Electronic Supporting Information

for

Development of Bis(arylimino)acenaphthene (BIAN) Copper Complexes as Visible Light Harvesters for Potential Photovoltaic Applications

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General information

The copper (Cu) complexes used in this study were synthesized in a glovebox under a N\textsubscript{2} atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were distilled prior to use. The other chemicals were obtained from Sigma-Aldrich and were used as received. Tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate\textsuperscript{1, 2} (n-Bu\textsubscript{4}NBAr\textsubscript{F\textsubscript{4}}), bromoacenaphthylene-1,2-dione,\textsuperscript{3} methyl 4-amino-3-iodobenzoate,\textsuperscript{4} and sodium 4-aminobenzenesulfonate\textsuperscript{5} were synthesized according to previously published procedures. The \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, and \textsuperscript{31}P NMR spectra were recorded at room temperature on a Bruker AVANCE 400 MHz spectrometer. The \textsuperscript{1}H and \textsuperscript{13}C chemical shifts (\(\delta\) reported in ppm) are referenced to the residual solvent signal(s). \textsuperscript{31}P NMR spectra were referenced externally using 85\% H\textsubscript{3}PO\textsubscript{4} (\(\delta = 0\) ppm). For the X-ray crystal structures, dihedral angles between the planes formed by the chelating rings around the Cu(I) center were determined by the Diamond 3.2 software, whereas centroid distances between aryl rings were obtained from the Mercury 3.5 software. UV-visible spectroscopic measurements were performed using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer.

Variable temperature NMR studies for Ar\textsuperscript{1COOMe-}BIAN (2)

Variable temperature (VT) NMR experiments at low (Figure S1, ESI) and high (Figure S2, ESI) temperatures were conducted in CDCl\textsubscript{3} to obtain thermodynamic parameters of this isomeric equilibrium of 2. Compound 2 was dissolved in CDCl\textsubscript{3} and sealed in a J. Young NMR tube. In order to collect the \textsuperscript{1}H NMR spectra at various temperatures between 333K and 223K (Figures S1 and S2), the tube was inserted into a temperature-controlled NMR probe before leaving the sample to equilibrate for 10 minutes at the desired temperature. The exact temperatures are indicated in the stack plots of Figures S1 and S2. Through the relative concentrations of the two isomers, obtained from the relative integration of peaks belonging to (\(E,E\))-isomer (doublet at \(\delta = 8.66\) ppm, corresponding to two protons) and (\(E,Z\))-isomer (doublet at \(\delta = 6.65\) ppm, corresponding to one proton), the equilibrium constants for the isomerisation from the (\(E,E\))-isomer to the (\(E,Z\))-isomer at each temperature can be determined by the following expression:

\[
K_{eq} = \frac{[\text{(E,Z)-isomer}]}{[\text{(E,E)-isomer}]}. 
\]

Subsequently, a Van’t Hoff plot of ln \(K_{eq}\) as a function of \(T\)^{-1} was fit to a line according to the expression:
\[ \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

where \(\Delta H^\circ\) and \(\Delta S^\circ\) have been determined to be +13.3 kJ mol\(^{-1}\) and +39.0 J mol\(^{-1}\) K\(^{-1}\) respectively (Figure S3, ESI). The conversion of \((E,E)-2\) to \((E,Z)-2\) is endothermic with the \((E,Z)\)-isomer being the product of the equilibrium, while \((E,E)-2\) is the starting material. NMR experiments at elevated temperatures (Figure S2, ESI) indicated that the coalescence temperature is 333 K in CDCl\(_3\).

**Fig. S1** Low temperature \(^1\)H NMR spectra of 2 in CDCl\(_3\) between 223 and 301 K. The solvent residual peak is at 7.26 ppm (singlet). The signal for the \((E,E)\)-isomer used in the Van’t Hoff plot is represented by the blue squares, while the signal for the \((E,Z)\)-isomer is represented by red triangles.
Fig. S2 High temperature $^1$H NMR spectra of 2 in CDCl$_3$ between 301 and 333 K. The solvent residual peak is at 7.26 ppm (singlet).

Fig. S3 Van’t Hoff plot for the isomerization equilibrium between the $(E,E)$-isomer and the $(E,Z)$-isomer.
Fig. S4 Space-filling model of 2 from single crystal X-ray diffraction experiments.
Fig. S5 Oak Ridge Thermal Ellipsoid Plots (ORTEPs) from single crystal X-ray diffraction experiments of 4. Top a) and side views b) of crystals grown from DCM/Et₂O. Space-filling model of 4 from the crystal structures. Top ((c) and (e)) and side views ((d) and (f)) of the crystals grown from THF/toluene and DCM/Et₂O respectively. The PF₆⁻ counteranion and the calculated hydrogen atoms are omitted for clarity.

Cu: orange; C: grey; I: green; N: blue; O: red
Electrochemical experiments

Cyclic voltammetry (CV) experiments were conducted using a Biologic SP-300 potentiostat with 1.0 mM solutions of each sample and 0.10 M of either $n$-Bu$_4$NBAr$_4^+$ or tetrabutylammonium hexafluorophosphate ($n$-Bu$_4$NPF$_6$) as the electrolyte. The measurements of all four compounds 1 – 4 were conducted in DMF/DMSO 1:1 (v/v) for comparison among them, but additional CVs were run in dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), or a mixture of DMF/DMSO 10:1 (v/v), each at a scan rate of 100 mV s$^{-1}$ in a glovebox. A standard three-electrode electrochemical cell was used with a glassy carbon working electrode (3 mm in diameter from BAS), a Pt wire as the counter electrode, and another Pt wire as the pseudoreference electrode. The potentials were calibrated by addition of ferrocene as an internal reference (0 V) after the CV measurements on the compound have been conducted to avoid obscuring signals from our samples. Before each experiment, the working electrode (glassy carbon) was polished using a polishing pad infused with a 0.05 µm alumina suspension, followed by sonication in DI water for 10 min, washed with methanol and acetone, before drying in air.
Fig. S6 Cyclic voltammograms of 1.0 mM of 1, with 0.10 M \( n\text{-Bu}_4\text{NBAr}^{+}_4 \) as the electrolyte in DMSO/DMF 1:1 (v/v), each at a scan rate of 100 mV s\(^{-1}\), within the potential windows of a) -2.6 to +0.9 V, and b) -2.6 to -0.6 V respectively, relative to Fc\(^+\)/Fc. Additional cyclic voltammograms were performed similarly with 0.10 M \( n\text{-Bu}_4\text{NPF}_6 \) as the electrolyte in DMSO only, within the potential windows of c) -3.1 to +1.0 V, and d) -3.1 to -0.5 V respectively, relative to Fc\(^+\)/Fc. The red arrows indicate the scan directions, with red vertical lines indicating the initial potentials for each scan. The blue arrows indicate the ligand redox events of 1 as well as additional reduction waves that appear after reversing the anodic scan in c).
Fig. S7 Cyclic voltammograms of 1.0 mM of 2, with 0.10 M \( n\)-Bu\(_4\)NBAr\(_4\) as the electrolyte in DMSO/DMF 1:1 (v/v), each at a scan rate of 100 mV s\(^{-1}\), within the potential windows of a) -2.6 to +0.3 V, and b) -1.9 to +0.3 V respectively, relative to Fc\(^+/\)Fc. Additional cyclic voltammograms were performed similarly with 0.10 M \( n\)-Bu\(_4\)NPF\(_6\) as the electrolyte in THF instead, within the potential windows of c) -3.7 to -0.7 V and d) -3.7 to +1.3 V respectively, relative to Fc\(^+/\)Fc. The red arrows indicate the scan directions, with red vertical lines indicating the initial potentials for each scan. The blue arrows indicate the ligand redox events of 2 as well as additional reduction waves that appear after reversing the anodic scan in d).
Fig. S8 Cyclic voltammograms of 1.0 mM of 3 with 0.10 M \textit{n}-Bu$_4$NBAr$^F_4$ as the electrolyte in DMF/DMSO 1:1 (v:v), each at a scan rate of 100 mV s$^{-1}$, within the potential windows of a) -2.1 to +0.5 V and b) -2.1 to -0.5 V respectively, relative to Fc$^+/Fc$. Additional cyclic voltammograms were performed similarly with 0.10 M \textit{n}-Bu$_4$NPF$_6$ as the electrolyte in DMF/DMSO 10:1 (v:v), each at a scan rate of 100 mV s$^{-1}$, within the potential windows of c) -2.1 to +1.0 V, and d) -2.1 to -0.5 V respectively, relative to Fc$^+/Fc$. The red arrows indicate the scan directions, with red vertical lines indicating the initial potentials for each scan. The blue arrows indicate the ligand reductions of 3.
Fig. S9 Cyclic voltammograms of 1.0 mM of 4 with 0.10 M \(n\)-Bu\textsubscript{4}NBAr\textsubscript{4} as the electrolyte in DMSO/DMF 1:1 (v/v) at a scan rate of 100 mV s\textsuperscript{-1}, within the potential windows of a) -2.6 to +0.3 V, and b) -2.0 to +0.7 V respectively. Additional cyclic voltammograms were performed similarly with 0.10 M \(n\)-Bu\textsubscript{4}NPF\textsubscript{6} as the electrolyte in THF, each at a scan rate of 100 mV s\textsuperscript{-1}, within the potential windows of c) -0.40 to +1.1 V, and d) -2.0 to +1.2 V respectively, relative to Fc\textsuperscript{+}/Fc. The red arrows indicate the scan directions, with red vertical lines indicating the initial potentials for each scan. The blue arrows indicate the ligand reductions of 4.

Peak-fitting for the UV-visible spectra of the solution samples of 3 and 4

The spectra were treated with a Peakfit algorithm by using the second-derivative technique for locating the maxima between 450 nm and 800 nm. The initial parameters were set up to fit three bands with the initial wavelengths set to 560, 620, and 720 nm, before the amplitudes and widths of the Gaussian curves were optimized until a satisfactory fit was obtained (Fig S20). The molar extinction coefficients (ε) were then obtained from the amplitudes of the Gaussian curves fitted into the spectrum.
Fig S10. Simulated UV-visible-NIR spectra obtained from fitting the MLCT bands I (pink), II (blue), and III (green) into the spectra of a) 3 and b) 4 between the dashed lines. The black line represents the experimental data, while the red line depicts the overall combined fit of all three bands.

Table S1. Fitted Parameters for 3

<table>
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<th>Amplitude</th>
<th>Width</th>
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<td>2930</td>
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Table S2. Fitted Parameters for 4

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<td>3040</td>
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Diffuse reflectance spectroscopy (DRS)

Relative reflectance measurements for the solids of 3 and 4 were recorded using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer equipped with an ISR-3100 integrating sphere attachment and barium sulfate was used as the reference standard. The samples were mixed and ground with barium sulfate in the glovebox prior to measurement. The Kubelka-Munk function, \( f(R) \), for each wavelength were computed from the relative reflectance, \( R \), of the complexes using the following equation:

\[
f(R) = \frac{(1 - R)^2}{2R}
\]

The spectra were treated with a Peakfit algorithm by using the second-derivative technique for locating the maxima between 450 nm and 1200 nm. The initial parameters were set up to fit three bands with the initial wavelengths set to 560, 620, and 720 nm before the amplitudes and widths of the Gaussian curves were optimized until a satisfactory fit was obtained (Fig S11 and S12). The Kubelka-Munk functions were then obtained from the amplitudes of the individual Gaussian curves fitted into the spectrum.

Table S3. Band maxima related to the excitations for the compounds measured using DRS and the ratio of the Kubelka-Munk functions, \( K/S \).

<table>
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<tr>
<th>Complex</th>
<th>Band</th>
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<th>Fitted ( f(R) )</th>
<th>( f(R) ) ratio of I:II</th>
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<td></td>
<td>II</td>
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<td></td>
<td>I</td>
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<td>III</td>
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<td></td>
<td>II</td>
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</tr>
<tr>
<td></td>
<td>I</td>
<td>829</td>
<td>0.0103</td>
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</table>
Fig. S11 a) Diffuse reflectance spectrum of 3. b) Simulated spectrum obtained from fitting the MLCT bands I (pink), II (blue), and III (green) into the diffuse reflectance spectrum of 3 between the dashed lines. The black line represents the experimental data while the red line depicts the combined fit of all three bands.

Table S4. Fitted Parameters for the diffuse reflectance spectrum of 3

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<th>Width</th>
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<tr>
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<td>602</td>
<td>0.0728</td>
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<tr>
<td>I</td>
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<td>0.0909</td>
<td>266</td>
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</table>

Fig. S12 a) Diffuse reflectance spectrum of 4. b) Simulated spectrum obtained from fitting the MLCT bands I (pink), II (blue), and III (green) into the diffuse reflectance spectrum of 4
between the dashed lines. The black line represents the experimental data while the red line depicts the combined fit of all three bands.

### Table S5. Fitted Parameters for the diffuse reflectance spectrum of 4

<p>| | | | |</p>
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<tr>
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<td>Wavelength</td>
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<tr>
<td>I</td>
<td>829</td>
<td>0.0103</td>
<td>188</td>
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</table>

**Fig. S13** The $^1$H NMR spectrum of 1 recorded in DMSO-d$_6$. The solvent residual peak is at 2.50 ppm (quintet), while the peak at 3.31 ppm is due to water in the NMR solvent. Inset: Magnification of the aromatic region.
Fig. S14 The $^{13}$C{H} NMR spectrum of 1 recorded in DMSO-d$_6$. The solvent residual peak is at 39.5 ppm (septet). Inset: Magnification of the aromatic region.

Fig. S15 $^1$H NMR spectrum of 2 recorded in CDCl$_3$. The solvent residual peak is at 7.26 ppm (singlet).
Fig. S16 The $^{13}$C{H} NMR spectrum of 2 recorded in CDCl$_3$. The solvent residual peak is at 77.2 ppm (triplet). Inset: Magnification of the aromatic region.

Fig. S17 The $^{13}$C DEPT-90 NMR spectrum of 2 recorded in CDCl$_3$. The signals with positive phase correspond to the CH carbons.
Fig. S18 The $^1$H NMR spectrum of 3 recorded in MeOD-$d_4$. The solvent residual peak is at 3.31 ppm (quintet), while the peak at 4.84 ppm is due to water in the NMR solvent. Inset: Magnification of the aromatic region.

Fig. S19 The $^{13}$C NMR spectrum of 3 recorded in DMSO-$d_6$. The solvent residual peak is at 39.5 ppm (septet). Inset: Magnification of the aromatic region.
Fig. S20 The $^1$H NMR spectrum of 4 recorded in CDCl$_3$. The solvent residual peak is at 7.26 ppm (singlet).

Fig. S21 The $^{13}$C{$^1$H} NMR spectrum of 4 recorded in CDCl$_3$. The solvent residual peak is at 77.2 ppm (triplet). Inset: Magnification of the aromatic region.
Fig. S22 The $^{31}$P NMR spectrum of 4 recorded in CDCl$_3$.

Fig. S23 The $^{19}$F NMR spectrum of 4 recorded in CDCl$_3$.
Fig. S24 (a) J-V plot for DSSCs after 4 had been incorporated by dye-sensitization. (b) Band alignment for DSSC sensitized with 4 showing the relative energy levels (in eV against vacuum) for 4, TiO₂, and the I⁻/I₃⁻ electrolyte.
Single crystal X-ray structure of compounds

\( \text{Ar}^{\text{LCOOMe}}\text{-BIAN} (2) \)

An orange block of \( \text{C}_{28}\text{H}_{16}\text{I}_{2}\text{N}_{2}\text{O}_{4} \) \((\text{Ar}^{\text{LCOOMe}}\text{-BIAN}, 2)\), with approximate dimensions \(0.100 \text{ mm} \times 0.180 \text{ mm} \times 0.280 \text{ mm}\), was used for the single crystal X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 0.26 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 24090 reflections to a maximum \(\theta\) angle of 31.15° (0.69 Å resolution), of which 8056 were independent (average redundancy = 2.990, completeness = 99.7%, \(R_{\text{int}} = 4.60\%\), \(R_{\text{sig}} = 5.35\%\)) and 6189 (76.82%) were greater than 2\(\sigma(F^2)\). The final cell constants of \(a = 9.8551(5)\ \text{Å}, \ b = 10.0192(6)\ \text{Å}, \ c = 14.2431(7)\ \text{Å}, \ \alpha = 87.110(2)^\circ, \ \beta = 78.367(2)^\circ, \ \gamma = 65.0268(19)^\circ\), volume = 1247.74(12) Å\(^3\), are based upon the refinement of the XYZ-centroids of 5155 reflections above 20\(\sigma(I)\) with 5.259° < \(\theta\) < 57.45°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.799. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5340 and 0.7840. The final anisotropic full-matrix least-squares refinement on \(F^2\) with 327 variables converged at \(R_1 = 3.33\%\) for the observed data, and \(wR_2 = 7.44\%\) for all data. The goodness-of-fit was 1.011. The largest peak in the final difference electron density synthesis was 1.020 \(e/Å^3\) and the largest hole was -0.742 \(e/Å^3\) with an RMS deviation of 0.136 \(e/Å^3\). On the basis of the final model, the calculated density was 1.864 \(g/cm^3\) and \(F(000), 676 e^-\).

\( [(\text{Ar}^{\text{LCOOMe}}\text{-BIAN})_2\text{Cu}]\text{PF}_6 (4) \).

For the crystal grown from dichloromethane and diethyl ether, a green block of \( \text{C}_{58}\text{H}_{40}\text{Cl}_4\text{CuF}_6\text{I}_4\text{N}_4\text{O}_8\text{P} \) \(([(\text{Ar}^{\text{LCOOMe}}\text{-BIAN})_2\text{Cu}]\text{PF}_6, 4)\), with approximate dimensions \(0.080 \text{ mm} \times 0.120 \text{ mm} \times 0.180 \text{ mm}\), was used for the single crystal X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 3.81 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 16485 reflections to a maximum \(\theta\) angle of 29.34° (0.73 Å resolution), of which 16485 were independent (average redundancy 1.000, completeness = 99.3%, \(R_{\text{int}} = 8.98\%\), \(R_{\text{sig}} = 12.29\%) and 9570 (58.05%) were greater than 2\(\sigma(F^2)\). The final cell
constants of $a = 11.844(4)$ Å, $b = 13.707(5)$ Å, $c = 20.634(8)$ Å, $\alpha = 94.692(7)^\circ$, $\beta = 97.346(7)^\circ$, $\gamma = 113.076(5)^\circ$, volume $=3024.4(19)$ Å$^3$, are based upon the refinement of the XYZ-centroids of 8822 reflections above $20 \sigma(I)$ with $6.301^\circ < 20 < 42.27^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.713. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6440 and 0.8140. The final anisotropic full-matrix least-squares refinement on $F^2$ with 808 variables converged at $R_1 = 8.65\%$ for the observed data, and $wR_2 = 20.71\%$ for all data. The goodness-of-fit was 1.076. The largest peak in the final difference electron density synthesis was $2.540$ e$^-$/Å$^3$ and the largest hole was $-1.644$ e$^-$/Å$^3$ with an RMS deviation of 0.250 e$^-$/Å$^3$. On the basis of the final model, the calculated density was $1.953$ g/cm$^3$ and $F(000)$, 1716 e$^-$.

For the crystal grown from toluene and tetrahydrofuran, a green plate of $C_{82}H_{75}CuF_6I_4N_4O_{11}P(\{(Ar^1L^1COOMe-BIAN)\_2Cu|PF_6, 4\}$, with approximate dimensions 0.020 mm x 0.060 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 10.24 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 84854 reflections to a maximum $\theta$ angle of $26.27^\circ$ (0.80 Å resolution), of which 15930 were independent (average redundancy 5.327, completeness $= 98.6\%$, $R_{int} = 14.56\%$, $R_{sig} = 12.75\%$) and 7983 (50.11%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 15.3314(9)$ Å, $b = 15.4957(9)$ Å, $c = 18.5347(10)$ Å, $\alpha = 98.846(4)^\circ$, $\beta = 110.128(3)^\circ$, $\gamma = 98.427(4)^\circ$, volume $=3989.7(4)$ Å$^3$, are based upon the refinement of the XYZ-centroids of 7944 reflections above $20 \sigma(I)$ with $5.377^\circ < 20 < 42.08^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.664. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8030 and 0.9630. The final anisotropic full-matrix least-squares refinement on $F^2$ with 1035 variables converged at $R_1 = 8.40\%$ for the observed data and $wR_2 = 29.16\%$ for all data. The goodness-of-fit was 1.115. The largest peak in the final difference electron density synthesis was $2.906$ e$^-$/Å$^3$ and the largest hole was $-2.189$ e$^-$/Å$^3$ with an RMS deviation of 0.278 e$^-$/Å$^3$. On the basis of the final model, the calculated density was $1.672$ g/cm$^3$ and $F(000)$, 1986 e$^-$. 

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X-ray crystallographic coordinates for structures

Compounds 2 and 4 (grown from both solvent combinations) reported herein have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC1431314 – 1431316. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S6. Crystal data and structure refinement for $\text{Ar}^{1\text{COOMe}}$-BIAN (2)

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| Unit cell dimensions | $a = 9.8551(5)$ Å  $\alpha = 87.110(2)^\circ$  
                                | $b = 10.0192(6)$ Å  $\beta = 78.367(2)^\circ$  
                                | $c = 14.2431(7)$ Å  $\gamma = 65.0268(19)^\circ$  |
| Volume           | 1247.74(12) Å³                                               |
| Z                | 2                                                             |
| Density (calculated) | 1.864 g/cm³                                                  |
| Absorption coefficient | 2.559 mm⁻¹                                                  |
| F(000)           | 676                                                           |
| Theta range for data collection | 2.46 to 31.15°                               |
| Index ranges     | -14<=h<=14, -14<=k<=14, -20<=l<=20                            |
| Reflections collected | 24090                                                   |
| Independent reflections | 8056 [R(int) = 0.0460]                                       |
| Coverage of independent reflections | 99.7%                                                      |
| Absorption correction | multi-scan                                                   |
| Max. and min. transmission | 0.7840 and 0.5340                                           |
| Refinement method | Full-matrix least-squares on $F^2$                           |
| Refinement program | SHELXL-2014/6 (Sheldrick, 2014)                              |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$                                 |
| Data / restraints / parameters | 8056 / 0 / 327                                           |
| Goodness-of-fit on $F^2$ | 1.011                                                     |
Δ/σ_{max} \quad 0.001
Final R indices \quad 6189 \text{ data}; I>2σ(I) \quad R1 = 0.0333, wR2 = 0.0664
\quad \text{all data} \quad R1 = 0.0502, wR2 = 0.0744
Weighting scheme \quad w=1/\left[σ^2(F_o^2)+(0.0277P)^2+0.1106P\right]
Largest diff. peak and hole \quad 1.020 \text{ and } -0.742 \text{ eÅ}^{-3}
R.M.S. deviation from mean \quad 0.136 \text{ eÅ}^{-3}

Table S7. Select bond lengths (Å) for Ar^{LCOOME}-BIAN (2)

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Table S8. Select bond angles (°) for Ar^{LCOOME}-BIAN (2)

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Table S9. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å$^2$) for Ar$^{\text{COO}Me}$-BIAN (2)

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<tr>
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<tr>
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The anisotropic atomic displacement factor exponent takes the form:

\[ -2\pi^2 \left[ h^2 a^* a^2 U_{11} + \ldots + 2 h k a^* b^* U_{12} \right] \]

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<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{23}</th>
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Table S11. Crystal data and structure refinement for [(Ar\textsuperscript{I-LCOOMe-BIAN})\textsubscript{2}Cu]PF\textsubscript{6} (4) grown from dichloromethane and diethyl ether

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<tr>
<td>Crystal size</td>
<td>0.080 x 0.120 x 0.180 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>red block</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 11.844(4) Å, α = 94.692(7)°</td>
</tr>
<tr>
<td></td>
<td>b = 13.707(5) Å, β = 97.346(7)°</td>
</tr>
<tr>
<td></td>
<td>c = 20.634(8) Å, γ = 113.076(5)°</td>
</tr>
<tr>
<td>Volume</td>
<td>3024.4(19) Å\textsuperscript{3}</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.953 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.682 mm\textsuperscript{-1}</td>
</tr>
<tr>
<td>F(000)</td>
<td>1716</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.01 to 29.34°</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16485</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>16485 [R(int) = 0.0898]</td>
</tr>
<tr>
<td>Coverage of independent reflections</td>
<td>99.3%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8140 and 0.6440</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F2</td>
</tr>
<tr>
<td>Refinement program</td>
<td>SHELXL-2014/6 (Sheldrick, 2014)</td>
</tr>
<tr>
<td>Function minimized</td>
<td>Σ w(Fo\textsuperscript{2} - Fc\textsuperscript{2})2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>16485 / 82 / 808</td>
</tr>
<tr>
<td>Goodness-of-fit on F2</td>
<td>1.076</td>
</tr>
<tr>
<td>Δ/σmax</td>
<td>0.001</td>
</tr>
<tr>
<td>Final R indices</td>
<td>9570 data; I&gt;2σ(I) R1 = 0.0865, wR2 = 0.1658</td>
</tr>
<tr>
<td></td>
<td>all data R1 = 0.1677, wR2 = 0.2071</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>w=1/[σ\textsuperscript{2}(Fo\textsuperscript{2})+(0.0624P\textsuperscript{2})\textsuperscript{2}+24.7871P]</td>
</tr>
<tr>
<td>where P=(Fo\textsuperscript{2}+2Fc\textsuperscript{2})/3</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.540 and -1.644 eÅ\textsuperscript{-3}</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.250 eÅ\textsuperscript{-3}</td>
</tr>
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</table>
Table S12. Select bond lengths (Å) for [(Ar\(^{I,COOMe}\)-BIAN)\(_2\)Cu]PF\(_6\) (4) grown from dichloromethane and diethyl ether

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
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<tbody>
<tr>
<td>Cu1-N3</td>
<td>1.892(8)</td>
</tr>
<tr>
<td>Cu1-N2</td>
<td>2.460(9)</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.268(14)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.461(15)</td>
</tr>
<tr>
<td>C1-C11</td>
<td>1.518(14)</td>
</tr>
<tr>
<td>C11-N2</td>
<td>1.262(13)</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.477(15)</td>
</tr>
<tr>
<td>C14-I1</td>
<td>2.083(10)</td>
</tr>
<tr>
<td>C22-I2</td>
<td>2.072(13)</td>
</tr>
</tbody>
</table>

Table S13. Select bond angles (°) for [(Ar\(^{I,COOMe}\)-BIAN)\(_2\)Cu]PF\(_6\) (4) grown from dichloromethane and diethyl ether

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3-Cu1-N1</td>
<td>170.7(4)</td>
</tr>
<tr>
<td>N1-Cu1-N2</td>
<td>76.1(4)</td>
</tr>
<tr>
<td>N1-Cu1-N4</td>
<td>99.9(4)</td>
</tr>
<tr>
<td>N1-C1-C11</td>
<td>117.8(9)</td>
</tr>
<tr>
<td>C1-N1-C13</td>
<td>119.9(10)</td>
</tr>
<tr>
<td>C13-N1-Cu1</td>
<td>117.0(7)</td>
</tr>
<tr>
<td>C11-N2-Cu1</td>
<td>103.9(7)</td>
</tr>
<tr>
<td>C29-N3-C41</td>
<td>116.8(8)</td>
</tr>
<tr>
<td>C41-N3-Cu1</td>
<td>118.4(6)</td>
</tr>
<tr>
<td>Cu1-N4-C39</td>
<td>100.1(6)</td>
</tr>
<tr>
<td>C2-C1-C11</td>
<td>108.1(9)</td>
</tr>
<tr>
<td>N3-C29-C39</td>
<td>120.0(9)</td>
</tr>
</tbody>
</table>
Table S14. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for [(Ar\(^{1,COOMe}\)-BIAN)\(_2\)CuPF\(_6\) (4) grown from dichloromethane and diethyl ether

U(eq) is defined as one third of the trace of the orthogonalized U\(_{ij}\) tensor.

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>0.56248(15)</td>
<td>0.75037(11)</td>
<td>0.26529(7)</td>
<td>0.0463(4)</td>
</tr>
<tr>
<td>C1</td>
<td>0.7082(10)</td>
<td>0.8703(8)</td>
<td>0.3857(5)</td>
<td>0.031(3)</td>
</tr>
<tr>
<td>C2</td>
<td>0.7764(11)</td>
<td>0.9496(9)</td>
<td>0.4441(5)</td>
<td>0.034(3)</td>
</tr>
<tr>
<td>C3</td>
<td>0.8102(12)</td>
<td>0.0590(8)</td>
<td>0.4602(6)</td>
<td>0.038(3)</td>
</tr>
<tr>
<td>C4</td>
<td>0.8748(14)</td>
<td>0.1073(10)</td>
<td>0.5245(6)</td>
<td>0.052(4)</td>
</tr>
<tr>
<td>C5</td>
<td>0.9089(13)</td>
<td>0.0514(10)</td>
<td>0.5701(6)</td>
<td>0.048(3)</td>
</tr>
<tr>
<td>C6</td>
<td>0.8781(12)</td>
<td>0.9422(9)</td>
<td>0.5548(6)</td>
<td>0.041(3)</td>
</tr>
<tr>
<td>C7</td>
<td>0.9005(12)</td>
<td>0.8720(10)</td>
<td>0.5975(6)</td>
<td>0.044(3)</td>
</tr>
<tr>
<td>C8</td>
<td>0.8583(11)</td>
<td>0.7652(9)</td>
<td>0.5760(5)</td>
<td>0.036(3)</td>
</tr>
<tr>
<td>C9</td>
<td>0.7920(11)</td>
<td>0.7181(9)</td>
<td>0.5133(6)</td>
<td>0.034(3)</td>
</tr>
<tr>
<td>C10</td>
<td>0.7675(10)</td>
<td>0.7806(8)</td>
<td>0.4698(5)</td>
<td>0.030(2)</td>
</tr>
<tr>
<td>C11</td>
<td>0.6985(10)</td>
<td>0.7615(8)</td>
<td>0.4018(5)</td>
<td>0.032(2)</td>
</tr>
<tr>
<td>C12</td>
<td>0.8113(11)</td>
<td>0.8931(8)</td>
<td>0.4922(5)</td>
<td>0.035(3)</td>
</tr>
<tr>
<td>C13</td>
<td>0.6633(10)</td>
<td>0.9756(7)</td>
<td>0.3112(5)</td>
<td>0.028(2)</td>
</tr>
<tr>
<td>C14</td>
<td>0.5588(10)</td>
<td>0.9985(8)</td>
<td>0.3002(5)</td>
<td>0.028(2)</td>
</tr>
<tr>
<td>C15</td>
<td>0.5678(9)</td>
<td>0.0932(8)</td>
<td>0.2789(4)</td>
<td>0.023(2)</td>
</tr>
<tr>
<td>C16</td>
<td>0.6836(9)</td>
<td>0.1666(7)</td>
<td>0.2690(5)</td>
<td>0.024(2)</td>
</tr>
<tr>
<td>C17</td>
<td>0.6918(10)</td>
<td>0.2694(8)</td>
<td>0.2450(5)</td>
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<tr>
<td>C18</td>
<td>0.8203(12)</td>
<td>0.4308(9)</td>
<td>0.2148(8)</td>
<td>0.053(4)</td>
</tr>
<tr>
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<tr>
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<td>0.2996(5)</td>
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<tr>
<td>C21</td>
<td>0.6255(11)</td>
<td>0.5789(8)</td>
<td>0.3775(5)</td>
<td>0.034(3)</td>
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<tr>
<td>C22</td>
<td>0.5158(11)</td>
<td>0.5090(8)</td>
<td>0.3962(5)</td>
<td>0.036(3)</td>
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<tr>
<td>C23</td>
<td>0.5076(12)</td>
<td>0.4076(8)</td>
<td>0.4116(5)</td>
<td>0.036(3)</td>
</tr>
<tr>
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<td>0.3783(9)</td>
<td>0.4074(5)</td>
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<tr>
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<td>0.2750(9)</td>
<td>0.4287(5)</td>
<td>0.037(3)</td>
</tr>
<tr>
<td>C26</td>
<td>0.4896(15)</td>
<td>0.1170(9)</td>
<td>0.4677(7)</td>
<td>0.053(4)</td>
</tr>
<tr>
<td>C27</td>
<td>0.7121(12)</td>
<td>0.4470(9)</td>
<td>0.3871(6)</td>
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<tr>
<td>C28</td>
<td>0.7191(11)</td>
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<tr>
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<td>0.4622(10)</td>
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<tr>
<td>C30</td>
<td>0.4018(10)</td>
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<tr>
<td>C31</td>
<td>0.3183(10)</td>
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</tr>
<tr>
<td>C</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>u</td>
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<td>-----</td>
<td>------</td>
<td>------</td>
<td>------</td>
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<tr>
<td>C32</td>
<td>0.2808(10)</td>
<td>0.4192(8)</td>
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<td>0.031(2)</td>
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<tr>
<td>C33</td>
<td>0.3268(11)</td>
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<tr>
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<tr>
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<td>0.5483(12)</td>
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<tr>
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<tr>
<td>C38</td>
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<td>0.7370(8)</td>
<td>0.0416(5)</td>
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<tr>
<td>C39</td>
<td>0.5410(9)</td>
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<td>0.1131(5)</td>
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<tr>
<td>C40</td>
<td>0.4473(10)</td>
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<td>0.205(5)</td>
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<tr>
<td>C41</td>
<td>0.3903(9)</td>
<td>0.5376(7)</td>
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<td>0.020(2)</td>
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<tr>
<td>C42</td>
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<td>0.5020(7)</td>
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<tr>
<td>C43</td>
<td>0.1951(10)</td>
<td>0.3993(7)</td>
<td>0.2252(5)</td>
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<tr>
<td>C44</td>
<td>0.2547(9)</td>
<td>0.3302(7)</td>
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<tr>
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<tr>
<td>C46</td>
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<td>0.060(4)</td>
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<td>0.3838(9)</td>
<td>0.3690(7)</td>
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<tr>
<td>C49</td>
<td>0.6681(9)</td>
<td>0.9396(7)</td>
<td>0.1359(5)</td>
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<tr>
<td>C50</td>
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<td>0.1127(5)</td>
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<td>0.6766(10)</td>
<td>0.1028(7)</td>
<td>0.0952(5)</td>
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<td>0.8053(10)</td>
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<td>0.1011(5)</td>
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<tr>
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<td>0.0821(5)</td>
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<td>0.3943(9)</td>
<td>0.0352(6)</td>
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<tr>
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<td>0.7945(10)</td>
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<td>0.0255(15)</td>
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<td>0.068(4)</td>
</tr>
<tr>
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<td>0.1306(4)</td>
<td>0.0201(4)</td>
<td>0.0641(3)</td>
<td>0.0785(13)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0975(4)</td>
<td>0.8039(4)</td>
<td>0.0846(2)</td>
<td>0.0761(12)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.045(4)</td>
<td>0.5662(18)</td>
<td>0.4718(11)</td>
<td>0.086(4)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0260(9)</td>
<td>0.4285(8)</td>
<td>0.4684(5)</td>
<td>0.090(3)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0788(9)</td>
<td>0.6032(7)</td>
<td>0.3924(5)</td>
<td>0.080(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.033(3)</td>
<td>0.5819(15)</td>
<td>0.349(2)</td>
<td>0.088(4)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0241(9)</td>
<td>0.4493(8)</td>
<td>0.3649(5)</td>
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</tr>
<tr>
<td>Cl</td>
<td>0.1805(11)</td>
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<td>0.4012(6)</td>
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<tr>
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<td>0.7719(8)</td>
<td>0.1626(5)</td>
<td>0.082(3)</td>
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<tr>
<td>Cl</td>
<td>0.0330(10)</td>
<td>0.8264(7)</td>
<td>0.2362(6)</td>
<td>0.102(4)</td>
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</table>
### Table S15. Anisotropic atomic displacement parameters (Å\(^2\)) for [(Ar\(^{13}\)COOMe-BIAN)\(_2\)Cu]PF\(_6\) (4) grown from dichloromethane and diethyl ether

The anisotropic atomic displacement factor exponent takes the form: 

\[-2\pi^2 \left( h^2 a^* a^* U_{11} + \ldots + 2 h k a^* b^* U_{12} \right) \]

<table>
<thead>
<tr>
<th></th>
<th>(U_{11})</th>
<th>(U_{22})</th>
<th>(U_{33})</th>
<th>(U_{23})</th>
<th>(U_{13})</th>
<th>(U_{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>0.0592(10)</td>
<td>0.0193(6)</td>
<td>0.0348(8)</td>
<td>0.0058(6)</td>
<td>-0.0108(7)</td>
<td>-0.0057(6)</td>
</tr>
<tr>
<td>C1</td>
<td>0.029(6)</td>
<td>0.019(5)</td>
<td>0.027(6)</td>
<td>0.002(4)</td>
<td>-0.002(4)</td>
<td>-0.007(4)</td>
</tr>
<tr>
<td>C2</td>
<td>0.042(7)</td>
<td>0.025(5)</td>
<td>0.027(6)</td>
<td>0.008(4)</td>
<td>0.006(5)</td>
<td>0.004(5)</td>
</tr>
<tr>
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<td>R1 = 0.0840, wR2 = 0.2135</td>
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<td>(w = 1/\left[\sigma^2(F_o^2) + (0.1089P)^2 + 53.1825P\right])</td>
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<td></td>
<td>where (P = (F_o^2 + 2F_c^2)/3)</td>
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<td>Largest diff. peak and hole</td>
<td>2.906 and -2.189 eÅ(^{-3})</td>
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<td>0.278 eÅ(^{-3})</td>
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Table S17. Select bond lengths (Å) for [(Ar^LCOOME-BIAN)_2Cu]PF_6 (4) grown from toluene and tetrahydrofuran

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<td>Cu1-N3</td>
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<td>Cu1-N1</td>
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<tr>
<td>Cu1-N2</td>
<td>2.463(11)</td>
<td>Cu1-N4</td>
<td>2.517(13)</td>
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<tr>
<td>C9-N1</td>
<td>1.288(16)</td>
<td>C37-N3</td>
<td>1.305(17)</td>
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<tr>
<td>C9-C19</td>
<td>1.510(17)</td>
<td>C37-C47</td>
<td>1.490(17)</td>
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<tr>
<td>C19-N2</td>
<td>1.253(16)</td>
<td>C47-N4</td>
<td>1.298(16)</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.458(18)</td>
<td>C37-C38</td>
<td>1.442(18)</td>
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<td>C18-C19</td>
<td>1.484(18)</td>
<td>C46-C47</td>
<td>1.473(18)</td>
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<td>C2-I1</td>
<td>2.065(13)</td>
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<td>C50-I4</td>
<td>2.114(15)</td>
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Table S18. Select bond angles (°) for [(Ar^LCOOME-BIAN)_2Cu]PF_6 (4) grown from toluene and tetrahydrofuran

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<td>N1-Cu1-N2</td>
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<td>N2-Cu1-N4</td>
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<td>N1-Cu1-N4</td>
<td>102.3(4)</td>
<td>N3-Cu1-N4</td>
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<tr>
<td>C1-N1-Cu1</td>
<td>120.5(8)</td>
<td>C9-N1-C1</td>
<td>118.2(11)</td>
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<tr>
<td>C9-N1-Cu1</td>
<td>120.8(9)</td>
<td>C21-N2-Cu1</td>
<td>136.4(9)</td>
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<td>C19-N2-Cu1</td>
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<td>C29-N3-Cu1</td>
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<td>C37-N3-C29</td>
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<td>N4-C47-C37</td>
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**Table S19.** Atomic coordinates and equivalent isotropic atomic displacement parameters (Å\(^2\)) for [(Ar\(^{1,COOMe}\)-BIAN)\(_2\)Cu(PF\(_6\))\(_4\)] grown from toluene and tetrahydrofuran

U(eq) is defined as one third of the trace of the orthogonalized U\(_{ij}\) tensor.

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<th>x/a</th>
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<td>C1</td>
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<td>0.6124(8)</td>
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<td>C2</td>
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<td>0.6160(9)</td>
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<tr>
<td>C3</td>
<td>0.8140(11)</td>
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<td>C4</td>
<td>0.7378(11)</td>
<td>0.5147(9)</td>
<td>0.4487(8)</td>
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<td>0.4018(8)</td>
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<td>0.5642(9)</td>
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Table S20. Anisotropic atomic displacement parameters (Å²) for for [(Ar¹⁺COOMe⁻-BIAN)₂Cu]PF₆ (4) grown from toluene and tetrahydrofuran

The anisotropic atomic displacement factor exponent takes the form: \(-2\pi² [ h^2 a^2 U_{11} + \ldots + 2 h k a^* b^* U_{12}] \)

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**DFT and TD-DFT calculations on 4**

All calculations in this work were performed using the Gaussian 09 D01 package. The M06 functional was used in both DFT and TD-DFT calculations, and the def2 general basis sets were used (I and Cu: def2-TZVPPD; H, C, N and O: def2-TZVP). Also, def2-ECP was used for iodine atoms. Ultrafine grids were adopted for the numerical integration in the DFT and TD-DFT calculations. The geometries of the cation complexes were optimized from crystal structures and solvent effects were included using the CPCM model. Although two mixtures of solvents were used in the experiments, in the calculations, only two pure solvents, toluene and dichloromethane (DCM), were considered for simplicity. Using the optimized geometries, two additional theoretical analyses were performed to evaluate non-
covalent interactions within the molecule. First, non-covalent interaction (NCI) analysis was conducted using the NCIPLOT-3.0 software package with the promolecular approximation.\textsuperscript{12,13} Second, an Atoms in Molecules (AIM) analysis was performed using AIMAll (Version 13.05.06).\textsuperscript{14,15} Both of these analyses (Fig. S26 and S27) indicate that there are I-I interactions among the iodide atoms in the same ligand and different ligands, although it should be noted that the geometries around I do not necessarily fulfill the latest geometric criteria of halogen-halogen bonding proposed by Desiraju.\textsuperscript{16} According to Desiraju\textsuperscript{15}, there are two types (Type I and Type II) of geometries in halogen-halogen interactions (Fig. S28). However, the C-I bonds in 4 do not strictly satisfy these geometric requirements, but rather, are more or less parallel to one another.

\textbf{Fig. S25} Overlay of oscillator strengths calculated from TD-DFT results (black lines) with the UV-visible spectrum of 4 (blue) in DCM.
Fig. S26 NCI plot for 4. Left: xyz in DCM; right: xyz in toluene.
Fig. S27 AIM results for 4 in DCM.

Fig. S27 a) Type I and Type II I-I halogen bond. b) Electrostatic interactions in I-I halogen bond.
Table S21. Comparison of selected bond lengths [Å] and angles [°] for 4 from the geometry optimizations in the different solvents with the experimental values

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<td>274.68</td>
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Table S23. Frontier orbitals of 4 at different isovalues

<table>
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<tr>
<th>MO 298 (LUMO + 1)</th>
<th>MO298 (LUMO + 1) Isovalue = 0.03</th>
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<td>MO 297 (LUMO)</td>
<td>MO297 (LUMO) Isovalue = 0.03</td>
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<td>MO 296 (HOMO)</td>
<td>MO 296 (HOMO) Isovalue = 0.03</td>
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<tr>
<td>MO 295 (HOMO-1)</td>
<td>MO 295 (HOMO-1) Isovalue = 0.03</td>
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MO 294 (HOMO-2)  

MO 293 (HOMO-3)  

MO 292 (HOMO-4)  

MO 291 (HOMO-5)
Table S24. TD-DFT calculated oscillator strength and nature of electronic transitions for some of the lowest energy photoexcitations of 4

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Origin</th>
<th>Relative contribution</th>
<th>Nature of transition</th>
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</thead>
<tbody>
<tr>
<td>2: 2.18 eV; 567 nm; f = 0.0025; &lt;S**2&gt; = 0.000</td>
<td>296 -&gt; 298</td>
<td>0.67921</td>
<td>MLCT</td>
</tr>
<tr>
<td>3: 2.78 eV; 445 nm; f = 0.0606; &lt;S**2&gt; = 0.000</td>
<td>292 to 298</td>
<td>-0.25018</td>
<td>MLCT + π to π*</td>
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<tr>
<td></td>
<td>293 to 297</td>
<td>0.34994</td>
<td>MLCT + π to π*</td>
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<td></td>
<td>294 to 297</td>
<td>-0.14684</td>
<td>n to π*</td>
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<tr>
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<td>295 to 297</td>
<td>0.51019</td>
<td>n to π*</td>
</tr>
<tr>
<td>4: 2.82 eV; 439.70 nm; f = 0.0364; &lt;S**2&gt; = 0.000</td>
<td>291 to 298</td>
<td>-0.22307</td>
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<td>0.34073</td>
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Table S25. Geometry-optimized XYZ coordinates of the cation of 4 in the two solvents

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<td>Cu -0.031189 0.040205 0.556520</td>
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<tr>
<td>C 2.514219 2.067720 0.885705</td>
<td>C -0.186873 2.868223 0.789673</td>
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<tr>
<td>C 3.872589 2.196274 1.118599</td>
<td>C 0.008357 4.308949 0.769645</td>
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References
15. AIMAll (Version 13.05.06), T. A. Keith, TK Grimstmill Software, Overland Park KS, USA, 2013 (aim.tkgristmill.com).