Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION FOR:

Photo-Induced Ring-Expansion Reactions Mediated by B_{12}-TiO_2 hybrid catalyst

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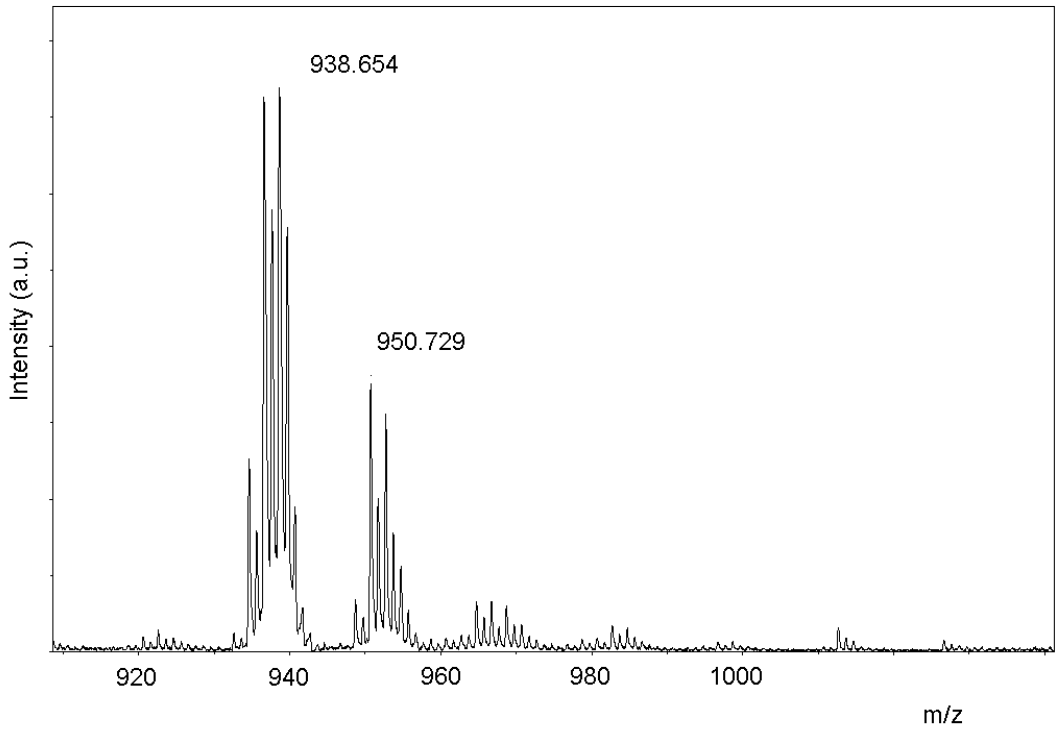

Fig. S1 MALDI-TOF mass spectrum for **B_{12}-TiO_2** (matrix: dithranol)

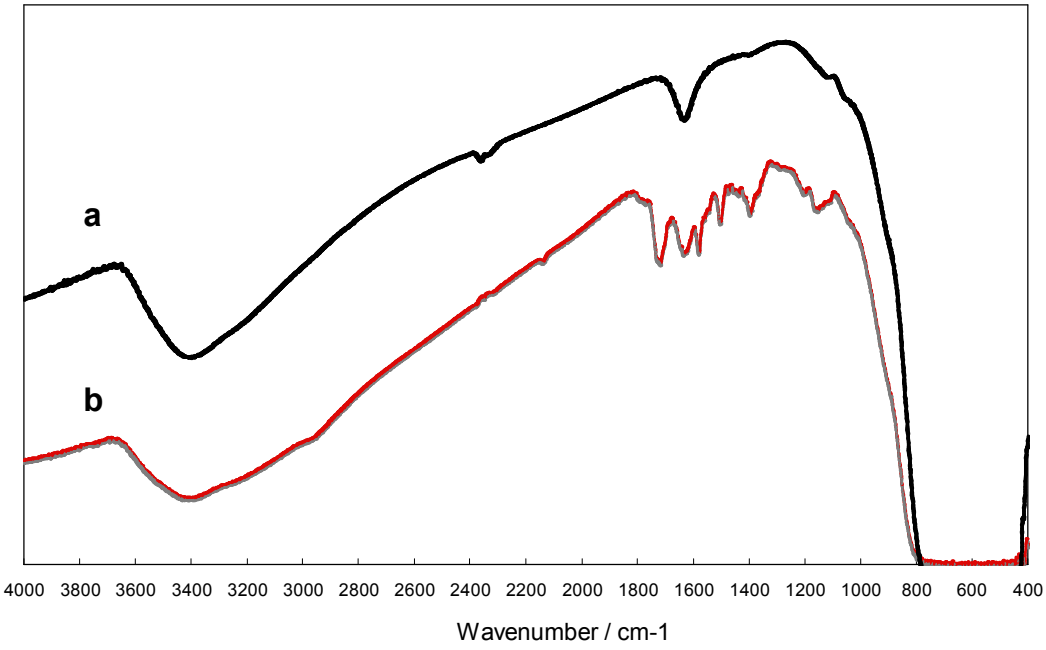

Fig. S2 FT-IR spectra for a) TiO_2 (black line) and b) **B_{12}-TiO_2** (red line)

Solvent effect

In addition to efficiency of hole scavenge, solvent viscosity also may influence the catalytic efficiency. In fact, solvent viscosity may influence the diffusion of substrate, catalyst according to Stokes-Einstein equation shown in equation S1.

$$D = k_B T / 6\pi r\eta \qquad (S1)$$

Where D is the diffusion coefficient and k_B is Boltzmann constant and r is the radius of the diffusing species. Brezova and co-workers found the correlation between rate constants of photocatalytic reduction and solvent viscosity.[S1] Indeed, the decay of the concentration of substrate **5a**, shown in Fig. 6, was found to be fitted to the exponential function in equation S2 kinetics as shown in Fig. S3, indicative of the first-order kinetics.

$$[\text{Substrate}] = A + B \cdot \exp(-k \cdot t) \qquad (S2)$$

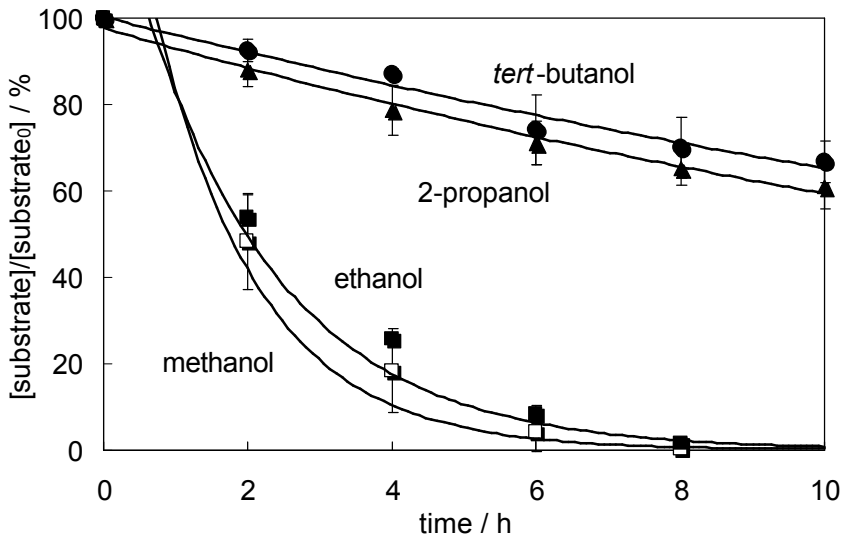

Fig. S3 concentration of substrate-time plot and kinetic curve fitting. □ methanol (y = 166.84exp(-0.6941x)), ■ ethanol (y = 138.56exp(-0.5161x)), ▲ 2-propanol (y = 97.692exp(-0.0498x)), ○ tert-butanol (y = 100.3exp(-0.043x)).

where *k* is the catalytic rate constant. Linear dependence on *k* versus 1/η (Fig. S4) suggests that viscosity η (Table S1) is another possible coefficient to determine catalytic efficiencies.

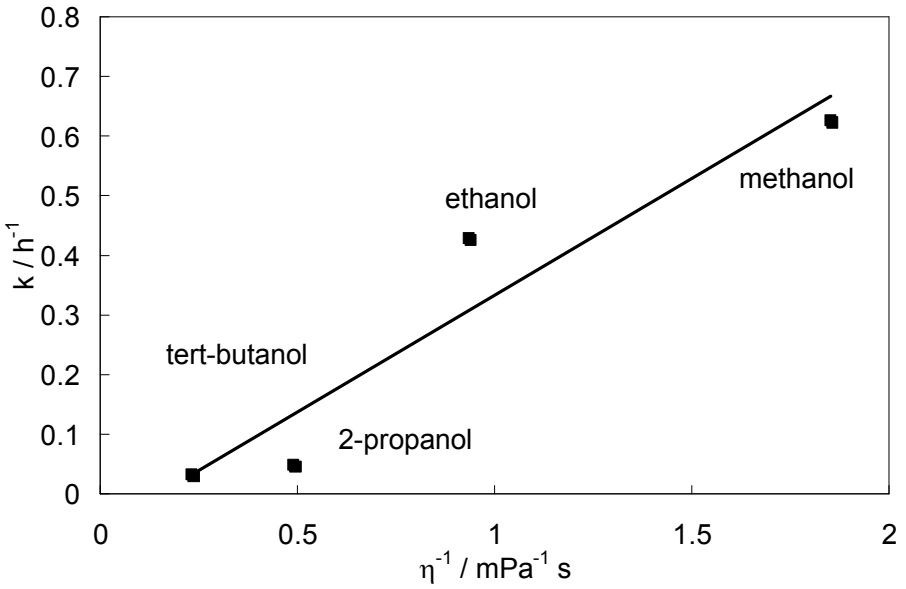

Fig. S4 Linear dependence on *k* versus 1/ η.

Table S1 Viscosity of various alcohols

Solvent	**η / mPa s^{-1}** [a]
methanol	0.54
ethanol	1.07
2-propanol	2.04
tert-butanol	4.31

[a] viscosity at 25℃, see ref. S2

References

S1) V. Brezová, B. Blazková, I. Surina and B. Havlínová, *J. Photochem. Photobiol., A,* 1997, **107**, 233-237.

S2) *Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC, Boca Raton, 74th edn., 1993 -1994. pp. 6-193.