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Surface Immobilized Copper(I)diimine Photosensitizers as Molecular Probes for Elucidating the Effects of Confinement at Interfaces for Solar Energy Conversion

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Heteroleptic copper(I) bis(phenanthroline) complexes with surface anchoring carboxylate groups have been synthesized and immobilized on nanoporous metal oxide substrates. The species investigated are responsive to the external environment and provide a new strategy to control charge transfer processes for efficient solar energy conversion.

Copper(I) coordination complexes have attracted interest for integration in solar energy conversion schemes because of their broad absorption in the visible region and the relative earth abundance of copper compared to the ruthenium centre of the prototype molecular photosensitizer $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine).¹⁻⁶ Recent work focused on ligand designs of Cu(I) photosensitizers has demonstrated the potential for these earth-abundant complexes to initiate light-driven H₂ catalysis in multimolecular systems.⁷⁻⁹ Herein, we describe a fundamentally new strategy for controlling and directing photochemical processes through dimensional control of a metal oxide environment.

For Cu(I)bis(phen) (phen = 1,10-phenanthroline) complexes, substitution of the phen ligands and accompanied distortions to the ideal tetrahedral symmetry profoundly influence their ground and excited state properties.¹⁰⁻¹³ By comparing Cu(I)(dmp)₂ and Cu(I)(dtbp)₂ (where dmp = 2,9-dimethyl-1,10-phen, dtbp = 2,9-di-*tert*-butyl-1,10-phen),¹⁴ we know that increasing the steric bulk at the 2,9-phen position from methyl to *tert*-butyl results in a 29 nm blue shift of the absorbance feature assigned to MLCT from λ_{max} = 454 nm to λ_{max} = 425 nm and a 0.20 V increase in the Cu(II/I) oxidation potential.¹⁵ Both observations are explained by the bulkier substituents yielding a more idealized D_{2d} symmetry in the Cu(I) state, increasing the

Cu—N bond length, and restricting flattening in the Cu(II) oxidation state. The light-induced structural dynamics of these two complexes are well understood from investigations using multiple time-resolved optical and X-ray spectroscopy methods.^{16, 17} In the non-coordinating solvent CH₂Cl₂, the ³MLCT decay for Cu(I)(dmp)₂ is ~90 ns, but increases to 1.9 μ s for Cu(I)(dtbp)₂ due to substituents preventing deactivation pathways associated with structural distortion in the Cu(II) MLCT state and minimizing Cu(II)—solvent interaction. These general design principles are well-established for homoleptic Cu(I)bis(phen) complexes, and the same trends apply to heteroleptic Cu(I)(phen^A)(phen^B) complexes.^{18, 19}

Short excited state lifetimes are problematic for diffusional reactions, but electrode surface immobilization provides a direct, well-defined pathway for interfacial electron transfer. Our group has shown that Cu(I)diimine complexes anchored to TiO_2 substrates inject photogenerated electrons from the ¹MLCT state on the sub-picosecond time scale while charge recombination occurs on the microsecond timescale, indicating a long lived charge separated state.^{5, 20} Indeed, these favourable charge separation kinetics have led to an interest in deploying Cu(I)diimine complexes as the photosensitizer in dye-sensitized solar cells.^{1, 21} In the pursuit of long-lived charge separated states from Cu(I) complexes, the immobilization approach provides more synthetic versatility than imposing the strict functionalization requirements for stable homoleptic complexes, and can also exploit what we have learned about the directional electron transfer in heteroleptic Cu(I)diimine complexes.6, 22

The primary goal of this work is to understand whether the structural factors that dominate the solution phase photophysical properties of Cu(I)diimine complexes also apply in heterogeneous environments. To this end, we have synthesized three new heteroleptic Cu(I)bis(phen) (CuHETPHEN) complexes functionalized with carboxylic acid groups which are capable of binding to metal oxide surfaces (Chart 1). These complexes were designed to evaluate two different ligand factors that we anticipate will impact the

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^c Department of Chemistry, Northwestern University, Evanston, IL 60208 Electronic Supplementary Information (ESI) available: Materials and methods for molecular synthesis and immobilization, description of physical characterization methods, additional spectra, and details of kinetic analysis. See DOI: 10.1039/x0xx00000x

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photophysical properties, particularly when immobilized or confined. Complex **1** has a short anchor which is directly connected to the phen ligand. In contrast, the imidazole-containing anchoring ligand of complexes **2** and **3** is approximately 6.5 Å longer than that of **1** and should allow studies to investigate the effect of distance and packing efficiency on the ground and excited state properties. Complexes **2** and **3** differ only in the 2,9-phen substitution on the anchor ligand and provide a direct comparison for how the known solution trends apply to immobilized CuHETPHEN complexes.

Complexes 1, 2, and 3 were synthesized by the two-step one-pot HETPHEN approach that yields kinetically stable complexes with no formation of the homoleptic analogues.²³⁻²⁶ However, we had to refine the standard synthesis methods because of the poor solubility of the phenanthroline ligands functionalized with carboxylic acids. We dissolved $Cu(CH_3CN)_4PF_6$ in de-aerated CH_2Cl_2 or THF depending on the target complex, then added a stoichiometric amount of 2,9dimesityl-1,10-phenanthroline (L) followed by one equivalent of carboxylate-functionalized ligands L1, L2, or L3 to form complexes 1, 2, and 3. The synthesis of 1 was accomplished in neat CH_2Cl_2 but the somewhat more Lewis basic solvent THF was required for synthesis of 2 and 3.

To systematically investigate the ground and excited state properties of immobilized CuHETPHEN complexes, we selected nanoporous anodic aluminium oxide (AAO) wafers as the metal oxide platform. AAO wafers are commercially available in a variety of pore sizes ranging from 10 nm to 200 nm,²⁷ and the controlled pore sizes offer a uniform chemical environment compared to the larger distribution of pore sizes that are present in more conventional metal oxide surfaces such as TiO₂ nanoparticle films.²⁸ Complexes **1**, **2**, and **3** were immobilized on AAO wafers by submerging the wafers in a CH₂Cl₂ or CH₃OH solution of each complex overnight. The AAO wafers adopted the characteristic red-orange colour of the CuHETPHEN complexes and upon removal from solution the wafers were rinsed, soaked in pure solvent, and rinsed again to remove any residual weakly adsorbed complex.

UV-Visible absorption spectra can be used to gather information on the coordination environment of Cu(I)diimine complexes.^{13, 29, 30} The AAO-immobilized MLCT band of 1 and 2



blue shift 10-30 nm as compared to each complex in CH₂Cl₂ solution (Figures S3, S4), which is consistent with increased restriction to geometric changes in the complex.14, 15 We observe only a minimal shift in the MLCT band for 3 between the immobilized complex and in solution (Figure 1), which suggests that immobilization has less of an impact on the spectral response than the increased sterics of the phen ligand environment. Additionally, we were able to correlate the density of immobilized 1-3 on the surface of the AAO wafers from the UV-Vis absorbance spectra and the AAO pore sizes and densities (Tables S3-S4). We determined that 1-3 were adsorbed on the surfaces at a density of approximately 1-2 complexes per square nanometre which correlates to roughly monolaver coverage based on related immobilized complexes.31

To further probe the impact of pore immobilization on molecular and electronic structure, we utilized EPR spectroscopy due to its high sensitivity for paramagnetic centres and ability to elucidate structural and electronic information of the copper centre in the immobilized complexes. Since Cu(I) is diamagnetic and therefore EPR silent, we immobilized **3** on 10, 20, and 40 nm pore size AAO, oxidized the surface bound Cu(I) to the corresponding Cu(II) species using a solution of AgNO₃ in CH₃CN, and recorded X-band EPR spectra at 20 K (Figure 2). For all of the AAO pore sizes, we observe spectra characteristic of Cu(II) $3d^9$ (S = $\frac{1}{2}$),^{32, 33} but with noticeable differences in the linewidth of the parallel, low field components as a function of AAO pore size. (We assign the sharp signal at 338 mT to an organic radical/defect, $g \approx 2.005$, that we also observed in the bare AAO lacking any immobilized copper species, see Figure S3.) The largest pore size of AAO investigated (40 nm) has the smallest linewidth (~290 MHz), which increases as the pore size decreases from 20 nm (~300 MHz) to 10 nm (~550 MHz). Since there is no evidence of a chemical change to 3 in the different pore sizes, we interpret the broadening as a response to shorter neighbour-neighbour distances between Cu(II) ions in the smaller pores, which leads to stronger magnetic dipole-dipole interaction. Using the assumption that there is no substantial contribution to line width from spin-spin interactions in glassy frozen dilute solutions of Cu(II) complexes (see Figure S7 and associated discussion), we estimate the distance between the immobilized Cu(II) neighbours to be ~12 Å for the 40 and 20 nm pores, and

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Figure 2. Continuous wave X-band EPR spectra of 3 in the Cu(II) oxidation state immobilized on 10, 20, and 40 nm AAO recorded at T = 20K.



Figure 3. Cyclic voltammograms of 1, 2, and 3 immobilized on *nano*ITO substrates in 0.1 M nBu_4PF_6 in CH₃CN.

~8.5 Å for 10 nm AAO pores.³⁴ This difference in spin-spin interaction likely arises from decreasing distance between neighbouring chromophore tethering sites with changes in pore size and may also be related in part to increased curvature with decreasing pores size.

Cyclic voltammetry of **1**, **2**, and **3** was performed in solution as well as immobilized on *nano*ITO which functions as both a substrate and working electrode since AAO is an insulator (Figure 3, S8). The dominant factor in determining the Cu(II/I) oxidation potential is the substitution at the 2,9-phen position of the anchor ligand, consistent with previous observations.¹⁸ As expected, the Cu(II/I) potential for **3** is substantially more positive than for **1** and **2**, both in solution and when immobilized (Figure 3, S8, and Table S6). Importantly, the potentials of **1** and **2** experience a more significant shift on immobilization than for **3** (230 mV for **1** and **2** vs. 50 mV for **3**) which suggests **3** is less influenced by the external environment, consistent with the observations based on UV-vis spectroscopy.

The excited state dynamics of the AAO-immobilized complexes were measured by ultrafast and nanosecond transient optical spectroscopy. Because of the complicated spectral changes and multiple photophysical processes of Cu(I)diimine complexes,^{13, 17, 29} we used global analysis to fit the transient absorption data over a broad range of wavelengths with multi-exponential functions (complete fitting details are found in the Supporting Information). Similar to the well-documented photophysical behaviour for related complexes in solution, the transient spectra for the immobilized complexes are characterized by an initial broad featureless excited state absorbance centred around 540 nm which evolves to a feature



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Figure 4. Ultrafast transient absorption spectra of 3 on 10 nm AAO in deaerated CH_2CI_2 . Excitation at 500 nm, time delay noted in legend.

with two local λ -maxima at 530 and 570 nm within 30 ps (see for example **3** immobilized on 10 nm AAO in Figure 4 and Figures S8-S39). As expected from literature precedent, methyl substitution in **3** results in a significant increase in excited state lifetimes compared to **1** and **2**, and the solution data are summarized in Table S7.

We immobilized complexes 1 and 3 on AAO and immersed the wafers in CH₂Cl₂ to investigate the impact of immobilization and pore size on the excited state kinetics. Both 1 and 3 showed significantly longer excited state lifetimes when immobilized on AAO than in solution, suggesting that immobilization restricts the ability of the complexes to undergo a flattening distortion and reduces exposure to solvent following photoexcitation. For complex 1, the ³MLCT lifetime is 1.0 ns in solution and increases to 1.7 ns when immobilized on 20 nm AAO. The average ³MLCT lifetime for **3** in CH₂Cl₂ is 49 ns, similar to that in 40 nm pores (51 ns), but the average ³MLCT lifetime increases to 69 ns for both 20 nm and 10 nm pores. This trend is similar to that previously observed for Cu(I)(dmp)₂ dispersed into a polymer matrix where the ³MLCT lifetime increased from 90 ns in CH₂Cl₂ to 210 ns with increasing polymer viscosity.³⁵ We interpret our results in a similar fashion: as 3 is immobilized in increasingly smaller pores and in closer proximity to other immobilized Cu centres (as measured by EPR), the typical flattening distortion is restricted which increases the lifetime of the excited state.

As a first step toward investigating the effect of nanoporous confinement on interfacial charge injection, we measured the electron transfer kinetics of **3** immobilized on mesoporous n-type semiconducting TiO₂ films immersed in CH₂Cl₂ (Figures S40-S41). Upon photoexcitation at 500 nm, we observe an average lifetime of 75 μ s for the recovery of the ground state bleach, which demonstrates that **3** does inject electrons into TiO₂. The recombination lifetime is comparable to analogous cases of other Cu(I) species bound to TiO₂.^{5, 20}

Immobilization of Cu(I)diimine complexes in nanoporous metal oxide materials presents an interesting opportunity to tune the photophysical properties of these complexes by external environmental factors. Here we have shown that decreasing the pore size of the AAO framework from 40 to 10 nm results in enhanced spin-spin interactions between Cu(II) centres, as well as a measurable increase in the ³MLCT lifetime, over twice that observed in solution. The increase in ³MLCT lifetime is consistent with inhibited structural flattening as pore size decreases and ongoing work is focused on restricting pore

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diameter even further to investigate the impact of extreme confinement on Cu(I)diimine excited state dynamics. These results present a fundamentally new strategy for controlling and directing photochemical processes.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, through Argonne National Laboratory under Contract No. DE-ACO2-06CH11357. Synthesis and electrochemistry were supported by the Early Career Research Program, EPR and TA facilities were supported by the Solar Photochemistry program. Transient optical spectroscopy was performed in part at the Center for Nanoscale Materials. The CNM is an Office of Science user facility supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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September 3, 2020

Dr. Alan Holder Publishing Editor, Journals (*ChemComm*) Royal Society of Chemistry Thomas Graham House Science Park, Milton Road Cambridge, UK

Dear Dr. Holder,

I have re-submitted a revised manuscript in response to the decision of **CC-COM-06-2020-004014**, "Surface Immobilized Copper(I)diimine Photosensitizers as Molecular Probes for Elucidating the Effects of Confinement at Interfaces for Solar Energy Conversion". My co-authors and I thank you for handling this manuscript, as well as the referees for their time evaluating the work and their insightful comments. We have revised the manuscript to address the referees' comments and have attached a point-by-point response to their comments below.

This work has not been submitted to another journal and has not been published elsewhere in any medium. All authors have approved of the manscript's contents and conclusions. In the revised manuscript, we have added David M. Kaphan as an author because of his contribution to the collection and analysis of the solid state absorbance spectra which were suggested by referee 1.

This work was orginally submitted in response to an invitation for the special issue of *Chemical Communications* on (Photo)electrocatalysis for renewable energy. The work presented in this manuscript describes a potentially seminal change in thinking about how to manipulate and optimize Cu(I) photophysics and photochemistry so that they may be ultimately deployed in photocatalytic systems. Given the overall positive reviewer comments on the novelty, broad interest, and scholarly presentation of the work, and that we have adequately addressed both referees' concerns with the original manuscript despite multiple constraints due to the ongoing coronavirus pandemic, we strongly advocate for publication within this special issue of *Chemical Communications*.

Sincerely,

Karen Mitz

Karen Mulfort



Response to referee comments: CC-COM-06-2020-004014

Referee: 1

Comments to the Author

The manuscript by Karen L. Mulfort and co-workers deals with an important and interesting topic, i.e. the immobilization of Cu(I) photosensitizers for later application in photochemical devices. The manuscript itself is well written, but the publication requires some improvements prior to publication in Chem. Comm. The following points need attention:

1.) Unfortunately, the presented complexes 1-3 are quite similar to a publication by Y. Pellegrin and F. Odobel et al. (c.f. Dalton Trans., 2013, 42, 10818-10827). The authors should comment on the novelty of their complexes and also compare with the previous one.

We are aware of this important paper which also provides relevant prior work for our immobilized Cu(I) complexes and we therefore cited this paper both in the original manuscript (ref. 22) and in the revised version (ref. 21). We acknowledge the reviewer's point that the complexes described by Sandroni et al. and those we describe are similar in that both manuscripts use carboxylate groups to immobilize Cu(I) complexes to metal oxide surfaces. However, this work differs from this previous literature in that we are specifically investigating heteroleptic Cu(I)bis(phenanthroline) complexes. While the complexes Pellegrin and Odobel discuss are also heteroleptic Cu(I) complexes, they feature a 2,2'-biquinoline-4,4'dicarboxylic acid ligand which serves to anchor the complex to metal oxide surfaces. The pairing of two different phenanthroline ligands around the Cu(I) center in our work prohibits any rotational flexibility that might be possible in the bpy-coordinated complexes described by Sandroni et al. Additionally, pairing two phenanthroline ligands allows for intramolecular pi stacking between the two ligands (this manuscript), which is absent in Cu(I)(phen)(bpy) complexes (Sandroni et al. Dalton 2013). The substantial differences in intramolecular ligand interactions in response to bpy v. phen as well as outer coordination sphere effects have been established by our group (Dalton Trans., 2016, 45, 9871-9883; Dalton Trans., 2017, 46, 13088-13100) and Gordon (Inorg. Chem., 2013, 52, 2980-2992) and have significant photophysical and photochemical consequences. Therefore, the complexes we describe here do have important differences from those in the cited paper, but we also acknowledge the importance of the previous work.

2.) The basic structural characterization of the complexes 1-3 is not complete in the Supporting Information. There are no 13C-NMR and no elemental analysis. Hence, it is very difficult to judge on the purity and quality of this compounds. Also IR or Raman spectra might be helpful to gain information about the carboxylic acid groups (on page 2 the authors speculate about the nature of the anchor group and suggest zwitterions, but strong evidences are missing).

We demonstrate the purity of **1**, **2**, and **3** by ¹H NMR and we have additionally definitively established their composition by high resolution mass spectrometry. Furthermore, we have now added ¹³C NMR spectra for the new organic ligands of **2** and **3**, as well as for complexes **2** and **3** to the Supporting Information to further establish the identity and purity of the new complexes (the synthesis of the carboxylated ligand of **1** has been previously reported). We chose to use ¹H NMR, ¹³C NMR, and HR-MS rather than elemental analysis to establish purity since the complexes are likely to co-crystallize with solvent molecules owing to their carboxylate and imidazole functional groups. Therefore, quantification of results from any CHN analysis would likely require the inclusion of some (arbitrary) quantity of solvent molecules. Work is in progress to obtain X-ray crystallographic data which would more clearly elucidate information about solvent species which co-crystallize with these complexes.

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We thank the reviewer for the suggestion about investigating carboxylic acid anchoring groups by IR or Raman spectroscopies; however, carboxylic acid anchoring groups for metal oxides are fairly well understood (from Grätzel cells and related work, as well as the Pellegrin and Odobel paper referenced in point #1 above). More in depth investigation of metal oxide anchoring is certainly important for the field in general, but it is more suitable subject matter for another manuscript and outside the scope of this work.

Following the reviewer's suggestion, we have removed the discussion of zwitterionic ligands from the main text because of its speculative nature.

3.) A very important point in my eyes is the (missing) comparison of the properties of the pure complexes 1-3 in the solid state (i.e. without solvent) with the immobilized samples. This comparison would clarify the effect of solvent, which can also cause deactivation of the excited states. Therefore, the authors should measure absorption and emission of their complexes in the solid state (powdered samples). For instance, diffuse reflectance absorption spectroscopy is a convenient method. This would help to explain, if the change in the UV-vis absorbance is caused by the solvent or by immobilization.

We thank the reviewer for this suggestion to help delineate the effect of solvent on the complexes from the effects of immobilization on the heterogeneous metal oxide. For the revised manuscript, we have measured the absorbance spectra of the solid state powders using diffuse reflectance and added this data to the Supporting Information as Figures S4 and S5. Additionally, in the revised manuscript we have presented all of the photophysical data in CH₂Cl₂, including for our surface immobilized samples, to make a consistent comparison between the surface and solution data. We note that the immobilized surfaces also open up a wide variety of solvents for investigation that would otherwise be impossible due to solubility constraints. Our preliminary results in that regard are that the effects of coordinating/non-coordinating solvents on the photophysics and photochemistry of immobilized Cu(I)bis(phenanthroline) complexes parallel what is known from solution phase work, and we are looking forward to publishing more data on this subject in the future.

4.) It is confusing that the UV-vis spectra (Fig. 1) and the amount of immobilized complex were presented for complex 1, but then the authors continue the EPR experiments with complex 3. 1 and 3 differ significantly from each other (one vs. two carboxyl groups). Therefore, the amount of immobilized 3 should also be determined by UV-vis.

On further reflection, we agree with the referee's comment regarding Figure 1. Therefore, we have moved (old) Figure 1 that compares the UV-Vis spectra of $\mathbf{1}$ in CH₂Cl₂ with that immobilized on AAO to the Supporting Information as Figure S3. Figure 1 in the revised manuscript compares the absorbance spectra of complex **3** with AAO-immobilized complex **3**, which correlates better with the EPR and TA results presented later in the manuscript.

5.) The photophysical and electrochemical properties (i.e. absorption an emission maxima, excited state lifetimes, redox potentials etc.) should be summarized in a table for all complexes. Some values are discussed in the text, but without a table it is more difficult to follow and to compare.

We have added Table S5 which summarizes the optical properties and Table S6 which summarizes the redox potentials to the Supporting Information. The kinetic data are summarized in Tables S7 and S8.

6.) Where are the cyclic voltammograms of 2 and 3 in solution? Only the CV of 1 in CH3CN is presented (Fig. S4). Furthermore, the UV-vis spectrum of 1 is given in solution, but not for 2 and 3. These spectra should be added (to the SI).

We have measured the UV-Vis and CV of **2** and **3** in solution and added this to the Supporting Information. The UV-Vis data for **3** are in the main text as Figure 1, the UV-vis data for **1** and **2** are in

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Supporting Information as Figures S3 and S4. The cyclic voltammograms for **2** and **3** in solution have been added to Figure S8 in the Supporting Information. The comparison of solution UV-Vis and CV to the immobilized response supports our conclusions regarding restrictions on geometric distortion imposed in the nanoscale confined environments, and how those plus immobilization impacts the electronic properties of the molecular species.

7.) I am very interested in the stability of the anchoring. Is any leaching of the immobilized Cu(I) complex from the heterogeneous support observed? The authors should state something about this issue in the manuscript, because it is essential for the samples immersed in CH2Cl2.

We did not observe desorption of the complexes from the metal oxide substrates during the optical, EPR, or electrochemical measurements performed in this work. We anticipate that the stability of the carboxylic acid anchoring groups on metal oxides parallels that of other carboxylic acid functionalized species such as N3 or other Ru(II) dyes for DSSCs which have been extensively discussed in the literature. In general, carboxylic acid binding to metal oxides is very stable under organic solvent conditions, less stable under aqueous conditions, and unstable in the presence of base. However, like the precise nature of carboxylate binding to metal oxide surfaces mentioned above in point #2, a detailed investigation of surface anchoring stability is outside the scope of this work and is more appropriate for a different study.

Referee: 2

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Comments to the Author

The manuscript submitted by Mulfort and coworkers requires very little commentary as it is a work of excellent scholarship and I cannot really find fault with any of it... I really enjoyed reading it and after multiple times couldn't even find any typos!

The work is extremely thorough and well executed and the SI is clear and should allow for easy reproducibility. The compounds are characterized well, one minor change I would suggest is that in complexes 2 and 3, the HRMS data is given after the NMR data whereas in complex 1 it is given prior to the NMR data. I'd simply recommend consistency in presentation.

We thank the reviewer for these positive comments and have adjusted the SI for consistent presentation.

My only hesitation with the manuscript is that it seems to follow on closely from earlier work. For example, as the authors themselves point out, charge injection characteristics of complex 3 are in agreement with the work of Chen and Stoddart (refs 5 and 21). Also, the lifetime is extended as a result of restricted flattening inside the AAO pores - similar to effects achieved in solution through the use of bulky substituents at the 2,9-position of the phen groups. Although significantly the lifetime is doubled in the pores versus the solution state lifetime which is a nice feature. It would have been nice for the casual reader to know the significance of these values... the manuscript starts by describing the motivation from moving away from Ru(bipy)3 - how do the copper complexes stack up in comparison to the more well-established ruthenium systems?

We believe ligand modification is an important tool for chemists, but it is only one of the many tools available that we can use to modulate a molecule's photophysical and photochemical properties. For example, changes to the greater chemical environment are also very important, particularly for Cu(I) complexes that are extremely responsive to their chemical environment. In this work, we are investigating the role of chemical environment *beyond* the ligand and *beyond* solvent interactions in the first coordination sphere to introduce an entirely new dimension to the factors that can be used to direct charge transfer processes. The observation that immobilizing complex **3** in pores of decreasing

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diameter results in a two-fold increase in the excited state lifetime, without any other structural modification, is quite a remarkable result! We acknowledge the reviewer's point that the excited state lifetimes of the complexes reported here do not compare with those reported for $[Ru(bpy)_3]^{2+}$ and its analogs, but that is not the goal of this work. The Cu(I) complexes reported here behave like "molecular probes" since the photophysical properties of the Cu(I)bis(phenanthroline) complexes are more responsive to their environment that the more common Ru(II)poly(pyridyl) chromophores.

Thus, based on the reviewer guidelines, I do not believe the manuscript meets the criteria to warrant publication in Chem Comm

I would recommend publication in Dalton Trans after the very minor points are addressed.

We respectfully disagree with the reviewer's assessment of the merit of this work and its meeting the high standards required to publish in *Chemical Communications*. As the reviewer stated, our "work is of excellent scholarship." The results in this manuscript demonstrate a fundamentally new strategy for controlling and directing photochemical processes. As such, we are eager to publish these exciting results in a timely manner and anticipate that these results will lead to a significant shift in thinking within the chemical community and inspire follow up research that will build on this early publication in an emerging field. Therefore, we are confident that *Chemical Communications* is the best place to publish these results.