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## Introduction

Toward the development of multi-functional molecular architectures, the structural diversity possible within transition metal coordination complexes presents an enormous potential to direct and tune the physical and chemical properties governing behavior.<sup>1–4</sup> Certainly the metal centered states guide the redox and optical properties of a complex, but the inner and outer sphere ligand environments surrounding the metal center also play a significant role in a molecule's response to external stimuli and chemical reactivity.<sup>5–13</sup> Transition metal coordinat-

# Synthesis, structure, and excited state kinetics of heteroleptic Cu(I) complexes with a new sterically demanding phenanthroline ligand<sup>†</sup>

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In this report we describe the synthesis of a new phenanthroline ligand, 2,9-di(2,4,6-tri-isopropylphenyl)-1,10-phenanthroline (bL2) and its use as the blocking ligand in the preparation of two new heteroleptic Cu(I)diimine complexes. Analysis of the CuHETPHEN single crystal structures shows a distinct distortion from an ideal tetrahedral geometry around the Cu(I) center, forced by the secondary phenanthroline ligand rotating to accommodate the isopropyl groups of **bL2**. The increased steric bulk of **bL2** as compared to the more commonly used 2,9-dimesityl-1,10-phenanthroline blocking ligand prohibits intramolecular ligand-ligand interaction, which is unique among CuHETPHEN complexes. The ground state optical and redox properties of CuHETPHEN complexes are responsive to the substitution on the blocking ligand even though the differences in structure are far removed from the Cu(I) center. Transient optical spectroscopy was used to understand the excited state kinetics in both coordinating and non-coordinating solvents following visible excitation. Substitution of the blocking phenanthroline ligand has a significant impact on the <sup>3</sup>MLCT decay and can be used to increase the excited state lifetime by 50%. Electronic structure calculations established relationships between ground and excited state properties, and general entatic state concepts are discussed for copper photosensitizers. This work contributes to the growing library of CuHETPHEN complexes and broadens the fundamental understanding of their ground and excited state properties.

> ing ligands can be used to directly link complementary functionalities (*i.e.* light absorption and catalysis) in mono- or multimetallic complexes and direct intra- *vs.* inter-molecular interactions.<sup>14</sup> Additionally, coordinating ligands will influence the dimensionality of supramolecular architectures and can be used to build up multidimensional molecular materials, coordination polymers, and extended crystalline frameworks from discrete molecules.<sup>15–25</sup> For these reasons, we are interested in developing new metal-coordinating ligands to explore their impact on molecular and supramolecular structure, ground and excited state properties, and photochemical reactivity.

> Copper(1)diimine complexes hold significant promise as earth-abundant light-absorbing modules in systems for solar energy conversion.<sup>26,27</sup> Importantly, Cu(1)bis(1,10-phenanthroline) complexes exhibit similar optical absorbance in the visible region to the more commonly used and well-understood Ru(1)tris(2,2'-bipyridyl) photosensitizers, even though the excited state lifetimes of Cu(1)(phen)<sub>2</sub> complexes are typically orders of magnitude shorter than their Ru(11) counterparts.<sup>28,29</sup> Homoleptic Cu(1)(phen)<sub>2</sub> complexes have been explored for over three decades, and early studies established key structural factors influencing the <sup>3</sup>MLCT (triplet metal-to-



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<sup>†</sup>Electronic supplementary information (ESI) available: NMR and FTIR characterization of **bL2**, **3**, and **4**; emission spectra; details of TA fitting and complete TA spectra and kinetics, supporting computational tables, figures and Cartesian coordinates. CCDC 1515480 and 1515481. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02476b

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#### Paper

ligand-charge-transfer) state properties on the sub-nanosecond and longer time scale.<sup>30–38</sup> These complexes have also been studied more recently using a variety of ultrafast optical and X-ray spectroscopies on the femtosecond and longer time scales to fully understand the factors that influence the excited state structural dynamics.<sup>39-46</sup> This work has formed the basis for a common excited state decay pathway that occurs through three distinct steps following excitation of the MLCT transition. First, light-induced formation of the <sup>1</sup>MLCT excited state is followed by a Jahn-Teller flattening distortion from the tetrahedral Franck-Condon structure in the 3d<sup>10</sup> Cu(I) ground state to accommodate the 3d<sup>9</sup> Cu(II) <sup>1</sup>MLCT state electronic configuration. The time constant for this process,  $\tau_1$ , is on the sub-picosecond time scale. Next, the <sup>1</sup>MLCT state undergoes intersystem crossing (ISC) to yield the triplet excited state (<sup>3</sup>MLCT), which usually occurs with a time constant  $(\tau_2)$  from a few to 20 picoseconds, depending on the <sup>1,3</sup>MLCT structures. Lastly, the flattened <sup>3</sup>MLCT state relaxes back to the ground state, and the kinetics of this process are highly dependent on the solvent (coordinating vs. non-coordinating) and accessibility of the Cu(II) center to solvent approach. Decay of the <sup>3</sup>MLCT state ( $\tau_3$ ) ranges from 20 ps for Cu(1)(1,10-phenanthroline)<sub>2</sub> to well over 2 µs for the highly substituted  $Cu(I)(2,9-di(t-butyl)-1,10-phenanthroline)_2^{44}$  and Cu(1)(2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenanthroline)<sub>2</sub>,<sup>47,48</sup> whose design exploits cooperative interaction between the substituents of the phenanthroline ligands.<sup>37</sup> Overall, the structural factors that influence the excited state kinetics and dynamics are quite well understood for homoleptic  $Cu(I)(phen)_2$  complexes. However, by comparison, there is a distinct lack of information regarding the excited state properties of well-defined heteroleptic  $Cu(I)(phen)_A(phen)_B$ , or CuHETPHEN, complexes.

Looking to expand the fundamental understanding of the physical properties of CuHETPHEN complexes, we recently reported the detailed characterization of the ground state and the ultrafast excited state dynamics of several CuHETPHEN model complexes.<sup>49</sup> Employing the most common strategy for CuHETPHEN synthesis, we used 2,9-dimesityl-1,10-phenanthroline as a sterically bulky blocking ligand (bL) to allow coordination of a second phenanthroline ligand (L) on which we varied the substitution adjacent to Cu(I), extended the phenanthroline conjugation, and added epoxide groups as facile handles for subsequent functionalization. We found that the excited state lifetime in acetonitrile can be tuned over two orders of magnitude within this family and is largely dictated by the steric bulk of the 2,9-substitution of L. Notably, Odobel and co-workers have made impressive use of the HETPHEN synthesis methodology in the development of linked electron donor-CuHETPHEN-acceptor triads and adsorbed CuHETPHEN sensitizers to TiO2 nanoparticles to measure charge injection in models of dye-sensitized solar cells.<sup>50–52</sup>

In this report, we have synthesized a new phenanthroline ligand and used it to access two new CuHETPHEN model complexes (Fig. 1). The new ligand increases the steric bulk at the



Fig. 1 Relevant features of CuHETPHEN complexes studied in this work. Blocking ligand (bL) shown in black and the second 1,10-phenan-throline ligand shown in blue.

2,9-phenanthroline position of bL from the typically used 2,4,6-trimethyl-phenyl (bL1) to 2,4,6-triisopropyl-phenyl (bL2). We postulated that the larger isopropyl groups of bL2 would increase the excited state lifetime of the CuHETPHEN complexes by (1) more effectively blocking solvent access to the Cu(II) center in the <sup>3</sup>MLCT state, and (2) preventing the ground state intramolecular  $\pi$ - $\pi$  interactions between phenanthroline ligands that we observed by single crystal analysis of bL1based CuHETPHEN complexes. As we will demonstrate using the new CuHETPHEN complexes based on bL2, the environment immediately surrounding the Cu(1) center influences its optical and redox properties as well as its excited state kinetics. Using electronic structure calculations, we show that entatic state concepts can be used to correlate ground and excited state properties of the CuHETPHEN complexes described here, and copper photosensitizers in general. In addition to CUHETPHEN complexes, we note that sterically crowded coordinating ligands have use in complexes of many transition metals to modify the chemical reactivity and that this new ligand could certainly find potential applications in a number of different areas.

## Results and discussion

## Ligand and CuHETPHEN synthesis

Our previous work on CuHETPHEN model complexes demonstrated that varying the steric bulk of **L** in complexes of the general formula Cu(I)(**bL1**)(**L**) dramatically influenced the excited state lifetime.<sup>49</sup> Therefore, we reasoned that increasing the steric bulk of the 2,9-substitution of **bL** would similarly influence the ground and excited state characteristics of CuHETPHEN complexes and also increase the structural diversity to select from when integrating such complexes into photocatalytic systems. The analogous 2,2'-bipyridine ligand with 6,6'-(di-2,4,6-triisopropyl-phenyl) substitution is known,<sup>53</sup> and our synthesis of the phenanthroline version proceeded similarly *via* Suzuki coupling of 2,4,6-triisopropylphenyl boronic acid and 2,9-dichloro-1,10-phenanthroline.

Using the general HETPHEN approach developed by Schmittel and co-workers,<sup>54–59</sup> we have obtained pure quantities of heteroleptic Cu(1)(**bL2**)(**L**) complexes incorporating the



Scheme 1 Synthesis of CuHETPHEN complexes. The top synthesis route follows the typical HETPHEN approach developed by Schmittel and coworkers using the  $[Cu(CH_3CN)_4](PF_6)$  reagent. The bottom synthesis route follows the approach developed by Gandhi *et al.* (ref. 60) *via* oxidation of Cu(0) in non-coordinating solvents.

new ligand bL2 (Scheme 1). The typical one-pot, two-step synthesis using the common [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) precursor proceeded flawlessly for the preparation of complex 3. However, when 2,9-dimethyl-1,10-phenanthroline (L2) was introduced to the reaction mixture containing the  $[Cu(bL2)(CH_3CN)_2](PF_6)$ intermediate, we obtained the homoleptic  $[Cu(L2)_2](PF_6)$ complex in approximately 10-20% yield. In this case, the homoleptic impurity could be cleanly separated from the desired [Cu(bL2)(L2)](PF<sub>6</sub>) by recrystallization from a dichloromethane/diethyl ether/pentane mixture. We also explored an alternative approach to CuHETPHEN synthesis where strongly coordinating solvents are excluded from the reaction mixture and one equivalent of bL2 is introduced to a suspension of Cu(0) powder in acetone in the presence of one equivalent of  $AgPF_6$ .<sup>60</sup> The  $[Cu(bL2)(OC(CH_3)_2)](PF_6)$  intermediate was then treated with the second phenanthroline ligand (L2 or L3) to generate the corresponding CuHETPHEN complex. In our hands this method resulted in exclusive formation of 4 with no contamination from the homoleptic  $[Cu(L2)_2](PF_6)$ . Complex 4 was very stable when dissolved in solvents such as dichloromethane, acetone, and methanol, but decomposed quickly in acetonitrile to form homoleptic  $[Cu(L2)_2](PF_6)$  as the major product. In attempts to use L3 as the second phenanthroline ligand and further increase the steric bulk around the Cu(I) center, we observed formation of the corresponding CuHETPHEN complex by mass spectrometry of the reaction mixture. However, the target  $[Cu(bL2)(L3)](PF_6)$  complex

decomposed quickly in all common solvents and could not be isolated. The instability of the heavily substituted [Cu(**bL2**) (**L3**)](PF<sub>6</sub>) juxtaposed with the relatively straightforward synthesis and isolation of [Cu(**bL1**)(**L3** $)](PF_6)$  that we previously described<sup>49</sup> suggests that we have approached the upper limit of 2,9-substitution possible in CuHETPHEN complexes.

## Single crystal structural characterization

The single crystal X-ray structures of the two new CuHETPHEN complexes 3 and 4 are shown in Fig. 2. The crystallographic data are summarized in Table 1, and selected interatomic bond lengths and angles are listed in Table 2. Both compounds crystallize in the space group  $P2_1/c$ . The asymmetric unit of 3 is occupied by one CuHETPHEN molecule and one dichloromethane molecule, and that of 4 is occupied by two independent CuHETPHEN molecules and two diethyl ether molecules. The average Cu-N bond length of 3 and 4 is very similar to that previously reported for 1 and 2 ( $\approx 2.05$  Å). However, more interesting are the individual bond lengths of complexes 3 and 4 containing bL2. The Cu-N distances are relatively similar toward bL2 (2.04–2.07 Å) whereas the Cu–N distances towards L skew unusually short (<2.01 Å) for one bond and unusually long (>2.08 Å) for the other. The longest Cu-N bond length in this series, 2.13 Å, is found in 4. This long Cu-N bond is likely the main contribution to the instability of 4 in the strongly coordinating solvent acetonitrile, and why the even more sterically congested complex  $[Cu(bL2)(L3)](PF_6)$ 



Fig. 2 Top: X-ray crystal structures of complexes 3 (A) and 4 (B). Ellipsoids represent 50% probability. Hydrogen atoms, solvent molecules, and counterions are omitted for clarity. Carbon, gray; nitrogen, blue; copper, orange. Bottom: Views along the phenanthroline plane of **bL2** illustrate ligand distortion from tetrahedral geometry around Cu(I) center in 3 (C) and 4 (D). **bL2**, light gray; L, black; copper, orange.

Table 1 Crystallographic data for complexes 3 and 4

Complex	3	4
Formula	C55H62Cl2CuF6N4P	C60H74CuF6N4OP
$M_{\rm w}$ (g mol <sup>-1</sup> )	1058.51	1075.77
Lattice type	Monoclinic	Monoclinic
Space group	P21/c	P21/c
a (Å)	12.2043(8)	22.851(9)
$b(\dot{A})$	22.7956(14)	19.517(7)
c (Å)	18.6567(12)	25.628(9)
$\alpha \beta \gamma (\circ)$	90.00/93.2555(9)/90.00	90.00/90.164(5)/90.00
$V(Å^3)$	5182.0(6)	11 430(7)
Z	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-1})$	1.357	1.250
T (K)	100	100
λ (Å) [Mo Kα]	0.71073	0.71073
$\mu (mm^{-1})$	0.618	0.472
S (GOF)	0.999	1.090
$R(F_{\rm o}), wR(F_{\rm o}^{2})$	0.037, 0.105	0.082, 0.21

could not be isolated. Similar stability issues were previously reported for the homoleptic complexes containing the bulky 2,9-di-*tert*-butyl-1,10-phenanthroline ligand, where crystal structures of this compound revealed a Cu–N bond longer than 2.14 Å.<sup>60</sup>

Our group and others have shown that CuHETPHEN complexes based on **bL1** contain a considerable distortion from the tetrahedral geometry expected for Cu(1)diimine complexes. This distortion is directed by  $\pi$ - $\pi$  interaction between one

Table 2 Selected bond length, bond angles, and geometry index parameter  $\ensuremath{s_4}$ 

		4			
Complex	3	Molecule A	Molecule B		
Selected bond lo	ength				
Cu1-N1	2.0445(9)	2.126(6)	1.997(5)		
Cu1-N2	2.0053(9)	2.005(5)	2.105(6)		
Cu1-N3	2.0614(8)	2.073(5)	2.070(5)		
Cu1-N4	2.0852(9)	2.051(5)	2.056(6)		
Selected bond a	ngles				
N2-Cu1-N1	138.52(4)	81.7(2)	82.3(2)		
N2-Cu1-N4	132.68(4)	133.4(2)	112.9(2)		
N1-Cu1-N4	81.81(3)	109.5(2)	137.7(2)		
N2-Cu1-N3	82.64(4)	136.6(2)	108.6(2)		
N1-Cu1-N3	109.45(3)	114.7(2)	131.5(2)		
N4-Cu1-N3	109.84(4)	81.0(2)	82.7(2)		
$s_4$ values					
-	0.630	0.638	0.644		

mesityl group of bL1 and the B-ring of the secondary phenanthroline ligand (L) and results in the so-called "pac-man" motif (Fig. 3).49,61 In contrast, CuHETPHEN complexes of the general formula [Cu(**bL1**)(2,2'-bipyridyl)](PF<sub>6</sub>), where 2,2'-bipyridine or an analog replaces 1,10-phenanthroline as L, do not show this sort of preferential interaction. Rather, these structures reveal two total  $\pi$ - $\pi$  interactions, one between each mesityl group of **bL1** and the second ligand, resulting in the bipyridine being "clamped" in the middle of the mesityl groups ("clamped down" motif, Fig. 3). The crystal structures of 3 and 4 clearly demonstrate that introducing isopropyl groups instead of methyl groups in bL results in a new type of motif where all inter-ligand  $\pi$ - $\pi$  interactions are prohibited by the very bulky isopropyl groups of bL2 ("centered" motif, Fig. 3). The distortion of the new CuHETPHEN complexes was quantified using the geometry index parameter  $s_4$ :

$$s_4 = \frac{360^\circ - a - b}{141^\circ} \tag{1}$$

where *a* and *b* represent the largest angles in the four coordinate geometry.<sup>62</sup> For a perfect square planar geometry,  $s_4 = 0$ , and for a perfect tetrahedral structure  $s_4 = 1$ . Analysis of complexes **3** and **4** reveals a greater distortion from tetrahedral geometry (0.63 and 0.64, respectively) in comparison to the



Fig. 3 Spacefilling diagrams of complexes  $Cu(mes_2bpy)(bpy)(BF_4)$ , 1, and 3, illustrating "clamped-down", "pac-man", and "centered" interactions between hetero-ligands coordinated to Cu(I).

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**bL1** containing compounds **1** and **2** (0.69 and 0.65, respectively). The coordination deviation in **3** and **4** cannot simply be described by the relative angle of ligand planes as for homoleptic complexes, as they introduce a distortion which may simply lower the symmetry from pseudo- $D_{2d}$  found in homoleptic complexes to a  $C_s$  symmetry. As with the  $[Cu(bL1)(L)](PF_6)$  complexes that we have previously analyzed, changes of L in  $[Cu(bL2)(L)](PF_6)$  had a relatively minor effect on  $s_4$ . In the CuHETPHEN complexes, **bL** determines not only the geometry of the ground state but also the ability to adopt a relaxed geometry in the excited state, both factors that contribute to the observed photophysics.

## **Electrochemical properties**

The electrochemical behavior of CuHETPHEN complexes containing **bL2** was measured by cyclic voltammetry in dichloromethane (Fig. 4). The Cu( $\pi/\pi$ ) oxidation potentials are well behaved and reversible for each CuHETPHEN complex studied here and are summarized in Table 3. The least sterically congested complex **1** was oxidized at the lowest potential, 0.77 V vs. SCE. As previously demonstrated for Cu( $\pi/\pi$ ) center leads to a more positive oxidation potential, but the magnitude of increase varied with each phenanthroline ligand (**bL** vs. **L**). Increasing the steric bulk of **bL** results in only a small increase in the Cu( $\pi/\pi$ ) oxidation potential (30–50 mV), whereas increas-



**Fig. 4** Cyclic voltammograms of 1 mM **1–4** in 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> comparing Cu( $_{||}$ ) oxidation potentials. Potential is referenced to SCE using ferrocene as an internal standard.

ing the 2,9-substitution of L from hydrogen to methyl increased the Cu( $\pi/\tau$ ) oxidation potential by ~200 mV. As a result, complex 4 was found to be the most difficult to oxidize at 1.01 V vs. SCE.

## Absorption and emission spectroscopy

The UV-Vis absorption spectra of complexes 1-4 were measured in dichloromethane and are shown in Fig. 5 and summarized in Table 3. All complexes exhibit a broad absorption band around 460 nm, which is associated with MLCT from Cu(1) to the phenanthroline ligands. We observe a blue shift of the MLCT band in response to increasing steric hindrance around the Cu(I) center by modifying both bL and L. For example, changing from bL1 to bL2 and keeping L constant resulted in a 6 nm blue shift between the L1 containing complexes 1 and 3 and a 15 nm shift between the L2 containing complexes 2 and 4. The difference in MLCT peak maximum between the complexes carrying **bL1** is smaller than the complexes containing bL2 (7 nm vs. 16 nm). We found a strong correlation between the sterics of the CuHETPHEN complexes and their absorption intensities. The least sterically congested complex 1 absorbs most strongly in the visible, and complex 4, carrying the bulkiest substituents, most weakly. Additionally, complexes 1 and 3 have a small shoulder on the low-energy side of the main MLCT absorbance peak centered around 550 nm. Both the decrease in extinction coefficient and the low-energy shoulder are correlated with increasing static or dynamic distortion from tetrahedral geometry. 45,63,64

To understand the impact of **bL2** on the excited state properties, the emission spectra of **1–4** were measured at room



Fig. 5 UV-Vis absorption spectra of complexes 1-4 in dichloromethane.

 Table 3
 Summary of redox and optical characteristics of CuHETPHEN 1-4 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. nd = not detected

Complex	$E(\operatorname{Cu}^{2+/+})$ (V vs. SCE)	$\lambda_{\max}$ (MLCT, nm)	$\varepsilon (M^{-1} cm^{-1})$	Emission max (nm)	$E_{00}$ , eV	$E(\operatorname{Cu}^{2+/+}*)$ (V vs. SCE)
1	+0.77	467	7326	nd	_	_
2	+0.96	460	5631	686	2.22	-1.26
3	+0.80	461	5253	nd	_	_
4	+1.01	445	4175	671	2.21	-1.20

temperature in dichloromethane (Fig. S1†). Complexes 1 and 3 carrying the unsubstituted phenanthroline ligand L1 showed no measurable emission at room temperature following excitation of the MLCT band, which has been noted previously for relatively unsubstituted CuHETPHEN complexes.<sup>38</sup> However, when the steric bulk near the Cu(1) center is increased by coordination of L2, as in complexes 2 and 4, we observe weak emission spectra following MLCT excitation. We estimate that the quantum yield is rather low, on the order of  $10^{-4}$ , comparable to other Cu(1)dimine complexes with similar ligand substitution.<sup>38,65</sup> For complexes 2 and 4 in non-coordinating solvent, the excited-state energy,  $E_{00}$ , is determined by extending a tangent from the blue side of the emission to y = 0 and the excited state reduction potential can then be calculated using eqn (2):

$$E(\mathrm{Cu}^{2+/+*}) = E(\mathrm{Cu}^{2+/+}) - E_{00}$$
(2)

The excited state reduction potentials of **2** and **4** are similar, -1.26 and -1.20 V vs. SCE, and in good agreement with values previously reported for homoleptic and hetero-leptic Cu(1)diimine complexes.<sup>38,48,49</sup>

#### Transient absorption spectroscopy

To understand the excited state kinetics of CuHETPHEN complexes 1–4, we performed room temperature ultrafast (femtosecond) and nanosecond transient absorption spectroscopy in both methanol and dichloromethane as representative coordinating and non-coordinating solvents. Overall, the TA spectra of 1-4 in both solvents resemble those typically found of Cu(1)diimine complexes,48,49,51,66 and the spectra of 3 and 4 in methanol are shown in Fig. 6 to illustrate the relevant features. Immediately following excitation of the MLCT band at 415 nm, we observe a negative feature at 460 nm associated with the ground state bleach and a broad positive excited state absorption feature centered at 550 nm that is correlated with the formation of a Cu(II)-based <sup>1</sup>MLCT charge separated state. In the first few picoseconds, this broad positive feature transitions into a well-resolved split vibronic feature, with peaks centered at 514 and 554 nm, which is attributed to the radical anion spectra of the phenanthroline ligands. This vibronic feature in the MLCT state then decays to the ground state on the nanosecond time scale. The kinetics of the ground state bleach and excited state absorption features were modeled using a global fit to a tri-exponential decay function, with the three time constants corresponding to: Jahn-Teller distortion (flattening) in the <sup>1</sup>MLCT Cu(II) excited state ( $\tau_1$ ); ISC from <sup>1</sup>MLCT to <sup>3</sup>MLCT  $(\tau_2)$ ; and <sup>3</sup>MLCT decay to the ground state  $(\tau_3)$ . A summary of the kinetic parameters for all CuHETPHEN complexes in both solvents is given in Table 4 and fitting details are in the ESI.†

The excited state kinetics of CuHETPHEN complexes are readily modulated by both solvent and ligand substitution, as



Fig. 6 Comparison of ultrafast transient absorption spectra of CuHETPHEN (A) 3 and (B) 4 following 415 nm excitation in methanol. Left panels depict early transient spectra up to 10 ps; right panels show transient spectra from 50–3000 ps.

Complex	CH <sub>2</sub> Cl <sub>2</sub>			CH <sub>3</sub> OH		
	$\tau_1 (ps)$	$ au_2 (\mathrm{ps})$	$\tau_3$ (ns)	$\overline{\tau_1(\mathrm{ps})}$	$ au_2 (\mathrm{ps})$	$\tau_3$ (ns)
1	$0.32 \pm 0.01$	$18.3 \pm 0.2$	$3.43 \pm 0.06$	$0.18 \pm 0.01$	$18.0 \pm 0.1$	$1.18 \pm 0.02$
2	$0.31 \pm 0.01$	$18.0 \pm 0.1$	$46.8 \pm 0.3$	$0.22 \pm 0.01$	$19.0 \pm 0.2$	$24.7 \pm 0.2$
3	$0.29 \pm 0.01$	$20.5 \pm 0.8$	$4.05 \pm 0.07$	$0.21 \pm 0.01$	$20.8 \pm 0.2$	$1.85\pm0.05$
4	$0.35\pm0.01$	$25.0\pm0.7$	$68.2 \pm 0.4$	$0.20\pm0.01$	$24.9\pm0.5$	$35.6\pm0.3$

Table 4 Summary of excited state kinetics for CuHETPHEN 1-4 in non-coordinating (CH<sub>2</sub>Cl<sub>2</sub>) and coordinating (CH<sub>3</sub>OH) solvents

has been demonstrated for homoleptic Cu(I)diimine complexes. The excited state kinetics of 1-4 in the coordinating solvent methanol show an interesting response to ligand structural modifications. Within the temporal resolution of our ultrafast TA set-up, we do not observe a difference in the earliest decay component,  $\tau_1$ , which suggests that the time scale of the Jahn-Teller distortion following <sup>1</sup>MLCT generation is not influenced dramatically in 1-4 by either the 2,9-substitution of L or increasing the steric bulk of bL from trimethyl to triisopropyl. However, given that the values of  $\tau_1$  reported in Table 4 are within the instrument response function of our ultrafast TA set-up, we cannot unambiguously rule out the possibility that the true values are shorter or have some meaningful variation on the sub-300 fs timescale. The second decay component,  $\tau_2$ , which is attributed to ISC to generate the <sup>3</sup>MLCT state, does show a small positive correlation with steric bulk. The least substituted CuHETPHEN 1 has the shortest decay component ( $\tau_2$  = 18.0 ps) and the most heavily substituted CuHETPHEN 4 has the longest decay component ( $\tau_2$  = 24.9 ps). Unlike the other kinetic components, decay from the <sup>3</sup>MLCT state does show a significant dependence on the ligand sterics. As documented in recent review articles,  $^{28,45}$   $\tau_3$ increases substantially when increasing the substitution at the 2,9-position of L; we observe an approximately 20-fold increase in <sup>3</sup>MLCT lifetime in going from hydrogen to methyl substitution (comparing 1 vs. 2 and 3 vs. 4). The effect of bL sterics on <sup>3</sup>MLCT lifetime is less dramatic (comparing 1 vs. 3 and 2 vs. 4), but there is still an increase in lifetime of about 50% in going from bL1 to bL2, demonstrating that even the remote ligand structural features influence excited state kinetics.

Ultrafast transient absorption studies have proven that the <sup>3</sup>MLCT state of Cu(I)diimine complexes has some interaction with solvent molecules when the metal center is sufficiently exposed to allow solvent molecule access, and X-ray transient absorption studies have suggested solvent "ligation" with the excited state which can be transiently formed with coordinating solvent molecules.40,41,67,68 Therefore, in this work we measured the excited state kinetics for 1-4 in a non-coordinating solvent (dichloromethane) and a coordinating solvent (methanol) to understand how the ligand modifications influence solvent access and excited state kinetics. The Jahn-Teller distortion in the Cu(II) <sup>1</sup>MLCT state is slightly slower in dichloromethane than in methanol ( $\tau_1 \sim 0.3$  ps in CH<sub>2</sub>Cl<sub>2</sub>, ~0.2 ps in  $CH_3OH$ ), which could be a result of better charge stabilization in a polar solvent such as methanol as opposed to the relatively non-polar dichloromethane. Again we note

that these values are not entirely reliable, as they are shorter than the ~0.3 ps instrument response of our spectrometer. Interestingly, the time constant attributed to ISC is nearly identical for each complex in both solvents, suggesting that the singlet-triplet gap is solvent independent as observed for homoleptic complexes, where both Jahn-Teller distortion and ISC are solvent-independent inner shell processes.<sup>41</sup> As noted previously for Cu(1)diimine complexes, the <sup>3</sup>MLCT decay is highly solvent dependent.<sup>43</sup> The <sup>3</sup>MLCT decay lifetime of 1–4 in methanol follows a similar trend as in dichloromethane, but the  $\tau_3$  values are two to three times shorter. This behavior can be explained by variations in solvent accessibility based on **bL** and **L** sterics (as discussed above) and the potential for interaction with coordinating solvent molecules that accelerates <sup>3</sup>MLCT-state decay.

#### **Electronic structure calculations**

DFT calculations were carried out to gain further insight into the ground and excited state properties of the CuHETPHEN complexes reported here and in a previous study.<sup>49</sup> Their structures are given in Fig. S40.† Here, electronic structure calculations are used to establish connections between the ground state redox potentials and the excited state lifetimes of copper photosensitizers.

Redox potentials were calculated from the adiabatic ionization energies as described in the Experimental section and are given in Table 5. While the absolute calculated value is sensitive to the amount of Hartree–Fock exchange in the functional, best agreement between theory and experiment for the relative potentials was found using BP86. The correlations between the calculated and experimental  $E^{\circ}s$  are given in Fig. 7A. Linear correlations were found for two groups of ligand combinations. The first group consists of complexes **1**, **2**, and Cu(**bL1**)(**L3**) (black circles throughout Fig. 7,  $R^2 = 0.96$ ) and the second group consists of the complexes **3**, **4**, and Cu(**L1**)<sub>2</sub> (red circles in Fig. 7,  $R^2 > 0.99$ ).

Table 5 summarizes the DFT-calculated redox potentials, singlet-triplet energy gaps, and reorganization energies for the CuHETPHEN complexes presented here, as well as for Cu(I) (**bL1**)(**L3**)<sup>49</sup> and Cu(I)(**L1**)<sub>2</sub>. We observe linear correlations between the calculated ground state (GS)-<sup>3</sup>MLCT energy gaps and the calculated  $E^{\circ}$ s ( $R^2 = 0.90$  for group 1 and >0.99 for group 2), as well as between the calculated GS-<sup>3</sup>MLCT gaps and the experimental  $E^{\circ}$ s (Fig. S41,†  $R^2 = 0.98$  and >0.99 for group 1 and 2, respectively). This correlation is largely expected

Table 5 Summary of the DFT calculated redox potentials, singlet-triplet energy gaps, and reorganization energies of selected CuHETPHEN complexes

Complex	<i>E</i> (Cu <sup>2+/+</sup> ) (V <i>vs.</i> SCE)	$\Delta E^{\circ a}$ (eV)	Energy gap (eV)	$\lambda_{i}$ (eV)	$\lambda_{\rm i}  ({\rm kcal \ mol}^{-1})$	Ligand repulsion (kcal mol <sup>-1</sup> )	$\Delta$ (kcal mol <sup>-1</sup> )
1	+1.01	-0.37/-0.26	1.54	0.74	17.2	2.0	15.2
2	+1.10	-0.18/-0.17	1.81	0.44	10.1	2.7	7.4
Cu(1)(bL1)(L3)	$+1.27^{b}$	0/0	1.97	0.37	8.5	2.8	5.7
3	+1.10	-0.34/-0.17	1.67	0.69	15.9	2.2	13.7
4	+1.17	-0.13/-0.10	1.83	0.38	8.7	3.1	5.5
$Cu(I)(L1)_2$	$+0.91^{c}$	-0.95/-0.35	1.36	0.63	14.6	1.4	13.2

<sup>a</sup> X/Y, where X and Y are the experimental and calculated E<sup>0</sup> differences relative to Cu(1)(**bL1**)(**L3**). <sup>b</sup> From ref. 49. <sup>c</sup> From ref. 43.



Fig. 7 Correlations between DFT calculations and experiment. (A) Linear relationships between experimental and calculated  $E^{\circ}s$ ; (B) linear relationships between GS- ${}^{3}$ MLCT energy gap and the calculated  $E^{\circ}s$ , and (C) linear relationships between the experimental  $E^{\circ}s$  and  $\ln(r_{3})$  in non-coordinating solvents. Group 1 (complexes 1, 2, and Cu(bL1)(L3)) and group 2 (complexes Cu(L1)<sub>2</sub>, 3, and 4) are colored black and red, respectively.

since the formation of the charge separated <sup>3</sup>MLCT state involves formal oxidation of the Cu center.

Given the good correlation between the GS-<sup>3</sup>MLCT energy gap and  $E^{\circ}$ , it is also interesting to consider a potential correlation between  $E^{\circ}$  and the <sup>3</sup>MLCT excited state lifetime,  $\tau_3$ ,  $\tau_3$  is related to the non-radiative decay of the <sup>3</sup>MLCT state, and thus should depend exponentially on the energy of the <sup>3</sup>MLCT state. Plots of the experimental  $\ln(\tau_3)$  (in DCM) vs. the calculated GS-<sup>3</sup>MLCT gaps are given in Fig. S42,† and again we observe good linear correlations ( $R^2 > 0.99$  and 0.98 for group 1 and 2, respectively). We also observe a roughly linear relationship between  $E^{\circ}$  and  $\ln(\tau_3)$  based upon both calculated  $E^{\circ}$  (Fig. S43,  $\dagger R^2 = 0.90$  and 0.97 for group 1 and 2, respectively) and experimental values (Fig. 7C,  $R^2 = 0.98$  and 0.95, respectively). Thus, the experimental data and electronic structure calculations establish a direct correlation between the ground state redox potential (E°) and the excited state lifetime of copper-based photosensitizers ( $\tau_3$ ).

The observation that groups based on **bL1** or **bL2** show different slopes in the correlation between  $E^{\circ}$  and  $\tau_3$  strongly indicates that the blocking ligand in CuHETPHEN complexes induces a different relationship between the ground and excited state properties. This too is not entirely unexpected since the crystal structures reveal different intramolecular ligand–ligand interactions (see Fig. 3). In **1** and **2**, which contain **bL1**, we observe the "pac-man" motif which has strong  $\pi$ – $\pi$  interaction between one mesityl group and the secondary phenanthroline. In 3 and 4, which contain **bL2**, the isopropyl substitution prevents intramolecular ligand–ligand interaction completely and yields the "centered" motif. Also, the absence of  $\pi$ – $\pi$  stacking in Cu(L1)<sub>2</sub> is likely why it correlates well with group 2 (**bL2**-containing CuHETPHEN) and we reason that Cu(I)(**bL1**)(L3) must have some intramolecular ligand–ligand interactions since it correlates well with group 1. The ligand set dependence is the subject of a future study to encompass a wider range of copper photosensitizers.

Structural contributions to the redox properties of copper complexes have been studied in detail;<sup>69-71</sup> however, a few useful observations are made here in the context of the entatic state<sup>72-74</sup> and its contributions to redox properties of copper complexes and electron transfer proteins.75,76 In the entatic state description, the ligand architecture or protein matrix imposes an 'energized' structure on the metal center, which in turn tunes the electronic structure for a specific function. One example of the entatic state in bioinorganic chemistry is the type one Cu proteins (e.g., plastocyanin), where the protein matrix enforces the weak Cu-S(Met) bond in both oxidized and reduced states and constrains the copper site to be pseudo-tetrahedral in both oxidized and reduced states (the latter contribution is relevant here). These structural constraints can increase the redox potential by ~500 mV while also significantly limiting the inner-sphere reorganization

energy ( $\lambda_i$ ) by eliminating the Jahn–Teller distortion upon oxidation.<sup>75</sup> Likewise, we propose that the ligand architectures of CuHETPHEN complexes can be utilized to apply entatic state concepts to tune the ground state redox potential ( $E^\circ$ ) and thus excited state lifetimes ( $\tau_3$ ).

In general, the energy of the entatic state can be difficult to measure, but for Cu complexes it can be estimated by considering the total inner-sphere reorganization energy,  $\lambda_i$ . Interestingly, we find the largest values for  $\lambda_i$  with 1, 3, and  $Cu(L1)_2$  (~17, 16, and 15 kcal mol<sup>-1</sup>, respectively), and the smallest values for 2, Cu(bL1)(L3), and 4 ( $\sim$ 10, 9, and 9 kcal mol<sup>-1</sup>, respectively). These can be grouped into complexes with no substitution on L (large  $\lambda_i$ ) or 2,9-dimethyl or di-sec-butyl on L (small  $\lambda_i$ ). We can understand the reorganization/entatic energies as a contribution from the second coordination sphere ligand-ligand interactions (*i.e.*, repulsion and  $\pi$ - $\pi$  stacking, largely governed by bL) and the first coordination sphere Cu-N bonding (i.e., bond-distances and angles, largely governed by 2,9-L substitution). The ligand-ligand interactions are a relatively minor component of  $\lambda_i$ , ~1.4–3.1 kcal mol<sup>-1</sup>, and the two extremes are represented by  $Cu(L1)_2$  (1.4 kcal mol<sup>-1</sup>) and 4  $(3.1 \text{ kcal mol}^{-1})$ . The changes in the first coordination sphere Cu-N bonding represent a large fraction of the total reorganization energies, where lower values are found for complexes that have large entatic constraints, which constrain the geometry to be pseudo-tetrahedral in both oxidized and reduced states.

Given these reorganization energies, we can roughly estimate the calculated entatic energy contributions to ground state redox for 2,9-phenanthroline substitution by comparing the total inner sphere reorganization energies of any complex to the Cu(L1)<sub>2</sub> reference (calculated  $\lambda_i = 14.6 \text{ kcal mol}^{-1}$ ). Relative to Cu(I)(L1)<sub>2</sub>,  $\lambda_i$  for 2 is ~6 kcal mol<sup>-1</sup> lower in energy, while it is  $\sim 7.5$  kcal mol<sup>-1</sup> lower in energy for both Cu(**bL1**) (L3) and 4. Thus, the entatic contribution across these ligand sets is  $\sim$ 6–7 kcal mol<sup>-1</sup>. Note that this value will likely be sensitive to computational methodology and is thus a preliminary estimate; however, future experimental and computational efforts will help define the ground state entatic energies of copper photosensitizers and how well these can be correlated to excited state reorganization energies for <sup>3</sup>MLCT formation. Interestingly, our estimated energy of entatic contribution  $(\sim 6-7 \text{ kcal mol}^{-1})$  is similar to ground state entatic energies estimated for bioinorganic and heterogeneous systems, including type one Cu proteins,<sup>77</sup> the O<sub>2</sub> binding type three binuclear copper proteins,<sup>78</sup> a methane oxidizing zeolite (Fe-ZSM-5),<sup>79</sup> and horse heart cytochrome c.80 Future studies will involve experimental measurements of ground and excited state enatic contributions from different ligand architectures for comparison to excited state lifetimes.

## Conclusions

Here we have described the synthesis of a new phenanthroline ligand (**bL2**) with sterically-demanding 2,4,6-tri-isopropyl-phenyl groups appended to the 2,9-phenanthroline positions.

ment of transition metal complexes whose properties are dependent on controlling small molecule access to the metal site. To demonstrate this effect, we synthesized two new heteroleptic Cu(I)diimine complexes using bL2 to prevent homoleptic coordination in place of the more commonly used bL1, which features 2,9-mesityl substitution. Analysis of the single crystal X-ray structures clearly shows that the increase in steric bulk of bL2 positions the secondary phenanthroline ligand in a more "centered" configuration and prevents the inter-ligand  $\pi$ - $\pi$  interaction which is observed in CuHETPHEN complexes containing **bL1**. The substitution of **bL2** for **bL1** in CUHETPHEN complexes results in moderate changes to the ground state redox and optical properties. With the increased steric bulk of bL2, the Cu(1/II) oxidation potential increases slightly (30-50 mV), and the MLCT absorption band shifts to slightly higher energy (5-6 nm) but decreases in intensity by approximately 30%. The excited state reduction potential of CUHETPHEN 4 is -1.20 V vs. SCE, aligned with that reported for related Cu(1)diimine complexes, and is notably a much stronger photoreductant than the common photosensitizer Ru(bpy)<sub>3</sub><sup>2+,81</sup> Transient optical spectroscopy was used to determine the excited state kinetics of the CuHETPHEN complexes in methanol and dichloromethane as representative coordinating and non-coordinating solvents. In general, the blocking ligand does not have a dramatic effect on the early kinetics, which are attributed to the flattening distortion in the <sup>1</sup>MLCT state  $(\tau_1)$  and ISC  $(\tau_2)$ . However, the lifetime of the <sup>3</sup>MLCT excited state increases by ~50% from CuHETPHEN complexes containing **bL1** to those with **bL2**, indicating that the change from methyl to isopropyl substitution, even far removed from the copper center, influences how solvent molecules interact with the metal site and thereby affect photophysical properties, as well as the dynamics of the first and second coordination spheres. DFT calculations established relationships between the ground state reduction potential and the excited state lifetime; these relationships were rationalized using entatic state concepts. In summary, this work adds to the growing library of CuHETPHEN complexes and the fundamental understanding of their ground and excited state properties. Current research is focused on the integration of CuHETPHEN complexes into molecular systems based on earth-abundant elements for light-harvesting and solar energy conversion.

We anticipate that this ligand will be useful in the develop-

## Experimental

## General materials and methods

All reagents and solvents were purchased from commercial sources and were used as received. Complexes 1 and 2<sup>49</sup> and 2,9-dichloro-1,10-phenanthroline<sup>82</sup> were prepared following previously published procedures.

<sup>1</sup>H NMR was performed on a Bruker DMX 500 and referenced to TMS or residual solvent peaks. ESI-MS was collected on a ThermoFisher LCQ Fleet from dilute methanol solutions in positive ionization mode. FTIR spectroscopy was performed

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#### Paper

on a Thermo Nicolet 6700 spectrophotometer in the region 400–4000 cm<sup>-1</sup>, with a resolution of 2 cm<sup>-1</sup> and averaging over 32 scans. Samples were dissolved in dichloromethane and a drop of the sample solution was added to a Real Crystal® KBr sample card; spectra were collected after complete evaporation of the solvent. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN, USA). UV-Vis absorption measurements were performed on a Beckman Coulter DU800 spectrophotometer. Steady state emission spectra were measured on a Quantamaster spectrophotometer from Photon Technology International; each sample was dissolved in spectrophotometric grade dichloromethane and thoroughly deaerated with  $N_2$ .

## Cyclic voltammetry

Cyclic voltammetry was conducted using a standard three-electrode cell on a BioAnalytical Systems (BAS) 100B potentiostat and cell stand with a 3 mm-diameter glassy carbon working electrode, a Pt wire auxiliary electrode, and a pseudo Ag/AgCl reference electrode (1.5 mm diameter Ag wire coated with AgCl). Each solution in anhydrous dichloromethane was purged with N<sub>2</sub> prior to measurement and maintained under a blanket of N<sub>2</sub> during measurement. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Ferrocene (purified by sublimation) was added as an internal standard and redox potentials were referenced to the ferrocene/ferrocenium couple (0.46 V  $\nu s$ . SCE (dichloromethane)).<sup>83</sup> All scans were performed at 100 mV s<sup>-1</sup>.

## Single crystal X-ray diffraction

Crystals suitable for single crystal X-ray diffraction measurements were affixed to glass micropipettes using a quick drying two-part epoxy and their diffraction patterns collected on a Bruker SMART diffractometer equipped with an APEXII CCD detector using Mo K<sub> $\alpha$ </sub> radiation. An Oxford Cryosystems 700 series cryostat was used for controlling the sample temperature. Data were corrected for absorption using SADABS.<sup>84</sup> Structure solutions and structure refinements on  $F^2$  were carried out using SHELXS<sup>85</sup> and SHELXL, respectively. The crystal structures of 3 and 4 are deposited at the Cambridge Crystallographic Data Centre as structures 1515480 and 1515481.<sup>†</sup>

## Transient absorption spectroscopy

Femtosecond transient absorption measurements were performed using an amplified Ti:sapphire laser system (Spectra Physics, Spitfire Pro) and an automated data acquisition system (Ultrafast Systems, Helios). The amplifier was seeded with the 100 fs output from the oscillator (Spectra Physics, Mai Tai) and was operated at 1.0 kHz, giving 3 mJ pulses centered at 830 nm. The beam was split 90/10, with the weaker beam being used to generate the white light continuum probe. The probe beam was delayed relative to the pump with a retroreflector mounted on a motorized delay stage and focused into a sapphire plate to generate a white light continuum spanning 420 to 650 nm. The continuum probe was focused to a spot size of 200 µm at the sample and subsequently focused into a

fiber optic coupled to a multichannel spectrometer and CMOS sensor. The other 830 nm beam was focused into a BBO crystal to generate the 415 nm pump beam used for the pump-probe measurements. This beam was passed through a depolarizer, chopped at 500 Hz, focused at the sample position to a spot size of 400  $\mu$ m, and attenuated to a pulse energy of 0.5  $\mu$ J. Transient absorption spectra were collected using the Helios control software. The data were corrected for temporal chirp in the probe beam using the separately collected nonresonant response of the blank solvent. The nonresonant response gave an instrument response time of approximately 300 fs. All experiments were performed at room temperature with constant stirring with samples in 2 mm quartz cuvettes that had been bubbled with nitrogen.

Nanosecond transient absorption spectroscopy was measured at the Center for Nanoscale Materials at Argonne National Laboratory using an amplified Ti:sapphire laser system (Spectra Physics, Spitfire Pro) and an automated data acquisition system (Ultrafast Systems, EOS). The amplifier was seeded with the 120 fs output from the oscillator (Spectra Physics, Tsunami) and was operated at 1.0 kHz for EOS. The output from the amplifier was split 90/10 with the majority used to pump an optical parametric amplifier (TOPAS) which provided the pump beam. For EOS experiments, a supercontinuum light source (Ultrafast Systems) was used for the probe.

## **Computational methods**

All DFT calculations were carried out using Gaussian 09, revision A.01,<sup>86</sup> software installed on the Blues or Fusion clusters at Argonne National Laboratory. Geometry optimizations (reduced, oxidized, and triplet structures) were carried out using the BP86 functional<sup>87-89</sup> (spin unrestricted for paramagnetic states), in combination with a split basis set (6-311G(d) for Cu and N, 6-31G(d) for C and H).90-92 Frequency calculations were carried out to ensure structures represented energetic minima. Single point energy calculations were carried out using the BP86 functional, but with a higher level split basis set (6-311+G(d) for Cu and N, 6-311G(d) for C and H). Solvation (dichloromethane) was included using the polarized continuum model (PCM).93 Standard reduction potentials (E°s vs. SCE) were calculated from the adiabatic ionization energies (*i.e.*, the difference in energy between the optimized oxidized and reduced structures) by subtracting 4.642 eV to correct the energy difference to vacuum. Total energies for  $E^{\circ}$  calculations have been enthalpy corrected using the results of frequency calculations on fully optimized structures. Note that several functionals were tested for  $E^{\circ}$  calculations and all results were qualitatively the same; however, best agreement between theory and experiment was found for BP86, and these results are discussed above. Results for the other functionals are provided in the ESI Table S1.<sup>†</sup> Inner sphere reorganization energies  $(\lambda_i)$ upon single electron oxidation were calculated as  $\lambda_i = \lambda_{ox} + \lambda_{red}$ ,  $(\lambda_{ox} = E(ox)(red) - E(ox)(ox) and \lambda_{red} = E(red)(ox) - E(red)(red),$ where E(1)(2) refers to the calculated energy of a molecule in the geometry of (2) and the oxidation state of (1)).<sup>69,70</sup>

#### Synthesis

2,9-Bis(2,4,6-triisopropylphenyl)-1,10-phenanthroline (bL2). 2,9-Dichloro-1,10-phenanthroline (0.38 g, 1.53 mmol), 2,4,6triisopropylphenylboronic acid (1.00 g, 4.03 mmol) and Ba (OH)<sub>2</sub>·8H<sub>2</sub>O (3.5 g, 11.09 mmol) were placed in a pressure tube. A dioxane/water mixture (16 mL, 3:1) was added and the reaction was deaerated for 15 minutes.  $Pd(PPh_3)_4$  (0.19 g, 0.16 mmol) was added and the reaction was stirred at 115 °C for 24 hours. The reaction mixture was allowed to cool to room temperature, was filtered and washed with dichloromethane. Aqueous NaOH solution (5%, 10 mL) was added to the filtrate, the organic layer was separated and the aqueous layer was washed with dichloromethane (2 times). The combined organic fraction was washed with water and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Chromatography on silica, eluting with dichloromethane/2% methanol afforded the product as an off-white solid in 89% yield (0.79 g). <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  8.25 (d, J = 8.2 Hz, 2H); 7.87 (s, 2H); 7.59 (d, J = 8.1 Hz, 2H); 7.04 (s, 4H); 2.92 (septet, J = 7.0 Hz, 2H); 2.51 (septet, J = 6.9 Hz, 4H); 1.28 (d, J = 6.9 Hz, 12H); 1.07 (d, J = 6.9 Hz, 12H); 1.06 (d, J = 6.8 Hz, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  160.5, 148.5, 146.2, 146.2, 137.2, 135.2, 127.2, 126.2, 124.9, 120.5, 34.4, 30.5, 24.1, 24.0, 24.0. ESI-MS (CH<sub>3</sub>OH): calcd  $[M + H^+]^+$  585.42; obsd 585.50. Anal. calcd for bL2, C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>·1/8CH<sub>2</sub>Cl<sub>2</sub>: C, 84.96; H, 8.84; N, 4.70. Found: C, 84.70; H, 8.81; N, 4.59.

Complex 3.  $[Cu(CH_3CN)_4]PF_6$  (29.0 mg, 0.078 mmol) was added to a round bottom flask and dissolved in dichloromethane (10 mL) with stirring. The clear colorless solution was deaerated with N<sub>2</sub>. A similarly deaerated solution of **bL2** (50 mg, 0.085 mmol) in dichloromethane (5 mL) was added to the reaction mixture. Upon addition of bL2, the solution turned bright yellow, and was allowed to stir at room temperature for one hour. A deaerated solution of L1 (14.0 mg, 0.078 mmol) in dichloromethane (5 mL) was then added to the reaction mixture which turned orange/red. The red solution was allowed to stir under N2 at room temperature for one hour. The solvent was evaporated, the residue was re-dissolved in a minimum volume of dichloromethane and the product precipitated with diethyl ether and pentane. The orange-red solid was isolated by filtration and allowed to dry in air to give complex 3 (59 mg, 0.061 mmol, 78% yield). Single crystals suitable for X-ray structure analysis were obtained via diffusion of diethyl ether into a concentrated dichloromethane product solution. <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  8.67 (d, J = 8.2 Hz, 2H), 8.30–8.25 (m, 4H), 8.17 (dd, J = 4.5, 1.5 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.84 (s, 2H), 7.57 (dd, J = 8.1 Hz, 4.7 Hz, 2H), 6.41 (s, 4H), 2.42 (septet, J = 6.8 Hz, 2H), 2.10 (septet, J = 6.8 Hz, 4H), 0.88 (d, J = 6.8 Hz, 12H), 0.79 (d, J = 7.0 Hz, 12H), 0.37 (d, J = 6.8 Hz, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 159.4, 149.4, 147.7, 145.7, 143.6, 142.9, 136.8, 136.2, 135.2, 128.7, 128.1, 127.6, 127.0, 126.7, 124.9, 119.6, 33.9, 30.3, 25.3, 23.7, 22.1. ESI-MS (CH<sub>3</sub>OH): calcd  $[M - PF_6^-]^+$  827.41; obsd 827.42. Anal. calcd for 3, C<sub>54</sub>H<sub>60</sub>CuF<sub>6</sub>N<sub>4</sub>P·1/4CH<sub>2</sub>Cl<sub>2</sub>: C, 65.20; H, 6.08; N, 5.63. Found: C, 65.52; H, 6.00; N, 5.61.

Complex 4, method A. The same procedure as described for the synthesis of 3 was followed using  $[Cu(CH_3CN)_4]PF_6$ 

(15.9 mg, 0.043 mmol), **bL2** (31 mg, 0.053 mmol) and **L2** (8.9 mg, 0.043 mmol). A slight excess of **bL2** was used to ensure complete coordination of Cu(1) by **bL2**. However, **4** was obtained contaminated with approximately 10% homoleptic  $[Cu(L2)_2]PF_6$ . The small impurities of  $[Cu(L2)_2]PF_6$  were removed *via* recrystallization from a dichloromethane/diethyl ether/pentane mixture to afford pure **4** (31 mg, 72% yield). Single crystals suitable for X-ray structure analysis were obtained *via* diffusion of pentane into a dichloromethane/diethyl ether product solution.

Complex 4, method B. Under a nitrogen atmosphere copper powder (1.00 g), AgPF<sub>6</sub> (22.4 mg; 0.089 mmol) and bL2 (51.8 mg, 0.089 mmol) were placed in a Schlenk flask. Dry degassed acetone (10 ml) was added and the mixture was stirred for 1.5 hours at room temperature. The reaction mixture was filtered and L2 (18.5 mg, 0.089 mmol) was added to the filtrate. The orange/red solution was stirred for two hours at room temperature and the product was precipitated by adding a diethyl ether/pentane mixture to the reaction. Filtration and washing with diethyl ether afforded 4 without any homoleptic  $[Cu(L2)_2]PF_6$  complex formation (71 mg, 80%) yield). <sup>1</sup>H NMR (CD<sub>3</sub>Cl):  $\delta$  8.69 (d, J = 8.2 Hz, 2H), 8.27 (s, 2H), 8.18 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.78 (s, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.47 (s, 4H), 2.55 (septet, J = 6.9 Hz, 2H), 2.10 (septet, J = 6.8 Hz, 4H), 1.83 (s, 6H), 0.93 (d, J = 6.9 Hz, 12H), 0.85 (d, J = 6.8 Hz, 12H), 0.23 (d, J = 6.7 Hz, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  159.9, 157.3, 149.7, 145.5, 144.5, 142.8, 136.8, 136.8, 135.3, 128.6, 127.9, 127.3, 127.0, 125.7, 125.0, 119.7, 34.1, 30.0, 25.8, 25.7, 23.8, 21.2. ESI-MS (CH<sub>3</sub>OH): calcd  $[M - PF_6^{-}]^+$  855.44; obsd 855.50. Anal. calcd for 4, C<sub>56</sub>H<sub>64</sub>CuF<sub>6</sub>N<sub>4</sub>P: C, 67.15; H, 6.44; N, 5.59. Found: C, 66.81; H, 6.35; N, 5.67.

## Conflicts of interest

There are no conflicts of interest to declare.

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