obtained (750 mg, 90 % yield). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.90 (t, 3H, CH_3), 1.43 (m, 2H, CH_2) 1.45 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 3.93 (t, 2H, CH_2), 6.78–6.97 (m, 4H, ar), 7.26 (d, 1H, ar), 7.12–7.16 (m, 2H, ar). MS (ESI), m/z [M^+]: 329.11, calcd: 329.52, $C_{19}H_{23}NS_2$, calcd: C, 69.25, H, 7.04, N, 4.25, S, 19.46; found: C, 69.22, H, 7.01, N, 4.24, S, 19.47.

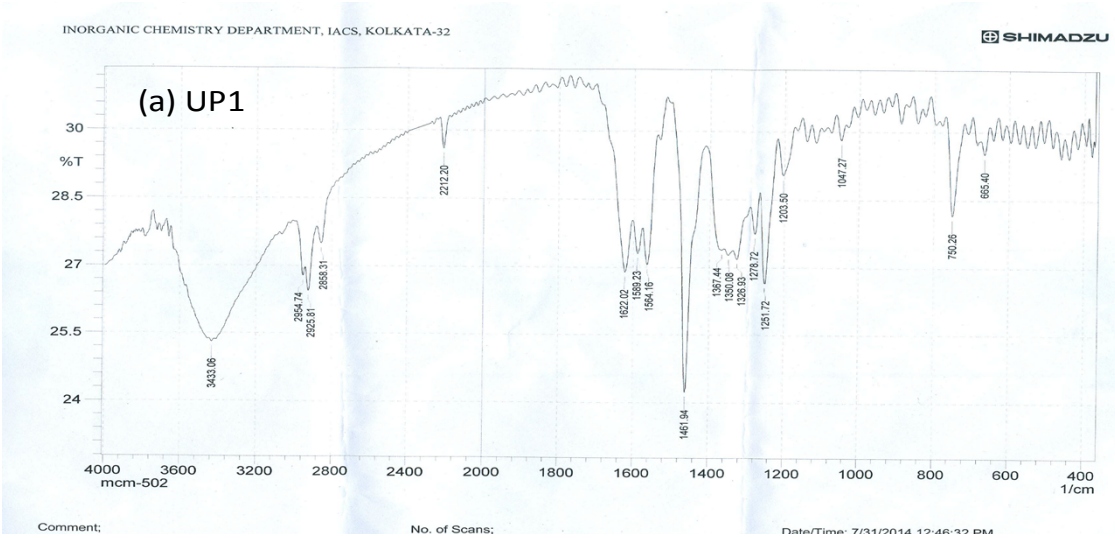
10-Hexyl-8-(methylthio)-10H-phenothiazine-3-carbaldehyde (3b). This compound was prepared by a procedure similar to that used for **1b**. The product **3b** was obtained as yellow oil. Yield: 500 mg (85 %). 0.92 (t, 3H, CH_3), 1.43 (m, 2H, CH_2) 1.46 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 2.48 (s, 3H, CH_3), 3.88 (t, 2H, CH_2), 6.87 – 6.97 (m, 4H, ar), 7.48 (d, 1H, ar), 7.09–7.26 (m, 2H, ar) 10.07 (s, 1H, CHO). MS (ESI), m/z [M^+]: 356.11, calcd: 357.12, $C_{20}H_{23}NOS_2$: calcd: C, 67.19; H, 6.48; N, 3.92; O, 4.47; S, 17.94; found: C, 67.18; H, 6.46; N, 3.93; O, 4.48; S, 17.92.

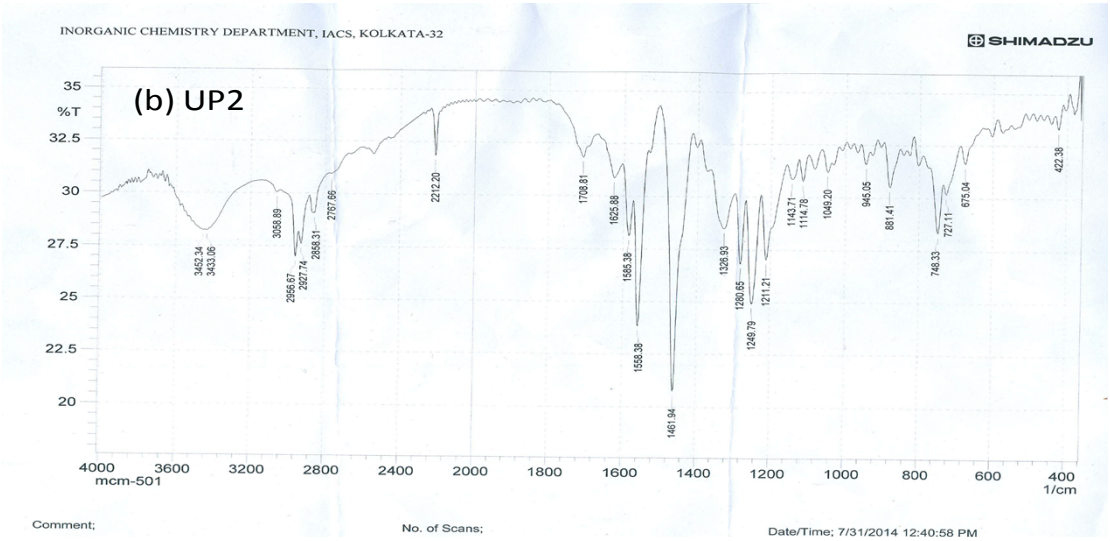
(E)-3-(10-Hexyl-8-(methylthio)-10H-phenothiazin-3-yl)-2-cyanoacrylic acid (3c). This compound was prepared by a procedure similar to that used for **1c**. The product was obtained as red solid, named as **UP3 (6)**. Yield: 160 mg (90 %). ^{1}H NMR (300 MHz, chloroform-d): d (ppm): 0.88 (s, 3H, CH_3), 1.45 (s, 2H, CH_2), 1.84 (s, 2H, CH_2), 1.86 (s, 2H, CH_2), 1.97 (s, 2H, CH_2), 2.49 (s, 3H, CH_3), 3.88 (s, 2H, CH_2), 6.86 (s, 1H, ar), 6.95 (d, 2H, ar), 6.97 (d, 2H, ar), 7.11 (d, 2H, ar), 7.26 (s, 1H, ar), 8.47 (s, 1H, ar). MS (ESI), m/z [M^+]: 423.43, calcd: 424.13; $C_{21}H_{20}N_2O_2S_2$: calcd: C, 65.06; H, 5.70; N, 6.60; O, 7.54; S, 15.10; found: C, 65.03; H, 5.72; N, 6.58; O, 7.51; S, 15.08.

Table S1. FTIR data

Wave number (cm^{-1})	Assignment and comment
3400 - 3450	Stretching vibration of –OH group associated

3000-3100	Stretching vibration of carboxylic moieties and/or –CH
2800 – 2950	Asymmetric stretching vibrations of $–CH_3$
2850-2950	Asymmetric stretching vibrations of $–CH_2$ group from the hydrocarbon skeleton
2210 - 2250	Stretching vibration of –C≡N group
1600 -1650	Alkenyl str vibration of C–C group
1550 -1600	Stretching vibration of aromatic ring C═C–C group; Bending vibration of –NH
1350 - 1450	Stretching vibration of aromatic ring C═C–C group; Symmetric str vibration of COO^- group
1330 - 1400	Symmetric bending vibration of $–CH_3$ group
1150 - 1250	Stretching vibration of C≡N group
1050 -1150	Stretching vibration of –CO group from carboxylic acid
1050 - 1100	Bending vibrations of –C– (C═O) –C group of ketone (probable overlapping with stretching vibration of –CO group from secondary alcohol and/or with stretching vibrations of –C═O groups from the ether)
750-680	Methylene $–(CH_2)n$ rocking,(n=3)
675-650	Out of plane bending vibration of aromatic C–H

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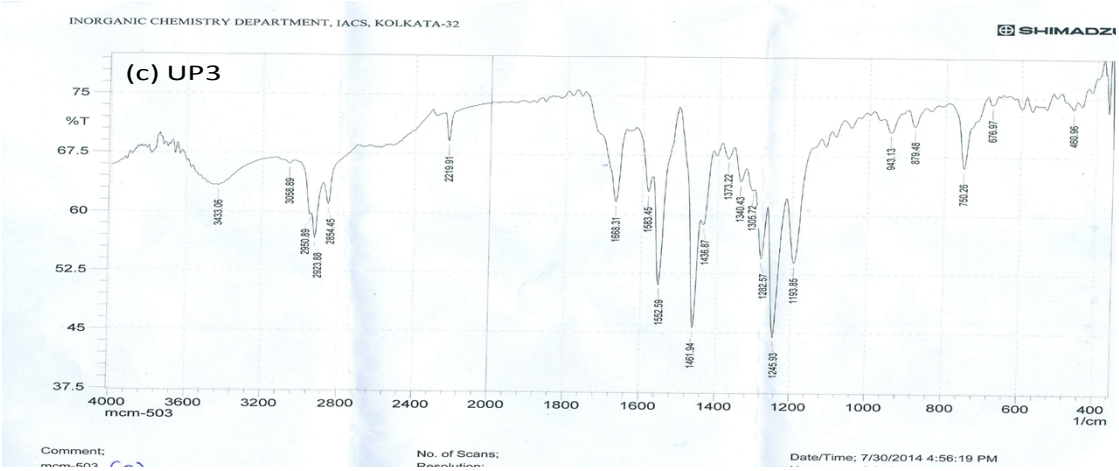
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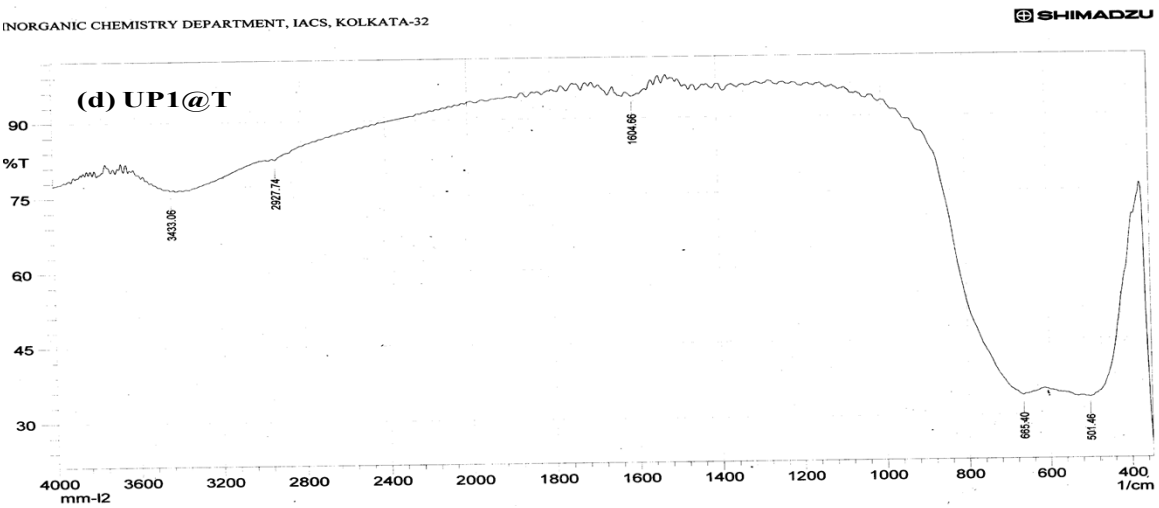
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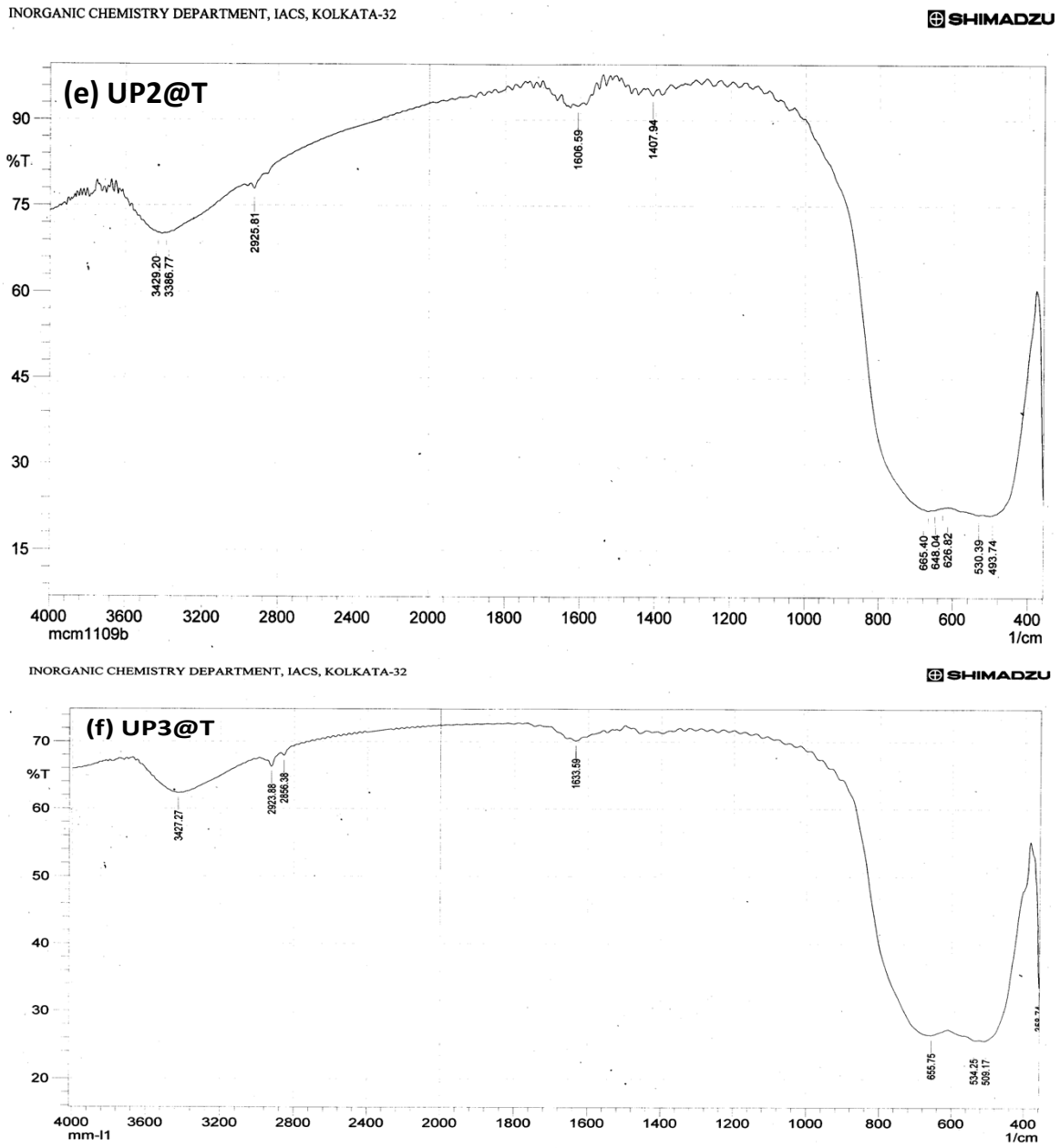

Figure S1. FTIR spectra of dyes (**UP1, UP2 and UP3**) and dye@TiO_2 (UP1@T, UP2@T and UP3@T) composites.

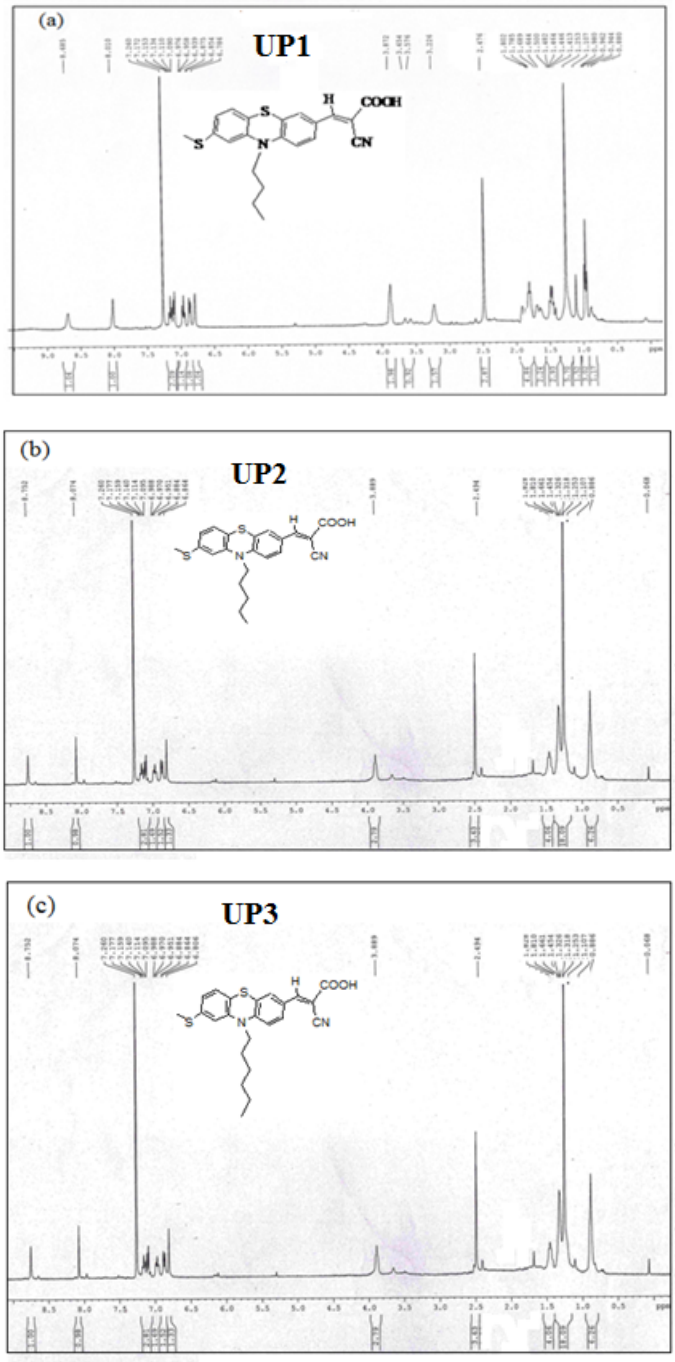

Figure S2. ^{1}H NMR spectra of dyes (**UP1, UP2 and UP3**).

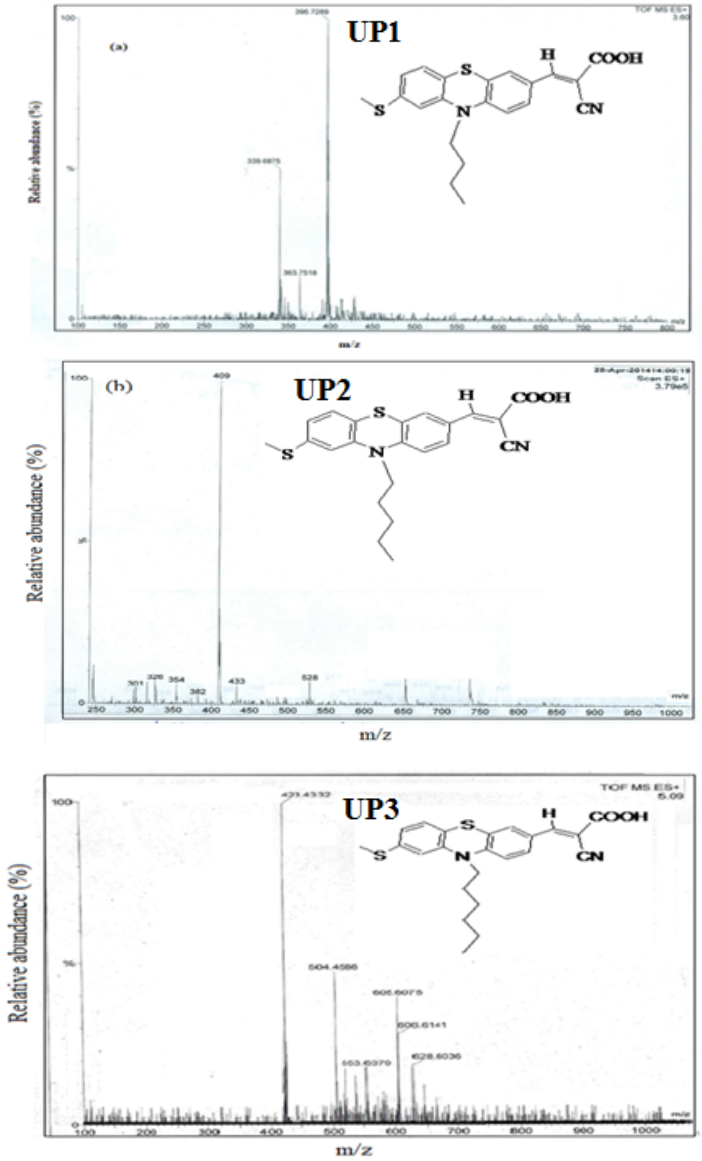

Figure S3. ESI-MS of dyes (**UP1, UP2 and UP3**).

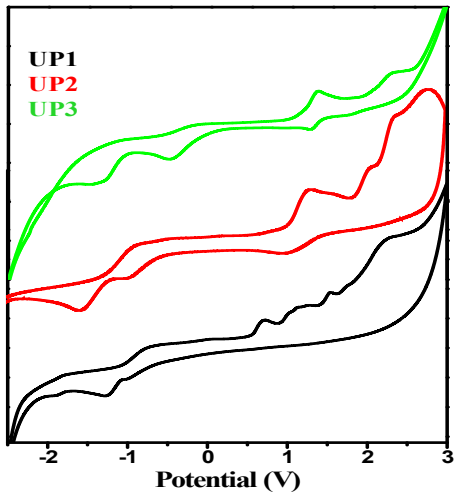

Figure S4. Cyclic voltammograms of UP-series of dyes traces at a scan rate of 50 mVs^{-1} measured in a 0.1 M ($TBABF_4$) CH_3CN solution.

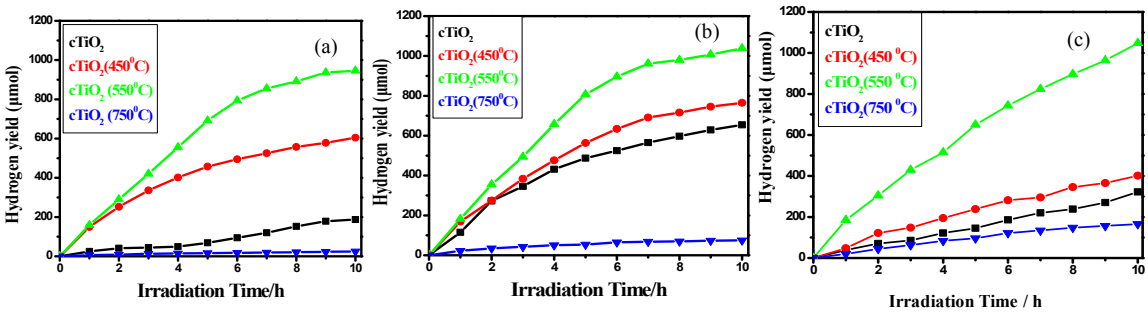

Figure S5. Photocatalytic activities of the (a) UP1@PT, (b) UP2@PT and (c) UP3@PT composites ($cTiO_2$ calcined at different temperatures) for water splitting. Reaction conditions: 2 mL of 10 vol % TEOA aq., 10 mg catalyst, pH = 7.

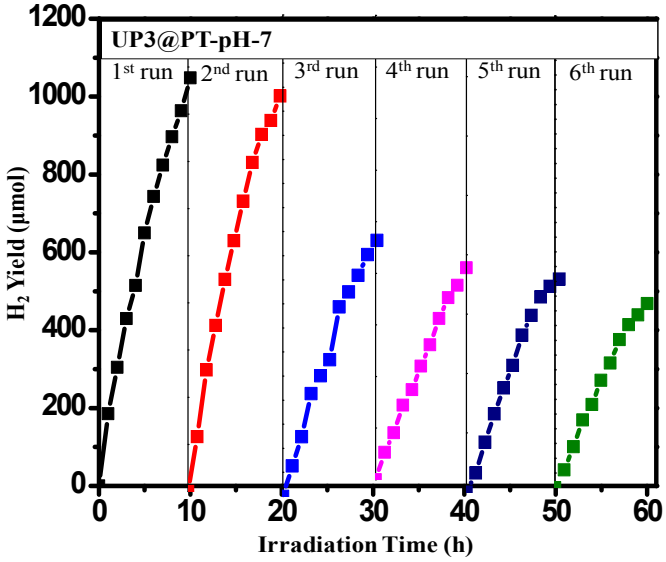

Figure S6. Cyclic H_2-evolution curve for the UP3@PT at pH-7.

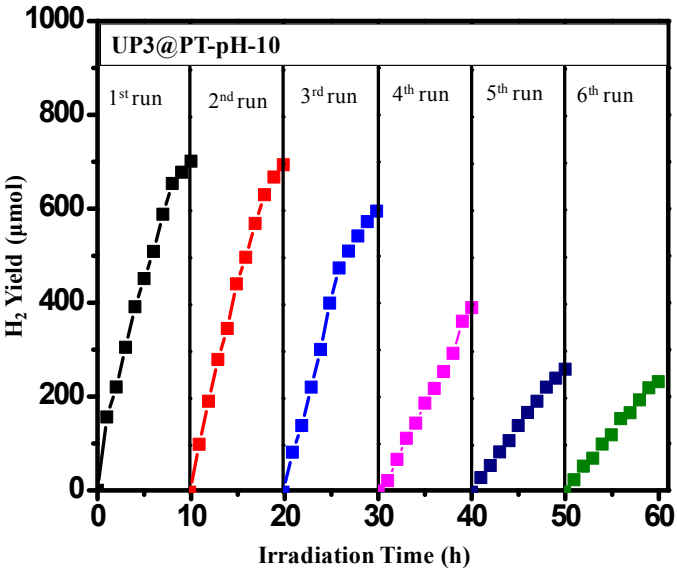

Figure S7. Cyclic H_2-evolution curve for the UP3@PT at pH-10.

XRD data:

In our report, the diffraction peaks (2θ) at 25.2º, 37.9º, 48.3º, 53.8º and 55.0º, represent the corresponding indices of (101), (103), (200), (105) and (211) planes respectively for anatase TiO_2 (Fig. 3). The occurrence of the prevalent peaks at 2θ of about 27.5º, 36.0º, 39.0º, 41.2º, 44.1º, 54.2º and 56.7º corresponds to the indices of (110), (101), (200), (111), (210), (211) and (220) planes respectively, indicating the presence of the rutile phase (Fig. 3).