Supporting Information

Impact of Average, Local and Electronic Structure on Visible Light Photocatalysis in Novel Bi*RE*WO_6 (*RE* = Eu & Tb) Nanomaterials

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Figures

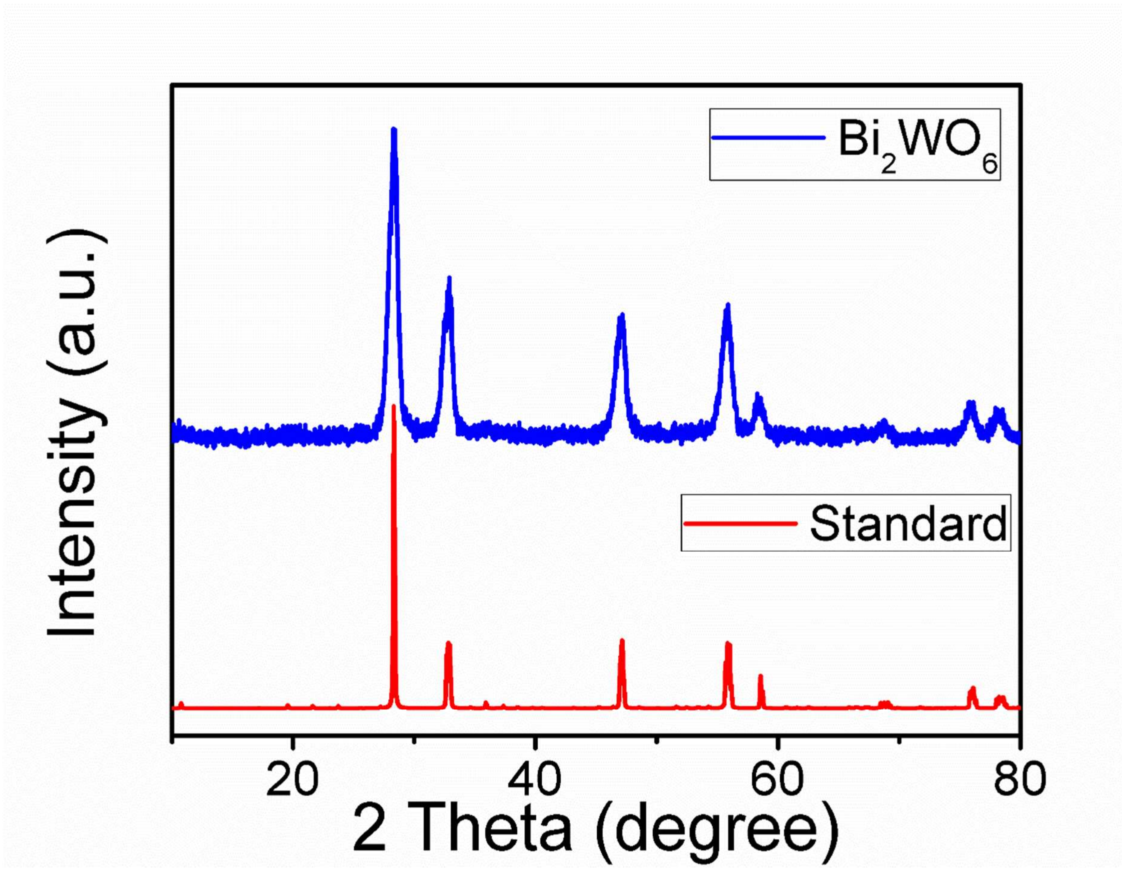

Figure S1. P-XRD patterns of hydrothermal synthesized Bi_2WO_6 which is matching with the LT-Bi_2WO_6 (orthorhombic) Phase.

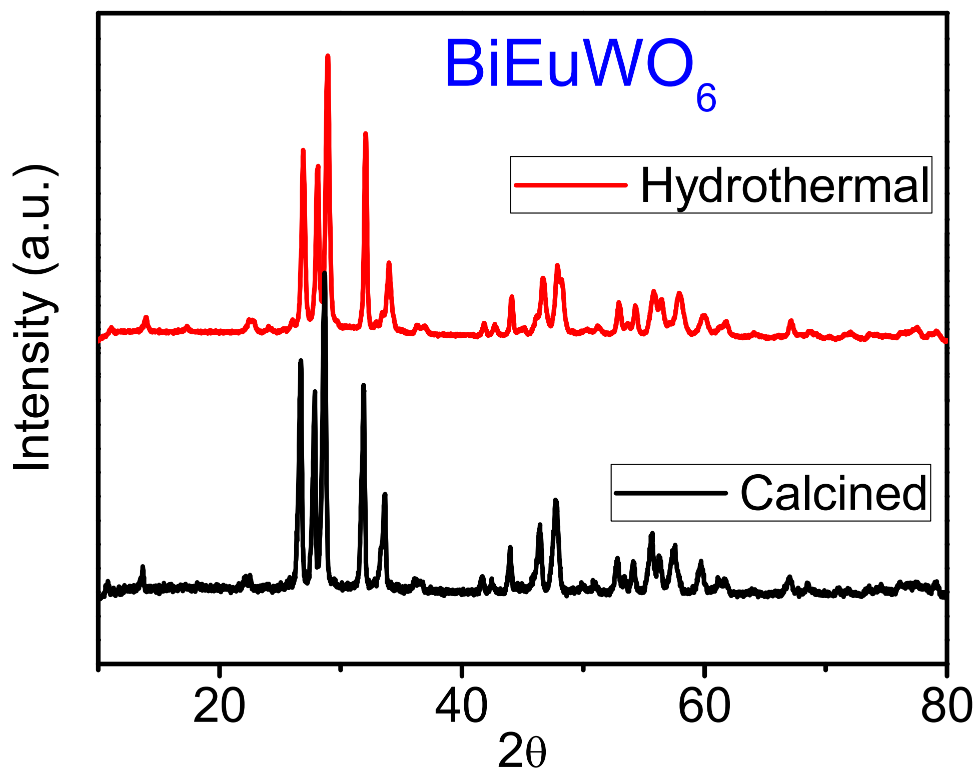

Figure S2. P-XRD patterns of hydrothermal synthesized $BiEuWO_6$ and Calcined $BiEuWO_6$ for 20 hours.

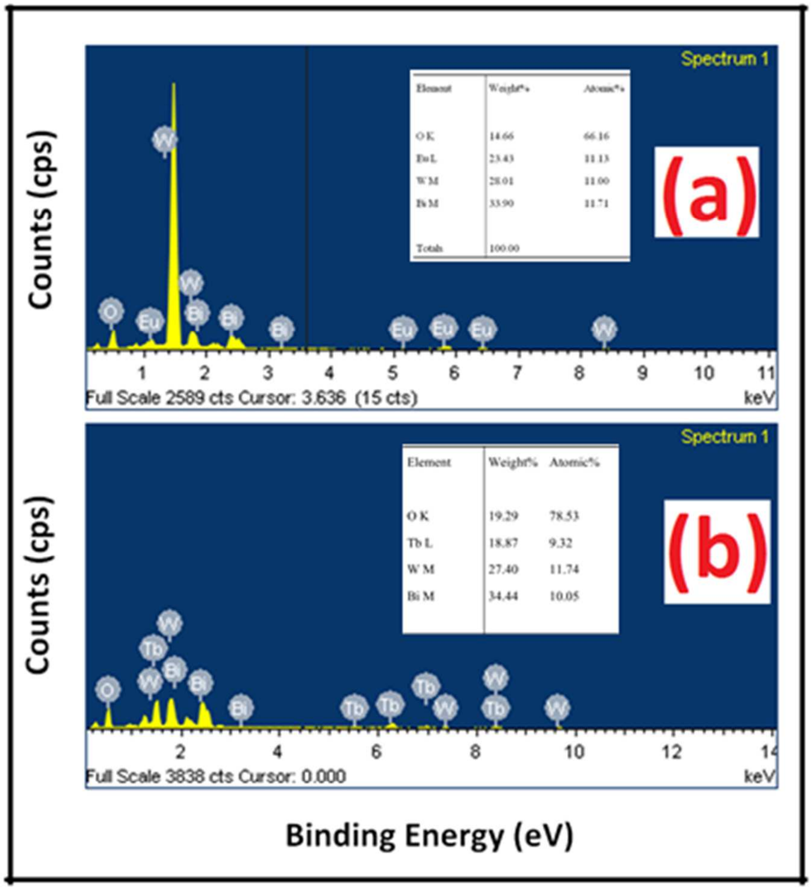

Figure S3. Energy Dispersive Absorption X-ray Spectrum of (a) $BiEuWO_6$ (b) $BiTbWO_6$ nanomaterials synthesized by hydrothermal method. Approximate composition of the materials is calculated as $Bi_1Eu_1WO_6$ and $Bi_{1.1}Tb_{0.9}WO_6$.

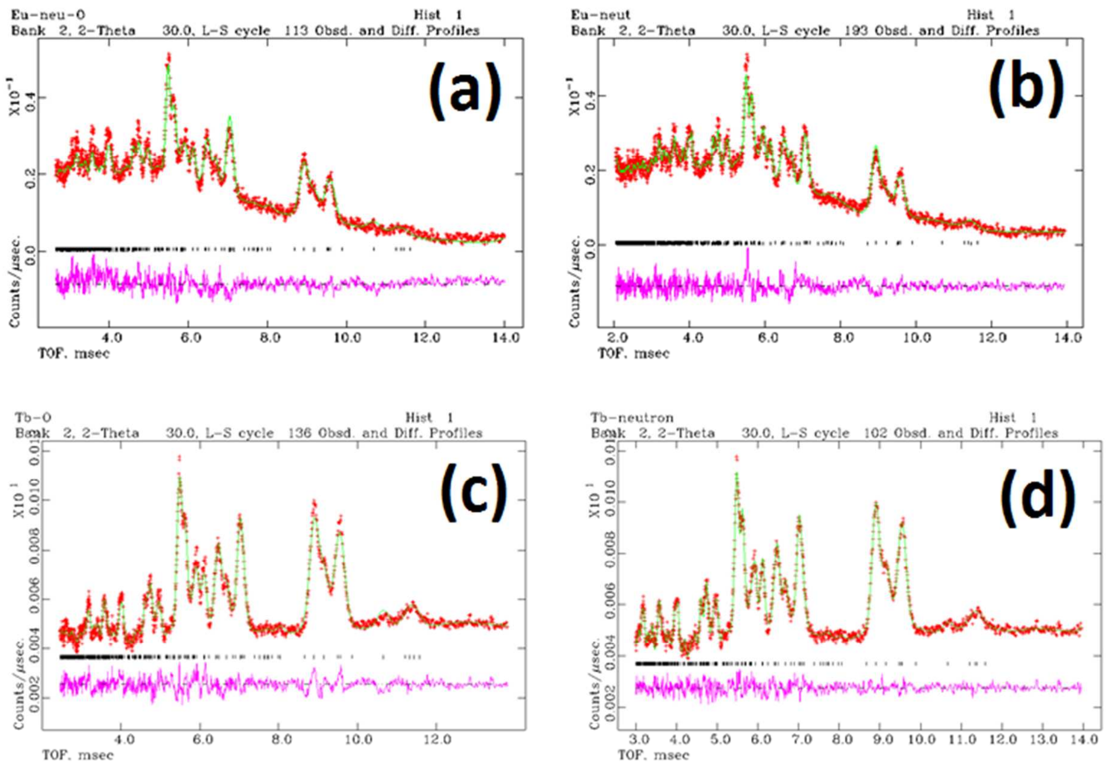

Figure S4: Observed (green), Calculated (red) and difference plot (indigo) obtained by Neutron data Rietveld refinement of (a). $BiEuWO_6$ Ordered model (b) $BiEuWO_6$ disordered model (c). $BiTbWO_6$ Ordered model (d). $BiTbWO_6$ Disordered model.

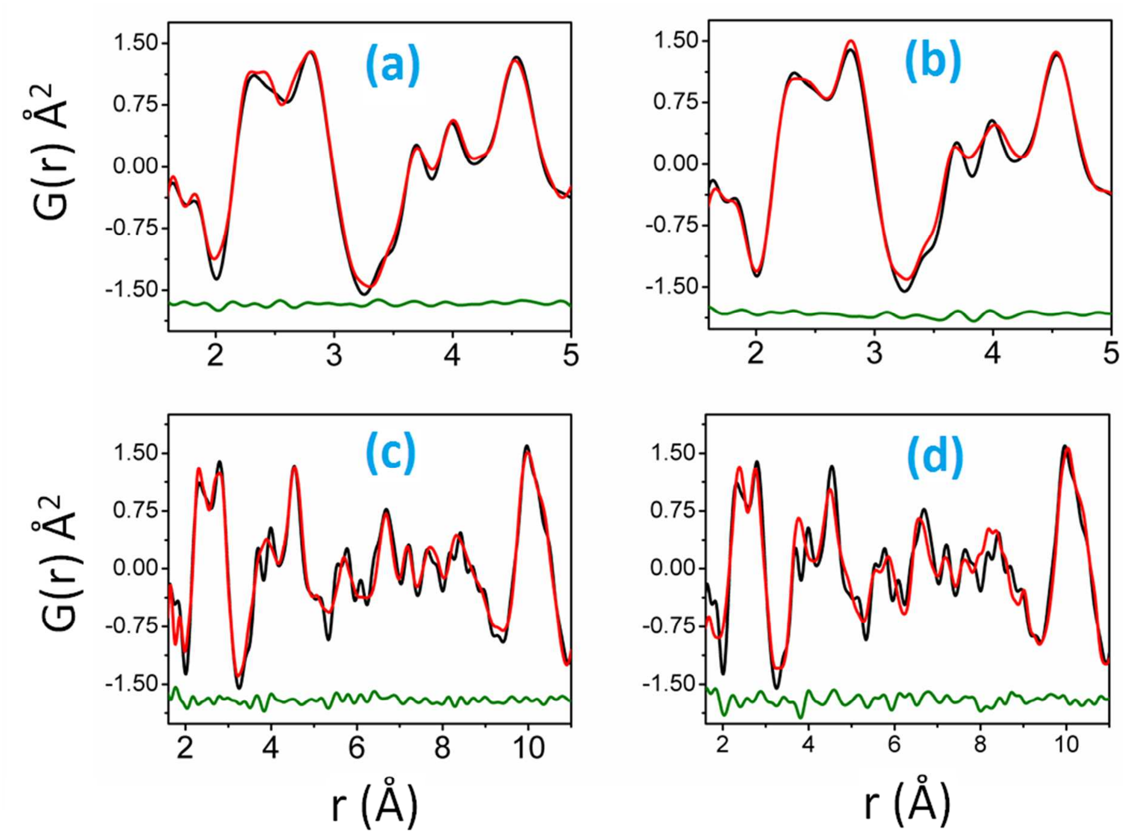

Figure S5: Observed (black), Calculated (red) and difference plot (green) obtained for PDF data of $BiEuWO_6$ (a). Short range (1.5 to 5Å) fit with Ordered model [R_{wp} = 9.9%]. (b). Short range (1.5 to 5Å) fit with Disordered model [R_{wp} = 11.8%]. (c) Medium range (1.5 to 11Å) fit with Ordered model [R_{wp} = 21.7%]. (d). long range (1.5 to 11Å) fit with Ordered model [R_{wp} = 32.47%].

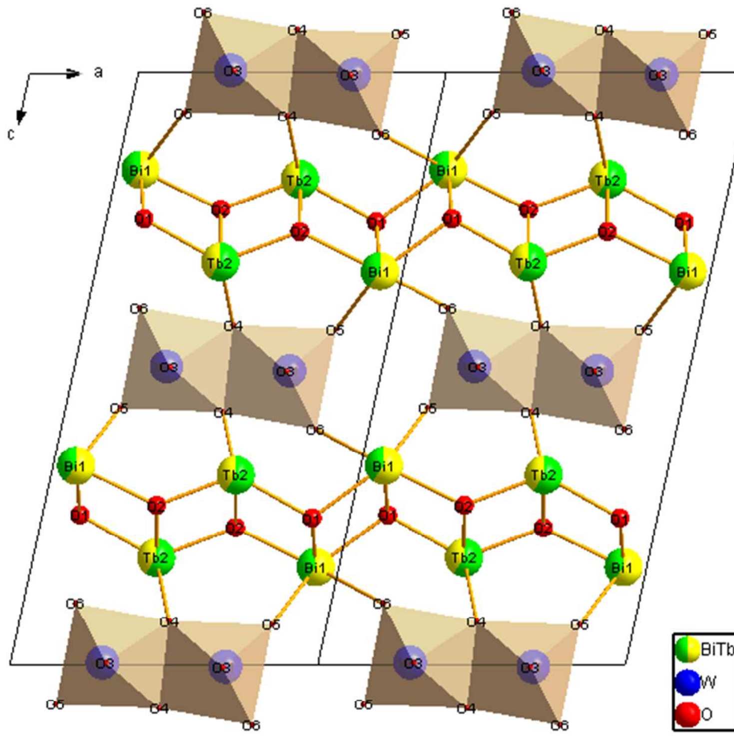

Figure S6: Crystal structure of $BiTbWO_6$ nanomaterial representing connectivity between Bi_2O_2 layer and edge shared WO6 octahedra.

Room Temperature Steady State Photoluminescence (PL) Spectroscopy:

Room Temperature steady state photoluminescence (PL) spectra of photocatalyst nanomaterials were recorded using Agilent Cary Eclipse fluorescence spectrophotometer. With a photomultiplier tube voltage of 600 V and a 150 W Xe lamp was used as the excitation source. Excitation and emission slit width was set as 5 nm. Corresponding room temperature excitation and emission spectra of LT-Bi_2WO_6[1], $BiEuWO_6$[2] and $BiTbWO_6$[3] are recorded according to literature (Figure S7), from which it is observed that Bi_2WO_6 has the fluorescence emission at 525 nm when excited at 378 nm, while $BiTbWO_6$ has an emission at 545nm when excited at 386 nm. Similarly $BiEuWO_6$ has an emission at 613 nm for 486 nm excitation.

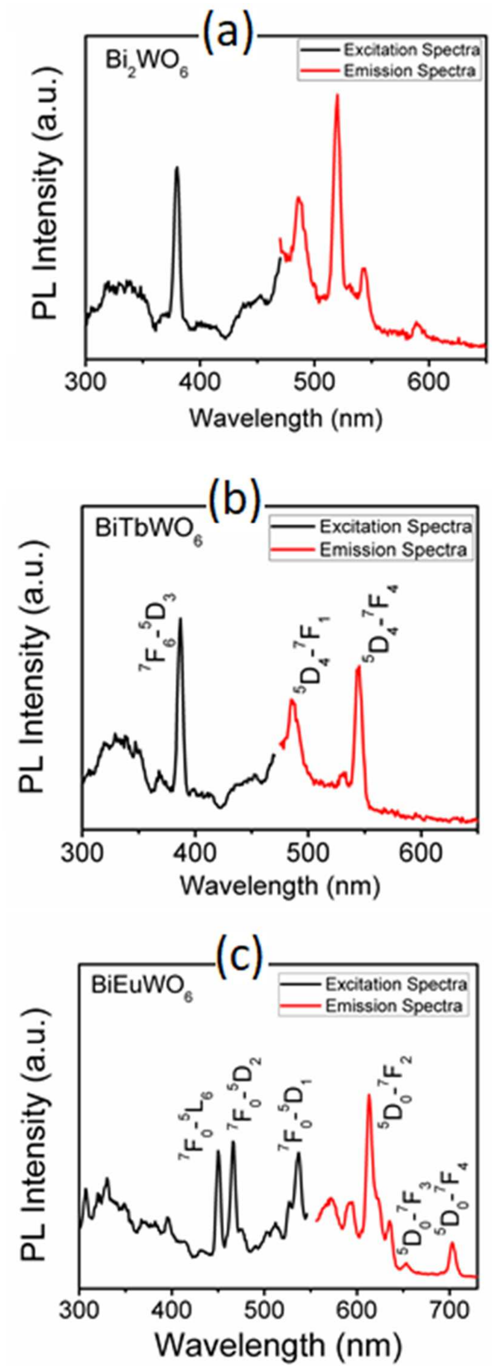

Figure S7: Room temperature steady state fluorescence excitation and corresponding emission spectra of (a) Bi_2WO_6, (b) $BiTbWO_6$ and (c) $BiEuWO_6$ nanomaterials.

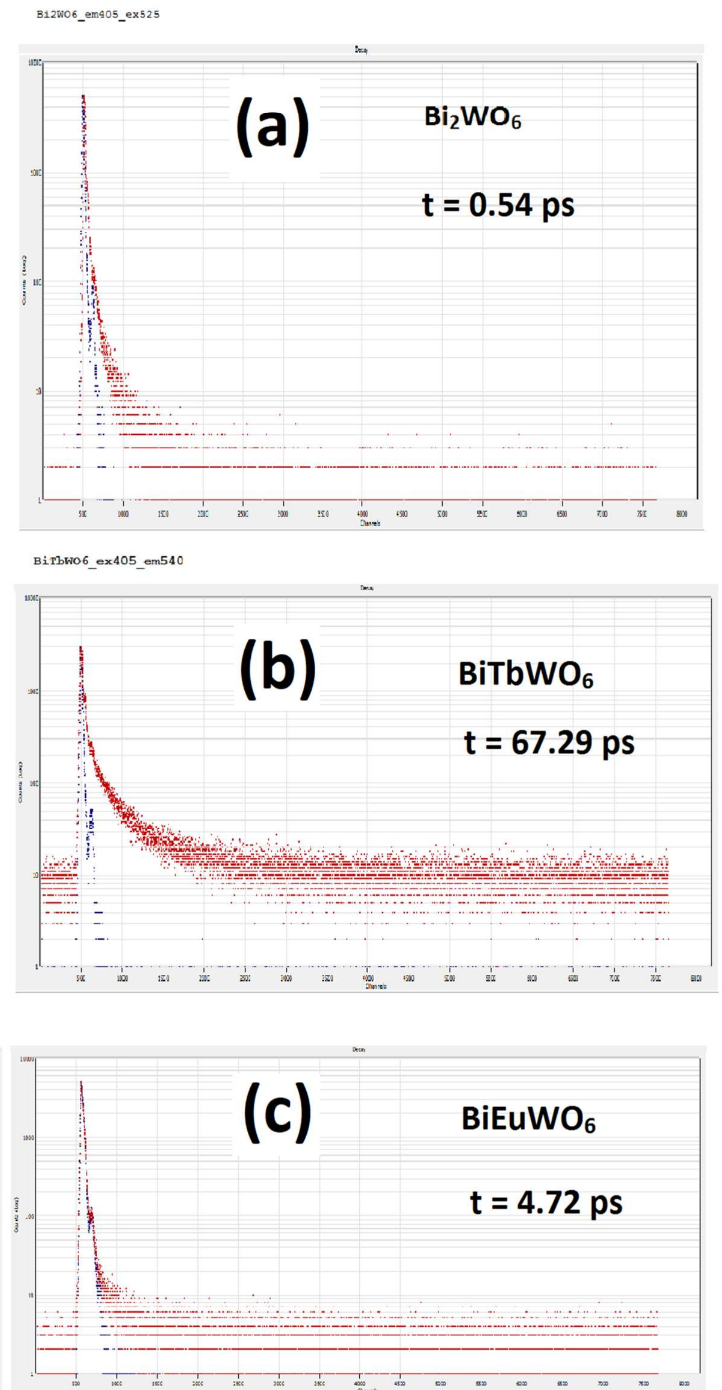

Figure S8: Time Resolved Fluorescence Spectra of (a) Bi_2WO_6 excited at 405 nm, (b) $BiTbWO_6$ excited at 405 nm and (c) $BiEuWO_6$ excited at 469 nm

BET surface area analysis:

Nitrogen sorption measurements of the catalysts were performed at 77 K using a BELSORP mini II instrument. The specific surface areas of the samples were calculated by using the Brunauer–Emmett–Teller (BET) method in the relative pressure (P/P_0) range of 0.05 to 0.25.

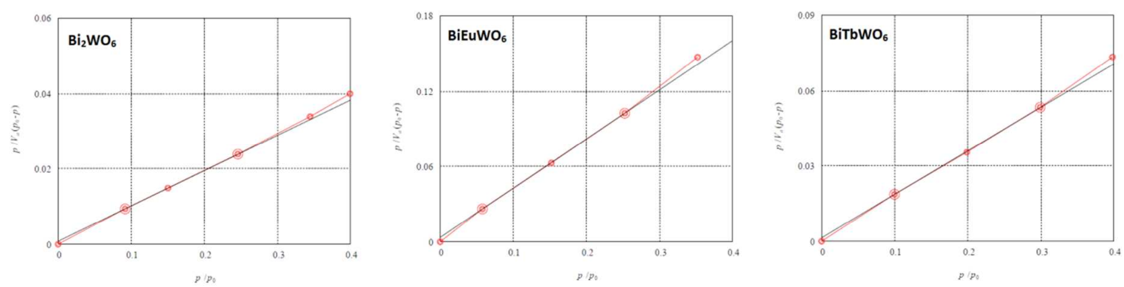

Figure S9: BET surface area analysis of Bi_2WO_6, $BIEuWO_6$ and $BiTbWO_6$ nanomaterials.

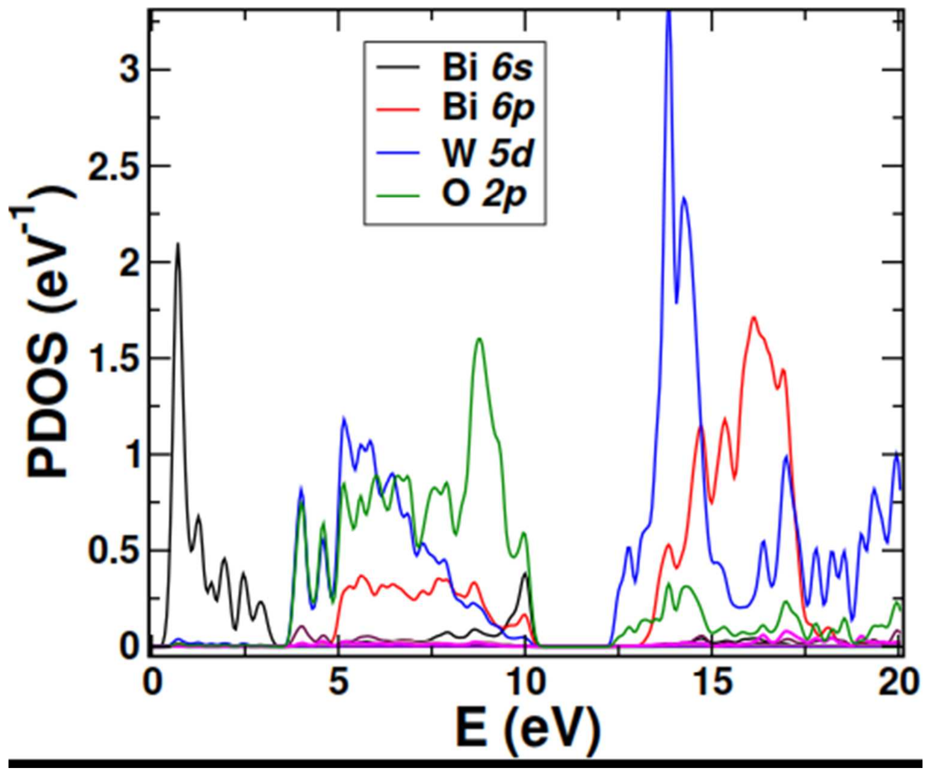

Figure S10: DFT-PDOS of Bi_2WO_6-monoclinic Phase.

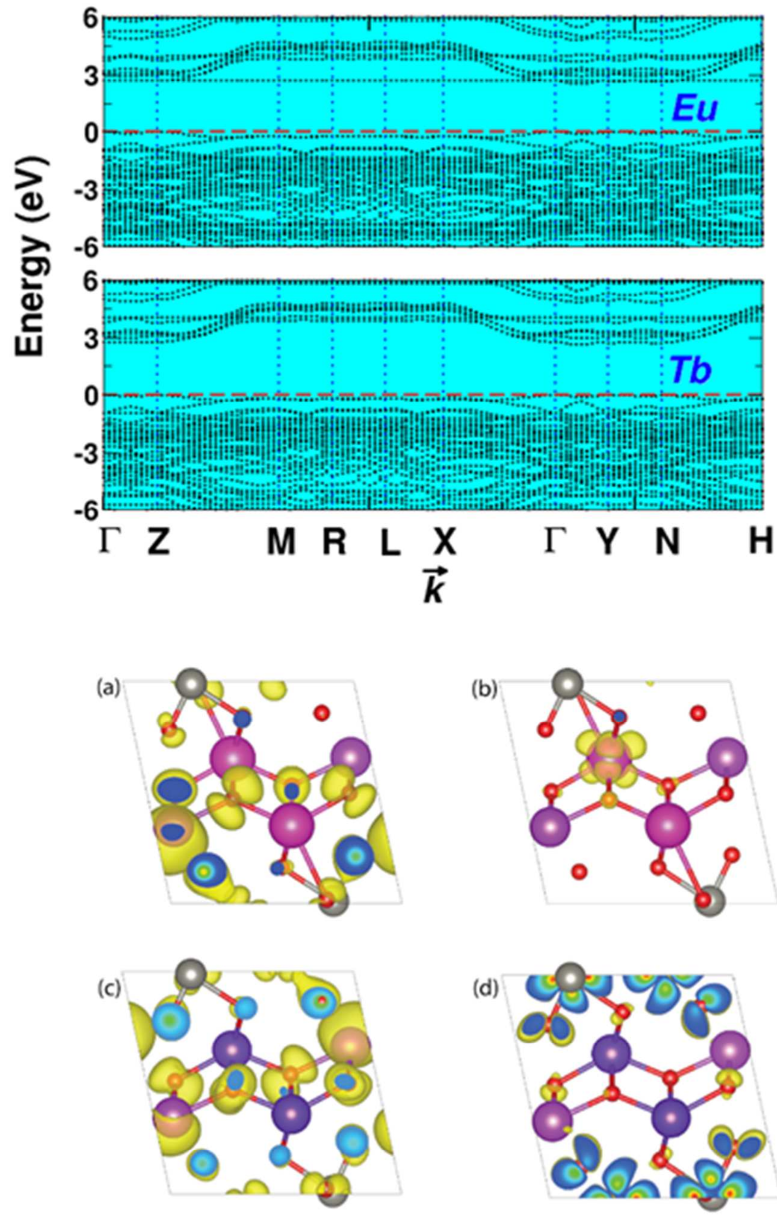

Figure S11: (Top) Electronic band structure of BiEuWO6 and BiTbWO6 compounds along various symmetry directions, for U_W=9.5 eV, $U_{Eu/Tb}$=7.5 eV and U_O=5 eV. **(Bottom).** Valence ((a) - Eu; (c) - Tb) and Conduction band (((b) - Eu; (d) - Tb) charge densities for Eu and Tb compounds at R point in the band structure plot.

References:

(1) Zhang, Y.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. Identification of Bi 2 WO 6 as a Highly Selective Visible-Light Photocatalyst toward Oxidation of Glycerol to Dihydroxyacetone in Water. *Chemical Science* **2013,** *4* (4), 1820-1824.
(2) Kirby, A. F.; Richardson, F. Optical Excitation and Emission Spectra of Europium(3+) in Microcrystalline Samples of Trigonal Na3[Eu(ODA)3].2NaClO4.6H2O. *The Journal of Physical Chemistry* **1983,** *87* (14), 2557-2563.
(3) Xia, F.; Liu, S.; Wang, Y.; Mao, J.; Li, X.; Wang, Y.; Chen, G. Fast and Intense Green Emission of Tb 3+ in Borosilicate Glass Modified by Cu+. *Scientific reports* **2015,** *5*, 15387.