

Supporting Information for

Analysis of Hydrogen Bonding Effects on Excited State Proton-Coupled Electron Transfer from a Series of Phenols to a Re(I) Polypyridyl Complex

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Materials and Preparation of the Re complexes

2,2'-bipyridine (bpy), 4,4'-bipyridine (4,4'-bpy), 4-phenylpyridine (4-phpy), potassium hexafluorophosphate (KPF₆), and silver nitrate (AgNO₃) were all purchased from Sigma Aldrich; Rhenium pentacarbonyl chloride, [Re(CO)₅Cl], was purchased from Acros Organics and used without further purification. Reagent grade solvents were used after being dried by conventional distillation techniques. All phenols were purchased from Sigma Aldrich. Phenol and BrPhOH were purified by recrystallization prior to use, while the remaining phenols were used as received.

Preparation of *fac*-[(CO)₃Re(bpy)(4,4'-bpy)]PF₆ (Re-N).

(CO)₃Re(bpy)Cl was prepared according to a previously reported method^{S1} by heating equimolar quantities of Re(CO)₅Cl and 2,2'-bipyridine in toluene to reflux for 1h. The yellow product precipitated from the cold reaction mixture, was filtered, washed with Et₂O, dried, and used without further purification in the next step. The chloro complex was converted to its acetonitrile counterpart via treatment with silver nitrate in MeCN.^{S2} For this, equimolar quantities of (CO)₃Re(bpy)Cl and AgNO₃ were refluxed in dry MeCN for 6 h under argon atmosphere in the dark. The resulting suspension was cooled to room temperature and the precipitated AgCl was separated by filtration through a sintered glass crucible (G-4). The volume of the filtrate was reduced to 10 mL and an excess of a saturated aqueous solution of KPF₆ was added. The pale yellow precipitate was filtered, washed with ice cold water, and dried in vacuum. The thus obtained [(CO)₃Re(bpy)(CH₃CN)]PF₆ and a 1.5-fold excess of 4,4'-bipyridine in THF were heated to reflux for 3h under argon atmosphere in the dark. After cooling to room temperature, Et₂O was added slowly to precipitate the product as a yellow solid. The crude product was purified by column chromatography on silica gel using a 2:1 (v/v) mixture of CH₂Cl₂ and CH₃CN as eluent. Evaporation of the solvent under reduced pressure afforded pure [(CO)₃Re(bpy)(4,4'-bpy)]PF₆. ¹H NMR (400 MHz, d₆-DMSO) δ = 9.35 (d, 2H), 8.74 (d, 2H), 8.70 (2d, 2H), 8.52 (d, 2H), 8.41 (t, 2H), 7.91 (t, 2H), 7.85 (d, 2H), 7.74 (d, 2H). ESI-MS (in acetonitrile): 582.61 [M – PF₆]. Anal. found: C 34.67, H 2.42, N 6.72 %; Calcd. for C₂₃H₁₆F₆N₄O₃PRe·H₂O·CH₂Cl₂: C 34.71, H 2.43, N 6.75 %.

Preparation of *fac*-[(CO)₃Re(bpy)(4-phpy)]PF₆ (Re-ref).

fac-[(CO)₃Re(bpy)(4-phpy)]PF₆ (Re-ref) was prepared by previous published procedure by Meyer.^{S3} (CO)₃Re(bpy)Cl (100.0 mg, 0.21 mmol) was suspended in 5mL DCM under N₂ atmosphere. After drop wise addition of trifluoromethanesulfonic acid (0.11 mL, 1.26 mmol) the clear orange mixture was stirred at RT for 1 h. A light yellow solid precipitated upon drop wise addition of Et₂O to the stirred reaction mixture. It was filtered, washed with Et₂O, and dried in vacuum (100.0 mg, 0.17 mmol, 81%). Subsequently, (CO)₃Re(bpy)OTf (100.0 mg, 0.17 mmol) was dissolved in 10 mL MeOH and 4-phenylpyridine (157.7 mg, 1.02 mmol, 4-phpy) in 1 mL CHCl₃ was added under N₂ atmosphere. After degassing for 10 min, the reaction mixture was heated to 85 °C for 24 h. Following cooling to RT, the solvents were evaporated, the residue was taken up in little DCM and precipitated in Et₂O. Final counter ion exchange afforded [(CO)₃Re(bpy)(4-phpy)]PF₆ as a yellow solid (94.5 mg, 0.13 mmol, 75%).

^1H NMR (400 MHz, $\text{d}_3\text{-MeCN}$) δ = 9.25 (2H), 8.39 (2H), 8.29 (2H), 8.25 (2H), 7.81 (2H), 7.64 (2H), 7.55 (2H), 7.49 (3H).

Equipment and Methods

All the samples were prepared in a $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 3:1 v/v mixture on same day of the measurements. In a typical experiment, the concentration of the Re^{I} complex was set to 0.1 mM. All the samples were degassed for 15 minutes prior to data acquisition. The concentration of the phenols can be extracted from the corresponding Stern-Volmer plots. Isotopic effect measurements were conducted by substituting water with deuterium oxide (Sigma Aldrich, 99.9%).

Ground-state absorption spectra were recorded on Agilent 8453 UV-Vis spectrometer. Regular monitoring of absorption spectra allows for the detection of any absorbing impurities or side reactions occurring during the course of the photochemical reaction between the Re^{I} complex and the phenols.

Fluorescence titrations were performed by exciting the samples at 400 nm using a Fluorolog-3 instrument from Horiba Jobin-Yvon and sequential addition of aliquots of a particular phenol to a sample of **Re-N** or **Re-ref**.

For transient absorption and kinetic emission measurements, optical excitation was afforded by using the third harmonic output of a Brilliant B Nd:YAG laser (355 nm, 10 Hz, ~ 20 mJ/pulse) as an excitation source. A pulsed Xenon lamp of an Applied Photophysics LKS60 setup provided the analyzing light that was passed through a 1×1 cm quartz sample cuvette in a right-angle configuration. Before hitting the P928 type photomultiplier the light was passed and through a monochromator. The PMT signal was converted and digitized using an HP Infiniium digital oscilloscope (2G samples/s). Transient absorption traces were generated from the raw data using the LKS60 software.

Transient absorption spectra measurements on the nanosecond time scale were performed with a frequency tripled Q-switch Nd:YAG laser to obtain 355 nm pump light of ~ 10 ns pulse duration at 10Hz. The pulse laser was coupled to a transient absorption detection system (Edinburgh Instruments), equipped with a monochromator and a pulsed Xe arc lamp. The sample was contained in a 1×1 cm quartz cell. Transient absorption data was collected at a right angle to the incoming laser beam by a Tektronix 500MHz digital oscilloscope coupled to a CCD camera to record the spectra. The output was processed with Edinburgh Instruments L900 software supplied by the manufacturer.

The raw spectral data was exported into either Origin 8.0 (Origin Lab corp., Northampton, Massachusetts, USA) or Igor 6.3 (WaveMetrics, Inc., USA) for further processing.

Ground State Association Constants

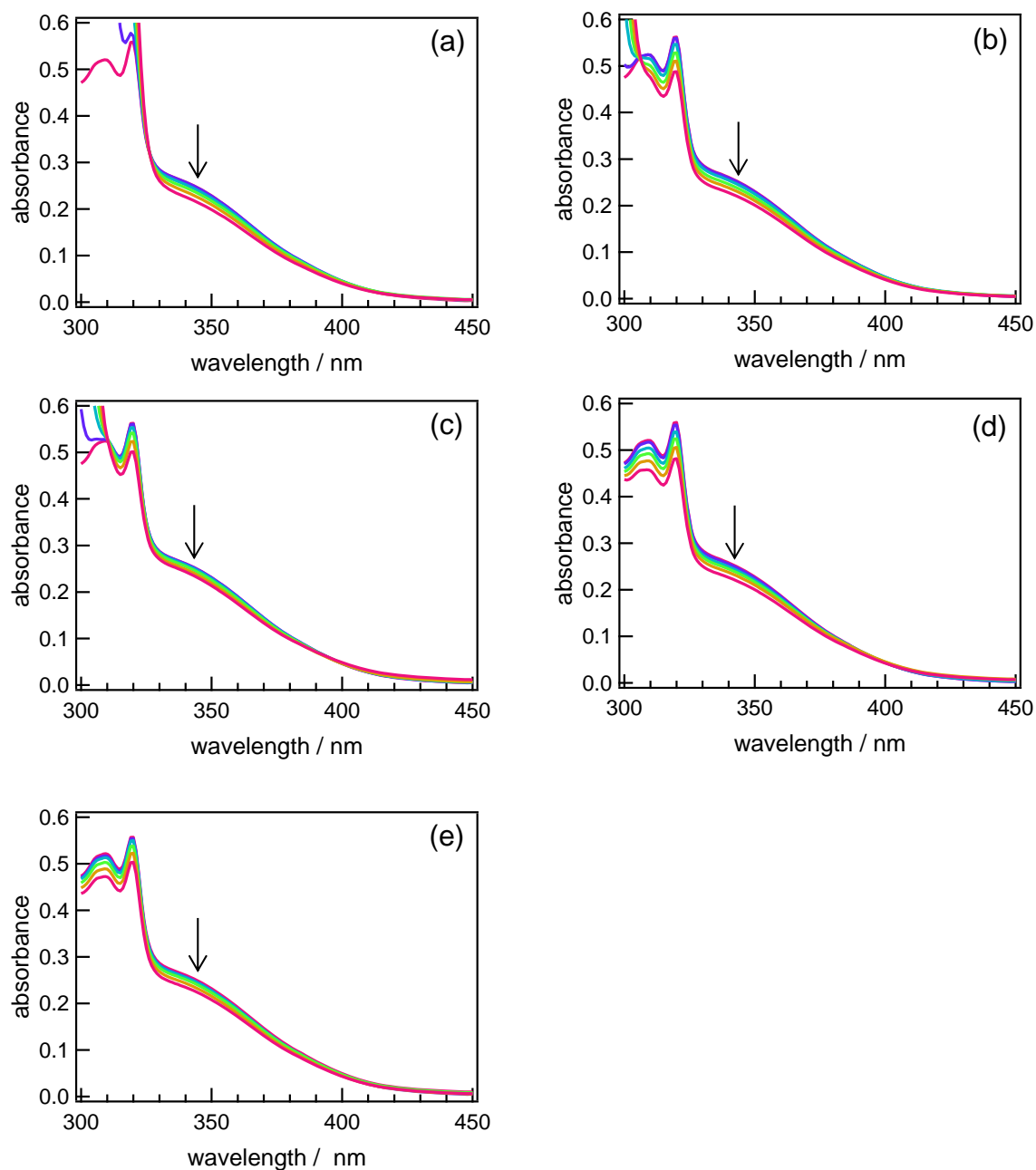


Figure S1. Absorption spectra obtained after sequential addition of phenol aliquotes to a $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 3:1 v/v solution of **Re-N**. (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. Direction of arrow indicates the spectral response upon phenol addition.

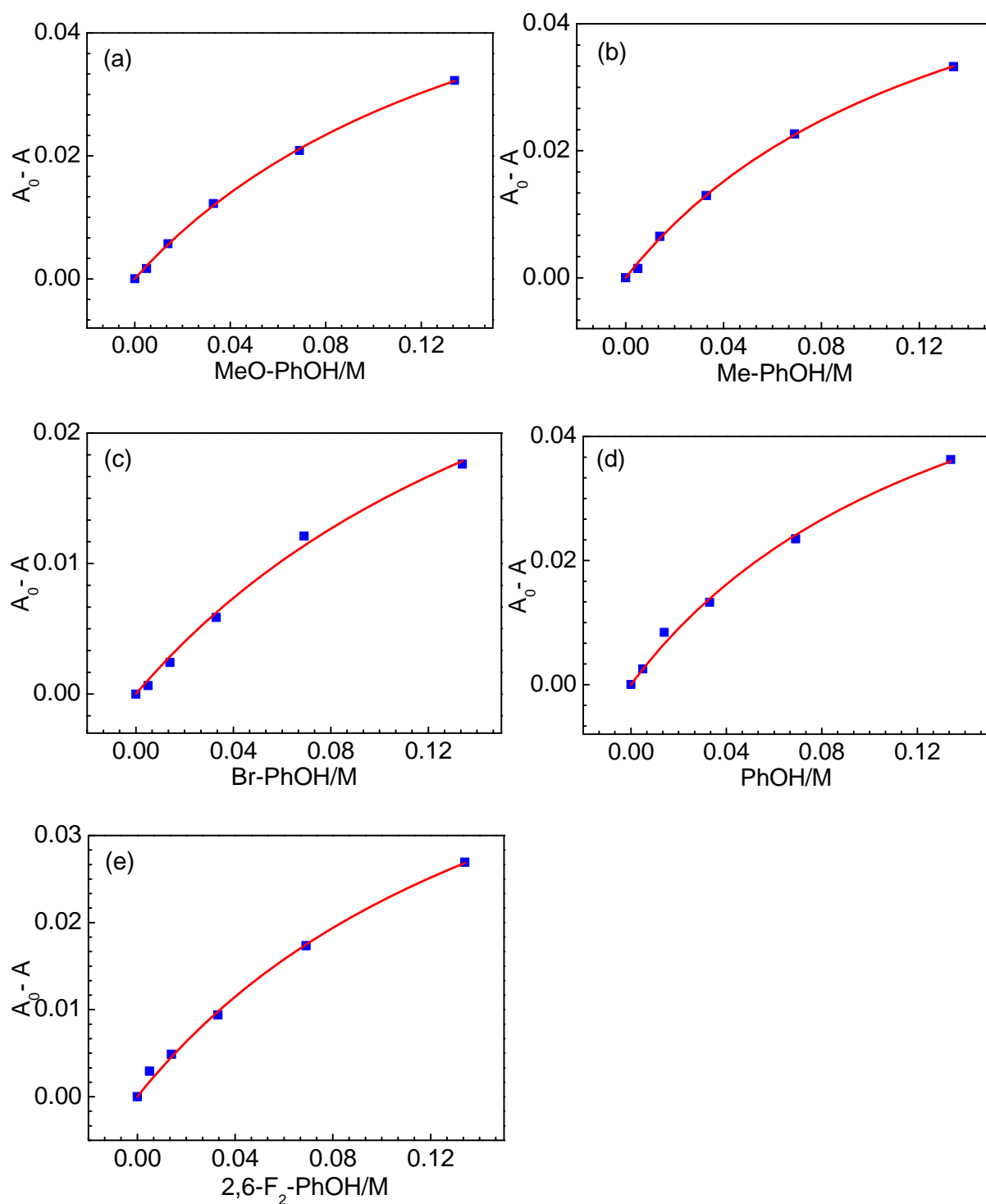


Figure S2. Plots of absorption change of **Re-N** as a function of the phenol concentration constructed from the corresponding spectra shown in Fig. S1. Blue squares: experimental data points; Red line: fit according to Eq 1. (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. The absorption change was monitored at 340 nm.

The ground state K_A can be extracted from the fits to the Stern-Volmer plots according to Eq. 1 in the main article, as previously described by Petersson *et al.*^{S4}

Excited State Association Constants

In a previous fitting model for the extraction of association constants by Concepcion *et al.*, the intensity change (ΔI) is plotted vs the concentration of the quencher $[Q]$.^{S5} There, the intensity plot appears to give evidence for saturation, but only because k_{obs} or $1/\tau$ vs $[Q]$ which is proportional to the observed rate is not plotted. Moreover, a simple diffusional quenching ($k = k_0 + k_q[Q]$) gives the same curvature (saturation plots) when it is plotted as ΔI vs $[Q]$ (see derivation below). Therefore, Concepcion *et al.* would observe only a straight line in the plot of k_{obs} vs $[Q]$. As a result, the data in that case can be explained by diffusional quenching. Bronner *et al.*^{S6} have adapted the same approach and their Stern-Volmer plots clearly suggest a simple diffusional quenching with $\tau_0/\tau = I_0/I$, which is essential for a model of fast equilibrium complexation. Thus, it can be concluded that the model reported by Concepcion *et al.* is not appropriate for a mixture of static and dynamic quenching where there is still significant emission from the association complex. Scheme S1 portrays the events occurring in the ground and excited state upon addition of phenol to the $[(\text{CO})_3\text{Re}^{\text{I}}(\text{bpy})(4,4'\text{-bpy})]^+$ (Re) complex.

For pure diffusional quenching, the ratio of luminescence lifetime (τ_0/τ) and intensity (I_0/I) as a function of quencher concentration $[Q]$ is given by the well-known Stern-Volmer expression:

$$\frac{\tau_0}{\tau} = \frac{I_0}{I} = 1 + K_{\text{SV}}[Q] = 1 + \frac{k_q}{k_0}[Q] \quad [\text{S1}]$$

where τ_0 and I_0 are the values in the absence of quencher, $k_0 = (\tau_0)^{-1}$ and k_q is the second-order quenching rate constant.

The difference in luminescence intensity, ΔI as defined in reference S5, is proportional to the difference in luminescence quantum yield, $\Delta\Phi$. This gives:

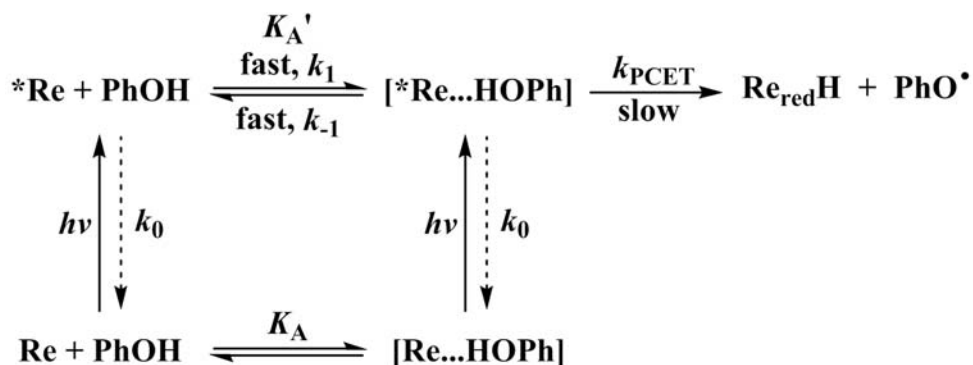
$$\Delta I = I_0 - I \propto \Phi_0 - \Phi = \frac{k_r}{k_0} - \frac{k_r}{k_0 + k_q[Q]} = \frac{k_r k_q [Q]}{k_0(k_0 + k_q[Q])} \quad [\text{S2}]$$

A plot of ΔI vs. $[Q]$ will thus show a downward curvature reaching “saturation”, but this is not related to formation of a complex.

Inversion of eq. S2 gives:

$$\frac{1}{\Delta I} \propto \frac{1}{\Phi_0 - \Phi} = \frac{k_0(k_0 + k_q[Q])}{k_r k_q [Q]} = \frac{k_0}{k_r} \left(\frac{k_0}{k_q[Q]} + 1 \right) \quad [\text{S3}]$$

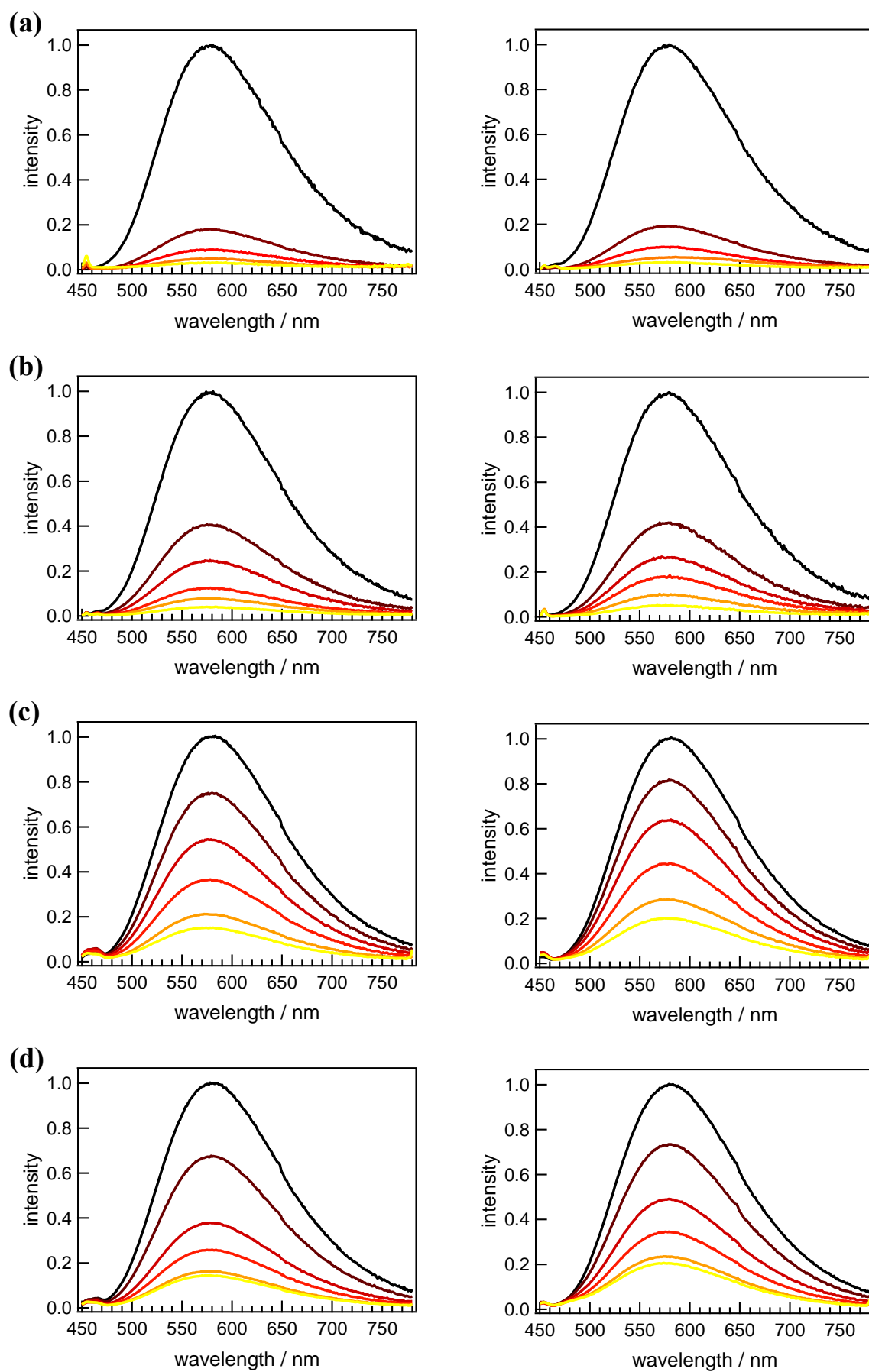
Thus, a plot of $(\Delta I)^{-1}$ vs. $([Q])^{-1}$ will result in a straight line, as observed in reference S5 and ref. 23 of the main paper. This is, however, perfectly consistent with pure diffusional quenching.



Scheme S1. Events occurring in the photochemical interaction of $[(CO)_3Re^I(bpy)(4,4'-bpy)]^+$ (denoted as Re) and phenol (represented as PhOH).

In the present study, phenol was added in great excess to ensure a rapid excited state equilibrium and for k_q to remain the same for both, the free and bound Re complex. At high phenol concentrations, curvature can be observed in $\frac{\tau_0}{\tau}$ or $\frac{I_0}{I}$ vs $[PhOH]$ plots. This indicates a saturation point, where $k_q = k_{PCET}$ and a separate excited state K_A' can be extracted by fitting according to Eq. S4.

$$k_{obs} = k_0 + k_{ET}[PhOH] + k_{PCET} \frac{K_A'[PhOH]}{1 + K_A'[PhOH]} \quad [S4]$$



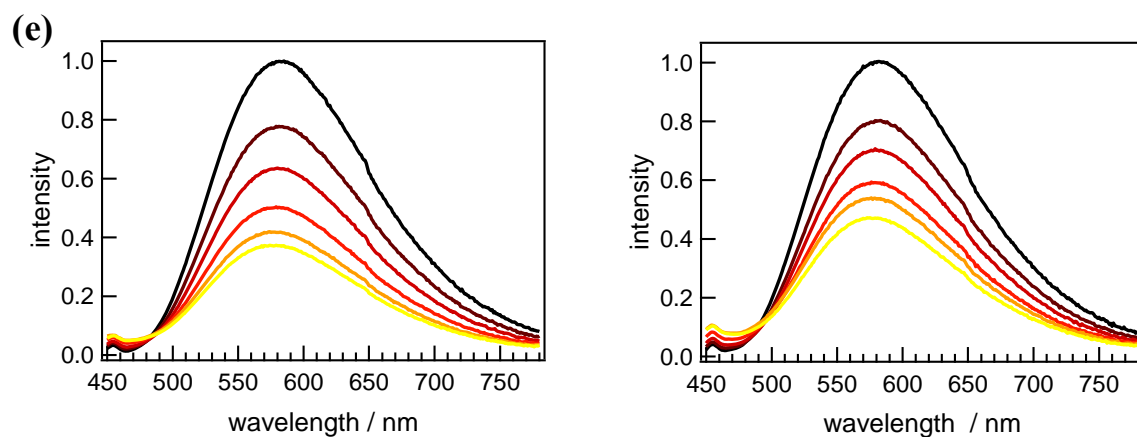
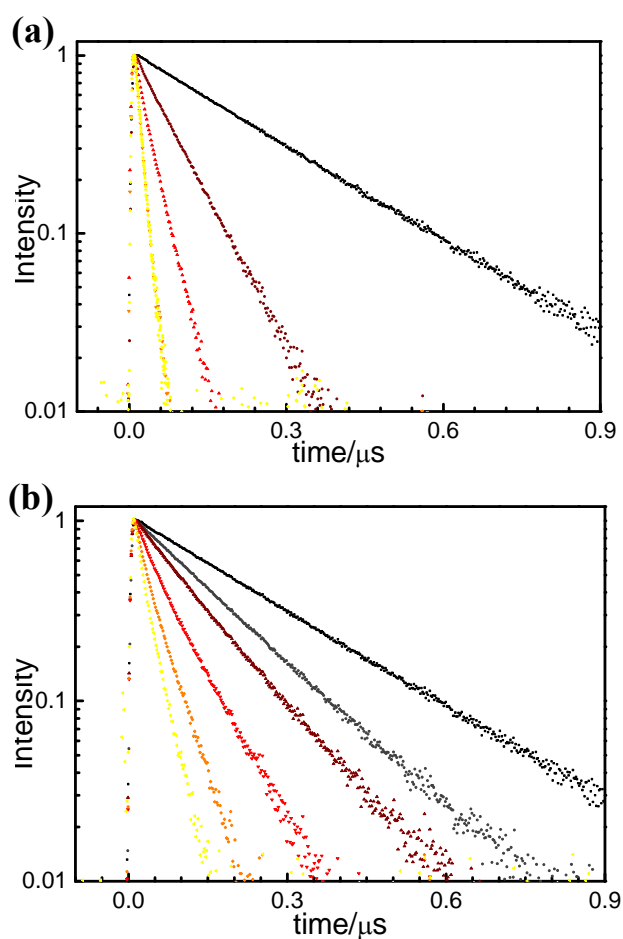


Figure S3. Steady-state luminescence spectra obtained as a function of phenol concentration acquired after exciting a deoxygenated 0.1 mM solution of **Re-N** at 400 nm. Left: spectra acquired in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ 3:1 (v/v); Right: corresponding spectra in $\text{CH}_3\text{CN}:\text{D}_2\text{O}$ 3:1 (v/v). (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. The amount of phenols added can be read from the corresponding Stern-Volmer plots.



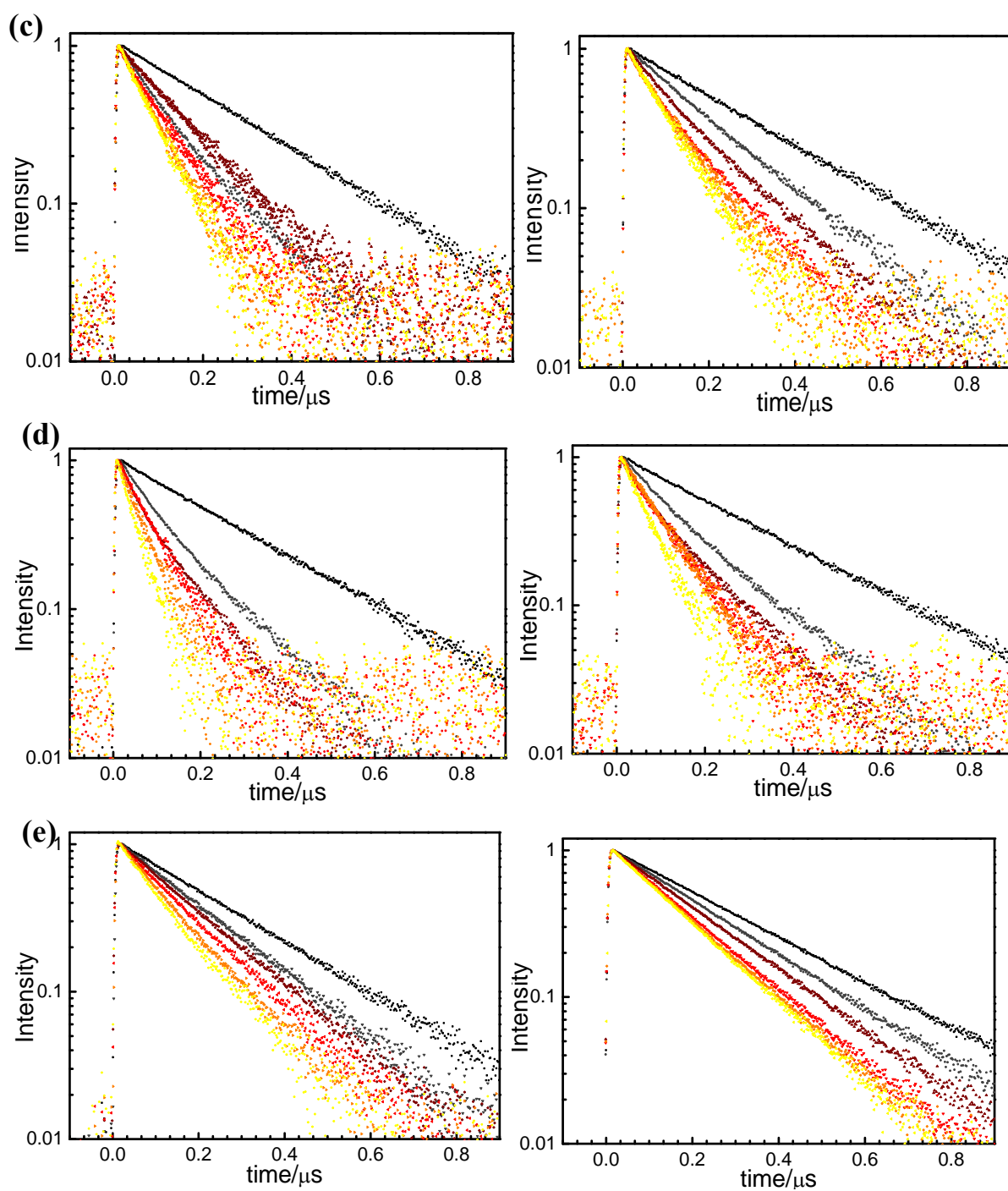
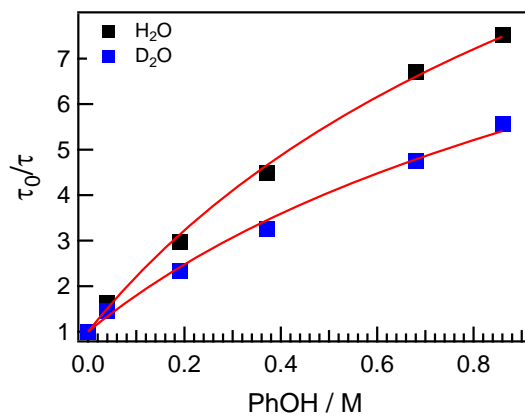
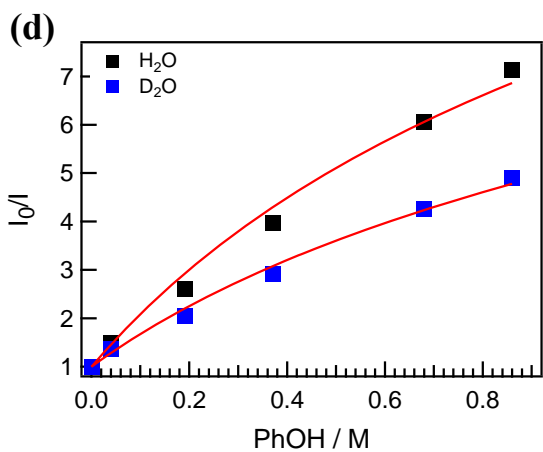
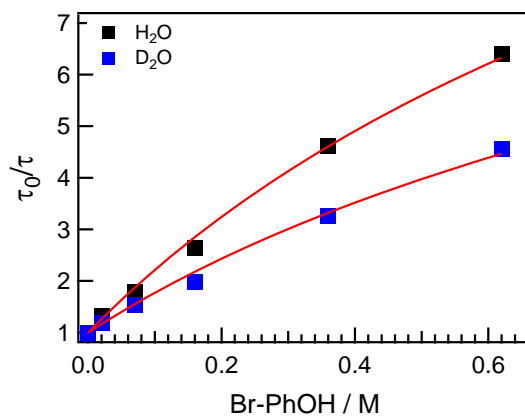
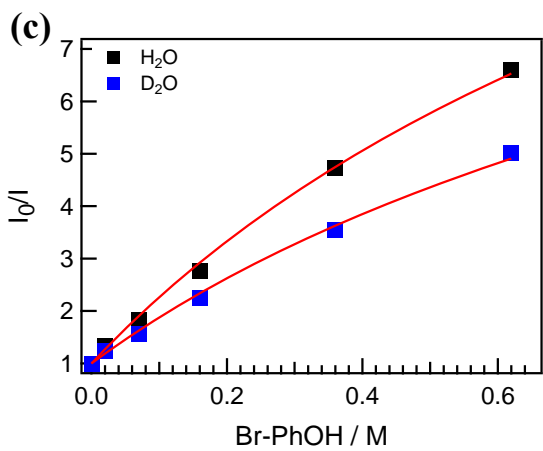
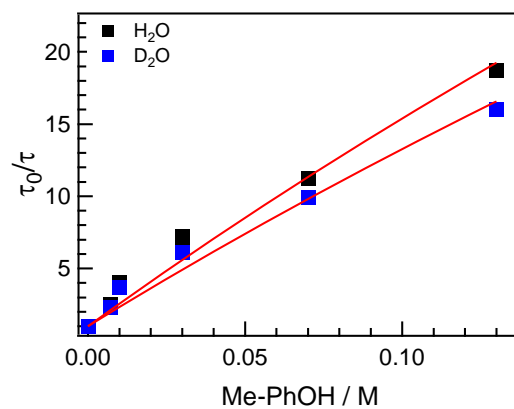
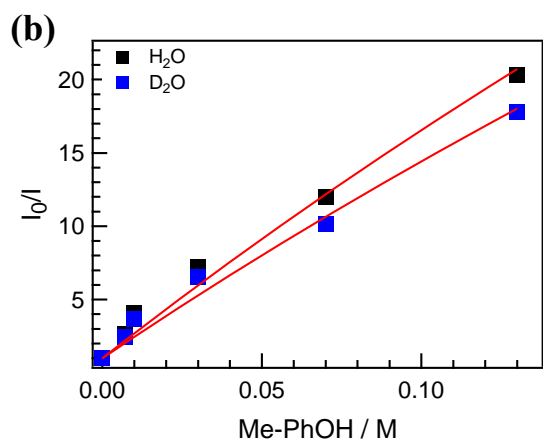
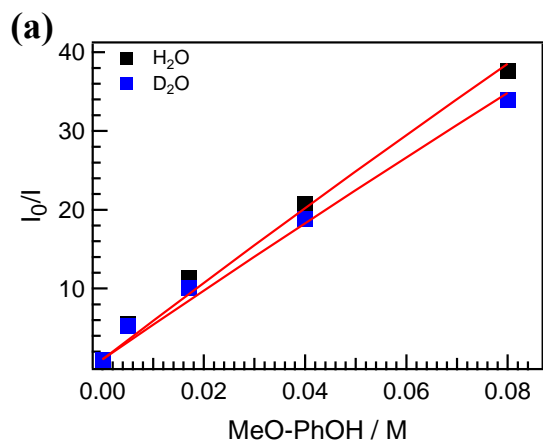


Figure S4. Time-resolved emission traces as a function of the phenol concentration acquired after excitation of a deoxygenated 0.1 mM solution of **Re-N** at 355 nm. Left: spectra in CH₃CN:H₂O 3:1 (v/v); Right: corresponding spectra in CH₃CN:D₂O 3:1 (v/v). (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. The amount of phenols added can be read from the corresponding Stern-Volmer plots.



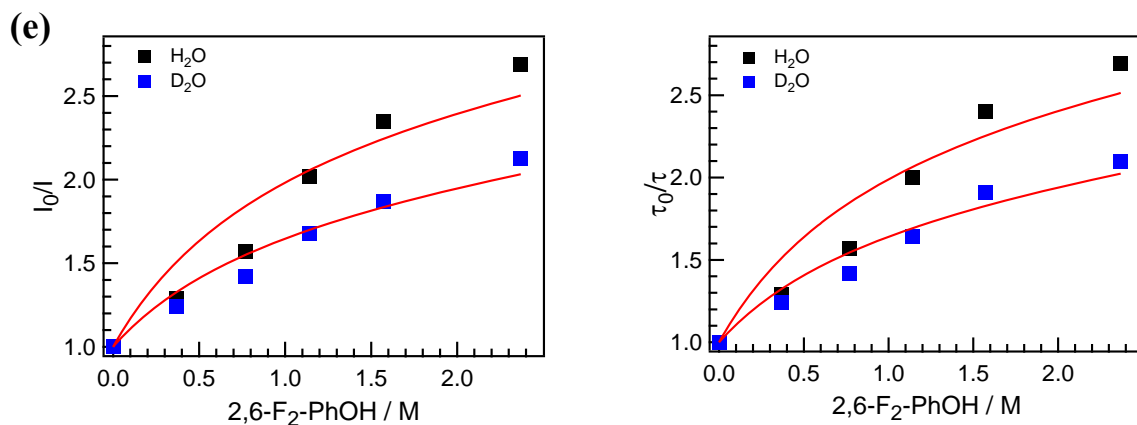
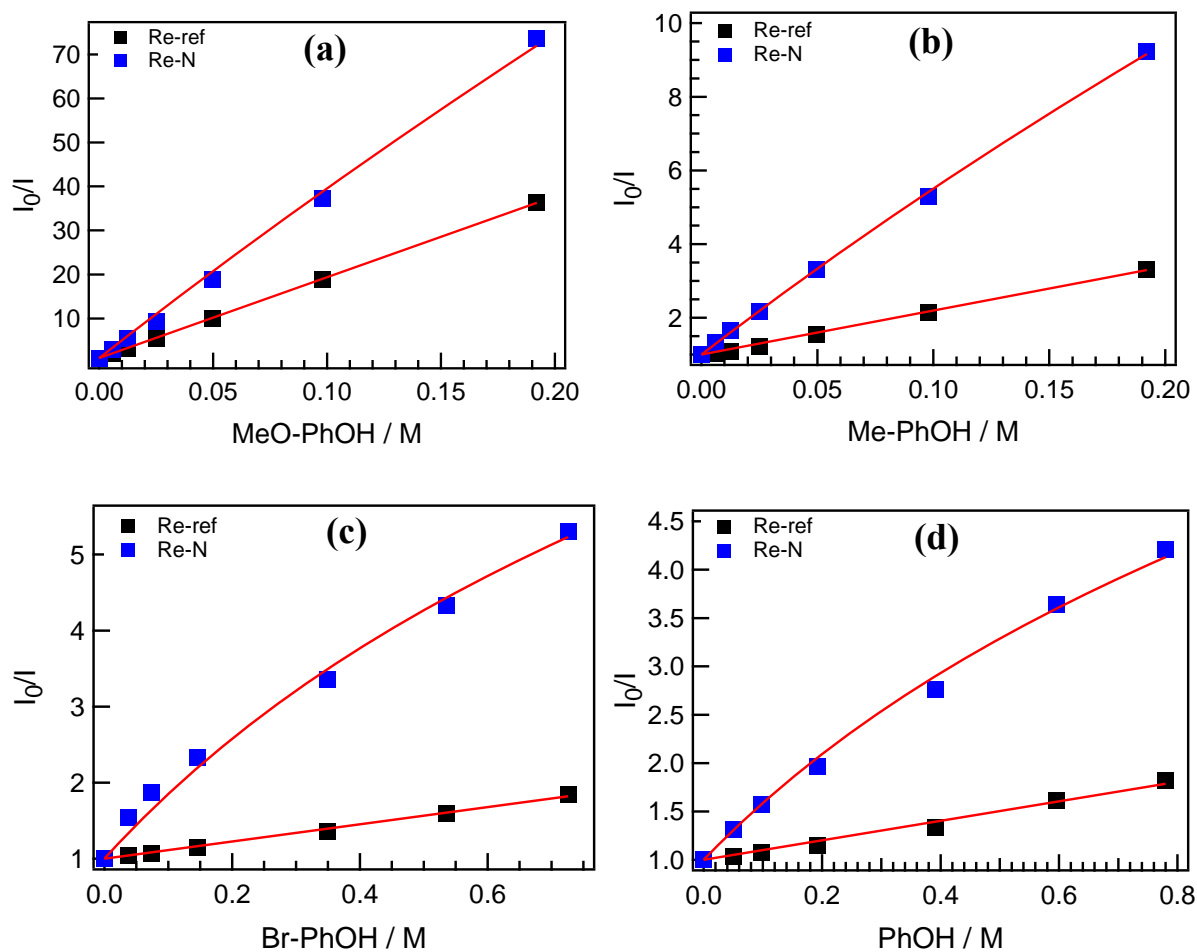


Figure S5. Stern-Volmer plots for **Re-N** constructed from the corresponding spectra shown in Fig. S3 and S4. Left: constructed from the luminescence quenching data; Right: constructed from lifetime quenching data. Quenching was monitored at 580 nm. (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. In all plots: black squares and blue squares correspond to data obtained in CH₃CN:H₂O 3:1 (v/v) and CH₃CN:D₂O 3:1 (v/v), respectively. The red line is a fit according to Eq. 2 in the main paper.



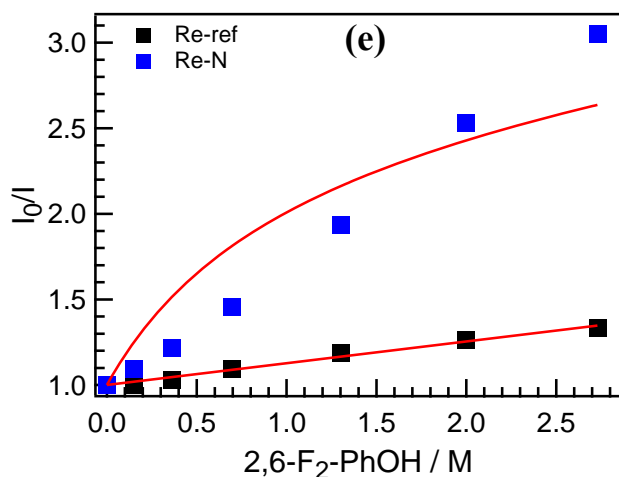


Figure S6. Stern-Volmer plots for **Re-Ref** (black squares) and **Re-N** (blue squares) acquired at equimolar concentrations constructed from the luminescence quenching data. For Re-Ref the quenching was monitored at 588 nm. (a) MeO, (b) Me, (c) Br, (d) H, and (e) 2,6-F₂. The data obtained in CH₃CN:H₂O 3:1 (v/v) by exciting at 400 nm. The red line is a fit according to Eq. 2 in the main paper.

Transient Absorption Spectra

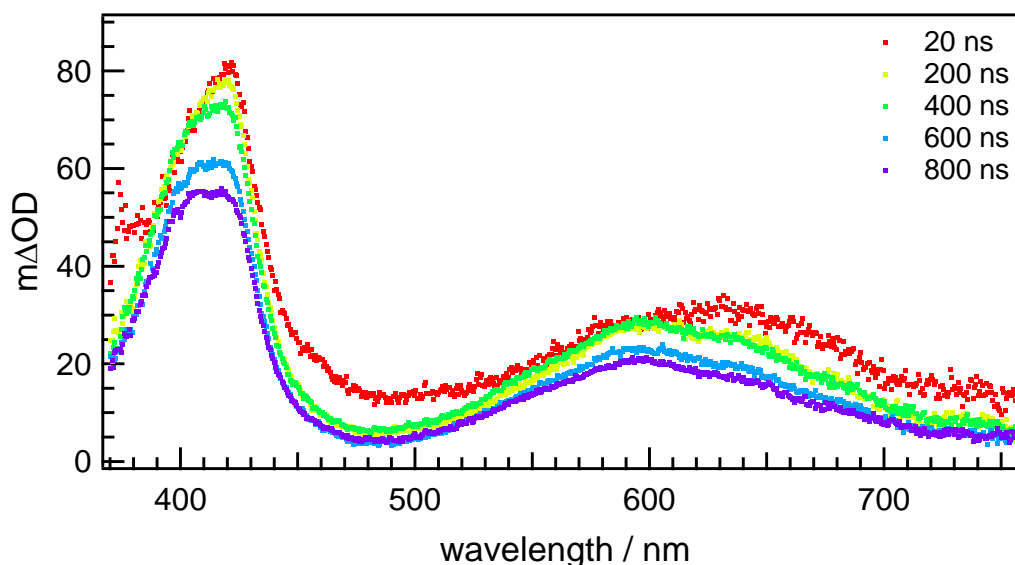


Figure S7. Time-resolved nanosecond absorption difference spectra for **Re-N** with 0.75 M BrPhOH in CH₃CN:H₂O 3:1 (1 atm N₂) acquired at room temperature after excitation at 355 nm with a 4 ns pulse and 3 mJ/pulse excitation.

Addition of 0.75 M BrPhOH to **Re-N** invokes a PCET reaction as illustrated in the TA spectra shown in Fig. S7. Upon irradiation, a positive and intense absorption in the 350-450 nm range appears within the laser pulse. Additionally, a broad absorption band in the range of 500-750 nm is assigned to a singly reduced, protonated 4,4'-bpy radical. This radical formation is a consequence of an ILET from 2,2'-bpy → 4,4'-bpy upon protonation of 4,4'-

bpy ($\Delta G = -0.49$ eV). The prompt positive absorption between 350-450 nm as well as 500-750 nm are similar to a previously observed singly reduced chromophore quencher complex $[(\text{CO})_3\text{Re}^{\text{II}}(\text{bpy})(\text{MQ}^*)]^{2+*}$ ($\text{MQ} = N\text{-methyl-4,4'-bipyridinium cation}$). It is noteworthy that the above mentioned transitions would be absent in the case of a pure PT reaction between ReN and 4-BrPhOH and their appearance here suggest that electron transfer is coupled to proton transfer. The observed transient features are well documented in the literature by the Meyer group.^{S7-S9} To further ensure that the the reaction pathway do not undergo a PT-ET, we aquired ReN emission with subsequent addition of trifluoroacetic acid (TFA) (fig S8). Upon each addition of TFA, a new weak emission band due to $[(\text{CO})_3\text{Re}^{\text{I}}(\text{bpy})(4,4'\text{-bpyH}^+)]^{2+}$, formed due to PT from TFA to ReN, becomes evident at ~ 30 mM TFA. This is similar to the feature observed earlier for the $[(\text{CO})_3\text{Re}^{\text{I}}(\text{bpy})(\text{MQ}^+)]^{2+}$ chromophore quencher assembly by Meyer and co-workers in ref S8. On the other hand, for the reaction of $[(\text{CO})_3\text{Re}^{\text{I}}(\text{bpy})(4,4'\text{-bpy})]^+$ and 2,6-F₂, no such feature due a PT is observed, ruling out a pure PT reaction mechanism.

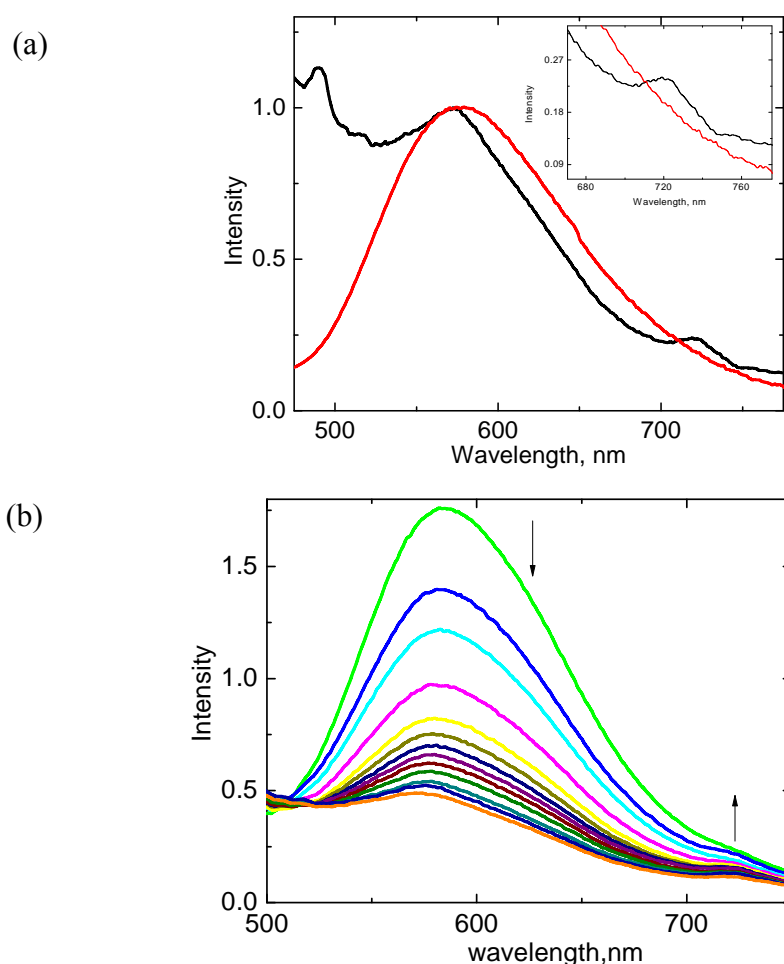


Figure S8. (a) Emission spectra of **ReN** with trifluoroacetic acid (black) [TFA] = 30.4 mM and **ReN** with 2,6-F₂ (red). Inset highlights the weak emission (b) Emission spectra of **ReN** with trifluoroacetic acid displaying conuinuous appearance of a weakly emissive band at 725 nm ([TFA] = 0 , 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.4, 4.8, 5.2, 6.4, 10.4, 30.4 mM). The data acquired in CH₃CN:H₂O 3:1 (1 atm N₂) acquired at room temperature after excitation at 400 nm. The arrow indicates trend in the spectral response.

In another piece of evidence to rule out a potential PT reaction pathway, we acquired an absorption decay trace of $[(\text{CO})_3\text{Re}^{\text{I}}(\text{bpy})(4,4'\text{-bpy})]^+$ and 2,6-F₂ obtained at 400 nm (fig S9). The prompt positive absorption at 400 nm is indicative of a reductive quenching of ReN complex by 2,6-F₂, (as described in the TA section) ruling out a PT product from this reaction.

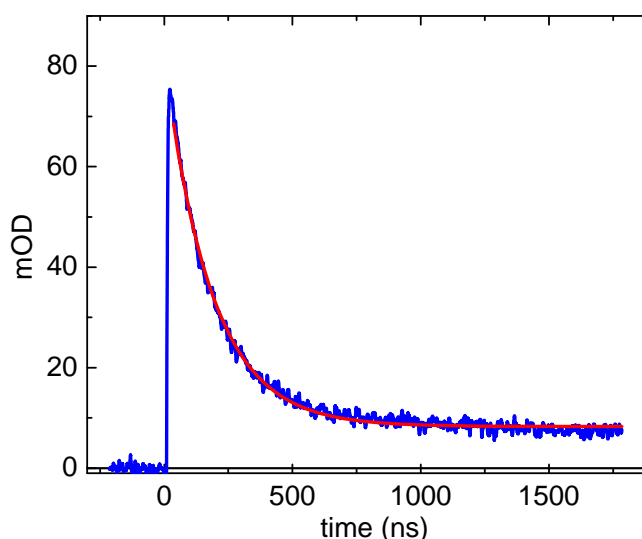


Figure S9. Absorption decay trace (blue) of **ReN** with 1.0 M of 2,6-F₂ in CH₃CN:H₂O 3:1 (1 atm N₂) acquired at room temperature after excitation at 355 nm along with the corresponding single exponential fit (red).

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