Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Precious-metal free Photocatalytic Production of a NADH Analogue using Cobalt Diimine-dioxime Catalysts under both Aqueous and Organic Conditions

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Experimental Section

Reagents and Materials

All chemicals commercially obtained (Sigma Aldrich and Acros) were of reagent grade and were used as purchased. For reactions and measurements, HPLC grade acetonitrile (LabScan) and purified water (MilliQ) was used. Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**$RuPS^{2+}$**), and the disodium salt of Eosin Y (**EY^{2-}**) and Rose Bengal (**RB^{2-}**) were purchased respectively from Sigma Aldrich and Acros. The cobalt diimine-dioxime complexes [Co(DO)(DOH)pnX_2] (**1** and **2**; X = Cl and Br; (DO)(DOH)pn = N^2, $N^{2'}$-propanediylbis(2,3-butandione-2-imine-3-oxime) and [Co($(DO)_2BF_2$)pnBr_2] (**3**) were prepared by reported procedures.[1,2] 1-Benzylnicotinamide chloride (BNACl) was prepared according to a reported method and the triflate salt (BNAOTf) was prepared by anion exchange using AgOTf.[3,4] The 1-benzyl-1,4-dihydronicotinamide (1,4-BNAH) was prepared by the reduction of BNACl using sodium dithionite as reported.[5] 4,8,12-Tri-*n*-butyl-4,8,12-triazatriangulenium hexafluorophosphate (**$TATA^+$**) was prepared by a modified procedure by using n-butylamine.[6,7]

Photocatalytic generation of 1,4-BNAH. Photogeneration of 1,4-BNAH was performed in a 10 mL Quickfit test tube (Lenz) sealed with a serrated rubber septum (Sigma Aldrich). Typically, an argon purged acetonitrile or aqueous solution (5 mL) containing the catalyst, photosensitizer (**$RuPS^{2+}$** or **$TATA^+$** in acetonitrile and **EY^{2-}** or **RB^{2-}** in aqueous solutions), triethanolamine (TEOA) and the conjugate cation 1-benzylnicotinamide triflate (BNAOTf) was irradiated using a white LED lamp (>420 nm) obtained from PRIME LED at room temperature. The amount of 1,4-BNAH produced from the reaction was determined by high-performance liquid chromatography (HP 1100) equipped with a reverse-phase C_{18} column (Alltech Allsphere ODS-25u, Length: 250 mm, ID: 4.6 mm) and a diode array detector (DAD) upon monitoring the absorption maximum (λ_{max} = 355 nm for 1,4-BNAH),[5] using acetonitrile-water (1:1) as the eluent. The concentration of the organohydride formed was also determined by photoluminescence measurement. A fixed portion of the reaction mixture was extracted every 30 min, and diluted by 400 folds with acetonitrile in a cuvette. Emission intensity at λ_{em} = 436 nm in acetonitrile was determined (λ_{ex} = 348 nm) with an Edinburgh Instruments FS5 spectrofluorometer. In both methods, the product concentration was then determined by comparison with a calibration curve prepared with the 1,4-BNAH standard (0.2 –10 mM) in acetonitrile. Uncertainty for the yields in the HPLC measurement are determined by reported method.[8]

^{1}H NMR analysis. Photolysis was performed as described above by using acetonitrile-D_3 (Cambridge Isotope Laboratories) as the solvent and ^{1}H NMR spectra of reaction mixtures were then collected by a Bruker Avance 400 MHz NMR spectrometer. The spectra of the reaction mixture thus obtained were compared to those of the 1,4-BNAH standards in the same solvent.

Measurement of quenching rate constants. Absorption spectra and lifetime of the transient species of **TATA$^+$** and **RB^{2-}** with different concentrations of Co catalyst, 1,4-BNAH and TEOA were measured by Edinburgh Instruments LP920 laser flash photolysis spectrometer, using 355 nm laser excitation (power = 10 mJ/pulse, pulse width = 10 ns). The sample were rigorously degassed by four freeze-pump-thaw cycles under reduced pressure.

Table S1. Photocatalytic reductive generation of 1,4-BNAH with **1** (100 µM) under varied conditions.

Trial	Solvent	PS	[PS]/mM	[BNA^{+}]/mM	[TEOA]/M	Yield[c]/µmol (TON)
1	CH_3CN	**RuPS^{2+}**	0.5	4	0.10	0.2 (0.4)
2		**RuPS^{2+}**	0.5	4	0.20	0.4 (0.8)
3		**RuPS^{2+}**	0.5	4	0.50	5.5 (10.9)
4		**RuPS^{2+}**	0.5	4	1.13[a]	11.1 (22.1)
5[b]		**RuPS^{2+}**	0.25	4	1.13	10.6 (21.3)
6[b]		**TATA^{+}**	0.25	4	1.13	11.8 (23.6)
7[c]		**TATA^{+}**	0.25	4	1.13	0.2 (0.4)
8	H_2O	**RB^{2-}**	0.25	4	0.10	0.5 (0.9)
9		**RB^{2-}**	0.25	4	0.50	1.8 (3.6)
10		**RB^{2-}**	0.25	4	1.13	3.3 (6.6)
11[b]		**RB^{2-}**	0.25	4	1.13	8.1 (16.3)
12[c]		**RB^{2-}**	0.25	4	1.13	2.1 (4.1)
13[b]		**EY^{2-}**	0.25	4	1.13	6.0 (12.0)

[a] 15% (v/v); [b] yield determined by photoluminescence; [c] result obtained in reactions performed in air

[d] data corrected from the blank obtained by control experiments without catalysts.

Table S2. Yield of H_2 generated during photocatalysis with and without added BNA^{+} (4 mM) by **1** (100 µM) under varied conditions.

Trial	Solvent	PS	[PS]/mM)	[BNA^{+}]/mM	[TEOA]/M	Yield/µmol (TON)
1	CH_3CN	**RuPS^{2+}**	0.25	4	1.13	0
2		**RuPS^{2+}**	0.25	0	1.13	16.8 (33.6)
3		**TATA^{+}**	0.25	4	1.13	0.6 (1.2)
4		**TATA^{+}**	0.25	0	1.13	18.9 (37.8)
5	H_2O	**RB^{2-}**	0.25	4	1.13	0
6		**RB^{2-}**	0.25	0	1.13	0.8 (1.5)
7		**EY^{2-}**	0.25	4	1.13	0
8		**EY^{2-}**	0.25	0	1.13	2.1 (4.1)

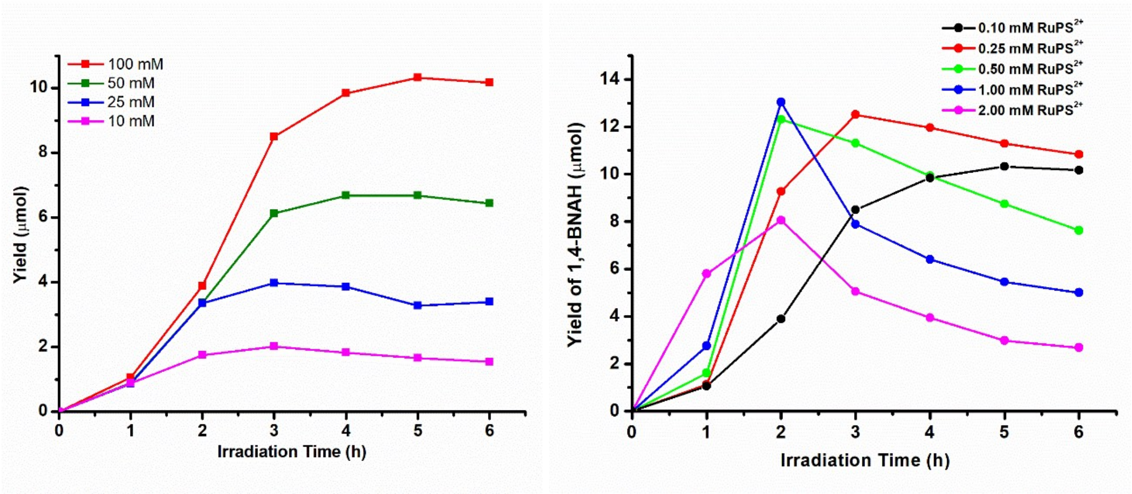

Figure S1. Photocatalytic (λ > 420 nm) generation of 1,4-BNAH in acetonitrile by a) varied concentrations of **1** (0 – 100 μM), in the presence of BNA^+ (4 mM), TEOA (15% v/v) and 0.10 mM **$RuPS^{2+}$** (left) and b) by **1** (100 μM) in the presence of TEOA (15% v/v) and varied concentrations (0.10 – 2.00mM) of **$RuPS^{2+}$** (right).

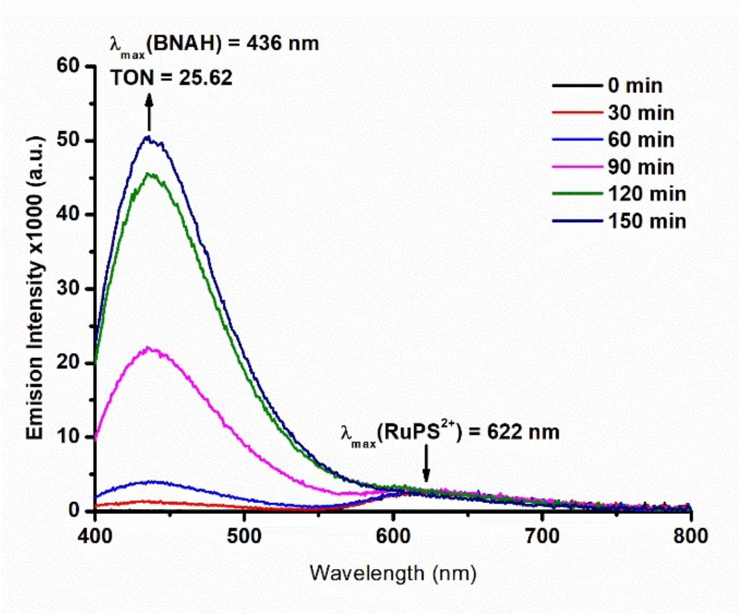

Figure S2. Emission spectral change for the photocatalytic (λ > 420 nm) generation of 1,4-BNAH from BNA^+ (4 mM) in acetonitrile by **1** (100 μM), in the presence of **$RuPS^{2+}$** (0.25 mM) and TEOA (15% v/v). The spectra were obtained with a diluted (400×) reaction mixture, upon photoexcitation (λ_{ex} = 348 nm).

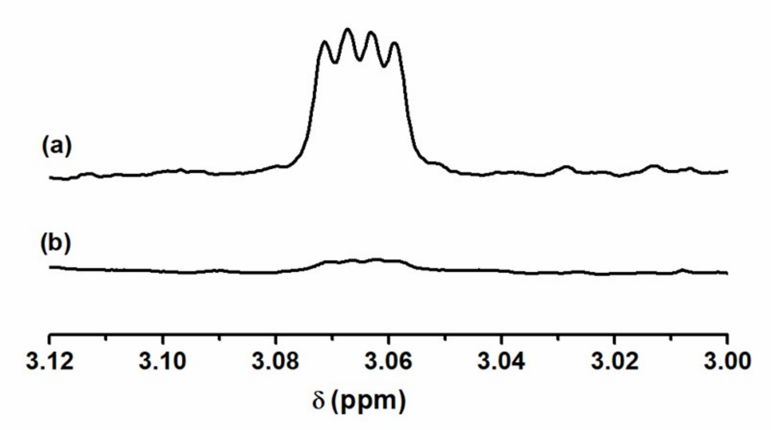

Figure S3. ^{1}H NMR (400 MHz) signal for a reaction mixture containing BNA$^+$ (8 mM), **1** (200 µM), **RuPS^{2+}** (0.50 mM) and TEOA (15% v/v) in a) CD_3CN and b) D_2O/CD_3CN (5% v/v) after 6 hours of irradiation (λ> 420 nm).

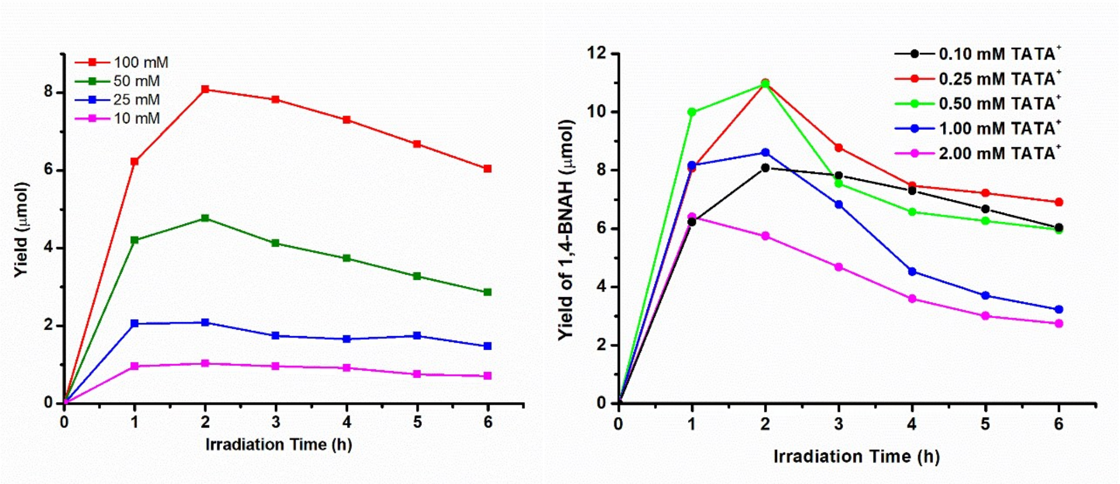

Figure S4. Photocatalytic (λ > 420 nm) generation of 1,4-BNAH in acetonitrile by a) varied concentrations of **1** (0 – 100 µM), in the presence of BNA$^+$ (4 mM), TEOA (15% v/v) and 0.10 mM **TATA$^+$** (left) and b) by **1** (100 µM) in the presence of TEOA (15% v/v) and varied concentrations (0.10 – 2.00mM) of **TATA$^+$** (right).

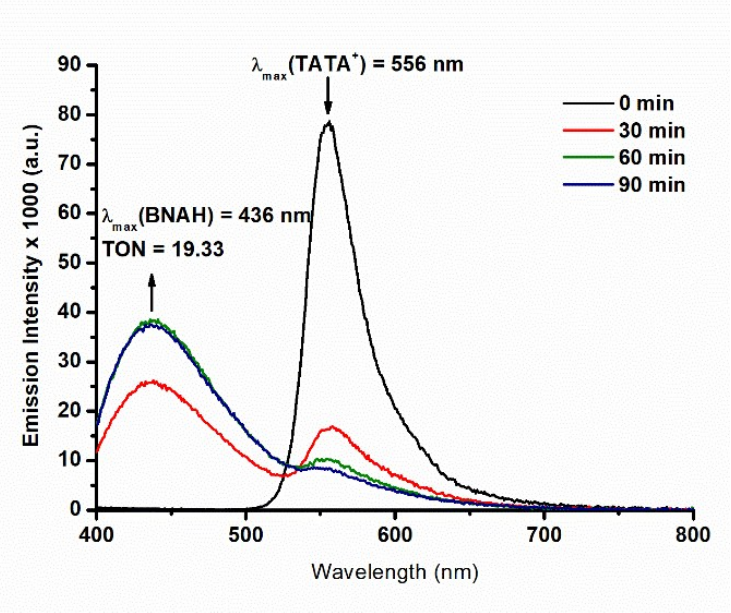

Figure S5. Emission spectral change for the photocatalytic (λ > 420 nm) generation of 1,4-BNAH from BNA^+ (4 mM) in acetonitrile by **1** (100 μM), in the presence of **TATA**$^+$ (0.25 mM) and TEOA (15% v/v). The spectra were obtained with a diluted (400×) reaction mixture, upon photoexcitation (λ_{ex} = 348 nm).

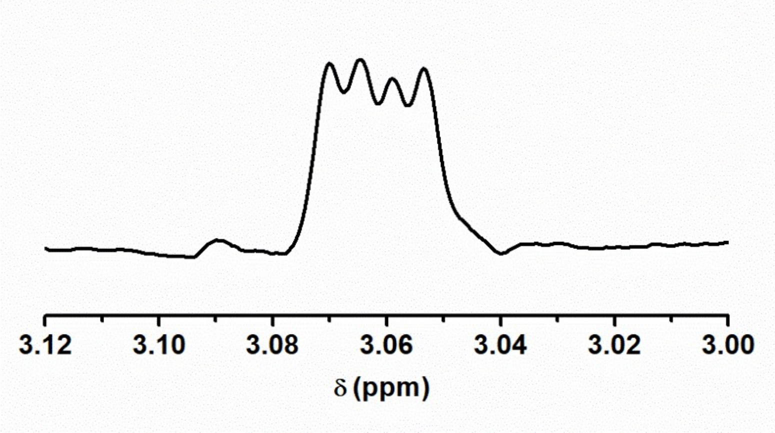

Figure S6. ^1H NMR (400 MHz) signal for a reaction mixture containing BNA^+ (8 mM), **1** (200 μM), **TATA**$^+$ (0.50 mM) and TEOA (15% v/v) in CD_3CN after 6 hours of irradiation (λ> 420 nm).

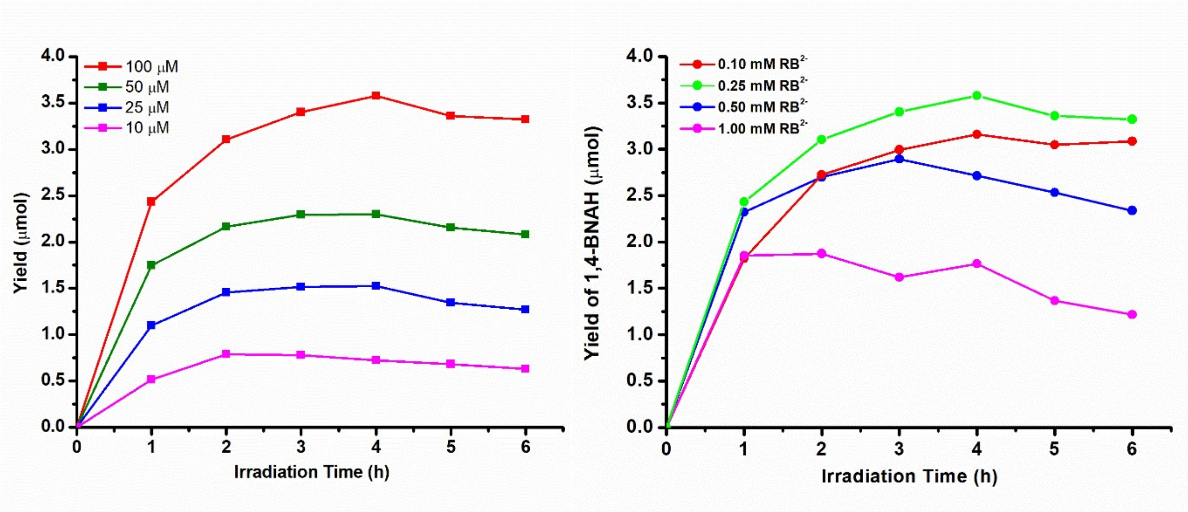

Figure S7. Photocatalytic (λ > 420 nm) generation of 1,4-BNAH in aqueous solution (pH 10.97) by a) varied concentrations of **1** (0 – 100 μM), in the presence of BNA^+ (4 mM), TEOA (15% v/v) and 0.25 mM $\mathbf{RB^{2-}}$ (left) and b) by **1** (100 μM) in the presence of TEOA (15% v/v) and varied concentrations (0.10 – 1.00 mM) of $\mathbf{RB^{2-}}$ (right).

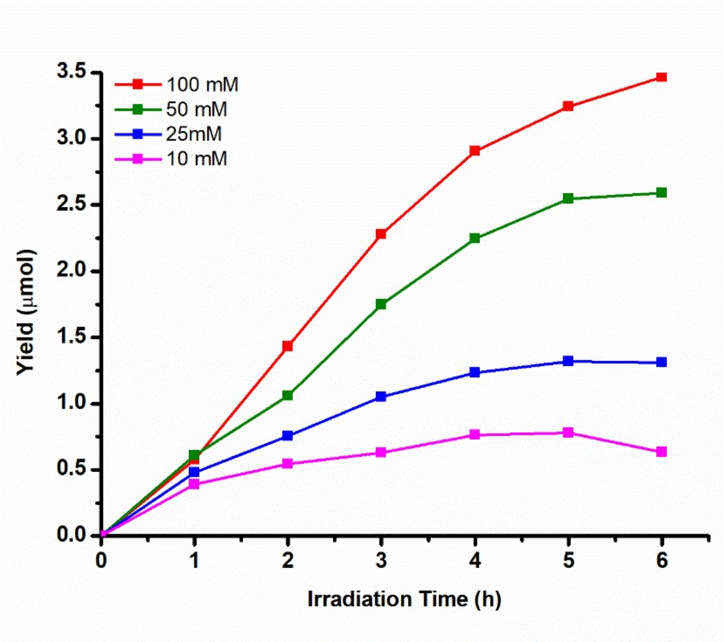

Figure S8. Photocatalytic (λ > 420 nm) generation of 1,4-BNAH in aqueous solution (pH 10.97) by varied concentrations of **1** (0 – 100 μM), in the presence of BNA^+ (4 mM), TEOA (15% v/v) and 0.25 mM $\mathbf{EY^{2-}}$.

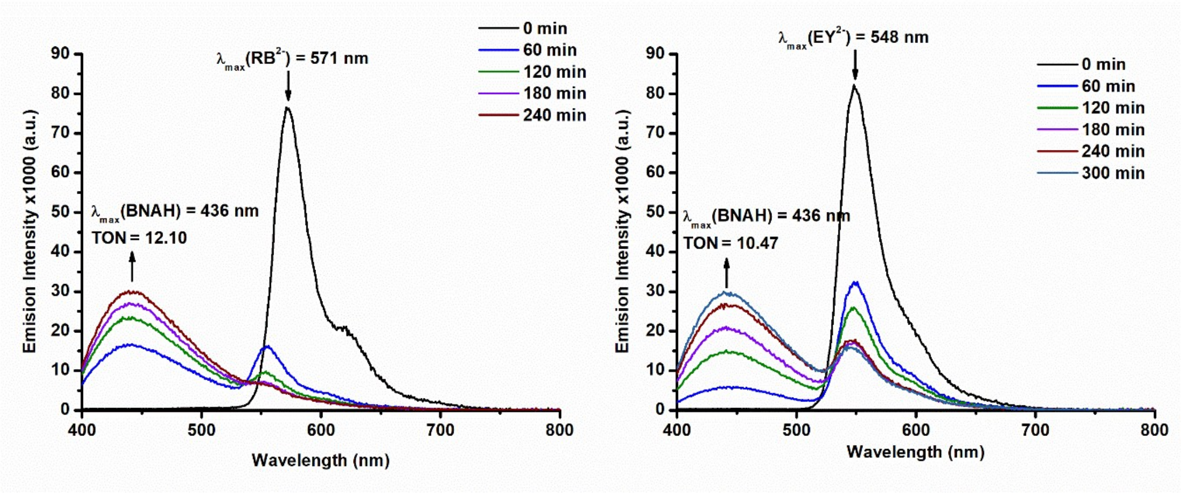

Figure S9. Emission spectral change for the photocatalytic (λ > 420 nm) generation of 1,4-BNAH from BNA^+ (4 mM) in an aqueous solution (pH 10.97) containing **1** (100 μM) and TEOA (15% v/v), in the presence of 0.25 mM of a) $\mathbf{RB^{2-}}$ (left) and b) $\mathbf{EY^{2-}}$ (right). The spectra were obtained with a diluted (400×) reaction mixture, upon photoexcitation (λ_{ex} = 348 nm).

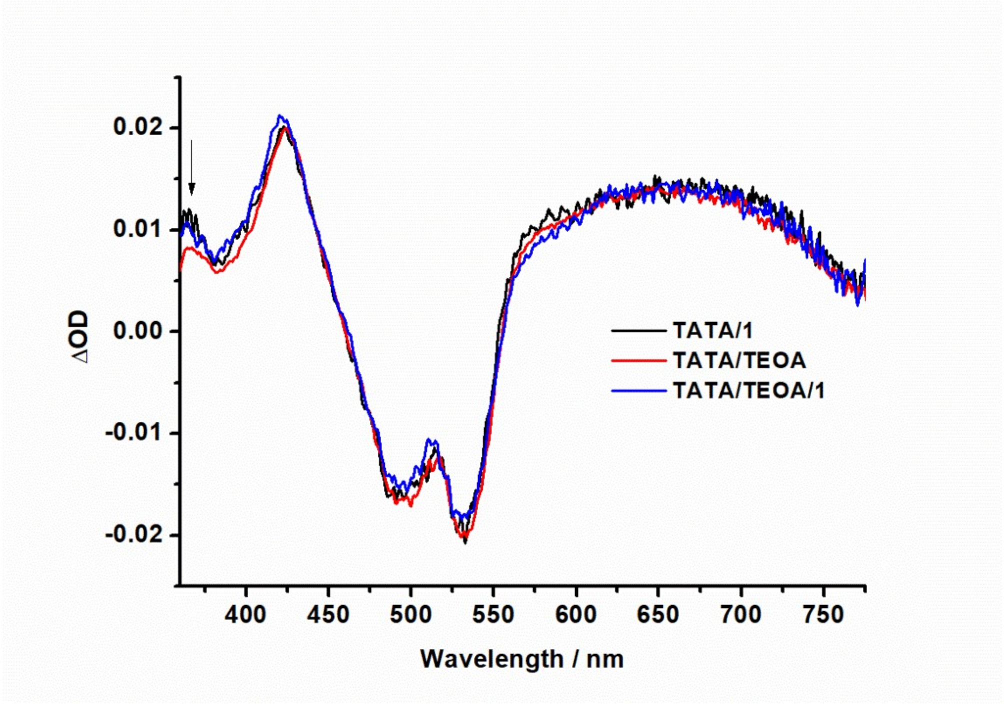

Figure S10. Transient absorption spectra of the degassed acetonitrile solution of 50 μM $\mathbf{TATA^+}$ in the presence of 50 μM **1** (black), 0.01 M TEOA (red) or both **1** and TEOA (blue).

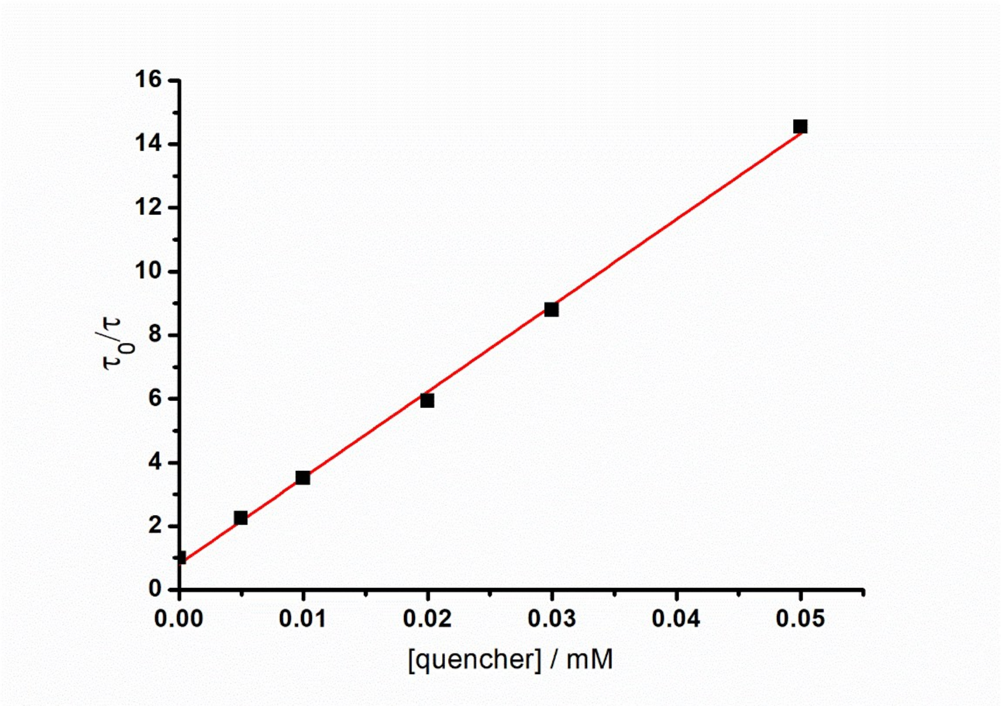

Figure S11. Stern-Volmer plot of transient absorption lifetime of **TATA$^+$** at varied [**1**]. $R^2 = 0.999$ and $k_q = 3.73 \times 10^9$ M^{-1} s^{-1}.

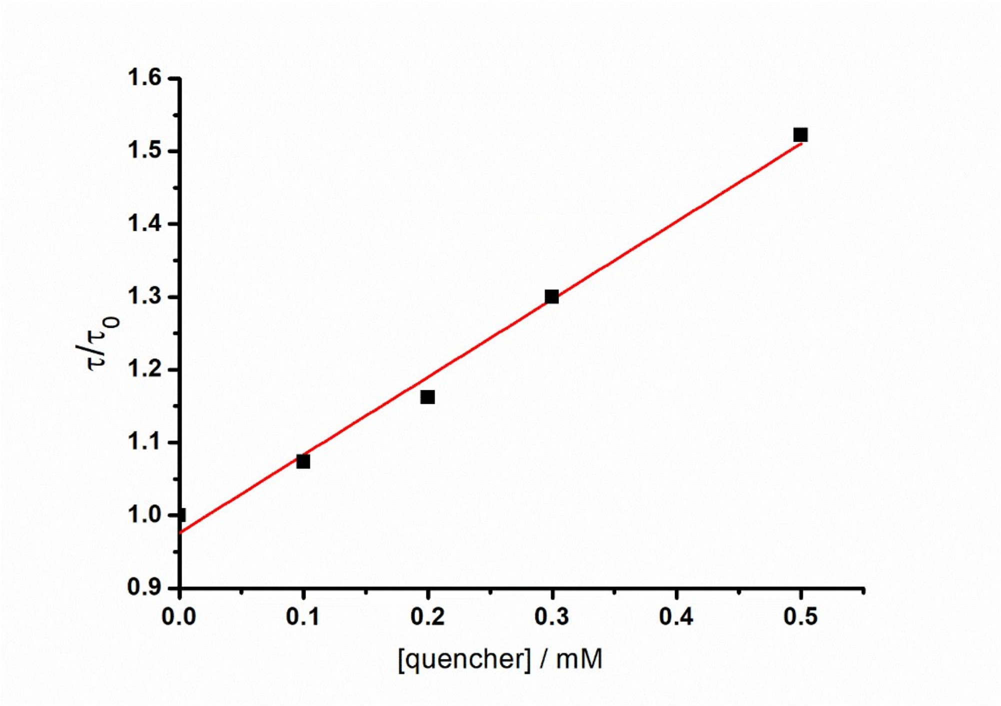

Figure S12. Stern-Volmer plot of transient absorption lifetime of **TATA$^+$** at varied [TEOA]. $R^2 = 0.991$ and $k_q = 1.48 \times 10^7$ M^{-1} s^{-1}.

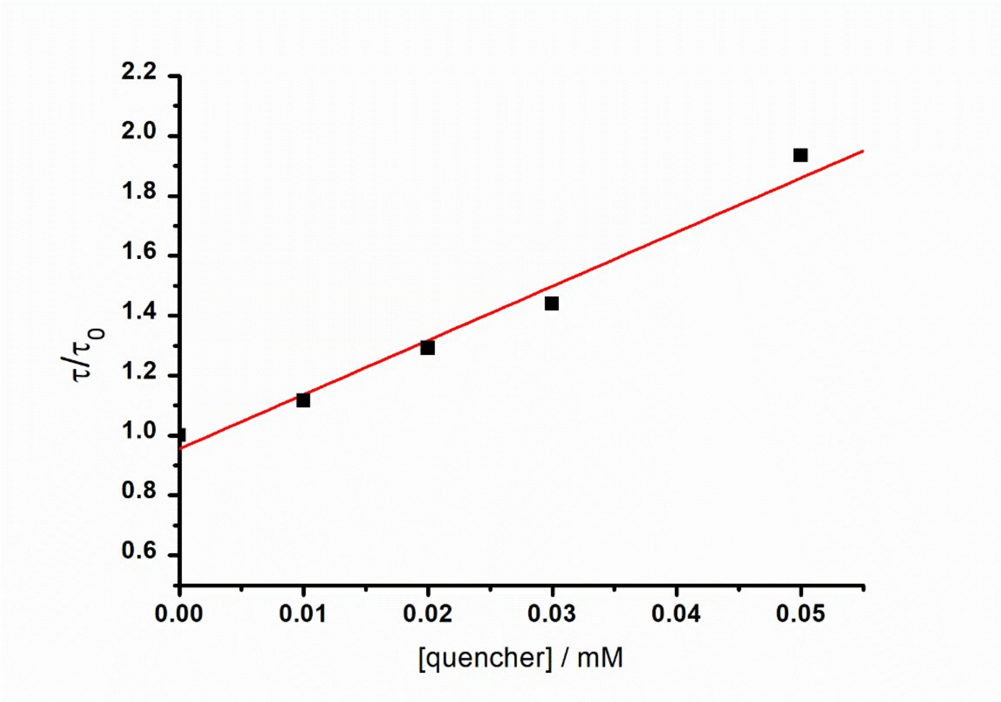

Figure S13. Stern-Volmer plot of transient absorption lifetime of **TATA⁺** at varied [BNAH]. $R^2 = 0.994$ and $k_q = 2.10 \times 10^8$ M^{-1} s^{-1}.

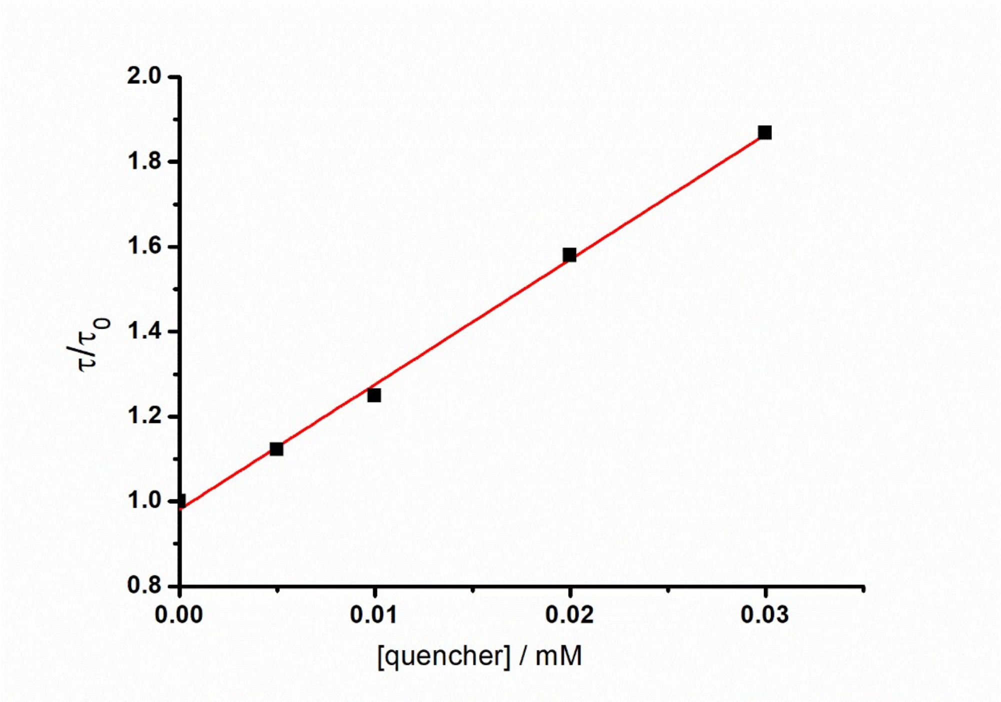

Figure S14. Stern-Volmer plot of transient absorption lifetime of $\mathbf{RB}^{2-}$ at varied [**1**]. $R^2 = 0.998$ and $k_q = 5.55 \times 10^8$ M^{-1} s^{-1}.

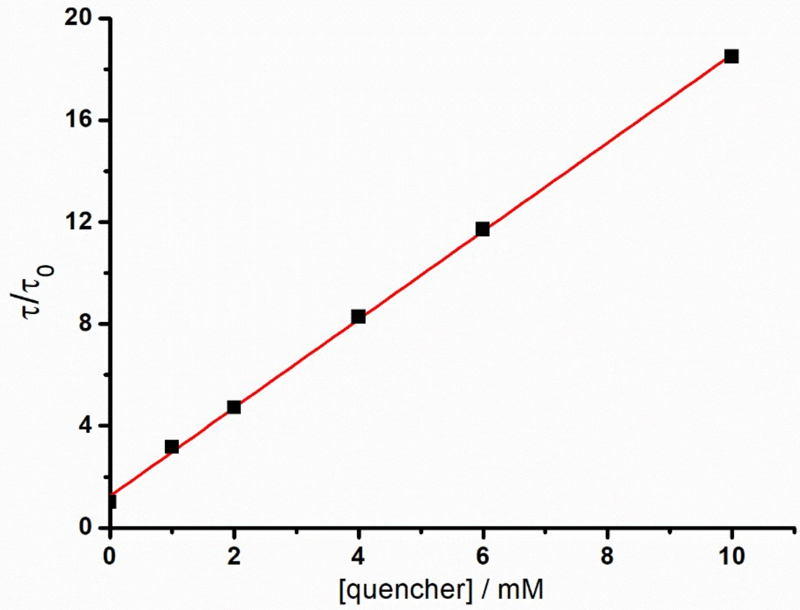

Figure S15. Stern-Volmer plot of transient absorption lifetime of **RB^{2-}** at varied [TEOA]. $R^2 = 0.999$ and $k_q = 3.27 \times 10^7$ M^{-1} s^{-1}.

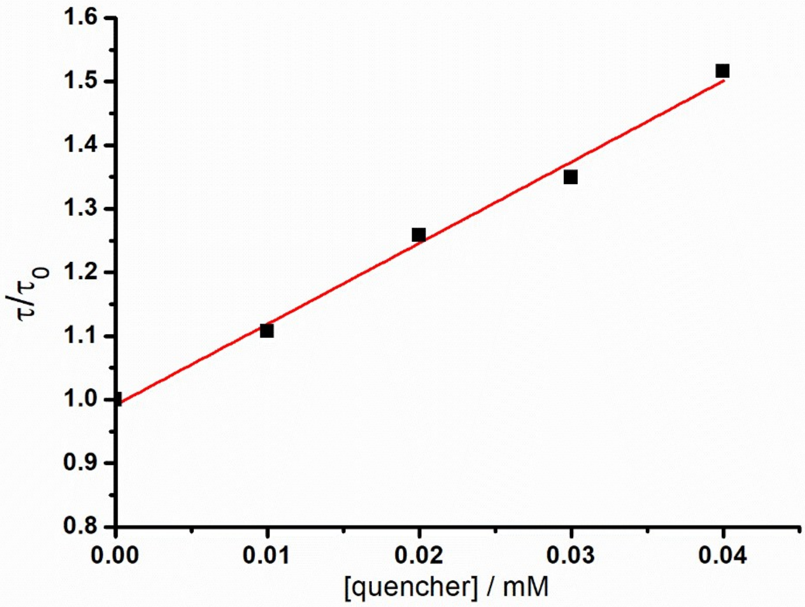

Figure S16. Stern-Volmer plot of transient absorption lifetime of **RB^{2-}** at varied [BNAH]. $R^2 = 0.993$ and $k_q = 2.10 \times 10^8$ M^{-1} s^{-1}.

Reference:

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