Supporting Information

In Situ Synthesis of CdS@NH_2-MIL-125 Nanocomposite for Enhanced Photocatalytic Oxidative Desulfurization of Dibenzothiophene

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Table of contents **Pages**

1. Photocatalyst characterization

Table S1. Results of bandgap calculation for synthesis photocatalysts

Photocatalyst name	Bandgap (eV)
CdS	2.1
NH_2-MIL-125	2.6
CdS@NH_2-MIL-125	2.52

2. Optimization of reaction conditions

Table S2: Solvent Screening [a]

Entry	Solvent	DBT removal percent (%)
1	Toluene	76.8
2	*n*-Octane	3.5
3	*n*-Heptane	2
4	CH_3CN	56 (after 3 days)
5	EtOH	82 (after 3 days)
6	DMSO	3
7	THF	26.2
8	MeOH	2
9	*n*-Octane/CH_3CN	6.5
10	Toluene/ CH_3CN	27
11	EtOH/ CH_3CN	12
12	EtOH/ H_2O	5.5
13	Toluene/H_2O	15
14	Toluene/EtOH	20

[a] Reaction conditions: CdS@NH_2-MIL-125 (20 mg), t = 24 h, T = r.t, DBT = 100 ppm, 12 W blue LED under oxygen gas.

3. HPLC chromatograms in the photocatalytic oxidative desulfurization of DBT

The concentration obtained of DBT after the reaction was determined by reversed-phase HPLC on an Agilent 1100 using Merck SP-18 column and Lichrospher C-18 bonded packing. The mobile phase was acetonitrile and water (75/25 V/V) and UV detector at 245 nm with a flow rate of 0.8 mL/min. An external standard of DBT was found to elute under these conditions at 6.7 min according to the method used in reference [1]. It seems that the peak appeared in retention time of 3.15-3.40 is related to DBT sulfone. Thus DBT sulfone obtained by the photo-oxidation was found to elute around 3.15-3.40 min [1].

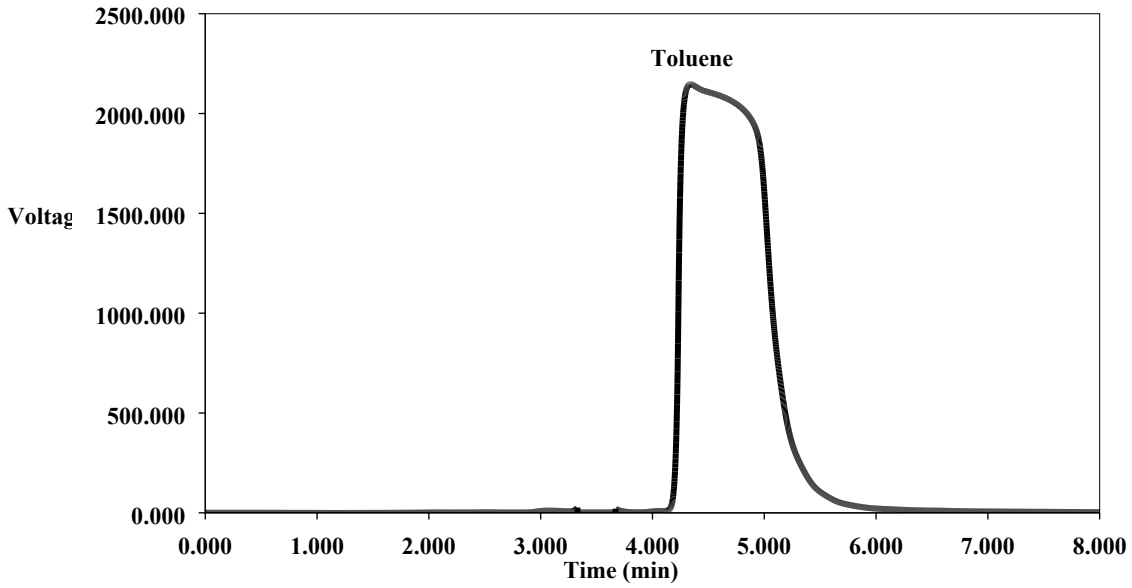

Figure S1. HPLC Chromatogram of toluene as solvent (retention time 4.145-5.79 min).

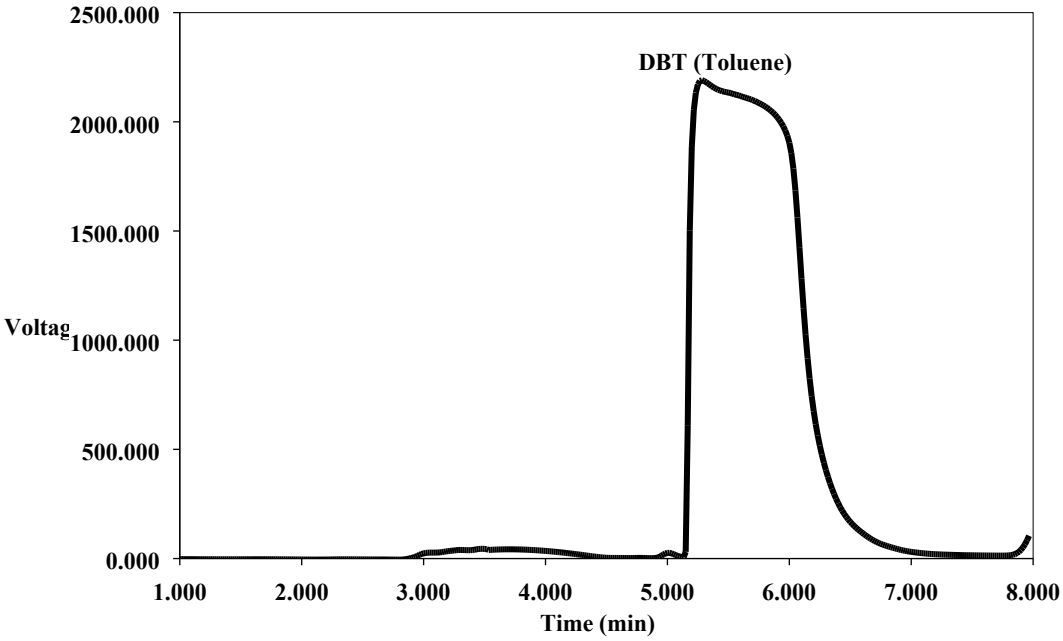

Figure S2. HPLC Chromatogram of 100 ppm standard of DBT in toluene (retention time 5.5-6.7 min).

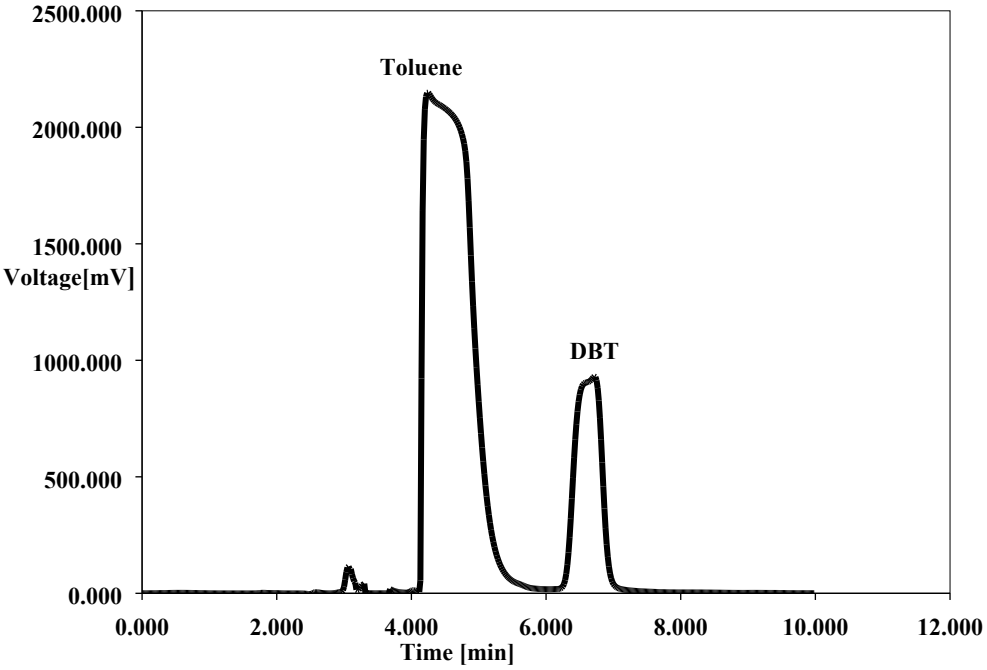

Figure S3. HPLC Chromatogram [Reaction condition: Without catalyst, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under oxygen gas]

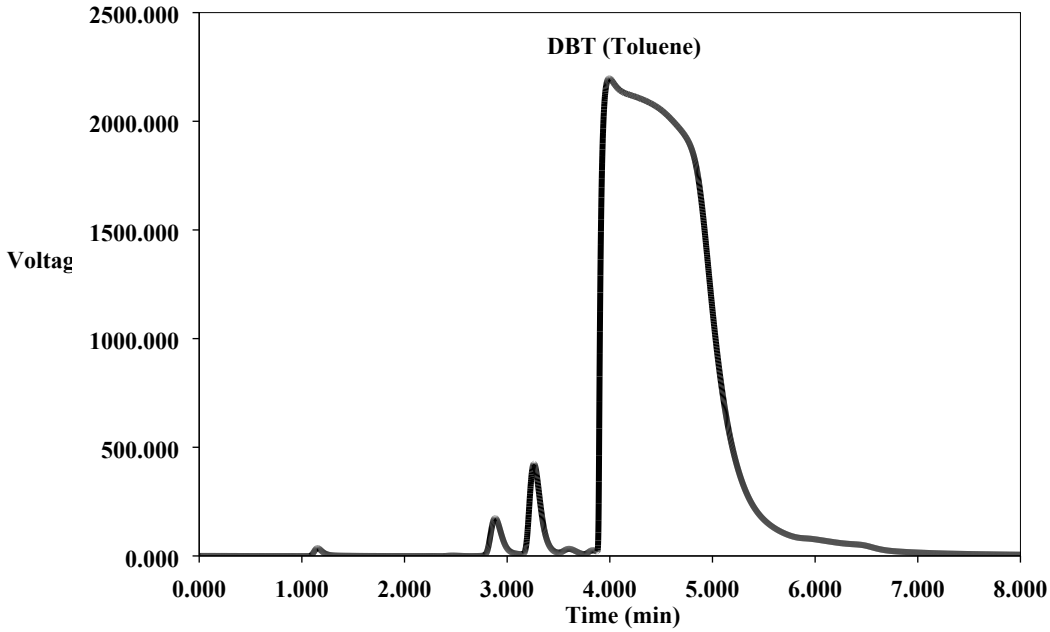

Figure S4. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 2 h in the dark and under oxygen gas], (Retention time 3.30 min)

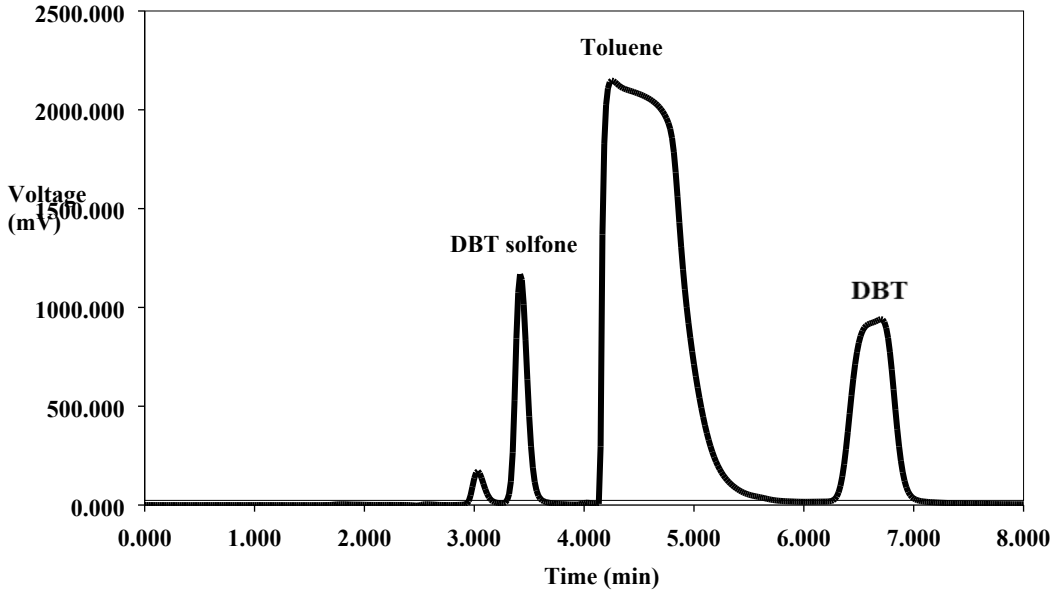

Figure S5. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 5 h under visible light irradiation and oxygen gas] (Retention time 3.43 min).

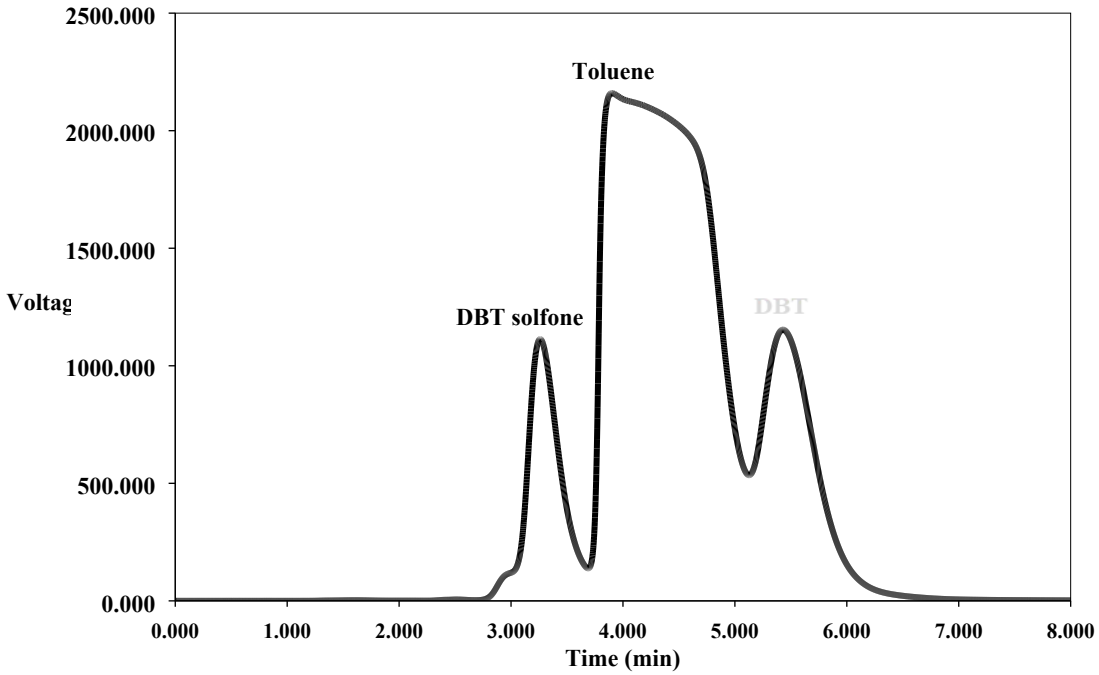

Figure S6. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 8 h under visible light irradiation and oxygen gas] (Retention time 3.30 min).

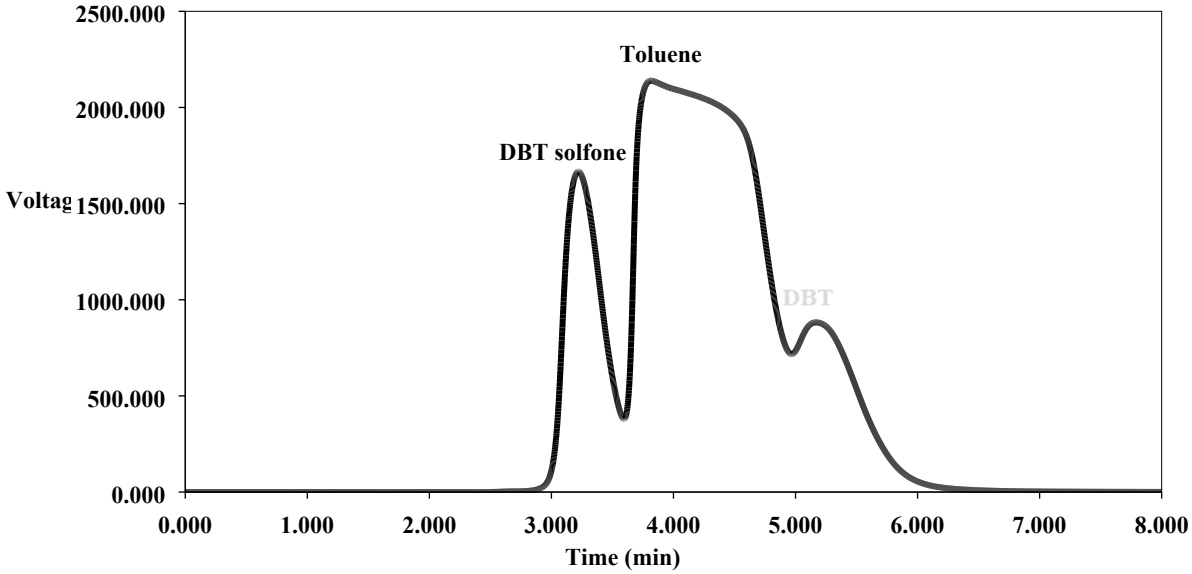

Figure S7. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 12 h under visible light irradiation and oxygen gas] (Retention time 3.28 min).

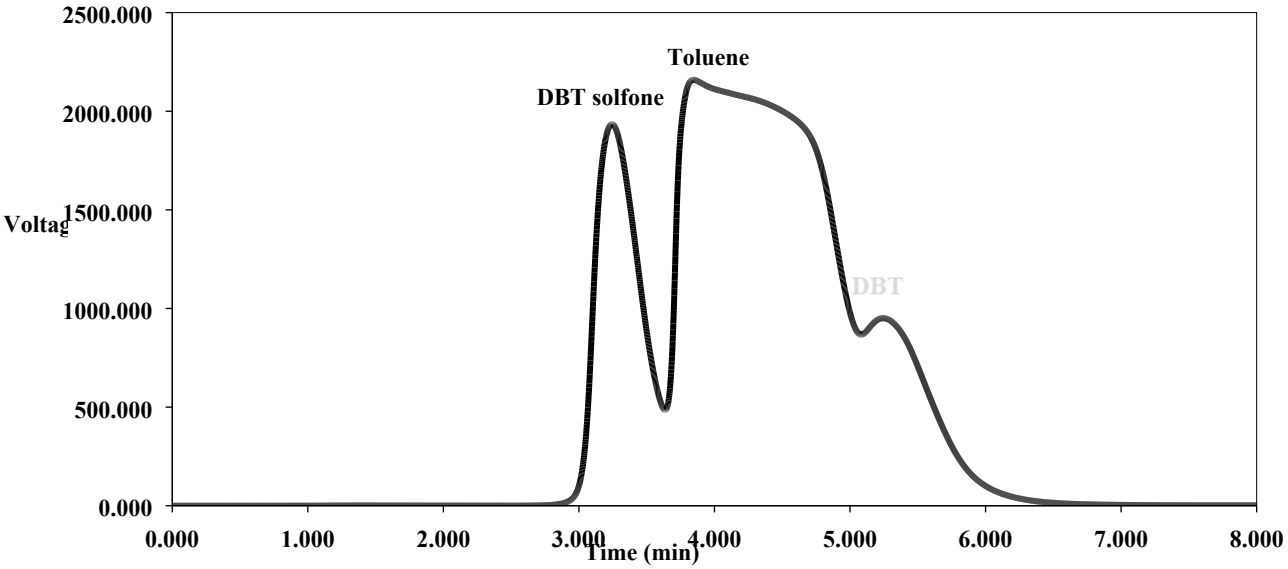

Figure S8. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 17 h under visible light irradiation and oxygen gas] (Retention time 3.28 min).

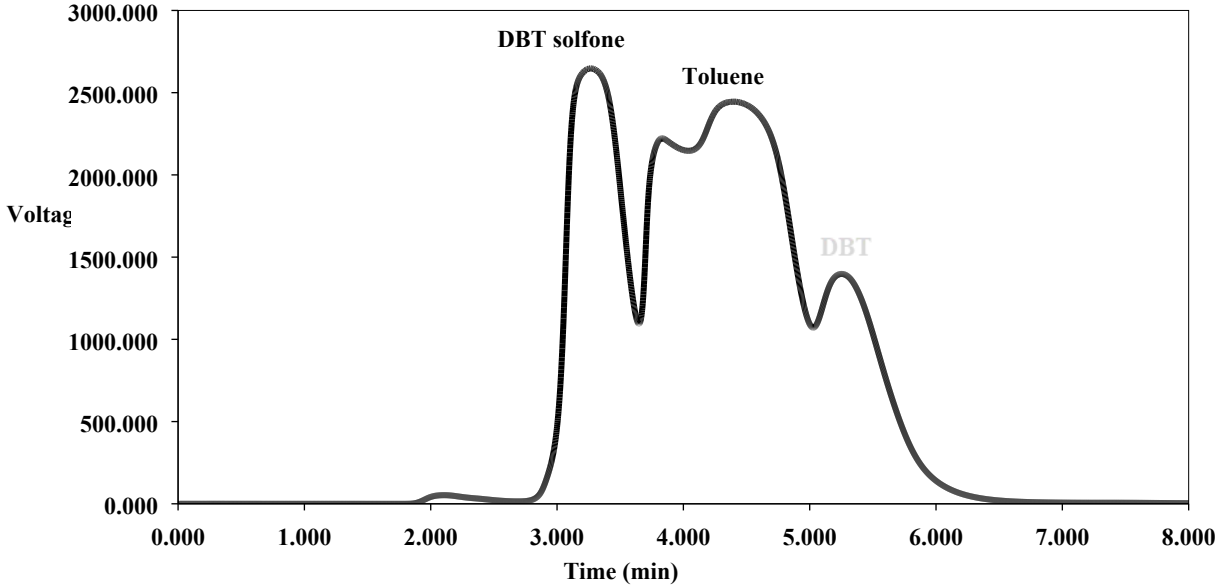

Figure S9. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 20 h under visible light irradiation and oxygen gas] (Retention time 3.30 min).

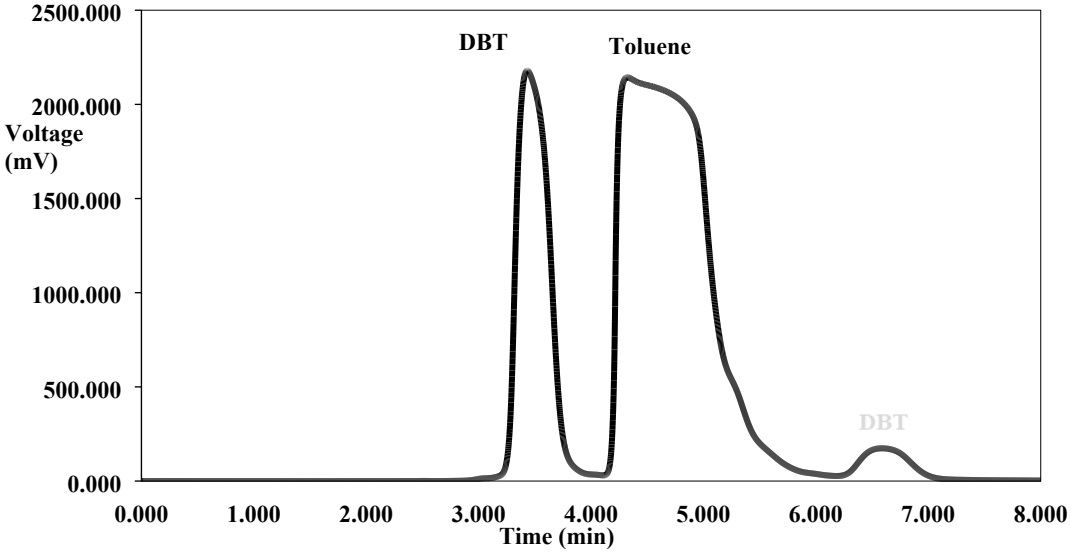

Figure S10. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 24 h under visible light irradiation and oxygen gas] (Retention time 3.40 min).

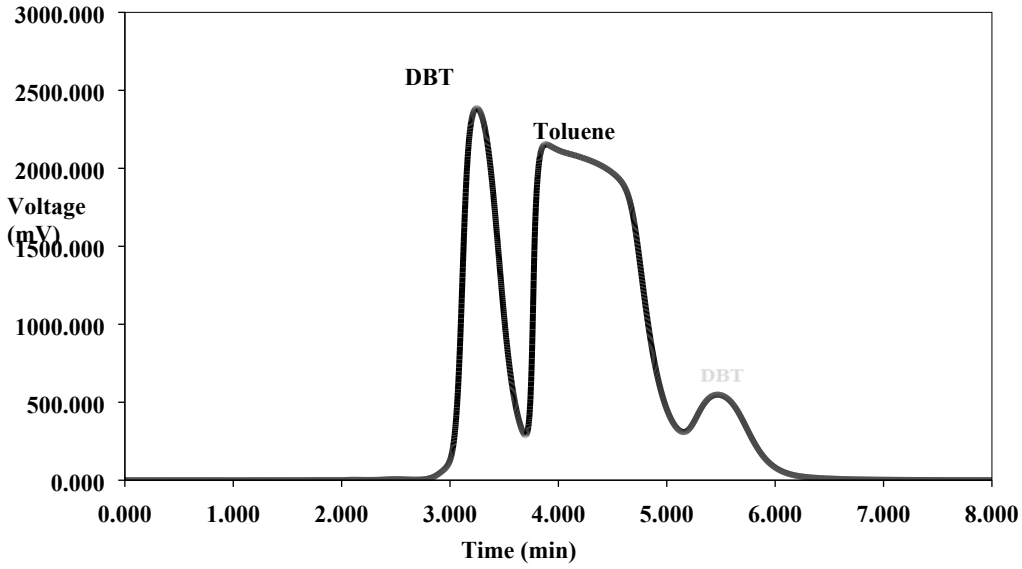

Figure S11. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, for 26 h under visible light irradiation and oxygen gas] (Retention time 3.28 min).

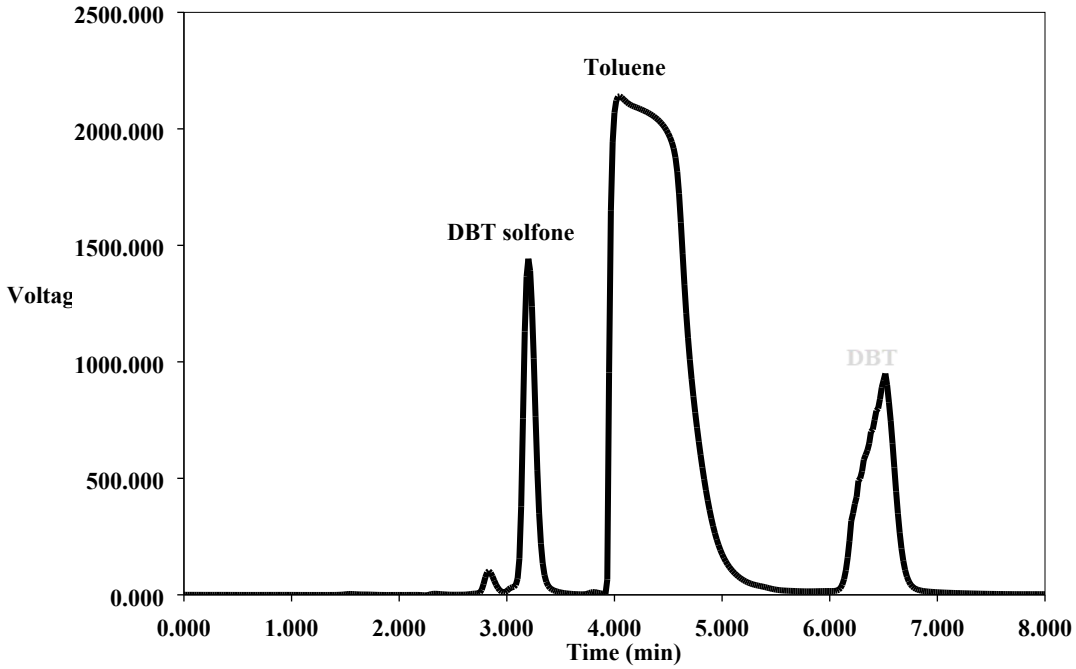

Figure S12. HPLC Chromatogram [Reaction condition: 5 mg CdS@NH_2-MIL-125, , t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under oxygen gas] (Retention time 3.21 min)

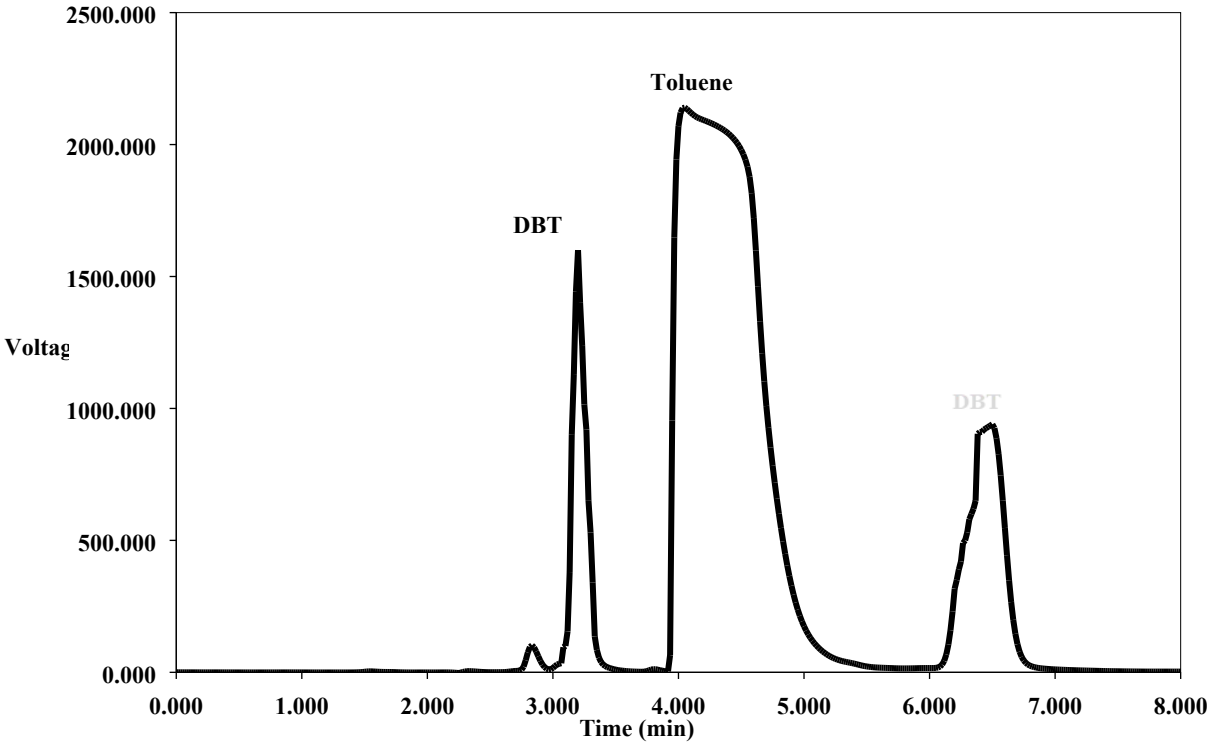

Figure S13. HPLC Chromatogram [Reaction condition: 10 mg CdS@NH_2-MIL-125, , t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under oxygen gas] (Retention time 3.18 min)

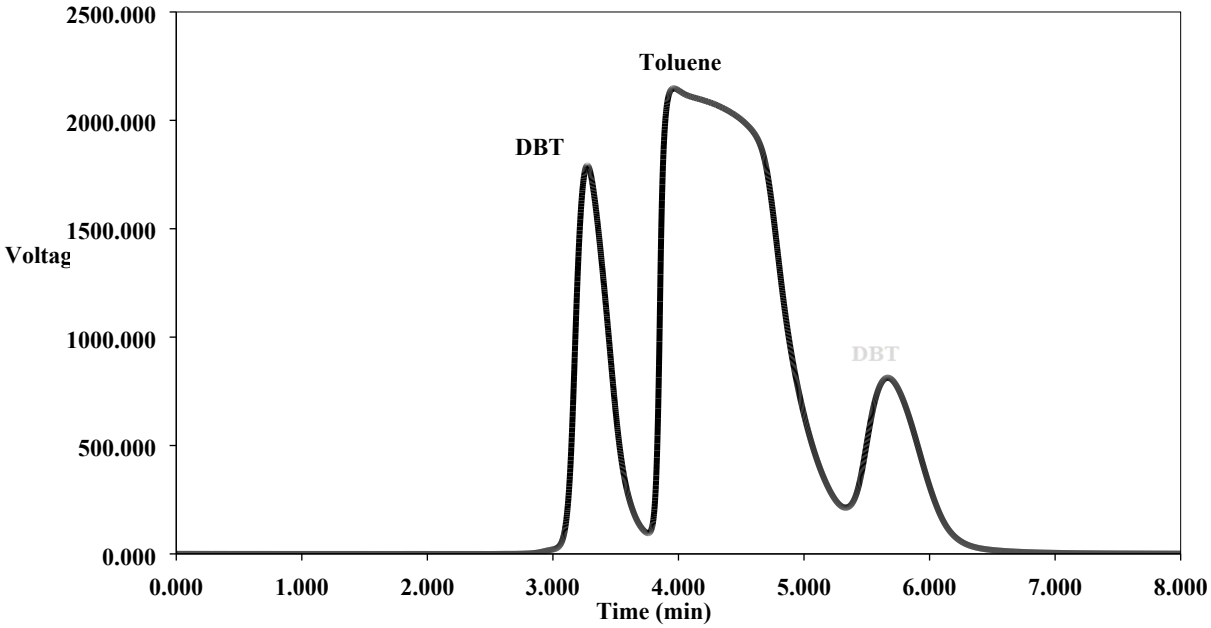

Figure S14. HPLC Chromatogram [Reaction conditions: 15 mg CdS@NH_2-MIL-125, , t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under oxygen gas]

(Retention time 3.18 min)

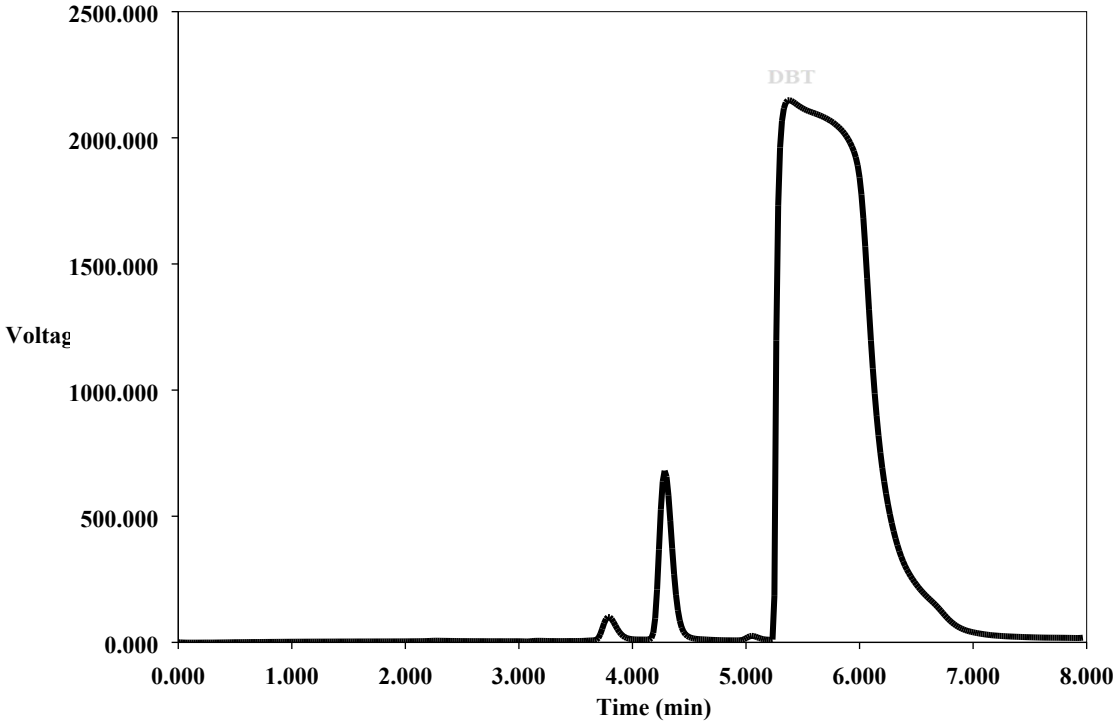

Figure S15. HPLC Chromatogram in dark conditions [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under oxygen gas]

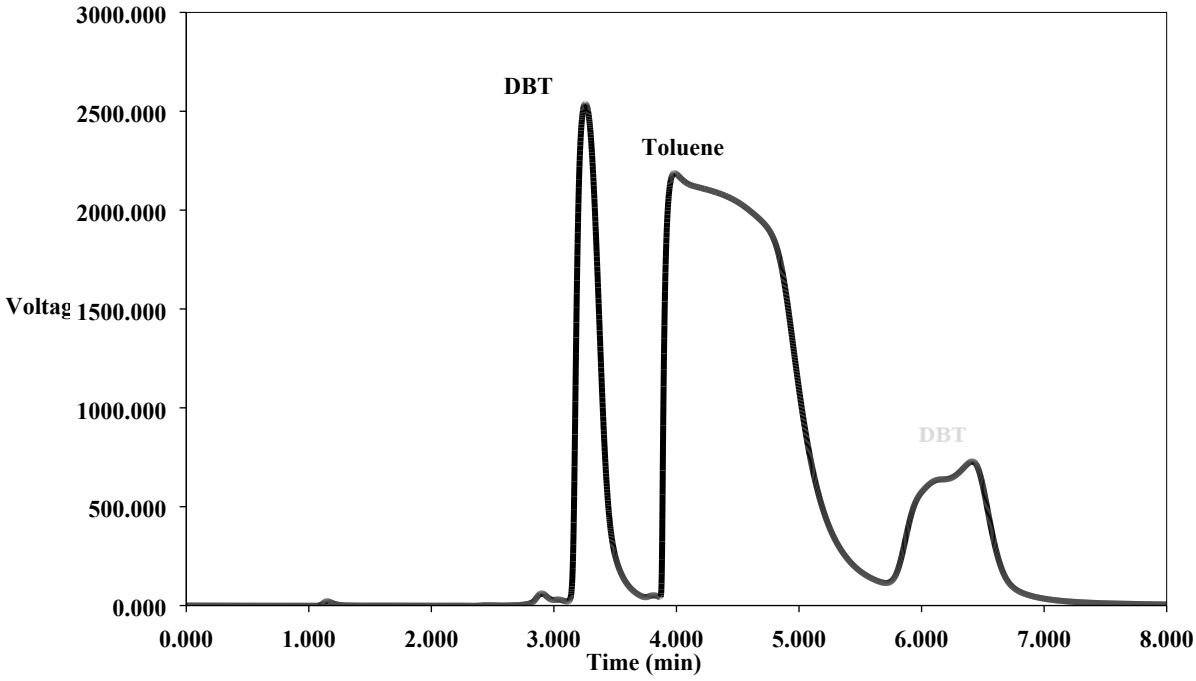

Figure S16. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, , t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W blue LED, under natural sunlight and oxygen gas] (Retention time 3.18 min).

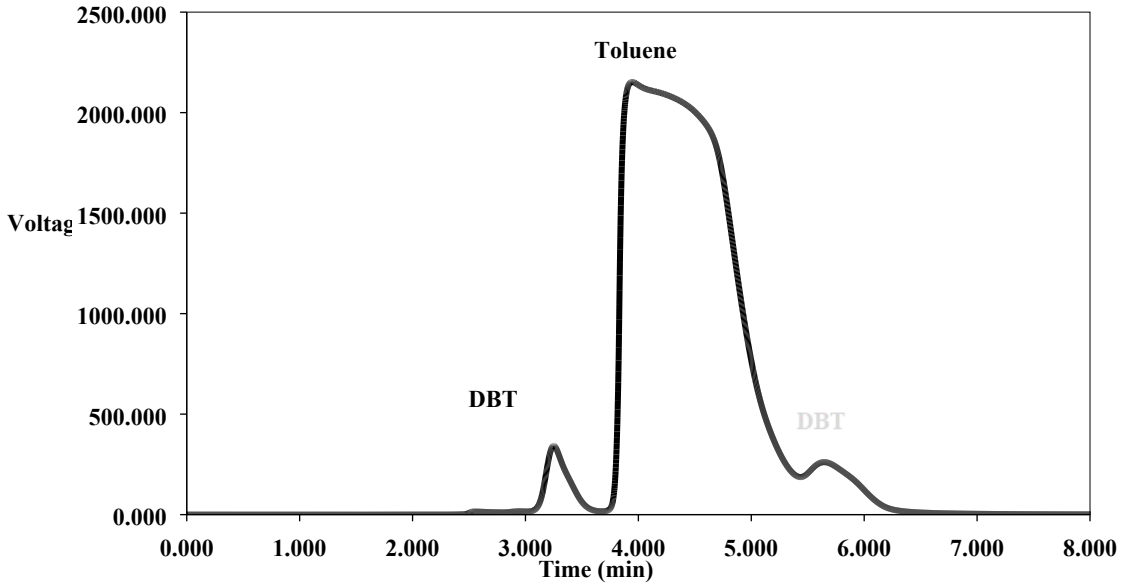

Figure S17. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, , t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 12 W white CFL, under oxygen gas] (Retention time 3.18 min).

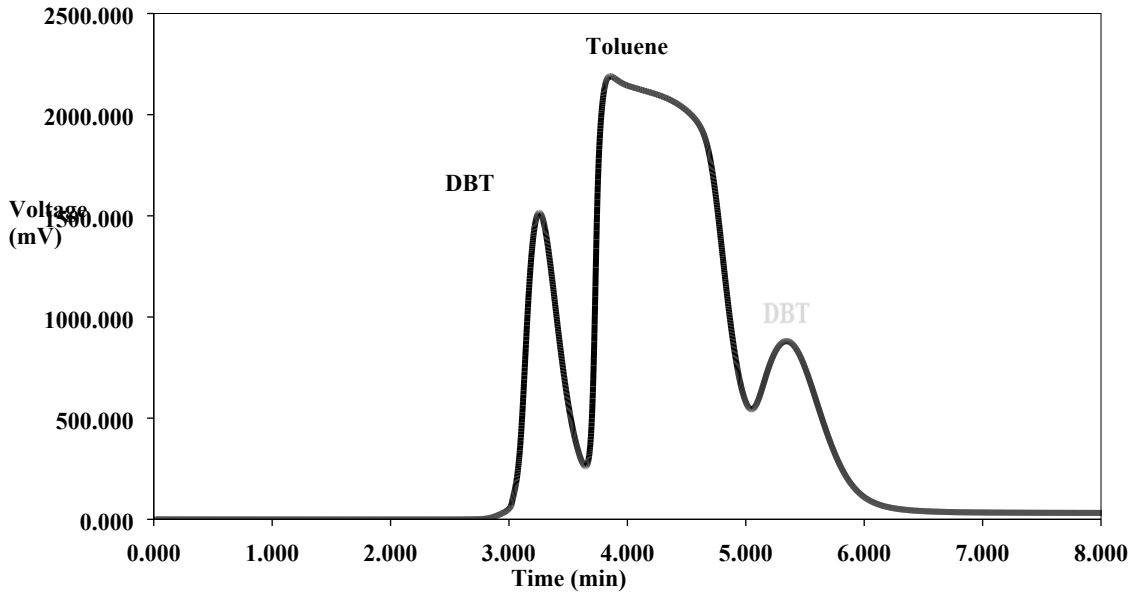

Figure 1

Figure S18. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, TEA scavenger under oxygen gas] (Retention time 3.18 min).

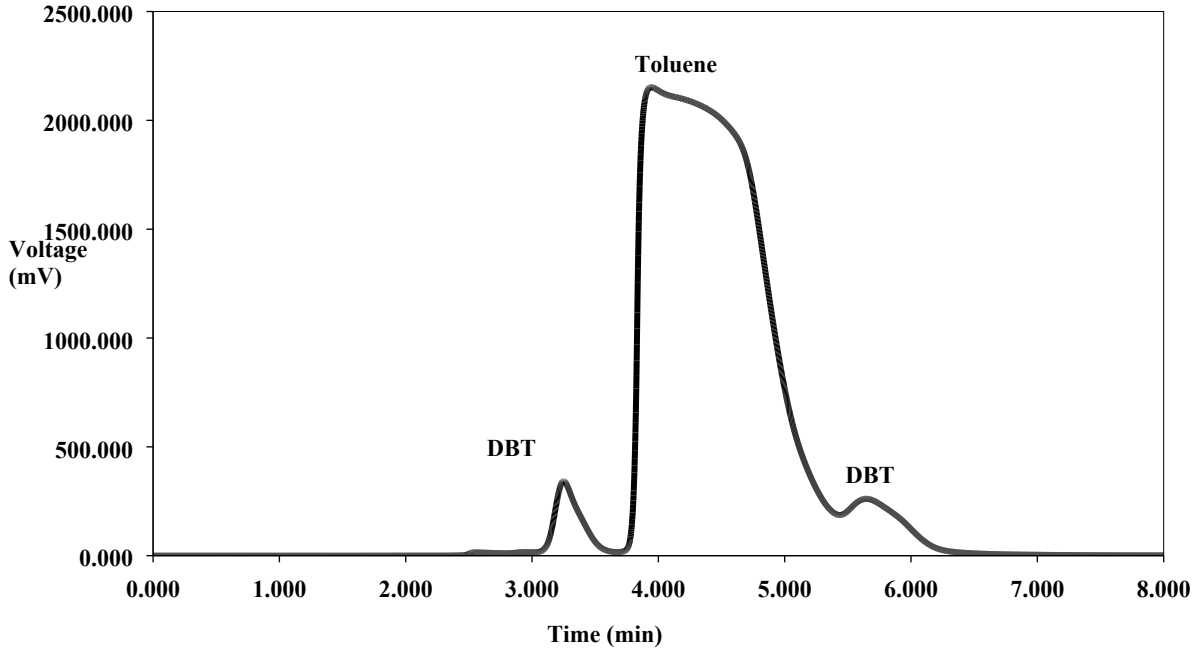

Figure S19. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, TEMPO scavenger under oxygen gas] (Retention time 3.18 min).

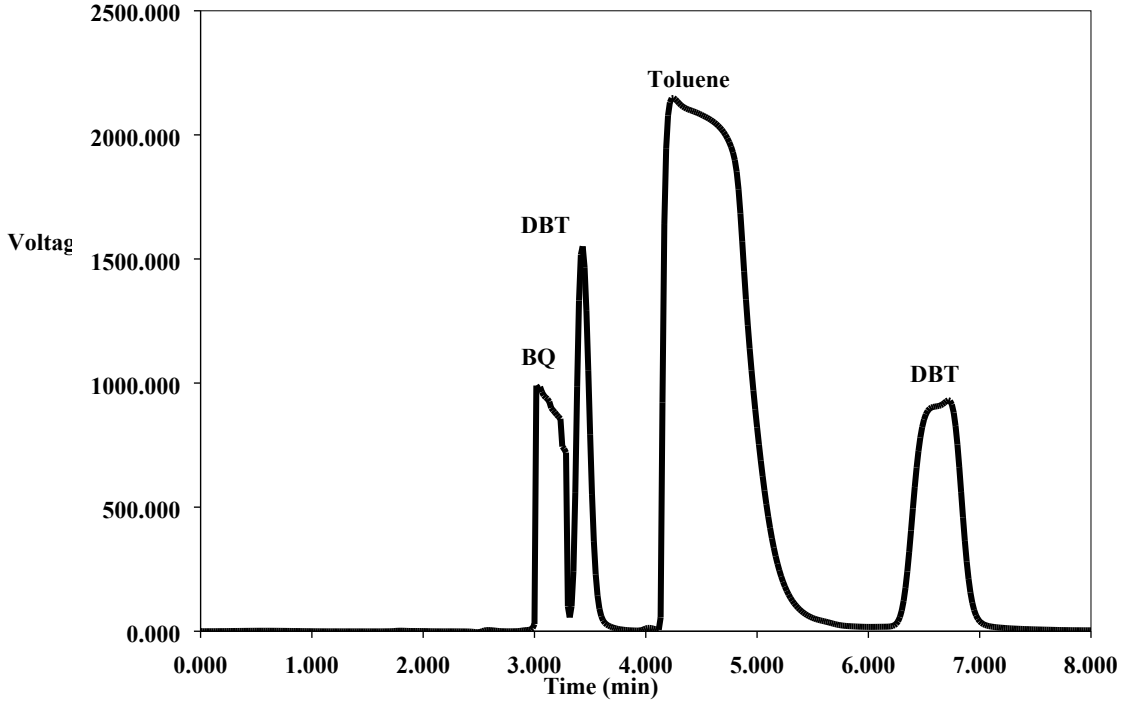

Figure S20. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, BQ scavenger under oxygen gas] (Retention time 3.18 min).

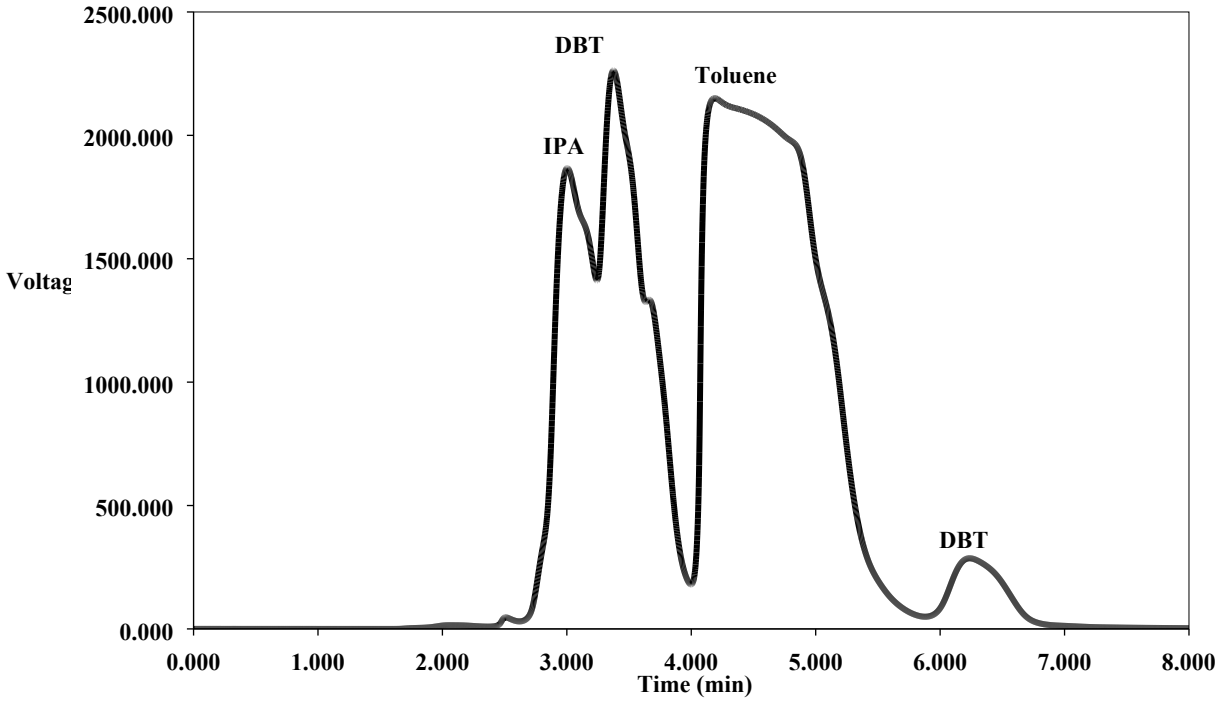

Figure S21. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, IPA scavenger under oxygen gas] (Retention time 3.18 min).

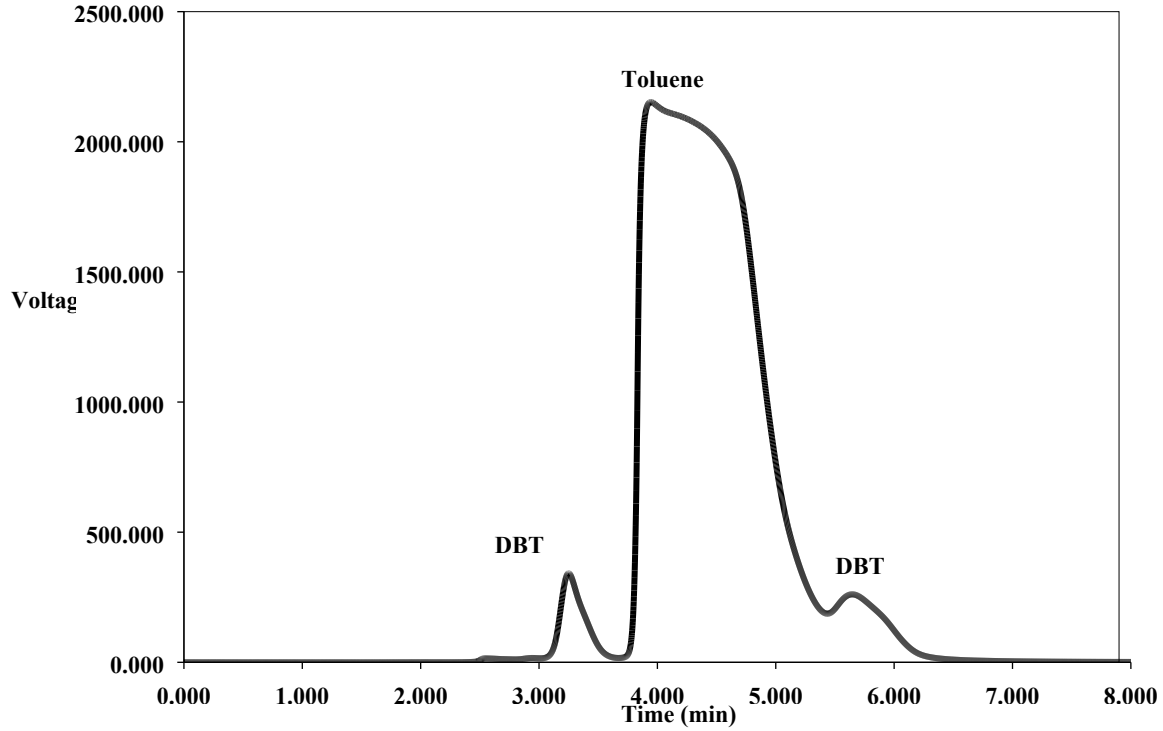

Figure S22. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 4 h On under oxygen gas] (Retention time 3.18 min).

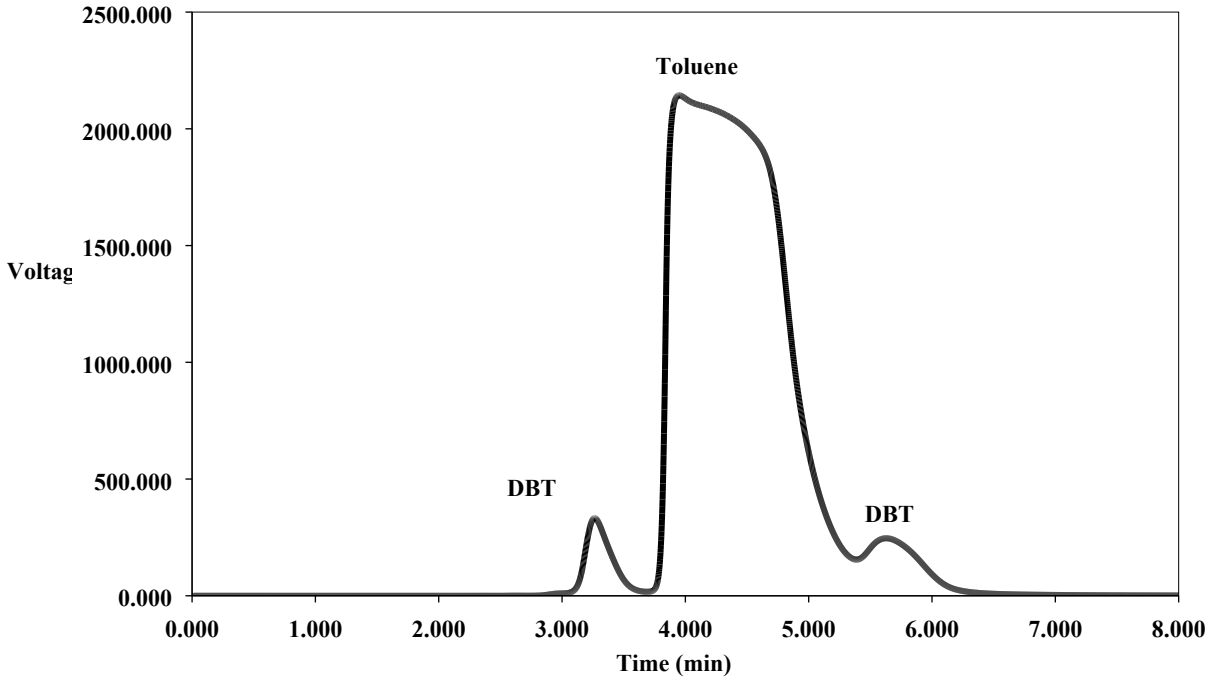

Figure S23. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 3 h Off under oxygen gas] (Retention time 3.18 min).

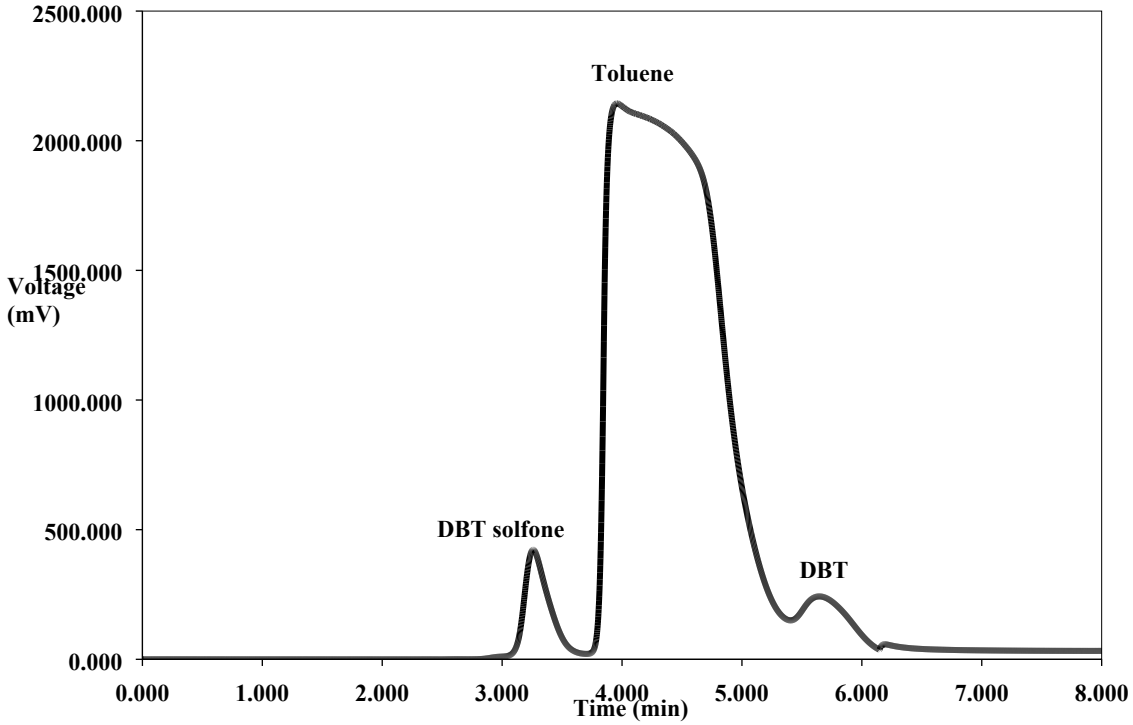

Figure S24. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 3 h On under oxygen gas] (Retention time 3.18 min).

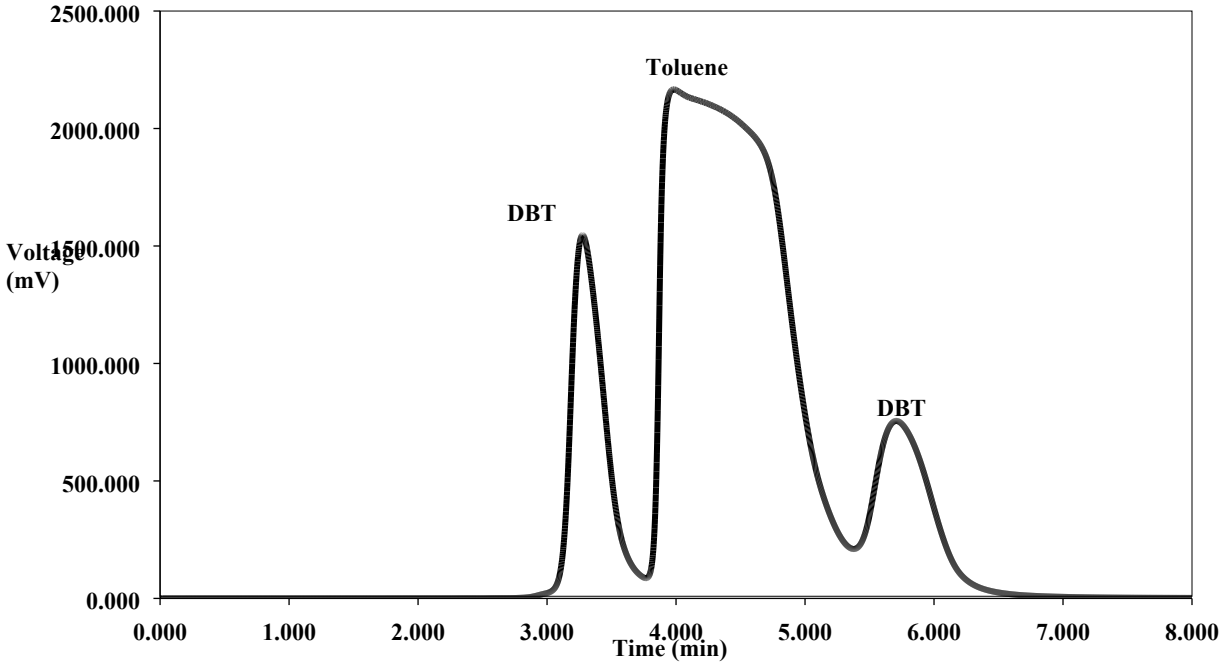

Figure S25. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, 3 h Off under oxygen gas] (Retention time 3.18 min).

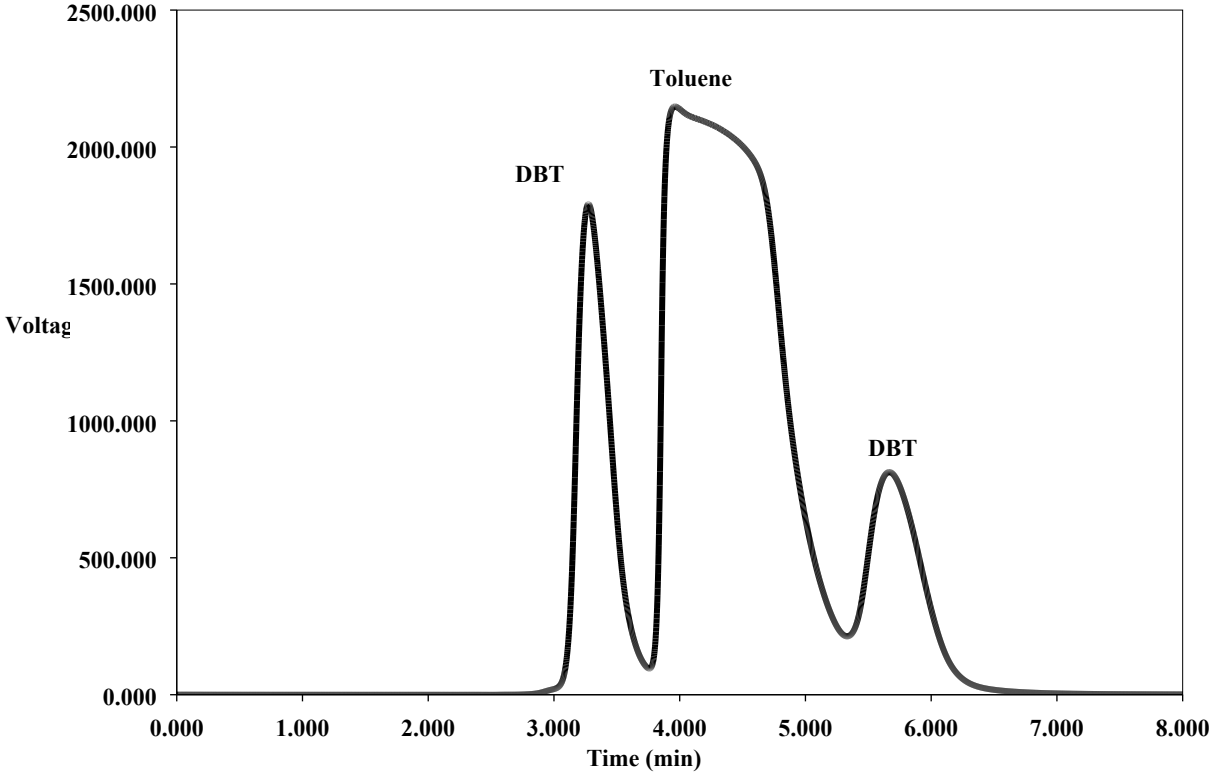

Figure S26. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 500 ppm, solvent = Toluene, 3 h On under oxygen gas] (Retention time 3.18 min)

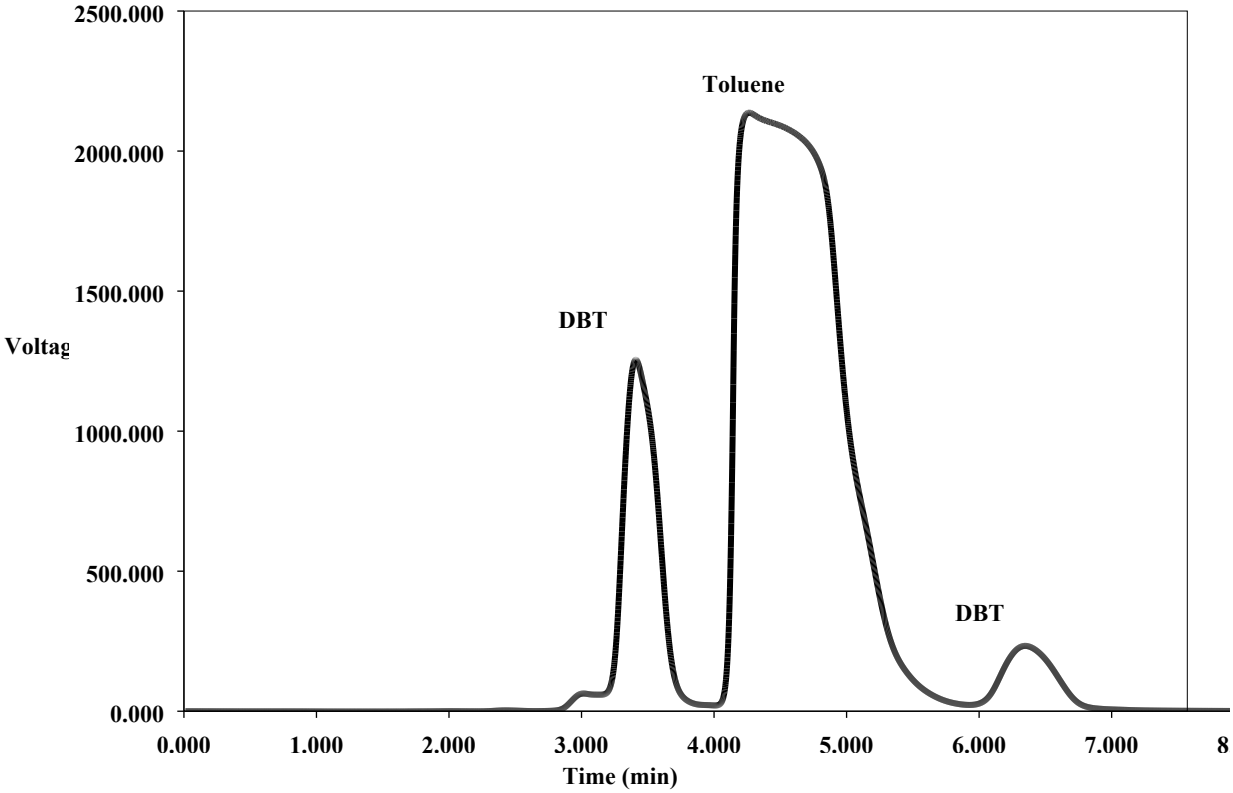

Figure S27. HPLC Chromatogram [Reaction condition: 20 mg recycled photocatalyst after 5 runs, t = 24 h, T = r.t, DBT = 100 ppm, solvent = Toluene, under oxygen gas] (Retention time 3.18 min).

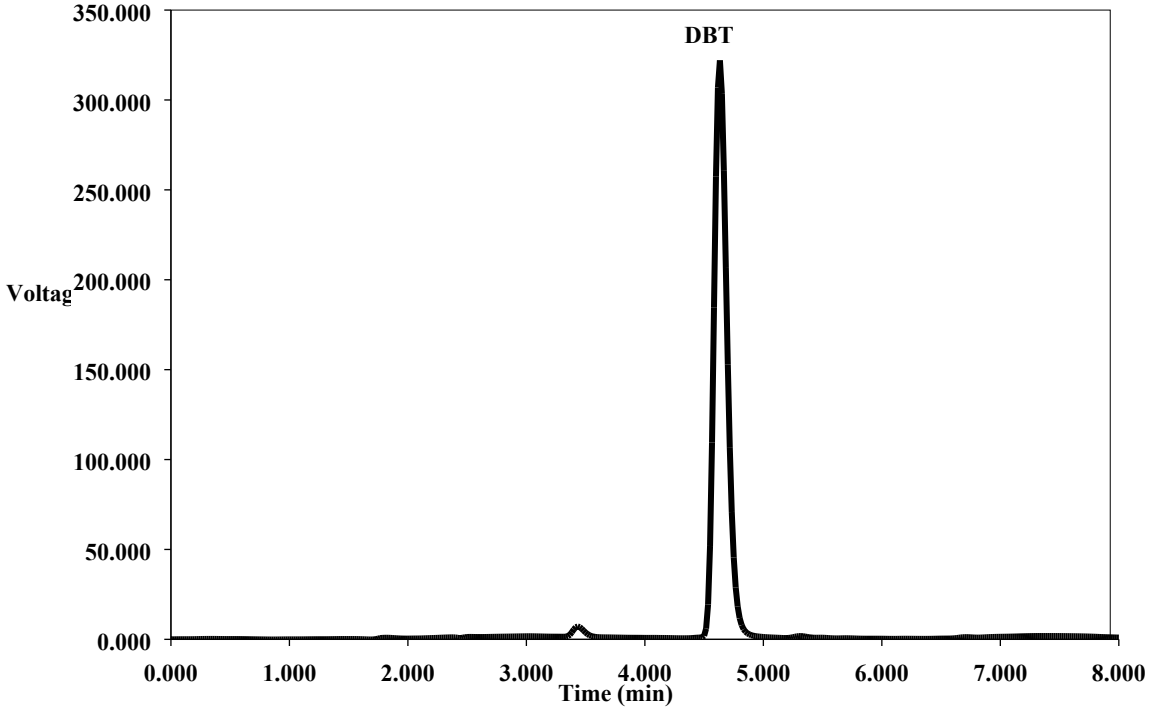

Figure S28. HPLC Chromatogram of 100 ppm standard of dibenzothiophene in CH_3CN as solvent (Retention time 4.5-5 min).

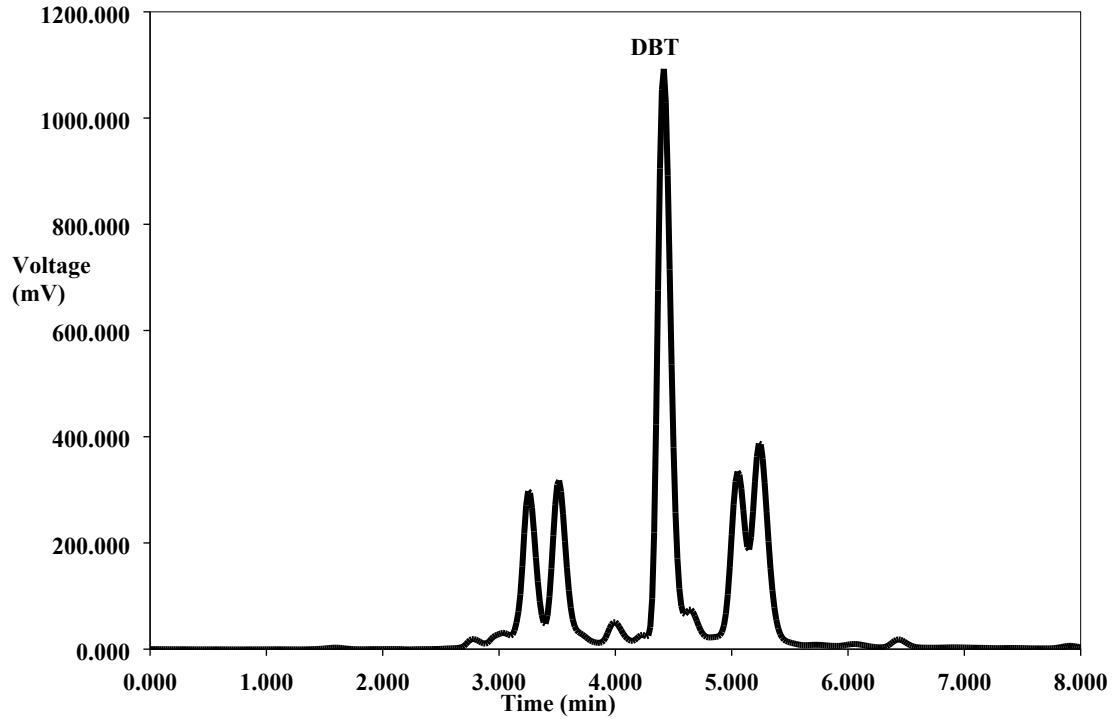

Figure S29. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = CH_3CN ,12 W blue LED, under oxygen gas] (Retention time 3.18-5.5 min)

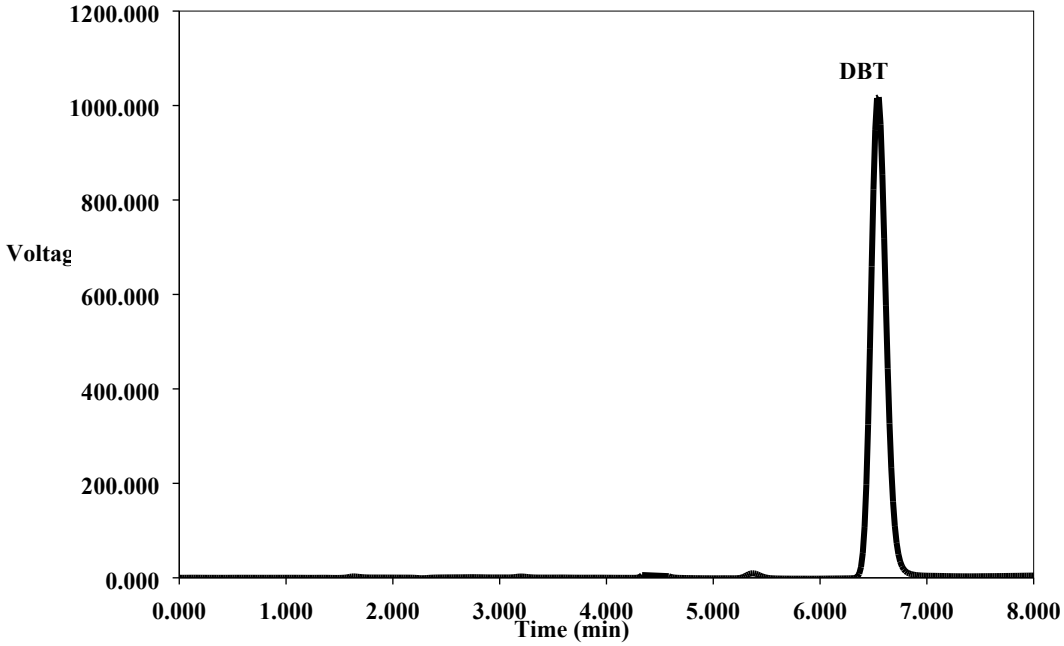

Figure S30. HPLC Chromatogram of 100 ppm standard of dibenzothiophene in EtOH as solvent (retention time 6.5-7 min).

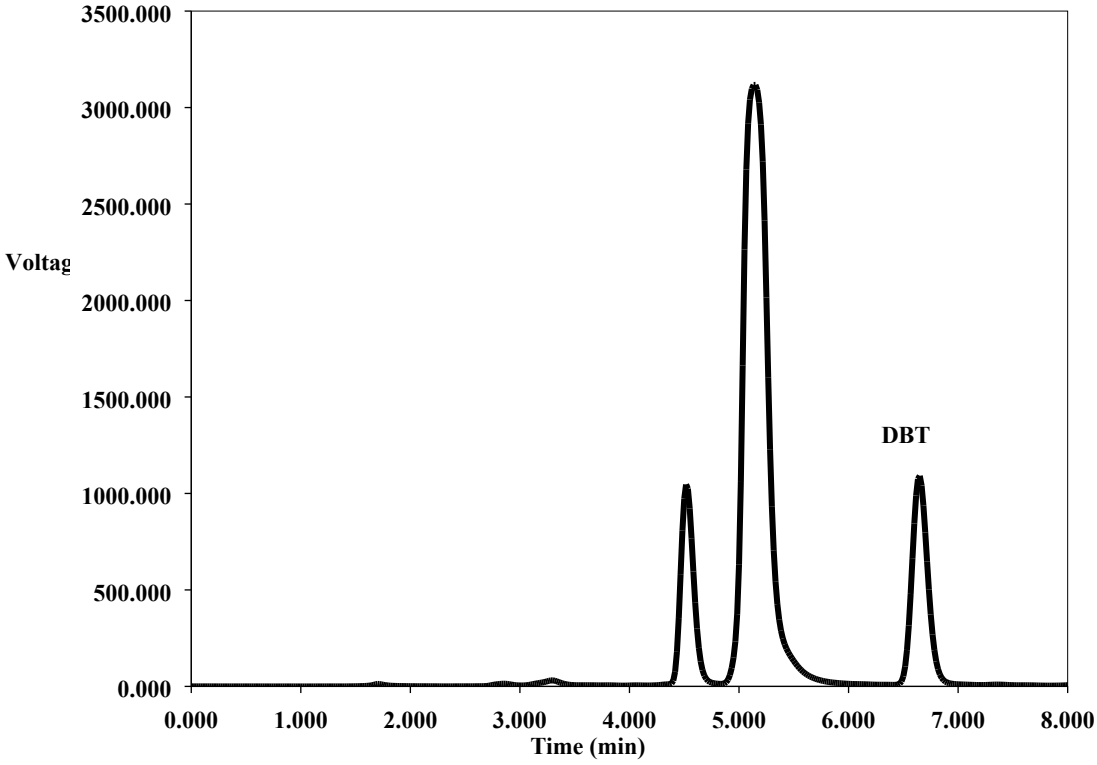

Figure S31. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = EtOH,12 W blue LED, under oxygen gas] (Retention time 4.5-6 min)

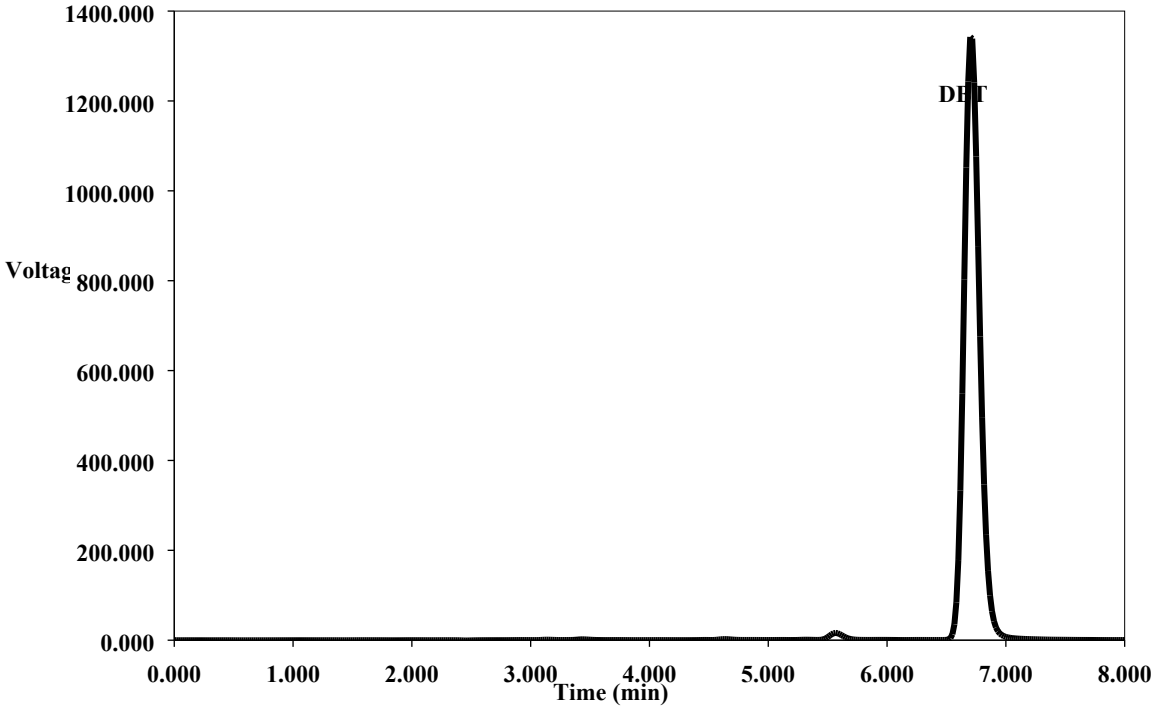

Figure S32. HPLC Chromatogram of 100 ppm standard of dibenzothiophene in *n*-Octane as solvent (retention time 6.5-7 min).

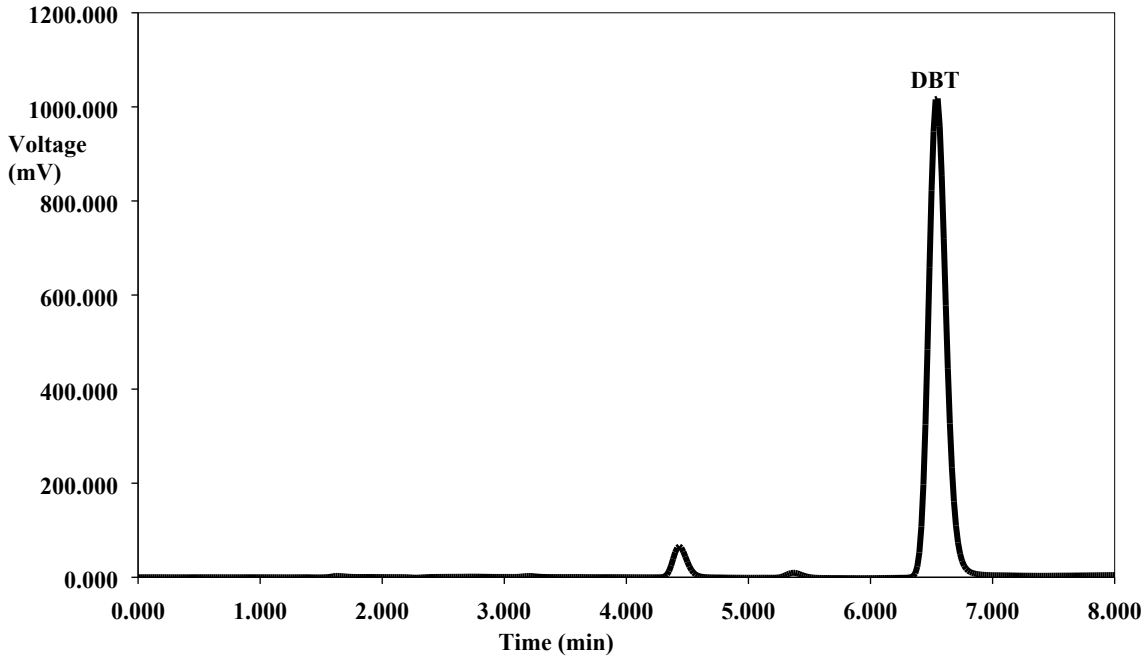

Figure S33. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = *n*-Octane, 12 W blue LED, under oxygen gas] (Retention time 6.5-7 min)

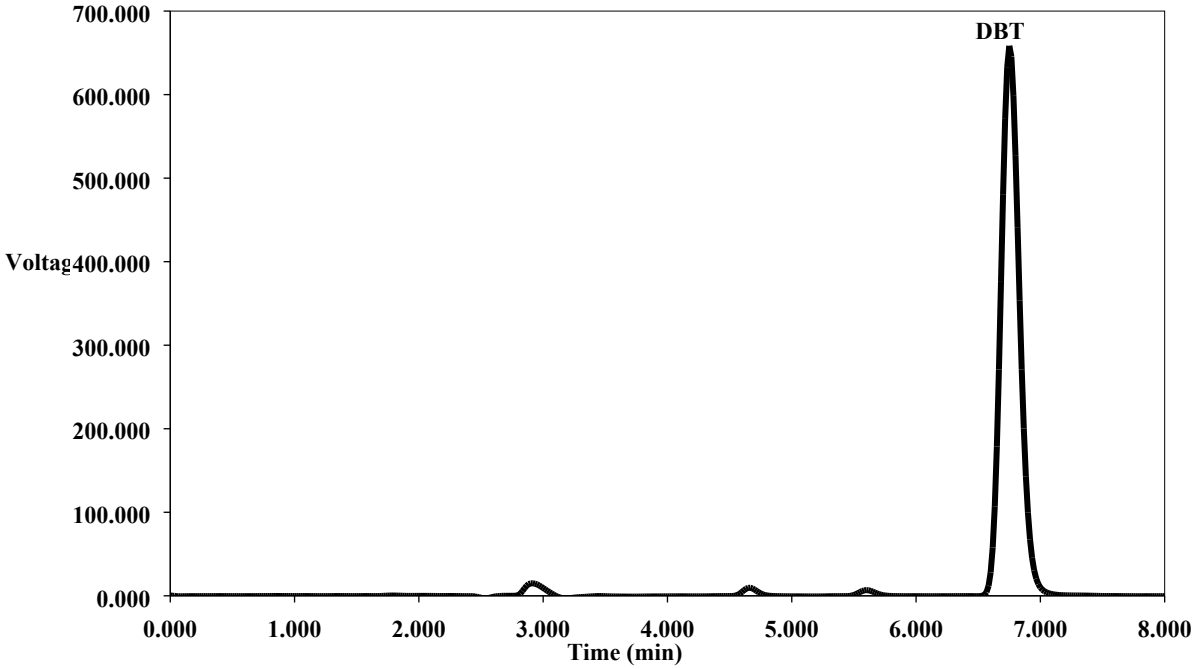

Figure S34. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = *n*-Octane/H_2O (98:2),12 W blue LED, under oxygen gas] (Retention time 6.5-7 min)

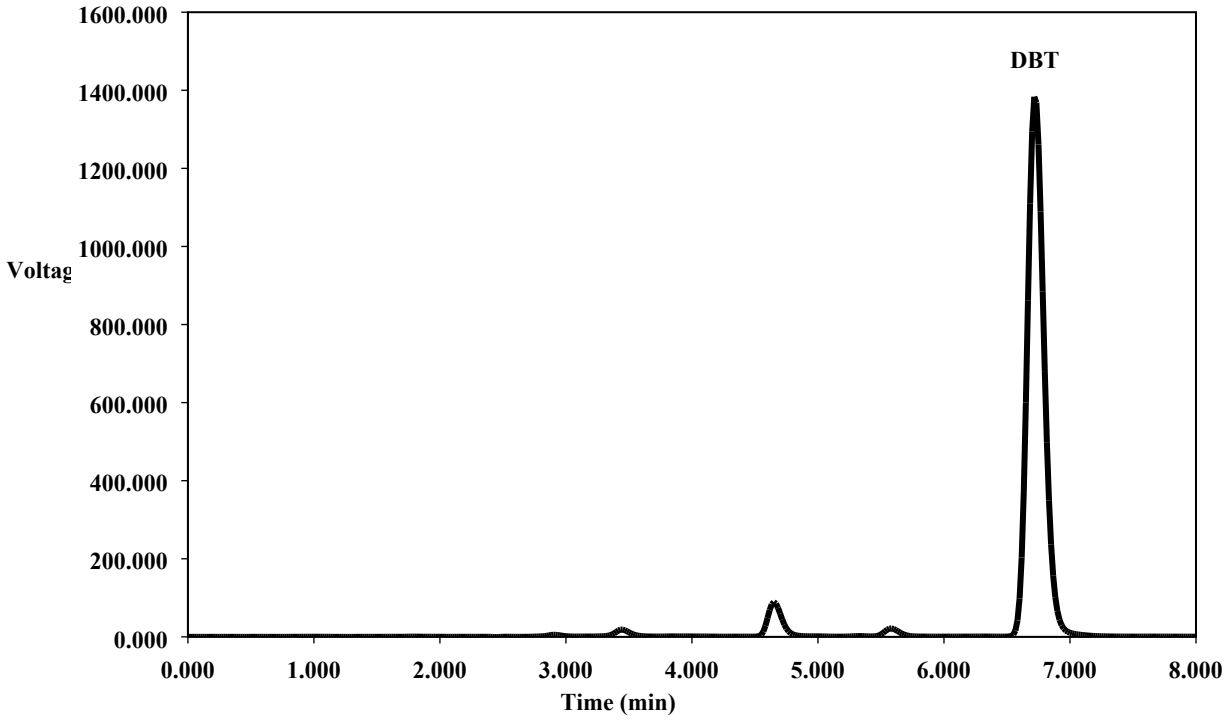

Figure S35. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = *n*-Octane/CH_3CN (98:2),12 W blue LED, under oxygen gas] (Retention time 6.5-7 min)

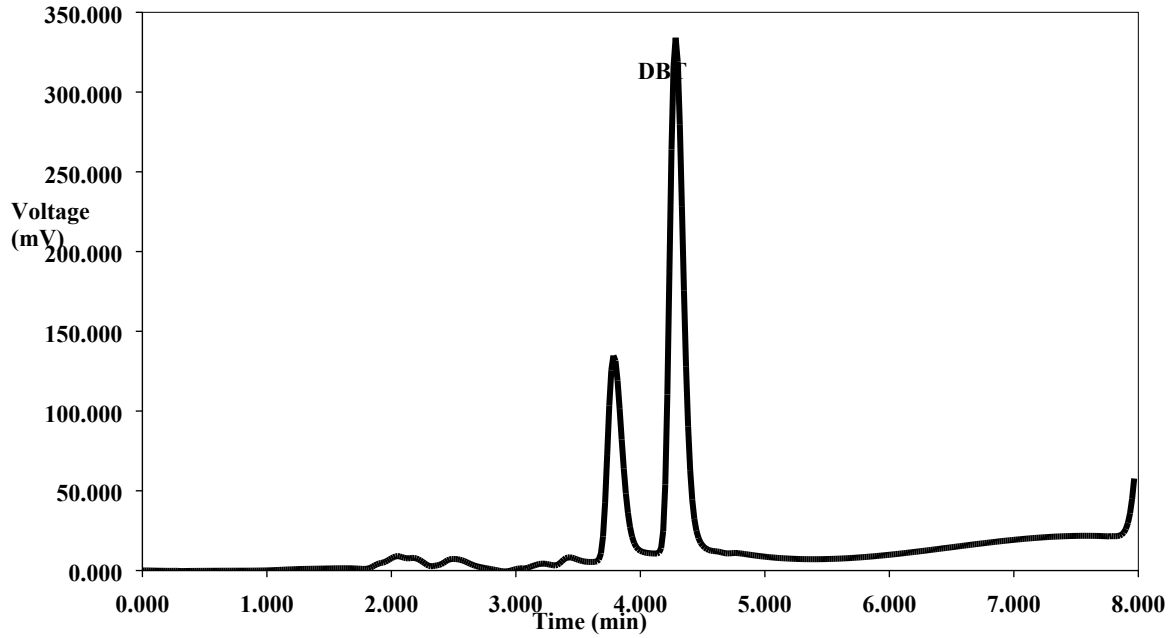

Figure S36. HPLC Chromatogram [Reaction condition: 20 mg CdS@NH_2-MIL-125, t = 24 h, T = r.t, DBT = 100 ppm, solvent = CH_3CN /Toluene (98:2), 12 W blue LED, under oxygen gas] (Retention time 4.5-6 min)

References

1. J. Robertson, T. Bandosz, Photooxidation of dibenzothiophene on TiO_2/hectorite thin films layered catalyst, J. Colloid Interface Sci.,2006, **299.1,** 125-135.