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## **Supporting information**

# Control of emission color with N-heterocyclic carbene (NHC) ligands in phosphorescent threecoordinate Cu(I) complexes

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#### General information.

**Synthesis.** All reactions were performed under nitrogen atmosphere in oven dried glassware. Chloro[1,3-bis(2,6-di-i-propylphenyl)imidazol-2-ylidene]copper(I) (IPr)CuCl and potassium dihydrobis(1-pyrazolyl)borate K[pz<sub>2</sub>BH<sub>2</sub>] were purchased from TCI America, all other commercially available reagents were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran was purified by Glass Contour solvent system by SG Water USA, LLC and CDCl<sub>3</sub>, which was passed through a plug of Al<sub>2</sub>O<sub>3</sub>. 1,3-bis(3,5-dimethylphenyl)-1*H*benzo[*d*]imidazol-3-ium chloride<sup>1</sup> (BzI-3,5Me)CuCl, sodium dimethyldi(2-pyridyl)borate<sup>2, 3</sup> Na(py<sub>2</sub>BMe<sub>2</sub>), 7,9-bis(2,6-diisopropylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium chloride<sup>4</sup> (IPrBIAN)Cl were synthesized according to literature procedures. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 400 or Varian VNMRS 500 spectrometer. The chemical shifts are given in units of ppm and referenced to the residual solvent signals. Elemental analyses were performed by the Microanalysis Laboratory at the University of Illinois, Urbana-Champaign, IL.

**DFT Calculations.** Density functional theory (DFT) calculations were carried out using the Gaussian03<sup>5</sup> (Revision E.01) package employing the B3LYP<sup>6, 7</sup> functional using LANL2DZ<sup>8</sup> basis set for Cu and 6-31G<sup>\*9</sup> for C, N, H and B. Geometric parameters obtained from XRD analyses were used as a starting point for geometry optimization in the ground state. The optimized geometries were used for time-dependent density functional calculations (TD-DFT).

**Photophysical characterization.** The UV-visible spectra were recorded on a Hewlett-Packard 4853 diode array spectrometer. Steady state emission measurements were performed using a Photon Technology International QuantaMaster model C-60 fluorimeter. All reported spectra are corrected for photomultiplier response. Phosphorescence lifetime measurements were performed using an IBH Fluorocube instrument equipped with a 405 nm LED excitation source using time-correlated single photon counting method. Quantum yields at room temperature were measured using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere and model C10027 photonic multichannel analyzer.

## X-ray Crystallography.

Single-crystal X-ray diffraction data for compound **1** were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The cell parameters for the complexes were obtained from a least-squares refinement of the spots (from 60 collected frames) using the SMART program. One hemisphere of crystal data was collected up to a resolution of 0.80 Å, and the intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (Version 5.1).<sup>10</sup> Absorption corrections were applied by using SADABS.<sup>11</sup> Hydrogen positions were input and refined in a riding manner along with the attached carbons.

The single crystal X-ray diffraction data for other compounds were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD detector with the  $\chi$ -axis fixed at 54.74°, and using Mo  $K_{\alpha}$  radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. A complete hemisphere of data was scanned on  $\omega$  and  $\phi$  (0.5°) at a detector resolution of 512 x 512 pixels using the BIS software package.<sup>12</sup> The frames were integrated using the SAINT algorithm<sup>13</sup> to give the hkl files corrected for Lp/decay. The absorption correction was performed using the SADABS program.<sup>14</sup> The structures were solved by direct methods and refined on  $F^2$  using the Bruker SHELXTL Software Package.<sup>15, 16</sup> All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the software ORTEP-3 for Windows V2013.1.<sup>17</sup>

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## Synthesis of (BzI-3,5Me)CuCl (2a).



(BzI-3,5Me)CuCl (2a)

1,3-bis(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazol-3-ium chloride (BzI-3,5Me)Cl (500 mg, 1.38 mmol), CuCl (164 mg, 1.66 mmol) and NaOtBu (132.5 mg, 1.38 mmol) were mixed in 40 ml of THF and stirred at room temperature overnight. The reaction mixture was then filtered under inert atmosphere through a plug of Celite and the solvent was evaporated in vacuo. The resulting solid was exposed to air and washed with pentane (50 ml). The product was obtained as white air stable solid (466 mg, 79%). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 2.45 (s, 12H, ArCH<sub>3</sub>), 7.27 (br s, 2H, H<sup>Ar</sup>), 7.48 ( br s, 4H, H<sup>Ar</sup>), 7.51 (AA'BB', 2H, H<sup>Ar</sup>), 7.62 (AA'BB', 2H, H<sup>Ar</sup>). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 21.27, 113.26, 124.62, 125.78, 131.67, 134.89, 138.50, 140.84, 184.75. Anal. Calcd for C<sub>23</sub>H<sub>22</sub>ClCuN<sub>2</sub>: C, 64.93; H, 5.21; N, 6.58. Found; C, 65.12; H, 5.45; N, 6.31.

## Synthesis of (PzI-3,5Me)CuCl (3a).



#### nthesis of N<sup>2</sup>,N<sup>3</sup>-bis(3,5-dimethylphenyl)pyrazine-2,3-diamine (3c).

2,3-Dichloropyrazine (5.58 g, 0.037 mol) and 3,5-dimethylaniline (11.21 g, 0.0925 mol) were heated neat at 140°C overnight under nitrogen atmosphere. The resulting solid was suspended in 200 ml of water and the mixture was made alkaline with 25% NaOH. The mixture was extracted with  $3\times75$  ml of CH<sub>2</sub>Cl<sub>2</sub> and  $3\times75$  ml of ethyl acetate. Combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and volatiles were removed by rotary evaporation to give a brown residual oil. Addition of pentane afforded the off-white solid, which was filtered, washed with pentane and dried (7.145 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 2.28 (s, 12H), 6.19 (br s, 2H), 6.69 (s, 2H), 6.87 (s, 4H), 7.76 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ) 21.58, 117.45, 124.92, 133.63, 138.99, 140.11, 142.80. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>: C, 75.44; H, 6.96; N, 17.6. Found: C, 75.61; H, 7.01; N, 17.39.

## Synthesis of (PzI-3,5Me)OEt (3b).

To N<sup>2</sup>,N<sup>3</sup>-bis(3,5-dimethylphenyl)pyrazine-2,3-diamine **3c** (750 mg, 2.35 mmol) was added 10 ml of triethylorthoformate, followed by 0.193 ml of HCl<sub>conc</sub>. The mixture was stirred overnight in a closed vessel at 110°C. The product was precipitated from dark yellow reaction mixture upon addition of pentane and cooling (0°C). Beige solid was collected by filtration, washed with pentane and dried (610 mg, 69%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ) 1.10 (t, J = 7.0 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 2.39 (s, 12H, ArCH<sub>3</sub>), 3.33 (q, J = 7.0 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 6.84 (br s, 2H, H<sup>Ar</sup>), 7.18 (s, 1H, NCHN), 7.52 (s, 2H, H<sup>Pz</sup>), 7.62 (br s, 4H, H<sup>Ar</sup>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$ ) 14.71, 21.81, 55.29, 96.37, 116.68, 126.20, 130.62, 138.05, 139.02, 143.81. Anal. Calcd for C<sub>23</sub>H<sub>26</sub>N<sub>4</sub>O: C, 73.77; H, 7.0; N, 14.96. Found: C, 73.68; H, 7.02; N, 14.81.

## Synthesis of (PzI-3,5Me)CuCl (3a).

(PzI-3,5Me)OEt (**3b**) (300 mg, 0.8 mmol) and CuCl (72.3 mg, 0.73 mmol) were refluxed overnight in 20 ml of THF. The resulting bright-yellow suspension was filtered; the solid was collected, washed with THF and dried in vacuo (273 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ) 2.46 (s, 12H, ArCH<sub>3</sub>), 7.21 ( br s, 2H, H<sup>Ar</sup>), 7.45 (s, 4H, H<sup>Ar</sup>), 8.55 (s, 2H, H<sup>Pz</sup>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>,  $\delta$ ) 21.54, 123.56, 131.86, 135.59, 139.71, 140.22, 140.55, 189.04. Anal. Calcd for C<sub>21</sub>H<sub>20</sub>ClCuN<sub>4</sub>: C, 59.01; H, 4.72; N, 13.11. Found: C, 58.79; H, 4.64; N, 12.97.

## Synthesis of (IPrBIAN)CuCl (4a).



(IPrBIAN)CuCl (4a)

7,9-bis(2,6-diisopropylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium chloride (IPrBIAN)Cl (492 mg, 0.89 mmol), CuCl (105.7 mg, 1.068 mmol) and NaOtBu (85.4 mg, 0.89 mmol) were mixed in 30 ml of THF and stirred at room temperature overnight. The reaction mixture was exposed to air, filtered through a plug of Celite and solvent was removed by rotary evaporation. Toluene (30 ml) was added to the crude product and the resulting suspension was filtered. The obtained filtrate was collected and solvent was evaporated to dryness to give yellow solid (175 mg, 32%). The sample was used without further purification for the next reaction. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 1.12 (d, *J* = 6.8 Hz, 12H, ArCHCH<sub>3</sub>), 1.35 (d, *J* = 6.8 Hz, 12H, ArCHCH<sub>3</sub>), 2.84 (septet, *J* = 6.8 Hz, 4H, ArCHCH<sub>3</sub>), 7.00 (d, *J* = 6.8 Hz, 2H, H<sup>Ar</sup>), 7.40-7.45 (m, 6H, H<sup>Ar</sup>), 7.59 (t, *J* = 7.8 Hz, 2H, H<sup>Ar</sup>), 7.80 (d, *J* = 8.3 Hz, 2H, H<sup>Ar</sup>).

## Synthesis of (IPr)Cu(py<sub>2</sub>BMe<sub>2</sub>) (1).

(IPr)CuCl (122.15 mg, 0.25 mmol) and sodium dimethyldi(2-pyridyl)borate (55 mg, 0.25 mmol) were mixed in 10 ml of THF and stirred at RT for 1 h under  $N_2$  atmosphere. The resulting light-yellow solution was filtered through Celite and the solvent was evaporated under reduced pressure. The product was obtained as light yellow solid by slow crystallization from acetone/hexanes solvent mixture under  $N_2$  atmosphere (75 mg, 46%). Alternatively, the crude

product obtained after removal of solvent can be purified by zone vacuum sublimation (220 °C, 10<sup>-6</sup> torr). Sublimation yield 66%. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) -0.15 (br s, 6H, BC*H*<sub>3</sub>), 1.16 (d, *J* = 6.9 Hz, 12H, ArCHC*H*<sub>3</sub>), 1.22 (d, *J* = 6.9 Hz, 12H, ArCHC*H*<sub>3</sub>), 3.04 (septet, *J* = 6.9 Hz, 4H, ArC*H*CH<sub>3</sub>), 6.50-6.53 (m, 2H, H<sub>py</sub>), 7.20 (tdd, *J* = 7.6 Hz, *J* = 1.9 Hz, *J* = 0.8 Hz, 2H, H<sub>py</sub>), 7.30-7.35 (m, 8H, H<sup>Ar</sup>, H<sub>py</sub>), 7.49 (t, *J* = 8 Hz, 2H, H<sup>Ar</sup>), 7.62 (s, 2H, NC*H*=). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 14.19 (B-CH<sub>3</sub>), 23.70, 25.35, 29.30, 118.04, 124.42, 124.72, 127.13, 130.58, 134.08, 137.79, 146.93, 149.31, 187.82. Pyridine *ipso*-carbon connected to boron was not observed. Anal. Calcd. for C<sub>39</sub>H<sub>50</sub>BCuN<sub>4</sub>: C, 72.15; H, 7.76; N, 8.63. Found: C, 72.2; H, 7.8; N, 8.58.

#### Synthesis of (BzI-3,5Me)Cu(py<sub>2</sub>BMe<sub>2</sub>) (2).

(BzI-3,5Me)CuCl (319 mg, 0.75 mmol) and sodium dimethyldi(2-pyridyl)borate (165 mg, 0.75 mmol) were mixed in 30 ml of THF and stirred at RT for 1 h under N<sub>2</sub> atmosphere. The resulting yellow solution was filtered through a pad of Celite in glove box. The filtrate was concentrated under reduced pressure to ~5 ml. Pentane was added dropwise resulting in precipitation of yellow solid that was collected by filtration and dried. (310 mg, 70%). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) -0.06 (br s, 6H, BCH<sub>3</sub>), 2.27 (s, 12H, ArCH<sub>3</sub>), 6.73-6.76 (m, 2H, H<sub>py</sub>), 7.13 (s, 2H, H<sup>Ar</sup>), 7.35 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 2H, H<sub>py</sub>), 7.50 (d, *J* = 7.8 Hz, 2H, H<sub>py</sub>), 7.41-7.44 (AA'BB', 2H, H<sup>Ar</sup>), 7.47 (d, *J* = 7.8 Hz, 2H, H<sub>py</sub>), 7.52-7.56 (m, 6H, H<sup>Ar</sup>), 7.97 (d, *J* = 5.1 Hz, 2H, H<sub>py</sub>). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 14.34 (B-CH<sub>3</sub>), 21.18, 112.40, 118.71, 124.62, 125.08, 127.61, 130.92, 134.62, 135.53, 139.48, 140.41, 149.42, 190.51, 190.64 (B-C<sub>py</sub>). Anal. Calcd. for C<sub>35</sub>H<sub>36</sub>BCuN<sub>4</sub>: C, 71.61; H, 6.18; N, 9.54. Found: C, 71.23; H, 6.15; N, 9.64.

#### Synthesis of (PzI-3,5Me)Cu(py<sub>2</sub>BMe<sub>2</sub>) (3).

(PzI-3,5Me)CuCl (427.4 mg, 1 mmol) and sodium dimethyldi(2-pyridyl)borate (220.11 mg, 1 mmol) were mixed in 30 ml of THF and stirred at RT for 1 h under N<sub>2</sub> atmosphere. The resulting orange solution was filtered through a pad of Celite in glove box. The filtrate was concentrated under reduced pressure to ~5 ml. Pentane was added dropwise resulting in precipitation of bright orange solid that was collected by filtration and dried. (444 mg, 75%). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) -0.05 (br s, 6H, BC*H*<sub>3</sub>), 2.25 (s, 12H, ArC*H*<sub>3</sub>), 6.77-6.80 (m, 2H, H<sub>py</sub>), 7.13 (s, 2H, H<sup>Ar</sup>), 7.39 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 2H, H<sub>py</sub>), 7.50 (d, *J* = 7.8 Hz, 2H, H<sub>py</sub>),

7.67 (s, 4H, H<sup>Ar</sup>), 8.06 (d, J = 5.3 Hz, 2H, H<sub>py</sub>), 8.49 (s, 2H, H<sub>pz</sub>). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 14.39 (B-CH<sub>3</sub>), 21.18, 118.91, 125.22, 127.80, 131.09, 134.09, 138.11, 139.44, 139.95, 141.92, 149.61, 191.72 (B-C<sub>py</sub>), 193.66. Anal. Calcd. for C<sub>33</sub>H<sub>34</sub>BCuN<sub>6</sub>: C, 67.29; H, 5.82; N, 14.27. Found: C, 67.2; H, 5.86; N, 14.02.

#### Synthesis of (IPrBIAN)Cu(py<sub>2</sub>BMe<sub>2</sub>) (4).

(IPrBIAN)CuCl (170 mg, 0.28 mmol) and sodium dimethyldi(2-pyridyl)borate (61.63 mg, 0.25 mmol) were mixed in 20 ml of THF and stirred at RT for 1 h under N<sub>2</sub> atmosphere. The resulting light-yellow solution was filtered through Celite and the solvent was evaporated under reduced pressure. The product was obtained as dark orange solid by crystallization from its toluene solution by layering with *n*-pentane under N<sub>2</sub> atmosphere (136 mg, 63%). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) -0.09 (br s, 6H, BCH<sub>3</sub>), 1.09 (d, *J* = 6.9 Hz, 12H, ArCHCH<sub>3</sub>), 1.19 (d, *J* = 6.9 Hz, 12H, ArCHCH<sub>3</sub>), 3.29 (septet, *J* = 6.9 Hz, 4H, ArCHCH<sub>3</sub>), 6.55-6.58 (m, 2H, H<sub>py</sub>), 7.01 (d, *J* = 7.0 Hz, 2H, H<sup>Ar</sup>), 7.24 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 2H, H<sub>py</sub>), 7.36 (d, *J* = 7.7 Hz, 2H, H<sub>py</sub>), 7.40 (d, *J* = 5.2 Hz, 2H, H<sub>py</sub>), 7.50 (d, *J* = 7.8 Hz, 4H, H<sup>Ar</sup>), 7.54 (dd, *J* = 8.3 Hz, *J* = 7.0 Hz, 2H, H<sup>Ar</sup>), 7.66 (t, *J* = 7.8 Hz, 2H, H<sup>Ar</sup>), 7.90 (d, *J* = 8.0 Hz, 2H, H<sup>Ar</sup>). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 24.10, 24.81, 29.56, 118.20, 121.90, 125.32, 127.02, 127.24, 128.76, 128.93, 130.86, 131.22, 131.47, 134.23, 136.11, 139.91, 146.90, 149.37. Carbon atoms connected to boron and carbene carbon were not observed. Anal. Calcd. for C<sub>49</sub>H<sub>54</sub>BCuN<sub>4</sub>: C, 76.1; H, 7.04; N, 7.24. Found: C, 76.07; H, 6.97; N, 7.22.

#### Synthesis of (IPr)Cu(pz<sub>2</sub>BH<sub>2</sub>).

(IPr)CuCl (195.04 mg, 0.4 mmol) and potassium dihydrobis(1-pyrazolyl)borate K[pz<sub>2</sub>BH<sub>2</sub>] (74.4 mg, 0.4 mmol) were mixed in 10 ml of THF and stirred at RT for 1 h under N<sub>2</sub> atmosphere. The resulting solution was filtered through a pad of Celite and the solvent was evaporated under reduced pressure. The product was obtained as white solid. (132 mg, 55%). <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 1.20 (d, *J* = 6.9 Hz, 12H, ArCHCH<sub>3</sub>), 1.23 (d, *J* = 6.9 Hz, 12H, ArCHCH<sub>3</sub>), 2.88 (septet, *J* = 6.9 Hz, 4H, ArCHCH<sub>3</sub>), 5.72 (t, *J* = 1.7 Hz, 2H, H<sub>pz</sub>), 5.91 (d, *J* = 1.8 Hz, 2H, H<sub>pz</sub>), 7.24 (d, *J* = 1.8 Hz, 2H, H<sub>pz</sub>), 7.38 (d, 4H, *J* = 7.8 Hz, H<sup>Ar</sup>), 7.53 (t, *J* = 7.8 Hz, 2H, H<sup>Ar</sup>), 7.63 (s, 2H, NC*H*=). <sup>13</sup>C NMR (126 MHz, acetone-d<sub>6</sub>,  $\delta$ ) 24.35, 24.40, 29.46, 102.89, 124.21, 124.82, 130.58, 134.32, 137.66, 140.00, 146.86, 186.88. Anal. Calcd. for C<sub>33</sub>H<sub>44</sub>BCuN<sub>6</sub>: C, 66.16; H,

7.4; N, 14.03. Found: C, 66.17; H, 7.46; N, 13.75.



Scheme S1.

 

 Table S1. Selected bond lengths (Å) and angles (deg) for complexes 1-4 obtained from singlecrystal X-ray diffraction studies.

	1	2a	2b	3	4
C <sub>NHC</sub> -Cu	1.895(2)	1.8678(19)	1.8678(19)	1.8808(11)	1.8831(10)
Cu-N <sub>py</sub> '	2.0288(15)	1.9929(16)	1.9876(16)	2.010(9)	2.0081(9)
Cu-N <sub>py</sub> ''	2.0288(15)	1.9997(16)	1.9985(16)	2.014(9)	2.0224(9)
C <sub>NHC</sub> -Cu-N <sub>py</sub> '	132.78(4)	134.32(7)	133.95(7)	135.0(6)	133.84(4)
C <sub>NHC</sub> -Cu-N <sub>py</sub> ''	132.78(4)	129.27(7)	129.41(7)	128.1(7)	133.32(4)
N <sub>py</sub> '-Cu-N <sub>py</sub> ''	94.43(9)	96.14(6)	96.28(6)	95.51(4)	92.71(4)

**Table S2.** Selected bond lengths (Å) and angles (deg) for geometry optimized  $S_0$  and  $T_1$  states of complexes **1-4** obtained from DFT calculations.

		C <sub>NHC</sub> -Cu	Cu-N <sub>py</sub> '	Cu-N <sub>py</sub> ''	C <sub>NHC</sub> -Cu-N <sub>py</sub> '	C <sub>NHC</sub> -Cu-N <sub>py</sub> "	N <sub>py</sub> '-Cu-N <sub>py</sub> ''
1	Opt S <sub>0</sub>	1.97077	2.10038	2.10041	133.295	133.293	93.345
	Opt T <sub>1</sub>	2.00792	1.95625	2.00673	149.422	116.426	91.003
2	Opt S <sub>0</sub>	1.94833	2.08668	2.05941	129.459	133.848	95.517
	Opt T <sub>1</sub>	1.95961	1.99715	2.02352	156.769	108.346	93.082
3	Opt S <sub>0</sub>	1.94125	2.06033	2.07146	130.573	132.225	95.960
	Opt T <sub>1</sub>	1.95384	1.98865	2.02633	156.233	109.267	93.135
4	Opt S <sub>0</sub>	1.95539	2.08339	2.10510	137.251	130.254	91.480
	Opt T <sub>1</sub>	1.93525	2.05113	2.06032	137.061	129.741	92.314



**Figure S1.** Absorption spectra of precursors (IPr)CuCl (1a), (BzI-3,5Me)CuCl (2a), (PzI-3,5Me)CuCl (3a) and (IPrBIAN)CuCl (4a) in CH<sub>2</sub>Cl<sub>2</sub> and Na[py<sub>2</sub>BMe<sub>2</sub>] in acetonitrile.



Figure S2. Absorption spectra of (IPr)Cu(py<sub>2</sub>BMe<sub>2</sub>) (1) and (IPr)Cu(pz<sub>2</sub>BH<sub>2</sub>) in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S3.** Excitation (open symbols) and emission (closed symbols) spectra of complexes **1-3** in the solid state at 77 K.



**Figure S4.** Excitation (open symbols) and emission (closed symbols) spectra of complexes **1-3** in methylcyclohexane at 77 K.

	solid powder		methylcyclohexane glass		
	$\lambda_{max}$ (nm)	τ (μs)	$\lambda_{max}$ (nm)	τ (μs)	
1	492	36	460	29	
2	586	17	570	19	
3	650	21	638	23	

**Table S3.** Emission properties of complexes 1-3 at 77 K.

Table S4. Lowest energ	y transitions f	for complexes	1-4 obtained	from TD-DFT	calculations.
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complex	states	vertical excitation energy (nm)	oscillator strength	major contribution <sup>a</sup>	character
1	T <sub>1</sub>	381	0	HOMO→LUMO (76%)	(M+L)LCT/ILCT
				HOMO→LUMO+4 (18%)	
	$\mathbf{S}_1$	375	0.0028	HOMO→LUMO (81%)	(M+L)LCT/ILCT
				HOMO→LUMO+4 (8.8%)	
2	T <sub>1</sub>	400	0	HOMO→LUMO (100%)	(M+L)LCT
	T <sub>2</sub>	367	0	HOMO-2→LUMO (61%)	(M+L)LCT
				HOMO-1→LUMO (35%)	
	<b>S</b> <sub>1</sub>	364	0.1440	HOMO→LUMO (96%)	(M+L)LCT
3	T <sub>1</sub>	522	0	HOMO→LUMO (100%)	(M+L)LCT
	<b>S</b> <sub>1</sub>	451	0.1645	HOMO→LUMO (100%)	(M+L)LCT
4	T <sub>1</sub>	671	0	HOMO→LUMO (80%)	(M+L)LCT
				HOMO-3→LUMO (10%)	
				HOMO-5→LUMO (10%)	
	<b>S</b> <sub>1</sub>	597	0.0044	HOMO→LUMO (100%)	(M+L)LCT

<sup>a</sup> transitions with >5% contribution

 Table S5. Sample and crystal data for complex 1.

Chemical formula	$C_{39}H_{50}BCuN_4$	
Formula weight	649.18	
Temperature	145(2) K	
Wavelength	0.71073 Å	
Crystal size	0.19 x 0.20 x 0.27 mm	
Crystal habit	clear colourless prism	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 16.5350(15) Å	$\alpha = 90^{\circ}$ .
	b = 20.3273(19) Å	$\beta = 90^{\circ}$ .
	c = 11.0518(10) Å	$\gamma = 90^{\circ}$ .
Volume	3714.6(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.161 g/cm <sup>3</sup>	
Absorption coefficient	0.619 mm <sup>-1</sup>	
F(000)	1384	

Bruker SMART APEX CCD diffractometer		
fine-focus tube, MoKa		
2.00 to 27.51°.		
-21<=h<=21, -26<=k<=26, -14<=l<=13		
31313		
4375 [R(int) = 0.0972]		
100.0%		
None		
direct methods		
SHELXS-97 (Sheldrick, 2008)		
Full-matrix least-squares on F <sup>2</sup>		
SHELXL-97 (Sheldrick, 2008)		
$\Sigma \mathrm{w}(\mathrm{F_o}^2 - \mathrm{F_c}^2)^2$		
4375 / 0 / 215		
1.524		
0.000		
$I > 2\sigma(I)$ R1 = 0.0439, wR2 = 0.0748		
all data $R1 = 0.0638$ , $wR2 = 0.0769$		
w=1/[ $\sigma^2(F_o^2)$ +(0.0420P) <sup>2</sup> +0.7503P] where P=( $F_o^2$ +2 $F_c^2$ )/3		
0.493 and -0.659 e.Å <sup>-3</sup>		
0.05 eÅ <sup>-3</sup>		

 Table S6. Data collection and structure refinement for complex 1.

Chemical formula	$C_{35}H_{36}BCuN_4$			
Formula weight	587.03			
Temperature	100(2) K			
Wavelength	0.71073 Å			
Crystal size	0.170 x 0.253 x 0.335 mm			
Crystal habit	clear colourless prism			
Crystal system	Triclinic			
Space group	P -1			
Unit cell dimensions	a = 11.5950(5) Å	$\alpha = 95.8960(10)^{\circ}$		
	b = 11.6113(5) Å	$\beta = 102.6010(10)^{\circ}$		
	c = 24.2450(10)  Å	$\gamma = 102.6940(10)^{\circ}$		
Volume	3068.5(2) Å <sup>3</sup>			
Z	4			
Density (calculated)	1.271 g/cm <sup>3</sup>			
Absorption coefficient	0.742 mm <sup>-1</sup>			
F(000)	1232			

 Table S7. Sample and crystal data for complex 2.

 Table S8. Data collection and structure refinement for complex 2.

Diffractometer	Bruker APEX II CCD		
Radiation source	fine-focus tube, MoKα		
Theta range for data collection	1.74 to 30.59°		
Index ranges	-16<=h<=16, -16<=k<=16, -34<=l<=34		
Reflections collected	66941		
Independent reflections	18417 [R(int) = 0.0613]		
Coverage of independent reflections	97.5%		
Absorption correction	multi-scan		
Max. and min. transmission	0.8840 and 0.7890		
Structure solution technique	direct methods		
Structure solution program	SHELXS-97 (Sheldrick, 2008)		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Refinement program	SHELXL-2012 (Sheldrick, 2012)		
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$		
Data / restraints / parameters	18417 / 0 / 751		
Goodness-of-fit on F <sup>2</sup>	1.017		
$\Delta / \sigma_{max}$	0.001		
Final R indices	12834 data; I> $2\sigma(I)$ R1 = 0.0448, wR2 = 0.0933		
	all data $R1 = 0.0784, wR2 = 0.1045$		
Weighting scheme	w=1/[ $\sigma^2(F_o^2)$ +(0.0420P) <sup>2</sup> +0.7503P] where P=( $F_o^2$ +2 $F_c^2$ )/3		
Largest diff. peak and hole	0.457 and -0.459 eÅ <sup>-3</sup>		
R.M.S. deviation from mean	0.075 eÅ <sup>-3</sup>		

Table S9.	Sample and	crystal data	for complex <b>3</b> .
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Chemical formula	$C_{33}H_{34}BCuN_6$	
Formula weight	589.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.380 x 0.470 x 0.620 mm	
Crystal habit	clear orange prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 19.1311(10) Å	$\alpha = 90^{\circ}$
	b = 8.4051(5)  Å	$\beta = 107.483(2)^{\circ}$
	c = 19.2334(10) Å	$\gamma = 90^{\circ}$
Volume	2949.8(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.326 g/cm <sup>3</sup>	
Absorption coefficient	0.774 mm <sup>-1</sup>	
F(000)	1232	

 Table S10. Data collection and structure refinement for complex 3.

Diffractometer	Bruker APEX II CCD	
Radiation source	fine-focus tube, MoKα	
Theta range for data collection	1.32 to 30.48°	
Index ranges	-27<=h<=26, -11<=k<=11, -27<=l<=27	
Reflections collected	70436	
Independent reflections	8876 [R(int) = 0.0278]	
Coverage of independent reflections	98.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7576 and 0.6456	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8876 / 0 / 377	
Goodness-of-fit on F <sup>2</sup>	1.056	
$\Delta / \sigma_{max}$	0.010	
Final R indices	8132 data; I> $2\sigma(I)$ R1 = 0.0279, wR2 = 0.0762	
	all data $R1 = 0.0314$ , $wR2 = 0.0783$	
Weighting scheme	w=1/[ $\sigma^2(F_o^2)$ +(0.0380P) <sup>2</sup> +1.5888P] where P=( $F_o^2$ +2 $F_c^2$ )/3	
Extinction coefficient	0.0016(3)	
Largest diff. peak and hole	0.440 and -0.288 eÅ <sup>-3</sup>	
R.M.S. deviation from mean	0.056 eÅ <sup>-3</sup>	

Chemical formula	$C_{49}H_{54}BCuN_4$	
Formula weight	773.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.460 x 0.480 x 0.500 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.4316(4) Å	$\alpha = 90^{\circ}$
	b = 20.5365(8) Å	$\beta = 105.3710(10)^{\circ}$
	c = 18.7320(7) Å	$\gamma = 90^{\circ}$
Volume	4240.3(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.211 g/cm <sup>3</sup>	
Absorption coefficient	0.553 mm <sup>-1</sup>	
F(000)	1640	

 Table S11. Sample and crystal data for complex 4.

Diffractometer	Bruker APEX DUO	
Radiation source	fine-focus tube, MoKa	
Theta range for data collection	1.50 to 30.52°	
Index ranges	-16<=h<=16, -29<=k<=29, -26<=l<=26	
<b>Reflections collected</b>	101321	
Independent reflections	12842 [R(int) = 0.0256]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7850 and 0.7700	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XS 2013/1 (Bruker AXS)	
<b>Refinement method</b>	Full-matrix least-squares on F <sup>2</sup>	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$	
Data / restraints / parameters	12842 / 6 / 548	
Goodness-of-fit on F <sup>2</sup>	1.032	
$\Delta/\sigma_{max}$	0.002	
Final R indices	11404 data; I> $2\sigma(I)$ R1 = 0.0302, wR2 = 0.0831	
	all data $R1 = 0.0356$ , $wR2 = 0.0867$	
Weighting scheme	w=1/[ $\sigma^2(F_o^2)$ +(0.0460P) <sup>2</sup> +1.7572P] where P=( $F_o^2$ +2 $F_c^2$ )/3	
Largest diff. peak and hole	0.762 and -0.348 eÅ <sup>-3</sup>	
R.M.S. deviation from mean	0.052 eÅ <sup>-3</sup>	

 Table S12. Data collection and structure refinement for complex 4.









