Supporting Information:
The importance of finite temperature and vibrational sampling in the absorption spectrum of a nitro-functionalized Ru(II) water oxidation catalyst

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S1 Excited state characterization with TheoDORE

The excited state characters were determined with the TheoDORE$^{S1-S3}$ program package, based on a charge transfer (CT) analysis of the one electron transition density matrix. This allows for a quantitative analysis of the excited states and, being automatized, is especially useful for analyzing the characters in the spectra computed from an ensemble of geometries like in the Wigner spectra. The starting point of the CT analysis is a partitioning of the one electron transition density matrix between the ground state and an excited state among predefined molecular fragments (A, B, ...).$^{S2,S3}$ The Ru-complexes were divided into the
Figure S1: Fragmentation of Ru-complexes for CT analysis with TheoDORE. (a) Four fragments of Ru(dppip-NO$_2$): 1. Ru, 2. dppi, 3. pic, 4. nitrophenyl (ph-NO$_2$); (b) three fragments of Ru(dpp): 1. Ru, 2. dpp, 3. pic. (c) Matrix plot of CT numbers $\Omega_{AB}$ showing the excitation hole on the vertical axis and the excited electron on the horizontal axis.
fragments shown in Fig. S1a–b based on a hierarchical clustering\textsuperscript{S4} ansatz; Ru(dppip-NO\textsubscript{2}) is divided in four fragments (1 is the Ru atom, 2 the dppi fragment, 3 the nitrophenyl fragment and 4 the pic ligands) and Ru(dpp) in three (Ru, dpp ligand, and pic ligands). A Löwdin-type population analysis scheme was used to yield the CT numbers $\Omega_{AB}$ for a particular excited state, which can be visualized in the form of a matrix plot or so-called electron–hole correlation plot (Fig. S1c).\textsuperscript{S2,S4} Here, the diagonal elements $\Omega_{AA}$ correspond to local excitations (on fragment A), whereas off-diagonal elements $\Omega_{AB}$ $A \neq B$ correspond to CT contributions to the excited state character.\textsuperscript{S2,S4} Figure S1c shows an example plot of the $4 \times 4$ $\Omega$-matrix of Ru(dppip-NO\textsubscript{2}), where the excitation hole coordinate is plotted along the vertical axis and the excited electron coordinate along the horizontal axis. Different excited state characters are indicated in the figure: Ru $\rightarrow$ dpdi and Ru $\rightarrow$ nitrophenyl metal-to-ligand charge transfer (MLCT) excitations are shown in blue, dpdi $\rightarrow$ dpdi ligand-centered (LC) and dpdi $\rightarrow$ nitrophenyl ligand-to-ligand charge transfer (LLCT) excitations in red, nitrophenyl $\rightarrow$ dpdi LLCT and nitrophenyl $\rightarrow$ nitrophenyl LC excitations in green, excitations from/to the axial pic ligands in gray, and metal-centered (MC) Ru d–d and ligands $\rightarrow$ Ru ligand-to-metal charge transfer (LMCT) excitations in violet. This color scheme is used below and in the main paper in the discussion of the absorption spectra of the Ru-complexes.

The relative character ($char_x$) of the vis absorption band was determined by summing over all states $i$ within the respective energy range and weighting them by their oscillator strength ($f_{osc}$) according to

$$char_x = \frac{\sum_{i \in \text{vis band}} \text{char}_x(i) \cdot f_{osc}(i)}{\sum_{i \in \text{vis band}} f_{osc}(i)} \quad (1)$$

such that all characters $x$ ($x = \text{Ru} \rightarrow \text{dpdi MLCT}, \text{Ru} \rightarrow \text{nitrophenyl MLCT}, \text{dpdi LC}, \text{dpdi} \rightarrow \text{nitrophenyl LLCT}, \text{nitrophenyl} \rightarrow \text{dpdi LLCT}, \text{nitrophenyl LC}, \text{transitions from/to pic}, \text{Ru MC and ligands} \rightarrow \text{Ru LMCT}$) sum up to 100% ($\sum_x char_x = 1$).
For comparison to the B3LYP spectra presented in the main paper, we additionally report here TD-DFT calculations using the range-separated CAM-B3LYP\textsuperscript{S5} functional. The B3LYP and CAM-B3LYP excitation energies are shown in Fig. S2, where the bright states are highlighted and labeled. We performed state overlap calculations with WFoverlap\textsuperscript{S6} to compare the nature of the B3LYP and CAM-B3LYP excited states. The black lines connecting the bright states in Fig. S2 indicate the overlap between the respective excited states. It can be seen that CAM-B3LYP generally predicts higher excitation energies than B3LYP.

Figure S2: Comparison of B3LYP excitation energies with CAM-B3LYP results. States with a high oscillator strength are highlighted, while dark states are shown as dotted lines. The correlation of the bright B3LYP and CAM-B3LYP states is shown by the black lines, where the line width corresponds to the overlap of the excited states. (a) 2H-Ru(dppip-NO\textsubscript{2}), (b) 1H-Ru(dppip-NO\textsubscript{2}), (c) 0H-Ru(dppip-NO\textsubscript{2}).

Thus, a blue shift of the CAM-B3LYP spectra is observed compared to the experiments, which can be seen in Fig. S3. The main band character, represented by the pie charts in Fig. S3 on the right, is similar to that of the B3LYP spectra: the intense band is dominated by Ru → dpdi MLCT and dpdi → dppip-NO\textsubscript{2} LC/LLCT excitations. CAM-B3LYP predicts a higher contribution of excitations to dpdi, whereas the importance of excitations to ph-NO\textsubscript{2} decreases to some extent compared to the B3LYP equilibrium spectra. Besides the similar characters of the underlying excited states, both B3LYP and CAM-B3LYP predict a red shift of the absorption band with decreasing degree of protonation of the dppip-NO\textsubscript{2} ligand. This red shift also agrees with the experimental observation\textsuperscript{S7} of a higher intensity at longer wavelengths with increasing pH. Due to the better agreement of the B3LYP spectra with
Figure S3: CAM-B3LYP absorption spectra of 0H,1H,2H-Ru(dppip-NO\textsubscript{2}) based on the equilibrium (eq.) structures (blue lines). The computed spectra are compared to the experimental (exp.) spectra (dotted lines, adapted from Ref. S7) of Ru(dppip-NO\textsubscript{2}) in Britton-Robinson buffer/MeCN at a pH of 1.95 (Ru-2H) and of 12.15 (Ru-1H, Ru-0H). The corresponding \( f_{\text{osc}} \)-weighted average band characters according to eqn (1) are shown on the right; the energy range of the band is shown above the pie charts.

the experiments, which was also observed previously for other Ru-complexes,\textsuperscript{S8–S11} we chose B3LYP for the spectra in the main paper. In addition, for illustrative purposes, we compare here the experimental pH-dependent spectra (adapted from Ref. S7) with the B3LYP and CAM-B3LYP pH-dependent spectra in Fig. S4. For the latter, we considered the computed spectra of all three 2H,1H,0H-Ru(dppip-NO\textsubscript{2}) species and scaled their intensities using the experimental pK\textsubscript{a,1} value of 6.8\textsuperscript{S7} and an estimated pK\textsubscript{a,2} of 14 to demonstrate the influence of a third species on the pH-dependent spectra. Further details can be found in Ref. S7. Please note the different x axis scale for the CAM-B3LYP spectra in Fig. S4b. The figure illustrates that both B3LYP and CAM-B3LYP would predict a third rising band at high pH values in the low energy region if the 0H-Ru(dppip-NO\textsubscript{2}) species contributed to the spectra to a greater extent. Since this is not observed in the experiments, this could indicate that large amounts of 0H-Ru(dppip-NO\textsubscript{2}) do not occur in the experimentally investigated pH range.
Figure S4: Ru(dppip-NO$_2$) pH-dependent absorption spectra: experimental spectra in Britton-Robinson buffer/MeCN (reproduced from Ref. S7) compared to (a) B3LYP 300 K Wigner spectra (adapted from Ref. S7) and (b) CAM-B3LYP eq. spectra (employing a large full width at half maximum of 0.7 eV to be better comparable to the Wigner spectra).
Furthermore, we investigated the role of spin–orbit coupling for the absorption spectra of the 2H,1H,0H-Ru(dppip-NO₂) complexes. Fig. S5 presents the B3LYP spectra without and with spin–orbit coupling between singlet and triplet states\textsuperscript{S12} taken into account. As can be seen, no significant differences are observed in the spectra. Therefore, we have calculated only singlet excited states in the main paper and have not considered spin–orbit coupling further.

Figure S5: B3LYP absorption spectra without spin–orbit coupling (solid lines) and including spin–orbit coupling (dashed lines): (a) 2H-Ru(dppip-NO₂), (b) 1H-Ru(dppip-NO₂), (c) 0H-Ru(dppip-NO₂).
S3  Absorption spectra of Ru(dppip-NO$_2$) and Ru(dpp)

The equilibrium spectra of the Ru-complexes were reported by us previously in Ref. S7. Here, we focus on the nature of the absorption bands in the Wigner spectra compared to the equilibrium spectra and show natural transition orbitals of the most intense states of the equilibrium spectra for clarity. Fig. S6 (Ru(dpp)) and Figs. S7 – S9 (0H,1H,2H-Ru(dppip-NO$_2$)) present a comparison of the absorption spectra calculated using the equilibrium geometries of the Ru-complexes (at the top) with the spectra calculated from the respective 300 K Wigner ensembles (at the bottom). The spectra were decomposed into contributions from different excitation characters indicated by the color scheme. The equilibrium geometries and superimposed structures of the 300 K Wigner ensembles of Ru(dpp) and of 0H,1H,2H-Ru(dppip-NO$_2$) are presented in Figs. S6 – S9 on the right.

Figure S6: Absorption spectrum of Ru(dpp) and decomposition into different excitation characters: (a) equilibrium geometry, (b) 300 K Wigner ensemble (50 geometries).

First, we focus on the character of the low-energy bands in the spectra. MLCT excitations to the equatorial ligand are mainly important in the low-energy range of the spectra of Ru(dpp) and 1H,2H-Ru(dppip-NO$_2$), whereas the contribution of ligand-based LC and
Figure S7: Absorption spectrum of 0H-Ru(dppip-NO₂) and decomposition into different excitation characters: (a) equilibrium geometry, (b) 300 K Wigner ensemble (50 geometries).

Figure S8: Absorption spectrum of 1H-Ru(dppip-NO₂) and decomposition into different excitation characters: (a) equilibrium geometry, (b) 300 K Wigner ensemble (50 geometries).
LLCT transitions increases at higher energies. In the 2H,1H,0H-Ru(dppip-NO₂) equilibrium spectra, MLCT excitations from dRu-based HOMOs to the π⁺₉₄⁻₆ LUMO and to higher-lying LUMO+1,2 of π⁺₆ LUMO and LUMO+1,2 above 400 nm. Similarly, Ru(dpp) exhibits MLCT excitations from the dRu HOMOs to the π⁺₆ LUMO and LUMO+1,2 above 400 nm. In contrast to the rather weak dRu HOMOs → π⁺₉₄⁻₆ LUMO MLCT transitions in 1H,2H-Ru(dppip-NO₂) (oscillator strengths fosc ≈ 0.05 – 0.1), 0H-Ru(dppip-NO₂) has a state with a high fosc of 0.45 at low energies of mainly HOMO → LUMO character, the S₂ at 637 nm. The character of this S₂ state can be described as dRu/πim-dpp → π⁺₉₄⁻₆ LLCT/MLCT transition as shown by the natural transition orbitals depicted in Fig. S10. It should be noted that the HOMO in 0H-Ru(dppip-NO₂) corresponds to a dRu/πim-dpp orbital, whereas 1H,2H-Ru(dppip-NO₂) (and also Ru(dpp)) have nearly degenerate HOMOs of dRu character.⁷⁷

The most remarkable difference in the spectra of Ru(dpp) and 0H,1H,2H-Ru(dppip-NO₂) is the strong absorption band of the latter complexes in the visible (vis) energy range.⁷⁷ The underlying bright states can be characterized as dRu/πim-dpp-ph → π⁺₉₄⁻₆ LLCT/MLCT excitations⁷⁷ as shown by the natural transition orbitals in Fig. S11. Hence, excitations

Figure S9: Absorption spectrum of 2H-Ru(dppip-NO₂) and decomposition into different excitation characters: (a) equilibrium geometry, (b) 300 K Wigner ensemble (50 geometries).
Figure S10: Natural transition orbitals of (a) the S$_2$ state and (b) the S$_{12}$ state of 0H-Ru(dppip-NO$_2$). The two dominant contributions to the S$_{12}$ state are shown.

to the electron-withdrawing nitrophenyl group seem to be the main reason for the different absorption properties of Ru(dpp) and 0H,1H,2H-Ru(dppip-NO$_2$) in the vis region.$^{57}$ Another bright state, the S$_{12}$ at 448 nm, of mostly of Ru $\rightarrow$ dpp MLCT character (see the natural transition orbitals in Fig. S10) contributes to the vis absorption band in 0H-Ru(dppip-NO$_2$).$^{57}$

An intense MLCT state that is observed in all complexes in the near UV range is the excitation from Ru to the axial pic ligands ($d_{Ru} \rightarrow \pi^*_{pic}$). This transition is not affected by the modification of the equatorial ligand, i.e., it occurs at about the same energy with similar oscillator strengths $f_{osc}$ in both the Ru(dpp) and 1H-Ru(dppip-NO$_2$) equilibrium spectra (at 339 nm with $f_{osc}$ of 0.32 and at 338 nm with $f_{osc}$ of 0.29 in Ru(dpp) and in 1H-Ru(dppip-NO$_2$), respectively, see Fig. S12). Also (de)protonation of the imidazole group has only small effects shifting the wavelength to 330 nm ($f_{osc}$ of 0.32) in 2H-Ru(dppip-NO$_2$) and to 349 nm ($f_{osc}$ of 0.31) in 0H-Ru(dppip-NO$_2$).

In the UV range, the spectra are dominated by intense transitions involving the equatorial
Figure S11: Natural transition orbitals of bright vis states (a) $S_{10}$ in 0H-Ru(dppip-NO$_2$), (b) $S_{11}$ in 1H-Ru(dppip-NO$_2$), and (c) $S_{13}$ in 2H-Ru(dppip-NO$_2$); reproduced from Ref. S7.

Figure S12: Natural transition orbitals of $d_{Ru} \rightarrow \pi^*_{pic}$ MLCT states (a) $S_{25}$ in 1H-Ru(dppip-NO$_2$) and (b) $S_{15}$ in Ru(dpp).
dpp or dppip-NO$_2$ ligand and excitations at the pic ligands, whose importance increases in the Wigner spectra compared to the equilibrium spectra.

These assignments agree with literature on Ru(dpp), where low-energy bands in the vis region were usually attributed to $d_{\text{Ru}} \rightarrow \pi^*_{\text{dpp}}$ MLCT transitions followed by MLCT transitions to the axial pic ligands at higher energies, and the intense UV band was suggested to be mainly caused by dpp-ligand-based $\pi \rightarrow \pi^*$ LC transitions.$^{13,14}$ Previous TD-DFT (B3LYP) calculations of Ru(dpp) in water found MLCT transitions at 519 nm,$^{15}$ similar to the MLCT band at 517 nm calculated for the Ru(dpp) equilibrium geometry in acetonitrile (MeCN) in this work.
As mentioned in the main text, care must be taken when applying the finite temperature Wigner sampling to systems that have low-frequency modes or for torsional motions. We therefore excluded low-frequency modes below 40 cm\(^{-1}\) in the Wigner sampling. To check for a possible deformation of the dppip-NO\(_2\) ligand, the distances between two opposite C atoms or H atoms in the nitrophenyl ring were analyzed as a function of the NO\(_2\) and nitrophenyl dihedral angles in the Wigner ensemble; this is shown in Fig. S13 taking 1H-Ru(dppip-NO\(_2\)) as an example. The figure shows that no deformation of the nitrophenyl group of the dppip-NO\(_2\) ligand is observed at higher deviations of the dihedral angles from their equilibrium values in the 300 K Wigner ensemble. This may also be seen in the superimposed structures of the 300 K Wigner ensembles of the Ru-complexes shown above in Figs. S6 – S9. That is, no exaggerated distances are seen here for 1H-Ru(dppip-NO\(_2\)) such as those reported for a 300 K Wigner ensemble of a Re-complex that exhibits a nearly free ligand torsion.

Figure S13: C–C and H–H distances in nitrophenyl group of dppip-NO\(_2\) as a function of (a)–(b) the NO\(_2\) and (c)–(d) the nitrophenyl dihedral angle in 1H-Ru(dppip-NO\(_2\)) 300 K Wigner ensemble (500 geometries). The equilibrium distances are shown as dashed lines.
S5  NO$_2$ and nitrophenyl dihedral angle scans

To determine the influence of torsional motions of or within the nitrophenyl group on the absorption spectra of 0H,1H,2H-Ru(dppip-NO$_2$) separately, scans of the NO$_2$ and nitrophenyl dihedral angles were performed and the spectra computed from these structures.

S5.1  Relaxed scans of 1H-Ru(dppip-NO$_2$)

In the main text, the absorption spectra and excited state characters obtained from unrelaxed NO$_2$ and nitrophenyl dihedral angle scans of 1H-Ru(dppip-NO$_2$) were shown and compared to the corresponding unrelaxed scans of the 0H,2H-Ru(dppip-NO$_2$) complexes. For comparison, the absorption spectra were additionally calculated from 1H-Ru(dppip-NO$_2$) structures from relaxed scans of the NO$_2$ and nitrophenyl dihedral angles, respectively, which are shown below in Fig. S14a–b. As in the unrelaxed scans, a significant decrease in intensity of the vis peak is observed. Fig. S14c–d presents the changes in the oscillator strength, CT number, and character of $S_{11}$, i.e., of the bright vis state in the 1H-Ru(dppip-NO$_2$) equilibrium spectrum, with increasing deviations of the NO$_2$ dihedral angle (Fig. S14c) and nitrophenyl dihedral angle (Fig. S14d) from their equilibrium values. The same results are observed as before in the unrelaxed scans, i.e., the oscillator strength of $S_{11}$ drops quickly at higher dihedral angles. In the case of the NO$_2$ dihedral angle scan, this is accompanied by a decrease in the CT character, which is mainly due to a decrease of the dppi $\rightarrow$ nitrophenyl LLCT contribution shown in dark red in Fig. S14c. At high NO$_2$ dihedral angles $\varphi_{NO_2} \geq 50^\circ$, states other than $S_{11}$ become more important for the vis absorption band. Therefore, only the range between 0$^\circ$ and 40$^\circ$ is shown in Fig. S14c. The nitrophenyl dihedral angle scan (Fig. S14d) shows an opposite effect, i.e., the CT character, especially the dppi $\rightarrow$ nitrophenyl LLCT character, increases at higher dihedral angles.
Figure S14: (a) Effect of NO$_2$ and (b) nitrophenyl torsion on the absorption spectra of 1H-Ru(dppip-NO$_2$). The spectra were calculated from structures from relaxed scans of the NO$_2$ and nitrophenyl dihedral angles, respectively. Influence of (c) NO$_2$ and (d) nitrophenyl torsion on the bright vis state (S$_{11}$) in 1H-Ru(dppip-NO$_2$) structures from relaxed dihedral angle scans, showing changes in oscillator strength f$_{osc}$, CT number, and character of S$_{11}$. 
S5.2 Unrelaxed scans

Fig. S15 presents unrelaxed scans along the NO$_2$ and nitrophenyl dihedral angles in 1H-Ru(dppip-NO$_2$) (Fig. S15a–b) as well as along the nitrophenyl dihedral angle in 0H,2H-Ru(dppip-NO$_2$) (Fig. S15b). The estimated torsion barriers are higher than the values from the corresponding relaxed scans (Fig. 6 in the main text), e.g., 0.24 eV compared to 0.22 eV and 0.23 eV in the relaxed scans of the NO$_2$ and nitrophenyl dihedral angles in 1H-Ru(dppip-NO$_2$). However, the differences are rather small and both unrelaxed and relaxed scans follow the same trend: the nitrophenyl torsion barrier increases in the order of 2H-Ru(dppip-NO$_2$) 0.17 eV < 1H-Ru(dppip-NO$_2$) 0.24 eV < 0H-Ru(dppip-NO$_2$) 0.34 eV.

Figure S15: Unrelaxed dihedral angle scans: (a) NO$_2$ dihedral angle $\varphi_{NO_2}$ in 1H-Ru(dppip-NO$_2$) and (b) nitrophenyl dihedral angle $\varphi_{ph-NO_2}$ with respect to im–dpp ring system in 0H,1H,2H-Ru(dppip-NO$_2$).

As no significant differences were observed between the unrelaxed and the relaxed dihedral angle scans, neither in the effect on the absorption spectra and excited state characters in 1H-Ru(dppip-NO$_2$) structures (Fig. 7 and Fig. S17 compared to Fig. S14) nor in the trend of the torsion barriers (Fig. S15 compared to Fig. 6), we focused on the unrelaxed scans in the following and in the main text.
S5.2.1 0H-Ru(dppip-NO$_2$)

The absorption spectra of 0H-Ru(dppip-NO$_2$) structures, where the nitrophenyl dihedral angle was scanned from $-0.8^\circ$ to $-50^\circ$ (unrelaxed scan), are presented in Fig. S16a. Both the vis band at about 460 nm and the low-energy peak below 600 nm are affected by the torsional motion. Fig. S16b shows the effect of the nitrophenyl dihedral angle scan on the oscillator strength and character of the $S_{10}$ state, which is the bright vis state in the 0H-Ru(dppip-NO$_2$) equilibrium spectrum. The oscillator strength decreases and the CT character increases with the nitrophenyl dihedral angle, which is mainly due to a higher Ru $\rightarrow$ dppip-NO$_2$ MLCT character, whereas the LC and LLCT contributions decrease.

Figure S16: (a) Absorption spectra of 0H-Ru(dppip-NO$_2$) structures, where the nitrophenyl dihedral angle was scanned from $-0.8^\circ$ to $-50^\circ$ (eq.: $-0.8^\circ$). (b) Effect of nitrophenyl torsion on the oscillator strength $f_{osc}$ and character of the bright vis state ($S_{10}$); the eq. angle is indicated by the dashed gray line. Distribution of dihedral angles in the 300 K Wigner ensemble (50 geometries).
S5.2.2 1H-Ru(dppip-NO$_2$)

The influence of changes in the dihedral angles on the vis band of 1H-Ru(dppip-NO$_2$) is presented in Fig. S17. As anticipated, we see significant effects. A decrease in the intensity of the vis band is found for a torsional motion of both the NO$_2$ group (Fig. S17a) and of the nitrophenyl ring (Fig. S17b). Moreover, both dihedral angle scans show a shift in the computed vis band position. However, it is plausible that the latter is due to changes in the charge transfer vs. local character of the bright state, keeping in mind that B3LYP is known to underestimate charge transfer excitation energies. And yet, in 2H-Ru(dppip-NO$_2$) an increase of the excitation energy with increasing CT character of the transition is observed at higher nitrophenyl dihedral angles $\varphi_{\text{ph-NO}}$ (see below in Fig. S19).

Figure S17: (a) Effect of NO$_2$ and (b) nitrophenyl torsion on the absorption spectra of 1H-Ru(dppip-NO$_2$). The spectra were calculated from structures in which the NO$_2$ and nitrophenyl dihedral angles were scanned from 0° to 90° or from 0° to -90°, respectively (unrelaxed scans).

The effect of a torsional motion of the NO$_2$ group and nitrophenyl group (unrelaxed
dihedral angle scans) on the character of the $S_{11}$ state, which dominates the vis absorption band in the equilibrium spectrum of 1H-Ru(dppip-NO$_2$), was discussed in the main text. The changes in the CT character, or in the localization of the excited electron, with increasing NO$_2$ and nitrophenyl dihedral angles can also be shown by the matrix plot of the TheoDORE CT numbers of $S_{11}$ of 1H-Ru(dppip-NO$_2$) in Fig. S18a–b (cf. Fig. S1c for an explanation of the matrix plot of the CT numbers). The figure compares dihedral angles of $0^\circ$, $|40|\circ$, and $|90|\circ$ to show the effect more clearly. It demonstrates the opposing effects of NO$_2$ and nitrophenyl torsion. While the former increases the dppi-centered local excitation character and effectively quenches CT excitations to the nitrophenyl group (Fig. S18a), the latter increases the dppi $\rightarrow$ nitrophenyl LLCT character of the excited state and the localization of the electron on the nitrophenyl ring (Fig. S18b).
Figure S18: Matrix plot of CT numbers of S\textsubscript{11} state of 1H-Ru(dppip-NO\textsubscript{2}) showing (a) the increasing localization of the excited electron on the im–dpp ring (dppi fragment) with increasing NO\textsubscript{2} dihedral angle $\varphi_{NO_2}$ (dppi LC excitation). In the planar structure ($0^\circ$), the excited electron is more distributed over the equatorial dppip-NO\textsubscript{2} ligand and there is a greater CT character to the nitrophenyl group. (b) Increasing localization of the excited electron on the nitrophenyl ring (ph-NO\textsubscript{2} fragment) with increasing nitrophenyl dihedral angle $\varphi_{ph-NO_2}$. The corresponding 1H-Ru(dppip-NO\textsubscript{2}) structures with varying dihedral angles ($\varphi_{NO_2}$ or $\varphi_{ph-NO_2} = 0^\circ$, $|40|^\circ$, $|90|^\circ$) are shown below the matrix plots.
S5.2.3 2H-Ru(dppip-NO₂)

Fig. S19a shows the absorption spectra of 2H-Ru(dppip-NO₂) structures, where the nitrophenyl dihedral angle was scanned from 0° to -50° (unrelaxed scans). The effect of the scan on the oscillator strength and character of the S₁₃ state, which is the bright vis state in the 2H-Ru(dppip-NO₂) equilibrium spectrum, is presented in Fig. S19b. Like in 0H,1H-Ru(dppip-NO₂), higher dihedral angles lead to a decrease in oscillator strength and increase in the CT character of the excited state. In 2H-Ru(dppip-NO₂), mainly the dppi-centered LC character is reduced, whereas the dppi → nitrophenyl LLCT contribution is increased at higher nitrophenyl dihedral angles. However, these changes in the character of S₁₃ are small in 2H-Ru(dppip-NO₂).

Figure S19: (a) Absorption spectra of 2H-Ru(dppip-NO₂) structures, where the nitrophenyl dihedral angle was scanned from 0° to -50° (eq.: -25°). (b) Effect of nitrophenyl torsion on the oscillator strength fosc and character of the bright vis state (S₁₃); the eq. angle is indicated by the dashed gray line. Distribution of dihedral angles in the 300 K Wigner ensemble (50 geometries).
S5.2.4 Comparison of 0H,1H,2H-Ru(dppip-NO$_2$)

Matrix plots of the TheoDORE CT numbers of the bright vis states $S_{10}$, $S_{11}$, $S_{13}$ in 0H,1H,2H-Ru(dppip-NO$_2$) are shown in Fig. S20 for ca. planar geometries and for structures with a nitrophenyl dihedral angle of -40°. The excited electron is more distributed over the equatorial dppip-NO$_2$ ligand in the nearly planar structures compared to the structures with a rotated nitrophenyl ring, where the excited electron is rather localized on the nitrophenyl ring. In the deprotonated 0H-Ru(dppip-NO$_2$) complex, MLCT excitations are more important than dpipi $\rightarrow$ dppip-NO$_2$ LLCT/LC excitations. In contrast, dpipi $\rightarrow$ nitrophenyl excitations dominate the character of $S_{13}$ in the protonated 2H-Ru(dppip-NO$_2$).

Figure S20: Matrix plot of CT numbers of $S_{10}$, $S_{11}$, $S_{13}$ states of 0H,1H,2H-Ru(dppip-NO$_2$) at nitrophenyl dihedral angles of 0° (ca. -1° for 0H-Ru(dppip-NO$_2$)), and -40°.
The Cartesian coordinates of the optimized geometries of the $0H_1H_2H-Ru$($dppip$-$NO_2$) complexes and of $Ru$($dpp$) are reported below (B3LYP-D3BJ/def2-TZVP and def2-ECP on Ru, C-PCM acetonitrile, RIJCOSX SARC/J). Frequency calculations based on these geometries were used for generating the Wigner ensembles.

![Table of coordinates](#)
|   |   |   |   |
|---|---|---|---|
| C | -4.039897 | -2.124508 | 12.617789 |
| C | -1.580055 | -1.506907 | 16.279518 |
| C | -0.565182 | -1.147312 | 17.149480 |
| C | 0.598020  | -0.521307 | 16.661046 |
| C | -5.333099 | -2.667520 | 12.225812 |
| C | -6.195218 | -3.232120 | 13.180820 |
| C | -7.423201 | -3.745355 | 12.813630 |
| C | -7.803398 | -3.697492 | 11.474006 |
| C | -6.970395 | -3.145096 | 10.503094 |
| C | -5.744780 | -2.635472 | 10.882664 |
| C | 1.785352  | -0.052912 | 17.395317 |
| C | 3.867099  | 0.976284  | 17.239839 |
| C | 4.068460  | 0.878930  | 18.609566 |
| C | 3.081401  | 0.290799  | 19.386613 |
| C | 1.929349  | -0.178825 | 18.770859 |
| C | -0.061999 | 6.474669  | 15.530100 |
| C | 2.651414  | -2.379246 | 13.890347 |
| C | 3.330561  | -3.574246 | 13.745011 |
| C | 4.698755  | -3.638296 | 14.003351 |
| C | 5.314838  | -2.453932 | 14.409279 |
| C | 4.574826  | -1.295006 | 14.533582 |
| C | 5.474235  | -4.908327 | 13.831362 |
| O | -9.816939 | -4.718293 | 11.949780 |
| O | -9.415988 | -4.180359 | 9.896665 |
| H | 5.117087  | 2.051446  | 14.042460 |
| H | 6.355925  | 2.951868  | 12.090418 |
| H | 5.306328  | 2.781885  | 9.820228 |
| H | 3.071564  | 1.721463  | 9.615584 |
| H | 1.038769  | 0.743697  | 9.590742 |
| H | -1.135209 | -0.350968 | 9.925878 |
| H | -2.470627 | -1.985881 | 16.662980 |
| H | -0.669573 | -1.348199 | 18.206344 |
| H | 1.145280  | -0.641253 | 19.353366 |
| H | 3.202693  | 0.197041  | 20.457604 |
| H | 4.981585  | 1.259137  | 19.045667 |
| H | 4.612171  | 1.427909  | 16.598274 |
| H | 3.287187  | 3.226050  | 15.385085 |
| H | 2.512552  | 5.525564  | 15.788869 |

S26
H  -1.424320  4.241137  14.658970
H  -0.503073  1.997954  14.297354
H   5.040363 -0.372676  14.848680
H   6.373211 -2.429356  14.633731
H   2.784203 -4.454488  13.432313
H   1.591399 -2.327588  13.692859
H  -0.934625  6.688741  14.913058
H  -0.365893  6.565140  16.577160
H    0.703345  7.228094  15.343156
H    4.840406 -5.781181  13.987791
H    5.873862 -4.966412  12.814609
H    6.318407 -4.949946  14.519869
H  -5.087881 -2.203333  10.141771
H  -7.286751 -3.119421   9.471277
H  -8.085317 -4.178751  13.547869
H  -5.887671 -3.262460  14.215891

84
Coordinates Ru-1H
Ru  2.256232  0.599088  14.479334
N  2.703867   0.712270  16.604866
N  0.661192 -0.160044  15.326554
N  1.243951  0.213156  12.846103
N  3.580315  1.268242  12.886381
N  1.498699  2.558422  14.595005
N  3.228943 -1.265492  14.435354
N  3.639580 -2.029416  13.900592
N -3.143273 -1.706133  11.756589
N  9.148893  4.320058  11.272730
C  1.688117  0.215162  17.379319
C  1.784764  0.196774  18.763459
C  2.928539  0.690368  19.377282
C  3.951672  1.193343  18.588411
C  3.796285  1.184361  17.208850
C  0.513079 -0.285586  16.643846
C -0.293063 -0.552948  14.449848
C -1.500596  1.116169  14.874587
C -1.673102 -1.256790  16.268303
H  1.219969  0.360845  9.513157
H  -0.987528 -0.651791  9.858215
H  -2.586450 -1.686421  16.655849
H  -0.821996  -0.959543  18.205515
H   0.972696 -0.201054  19.355120
H   3.014604  0.680474  20.455635
H   4.859443  1.588436  19.022405
H   4.571068  1.567568  16.558201
H   3.356270  3.280116  15.145404
H   2.642393  5.625448  15.324577
H  -1.299830  4.360099  14.191346
H  -0.440543  2.069985  14.054583
H    5.009563 -0.389831  15.015615
H    6.295601 -2.485251  15.030882
H    2.712017 -4.522965  13.833675
H   1.564973 -2.358083  13.863068
H  -0.726977  6.810950  14.227809
H  -0.245714  6.804663  15.923328
H    0.905627  7.333931  14.698234
H    4.707692 -5.843564  14.596005
H    5.805372 -5.155298  13.400718
H    6.185328 -5.002338  15.114769
H  -3.226026  1.715554  10.751098
H  -5.185706  2.320442  10.153450
H  -7.376295 -3.262274   9.586272
H  -8.082220 -4.174853  13.714284
H  -5.868402 -3.234212  14.300180

85
Coordinates Ru-2H
Ru  2.250451  0.609630  14.488055
N  3.566097  1.254206  12.880284
N  1.226968  0.212075  12.867543
N  0.659589 -0.133832  15.352632
N  2.713225  0.740567  16.607438
N  1.511984  2.577749  14.589709
N  3.219924  1.258655  14.459790
N  3.157938 -1.734555  11.807758
N  -3.632618 -2.034939  13.892393
N  -9.076180 -4.491204  11.172188
C   0.234721  2.906238  14.336746
C   2.358450  3.568584  14.920906
C   1.963616  4.888490  15.007167
C   0.639040  5.241872  14.748256
C  -0.228535  4.206202  14.404417
C   3.013887  1.055846  11.641457
C   3.695748  1.404689  10.485140
C   4.962521  1.966269  10.581119
C   5.515931  2.164650  11.836134
C   4.783522  1.794382  12.956615
C   1.668280  0.456001  11.633991
C  -0.301051 -0.534299  14.487243
C  -1.502194 -1.096646  14.931376
C  -2.382757 -1.459539  13.863844
C  -2.076574 -1.266170  12.516763
C  -4.097902 -2.201187  12.644497
C  -1.667263 -1.227949  16.326204
C  -0.665005 -0.808224  17.184002
C   0.521126 -0.250288  16.673021
C  -5.373515 -2.784418  12.267964
C  -6.016566 -3.675210  13.135867
C  -7.230255 -4.234452  12.779579
C  -7.785536 -3.895824  11.553894
C  -7.168309 -3.017059  10.675182
C  -5.955768 -2.458429  11.037056
C   1.702658  0.253474  17.395088
C   3.811667  1.213906  17.198256
C   3.977028  1.233689  18.577064
C   2.959354  0.741038  19.378533
C   1.808882  0.245740  18.777995
C   0.168529  6.659231  14.857650
C   2.602086 -2.411112  14.154264
| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| C    | 3.253468      | -3.629582     | 14.153628     |
| C    | 4.607641      | -3.699730     | 14.477108     |
| C    | 5.238230      | -2.496317     | 14.794564     |
| C    | 4.525806      | -1.314043     | 14.775315     |
| C    | 5.353824      | -4.997930     | 14.462524     |
| O    | -9.608400     | -5.258384     | 11.960740     |
| O    | -9.548486     | -4.187369     | 10.086734     |
| H    | 5.181345      | 1.932612      | 13.952992     |
| H    | 6.498495      | 2.598221      | 11.958877     |
| H    | 5.504581      | 2.242657      | 9.686755      |
| H    | 3.240411      | 1.238508      | 9.519301      |
| H    | 1.181564      | 0.321100      | 9.532335      |
| H    | -1.026555     | -0.684856     | 9.901557      |
| H    | -2.573516     | -1.656860     | 16.731644     |
| H    | -0.799930     | -0.913212     | 18.250734     |
| H    | 1.000535      | -0.144679     | 19.379550     |
| H    | 3.054209      | 0.739998      | 20.456089     |
| H    | 4.889541      | 1.629321      | 19.000455     |
| H    | 4.583033      | 1.588582      | 16.538801     |
| H    | 3.381821      | 3.285943      | 15.118476     |
| H    | 2.695196      | 5.639640      | 15.274391     |
| H    | -1.269107     | 4.405280      | 14.184345     |
| H    | -0.437195     | 2.104995      | 14.068977     |
| H    | 5.004399      | -0.378032     | 15.022721     |
| H    | 6.286538      | -2.474192     | 15.061946     |
| H    | 2.696586      | -4.522794     | 13.902691     |
| H    | 1.553011      | -2.358138     | 13.905799     |
| H    | -0.673704     | 6.847282      | 14.191956     |
| H    | -0.165358     | 6.861791      | 15.879678     |
| H    | 0.971987      | 7.359324      | 14.628887     |
| H    | 4.692699      | -5.834796     | 14.687329     |
| H    | 5.780009      | -5.170193     | 13.469661     |
| H    | 6.176934      | -4.986982     | 15.176941     |
| H    | -3.220988     | -1.775121     | 10.798986     |
| H    | -5.482236     | -1.754087     | 10.367323     |
| H    | -7.631919     | -2.770193     | 9.732553      |
| H    | -7.734468     | -4.927117     | 13.435469     |
| H    | -5.565109     | -3.955332     | 14.077578     |
H  -4.152392  -2.261999  14.730463

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Coordinates Ru(dpp)

Ru  -0.069433  -0.540387  16.564127
N   0.452990  -2.482304  17.419970
N   0.887048  -1.458925  15.120808
N  -0.183076   0.883644  15.222523
N  -1.157859   1.062204  17.576555
N  -1.921060  -1.355884  15.988849
N   1.711210   0.227187  17.378074
C   1.141765  -3.276585  16.539609
C   1.563243  -4.549086  16.897249
C   1.284646  -5.030258  18.169985
C   0.588229  -4.223043  19.055892
C   0.192823  -2.958832  18.638791
C   1.392215  -2.684380  15.213610
C   0.996575  -0.721616  13.989374
C   1.640711  -1.185823  12.842575
C   2.184028  -2.491636  12.930677
C   2.061630  -3.227011  14.096264
C   1.673016  -0.287912  11.721936
C   1.102037   0.956364  11.775177
C   0.438174   1.436279  12.955017
C   0.406367   0.566147  14.044712
C  -0.777623   2.055772  15.417970
C  -0.789640   2.993080  14.363373
C  -0.192117   2.689816  13.152905
C  -1.341852   2.159762  16.775290
C  -1.642341   1.092359  18.819487
C  -2.326390   2.184281  19.337439
C  -2.517180   3.295515  18.531044
C  -2.017699   3.280746  17.235211
C  -2.786011  -1.737892  16.944828
C  -4.020430  -2.285571  16.657763
C  -4.416340  -2.464636  15.331937
C  -3.513184  -2.060516  14.349984
C  -2.293392  -1.519352  14.708961

S32
| At. | X      | Y      | Z      | U      | V      | W      |
|-----|--------|--------|--------|--------|--------|--------|
| C   | -5.735 | -3.082 | 14.982 | 14.982 | 0.000  | 0.000  |
| C   | 2.714  | 0.723  | 16.635 | 16.635 | 0.000  | 0.000  |
| C   | 3.878  | 1.219  | 17.190 | 17.190 | 0.000  | 0.000  |
| C   | 4.050  | 1.218  | 18.573 | 18.573 | 0.000  | 0.000  |
| C   | 3.001  | 0.704  | 19.335 | 19.335 | 0.000  | 0.000  |
| C   | 1.865  | 0.224  | 18.714 | 18.714 | 0.000  | 0.000  |
| C   | 5.310  | 1.720  | 19.210 | 19.210 | 0.000  | 0.000  |
| H   | -1.473 | 0.207  | 19.417 | 19.417 | 0.000  | 0.000  |
| H   | -2.697 | 2.151  | 20.352 | 20.352 | 0.000  | 0.000  |
| H   | -3.046 | 4.164  | 18.900 | 18.900 | 0.000  | 0.000  |
| H   | -2.152 | 4.134  | 16.585 | 16.585 | 0.000  | 0.000  |
| H   | -1.267 | 3.953  | 14.499 | 14.499 | 0.000  | 0.000  |
| H   | -0.206 | 3.416  | 12.350 | 12.350 | 0.000  | 0.000  |
| H   | 1.147  | 1.604  | 10.909 | 10.909 | 0.000  | 0.000  |
| H   | 2.165  | -0.614 | 10.814 | 10.814 | 0.000  | 0.000  |
| H   | 2.698  | -2.917 | 12.079 | 12.079 | 0.000  | 0.000  |
| H   | 2.481  | -4.222 | 14.148 | 14.148 | 0.000  | 0.000  |
| H   | 2.104  | -5.157 | 16.186 | 16.186 | 0.000  | 0.000  |
| H   | 1.608  | -6.021 | 18.460 | 18.460 | 0.000  | 0.000  |
| H   | 0.349  | -5.556 | 20.056 | 20.056 | 0.000  | 0.000  |
| H   | -0.353 | -2.299 | 19.300 | 19.300 | 0.000  | 0.000  |
| H   | -2.472 | -1.592 | 17.967 | 17.967 | 0.000  | 0.000  |
| H   | -4.673 | -2.569 | 17.473 | 17.473 | 0.000  | 0.000  |
| H   | -3.754 | -2.161 | 13.299 | 13.299 | 0.000  | 0.000  |
| H   | -1.594 | -1.205 | 13.949 | 13.949 | 0.000  | 0.000  |
| H   | 1.046  | -0.176 | 19.293 | 19.293 | 0.000  | 0.000  |
| H   | 3.061  | 0.677  | 20.415 | 20.415 | 0.000  | 0.000  |
| H   | 4.647  | 1.609  | 16.536 | 16.536 | 0.000  | 0.000  |
| H   | 2.579  | 0.724  | 15.564 | 15.564 | 0.000  | 0.000  |
| H   | -6.099 | -2.716 | 14.021 | 14.021 | 0.000  | 0.000  |
| H   | -5.629 | -4.168 | 14.904 | 14.904 | 0.000  | 0.000  |
| H   | -6.481 | -2.878 | 15.750 | 15.750 | 0.000  | 0.000  |
| H   | 5.786  | 2.483  | 18.594 | 18.594 | 0.000  | 0.000  |
| H   | 5.113  | 2.130  | 20.201 | 20.201 | 0.000  | 0.000  |
| H   | 6.021  | 0.897  | 19.328 | 19.328 | 0.000  | 0.000  |
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