Electronic Supplementary Information

Excited-state hydrogen detachment from a tris-(*o*-phenylenediamine) iron(II) complex in THF at room temperature

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Experimental details

General procedures

UV-visible absorption spectra were recorded using a HITACHI U-4100 spectrophotometer at room temperature. ^{1}H NMR (500 MHz) spectra were recorded on a JEOL EX-500 spectrometer using THF-d_8 as the solvent. A Hamamatsu Photonics LC8 Hg–Xe lamp (200 W) was used as the light source in conjunction with a bandpass filter ($\lambda = 300 \pm 10$ nm, Asahi Spectra). Gas analyses were conducted using a Shimadzu GC-2014 gas chromatograph connected to a thermal conductivity detector (GC-TCD).

The ligand opda and iron(II) perchlorate hexahydrate ($[Fe(H_2O)_6](ClO_4)_2$) were purchased from Wako Pure Chemical Industries (Japan). *t*-Butylthiol (^{t}BuSH), *t*-butyldisulfide ($^tBu_2S_2$), 2,2,3,3-tetramethylbutane (TMB), and 2-methylpropane (MPA) were purchased from Tokyo Chemical Industries Co. Ltd. (Japan). Dichloromethane (CH_2Cl_2), ethyl acetate ($CH_3COOC_2H_5$), *n*-hexane, dehydrated THF, and THF-d_8 were purchased from Kanto Chemical Co. Inc. (Japan). Deuterium oxide (D_2O), magnesium sulfate ($MgSO_4$), 2-methylpropene (MPE), and 10% palladium on charcoal (10% Pd/C) were purchased from Sigma-Aldrich. Prior to use, the solvents were degassed using at least five freeze–pump–thaw cycles. Complex $[Fe(opda)_3](ClO_4)_2$ was prepared from $[Fe(H_2O)_6](ClO_4)_2$ and opda according to a previously reported procedure.[S1]

Caution! *Although we did not experience any difficulties manipulating the perchlorate salts, they should be regarded as potentially explosive and therefore be handled with the utmost care.*

Synthesis

$C_6D_4(NH_2)_2$.[S2] Opda (205 mg, 1.90 mmol) and 10% Pd/C (23.4 mg) were placed in an autoclave (10 mL), and D_2O (6 mL) was added. After being purged with H_2 for 20 min, the vessel was sealed and heated at 453 K for 90 h. The obtained black suspension was filtered, and the filtrate was extracted three times using CH_2Cl_2 (15 mL). The organic phases were combined, washed with H_2O, and dried with $MgSO_4$. After evaporation of the solvent, the obtained pale-orange powder was dissolved in $CH_3COOC_2H_5$ (3 mL). *n*-Hexane (6 mL) was then slowly added, resulting in the formation of colorless crystals of $C_6D_4(NH_2)_2$. ^{1}H NMR (THF-d_8, 500 MHz): δ (ppm) = 6.51 (m, 0.1H), 6.43 (m, 0.1H), 3.81 (s, 4H).

$C_6H_4(ND_2)_2$.[S3] Opda (29.1 mg, 0.27 mmol) was placed in a Schlenk flask (10 mL) to which degassed D_2O (1 mL) and $CDCl_3$ were added under an N_2 atmosphere. The mixture was stirred at room temperature for 1 h. Subsequently, the solvent was removed by evacuation to obtain $C_6H_4(ND_2)_2$ as a white powder, which was immediately used for the photochemical reaction to avoid proton exchange with moisture in the air. ^{1}H NMR (THF-d_8, 500 MHz): δ (ppm) = 6.51 (m, 4H), 6.43 (m, 4H), 3.81 (s, 0.2H).

Photochemical radical trapping experiments

A THF solution (3 mL) containing $[Fe(opda)_3](ClO_4)_2$ (1 mM) and ^{t}BuSH (6 mM) was prepared in a custom-built quartz vessel equipped with a Schlenk flask (V = 165 mL) under an N_2 atmosphere. After irradiation of the solution with UV light (λ = 300 ± 10 nm), the gaseous product was analyzed via a GC-TCD with a molecular sieve 5A column (Shinwa Chemical Industries LTD., 2 m, T = 343 K, carrier gas: Ar), while the products in solution were evaluated using ^{1}H NMR spectroscopy. As a control experiment, the same procedure was carried out using $^tBu_2S_2$ (6 mM).

Calculation of the external quantum efficiency for the photochemical H_2 evolution

The external quantum efficiency (Φ) of the H_2 evolution from a THF solution containing $[Fe(opda)_3](ClO_4)_2$ (1 mM) and ^{t}BuSH (6 mM) was calculated according to:

$$\Phi = N_e/N_p = 2N_{H2}/N_p$$

where N_e, N_{H2}, and N_p denominate the number of reacted electrons, the number of the evolved H_2 molecules, and the number of incident photons, respectively.

Deuterium labeling experiments for photochemical hydrogen gas evolution

A THF solution (3 mL) containing $[Fe(H_2O)_6](ClO_4)_2$ (0.09 mmol) and ^{t}BuSH (0.54 mmol), which had been dehydrated using molecular sieves 4A (0.3 g) for 5 h prior to the experiment, was transferred to a quartz vessel equipped with a three-way cock (V = 12.2 mL) containing labelled or non-labelled opda (0.27 mmol) under an N_2 atmosphere. After irradiating the solution with UV light (λ = 300 ± 10 nm), the gaseous product was analyzed using GC-TCD with an OGO-SP column (Shinwa Chemical Industries LTD., 2 m, T = 77 K, carrier gas: He).

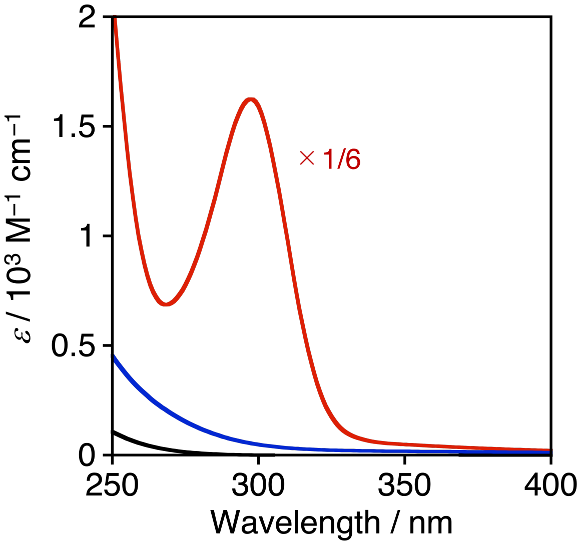


Fig. S1 UV-visible absorption spectra of ^{t}BuSH (black), ${}^{t}Bu_2S_2$ (blue), and $[Fe(opda)_3](ClO_4)_2$ (red) in THF.

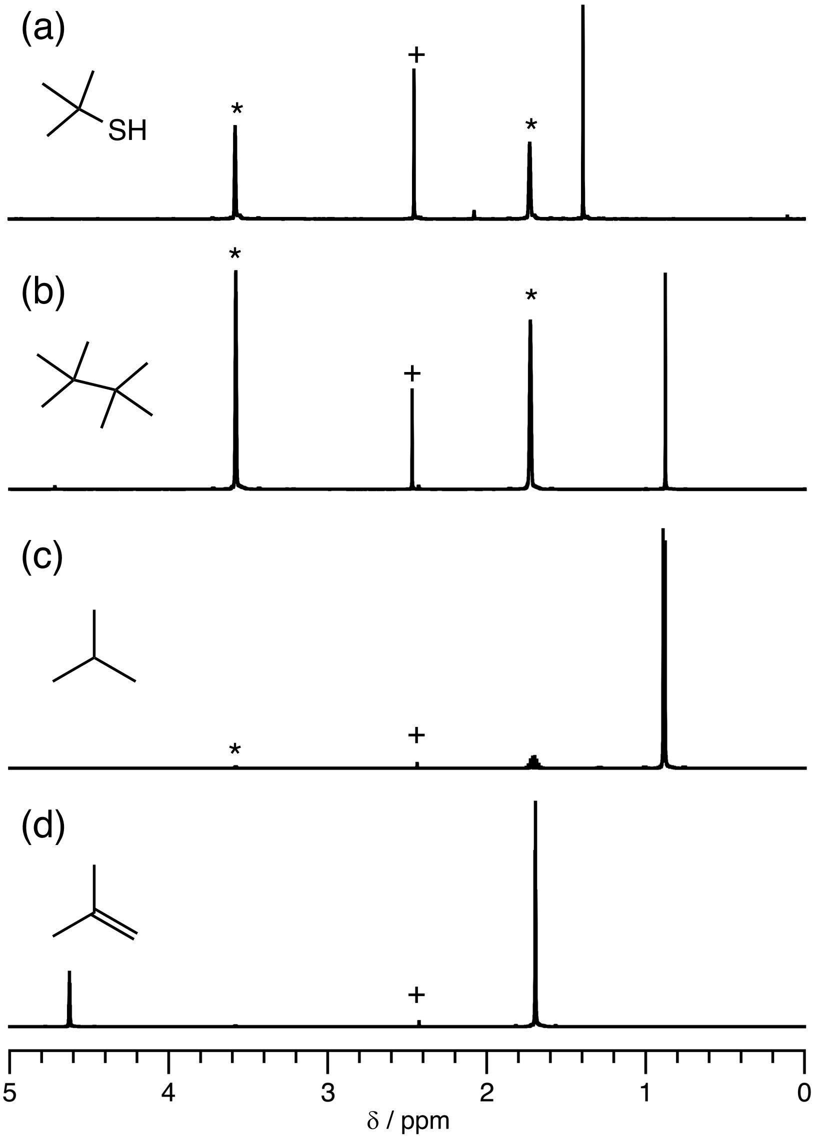


Fig. S2 ^{1}H NMR spectra of (a) ^{t}BuSH, (b) 2,2,3,3-tetramethylbutane (TMB), (c) 2-methylpropane (MPA), and (d) 2-methylpropene (MPE) in THF-d_8. The signals ‘*’ and ‘+’ indicate signals assignable to THF and water, respectively.

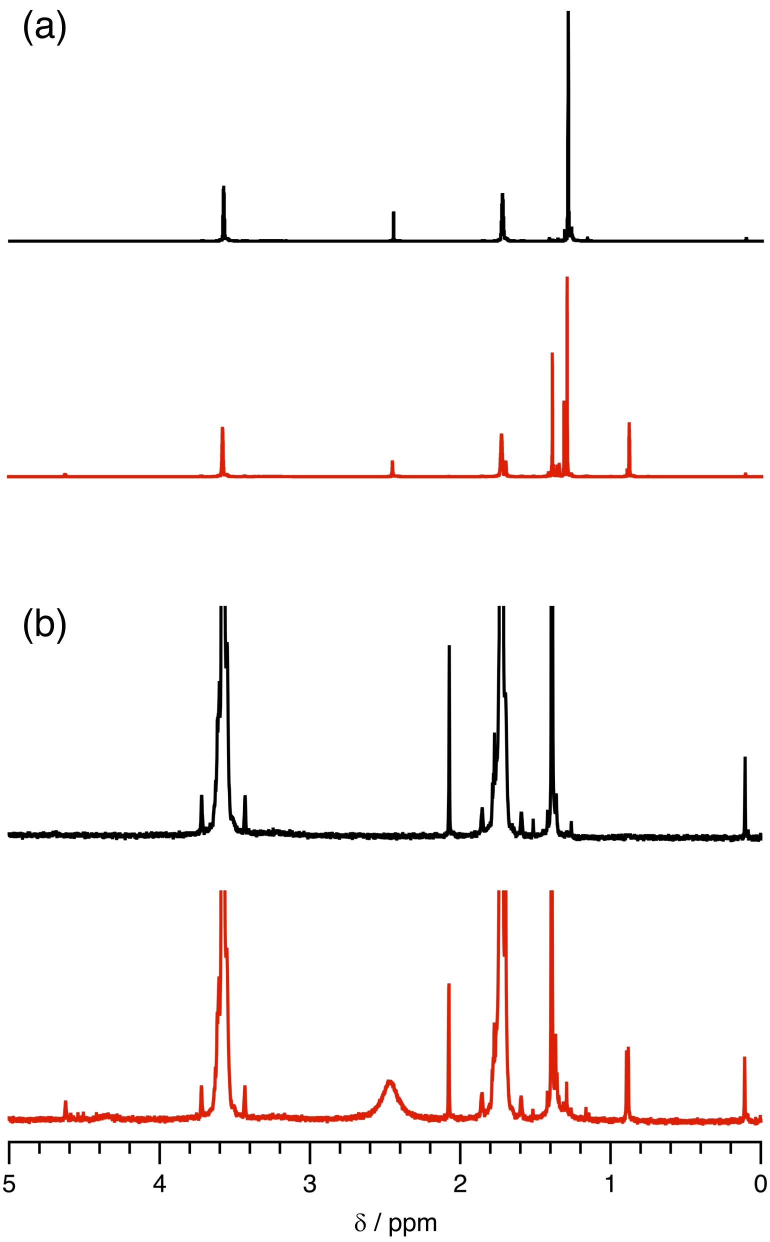


Fig. S3 ^{1}H NMR spectra of THF-d_8 solutions containing (a) ^{t}Bu$_2$S$_2$ (6 mM) or (b) a mixture of [Fe(opda)$_3$](ClO$_4$)$_2$ (1 mM) and ^{t}BuSH (6 mM) before (black) and after (red) photoirradiation (λ = 300 nm) for 1 h.

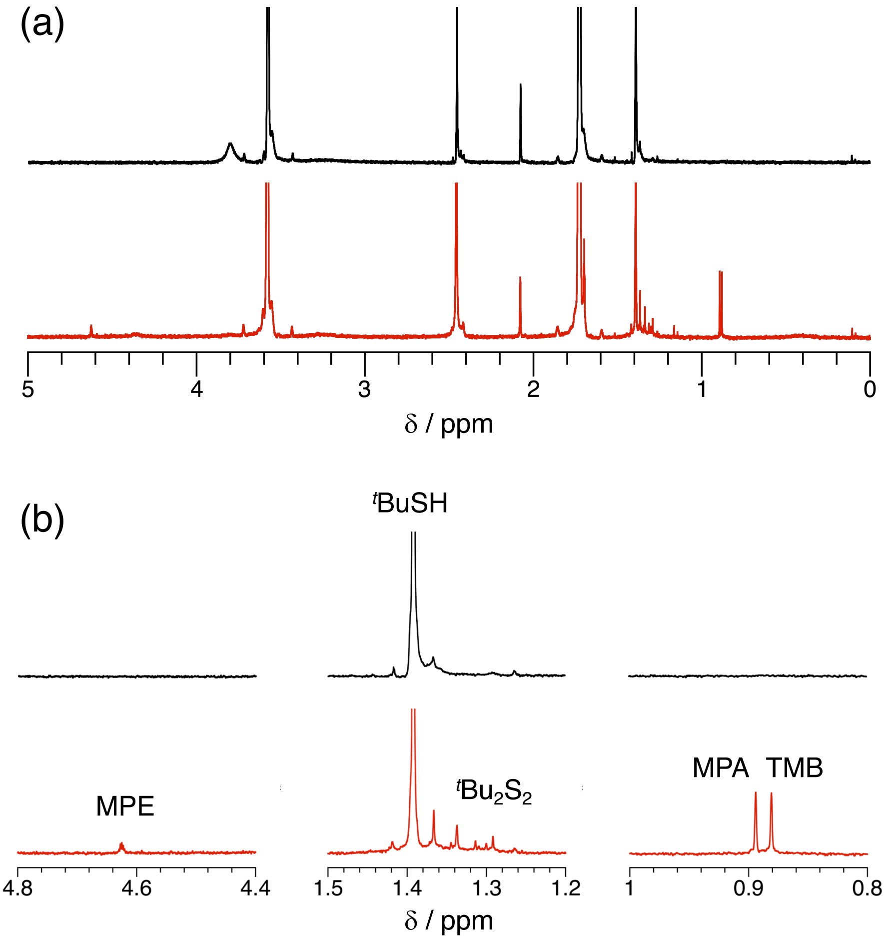


Fig. S4 (a) ^{1}H NMR spectra of a THF-d_8 solution containing opda (3 mM) and ^{t}BuSH (6 mM) before (black) and after (red) photoirradiation (λ = 300 nm) for 1 h. (b) Magnifications of selected regions of the spectra in (a).

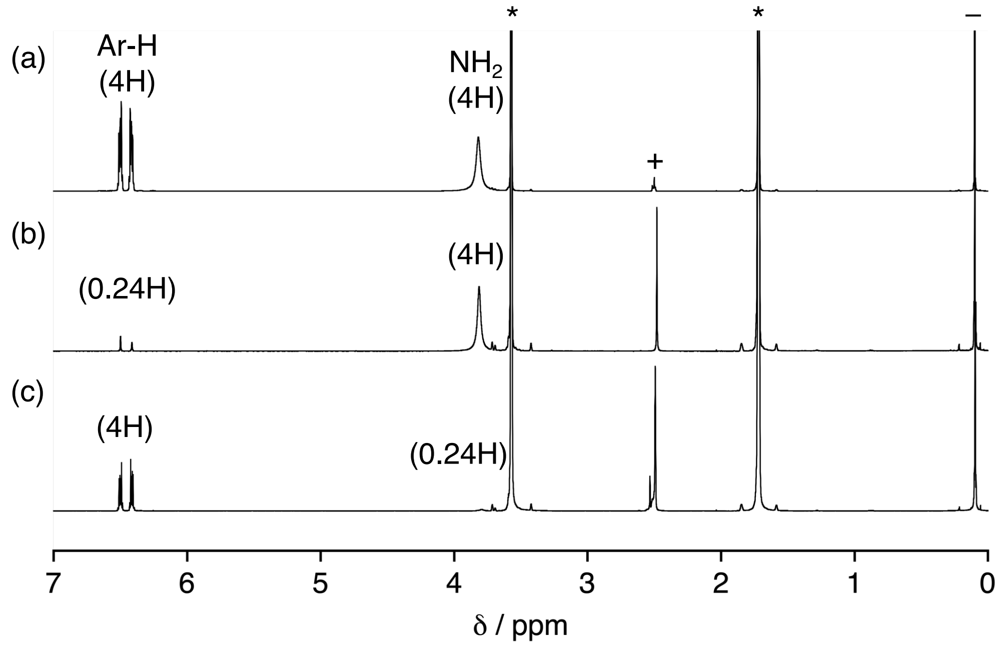
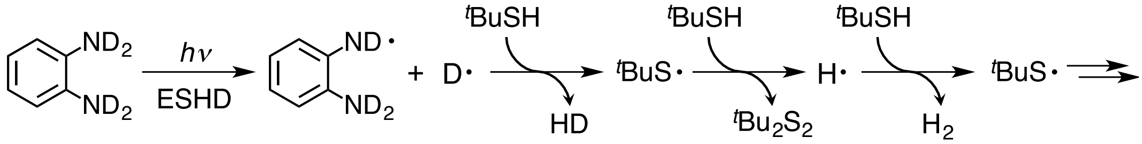


Fig. S5 ^{1}H NMR spectra of THF-d_8 solutions containing (a) opda, (b) o-$C_6D_4(NH_2)_2$, or (c) o-$C_6H_4(ND_2)_2$. The signals '*', '$^+$', and '$^-$' indicate peaks assignable to THF, water and silicone grease contamination, respectively.



Scheme S1 Plausible side radical reactions of ^{t}BuSH followed by ESHD of $C_6H_4(CD_2)_2$ for H_2 formation.

References

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S3. H. Chikashita, S. Nishida, M. Miyazaki, Y. Morita and K. Itoh, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 737–746.