

Supplementary Information

Dioxetane formation and chemiluminescent emission upon the combination of a vinylphenol derivative with naphthalene endoperoxide

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Experimental Section

General Methods. Melting points were determined by Yanagimoto micro melting point apparatus and uncorrected. ¹H-NMR spectra were measured with JEOL JMN-AL-300 (300 MHz) or JOEL JNM-ECA600P (600 MHz) spectrophotometers. Coupling constants (*J* values) are reported in hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane ($\delta = 0$) or residual chloroform ($\delta = 7.24$) as an internal standard. ¹³C NMR spectra were measured with JEOL JMN-AL-300 (75 MHz) or JOEL JNM-ECA600P (600 MHz) spectrophotometers. Mass spectra were recorded on a JOEL JMS-SX102A spectrometer, using nitrobenzylalcohol matrix. Wakogel C-300 was used for silica gel column chromatography. Precoated TLC plates Merck silica gel 60 F₂₅₄ was used for monitoring reactions. VPA was synthesized as described previously (Simsek Turan; Engin U. Akkaya, *Org. Lett.*, **2014**, *16*, 1680–1683). All aqueous solutions were prepared using purified water (YAMATO, WR600A).

Compound 2. 4-methyl-1-naphthalenepropionic acid (199 mg, 0.93 mmol), N- (tert-Butoxycarbonyl)-1, 2-diaminoethane (148 μ L, 0.93 mmol), 1- (3-

Dimethylaminopropyl)-3-ethylcarbodiimide (EDCI) (179 mg, 0.93 mmol), and 1-Hydroxybenzotriazole (HOBT) (128 mg, 0.93 mmol) were dissolved in 5 mL DMF, and stirred at room temperature for 22 h. After addition of saturated NaHCO₃, reaction mixture was extracted with EtOAc. Combined organic layer was washed by brine, and dried with MgSO₄. After removal of the solvent, the residue was purified by column chromatography (SiO₂, CHCl₃). Compound **2** was obtained as white solid (258 mg, 78%): m.p. 133 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.08–8.06 (m, 1H), 8.04–8.02 (m, 1H), 7.55–7.52 (m, 2H), 7.24 (s, 1H), 5.94 (brs, 1H), 4.66 (brs, 1H), 3.41 (t, *J* = 7.8 Hz, 2H), 3.29 (q, *J* = 5.4 Hz, 2H), 3.15 (d, *J* = 5.4 Hz, 2H), 2.67 (s, 3H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.41 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 172.84, 156.75, 134.92, 133.14, 132.95, 131.57, 126.29, 125.93, 125.75, 125.47, 125.00, 124.05, 79.64, 40.65, 40.25, 37.88, 28.87, 28.34, 19.44;. FABMS (matrix; 3-nitrobenzyl alcohol) *m/z* 356 [M⁺]; HRMS calcd. for C₂₁H₂₈O₃N₂⁺: [M⁺], 356.2100, found 356.2092.

Compound 3. Compound **2** (300 mg, 0.84 mmol) was dissolved in 0.5 M HCl in methanol solution (5 mL) and the mixture was stirred at room temperature for 4 h. After addition of saturated NaHCO₃, the reaction mixture was extracted with EtOAc.

Combined organic layer was washed by brine, and dried with MgSO₄. After removal of the solvent, the residue was purified by column chromatography (SiO₂, 20% MeOH-CHCl₃). Compound **3** was obtained as pale yellow oil (32 mg, 15%): ¹H NMR (300 MHz, DMSO-d₆) δ 8.11–8.08 (m, 1H), 8.04-8.01 (m, 1H), 7.86 (brs, 1H), 7.58-7.55 (m, 2H), 7.28-7.22 (m, 2H), 3.25 (t, *J* = 7.3 Hz, 2H), 3.08 (q, *J* = 5.9 Hz, 2H), 2.61 (s, 3H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.46 (t, *J* = 7.3 Hz, 2H); ¹³C NMR (125 MHz, DMSO-*d*) δ 172.15, 135.39, 132.44, 132.29, 131.34, 126.26, 125.74, 125.54, 125.42, 124.80, 124.13, 38.52, 36.61, 36.43, 28.03, 19.05;. FABMS (matrix; 3-nitrobenzyl alcohol) *m/z* 257 [(M + H)⁺]; HRMS calcd. for C₁₆H₂₁ON₂⁺: 257.1654, found 257.1655.

Preparation of silica nanoparticles bearing naphthalene units (MSN-NA).

Mesoporous silica nanoparticle (20 mg, 0.8 μmol), compound **3** (15.9 mg, 62 μmol), EDCI (12 mg, 62 μmol) and HOBt (8.4 mg, 62 μmol) were dissolved in 1 mL DMF and the mixture was stirred for 12 h. The precipitate was produced by the addition of water (9 mL) and isolated by centrifuging at 3000 rpm for 3 min. Wash of the precipitate with water twice gave MSN-NA.

Oxidation of MSN-NA (MSN-NEP). MSN-NA (2.7 mg, 0.11 mmol) was dissolved in 50 mM methylene blue solution (5 mL) in the solvent (DMSO: H₂O = 1: 1). After bubbling of oxygen gas (15 min), the mixture was photo-irradiated (665 nm) for 1 h. After irradiation, the precipitate was produced by the addition of water and isolated by centrifuging at 3000 rpm for 3 min. Wash of the precipitate with water twice gave MSN-NEP.

Measurement of Absorption Spectra. All UV-vis absorption spectra of the sample were recorded using a JASCO V-630 spectrophotometer with a 1 cm quartz cell.

Measurement of chemiluminescent spectra. Chemiluminescent spectra of the samples were recorded using a JASCO FP-8300 spectrofluorometer with a 1 cm quartz cell. The sample in aqueous solution containing phosphate buffer at various pH conditions were prepared and subjected to spectrometer.

Measurement of emission of singlet oxygen. Phosphorescence emission of singlet

oxygen from MSN-NEP and NEP were measured by means of spectrometer consisted of XeCl excimer laser (Lambda Physik Complex102, 308 nm, Pulse width 20 ns) equipped with photomultiplier tube (Hamamatsu Photonics H10330B-45). The samples in DMSO were prepared and subjected to spectrometer.

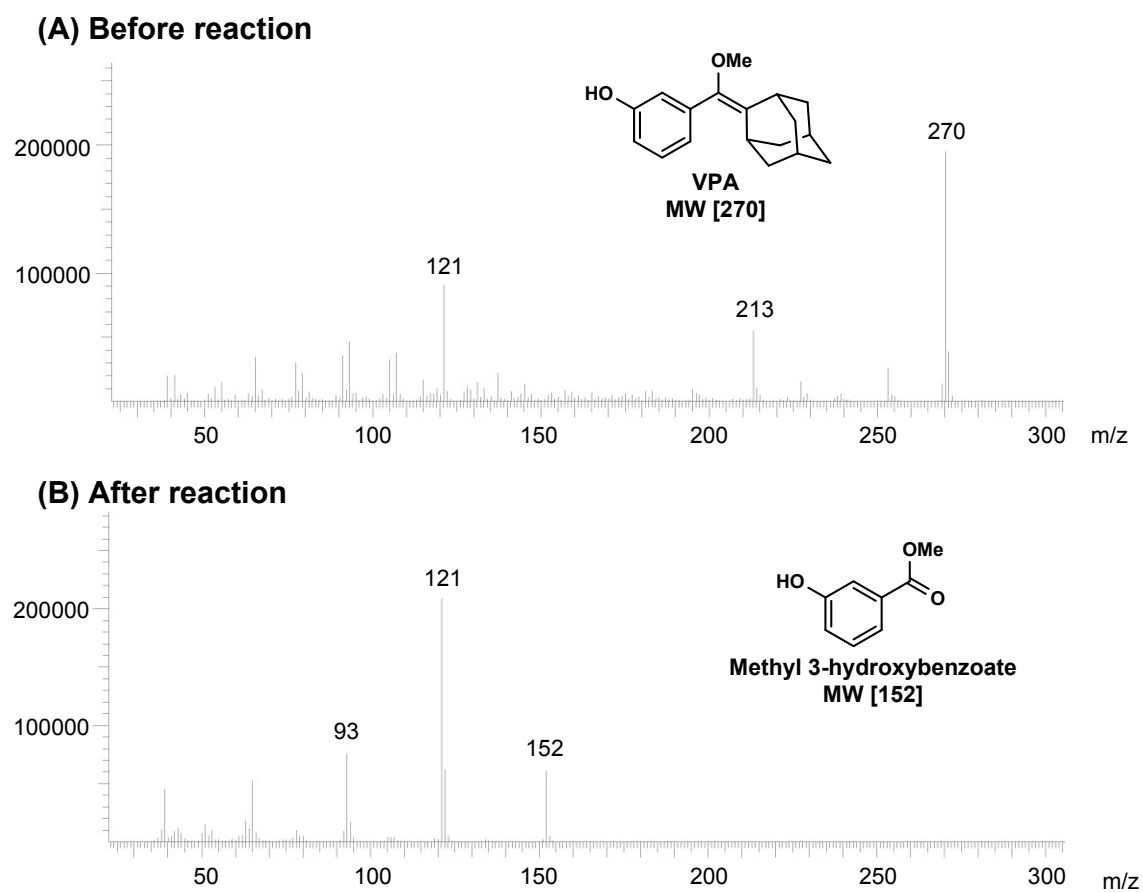


Figure S1. Analysis of the reaction of VPA (10 mM) and NEP (90 mM) by GC-MS.

MS spectra were measured before (A) or after the reaction for 1 h (B).

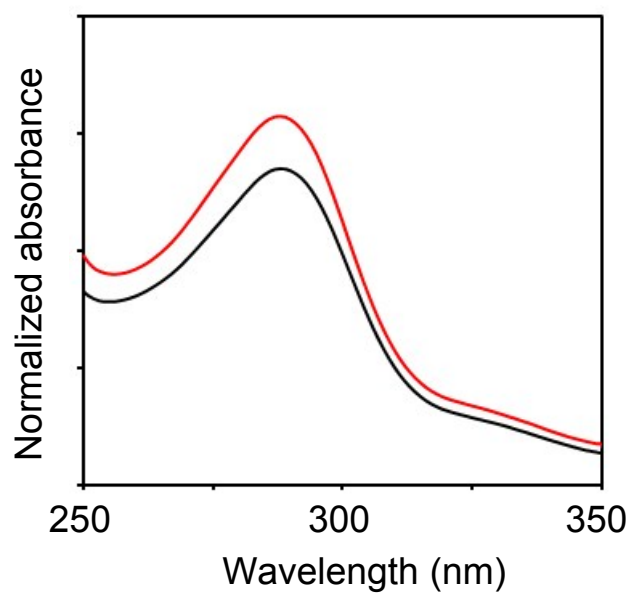


Figure S2. Absorption spectra of MSN-NEP before (black) or after release of $^1\text{O}_2$ (red).

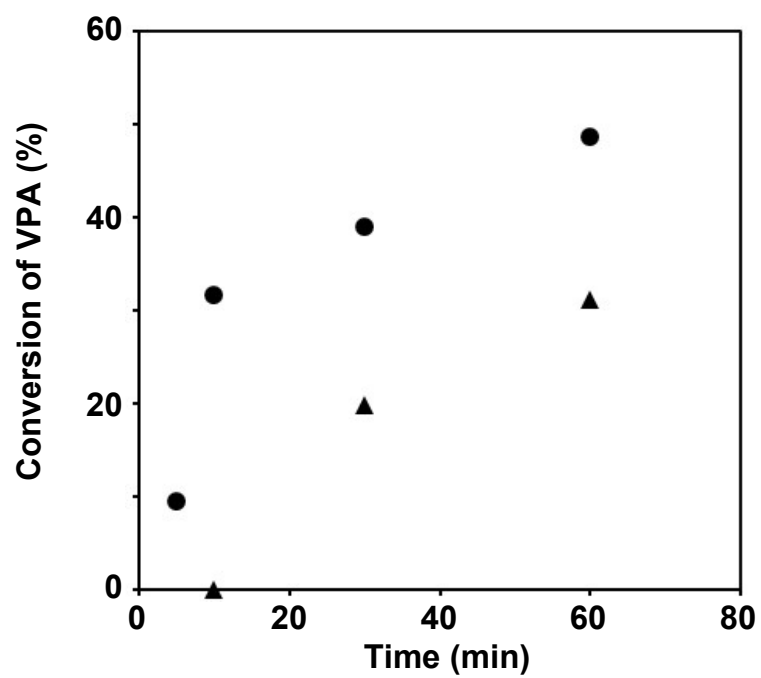


Figure S3. Time profile of VPA consumption during the reaction with NEP (circle) or MSN-NEP (triangle).