Strong Steric Hindrance Effect on Excited State Structural Dynamics of Cu(I) Diimine Complexes

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SUPPLIMENTAL INFORMATION

General Procedures. Commercial solvents and reagents were used without further purification, unless otherwise stated. Reactions were carried out under an atmosphere of nitrogen. Reaction progress was monitored by thin-layer chromatography (TLC) and carried out on 250 μm silica gel polyester plates on fluorescent silica gel with UV visualization. Column chromatography was performed on 40–63 μm silica gel using flash chromatography. Solvents were removed by rotary evaporation. Residual solvents were removed under vacuum (< 0.01 mmHg). Precipitated and recrystallized products were dried under vacuum (< 0.01 mmHg) or by air suction through a filter funnel. Mass spectra were obtained by electrospray ionization (ESI). NMR spectra were recorded using a 500 MHz Bruker spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale. ^{1}H and ^{13}C NMR spectra in CD_2Cl_2 were referenced with TMS (δ = 0.00 ppm).

2-*tert*-Butyl-1,10-phenanthroline. The synthesis of 2-*tert*-butyl-1,10-phenanthroline has been previously described.[1] Briefly, 30 mL of dry THF was taken in a flame dried 250 ml

round bottom flask equipped with N_2 adapter and stir bar. (2g, 11 mmoles) 1,10-phenanthroline was added and stirred at room temperature for 15 min. to partially dissolve the solid material. (22 mmoles, 32 ml) t-butylithium was added dropwise to a stirred suspension at 30 °C. The deep reddish purple mixture was stirred at room temperature for overnight. 10 mL of water was added under N_2 atmosphere, color change was observed from purple to yellow. The organic phase is separated and aqueous phase was extracted with dichloromethane (3x 20 mL). Organic layers were combined and 40 g MnO_2 was added and the mixture was stirred for 2 h, the aromatization was monitored by TLC (EtOAc:Hx 8:2). Na_2SO_4 was added and stirred for additional 30 min. The mixture was filtered over ceilite bed and solvent was evaporated under vacuum. The product was purified over silica (EtOAc:Hx 8:2). Semi pure samples were collected and recrystallization was done in dichloromethane and hexane. The product was collected as a white powder in 35% yield. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 1.47 (s, 9 H, CH_3), 7.54 (dd, ^3J = 4.3 Hz, ^3J = 8.1 Hz, 1 H, CH), 7.69 (m, 3 H), 8.12 (d, J = 8.4 Hz 1 H, CH), 8.18 (dd, ^3J = 1.7 Hz, ^3J = 7.9 Hz, 1 H, CH), 9.08 (dd, ^3J = 1.7 Hz, ^3J = 4.4 Hz, 1 H, CH) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ 32.11, 40.40, 121.59, 124.47, 127.58, 128.31, 128.68, 130.87, 137.85, 138.07, 146.96, 1 48.27, 151.79, 171.35 ppm.

Bis(2-*tert*-butyl-1,10-phenanthroline)copper(I), [Cu(tbp)$_2$][PF$_6$]. The synthesis of bis(2-*tert*-butyl-1,10-phenanthroline)copper(I), $[Cu(tbp)_2]^+$ has been previously described.[2] Briefly, two equivalents (2 mmol) of 2-*tert*-butyl-1,10-phenanthroline was dissolved in 10 mL of acetonitrile, and the solution was purged with N_2. $Cu(CH_3CN)_4(PF_6)$, 2 mmol was added under N_2. Red color was immediately observed,

and the reaction mixture was stirred for additional 30 min. The solvent was evaporated under vacuum. The product was purified by recrystallization with dichloromethane and hexane in a 95% yield. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 1.23 (s, 18 H, CH_3), 7.75 (t, 2 H, CH), 8.08 (m, 6 H), 8.45 (d, *J* = 8.7 Hz 2 H, 8.52 (d, *J* = 8.7 Hz 2 H,CH), 8.75 (d, *J* = 5.7 Hz 2 H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ 29.9, 32.22, 121.67, 126.45, 128.52, 136.66 ppm

2,9-di-tert-butyl-1,10-phenanthroline. The synthesis of 2,9-di-tert-butyl-1,10-phenanthroline has been previously described.[1] Briefly, 30 mL of dry THF was taken in a flame dried 250 ml round bottom flask equipped with N_2 adapter and stir bar. (2g, 11 mmoles) 1,10-phenanthroline was added and stirred at room temperature for 15 min. to partially dissolve the solid material. (44 mmoles, 64 ml) *t*-butylithium was added dropwise to a stirred suspension at 30 °C. The deep reddish purple mixture is stirred at room temperature overnight. 10 mL of water was added under N_2 atmosphere, color change was observed from purple to yellow. The organic phase is separated and aqueous phase was extracted with dichloromethane (3x 20mL). Organic layers were combined and 40 g MnO_2 was added and the mixture was stirred for 2 h, the aromatization was monitored by TLC (EtOAc:Hx 8:2). Na_2SO_4 was added and stirred for additional 30 min. The mixture was filtered over ceilite bed and solvent was evaporated under vacuum. The product was purified over silica (EtOAc:Hx 8:2). Semi pure samples were collected and recrystallization was done in dichloromethane and hexane. The product was collected as a white powder in 40% yield. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 1.45 (s, 18 H, CH_3), 7.74 (d, *J* = 7.7 Hz, 2 H, CH), 7.86 (s, 2 H), 8.34 (d, *J* = 9.3 Hz 2 H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ 29.9, 37.22, 117.67, 127.45, 136.52, 144.66, 168.45 ppm

Bis(2,9-di-*tert*-butyl-1,10-phenanthroline)copper(I), [Cu(dtbp)$_2$][SbF$_6$] The synthesis of bis(2,9-di-*tert*-butyl-1,10-phenanthroline)copper(I), $[Cu(dtbp)_2]^+$ has been previously describe.[3] Briefly, In a N_2 filled dry box a 50 ml schlenk flask, charged with acetone (10 mL) di-tert-butyl-1,10-phenanthroline (200 mg, 0.6 mmol), $AgSbF_6$ (129 mg, 0.2 mmol) and an excess of Cu powder (2 g) was taken. The reaction mixture was stirred for 30 min and then filtered through celite. The resulting orange solution was evaporated under vacuum and recrystallized with dichloromethane and hexanes yielding 160 mg (85%) of bright orange crystals. The product was purified by recrystallization with dichloromethane and hexane.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 1.22 (s, 36 H, CH_3), 8.03 (s, 4 H, CH), 8.08 (d, *J* = 8.4 Hz, 2 H), 8.52 (d, *J* = 8.7 Hz 2 H, CH) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ 29.74, 36.22, 123.67, 126.45, 128.52, 137.66 ppm.

Time-Correlated Single Photon Counting of 2,9-di-*tert*-butyl-1,10-phenanthroline

A solution of 2,9-di-*tert*-butyl-1,10-phenanthroline (dtbp) in dichloromethane was analyzed by time-correlated single photon counting as a control experiment to identify the 3.5 ns feature seen in the TCSPC scan of $Cu(dtbp)_2$ at 500 nm emission. The data was fitted with a single exponential decay convoluted with a 150 ps, Gaussian response function and yielded a 2.4 ns decay lifetime, consistent with the 3.5 ns determined from the $Cu(dtbp)_2$ decay. Therefore, it is reasonable to assign the 3.5 ns decay to emission from free dtbp ligand in solution.

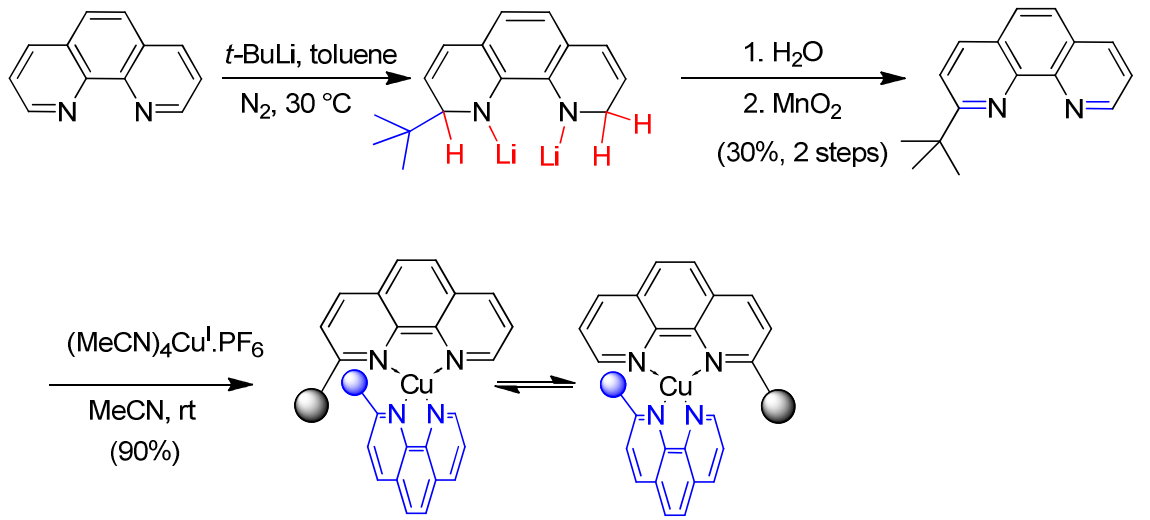
Determination of Transient Absorption Rise Times for Cu(dtbp)$_2$ and Cu(tbp)$_2$

Transient absorption data for $[Cu(dmp)_2]^+$ typically exhibit a <1 ps rise time indicative with flattening from a D_{2d} to D_2 geometry. In order to confirm the validity of the rise time

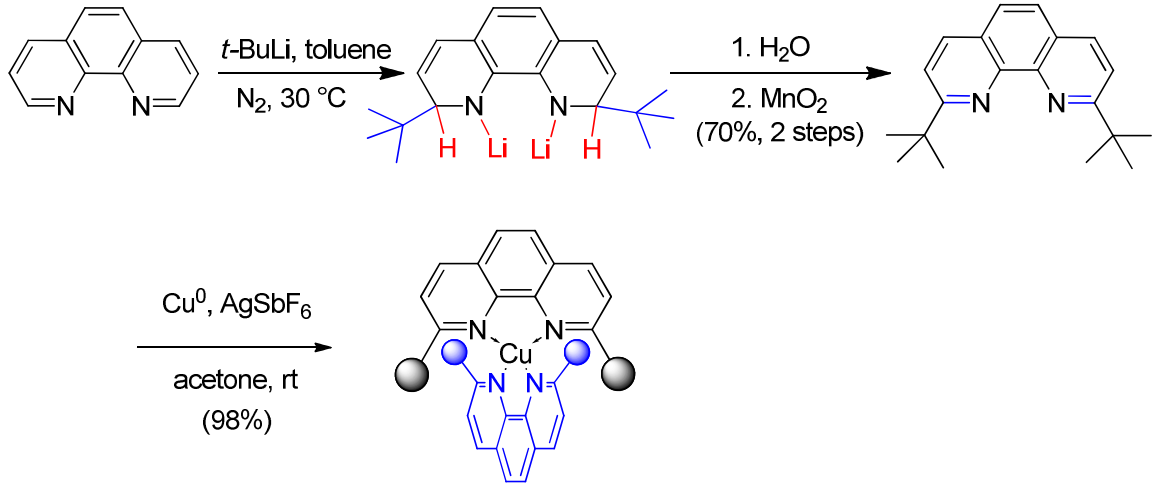
for $Cu(tbp)_2$, the data was refitted without this rise time. Both fits required a 10-15 ps decay and a >3 ns decay. The fit without the 600 fs rise component was quite poor (χ^2 = 2.87×10^{-6}) while the fit with the fast rise time improved goodness of the fit significantly (χ^2 =1.88×10^{-6}), confirming the presence of the ultrafast rise time.

In order to confirm the absence of the rise time for $[Cu(dtbp)_2]^+$, the data was refit without and with a fast rise time. Both fits required dual decay components with time constants of 4-5 ps and > 3 ns. There was no improvement in the goodness of fits with and without the fast rise time, resulting in χ^2 values of 1.91×10^{-5} and 2.08×10^{-5} respectively, confirming that the short rise time is unnecessary in the kinetics of the MLCT state of $[Cu(dtbp)_2]^+$.

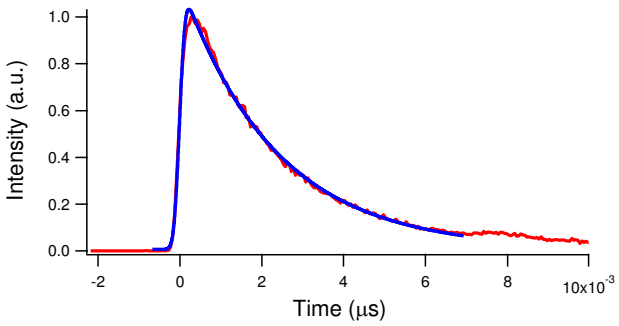
Electrochemical Measurements. Cyclic voltammetry was performed in a one-compartment cell with a Pt disk working electrode, Pt gauze counter electrode and Ag wire reference electrode. The sample, 5 mM solution of complex with 0.1 M tetrabutylammonium hexafluorophosphate, TBA(PF_6) as a supporting electrolyte, in dichloromethane. Potential measured *vs.* SCE using Fc^+/Fc as an internal standard. Data were collected at a scan rate of 100, 200 and 50 mV/s. The $E_{1/2}$ of ferrocene$^{0/+}$ couple was 0.46 V versus SCE in CH_2Cl_2 under identical experimental conditions to those used for studying complexes **1**-**3**.



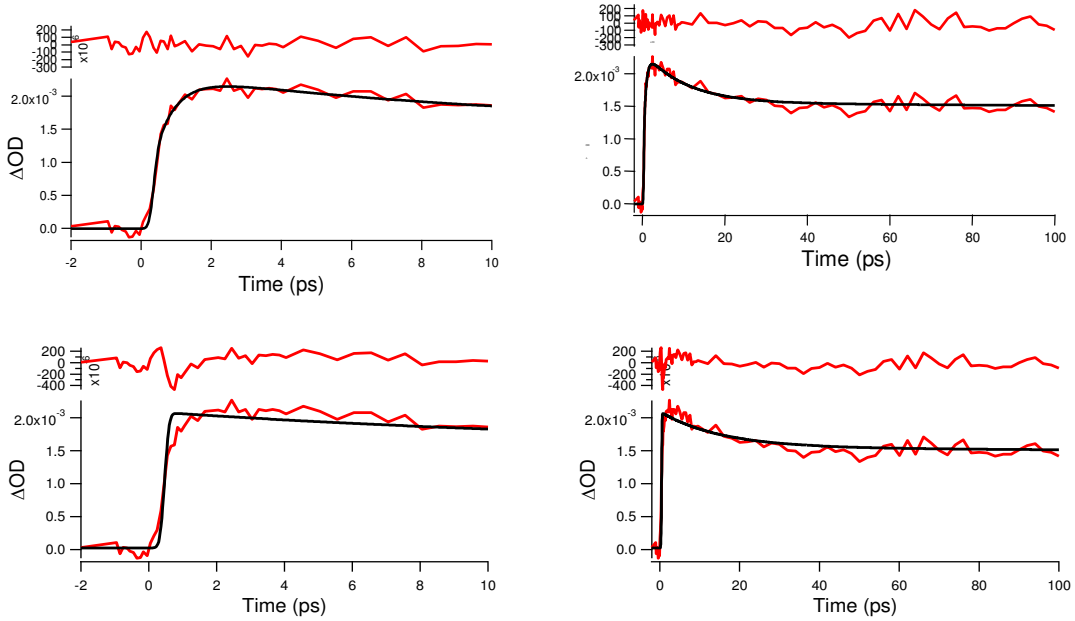
SI Scheme 1. Synthetic scheme for Bis(2-*tert*-butyl-1,10-phenanthroline)copper(I), $[Cu(tbp)_2][PF_6]$



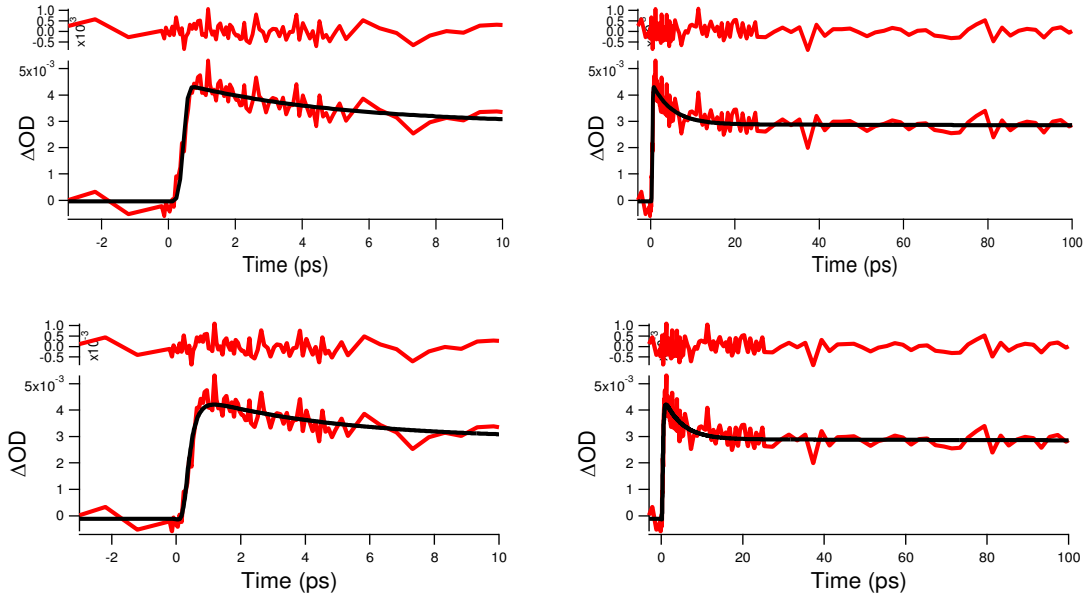
SI Scheme 2. Synthetic scheme for Bis(2,9-di-*tert*-butyl-1,10-phenanthroline)copper(I), $[Cu(dtbp)_2][SbF_6]$



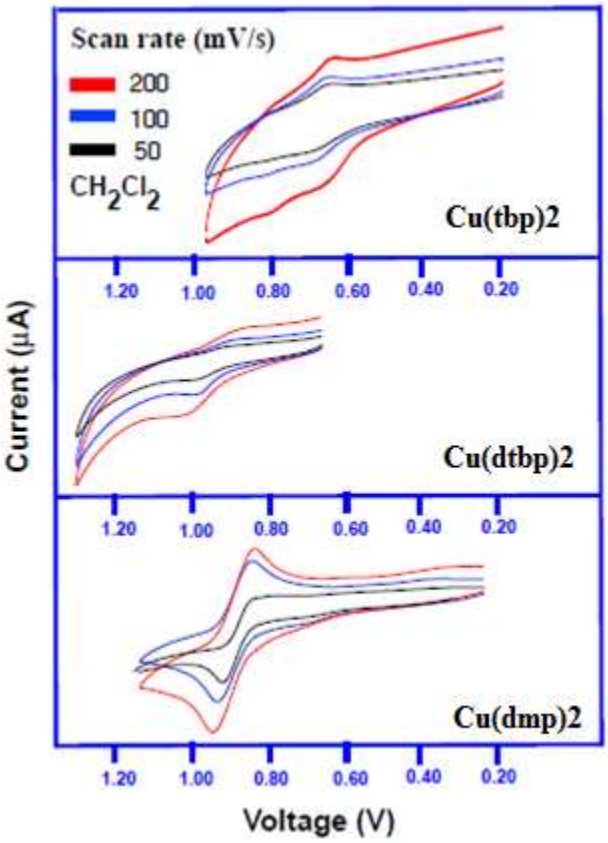
SI Figure 1: TCSPC of dtbp ligand in dichloromethane with 400 nm excitation, 500 nm emission; fits to single exponential with 2.4 ns lifetime



SI Figure 2: Top: TA of $Cu(tbp)_2$ with 415 nm excitation, 610 nm absorption; fit with 580 fs rise, a 10.3 ps decay, and a >3000 ns decay (χ^2 = 1.88 E-6). Bottom: TA of $Cu(tbp)_2$ with 415 nm excitation, 610 nm absorption; fit without rise time (χ^2 = 2.87 E-6).



SI Figure 3: Top: TA of $Cu(dtbp)_2$ with 415 nm excitation, 610 nm absorption; fit with a 4.8 ps decay and a >3000 ns decay (χ^2 = 2.08 E-5). Bottom: TA of $Cu(dtbp)_2$ with 415 nm excitation, 610 nm absorption; fit after addition of ~200 fs rise time (χ^2 = 1.92 E-5).



SI Figure4: Cyclic voltammogram of complexes **1-3** in CH_2Cl_2

SI Table 1. $Cu^{2+/+}$ potentials of complexes **1-3**

Compound	**λ_{abs}** **nm**	**λ_{PL}** **nm**	**$E_{(0-0)}$** **(eV Abs/Em)**	**$E_{1/2}^{OX}$** **(V vs SCE)**	**$E^*_{1/2}{}^{OX}$** **(V)**
				CH_2Cl_2	CH_2CL_2
$[Cu(dmp)_2][PF_6]$	454	740	2.04	0.90	- 1.14
$[Cu(tbp)_2][PF_6]$	432	-	-	0.70	-
$[Cu(dtbp)_2][SbF_6]$	425	599	1.99	1.00	- 1.36

References:

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(2) Hebbe-Viton, V.; Desvergnes, V.; Jodry, J. J.; Dietrich-Buchecker, C.; Sauvage, J.-P.; Lacour, J. *Dalton Transactions* **2006**, 2058.

(3) Gandhi, B. A.; Green, O.; Burstyn, J. N. *Inorganic Chemistry* **2007**, *46*, 3816.