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Increasing excited state lifetimes of Cu(I) coordination complexes *via* strategic surface binding†

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Molecules undergo a structural change to minimize the energy of excited states generated *via* external stimuli such as light. This is particularly problematic for Cu(I) coordination complexes which are an intriguing alternative to the rare and expensive transition metal containing complexes (e.g., Pt, Ir, Ru, etc.) but suffer from short excited state lifetimes due to D_{2d} to D_2 distortion and solvent coordination. Here we investigate strategic surface binding as an approach to hinder this distortion and increase the excited state lifetime of Cu(I) polypyridyl complexes. Using transient absorption spectroscopy, we observe a more than 20-fold increase in excited state lifetime, relative to solution, for a Cu(I) complex that can coordinate to the ZrO_2 *via* both carboxylated ligands. In contrast, the Cu(I) complex that coordinates *via* only one ligand has a less pronounced enhancement upon surface binding and exhibits greater sensitivity to coordinating solvents. A combination of ATR-IR and polarized visible ATR measurements as well as theoretical calculations suggest that the increased lifetime is due to surface binding which decreases the degrees of freedom for molecular distortion (e.g., D_{2d} to D_2), with the doubly bound complex exhibiting the most pronounced enhancement.

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Introduction

Molecules undergo a structural change to minimize the energy of transient excited states that are generated *via* external stimuli such as pressure, oxidants/reductants, magnetic fields, or light. This process is intrinsic to all molecules but large changes in structure, particularly of transition metal coordination complexes, can have a debilitating impact on their properties including decreased stability, lowered reactivity, and shortened excited state lifetimes.^{1–4} This hinders their utility in catalysis, lighting, solar energy conversion, and more.^{5,6} For example, in lighting/light harvesting applications, tetrahedral Cu(I) coordination complexes are an intriguing alternative to molecules containing expensive and low abundance transition metals like Ru(II), Pt(II), and Ir(III).² However, the lowest energy excited state of these Cu(I) complexes is typically dominated by

metal-to-ligand charge transfer character where the resulting d^9 , Cu(II) center favors a square planar geometry, resulting in a D_{2d} to D_2 distortion (Fig. 1).^{7–9} This distortion decreases the energy of the excited states, enables access to additional relaxation modes, and opens sites for solvent coordination resulting in rapid, non-radiative decay.^{10–13}

The most popular strategy to inhibit this type of distortion, particularly in the prototypical Cu(I) bis(1,10-phenanthroline) (phen) complexes, is *via* the addition of steric bulk to the ligands.¹⁴ Increasing the size of the moiety at the 2,9-position from methyl groups (dmp) introduced by McMillin in the 1980s,¹⁵ to phenyl,¹⁶ *sec*-butyl,¹⁷ cyclohexyl,¹⁸ and *tert*-butyl,¹⁹ has resulted in Cu(I) phen-based emitters with lifetimes >1 μ s and emission quantum yields >5%, as compared 90 ns and

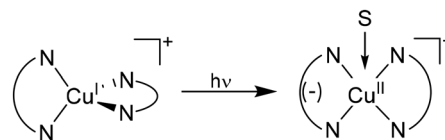


Fig. 1 General depiction of the tetrahedral to square planar (*i.e.*, D_{2d} to D_2) distortion in the excited state of Cu(I) polypyridyl complexes, and subsequent solvent (S) coordination.

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0.4% for the parent $[\text{Cu}(\text{dmp})_2]^+$.¹⁵ While effective, this steric bulk strategy can suffer from limitations like increased synthetic complexity and decreased stability of the coordination sphere.¹⁹ One can also hinder distortions by embedding the molecules in a rigid matrix or glass^{20,21} but this strategy hinders mobility and access to the molecules for use in catalysis and photoinduced electron transfer.

Here, we introduce strategic surface binding as an alternative approach to hinder the distortion of Cu(I) polypyridyl complexes. We use metal ion-coordinating functional groups on the ligands to bind to a metal oxide substrate with the goal of hindering the D_{2d} to D_2 -type distortion. We demonstrate that there is a >20-fold increase in excited state lifetime, relative to solution when both ligands are bound to the surface. This offers a new paradigm to extend the excited state lifetime of Cu(I) coordination complexes and hinder undesirable distortion pathways for molecules in response to stimuli.

Results and discussion

Synthesis and surface loading

The two Cu(I) complexes used for this study (**1** and **2**) are shown in Fig. 2. The 6,6'-dimethyl-2,2'-bipyridine scaffolding was selected, as opposed to the more common phenanthroline ligands, because of the relative ease of synthesizing COOH functionalized ligands.²² The same or similar complexes were previously bound to metal oxide surfaces for application in dye-sensitized solar cells (DSSCs).²² The position and number of ligands with the COOH functional groups were selected in such a way to allow only one (for **1**) or both (for **2**) ligands to bind to the metal oxide surface (Fig. 2; bottom).

Complexes **1** and **2** were prepared following previously published procedures.^{22,23} Synthetic details and structural characterization are provided in the ESI.† Both **1** and **2** exhibits strong absorbance (Fig. 3a and Fig. S1†) from 250–350 nm and a weaker

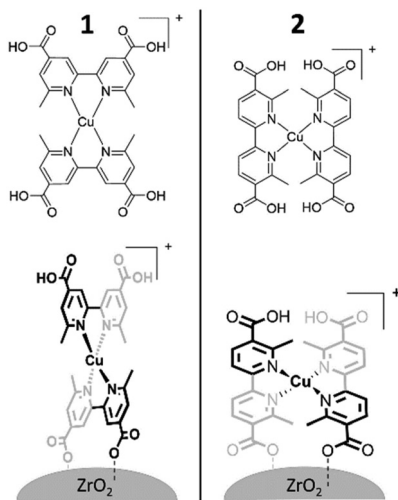


Fig. 2 Molecular structure (top) and envisioned ZrO_2 binding modes (bottom) for complexes **1** and **2**.

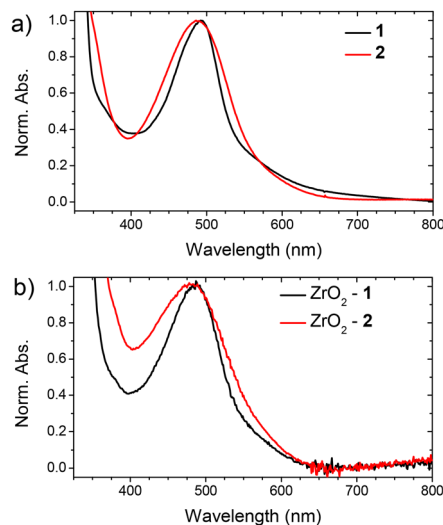


Fig. 3 Normalized absorption spectrum of **1** and **2** in MeOH (a) and on ZrO_2 (b).

feature at 400–600 nm that are attributed to π - π^* and metal-to-ligand charge transfer (MLCT) transitions, respectively.²⁴

The complexes were loaded onto the surface *via* soaking a ZrO_2 film in a 500 μM MeOH solution of **1** and **2**. The adsorption isotherms are provided in the ESI (Fig. S2†). As opposed to the more ubiquitous TiO_2 , ZrO_2 was selected as the mesoporous oxide substrate²⁵ for these studies because its relatively high conduction band²⁶ allows for the excited state dynamics of the molecule to be studied in the absence of electron transfer quenching to the substrate. From fits to the absorption isotherms,²⁷ the complexes exhibit maximum surface coverages of 2.1×10^{-7} mol cm^{-2} for **1** and 3.6×10^{-8} mol cm^{-2} for **2**.

When bound to the surface (ZrO_2 -X), the complexes maintain the same spectral features and energies, (Fig. 3b) albeit with peak broadening that is commonly attributed to inhomogeneous environments for molecules on metal oxide surfaces.²⁸ The lack of shift in the absorption energy/features suggests that the surface binding has minimal impact on energetics or protonation state, for example, and that the ground state structure of the molecule in solution is largely retained when bound to the surface.

Excited state dynamics

The excited-state dynamics of the Cu(I) complexes in MeOH and on ZrO_2 submerged in MeOH were measured by transient absorption (TA) spectroscopy and the results can be seen in Fig. 4. TA was chosen to monitor the excited state because the complexes were non-emissive even in rigid glass and at 77 K.

Upon 500 nm excitation, the complexes exhibit a bleach of the MLCT absorption band at <550 or 600 nm and an excited state absorption (ESA) feature at >550 or 600 nm, analogous to $[\text{Cu}(\text{phen})_2]^+$ derivatives.¹³ Worth noting is that the spectral features of **1** are redshifted relative to **2** (Fig. 4) presumably due to the 4,4', rather than 5,5'-position of the COOH groups, respectively, similar to the shift observed in ruthenium poly-



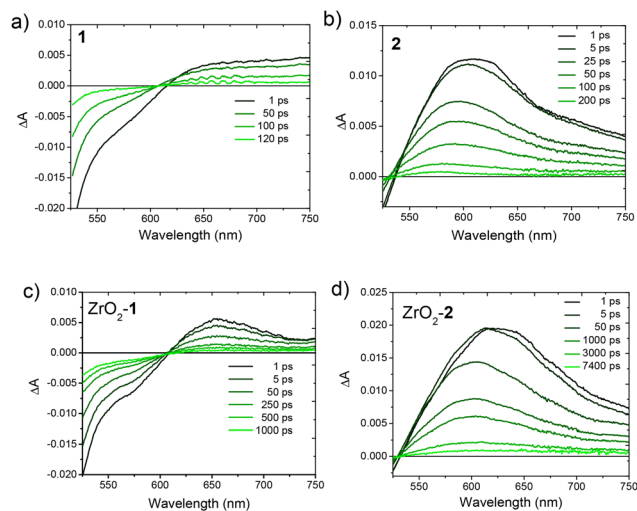


Fig. 4 Transient absorption spectra of complex **1** (a and c) and **2** (b and d) in MeOH (a and b) and on ZrO₂ in MeOH (c and d) ($\lambda_{\text{ex}} = 500$ nm).

pridyl complexes.²⁹ For all the complexes in solution, at early time scales (<30 ps) there is a blueshift of the ESA feature (Fig. 4) that is often attributed to vibrational cooling.³⁰ In contrast, a more subtle blue shift occurs in ~500 ps for the surface bound complexes.

Comparing the solution and surface bound TA spectra, perhaps the most notable observation is the dramatic change in decay kinetics. Whereas the solution samples have returned to baseline in <300 ps, spectral features for the surface bound complexes are observed for several nanoseconds. Attempts to globally fit the decay kinetics using either sequential or parallel models were unsuccessful for the surface bound complexes (ZrO₂-X). This difficulty is not uncommon for these types of samples and again is attributed to inhomogeneous environments for molecules on metal oxide surfaces.²⁸ However, the single wavelength decay dynamics were fit with a single and biexponential function for solvated and ZrO₂ bound species, respectively (Table S1†). Regardless of wavelength, the biexponential fits to the ESA feature of ZrO₂-X samples (X = 1 or 2) gave a consistent trend in both the fast (~50 and ~270 ps for **1** and **2**) and slow (~600 and ~2000 ps for **1** and **2**) components with approximately equal amplitude contribution for each (Table S1†). Given that the trends in decay were similar across ESA features (and across several independent samples), we chose representative wavelengths and weighted average lifetimes and the results are shown in Fig. 5 and Table 1, respectively.

When solvated in MeOH, the complexes exhibit excited state lifetimes <80 ps. In contrast, the lifetime for surface bound complexes is much longer and when compared solution, the lifetime increases ~8-fold for **1** and 22-fold for **2** (Table 1). Increased excited state lifetime for surface bound Cu(I) complexes has been observed before and was attributed to intermolecular packing hindering non-radiative distortions.³¹ For the complexes studied here, the lifetimes did decrease

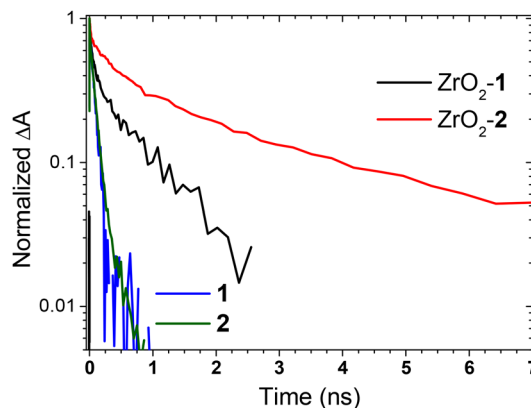


Fig. 5 Excited state decay traces for **1** and **2** solvated and on ZrO₂ in MeOH at 690 nm and 610 nm, respectively ($\lambda_{\text{ex}} = 500$ nm).

Table 1 Excited state lifetime for solvated and surface bound complexes **1** and **2** in MeOH^a

	τ in solution ^b (ps)	τ on ZrO ₂ ^c (ps)	τ in PMMA ^{c,d} (ps)
1	80	640	2560
2	90	1960	4600

^a Fits at 690 nm for **1** and 610 nm for **2**. ^b Single exponential fits. ^c Weighted average of biexponential fits. ^d The ethyl ester protected versions of the molecule (**1**_{Et} and **2**_{Et}).

when the surface loading was reduced by half (Fig. S3 and Table S2†), from 640 to 430 ps for **1** and 1960 to 1060 ps for **2** indicating the intermolecular interactions are not solely responsible for the lifetime increase. Instead, we attribute it to the surface binding decreasing excited state distortion of the complexes, and solvent coordination (*vide infra*), with the most pronounced behavior being complex **2** where both ligands are bound to the surface. For reference, we have included the excited state spectra (Fig. S4†) and lifetime (Table 1) for **1** and **2** in PMMA where the rigid matrix significantly hinders molecular mobility/flexibility.^{32,33} Relative to the molecules in PMMA, ZrO₂-**2** more closely (43% of the PMMA lifetime) resembles that of the rigid environment than ZrO₂-**1** (25%).

As mentioned above, solvent coordination to the planarized, D₂ distorted Cu(I) complex can play a role in the excited state decay dynamics. Previous theoretical, time-resolved emission, and X-ray absorption studies on [Cu(dmp)₂]⁺ derivatives, have indicated that structural distortion can occur on the sub-picosecond timescale, followed by solvent coordination and relaxation on the 1–10 ps time scale.^{7,34} MeOH was selected as the solvent of choice for the preliminary measurements due to the limited solubility and surface stability of **1** and **2** in other solvents. MeOH is known to serve as a coordinating Lewis Acid and excited state quencher for Cu(I) complexes.³⁵ Consequently, MeOH can serve as an indirect probe of the structural distortion that enables quenching *via* coordination.

To investigate the role of solvent in the excited state decay of solvated and surface bound Cu(I) complexes, we generated



the more soluble ethyl protected version of **1** and **2** (**1_{Et}** and **2_{Et}**). As can be seen in Fig. S5 and 6,[†] the steady-state and time-resolved absorption spectral features of **1** and **1_{Et}**, **2** and **2_{Et}** are similar. This indicates that other than increasing the solubility, the ethyl group has minimal impact on the photo-physical properties of the complexes. The absorption and TA spectra (Fig. S7 and S8[†]) were measured in CHCl₃, the decay traces fit and the results are summarized in Table 2.

For both **1_{Et}** and **2_{Et}**, there is an ~40-fold increase in lifetime from MeOH to CHCl₃ which we attribute to the absence of excited state quenching *via* solvent coordination in CHCl₃.³⁵ Likewise, for ZrO₂-**1** there is a nearly 4-fold increase in lifetime in the non-coordinating CHCl₃. In contrast, for ZrO₂-**2** the lifetime slightly decreases from MeOH to CHCl₃ suggesting that the solvent dependent quenching mechanism for **2** in solution (*i.e.*, MeOH coordination) is significantly less prominent when it is bound to the surface. This outcome is consistent with inhibited *D*_{2d} to *D*₂ distortion for ZrO₂-**2** which hinders access for coordinating solvents to the metal center. Interestingly, the lifetime decrease for ZrO₂-**2** in CHCl₃ suggests that alternative non-radiative modes are available when bound to the surface.

Computational analysis

To gain insights into the electronic structure and degree of distortion upon excitation, we used density functional theory (DFT) (B3LYP,^{36,37} SDD/6-311G*;^{38,39} details in the ESI[†]) to optimize the geometries of compounds **1** and **2** in their singlet ground and lowest-energy triplet state. The ground state MO diagrams for the complexes are shown in Fig. 6 and Fig. S10.[†] Both complexes exhibit ligand-based LUMOs and Cu-based HOMOs (Fig. 6), where HOMO through HOMO-4 can be described as primarily metal centered, 3d orbitals (see Table S3[†]).

Using the ground state optimized geometry, the excited state transitions for **1** and **2** were then calculated using time-dependent density functional theory (TD-DFT) with the same model and the results are summarized in Tables S4 and 5[†] with the simulated spectrum shown in Fig. S12.[†] In agreement with experiment, the complexes exhibit strong, higher-energy peaks (<350 nm) that have ligand centered character (*i.e.*, π - π^*) and lower-intensity peaks at ~500 nm that are MLCT in character. Transition dipole moments for the MLCT band were obtained from TD-DFT calculations and the results are summarized in Table S6[†] with the transition dipole moment

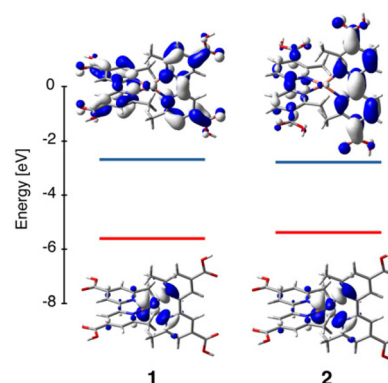


Fig. 6 Energy level diagrams for **1** and **2** with the HOMO (bottom, red line) and LUMO (top, blue line) orbitals.

vectors visualized in Fig. S13.[†] For both complexes, the MLCT transition dipoles are oriented from the metal center and bisect the bipyridine ligands. This orientation is consistent with previously reported Ru(II) and Os(II) tris-bipyridine complexes.^{40,41} From the geometry optimized lowest-energy triplet state, **1** and **2** also exhibits MLCT character as confirmed by the spin density and natural orbital analysis (Fig. S14[†]).

Given our interest in the structural distortion of the complexes, we used the interligand dihedral angle (φ)⁴² to evaluate the degree of planarization between the ground and lowest-energy ³MLCT states (Table 3). The interligand dihedral angle (φ)⁴² is the angle between planes of the bipyridine ligand (Fig. S11[†]). Note that since the complexes do not exhibit perfect *D*_{2d} symmetry, there are two different measurements of this angle, so the values reported in Table 3 correspond to their average. The $\varphi = 90^\circ$ corresponds to the tetrahedral structure, while $\varphi = 0^\circ$ or 180° describe a square planar structure. We have also calculated $\Delta\varphi = |90^\circ - \varphi|$ that provides an information on deviation from tetrahedral conformation. The results are summarized in Table 3. For **1** and **2** we see flattening of the structure going from singlet to triplet state. The change is more pronounced for complex **2**, where the complex flattens by 9° going from singlet to triplet (this can be seen by comparing $\Delta\varphi$), and less apparent for complex **1** where it only flattens by additional 2° .

Collectively, the theoretical outcomes describe behavior analogous between **1** and **2** and prior Cu(I)(phen)₂ complexes.¹⁵⁻¹⁹ Namely, excitation into a MLCT transition results in a ligand-centered reduction and oxidation of the Cu

Table 2 Excited state lifetime in MeOH and CHCl₃ for solvated **1_{Et}** and **2_{Et}** and ZrO₂ bound **1** and **2**

	τ in solution ^a (ps)		τ on ZrO ₂ (ps)		
	In MeOH	In CHCl ₃	In MeOH	In CHCl ₃	
1_{Et}	70	2660	1	640	2420
2_{Et}	55	2640	2	1960	1660

^a For **1_{Et}** and **2_{Et}**. From weighted average of biexponential fits at 690 nm for ZrO₂-**1** and 610 nm for ZrO₂-**2**.

Table 3 Interligand dihedral angle (φ) and $\Delta\varphi = |90^\circ - \varphi|$ for singlet ground state and triplet states of **1** and **2**

	Singlet		Triplet	
	φ	$\Delta\varphi$	φ	$\Delta\varphi$
1	81°	9°	101°	11°
2	74°	16°	65°	25°



(i) to Cu(II), which results in molecular distortion to a more square planar geometry (see Fig. 1). Our experimental results suggest that this process is inhibited by strategic surface binding.

Structural characterization

To gain insights into the structures of these interfaces we performed attenuated total reflectance infrared spectroscopy (ATR-IR) measurements on both the neat powders and ZrO₂ films of **1** and **2** and the results are shown in Fig. 7 and Fig. S15.†

In the neat powder, the complexes exhibit prominent peaks at 1715 cm⁻¹ and 1700 cm⁻¹ for **1** and **2**, respectively, that are assigned to the C=O stretching mode ($\nu_{\text{C=O}}$) and peaks at 1225–1245 cm⁻¹ for the C–O stretching mode ($\nu_{\text{C-O}}$).⁴³ The C=O stretching assignment is consistent with the calculated vibrational spectra (Fig. S16 and 17†) where the highest energy feature in the fingerprint region is the $\nu_{\text{C=O}}$ mode, along with a C–O stretch and O–H bands in the 1000–1700 cm⁻¹ region. Upon binding to the surface, there is a notable decrease in the relative amplitude of the unbound $\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$ modes and an increase in the intensity of the carboxylate symmetric (ν_{s}) and asymmetric (ν_{as}) stretching in the 1600–1650 cm⁻¹ region, which is attributed to surface binding.⁴³ It is important to note that while the amplitude of the unbound COOH modes decreases, they are still present in the surface bound samples. Given the geometric limitations of the molecules (*i.e.*, COOH groups on opposite sides), presumably, only half of the COOH groups are capable of binding to the surface and thus signal due to the unbound COOH groups is still observed.

Polarized UV-Vis attenuated total reflection (p-ATR) spectroscopy offers a powerful means of determining the orientation of molecular transition dipole moments relative to the surface normal.^{44–47} Here we performed p-ATR on **1** and **2** bound to an indium tin oxide (ITO) surface and the results are summarized in Table 4 and Table S8† with the loading con-

Table 4 Transition dipole moment tilt angles and surface coverage of **1** and **2** on ITO as determined from p-ATR^a

ITO-X	Tilt angle (°)	Surface coverage (mol cm ⁻²)
1	47 ± 2	1.1 × 10 ⁻¹⁰ (±0.12)
2	62 ± 2	9.0 × 10 ⁻¹¹ (±2.3)

^a All values are the average of three measurements with the standard deviation reported as the relative error.

ditions shown in Table S7.† ITO was selected as the substrate because it is commercially available, has a low surface roughness (0.5 ± 0.1 nm), and the molecular orientation of absorbates is expected to be similar to that on ZrO₂.⁴⁸ In agreement with that observed for the ZrO₂ films (*vide supra*), the surface coverage was found to be similar between the complexes (~1 × 10⁻¹⁰ mol cm⁻²). Assuming a hexagonal packing on a planar (*i.e.*, atomically flat) surface, this equates to a center-to-center intermolecular distance of ~15 Å,⁴⁶ which is in good agreement with full monolayers of related transition metal-polypyridyl complexes.⁴⁹

The tilt angle of the molecules was determined from the dichroic ratio (Fig. S18–20†) of the absorbance values measured using transverse magnetic and transverse electric polarized light at the MLCT transition (350–600 nm).⁵⁰ The complexes with carboxylic acid groups in the 5,5' position of the bipyridine, **2** exhibited tilt angles of 62°. In contrast, for **1**, where the COOH groups are in the 4,4' position, the tilt was 47° relative to surface normal.

Based on the combination of theoretical and experimental results described above, Fig. 8 shows the proposed orientation of the molecules on a metal oxide surface. The ground state optimized geometry of the complexes was oriented relative to the surface normal based on the calculated transition dipole moment and the p-ATR results. Based on the ATR-IR results, we assume that two of the four COOH groups of **1** and **2** were bound to the surface. These structures are consistent with the anticipated structure depicted in Fig. 2 and further support the hypothesis that in **1** only one of the ligands can bind, whereas in **2** both can bind which hinders the tetrahedral to square planar distortion.

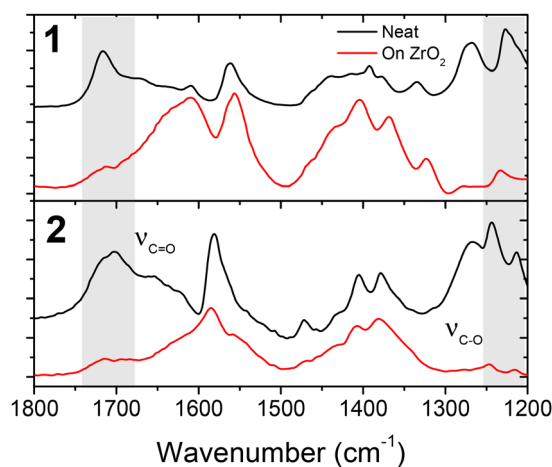


Fig. 7 ATR-IR absorption spectra of neat powder (black) and ZrO₂ bound (red) **1** and **2**.

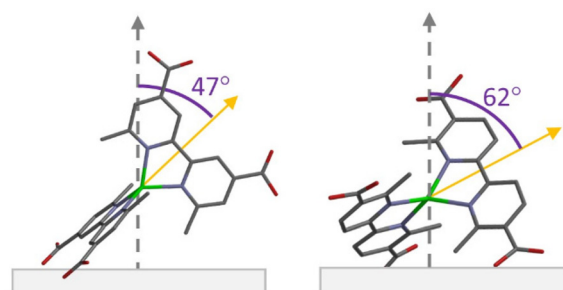


Fig. 8 Proposed structure of **1** (left) and **2** (right) on a metal oxide surface with the transition dipole moment in orange (H atoms omitted for clarity).



Conclusions

Here we studied the structural and excited state properties of two Cu(I) bipyridine complexes (*i.e.*, **1** and **2**) with variation in the position of the COOH surface binding group. Theoretical calculations for the complexes in solution point to a mechanism consisting of (1) excitation into a MLCT transition, (2) ligand-centered reduction and oxidation of the Cu(I) to Cu(II), and (3) molecular distortion from a tetrahedral to a square planar geometry. Upon ZrO₂ surface loading, ATR-IR and p-ATR measurements as well as geometric considerations indicate that molecules **1** are bound to the surface *via* a single ligand and molecule **2** coordinates *via* both carboxylated ligands. Using transient absorption, we observe a dramatic increase in the excited state lifetime for the molecules on a ZrO₂ surface, relative to solution, with the most pronounced increase for complex **2**. Furthermore, for **2** bound to the surface, the excited state quenching by a coordinating solvent like MeOH, was less pronounced than the singly bound derivative (*i.e.*, **1**) and it behaves more like that in a rigid matrix like PMMA. The increase in lifetime is not due to intermolecular interactions or energetic changes of the complex. Instead, we attribute it to surface binding decreasing the degrees of freedom for the molecules to distort with the doubly bound complex **2** having the greatest barrier to distortion. The hindered mobility decreases the excited state quenching *via* D_{2d} to D₂-type distortion and subsequent solvent coordination. Collectively, these results demonstrate that molecular immobilization *via* strategic surface binding is an alternative and innovative means of inhibiting undesired structural distortion for molecules responding to stimuli like light. However, it is important to acknowledge that the utility of these particular molecules is limited by their relatively short lifetime and non-emissive nature. But we hope these results will usher in a new paradigm for the design of molecule-metal oxide interfaces resulting in increased excited state lifetimes and efficiencies for light emission/harvesting applications as well as in electro-/photocatalysts where structural trapping at the interface could lead to coordinatively unsaturated sites and high energy species favorable for increased/unique reactivities.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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