Electronic Supplementary Information for

DDQ as an electrocatalyst for Amine Dehydrogenation in a Virtual Virtual Hydrogen Storage Model System

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S1: Experimental details

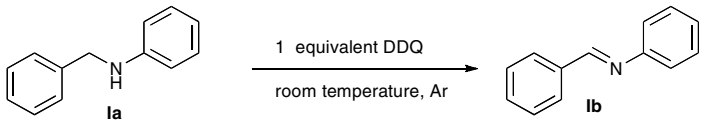
All reagents were received from commercial sources and used without further purification unless otherwise specified. Toluene, dichloromethane, acetonitrile and tetrahydrofuran were dried with a solvent purification system using a 1 m column containing activated alumina. Benzene was distilled from CaH_2 and stored under molecular sieves. ^{1}H and ^{13}C NMR spectra were obtained at room temperature using $CDCl_3$ as solvent on 400 and 500 MHz Bruker spectrometers.

Voltammograms and bulk electrolysis experiments were performed on a Pine Instruments AFCBP1 Bipotentiostat system in a two chamber Basi Bulk Electrolysis cell setup (MF-1056) with a platinum mesh (50x50mm) working electrode. All potentials are reported as referenced vs. NHE using a double junction Ag/AgCl non-aqueous reference electrode and the ferrocene/ferrocenium couple as external standard. A platinum coil was used as counter electrode. Electrolyses were run under continuous Ar purge.

Data workup was performed on OriginPro v8.0988 and AfterMath Data Organizer Version 1.2.3383.

S2: General Procedure

Stoichiometric experiments general procedure: 0.135 mmol amine substrate (15.4µL indoline or 25.4 mg N-phenylbenzylamine) were added to a flame dried 5-mL round bottom flask. After evacuating/backfilling the headspace with argon three times, 2.5 mL solvent were added via a degassed volumetric syringe. 0.135 mmol DDQ (30.8mg) were weighed in a flame dried 5mL round bottom flask equipped with a magnetic stir bar (cooled under vacuum) and placed under argon. The headspace was evacuated/backfilled with the inert gas three times and 2.5 mL solvent were added. The amine solution was transferred into the DDQ solution via a steel cannula. After consumption of the starting material, the reaction mixture was reduced in volume under vacuum, taken in 10 mL diethylether and washed with 3x10mL 3M NaOH solution cooled to 0°. The organic layer was dried over $MgSO_4$ and the ether evaporated in vacuo. The workup yielded pure product in yields presented below.

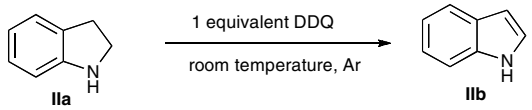


Ia **Ib**

Table 1. Stoichiometric N-phenylbenzylamine (Ia) oxidation[a]

Entry	Solvent	Time	Product[b] %
1	Benzene	30s	86%
2	THF	1min	33%
3	Toluene	3min	66%
4	Acetonitrile	1min	52%
5	Dichloromethane	1min	28%
6	CF_3Ph	30s	51%

[a]1:1 DDQ:substrate ratio, under Ar. 21°C.
[b] Yield confirmed by NMR with trimethoxybenzene as internal standard.



IIa **IIb**

Table 2. Stoichiometric indoline (IIa) oxidation[a]

Entry	Solvent	Time	Product[b] %
1	Benzene	30s	97%
2	THF	30s	28%
3	Toluene	4min	56%
4	Acetonitrile	2min	53%
5	Dichloromethane	1min	69%
6	CF_3Ph	2min	61%

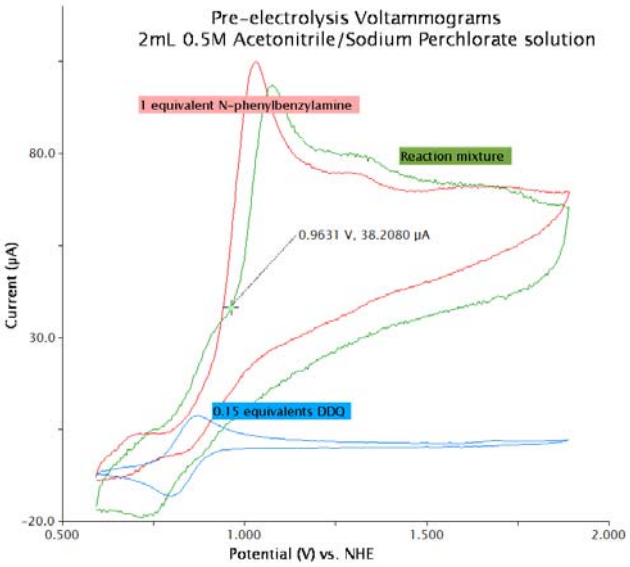
[a]1:1 DDQ:substrate ratio, under Ar. 21°C.
[b] Yield confirmed by NMR with trimethoxybenzene as internal standard.

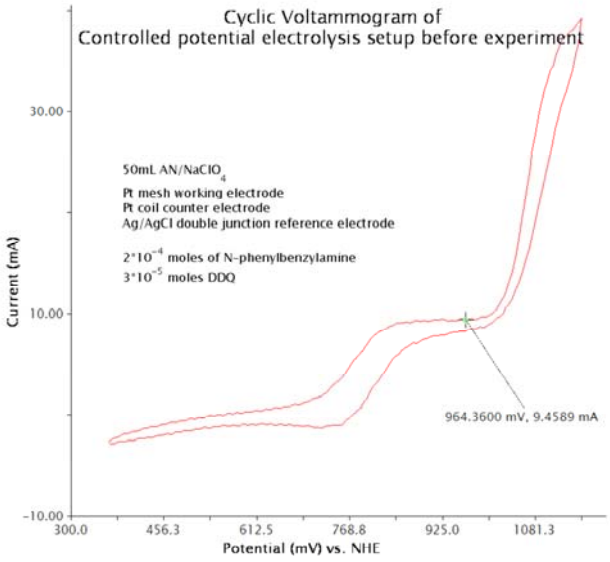
N-benzylideneaniline (Ib): ^{1}H NMR: (400 MHz, $CDCl_3$) 8.38 (1H, s, CH=N), 7.84 (2H, m), 7.36-7.43 (3H, m), 7.31 (2H, m), 7.12-7.18 (3H, m) ^{13}C NMR (500 MHz, $CDCl_3$) 160.58, 152.22, 136.33, 131.53, 129.29, 128.95, 128.92, 126.08, 121.00.

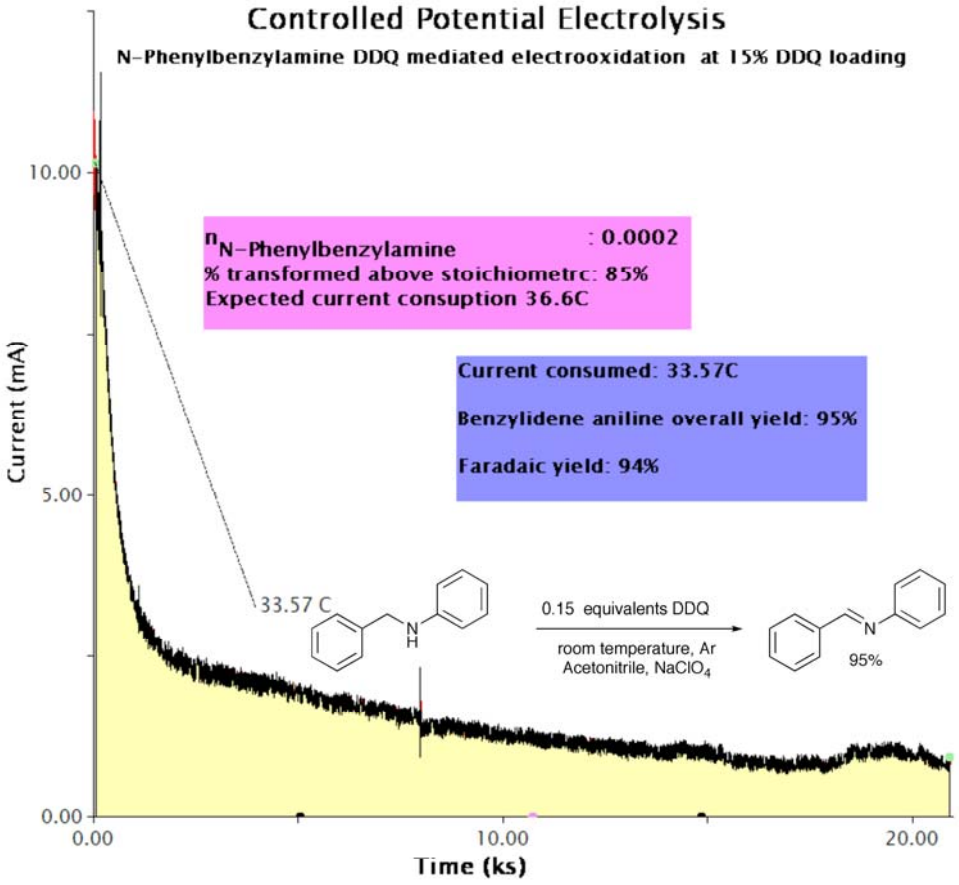
Indole (IIb): ^{1}H NMR (400MHz, $CDCl_3$) 7.83 (1H, br s, NH), 7.67 (1H, d), 7.30 (1H, d), 7.21 (1H, t), 7.14 (1H, t), 7.07(1H, d), 6.54 (1H, d) ^{13}C NMR: (500MHz, $CDCl_3$) 135.69, 127.77, 124.3, 121.89, 119.78, 111.10, 102.25.

S3: Controlled potential electrolysis

Catalytic experiment The Basi cell was charged with 3.061 g sodium perchlorate and 50 mL dry acetonitrile and a dry magnetic stir bar. The solution was degassed for 30 minutes prior to the start of the experiment. 3mL of the solution were added to the cathode chamber (the chambers were separated by an E type ceramic frit). Substrate and DDQ were weighed out and added to the anode chamber. After setting up the working, reference and counter electrode, the experiment was set to proceed at 0.964V vs. NHE with continuous Ar purge. The crude product was concentrated in vacuo and 50mL ether added. The resulting suspension was filtered and the organic layer was washed with 2 x 50mL 3M cold (0°) NaOH and subsequently dried over $MgSO_4$ to yield the desired imine product in 95% yield.

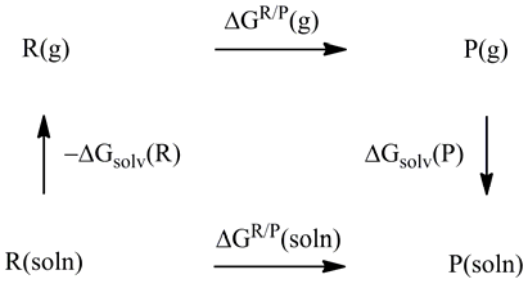






S4: Electronic Structure Calculations

All calculations were performed using Gaussian 03 and Gaussian 09 programs.[1,2] The BH&H hybrid density functional (50% Hartree-Fock exchange and 50% LSDA exchange), which is known to be capable of correctly reproducing π-stacking geometry and interactions,[3,4] was selected. All calculations were done with the 6-311++G(d,p) basis. Changes in the free energy in solution $\Delta G(soln)$ from states R to P were found using the thermodynamic cycle:



and

$$\Delta G^{R/P}(soln) = \Delta G^{R/P}(g) + \Delta G_{solv}(P) - \Delta G_{solv}(R), \quad (1)$$

where $\Delta G(g) = \Delta H(g) - T\Delta S(g)$ is the free energy state transition in the gas phase. The solvation free energies ΔG_{solv} were computed using the standard self-consistent reaction field (SCRF) approach[5,6] based on gas-phase geometries with a dielectric constant of $\varepsilon = 2.27$ (benzene) for the continuum solvating medium. Enthalpy changes in the gas phase $\Delta H(g) = \Delta H_{SCF}(DFT) + \Delta H_{ZPE} + \Delta H_T$ were obtained from changes in the DFT self-consistent field energy $\Delta H_{SCF}(DFT)$ in the gas phase and vibrational frequency calculations that yield changes in the zero point energy ΔH_{ZPE}, corrections for molecular entropy changes $\Delta S(g)$, and corrections due to changes in thermal enthalpy ΔH_T.

Table 3. Atomic coordinates used for DFT calculations. Structures are referred to in Figure 1 in the main text.

1:1 Complex

C	-0.542759	0.794615	-0.821552
C	-0.910993	-0.581939	-1.174365
C	-2.159538	-1.040759	-1.007775
C	-3.247373	-0.157146	-0.549742
C	-2.877054	1.230258	-0.216653
C	-1.624411	1.665684	-0.329650
O	0.577561	1.189453	-0.962575
O	-4.370762	-0.544813	-0.478498
Cl	-4.135455	2.192323	0.363712
Cl	-1.152224	3.227039	0.103573
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C	-1.035387	-2.676281	1.386548
C	-2.018726	-1.800209	1.826915
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C	-0.400186	-0.042178	1.880646
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H	-1.291340	-3.706819	1.180665
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C	0.124533	-1.372718	-1.726583
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C	6.322309	0.307410	0.368281
H	6.925172	1.966989	-0.831391
H	4.681218	2.300314	-1.790309
H	2.823359	0.827262	-1.128833
H	5.444465	-1.305583	1.460823
H	7.305046	0.156541	0.793338

TS

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H	2.940236	1.057127	1.534711
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H	6.181728	-1.711394	-0.929657

Ion Pair

C	-0.125465	0.907432	-1.171133
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C	-1.182948	1.667334	-0.681365
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C	-0.489040	-2.128530	1.263816
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H	4.291754	-2.218609	0.288609
H	6.510448	-1.305377	-0.259657

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