## **Supporting Information**

Photo-Promoted Production of a New Monophenolic Compound from Larch Lignin with Polyoxometalates Supported on g-C3N4 under Ambient Conditions

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Instruments: Fourier Transform Infrared Spectroscopy (FT-IR, IRAffindedy-1, Shimadzu, Japan) was used to obtain the information of functional groups in the samples. The crystal structure of the samples was analyzed by X-ray diffractometer (Rigaku, D/max-2500X, Japan). Cu-K a rays were used as the radiation source, the radiation wavelength was 0.1542 nm with 40.0 kV voltage. The scanning angle was from  $10^{\circ}$ - $80^{\circ}$ , the stepping angle was  $0.02^{\circ}$ , and the scanning speed was  $5^{\circ}$ /min. The equipment used for SEM analysis was field emission environmental scanning electron microscope (Quanta FEG) of FEI in Netherlands, and the acceleration voltage is 20.00 kV, which is applied to characterize the sample morphology. A surface area and porosity analyzer (Micromeritics ASAP 2020, USA) was used to obtain the N<sub>2</sub> adsorption-desorption isotherms of the samples and thereby determine their Brunauer-Emmett-Teller (BET) specific surface areas and porosities. XPS (Thermo ESCALAB 250) was used to determine the elemental information (V, Mo, P, C, N and O) and calibrated with a C 1s peak at 284.6 eV. The optical absorption and band structure of the samples were evaluated by UV-Vis DRS (UV-2600i, Shimadzu, Japan). The photoluminescence spectra (PL, HORIBA Evolution, France) were recorded at the excitation wavelength of 325 nm to investigate the electron-hole recombination rate.

Agilent 6890N/5973i gas chromatography-mass spectrometry (GC-MS) was used to identify the structure of products and determine the yield of HMB. The detector is FID and the set temperature is 200 °C. The temperature of the injection port was 180 °C and the injection volume was 1  $\mu$ L. The carrier gas was high-purity helium with a split ratio of 5.01:1 and a flow rate of 2.05 mL/min. Gel Permeation Chromatography (GPC) analysis was performed to detect molecular weight of using Agilent Infinity 1260 HPLC. A standard sample of polystyrene with a calibrated molecular weight range of 910-28800 g/mol was used for calibration at a flow rate of 1 mL/min with the column oven temperature of 25 °C and THF as the mobile phase. The information of side chain region and aromatic region of larch lignin and bio-oil were characterized by a Bruker Avance II 500 MHz nuclear magnetic resonance spectrometer (2-dimension heteronuclear single-quantum coherence, 2D HSQC) with dissolving some samples in 0.5 mL solution of DMSO-d6/pyridine-d5.



Fig. S1 FT-IR of CN, HPMoV, and HPMoV/CN with different amount of HPMoV,

respectively.



Fig. S2 The power XRD patterns of CN, HPMoV, and HPMoV/CN with different amount of HPMoV, respectively.



Fig. S3 Comparation on the BET results of different catalysts.



Fig. S4 UV-Vis DRS (a) and optical band gap (b) of CN  $\sim$  HPMoV and 25% HPMoV/CN



Fig. S5 PL spectra of CN and 25% HPMoV/CN.



Fig. S6 Effect of different reaction factors in the production of HMB from larch lignin. Reaction conditions: a: DES 20 mL, 1 mL H<sub>2</sub>O, 80 °C, 6 h; b: DES 20 mL, 1 mL H<sub>2</sub>O,

80 °C, 6 h; c: 0.2 g 25% HPMoV/CN, 1 mL H<sub>2</sub>O, 80 °C, 6 h; d: 0.2 g 25% HPMoV/CN, DES 20 mL, 1 mL H<sub>2</sub>O, 6 h; e: 0.2 g 25% HPMoV/CN, DES 20 mL, 1 mL H<sub>2</sub>O, 80 °C; f: 0.2 g 25% HPMoV/CN, DES 20 mL, 80 °C, 6 h.



Fig.S7 GC-MS of products with the addition of D<sub>2</sub>O to DES instead of H<sub>2</sub>O under the

optimum conditions.



Fig. S8 Effect of different DES on the yields of HMB and the conversion of bio-oil under the optimum conditions.



Fig. S9 The reusability performances of 25% HPMoV/CN under the optimum

conditions.



Fig. S10 The results of GPC of larch lignin befor the reaction and bio-oil after

the depolymerization.



Fig. S11 Effect of various quenching agents on the degradation of lignin.



Fig. S12 The capture of free radicals of  $h^+$  (a) and  $\cdot OH$  (b) with the conditions of dark and light for 5 min.

Catalysts	guaiacol (%)	HMB (%)	conversion (%)
no catalyst	4.10	25.70	92.05
CN	5.85	33.19	93.84
HPMo	4.43	28.07	91.89
HPMoV	4.90	31.94	92.65
HPMo/CN	8.11	36.89	94.04
HPMoV/CN	9.22	48.43	94.58

Table S1 Performances of different catalysts on the degradation of GG under

optimum conditions.



Fig. S13 Comparation of GC-MS in fracturing GG with the addition of D<sub>2</sub>O instead of

H<sub>2</sub>O.

Catalysts	guaiacol (%)	BDT (%)	conversion (%)
no catalyst	3.07	31.47	92.86
CN	4.59	42.19	93.85
HPMo	3.93	35.07	93.34
HPMoV	4.90	41.94	93.37
HPMo/CN	4.71	40.89	94.00
HPMoV/CN	6.22	47.45	94.03

Table S2 Performances of different catalysts on the degradation of VG under

optimum conditions.



Fig. S14 Comparation of GC-MS in fracturing VG with the addition of D<sub>2</sub>O instead of

H<sub>2</sub>O.

Catalysts	BP (%)	ED (%)	MEPO (%)	conversion (%)
no catalyst	1.02	58.47	0.93	95.26
CN	4.34	60.33	1.24	93.37
НРМо	4.22	60.05	1.91	92.42
HPMoV	4.70	62.32	2.35	93.56
HPMo/CN	4.79	64.30	3.82	94.06
HPMoV/CN	5.38	65.92	9.04	96.36

Table S3 Performances of different catalysts on the degradation of Dpol under optimum conditions.



Fig. S15 The products in the degradation of Mpol (a), PP-ol (b), and Dpol (c), and the possible depolymerization pathways of Dpol (d) under optimum conditions.



Fig. S16 GC-MS of fracturing PP-ol, Mpol, and Dpol under optimum conditions.