Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Rapid Degradation of Oxidation Resistant Nitrophenols by TAML Activator and H_2O_2

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Instrumentation

A Waters HPLC system consisting of a Waters 600 controller, 2996 Photodiode Array Detector and 717 plus autosampler was used. Chromatographic separations were achieved using a Varian Polaris C-8 (150 mm × 2 mm, 5 μM) column. The mobile phase consisted of acetonitrile and water (0.1% formic acid). The mobile phase flow rate was 0.5 $mL.min^{-1}$. The column temperature was kept at 30 °C and the injection volume was 20 μL. The gradient profile used is shown in Table 1. Under the above mentioned conditions, the retention times of 2-NP, 3-NP, 4-NP, 2-Me-4-NP, 3-Me-4-NP, and 2,6-diMe-4-NP were 13.03, 16.81, 17.54, 32.46, 31.53, and 33.95 min, respectively. For DNPs, the retention times of 2,6-DNP, 2,5-DNP, 2,4-DNP, and 2-Me-4,6-DNP were 8.6, 11, 13, and 24.3 min, respectively. The percentage of degradation of each NP at different times was measured by HPLC, based on calibration curves generated for each NP using standard compounds. The UV detector in the HPLC was set at 283 and 333 nm for MNP and DNP detection, respectively.

Table 1S. Gradient program used for separation of nitrophenols

Time / min	0	20	21	25	30	35
CH_3CN	0	5	30	40	50	50
H_2O (0.1% formic acid)	100	95	70	60	50	50

For Ion Chromatography studies, a Dionex DX500 chromatography system consisting of a GP50 gradient pump, an AS40 automated sampler, an ED40 electrochemical detector, a LC25 chromatography oven, and an ASRS® 300 (P/N 064554) self-regenerating suppressor were used. Chromatographic data were analyzed using Chromeleon chromatography software (Version 6.70 Build 1820, S/N 50398). IonPac® AS9-HC (4 × 250 mm) analytical and IonPac® AG9-HC (4 × 50 mm) guard columns were obtained from Dionex. The IC analysis was performed under isocratic conditions with 9 mM Na_2CO_3 as the mobile phase at 1mL/min flow rate with the oven temperature set at 35°C and the SRS current set at 100 mA. The injection volume for all IC samples was 100 μL. The mobile phase for IC analysis was prepared with water from a Barnstead Nanopure system. The end products of NP degradation were detected as formate, nitrite and nitrate ions, which had retention times of 4.9, 8.6 and 13.2 min, respectively. The degradation reaction mixtures were quenched with catalase for these studies.

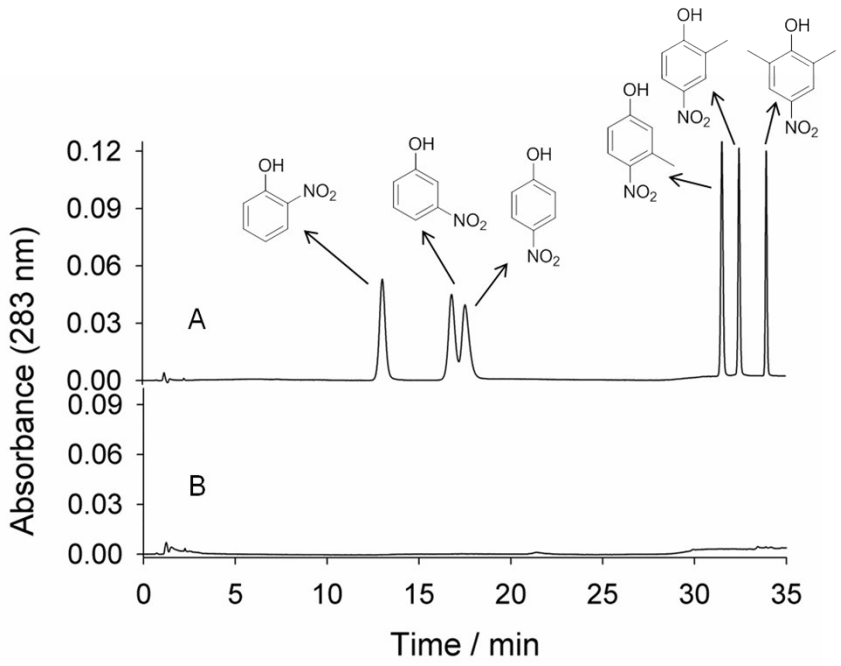

Figure 1S. (A) Untreated mixture of MNPs (1×10^{-4} M). (B) Treatment of MNPs (shown in A) with **1**/H_2O_2 under the previously optimized conditions (Table 1). Conditions: [2-NP]=[3-NP]=[4-NP]=[2-Me-4-NP]=[3-Me-4-NP]=[2,6-diMe-4-NP] = 1×10^{-4} M, [**1**] = 6.9×10^{-6} M (Total optimized **1**, Table 1), [H_2O_2] = 1.8×10^{-1} M (Total of optimized H_2O_2, Table 1), 30 min reaction time, pH 8 (0.1 M phosphate), room temperature.

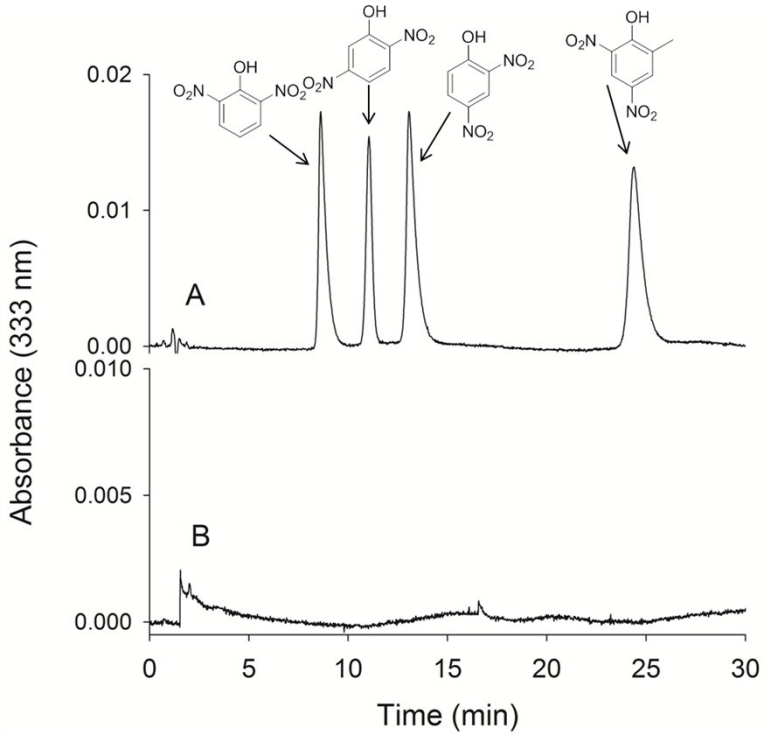

Figure 2S. (A) Untreated mixture of DNPs (1×10^{-4} M). (B) Treatment of DNPs (shown in A) with **1**/H_2O_2 under the previously optimized conditions (Table 1). Conditions: [2,6-DNP]=[3,5-DNP]=[4,6-DNP]=[2-Me-4,6-DNP] = 1×10^{-4} M, [**1**] = 11.3×10^{-6} M (Total optimized **1**, Table 1), [H_2O_2] = 1.8×10^{-1} M (Total of optimized H_2O_2, Table 1), 45 min reaction time, **1** and H_2O_2 added in two equal aliquots at *t*=0 and t=25 min, pH 8 (0.1 M phosphate), room temperature.

Table 2S. pK_a's of Mononitrophenols

Compounds	***pK$_a$***
2-Nitrophenol	7.21[1]
4-Nitrophenol	7.16[1]
3-methyl-4-Nitrophenol	7.33[2]
2-methyl-4-Nitrophenol	7.33[2]
2,6-dimethyl-4-Nitrophenol	7.07[3]

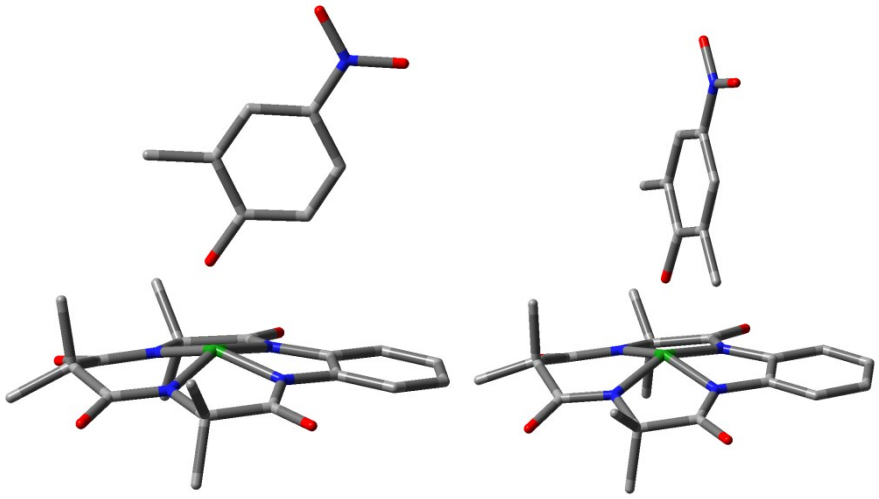

Figure 3S. Geometry optimized structure of 2-Me-4-NP and 2,6-diMe-4-NP bound to methyl substituted Fe(TAML) showing differences in the binding mode. Significant tilt was observed for 2-Me-4-NP and almost 90° turn was observed for 2,6-diMe-4-NP.

References

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