

Supporting information for:

# Kinetic Isotope Effects in Reductive Excited-State Quenching of Ru(2,2'-bipyrazine)<sub>3</sub><sup>2+</sup> by Phenols

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## Preparation of Ru(bpz)<sub>3</sub><sup>2+</sup>

[Ru(bpz)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was prepared from RuCl<sub>3</sub>·3H<sub>2</sub>O and 2,2'-bipyrazine following previously published protocols.<sup>1</sup> 2,2'-bipyrazine was synthesized from 2-chloropyrazine as described previously.<sup>2</sup>

## Preparation of deuterated phenols

Commercially available phenols were dissolved in methanol-d<sub>4</sub> (99.80 % D) and stirred for 1 hour at room temperature, under nitrogen atmosphere. The solvent was removed subsequently using a rotary evaporator, and the operation was repeated a second time. This procedure results in an isotope purity on the order of 99%, i. e., 1% of the phenol molecules remain un-deuterated.

The errors associated with the quenching rate constants ( $k_Q$  or  $k_{red}(H)$ ) and kinetic isotope effects (KIEs) are typically on the order of 4% to 8%.

## Experimental details regarding the spectroscopic investigations

Optical absorption spectra were measured on a Cary 300 instrument from Varian before and after the luminescence experiments in order to verify that no sample degradation had occurred during irradiation. By optical absorption spectroscopy we also ensured that there is no significant phenol absorption at the excitation wavelength (450 nm) used for the luminescence experiments.

CH<sub>3</sub>CN was distilled over P<sub>2</sub>O<sub>5</sub> prior to use in spectroscopic experiments. A referee pointed out to us that even the highest quality CH<sub>3</sub>CN usually contains concentrations of H<sub>2</sub>O on the order of 0.1 mM or higher.

Steady-state and time-resolved luminescence experiments were performed using a Fluorolog-3 instrument from Horiba Jobin-Yvon, equipped with a TBX-07C photomultiplier from Hamamatsu and a TCSPC option (Fluorohub FL-1061PC). Pulsed excitation occurred with a NanoLed-340 unit.

Transient absorption spectra and time-resolved luminescence was measured on an LP920-KS spectrometer from Edinburgh Instruments equipped with an iCCD from Andor. The excitation source was a Quantel Brilliant b laser equipped with an OPO from Opotek.

## Thermodynamic parameters for Ru(bpz)<sub>3</sub><sup>2+</sup> and the 6 phenols

**Table S1.** Electrochemical potentials ( $E$ ) for one-electron oxidation and  $pK_a$  values for the 6 phenol molecules and their radical cations as reported previously.<sup>3</sup> Electrochemical potentials are given in Volts vs. Fc<sup>+</sup>/Fc.

no.	R	$E(\text{R-PhOH}^+/\text{R-PhOH})^a$	$E(\text{R-PhO}\cdot/\text{R-PhO}^-)^b$	$pK_a(\text{R-PhOH})$ in DMSO <sup>b</sup>	$pK_a(\text{R-PhOH}^+)$ in DMSO <sup>b</sup>	$pK_a(\text{R-PhOH})$ in CH <sub>3</sub> CN <sup>c</sup>	$pK_a(\text{R-PhOH}^+)$ in CH <sub>3</sub> CN <sup>c</sup>
1	OCH <sub>3</sub>	1.05	-0.62	19.1	-5.6	31.0	6.8
2	CH <sub>3</sub>	1.16	-0.43	18.9	-4.0	30.8	8.4
3	Br	1.23	-0.19	16.4	-8.7	28.4	3.8
4	H	1.25	-0.33	18.0	-7.7	30.0	4.8
5	Cl	1.25	-0.23	16.8	-11	28.8	1.5
6	CN	1.40	0.15	13.2	-13	25.2	-0.4

<sup>a</sup> In acetonitrile. <sup>b</sup> In DMSO. <sup>c</sup> Calculated from the DMSO values using eq. 1.<sup>4</sup>

$$pK_a(\text{CH}_3\text{CN}) = 12.31 + 0.98 \cdot pK_a(\text{DMSO}) \quad (\text{eq. 1})$$

**Table S2.** Electrochemical potential ( $E_{red}$ ) for one-electron reduction of Ru(bpz)<sub>3</sub><sup>2+</sup> and  $pK_a$  values of the singly protonated forms of this complex as reported previously.<sup>5,6</sup> The electrochemical potentials are given in Volts vs. SCE. Conversion to Volts vs. Fc<sup>+</sup>/Fc occurred as described below.

	$E_{red}$	$pK_a$ in H <sub>2</sub> O	$pK_a$ in CH <sub>3</sub> CN <sup>d</sup>
[Ru(bpz) <sub>3</sub> ] <sup>2+</sup>	-0.71 <sup>a</sup>		
[Ru <sup>II</sup> (bpz) <sub>2</sub> (bpzH)] <sup>3+</sup>	0.05 <sup>a</sup>	-2.2	16.0
*[Ru <sup>II</sup> (bpz) <sub>2</sub> (bpzH)] <sup>3+</sup>		2.3 <sup>b</sup>	20.4
[Ru <sup>I</sup> (bpz) <sub>2</sub> (bpzH)] <sup>2+</sup>		7.1 <sup>c</sup>	25.1

<sup>a</sup> In acetonitrile.<sup>5c, 6</sup> <sup>b</sup> In the photoexcited <sup>3</sup>MLCT state. <sup>c</sup> For the one-electron reduced form. <sup>d</sup> Estimated values, see text below.

With respect to conversion of  $pK_a$  values determined for aqueous solution to  $pK_a$  values in CH<sub>3</sub>CN, there seem to be no systematic studies similar to the one cited above for conversion of  $pK_a$  values from DMSO to CH<sub>3</sub>CN.<sup>4</sup> There is definitely no literature available for this  $pK_a$ -conversion for the particular case of metal-2,2'-bipyrazine complexes. However, we note that for the 6 phenol molecules considered here (as well as for several other phenols),  $pK_a$  values were determined in DMSO and H<sub>2</sub>O. The experimental finding is that these  $pK_a$  values are between 3.7 and 8.0  $pK_a$  units higher in DMSO than in H<sub>2</sub>O.<sup>3b</sup>

Consequently, we are making the crude approximation (in analogy to eq. 1 and the procedure reported in ref. 4):

$$pK_a(\text{DMSO}) \approx pK_a(\text{H}_2\text{O}) + 6 \quad (\text{eq. 2})$$

The large discrepancy between  $pK_a$  values in DMSO and  $\text{H}_2\text{O}$  stems from large differences in the solvation energy of  $\text{H}^+$  in the two different solvents. Equation 2 is used to convert the  $pK_a$  values from the third column in Table S2 to  $pK_a$  values in DMSO. The resulting  $pK_a$  values for DMSO solution are then converted to  $pK_a$  values for  $\text{CH}_3\text{CN}$  using equation 1. This procedure yields the  $pK_a$  values reported in the last column of Table S2. This course of action is cumbersome and it can obviously yield only very crude estimates (there is no such clear and experimentally well documented correlation between  $pK_a(\text{DMSO})$  and  $pK_a(\text{H}_2\text{O})$  as in the case of  $pK_a(\text{CH}_3\text{CN})$  and  $pK_a(\text{DMSO})$ ), but in our opinion it is the best that can be done with the available experimental data.

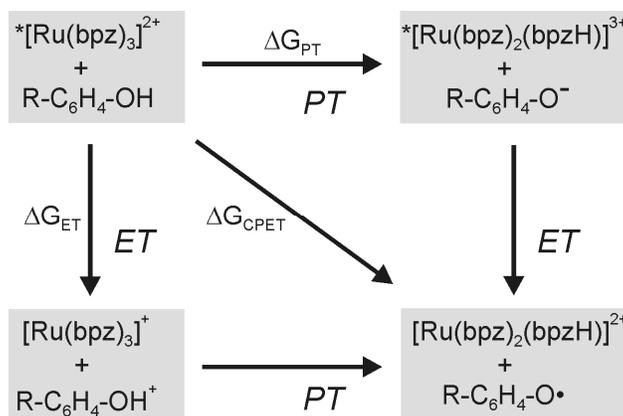
The electrochemical potential ( $E_{red}^*$ , 2<sup>nd</sup> column in Table S2) for one-electron reduction of photoexcited  $\text{Ru}(\text{bpz})_3^{2+}$  is calculated using the approximation<sup>7</sup>

$$E_{red}^* = E_{red} + E_{00} \quad (\text{eq. 3})$$

where  $E_{00}$  is the energy of the emissive  $^3\text{MLCT}$  state (2.01 eV).<sup>8</sup> This procedure yields  $E_{red}^* = 1.30$  V vs. SCE (in  $\text{CH}_3\text{CN}$ ). Conversion to V vs.  $\text{Fc}^+/\text{Fc}$  is possible through subtraction of 0.38 V,<sup>9</sup> yielding  $E_{red}^* = 0.92$  V vs.  $\text{Fc}^+/\text{Fc}$  in  $\text{CH}_3\text{CN}$ .

## Rough estimation of $\Delta G_{ET}$ , $\Delta G_{PT}$ , and $\Delta G_{CPET}$ for the 6 phenol / $\text{Ru}(\text{bpz})_3^{2+}$ couples

Photoexcited  $\text{Ru}(\text{bpz})_3^{2+}$ , abbreviated below as  $^*\text{Ru}(\text{bpz})_3^{2+}$ , and phenol molecules, abbreviated below as  $\text{R-C}_6\text{H}_4\text{-OH}$ , may exhibit PCET chemistry following three different reaction pathways as illustrated in Scheme S1: (i) proton transfer followed by electron transfer (PT, ET sequence) along the upper right corner of Scheme S1; (ii) electron transfer followed by proton transfer (ET, PT sequence) along the lower left corner of Scheme S1; (iii) concerted proton-electron transfer (CPET) along the diagonal of Scheme S1.



**Scheme S1.** PCET reaction pathways.

In the following we make an attempt to obtain at least rough estimates for the  $\Delta G_{ET}$ ,  $\Delta G_{PT}$ , and  $\Delta G_{CPET}$  values (reaction free energies) from Scheme S1 using the thermodynamic data summarized in Table S1 and Table S2. The phenol  $\text{pK}_a$  values were originally determined for DMSO solution (4<sup>th</sup> and 5<sup>th</sup> columns in Table S1),<sup>3b, c</sup> but these values can be converted to  $\text{pK}_a$  values in  $\text{CH}_3\text{CN}$  using the procedure described in reference 4 (6<sup>th</sup> and 7<sup>th</sup> column in Table S1). As seen from Table S1, the  $\text{pK}_a$  value of a given phenol differs by roughly 12  $\text{pK}_a$  units between DMSO and  $\text{CH}_3\text{CN}$ .

Unfortunately, there seems to be no analogous procedure for conversion of  $\text{pK}_a$  values determined in  $\text{H}_2\text{O}$  to  $\text{pK}_a$  values in  $\text{CH}_3\text{CN}$ , hence we applied the somewhat cumbersome procedure described on page S4 to obtain crude estimates for the  $\text{pK}_a$  values of the ruthenium complex in  $\text{CH}_3\text{CN}$  (4<sup>th</sup> column of Table S2). Large error bars are therefore associated with our subsequent driving-force estimates.

The driving-force for the first step of the ET, PT sequence ( $\Delta G_{ET}$ ) was calculated using the expression:<sup>7, 10</sup>

$$\Delta G_{ET} = -e \cdot [E_{red} - E(\text{R-PhOH}^+/\text{R-PhOH})] \quad (\text{eq. 4})$$

with  $E_{red}$  and  $E(\text{R-PhOH}^+/\text{R-PhOH})$  as defined in the captions to Tables S1 and S2.  $e$  is the elemental charge.

The driving-force for the first step of the PT, ET sequence ( $\Delta G_{PT}$ ) was calculated using the expression:<sup>11</sup>

$$\Delta G_{PT} = 0.059 \text{ eV} \cdot \{pK_a(\text{R-PhOH}) - pK_a([\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+})\} \quad (\text{eq. 5})$$

with  $pK_a(\text{R-PhOH})$  and  $pK_a([\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+})$  as defined in Tables S1 and S2 ( $\text{CH}_3\text{CN}$  values, i. e., 6<sup>th</sup> column of Table S1 for  $pK_a(\text{R-PhOH})$  and last column of Table S2 for  $pK_a([\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+})$ ). Equation 5 implies that protonation of the ruthenium complexes produces  $[\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+}$  in its <sup>3</sup>MLCT excited state. It is also conceivable that protonation is accompanied by electronic relaxation of the photoexcited metal complex to its ground state. The driving-force for this reaction can be estimated using the expression:

$$\Delta G_{PT}^{el. \text{ relax.}} = 0.059 \text{ eV} \cdot \{pK_a(\text{R-PhOH}) - pK_a([\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+})\} - E_{00}' \quad (\text{eq. 6})$$

with  $E_{00}'$  being the energy of the long-lived <sup>3</sup>MLCT excited state of  $[\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+}$  (= photoexcited and protonated  $\text{Ru}(\text{bpz})_3^{2+}$ ). A prior study reports  $E_{00}' = 1.51 \text{ eV}$ .<sup>8</sup>

The driving-force for concerted proton-electron transfer along the diagonal of Scheme S1 ( $\Delta G_{CPET}$ ) was calculated using the expression:<sup>11</sup>

$$\Delta G_{CPET} = -e \cdot [E_{red} - E(\text{R-PhOH}/\text{R-PhOH}^+)] + 0.059 \text{ eV} \cdot \{pK_a(\text{R-PhOH}^+) - pK_a([\text{Ru}^{\text{I}}(\text{bpz})_2(\text{bpzH})]^{2+})\} \quad (\text{eq. 7})$$

with  $E_{red}$ ,  $E(\text{R-PhOH}/\text{R-PhOH}^+)$ ,  $pK_a(\text{R-PhOH}^+)$  and  $pK_a([\text{Ru}^{\text{I}}(\text{bpz})_2(\text{bpzH})]^{2+})$  as defined in Tables S1 and S2.  $e$  is the elemental charge ( $\text{CH}_3\text{CN}$  values, 6<sup>th</sup> column of Table S1 for  $pK_a(\text{R-PhOH})$  and last column of Table S2 for  $pK_a([\text{Ru}^{\text{II}}(\text{bpz})_2(\text{bpzH})]^{3+})$ ).

Based on the mathematical expressions in eqs. 4 – 7, the redox potentials and  $pK_a$  values from Table S1 and Table S2, the following rough estimates for  $\Delta G_{ET}$ ,  $\Delta G_{PT}$ ,  $\Delta G_{PT}^{el. relax.}$ ,  $\Delta G_{CPET}$  are obtained:

**Table S3.** Driving-forces for elementary reaction steps between phenols and photoexcited  $Ru(bpz)_3^{2+}$ .

no.	R-PhOH / * $Ru(bpz)_3^{2+}$	$\Delta G_{ET}$	$\Delta G_{PT}$	$\Delta G_{PT}^{el. relax.}$ <sup>b</sup>	$\Delta G_{CPET}$ <sup>a</sup>
1	OCH <sub>3</sub>	0.13	1.69	0.18	-0.06
2	CH <sub>3</sub>	0.24	1.68	0.17	0.15
3	Br	0.31	1.54	0.03	-0.05
4	H	0.33	1.63	0.12	0.02
5	Cl	0.33	1.56	0.05	-0.17
6	CN	0.48	1.35	-0.16	-0.13

<sup>a</sup> Calculated using eq. 7 as described on page S6. <sup>b</sup> Calculated following the procedure described on page S9.

$\Delta G_{ET}$  values are accurate to  $\pm 0.1$  eV while  $\Delta G_{CPET}$  values are accurate to  $\pm 0.6$  eV. We estimate that our  $\Delta G_{PT}$  values are accurate to  $\pm 0.5$  eV. These error estimates are based on the following arguments:

$\Delta G_{ET}$ : Eq. 4 is commonly considered to be accurate to  $\pm 0.1$  eV.<sup>7</sup>

$\Delta G_{PT}$ : The main error in eq. 5 stems from the approximations made with equations 1 and 2, i. e., from the conversion of  $pK_a$  values measured in DMSO or H<sub>2</sub>O to  $pK_a$  values in CH<sub>3</sub>CN. Our  $pK_a$  estimates are presumably no more accurate than  $\pm 5$   $pK_a$  units. This translates into an uncertainty of 0.5 eV for  $\Delta G_{PT}$ .

$\Delta G_{PT}^{el. relax.}$ : The same arguments as for  $\Delta G_{PT}$  apply.

$\Delta G_{CPET}$ : There is an uncertainty on the order of 0.5 eV for the proton transfer component to CPET (see comments made above regarding the accuracy of  $\Delta G_{PT}$ ). Together with an uncertainty on the order of 0.1 eV for the electron transfer component (see comments made above regarding the accuracy of  $\Delta G_{ET}$ ), on overall uncertainty of  $\sim 0.6$  eV results for  $\Delta G_{CPET}$ .

The key observations from Table S3 are the following:

$\Delta G_{ET}$  increases with increasing electron-withdrawing nature of the phenol R-substituent.

$\Delta G_{PT}$  is calculated to be strongly endergonic in all cases. Even the large uncertainty of 0.5 eV permits the qualitative conclusion that proton transfer between phenols and photoexcited  $\text{Ru}(\text{bpz})_3^{2+}$  leading to deprotonated phenols and photoexcited  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  is thermodynamically unfavorable in all cases.

$\Delta G_{PT}^{el. relax}$  ranges from weakly endergonic to weakly exergonic among the 6 reaction couples considered here. Given the large error bars associated with these estimates ( $\pm 0.5$  eV), initial proton transfer involving relaxation of the protonated ruthenium complex to the electronic ground state cannot be excluded based on thermodynamic grounds. Further comments regarding excited-state deactivation by a PT, ET mechanism are made on page S9.

$\Delta G_{CPET}$  ranges from weakly endergonic to weakly exergonic. The error bars associated with our  $\Delta G_{CPET}$  estimates are larger than the variations in  $\Delta G_{CPET}$  among the 6 phenol –  $\text{Ru}(\text{bpz})_3^{2+}$  couples investigated here.

## Comments on excited-state deactivation by proton transfer involving electronic relaxation of the $\text{Ru}(\text{bpz})_3^{2+}$ complex

Our transient absorption spectra (page S12, Figure S1) provide clear evidence for the formation of  $\text{Ru}(\text{bpz})_3^+$ , i. e., a reduced ruthenium species. Consequently, if proton transfer involving relaxation of the photoexcited  $\text{Ru}(\text{bpz})_3^{2+}$  complex to the ground state (characterized by  $\Delta G_{\text{PT}}^{\text{el. relax}}$  in eq. 6) is the rate-determining excited-state deactivation process, this must be followed by subsequent electron transfer between deprotonated phenols ( $\text{R-PhO}^-$ ) and  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  (= protonated  $\text{Ru}(\text{bpz})_3^{2+}$  in the electronic ground state). Using eq. 8 we estimate the driving-force for this subsequent electron transfer step:

$$\Delta G_{\text{ET after PT}} = -e \cdot [E([\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}/[\text{Ru}(\text{bpz})_2(\text{bpz})]^{2+}) - E(\text{R-PhO}^-/\text{R-PhO}^-)] \quad (\text{eq. 8})$$

The electrochemical potentials for oxidation of the various phenolate anions to phenoxy radicals are given in the 4<sup>th</sup> column of Table S1 and range from -0.62 V for 4-methoxyphenol to +0.15 V vs.  $\text{Fc}^+/\text{Fc}$  for 4-cyanophenol. The respective reduction potentials were determined for DMSO solution, and in absence of analogous data for  $\text{CH}_3\text{CN}$  solution were used for our  $\Delta G_{\text{ET after PT}}$  estimates with eq. 8. The electrochemical potential for one-electron reduction of protonated  $\text{Ru}(\text{bpz})_3^{2+}$  ( $= [\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$ ) in the electronic ground state is 0.05 V vs. SCE in  $\text{CH}_3\text{CN}$  (Table S2),<sup>6</sup> corresponding to -0.33 V vs.  $\text{Fc}^+/\text{Fc}$ .

Based on these redox potential values, our estimates for  $\Delta G_{\text{ET after PT}}$  range from -0.29 eV for the 4-methoxyphenolate /  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  couple to +0.48 eV for the 4-cyanophenolate /  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  pair (Table S4).

**Table S4.** Driving-forces for electron transfer between phenolate anions and  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  in the electronic ground state.

no.	$\text{R-PhO}^- / [\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$	$\Delta G_{\text{ET after PT}}$
1	$\text{OCH}_3$	-0.29
2	$\text{CH}_3$	-0.10
3	Br	+0.14
4	H	0.00
5	Cl	+0.10
6	CN	+0.48

At least for the 4-cyanophenolate /  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  couple a  $\text{PT}_{\text{relax}}$ -ET sequence (with the  $\text{PT}_{\text{relax}}$  step involving electronic relaxation of the ruthenium complex to the ground state) seems incompatible with the experimental observation of photoreduced ruthenium: The estimated driving-force of the ground-state ET step which is expected to occur as part of this reaction sequence is too strongly exergonic – even in view of the error bars associated with calculation of  $\Delta G_{\text{ET after PT}} (\pm 0.1 \text{ eV})$ .

For all other phenolate /  $[\text{Ru}(\text{bpz})_2(\text{bpzH})]^{3+}$  couples  $\Delta G_{\text{ET after PT}}$  is either weakly exergonic or weakly endergonic. Therefore, based on thermodynamic arguments, one cannot definitely rule out the possibility of the abovementioned  $\text{PT}_{\text{relax}}$ -ET sequence.

Several photoacids, e. g. naphthol molecules, are known to undergo proton transfer with simultaneous relaxation to the electronic ground state. In this light the  $\text{PT}_{\text{relax}}$ -ET sequence discussed above does indeed make sense. On the other hand, photoexcitation of naphthol photoacids usually involves co-excitation of O-H vibrational modes, hence proton release and electronic relaxation are perhaps more intimately coupled in this case than in our samples. In our study, it is the proton *acceptor* that is excited selectively while the phenol proton donors remain in their electronic ground states.

## Comments on $\text{Ru}(\text{bpz})_3^{2+}$ excited-state deactivation by triplet-triplet energy transfer

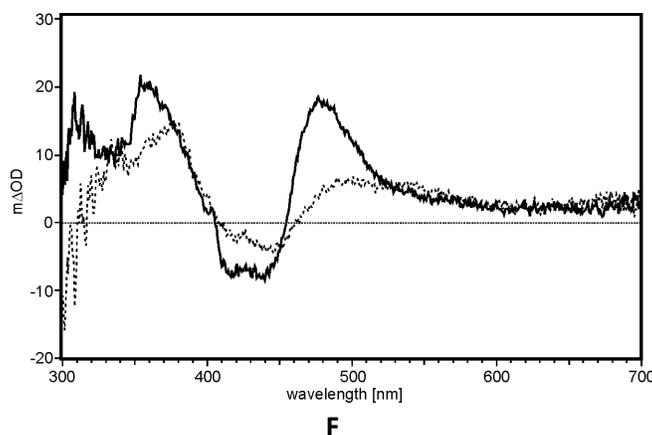
To the best of our knowledge, unsubstituted phenol is the only molecule among the 6 phenols investigated here for which the energy of the lowest triplet excited state ( $E_T$ ) is known. According to ref. 12, phenol has  $E_T = 3.55$  eV, hence triplet-triplet energy transfer from the lowest  $^3\text{MLCT}$  state of  $\text{Ru}(\text{bpz})_3^{2+}$  ( $E_{00} = 2.18$  eV)<sup>5a, 5c, 13</sup> is thermodynamically uphill by 1.37 eV.

Scaiano and Das explored the photochemistry of carbonyl triplet excited states with various 4-substituted phenols, among them the 5 *para*-substituted phenol molecules ( $R = \text{OCH}_3, \text{CH}_3, \text{Br}, \text{Cl}, \text{CN}$ ) used in our study.<sup>12, 14</sup> An important conclusion from the work by Scaiano and Das is that the lowest triplet state of benzophenone ( $E_T = 3.05$  eV) reacts with these 4-substituted phenols via hydrogen atom transfer at quantum yields near unity.<sup>12, 14</sup> In other words, triplet-triplet energy transfer from benzophenone to the phenols is extremely inefficient, suggesting that their triplet energies are well above 3.05 eV. This would make triplet-triplet energy transfer from photoexcited  $\text{Ru}(\text{bpz})_3^{2+}$  ( $E_{00} = 2.18$  eV)<sup>5a, 5c, 13</sup> thermodynamically uphill by at least 0.87 eV in all cases.

These thermodynamic considerations suggest that triplet-triplet energy transfer is an inefficient  $\text{Ru}(\text{bpz})_3^{2+}$  excited-state deactivation process. The transient absorption data presented below support this notion.

## Transient absorption data

Figure S1 shows the transient absorption spectra obtained from (i) a  $2.3 \cdot 10^{-5}$  M solution of  $\text{Ru}(\text{bpz})_3^{2+}$  in dry  $\text{CH}_3\text{CN}$  (dashed trace) at  $25^\circ\text{C}$ ; (ii) the same solution after addition of 4-methylphenol (concentration of  $\text{CH}_3\text{-PhOH}$ : 0.25 M) (solid trace). The excitation wavelength was 450 nm, detection occurred in a time window of 200 ns width, starting immediately after the excitation pulse (pulse width:  $\sim 8$  ns).



**Figure S1.** Transient absorption spectra.

The transient absorption spectrum obtained for the  $\text{Ru}(\text{bpz})_3^{2+} / \text{CH}_3\text{-PhOH}$  mixture bears great resemblance to the absorption spectrum of photoreduced  $\text{Ru}(\text{bpz})_3^+$  as reported in ref. 5a. From this we conclude that the  $^3\text{MLCT}$  excited state of  $\text{Ru}(\text{bpz})_3^{2+}$  is indeed quenched reductively rather than by triplet-triplet energy transfer. Similar transient absorption spectra can be obtained for the other phenols used in our study.

The spectral shifts associated with protonation of the photoreduced  $\text{Ru}(\text{bpz})_3^+$  species are minor, hence clear distinction between electron transfer and PCET products based on transient absorption spectroscopy is difficult. Transient EPR spectroscopy would be more useful in this context.<sup>15</sup>

Prior transient absorption spectroscopy studies of  $\text{Ru}(\text{bpz})_3^{2+}$  and related protonatable ruthenium complexes succeeded in determining  $\text{pK}_a$  values for the reduced  $\text{Ru}(\text{bpz})_3^+$  species by monitoring changes in optical density at a given wavelength as a function of solution pH. Pulse radiolytically generated  $\text{CO}_2^{\cdot -}$  was used as a reductant for these purposes. This method has the great advantage that absorption of the oxidation product does not interfere with absorption of the ruthenium reduction product. A similarly favorable scenario is unfortunately not encountered for our phenol /  $\text{Ru}(\text{bpz})_3^{2+}$  couples. In spite of significant efforts (recognizing the importance of detecting PCET photoproducts!) we were so far unable to clearly and unambiguously identify the (transient) absorption spectrum of protonated and reduced ruthenium complex in the simultaneous presence of oxidation products associated with the various phenols used in our investigations.

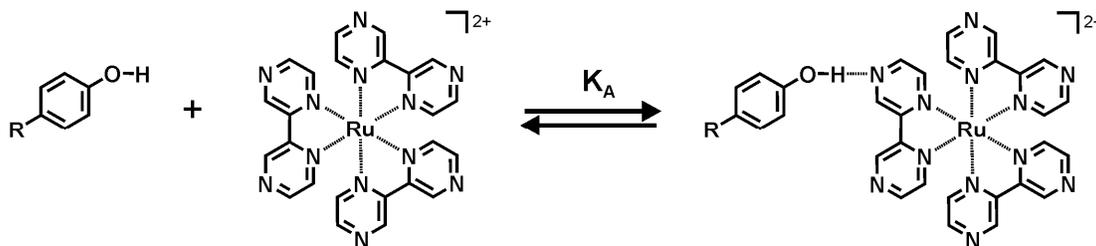
This unresolved issue remains of interest for future studies of thermal electron and proton transfer reactions occurring between the individual PCET photoproducts (leading back to the initially presented starting materials before photoexcitation), but this aspect is beyond the scope of the current article.

Our transient absorption spectra provide clear evidence for an electron transfer event – the spectral signature of the reduced ruthenium complex can be identified unambiguously. In other words, we truly observe reductive excited-state quenching as stated in the title of our article – and not triplet-triplet energy transfer or only proton transfer.

Our evidence for proton transfer is indirect and comes from the magnitudes of the KIEs, many of which cannot be reconciled with pure electron transfer in the rate-determining reaction step. The chemical similarity of our phenol / Ru(bpz)<sub>3</sub><sup>2+</sup> couples relative to Meyer's 1,4-dihydroquinone / Ru(bpy)<sub>2</sub>(bpz)<sup>2+</sup> system for which PCET products could be identified by transient EPR spectroscopy also supports our conclusion that reductive excited-state quenching in our systems is in fact coupled to proton transfer.<sup>15</sup>

## Adduct formation and association constants

In analogy to the study by Meyer and coworkers on the Ru(bpy)<sub>2</sub>(bpz)<sup>2+</sup> / 1,4-dihydroxybenzene reaction couple,<sup>15a</sup> we assume that prior to electron transfer or CPET, photoexcited Ru(bpz)<sub>3</sub><sup>2+</sup> and phenols form weakly hydrogen-bonded encounter complexes or adducts (Scheme S2).



**Scheme S2.** Formation of weakly hydrogen-bonded encounter adducts.

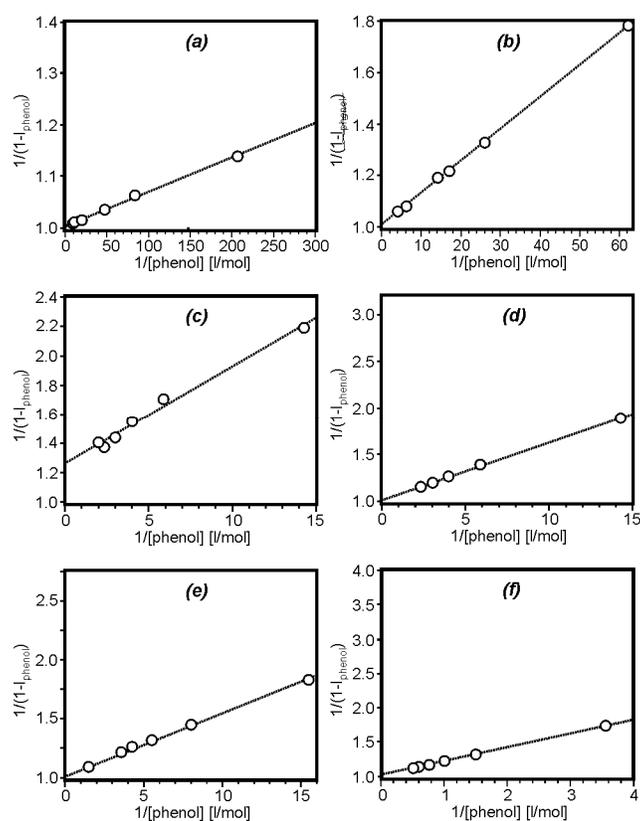
Meyer and coworkers previously developed a mathematical expression for estimating the association constants ( $K_A$ ) of such adducts based on the integrated luminescence intensity emitted by the metal complex in presence of variable amounts of quencher (see supporting information of ref. 12a). Here, we merely give the final result of their detailed mathematical derivation:<sup>15a</sup>

$$\frac{1}{I_0 - I_{phenol}} = \frac{1}{(I_0 - I_{phenol}) \cdot K_A} \cdot \frac{1}{[phenol]} + \frac{1}{(I_0 - I_{phenol})} \quad (\text{eq. 4})$$

In eq. 4,  $I_0$  is the  $\text{Ru}(\text{bpz})_3^{2+}$  emission intensity in absence of quencher,  $I_{\text{phenol}}$  the emission intensity in presence of quencher, and  $[\text{phenol}]$  is the concentration of phenol in mol/l. When normalizing  $I_0$  to a value of 1.0, plots of  $1/(1-I_{\text{phenol}})$  versus  $1/[\text{phenol}]$  are expected to give straight lines that can be fitted by linear regression. The association constants ( $K_A$ ) are obtained by dividing the intercepts from these fits through the respective slopes.

Figure S2 shows plots of  $1/(1-I_{\text{phenol}})$  versus  $1/[\text{phenol}]$  for our 6 phenol /  $\text{Ru}(\text{bpz})_3^{2+}$  couples. The resulting  $K_A$  values are summarized in Table 2 of the paper.

We found that the data quality obtained for R-PhOH /  $\text{Ru}(\text{bpz})_3^{2+}$  couples is better suited for determination of the association constants than those of the R-PhOD /  $\text{Ru}(\text{bpz})_3^{2+}$  couples. Consequently, Figure S2 shows data obtained from non-deuterated samples only.



**Figure S2.** Graphical determination of  $K_A$  for our R-PhOH /  $\text{Ru}(\text{bpz})_3^{2+}$  couples.<sup>15a</sup>  
 (a) R = OCH<sub>3</sub>, (b) R = CH<sub>3</sub>, (c) R = Br, (d) R = H, (e) R = Cl, (f) R = CN.

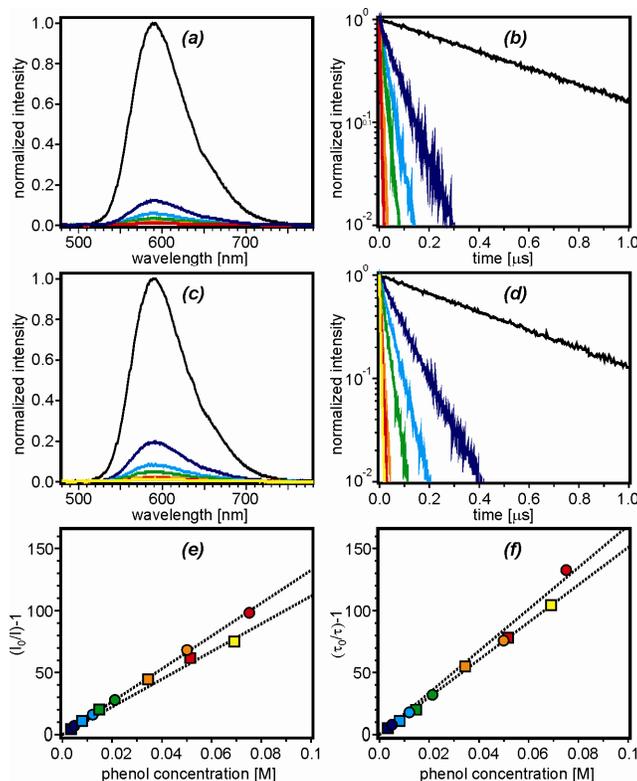
## Luminescence quenching data for 5 phenol / Ru(bpz)<sub>3</sub><sup>2+</sup> couples

In the following we present a series of five figures which are analogous to Figure 1 of the paper. These figures show (a) Ru(bpz)<sub>3</sub><sup>2+</sup> luminescence spectra in presence of increasing amounts of R-PhOH; (b) Ru(bpz)<sub>3</sub><sup>2+</sup> luminescence decays in presence of increasing amounts of R-PhOH; (c) Ru(bpz)<sub>3</sub><sup>2+</sup> luminescence spectra in presence of increasing amounts of R-PhOD; (d) Ru(bpz)<sub>3</sub><sup>2+</sup> luminescence decays in presence of increasing amounts of R-PhOD; (e) Stern-Volmer plots based on luminescence intensity data (circles: R-PHOH; squares: R-PhOD); (f) Stern-Volmer plots based on luminescence decay data (circles: R-PHOH; squares: R-PhOD).

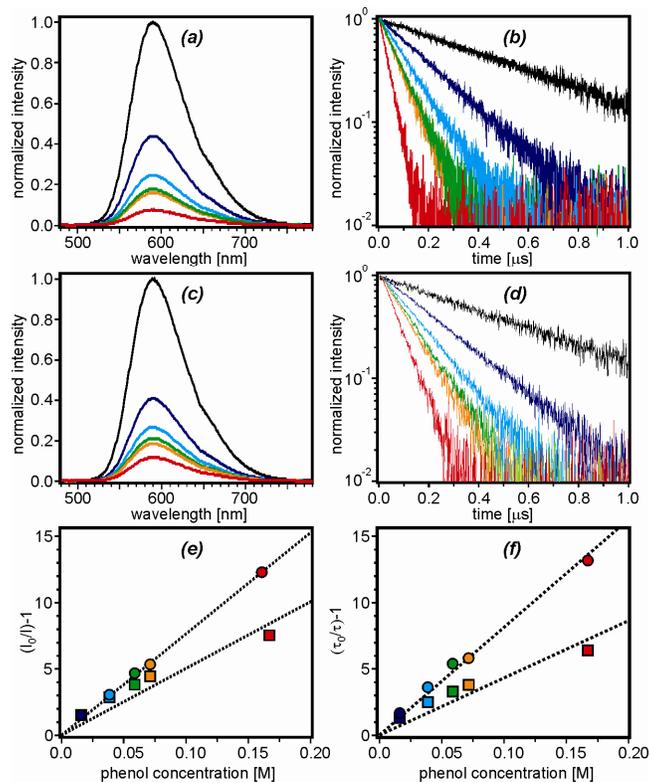
The solvent was dry CH<sub>3</sub>CN in each case, excitation occurred at 450 nm for measurement of the luminescence spectra and at 342 nm for measurement of the luminescence decay. Detection in the decay measurements occurred at 610 nm.

Bimolecular excited-state quenching rate constants ( $k_Q$ ) extracted from the Stern-Volmer plots are summarized in Table 1 of the paper.

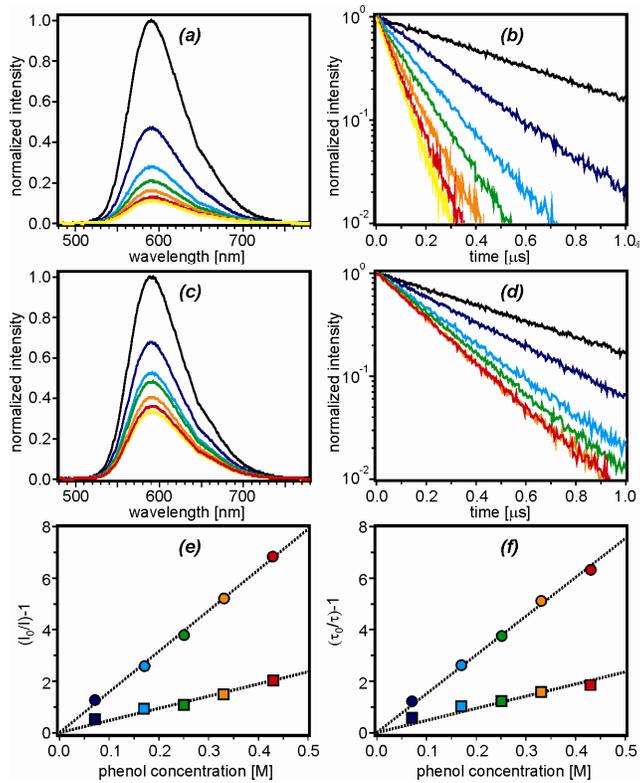
A general observation that is made in our data is that the Stern-Volmer fits are significantly better for ordinary phenols than for their deuterated analogues. This presumably reflects incomplete deuteration.



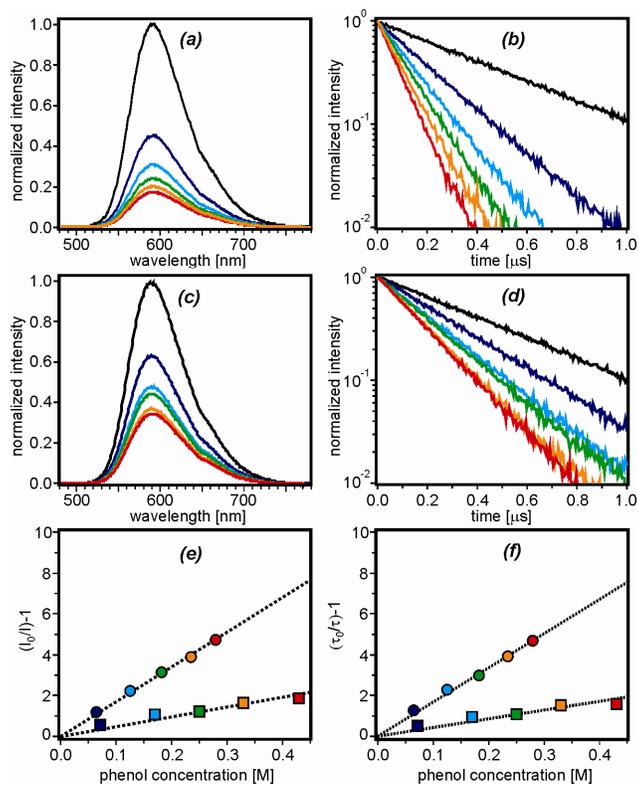
**Figure S3.** Luminescence quenching data for CH<sub>3</sub>O-PhOH / CH<sub>3</sub>O-PhOD.



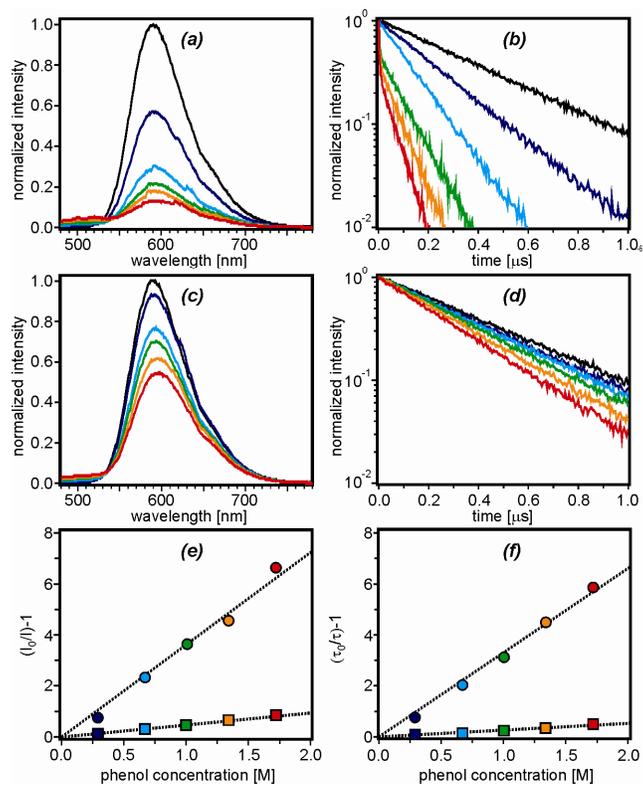
**Figure S4.** Luminescence quenching data for  $\text{CH}_3\text{-PhOH}$  /  $\text{CH}_3\text{-PhOD}$ .



**Figure S5.** Luminescence quenching data for H-PhOH / H-PhOD.



**Figure S6.** Luminescence quenching data for Cl-PhOH / Cl-PhOD.



**Figure S7.** Luminescence quenching data for CN-PhOH / CN-PhOD.

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