# Triboluminescence of a new family of Cu<sup>l</sup>-NHC complexes in crystalline solid and in amorphous polymer films

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#### I. General specifications

# Materials

(1,3-dibenzylbenzimidazoyl-2-ylidene)copper(I) chloride,<sup>1</sup> N,N'-dimethyl-2,11diaza[3,3](2,6)pyridinophane,<sup>2</sup> N,N'-di-tert-butyl-2,11-diaza[3,3](2,6)pyridinophane<sup>3</sup>, and complex  $3a^4$  were synthesized by the previously reported procedures. Powder of polymethylmethacrylate (PMMA) (Mw: 350,000), polystyrene (Mw: 35,000), and poly(vinyl 48,000) chloride) (Mw: were purchased from Aldrich. Chloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) and chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) were purchased from Tokyo Chemical Industry.

Instrumentation. NMR spectra were measured on JEOL ECZ600R or JEOL ECZ400S NMR spectrometers. The following abbreviations are used for describing NMR spectra: s (singlet), d (doublet), t (triplet), dd (double of doublets), quat (quaternary). Electrospray Ionization Mass Spectrometry (ESI-MS) measurements were performed on a Thermo Scientific ETD apparatus. Elemental analyses were performed using an Exeter Analytical CE440 instrument. FT-IR spectra were measured using an Agilent Cary 630 with an ATR module in an argon-filled glovebox. The following abbreviations are used for describing FT-IR spectra: s (strong), m (medium), w (weak), br (broad). Absorbance UV/vis spectra were collected using an Agilent Cary 60 instrument. Fluorescence microscopy images were taken using an inverted microscope (Olympus IX83) equipped with a spinning disk (Yokogawa CSU-W) where a back-illuminated sCMOS camera (Teledyne Photometrics Prime BSI) is equipped. ( $\lambda_{ex} = 405$  nm;  $\lambda_{em} = 520$  nm; Exposure time = 50 msec ). Polymer samples were put in glass bottom dish 35mm (Iwaki) and were sealed under Ar gas, then sealed and used for measurement.

*Photoluminescence properties.* Luminescence spectra and luminescence quantum yields were recorded by a Hamamatsu Quantaurus-QY Plus spectrometer (excitation wavelength is 380 nm). For PLQY measurements, a solid sample placed on a quartz dish was purged with nitrogen gas for 30 min and measured keeping nitrogen gas flow (excitation wavelength is 380 nm). Luminescence lifetime was measured with second harmonics of a Spectra-Physics Mai Tai pulsed laser and a Hamamatsu Photonics Streak scope camera (excitation wavelength is 380 nm). Fitting curves of photoluminescence of crystals were obtained as one exponential fit.

*Measurement of triboluminescence spectra in Ar*. In a glove box filled with Ar gas, crystals or PMMA films in glass tube or glass vial were rubbed by a glass tube (diameter: 9.0 mm), in which a fiber optic probe was placed inside. The TL spectra were collected using a QE-Pro 6200

spectrometer manufactured by Ocean Optics (integration time is 5 seconds).

*Measurement of triboluminescence spectra under atmosphere of different gases including carbon dioxide, nitrogen, helium, and sulfur hexafluoride.* Glass tube or vial containing crystals or PMMA films were capped with a septum, through which a glass tube (diameter: 9.0 mm) was inserted; a fiber optic probe was placed inside a glass tube. Prior to measurement, a gas was purged for 5 minutes through the needle. During measurement, the setup was protected from stray light by covering with aluminum foil. Samples were crushed or rubbed by the glass tube under a gas flow. The generated light was collected by a QE-Pro 6200 spectrometer manufactured by Ocean Optics (integration time is 5 seconds).

# Powder X-ray diffraction analysis.

The powder X-ray diffraction studies were performed on an automated Bruker D8 Discover diffractometer equipped with an EIGER R 500K detector. The CuK $\alpha$ 1 radiation was used. All experiments were carried out at room temperature (293(2) K). Before measurements, crystals were carefully ground using a mortar and a pestle. If films were measured, the sample thickness was of ca. 0.05-0.08 mm. Samples were placed in a Si-low-background holder. Patterns were recorded in the 20 range starting from 5°, in 0.015°steps, with an exposure time of 1 s. Simulated PXRD patterns were obtained by Mercury (version 3.9) using structural models based on single-crystal XRD data collected at low temperatures.

*High speed camera video recording*. A phantom v641 camera with a 105mm Nikon macro lens was used. The f-stop was 2.8. Frame rate of 2000 or 5000 fps was applied. During experiments, crystals were crushed between two glass microscope slides. The emission imaging was obtained by free software ImageJ (1.52a).

#### **II.** Synthesis of Cu complexes

#### Synthesis of complex 1



#### Scheme S1.Synthesis of 1.

In a glovebox, N,N'-dimethyl-2,11-diaza[3,3](2,6)-pyridinophane (100 mg, 0.373 mmol), chloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) (150 mg, 0.372 mmol), KPF<sub>6</sub> (688 mg, 3.74 mmol), and dry MeCN (10 mL) were placed in a 20 mL vial and stirred at room temperature for 2 h. After reducing volume of solvent to ca. 1 mL under reduced pressure, dichloromethane (2 mL) was added and the reaction mixture was filtered off to remove an insoluble white solid. Crystals of pure compound were then obtained by diethyl ether vapor diffusion to dichloromethane solution at least three times to provide yellow crystalline solid (278 mg, 96%). A crystal suitable for X-ray crystallography and triboluminescence study was obtained by vapor diffusion with MeCN-diethyl ether.

<sup>1</sup>H NMR (600 MHz, -30 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.24 (t, <sup>3</sup>J<sub>HH =</sub> 7.6 Hz, *p*-**H**<sub>py</sub>, 2H), 7.17 (s, C**H**<sub>Im</sub>, 2H), 6.90 (s, C**H**<sub>Mes-Ar</sub>, 4H), 6.72 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *m*-**H**<sub>py</sub>, 2H), 6.63 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, *m*-**H**<sub>py</sub>, 2H), 3.55 (d, <sup>2</sup>J<sub>HH</sub> = 15.3, Py-C**H**<sub>2</sub>-N,2H), 3.48 (s, Py-C**H**<sub>2</sub>-N, 4H), 3.32 (d, <sup>2</sup>J<sub>HH</sub> = 15.3 Hz, Py-C**H**<sub>2</sub>-N, 2H), 2.34 (s, N-C**H**<sub>3</sub>, 3H), 2.30 (s, N-C**H**<sub>3</sub>, 3H), 2.25 (s, C-C**H**<sub>3Mes-Ar</sub>, 6H), 2.14 (s, C-C**H**<sub>3Mes-Ar</sub>, 12H).

<sup>13</sup>C NMR (151 MHz, -30 °C, CD<sub>2</sub>Cl<sub>2</sub>): δ 186.3 (quat.  $C_{Im}$ ), 154.6 (quat.  $C_{Py}$ ), 153.9 (quat.  $C_{Py}$ ), 138.6 (N<sub>Im</sub>- $C_{Mes-Ar}$ ), 136.4 (*p*- $C_{Py}$ ), 135.99 (*p*-C(CH<sub>3</sub>)<sub>Mes-Ar</sub>), 134.7 (*o*-C(CH<sub>3</sub>)<sub>Mes-Ar</sub>), 128.8 (*C*H<sub>Mes-Ar</sub>), 123.7 (*m*- $C_{Py}$ ), 121.7 (*C*H<sub>Im</sub>), 121.2 (*m*- $C_{Py}$ ), 65.8 (Py-*C*H<sub>2</sub>-N), 64.5 (Py-*C*H<sub>2</sub>-N), 49.8 (N-*C*H<sub>3</sub>), 43.6 (N-*C*H<sub>3</sub>), 20.7 (C(*C*H<sub>3</sub>)<sub>Mes-Ar</sub>), 18.2 (-C(*C*H<sub>3</sub>)<sub>Mes-Ar</sub>).

<sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -73.4 (d,  $J_{P,F}$  = 714 MHz).

ESI-HRMS m/z calcd for  $[C_{37}H_{44}CuN_6]^+ = 635.2923$ , found: 635.2901, and  $[PF_6]^- = 144.9647$ , found: 144.9659

Elemental Analysis. Found (calcd for  $C_{37}H_{44}N_6CuF_6P$ ): C, 57.16 (56.88), H, 5.96 (5.68), N, 10.50 (10.76).

UV-vis (in dichloromethane): λ, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>) 228 (2000), 278 (8200).

FT-IR (ATR, solid): 691 (w), 735 (m), 761 (m), 831 (s), 872 (w), 927 (m), 973 (m), 1026 (w), 1095 (w), 1113 (m), 1165 (m), 1242 (w), 1266 (m), 1315 (m), 1380 (m), 1397 (m), 1446 (m), 1463 (m), 1487 (m), 1576 (w), 1599 (w), 2857 (br, w), 2921 (br, w).



**Figure S1.** <sup>1</sup>H NMR spectrum of **1** in  $CD_2Cl_2$  at -30 °C (600 MHz).



Figure S2. <sup>13</sup>C NMR spectrum of 1 in  $CD_2Cl_2$  at -30 °C (150 MHz).



Figure S3 VT-NMR spectra of 1 in CD<sub>2</sub>Cl<sub>2</sub>.

The broadening of the peaks of 1 at higher temperatures is caused by exchange process described in Scheme S2.<sup>4</sup>



Scheme S2. Exchange process observed in solution of complex 1.



Figure S4. <sup>19</sup>F-NMR spectrum of 1 in  $CD_2Cl_2$  at room temperature (376 MHz).



Figure S5. IR spectrum of 1.

#### Synthesis of complex 2



Scheme S3. Synthesis of 2.

Complex 2 was prepared by the same procedure as 1 using N,N'-dimethyl-2,11-diaza[3,3](2,6)-pyridinophane 0.303 (81.4 mg, mmol), chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (147 mg, 0.301 mmol), MeCN (8 mL), and KPF<sub>6</sub> (556 mg, 3.02 mmol) to provide a yellow crystalline solid (239 mg, 92%). Crystals suitable for X-ray crystallography and triboluminescence study were obtained by the vapor diffusion method with dichloromethane-diethyl ether.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.44 (t, <sup>3</sup>*J*<sub>HH =</sub> 7.9 Hz, Ar-*H*<sub>IPr</sub>, 2H), 7.30 (s, C*H*<sub>Im</sub>, 2H), 7.31 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, *p*-*H*<sub>py</sub>, 2H), 7.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.9 Hz, Ar-*H*<sub>IPr</sub>, 4H), 6.69 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, *m*-*H*<sub>py</sub>, 2H), 6.68 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.7 Hz, *m*-*H*<sub>py</sub>, 2H), 3.72 (d, <sup>2</sup>*J*<sub>HH</sub> = 14.3 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.59 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.4 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.50 (d, <sup>2</sup>*J*<sub>HH</sub> = 14.3 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.38 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.4 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.17 (septet, <sup>3</sup>*J*<sub>HH = 6.8 Hz, C*H*(CH<sub>3</sub>)<sub>2</sub>, 4H), 2.24 (s, N-C*H*<sub>3</sub>, 3H), 2.14 (s, N-C*H*<sub>3</sub>, 3H), 1.13 (d, <sup>3</sup>*J*<sub>HH = 6.8 Hz, CH(C*H*<sub>3</sub>)<sub>2</sub>, 12H), 1.00 (d, <sup>3</sup>*J*<sub>HH = 6.8 Hz, CH(C*H*<sub>3</sub>)<sub>2</sub>, 12H).</sub></sub></sub>

<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  186.3 (quat.  $C_{Im}$ ), 155.0 (quat.  $C_{Py}$ ), 154.2 (quat.  $C_{Py}$ ), 145.8 (quat.  $C_{Ar}$ ), 137.0 (p- $C_{Py}$ ) and (C $H_{Imd}$ ), 130.5 (p- $C_{Ar}$ ), 124.7 (m- $C_{Ar}$ ), 123.8 (m- $C_{Py}$ ), 123.7 ( $C_{Ar}$ -C(CH<sub>3</sub>)<sub>2</sub>), 121.7 (121.4 (m- $C_{Py}$ ), 66.3 (Py-CH<sub>2</sub>-N), 63.4 (Py-CH<sub>2</sub>-N), 51.9 (N-CH<sub>3</sub>), 38.9 (N-CH<sub>3</sub>), 29.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.8 (CH(CH<sub>3</sub>)<sub>2</sub>).

<sup>19</sup>F NMR (376 MHz,  $CD_2Cl_2$ ): -73.4 (d,  $J_{P,F}$  = 714 MHz).

ESI-HRMS m/z calcd for  $[C_{43}H_{56}CuN_6]^+ = 719.3862$ , found: 719.3833, and  $[PF_6]^- = 144.9647$ , found: 144.9665

Elemental analysis. Found (calcd for C43H56N6CuPF6) C, 59.51 (59.68), H, 6.80 (6.52), N, 9.40

(9.71) UV-vis (in dichloromethane): λ, nm (ε, M<sup>-1</sup>cm<sup>-1</sup>) 228 (15000), 287 (6700).

FT-IR (ATR, solid): 705 (m), 734 (s), 762 (s), 833 (s), 876 (m), 969 (m), 993 (m), 1013 (m), 1035 (m), 1094 (m), 1121 (m), 1165 (w), 1258 (w), 1273 (m), 1309 (m), 1328 (m), 1363 (w), 1391 (m), 1444 (m), 1461 (m), 1576 (w), 1599 (w), 2869 (m), 2927 (m), 2965 (m).



**Figure S6.** <sup>1</sup>H NMR spectrum of **2** in  $CD_2Cl_2$  at room temperature (400 MHz).



**Figure S7.** <sup>13</sup>C NMR spectrum of **2** in  $CD_2Cl_2$  at room temperature (100 MHz).



**Figure S8.** <sup>19</sup>F-NMR spectrum of **2** in  $CD_2Cl_2$  at room temperature (376 MHz).



Figure S9. IR spectrum of 2.

#### Synthesis of complex 3b



Scheme S4. Synthesis of 3b.

Complex 3b was prepared by the similar procedure to 1 using (1,3-dibenzylbenzimidazoyl-2-ylidene)copper(I) chloride (57.6 mg, 0.145 mmol), N,N'-di-t-butyl-2,11-diaza[3,3](2,6)-pyridinophane (50.1 mg, 0.142 mmol), dry MeCN (1 mL), dry THF (1 mL), and sodium trifluoromethanesulfonate (76.3 mg, 0.443 mmol) to provide yellow crystalline solid (60.1 mg, 49%). Crystals suitable for X-ray crystallography and triboluminescence study were obtained bv solvent diffusion method with dichloromethane-benzene.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.32-7.25 (m, *p*-*H*<sub>py</sub> and Ar-*H*<sub>benz</sub>, 12H), 7.06-7.03 (m, Ar-*H*<sub>benz</sub>, 4H), 6.81 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, *m*-*H*<sub>py</sub>, 2H), 6.77 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, *m*-*H*<sub>py</sub>, 2H), 6.08 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.1 Hz, C*H*<sub>2benz</sub>, 2H), 5.65 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.1 Hz, C*H*<sub>2benz</sub>, 2H), 4.73 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.1 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.76 (d, <sup>2</sup>*J*<sub>HH</sub> = 12.8 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.60 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.1 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.50 (d, <sup>2</sup>*J*<sub>HH</sub> = 12.8 Hz, Py-C*H*<sub>2</sub>-N, 2H), 1.36 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H), 1.02 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H).

<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 192.7 (quat.  $C_{Imd}$ ), 160.0 (quat.  $C_{Py}$ ), 155.4 (quat.  $C_{Py}$ ), 137.6 (*p*- $C_{Py}$ ), 136.2 (Ar- $C_{-benz}$ ), 134.6 (Ar- $C_{-benz}$ ), 129.0 (Ar- $CH_{-benz}$ ), 127.9 (Ar- $C_{-benz}$ ), 126.3 (Ar- $CH_{benz}$ ), 124.3 (*m*- $C_{Py}$ ), 123.8 (Ar- $CH_{-benz}$ ), 121.7 (*m*- $C_{Py}$ ), 112.2 (Ar- $CH_{-benz}$ ), 59.7 (Py- $CH_2$ -N), 59.2 (Py- $CH_2$ -N), 59.1 (Py- $CH_2$ -N), 56.3 (N- $C(CH_3)_2$ ), 52.3 ( $CH_{2benz}$ ), 27.5 (N- $C(CH_3)_3$ ).

<sup>19</sup>F NMR (376 MHz,  $CD_2Cl_2$ ):  $\delta$  -88.3 (s).

ESI-HRMS m/z calcd for  $[C_{43}H_{50}CuN_6]^+ = 713.3393$ , found: 713.3371, and  $[CF_3SO_3]^- = 148.9526$ , found: 148.9548.

Elemental Analysis. Found (calcd for C44H50N6CuO3SF3): C, 61.05 (61.20), H, 5.58 (5.84), N,

9.62 (9.73).

UV-vis (in dichloromethane):  $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) 230 (20000), 305 (17000).

FT-IR (ATR, solid): 697 (m), 716 (m), 747 (m), 762 (m), 795 (m), 809 (m), 845 (m), 865 (w), 891 (w), 928 (m), 974 (m), 1022 (s), 1076 (m), 1114 (s), 1137 (s), 1160 (m), 1193 (m), 1217 (m), 1266 (w), 1307 (w), 1356 (m), 1389 (m), 1456 (m), 1478 (m), 1497 (m), 1574 (w), 1600 (m), 2834 (m), 2975 (br, m).



Figure S10. <sup>1</sup>H NMR spectrum of 3b in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (400 MHz).



Figure S11. <sup>13</sup>C NMR spectrum of **3b** in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (100 MHz).



Figure S12. <sup>19</sup>F-NMR spectrum of 3b in  $CD_2Cl_2$  at room temperature (376 MHz).



Figure S13. IR spectrum of 3b.

#### Synthesis of complex 3c



Scheme S5. Synthesis of 3c.

In a glovebox, (1,3-dibenzylbenzimidazoyl-2-ylidene)copper(I) chloride (56.8 mg, 0.143 mmol), N,N'-di-t-butyl-2,11-diaza[3,3](2,6)-pyridinophane (50.1 mg, 0.142 mmol), dry MeCN (1 mL), and dry THF (1 mL) were stirred at room temperature for 2 h. Potassium trifluoroacetate (46.1 mg, 0.303 mmol) was dissolved in dry MeOH (3 mL) and added to the mixture. After stirring for 10 min, the reaction mixture was concentrated under reduced pressure. The obtained solid was suspended in dry dichloromethane (2 mL), then filtered off to remove insoluble white solid and concentrated under reduced pressure. Diethyl ether vapor diffusion into dichloromethane solution gave a yellow crystalline solid. The crystals were washed with diethyl ether. The obtained yellow crystal was further purified by crystallization with the vapor diffusion method using dichloromethane-diethyl ether at least three times to give yellow crystals suitable for X-ray crystallography and triboluminescence study. (90.5 mg, 77%).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.33-7.28 (m, *p*-*H*<sub>py</sub> and Ar-*H*<sub>benz</sub>, 12H), 7.06-7.03 (m, Ar-*H*<sub>benz</sub>, 4H), 6.82 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, *m*-*H*<sub>py</sub>, 2H), 6.77 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, *m*-*H*<sub>py</sub>, 2H), 6.08 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.1 Hz, C*H*<sub>2benz</sub>, 2H), 5.66 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.1 Hz, C*H*<sub>2benz</sub>, 2H), 4.73 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.1 Hz, -Py-C*H*<sub>2</sub>-N-, 2H), 3.76 (d, <sup>2</sup>*J*<sub>HH</sub> = 13.0 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.61 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.1 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.50 (d, <sup>2</sup>*J*<sub>HH</sub> = 13.0 Hz, Py-C*H*<sub>2</sub>-N, 2H), 1.36 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H), 1.02 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H).

<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 192.7 (quat.  $C_{Imd}$ ), 160.0 (quat.  $C_{Py}$ ), 155.5 (quat.  $C_{Py}$ ), 137.6 (*p*- $C_{Py}$ ), 136.2 (Ar- $C_{-benz}$ ), 134.6 (Ar- $C_{-benz}$ ), 129.0 (Ar- $CH_{-benz}$ ), 127.9 (Ar- $C_{-benz}$ ), 126.3 (Ar- $CH_{benz}$ ), 124.2 (*m*- $C_{Py}$ ), 123.8 (Ar- $CH_{-benz}$ ), 121.7 (*m*- $C_{Py}$ ), 112.2 (Ar- $CH_{-benz}$ ), 59.7 (Py- $CH_2$ -N), 59.1 (Py- $CH_2$ -N), 56.3 (N-C(CH<sub>3</sub>)<sub>2</sub>), 52.3 ( $CH_{2benz}$ ), 27.5 (N-C( $CH_3$ )<sub>3</sub>).

<sup>19</sup>F NMR (376 MHz,  $CD_2Cl_2$ ):  $\delta$  -74.7 (s).

ESI-HRMS m/z calcd for  $[C_{43}H_{50}CuN_6]^+ = 713.3393$ , found: 713.3371, and  $[CF_3CO_2]^- = 713.3393$ 

112.9856, found: 112.9876.

Elemental Analysis. Found (calcd for  $C_{45}H_{50}N_6CuO_2F_3$ ): C, 65.05 (65.32), H, 6.20 (6.09), N, 10.08 (10.16).

UV-vis (in dichloromethane):  $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) 230 (20000), 305 (17000).

FT-IR (ATR, solid): 715 (s), 746 (s), 763 (m), 794 (m), 809 (s), 845 (m), 865 (w), 892 (w), 928 (m), 975 (m), 1007 (m), 1034 (m), 1076 (m), 1105 (s), 1148 (m), 1191 (s), 1219 (m), 1268 (w), 1306 (w), 1354 (m), 1364 (m), 1389 (m), 1455 (m), 1478 (m), 1498 (m), 1573 (m), 1601 (m), 1690 (s), 2834 (br, m), 2967 (m).



Figure S14. <sup>1</sup>H NMR spectrum of 3c in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (400 MHz).



Figure S15. <sup>13</sup>C NMR spectrum of 3c in  $CD_2Cl_2$  at room temperature (100 MHz).



Figure S16. <sup>19</sup>F-NMR spectrum of **3c** in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (376 MHz)



Figure S17. IR spectrum of 3c.

#### Synthesis of 3d



Scheme S6. Synthesis of 3d.

In a glovebox, (1,3-dibenzylbenzimidazoyl-2-ylidene)copper(I) chloride (57.1 mg, 0.144 mmol), N,N'-di-t-butyl-2,11-diaza[3,3](2,6)-pyridinophane (50.5 mg, 0.143 mmol), dry MeCN (1 mL), and dry THF (1 mL) were stirred at room temperature for 2 h. NaBPh<sub>4</sub> (98.8 mg, 0.289 mmol) was dissolved in dry MeOH (3 mL) and added to the mixture. After stirring for 10 min, the reaction mixture was concentrated under reduced pressure, then suspended in a mixture of dry dichloromethane (1 mL) and dry MeCN (1 mL), then filtered off to remove white solid. A yellow crystalline solid was obtained by diethyl ether diffusion into the resulting solution. The obtained crystalline solid were collected and further purified by crystallization by diethyl ether diffusion to acetone solution three times to provide crystals suitable for X-ray crystallography and triboluminescence study (92.9 mg, 63%).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.34-7.25 (m, *p*-*H*<sub>py</sub> Ar-*H*<sub>benz</sub>, and B-*m*-*H*<sub>Ph</sub>, 20H), 7.07-7.04 (m, Ar-*H*<sub>benz</sub>, 4H), 7.01 (t, B-*o*-*H*<sub>Ph</sub>, 8H), 6.86, (t, B-*p*-*H*<sub>Ph</sub>, 4H), 6.77 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz, *m*-*H*<sub>py</sub>, 2H), 6.85 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, *m*-*H*<sub>py</sub>, 2H), 6.08 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.0 Hz, C*H*<sub>2benz</sub>, 2H), 5.66 (d, <sup>2</sup>*J*<sub>HH</sub> = 16.0 Hz, C*H*<sub>2benz</sub>, 2H), 4.70 (d, <sup>2</sup>*J*<sub>HH</sub> = 14.6 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.77 (d, <sup>2</sup>*J*<sub>HH</sub> = 12.8 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.51 (d, <sup>2</sup>*J*<sub>HH</sub> = 12.4 Hz, Py-C*H*<sub>2</sub>-N, 2H), 3.49 (d, <sup>2</sup>*J*<sub>HH</sub> = 15.1 Hz, Py-C*H*<sub>2</sub>-N, 2H), 1.37 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H), 1.00 (s, N-C(C*H*<sub>3</sub>)<sub>3</sub>, 9H).

<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 192.6 (quat.  $C_{Imd}$ ), 164.9-163.4 (B- $C_{ipso}$ ), 160.1 (quat.  $C_{Py}$ ), 155.2 (quat.  $C_{Py}$ ), 137.6 (p- $C_{Py}$ ), 136.1 (B-o-Ph), 135.9 (Ar-C-<sub>benz</sub>), 134.4 (Ar-C-<sub>benz</sub>), 129.0 (Ar-CH-<sub>benz</sub>), 128.0 (Ar-C-<sub>benz</sub>), 126.3 (Ar-CH<sub>benz</sub>), 125.7 (B-m-Ph), 124.4 (m- $C_{Py}$ ), 123.9 (Ar-CH-<sub>benz</sub>), 121.8 (B-p-Ph), 121.6 (m- $C_{Py}$ ), 112.2 (Ar-CH-<sub>benz</sub>), 59.6 (Py-CH<sub>2</sub>-N), 59.2 (Py-CH<sub>2</sub>-N), 59.1 (Py-CH<sub>2</sub>-N), 56.3 (N-C(CH<sub>3</sub>)<sub>2</sub>), 52.3 (CH<sub>2benz</sub>), 27.5 (N-C(CH<sub>3</sub>)<sub>3</sub>).

ESI-HRMS m/z calcd for  $[C_{43}H_{50}CuN_6]^+ = 713.3393$ , found: 713.3376, and  $[C_{24}H_{20}B]^- = 319.1664$ , found: 319.1682.

Elemental Analysis. Found (calcd for  $C_{67}H_{70}N_6BCu$ ) C, 77.81 (77.85), H, 6.80(6.83), N, 8.16 (8.13).

UV-vis (in dichloromethane):  $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) 230 (40000), 305 (16000).

FT-IR (ATR, solid): 700 (s), 732 (s), 811 (m), 845 (m), 918 (m), 975 (m), 1027 (m), 1076 (m), 1184 (m), 1263 (w), 1360 (s), 1389 (m), 1429 (m), 1472 (m), 1573 (m), 1596 (m), 1708 (w), 2974 (m), 3030 (br, m).



**Figure S18.** <sup>1</sup>H NMR spectrum of **3d** in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (400 MHz).



Figure S19. <sup>13</sup>C NMR spectrum of 3d in CD<sub>2</sub>Cl<sub>2</sub> at room temperature (100 MHz).



Figure S20. IR spectrum of 3d.

# Preparation of PMMA films containing Cu(I) complexes

In a glove box, the corresponding Cu(I) complex (2 mg), was added to a solution of PMMA (200 mg) in dry dichloromethane (2.5 mL) in a glass vial containing a magnetic stirring bar; the reaction mixture was stirred until complete dissolution. The solution was evaporated slowly under reduced pressure in a vial or a glass Petri dish, and then further dried under vacuum at room temperature for 1 day. The obtained film was carefully removed and used for characterization of photophysical properties. PMMA films containing different ratio of Cu(I) complexes to PMMA were prepared with the same method by altering the ratio of Cu(I) complex to PMMA.

# Air stability of 1, 2, and 3a in PMMA films

The PMMA films containing 1 wt% of Cu(I) complexes (1, 2, and 3a) were placed in the glass vials and kept in the air at ambient temperature. The samples were purged with a nitrogen gas for 1 hour prior to measuring PLQY in an integrating sphere. The PLQYs were measured under a nitrogen gas flow and were determined as an average of measurements for the three films.



Figure S21. PLQY of 1 wt% of 1, 2, and 3a in PMMA after exposing to air.

# III. Powder X-ray diffraction study

Experimental patterns (black) were collected at room temperature; theoretical ones (red) were simulated based on X-ray crystal structures collected at low temperatures.



Figure S22. Powder X-ray diffraction patterns of crystalline samples of 1.



Figure S23. Powder X-ray diffraction patterns of crystalline samples of 2.



Figure S24. Powder X-ray diffraction patterns of crystalline samples of 3a.



Figure S25. Powder X-ray diffraction patterns of crystalline samples of 3b.



Figure S26. Powder X-ray diffraction patterns of crystalline samples of 3c.



Figure S27. Powder X-ray diffraction patterns of crystalline samples of 3d.



Figure S28. Powder X-ray diffraction patterns of PMMA film.



Figure S29. X-ray diffraction patterns of PMMA films containing 1 wt% of Cu(I) complexes.



**Figure S30**. X-ray diffraction patterns of PMMA films containing different amounts of **3a**: (a) 10 wt%; (b) 50 wt%; and (c) 80 wt%.

IV. UV-vis spectra of Cu complexes



Figure S31. UV-vis absorption spectra of 1, 2, and 3a-d in dichloromethane at 25 °C.

# **V.** Photophysical properties

**Table S1.** Photophysical properties of **1**, **2**, and **3a-d** in argon-saturated dichloromethane solution  $(2-3 \times 10^{-5} \text{ M})$ .<sup>*a*</sup>

Complex	Counter anion	$PLQY^{b}$	$\lambda_{max}$
1	$PF_6$	0.49	576
2	$PF_6$	0.81	558
<b>3</b> a	$PF_6$	0.72	549
<b>3</b> b	OTf	< 0.01 <sup>c</sup>	-
3c	CF <sub>3</sub> COO	< 0.01 <sup>c</sup>	-
3d	BPh <sub>4</sub>	0.56	548

<sup>*a*</sup>Excitation at 380 nm. <sup>*b*</sup>Photoluminescence quantum yield. <sup>*c*</sup> The quench of photoluminescence can be ascribed to a formation of exciplex with Lewis basic counter anion.

Table S2. Photophysical properties of 1, 2, and 3a in crystalline state (under nitrogen).<sup>a</sup>

Complex	$\tau (\mu s)^b$	$k_{\rm r} \cdot 10^{-4}  ({\rm s}^{-1})^c$	$k_{\rm nr} \cdot 10^{-4} \ ({\rm s}^{-1})^d$
1	16.3	4.05	2.09
2	16.1	5.15	1.06
<b>3</b> a	15.0	5.07	1.60

<sup>*a*</sup>Excitation at 380 nm. <sup>*b*</sup>Emission lifetime at 298 K. <sup>*c*</sup>Radiative decay rate constants  $k_r$  were estimated as PLQY/ $\tau$ . <sup>*d*</sup>Non-radiative decay rate constants  $k_{nr}$  were calculated as  $k_r \cdot (1 - PLQY)/PLQY$ . PLQY is given in Table 1 of the manuscript.



Figure S32. Photoluminescence spectra of 1, 2, 3a, and 3d in dichloromethane solution.



**Figure S33**. Normalized photoluminescence decay profile of **1**, **2**, and **3a** in crystals at 25 °C under argon atmosphere. Excitation at 380 nm. Solid lines are fitting curves.

**Table S3**. Photophysical properties of polystyrene (PS) and polyvinyl chloride (PVC) films blended with 1 wt% of **1**, **2**, and **3a** under  $N_2$ .<sup>*a*</sup>

Complex	$PLQY^b$		$\lambda_{max}$ (nm)	
	PS	PVC	PS	PVC
1	0.38	0.51	552	552
2	0.71	0.71	539	539
<b>3</b> a	0.69	0.79	529	522

<sup>a</sup>Excitation at 380 nm. <sup>b</sup>Photoluminescence quantum yield.

# VI. Triboluminescent properties

Crystals or PMMA films were put in a glass vial or a glass tube equipped with a septum. A glass tube in which optical probe was placed was inserted through septum. Prior to measurement, gases were purged for 5 minutes through needle. The crystals or PMMA films were crushed or rubbed under gas flow.



Figure S34. Photograph of instrument for TL measurement.



Figure S35. Full TL spectra of crystals of 1, 2, and 3a-d under a nitrogen gas atmosphere



Figure S36. Full TL spectra of PMMA films containing 1 wt% of 1, 2, and 3a-d under a nitrogen gas atmosphere.



Figure S37. TL spectra of crystalline samples of 1, 2, and 3a-d under an argon gas atmosphere.



Figure S38. TL spectra of PMMA films containing 1 wt% of 1, 2, and 3a-d under an argon gas atmosphere.



Figure S39. TL spectra of polystyrene films containing 1 wt% of 1, 2, and 3a under an argon gas atmosphere.



Figure S40. TL spectra of polyvinyl chloride films containing 1 wt% of 1, 2, and 3a under an argon gas atmosphere.



Figure S41. TL spectra of crystalline samples of (a) 1, (b) 2, and (c) 3a under varied gas atmosphere.



Figure S42. TL spectra of crystalline samples of (a) 3b, (b) 3c, and (c) 3d under He and  $SF_6$  atmosphere.



**Figure S43**. TL spectra of **3a** in PMMA film with different weight ratio under argon: (a) 1 wt%; (b) 10 wt%; (c) 50 wt%; and (d) 80 wt% of complex **3a**; (e) overlay of normalized TL spectra.



Figure S44. TL spectra of PMMA films under vacuum of 0.5 Torr with 1 wt% of (a) 1, (b) 2, and (c) 3a.



Figure S45. Pictures of triboluminescence of crystal of (a) 1; (b) 2; (c) 3a; (d) 3b; (e) 3c; and (d) 3d under air in dimmed room light.



Figure S46. Pictures of triboluminescence of crystal of 1 compressed between two glass plates under air.



**Figure S47**. Picture of TL of PMMA film containing 10 wt% of **1** (left), **2** (center), and **3a** (right) under Ar gas. The film was rubbed using a glass rod (diameter of film: ca. 5 cm)



**Figure S48**. TL emission intensity imaging recorded by high speed camera for the crystal of **1** (size: ca. 2 mm) compressed between two glass plates under air (view from top). The video of this TL is also available.



**Figure S49**. TL emission intensity imaging for the crystal of **1** (size: ca. 2 mm) compressed between two glass plates under air (view from side); frame rate: 300 fps.



**Figure S50**. Pictures of PMMA films containing 10 wt% of **1** (left), **2** (center), and **3a** (right) that were used for experiments.



**Figure S51**. (a) PL spectrum of 9,10-diphenylanthracene (DPA) in 1 wt% PMMA film. (b) TL spectra of PMMA film containing 1 wt% of DPA under varied gas atmosphere. Crystals of DPA grown from toluene or *p*-xylene did not show discernible TL.



**Scheme S7**. Chemical structure of europium dibenzoylmethide trietylammonium (EuD4TEA). EuD4TEA was prepared according to the literature procedure<sup>5</sup> and showed triboluminescence in the solid state.



**Figure S52**. (a) Normalized PL spectra of EuD4TEA in crystal and in PMMA film (1 wt%). (b) TL spectra of PMMA film containing 1 wt% of EuD4TEA under varied gas atmosphere.

VII. Fluorescence microscopy images of PMMA films containing Cu complexes



**Figure S53.** Fluorescence microscopy images of PMMA blended with 10 wt% of **1**. (Scale bar: left, 200 and right, 20  $\mu$ m)



**Figure S54.** Fluorescence microscopy images of PMMA blended with 10 wt% of **2**. (Scale bar: left, 200 and right, 20  $\mu$ m)



Figure S55. Fluorescence microscopy images of PMMA blended with 10 wt% of 3a. (Scale bar: left, 200 and right, 20  $\mu$ m)



Figure S56. Fluorescence microscopy images of PMMA blended with 80 wt% of 3a. (Scale bar: left, 200 and right, 10  $\mu$ m)

#### VIII. X-ray structure determination details

The X-ray diffraction data for the single crystals 1, 2, and 3b-d were collected on a Rigaku XtaLab PRO instrument in an ω-scan mode with a PILATUS3 R 200K hybrid pixel array detector and MicroMax<sup>TM</sup>-003 microfocus X-ray tubes using MoKa (0.71073 Å) and  $CuK\alpha$  (1.54184 Å) radiation monochromated by means of multilayer optics. The performance mode of the X-ray tubes was 50 kV, 0.60 mA. The diffractometer was equipped with a Rigaku GN2 system for low temperature experiments. Suitable crystals of appropriate dimensions were mounted on loops in random orientations. The data were collected according to recommended strategies in an  $\omega$ -scan mode. Final cell constants were determined by global refinement of reflections from the complete data sets using the Lattice wizard module. Images were indexed and integrated with "smart" background evaluation using the CrysAlis<sup>Pro</sup> (versions 1.171.39.7b–1.171.40.79a) data reduction package. Analysis of the integrated data did not show any decay. Data were corrected for systematic errors and absorption using the ABSPACK module: Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module and the ASSIGN SPACEGROUP routine of the WinGX suite were used for the analysis of systematic absences and space-group determination. All structures were solved by the direct methods using SHELXT-2018/2<sup>6</sup> and refined by the full-matrix least-squares on  $F^2$  using SHELXL-2018/3,<sup>7</sup> which uses a model of atomic scattering based on spherical atoms. Calculations were mainly performed using the WinGX-2018.3 suite of programs.<sup>8</sup> Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The positions of the hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The disorder, if present, was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters. All the compounds studied have no unusual bond lengths and angles. Absolute crystal structure of complexes 2 and 3b-c was determined on the basis of the Flack parameter.<sup>9</sup>

Deposition numbers 2009593-2009597 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

## Crystallographic data for 1.

C<sub>37</sub>H<sub>44</sub>CuN<sub>6</sub><sup>+</sup> F6P<sup>−</sup> × 0.5 C<sub>4</sub>H<sub>10</sub>O, yellow prism (0.248 × 0.218 × 0.158 mm<sup>3</sup>), formula weight 818.35; monoclinic,  $P2_1/n$  (No. 14), a = 11.46796(15) Å, b = 19.4563(2) Å, c = 17.9268(3) Å,  $\beta = 106.3314(15)^\circ$ , V = 3838.52(9) Å<sup>3</sup>, Z = 4, Z' = 1, T = 103(2) K,  $d_{calc} = 1.416$  g cm<sup>-3</sup>, µ(MoKα) = 0.679 mm<sup>-1</sup>, F(000) = 1708;  $T_{max/min} = 1.000/0.401$ ; 111295 reflections were collected (2.093° ≤  $\theta \le 32.347^\circ$ , index ranges:  $-16 \le h \le 17$ ,  $-29 \le k \le 27$ ,  $-26 \le l \le 26$ ), 12827 of which were unique,  $R_{int} = 0.0308$ ,  $R_{\sigma} = 0.0183$ ; completeness to  $\theta_{max}$  93.5 %. The refinement of 515 parameters with 27 restraints converged to  $R_1 = 0.0321$  and  $wR_2 = 0.0867$  for 11273 reflections with  $I > 2\sigma(I)$  and  $R_1 = 0.0380$  and  $wR_2 = 0.0892$  for all data with S = 1.060 and residual electron density,  $\rho_{max/min} = 1.018$  and -0.475 e Å<sup>-3</sup>. The crystals were grown by vapor diffusion in an acetonitrile–diethyl ether system at r.t.

## Crystallographic data for 2.

C<sub>43</sub>H<sub>56</sub>CuN<sub>6</sub><sup>+</sup> F<sub>6</sub>P<sup>−</sup> × CH<sub>2</sub>Cl<sub>2</sub>, yellow prism (0.248 × 0.185 × 0.087 mm<sup>3</sup>), formula weight 950.37; orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), *a* = 12.1264(7) Å, *b* = 18.4915(15) Å, *c* = 19.9843(14) Å, *V* = 4481.2(5) Å<sup>3</sup>, *Z* = 4, *Z'* = 1, T = 95(2) K, *d<sub>calc</sub>* = 1.409 g cm<sup>-3</sup>, μ(MoKα) = 0.706 mm<sup>-1</sup>, *F*(000) = 1984; *T*<sub>max/min</sub> = 1.000/0.591; 41059 reflections were collected (1.964° ≤ θ ≤ 27.648°, index ranges: −15 ≤ *h* ≤ 15, −23 ≤ *k* ≤ 21, −26 ≤ *l* ≤ 24), 10348 of which were unique, *R<sub>int</sub>* = 0.0350, *R*<sub>σ</sub> = 0.0314; completeness to θ<sub>max</sub> 99.7 %. The refinement of 551 parameters with no restraints converged to *R*<sub>1</sub> = 0.0308 and *wR*<sub>2</sub> = 0.0739 for 9808 reflections with *I* > 2σ(*I*) and *R*<sub>1</sub> = 0.0330 and *wR*<sub>2</sub> = 0.0748 for all data with *S* = 1.049 and residual electron density, ρ<sub>max/min</sub> = 0.642 and −0.598 *e* Å<sup>-3</sup>. Flack parameter *x* = −0.005(3) determined using 4130 selected quotients by Parsons' method. The crystals were grown by vapor diffusion in a DCM−diethyl ether system at r.t.

# Crystallographic data for 3b.

C<sub>43</sub>H<sub>50</sub>CuN<sub>6</sub><sup>+</sup> CF<sub>3</sub>O<sub>3</sub>S<sup>−</sup>, yellow plank (0.078 × 0.062 × 0.025 mm<sup>3</sup>), formula weight 863.50; orthorhombic, *Pca*2<sub>1</sub> (No. 29), *a* = 20.1211(2) Å, *b* = 13.39232(18) Å, *c* = 15.13962(18) Å, *V* = 4079.64(9) Å<sup>3</sup>, *Z* = 4, *Z'* = 1, T = 95(2) K, *d<sub>calc</sub>* = 1.406 g cm<sup>-3</sup>, µ(CuKα) = 1.752 mm<sup>-1</sup>, *F*(000) = 1808; *T*<sub>max/min</sub> = 1.000/0.865; 29635 reflections were collected (3.965° ≤ θ ≤ 74.769°, index ranges:  $-24 \le h \le 25$ ,  $-16 \le k \le 16$ ,  $-18 \le l \le 18$ ), 8154 of which were unique, *R<sub>int</sub>* = 0.0383, *R*<sub>σ</sub> = 0.0380; completeness to θ<sub>max</sub> 99.8 %. The refinement of 603 parameters with 354 restraints converged to *R*<sub>1</sub> = 0.0371 and *wR*<sub>2</sub> = 0.1018 for 7899 reflections with *I* > 2σ(*I*) and *R*<sub>1</sub> = 0.0382 and *wR*<sub>2</sub> = 0.1029 for all data with *S* = 1.039 and residual electron density,  $\rho_{max/min}$  = 1.131 and - 0.394 *e* Å<sup>-3</sup>. Flack parameter *x* = 0.16(2); the structure was refined as an inversion twin. The crystals were grown by vapor diffusion in a DCM–diethyl ether system at r.t.

Crystallographic data for 3c.

 $C_{43}H_{50}CuN_6^+ C_2F_3O_2^-$ , light yellow plank (0.131 × 0.120 × 0.048 mm<sup>3</sup>), formula weight 827.45;

orthorhombic,  $Pca2_1$  (No. 29), a = 19.77529(5) Å, b = 13.53091(4) Å, c = 15.04125(5) Å, V = 4024.70(2) Å<sup>3</sup>, Z = 4, Z' = 1, T = 93(2) K,  $d_{calc} = 1.366$  g cm<sup>-3</sup>,  $\mu$ (CuK $\alpha$ ) = 1.261 mm<sup>-1</sup>, F(000) = 1736;  $T_{max/min} = 1.000/0.626$ ; 74939 reflections were collected ( $3.266^{\circ} \le \theta \le 79.715^{\circ}$ , index ranges:  $-25 \le h \le 25$ ,  $-17 \le k \le 17$ ,  $-19 \le l \le 19$ ), 8588 of which were unique,  $R_{int} = 0.0367$ ,  $R_{\sigma} = 0.0188$ ; completeness to  $\theta_{max}$  99.8 %. The refinement of 578 parameters with 218 restraints converged to  $R_1 = 0.0253$  and  $wR_2 = 0.0674$  for 8504 reflections with  $I > 2\sigma(I)$  and  $R_1 = 0.0256$  and  $wR_2 = 0.0676$  for all data with S = 1.046 and residual electron density,  $\rho_{max/min} = 0.188$  and -0.379 e Å<sup>-3</sup>. Flack parameter x = 0.174(17); the structure was refined as an inversion twin. The crystals were grown by vapor diffusion in a DCM–diethyl ether system at r.t.

# Crystallographic data for 3d.

C<sub>43</sub>H<sub>50</sub>CuN<sub>6</sub><sup>+</sup> C<sub>24</sub>H<sub>20</sub>B<sup>−</sup> × 0.175 C<sub>4</sub>H<sub>10</sub>O × 0.825 C<sub>3</sub>H<sub>6</sub>O, yellow prism (0.166 × 0.129 × 0.076 mm<sup>3</sup>), formula weight 1094.52; orthorhombic, *Pbca* (No. 61), *a* = 19.42866(14)Å, *b* = 20.15442(13) Å, *c* = 30.18361(19) Å, *V* = 11819.09(14) Å<sup>3</sup>, *Z* = 8, *Z'* = 1, T = 100(2) K, *d<sub>calc</sub>* = 1.230 g cm<sup>−3</sup>, µ(CuKα) = 0.894 mm<sup>−1</sup>, *F*(000) = 4654; *T<sub>max/min</sub>* = 1.000/0.666; 71255 reflections were collected (2.928° ≤ θ ≤ 77.389°, index ranges:  $-24 \le h \le 24$ ,  $-19 \le k \le 25$ ,  $-29 \le l \le 38$ ), 12385 of which were unique, *R<sub>int</sub>* = 0.0347, *R*<sub>σ</sub> = 0.0248; completeness to θ<sub>max</sub> 98.6 %. The refinement of 768 parameters with 119 restraints converged to *R*<sub>1</sub> = 0.0356 and *wR*<sub>2</sub> = 0.0948 for 11080 reflections with *I* > 2σ(*I*) and *R*<sub>1</sub> = 0.0398 and *wR*<sub>2</sub> = 0.0976 for all data with *S* = 1.041 and residual electron density,  $\rho_{max/min}$  = 0.328 and  $-0.657 e Å^{-3}$ . The crystals were grown by vapor diffusion in an acetone–diethyl ether system at r.t.



**Figure S57.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **1** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Cu1–N1 2.1280(9), Cu1–N2 2.1286(9), Cu1–N3 2.2048(9), Cu1–C1 1.9037(11).



**Figure S58.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **2** according to single crystal X-ray diffraction data. Selected interatomic distances [Å]: Cu1–N1 2.115(2), Cu1–N2 2.097(2), Cu1–N3 2.185(2), Cu1–C1 1.897(2).



**Figure S59.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **3b** according to single crystal X-ray diffraction data. The second disordered component is shown by dashed lines. Selected interatomic distances [Å]: Cu1–N1 2.108(2), Cu1–N2 2.163(3), Cu1–N3 2.194(2), Cu1–C1 1.901(3).



**Figure S60.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **3c** according to single crystal X-ray diffraction data. The second disordered component is shown by dashed lines. Selected interatomic distances [Å]: Cu1–N1 2.1268(17), Cu1–N2 2.1302(16), Cu1–N3 2.1904(17), Cu1–C1 1.9006(19).



**Figure S61.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for compound **3d** according to single crystal X-ray diffraction data. The second disordered component is shown by dashed lines. Selected interatomic distances [Å]: Cu1–N1 2.1078(11), Cu1–N2 2.0898(12), Cu1–N3 2.2010(11), Cu1–C1 1.8929(13).

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