Supporting Information for the manuscript:

**Ligand and Electronic Effects on Copper-Arylnitroso Self-Assembly**

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**Contents**

1. Examples of UV-vis multivariate fitting .................................................................................................................. 2

2. Selection of NMR spectra ........................................................................................................................................ 4
   2.1. DBED-Z species .................................................................................................................................................. 4
   2.2. TEED-Z species .................................................................................................................................................. 6
   2.3. MeDHN-Z species .............................................................................................................................................. 7
   2.4. MeTREN-Z species ............................................................................................................................................. 9

3. X-ray Crystallography .................................................................................................................................................. 10

4. DFT Details ............................................................................................................................................................... 12
   4.1. DBED-NMe₂ ..................................................................................................................................................... 13
   4.2. DBED-H ........................................................................................................................................................... 14
   4.3. DBED-Br .......................................................................................................................................................... 15
   4.4. DBED-NO₂ ....................................................................................................................................................... 16

5. Reference .................................................................................................................................................................... 17
1. Examples of UV-vis multivariate fitting

Figure S1. Screenshots of the fitting process with ReactLab™ Equilibria for TEED-H: (top) 1:1 Cu:ArNO model (bottom) 2:1 Cu:ArNO model.
Figure S2. Screenshots of the fitting process with ReactLab™ Equilibria for MesDIEN-H: (top) 1:1 Cu:ArNO model (bottom) 2:1 Cu:ArNO model.
2. Selection of NMR spectra

2.1. DBED-Z species

Figure S3. $^1$H-NMR (500 MHz) spectra of DBED-NMe$_2$ formed in situ in CDCl$_3$ at 23°C.

Figure S4. $^1$H-NMR (500 MHz) spectra of DBED-H formed in situ in CDCl$_3$ at 23°C.
Figure S5. $^1$H-NMR (500 MHz) spectra of DBED-Br formed in situ in CDCl$_3$ at 23°C.

Figure S6. $^1$H-NMR (500 MHz) spectra of DBED-NO$_2$ formed in situ in $d^6$-acetone at 23°C. The red * in the inset denote the azozy decomposition product.
2.2. TEED-Z species

Figure S7. $^1$H-NMR (500 MHz) spectra of TEED-NMe$_2$ formed in situ in CDCl$_3$ at 23°C.

Figure S8. $^1$H-NMR (300 MHz) spectra of TEED-H formed in situ from a 1:1 TEEDCu$^{1}$HArNO stoichiometry in CDCl$_3$ at 23°C.
2.3. Me$_5$DIEN-Z species

Figure S9. $^1$H-NMR (500 MHz) spectra of Me$_5$DIEN-NMe$_2$ formed in situ in d$_6$-acetone at 23°C.
Figure S10. $^1$H-NMR (500 MHz) spectra of (top to bottom) $\text{Me}_5\text{DIEN-H}$, $\text{Me}_5\text{DIEN-Br}$ and $\text{Me}_5\text{DIEN-NO}_2$ formed in situ in $d^6$-acetone at 23°C, showing the increasing amount of azoxy decomposition product (red *) on going to more electron-poor ArNO moieties.
2.4. Me₆TREN-Z species

Figure S11. $^1$H-NMR (500 MHz) spectra of Me₆TREN-NMe₂ in $d^6$-acetone at 50°C.

Figure S12. $^1$H-NMR (500 MHz) spectra of Me₆TREN-H with TfO⁻ (top) or SbF₆⁻ (bottom) counteranions in $d^8$-THF at 23°C.
3. X-ray Crystallography

X-ray crystallography analysis was performed using the Cu-Kα microfocus or Mo-Kα source of a Bruker APEX-DUO diffractometer or, for TEED-H, the Cu-Kα enhanced source of an Oxford Diffraction Gemini A Ultra. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS or TWINABS). The structures were solved by direct methods and refined using the Bruker APEX2 or APEX3 software package (SHELXL instructions). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters.

Table S1. X-ray crystallographic data for L-Z adducts

<table>
<thead>
<tr>
<th>Adduct name</th>
<th>DBED-NM2e</th>
<th>DBED-H</th>
<th>TEED-NM2e</th>
<th>M2eDIEN-NM2e</th>
<th>M2eTREN-NM2e</th>
<th>TEED-H</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="SbF6">DBEDCu(NMe2)ArNO</a></td>
<td><a href="SbF6">DBEDCu(NMe2)ArNO</a></td>
<td><a href="SbF6">TEEDCu(NMe2)ArNO</a></td>
<td><a href="TFO">Me2DIENCu(NMe2)ArNO</a></td>
<td><a href="TFO">Me2TRENCu(NMe2)ArNO</a></td>
<td><a href="CuTEED">TEEDCu(NMe2)ArNO</a>(TFO)</td>
<td></td>
</tr>
<tr>
<td>1823004</td>
<td>1823005</td>
<td>1823006</td>
<td>1823007</td>
<td>1823008</td>
<td>1823009</td>
<td></td>
</tr>
<tr>
<td>Chemical formula</td>
<td>CuH2CuF2N2O5Sb·CuH2O</td>
<td>CuH2CuF2N2O·F5Sb</td>
<td>CuH2CuF2N2O·CF3O3S</td>
<td>CuH2CuF2N2O·CF3O3S</td>
<td>CuH2CuF2N2O·CF3O3S</td>
<td></td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P21/n</td>
<td>Triclinic, P1</td>
<td>Monoclinic, P21/c</td>
<td>Monoclinic, P21/c</td>
<td>Monoclinic, P21/c</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>9.6745 (1)</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.2011 (3)</td>
<td>9.2011 (3)</td>
<td>9.2011 (3)</td>
<td>9.6745 (1)</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>b (Å)</td>
<td>21.4308 (6)</td>
<td>15.8106 (4)</td>
<td>15.1515 (9)</td>
<td>15.6108 (1)</td>
<td>12.7528 (15)</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>14.8258 (4)</td>
<td>108.077 (1)</td>
<td>13.3703 (3)</td>
<td>16.0592 (1)</td>
<td>18.7395 (5)</td>
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<tr>
<td>a(°)</td>
<td>94.433 (1)</td>
<td>0.9063 (2)</td>
<td>97.983 (7)</td>
<td>98.085 (1)</td>
<td>105.723 (7)</td>
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</tr>
<tr>
<td>β(°)</td>
<td>84.351 (1)</td>
<td>92.875 (1)</td>
<td>98.093 (1)</td>
<td>98.085 (1)</td>
<td>105.723 (7)</td>
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<tr>
<td>γ(°)</td>
<td>2914.71 (15)</td>
<td>2235.33 (11)</td>
<td>2481.03 (15)</td>
<td>2401.26 (3)</td>
<td>2740.7 (6)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
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</tr>
<tr>
<td>Radiation type</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
<td>Cu Kα</td>
<td></td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>8.62</td>
<td>11.32</td>
<td>10.25</td>
<td>10.25</td>
<td>10.25</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.31 × 0.17 × 0.12</td>
<td>0.20 × 0.15 × 0.05</td>
<td>0.32 × 0.15 × 0.14</td>
<td>0.16 × 0.14 × 0.08</td>
<td>0.14 × 0.09 × 0.07</td>
<td></td>
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<tr>
<td>Tmin, Tmax</td>
<td>0.492, 0.753</td>
<td>0.356, 0.753</td>
<td>0.407, 0.753</td>
<td>0.667, 0.753</td>
<td>0.617, 0.753</td>
<td></td>
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<tr>
<td>No. of measured, independent and observed (I &gt; 2σ(I)) reflections</td>
<td>43477</td>
<td>7984</td>
<td>36450</td>
<td>35778</td>
<td>37557</td>
<td></td>
</tr>
<tr>
<td>R1, wR2</td>
<td>0.097</td>
<td>0.044</td>
<td>0.049</td>
<td>0.029</td>
<td>0.039</td>
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<tr>
<td>(sinθ/λ)max (Å⁻¹)</td>
<td>0.603</td>
<td>0.603</td>
<td>0.603</td>
<td>0.603</td>
<td>0.603</td>
<td></td>
</tr>
<tr>
<td>R(F² &gt; 2σ(F²))</td>
<td>0.036</td>
<td>0.033</td>
<td>0.034</td>
<td>0.024</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
<td>1.04</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td></td>
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<tr>
<td>No. of reflections, parameters, restraints</td>
<td>5344, 333, 0</td>
<td>7984, 517, 0</td>
<td>4552, 286, 0</td>
<td>4408, 296, 0</td>
<td>4990, 333, 0</td>
<td></td>
</tr>
<tr>
<td>Amax, Amin (e Å⁻³)</td>
<td>1.09, −0.82</td>
<td>1.26, −0.74</td>
<td>0.69, −1.52</td>
<td>0.29, −0.30</td>
<td>0.34, −0.29</td>
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<tr>
<td>Absolute structure</td>
<td>Flack parameter</td>
<td>2.59, −1.12</td>
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Selected metrical parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>N−O (Å)</td>
<td>1.269</td>
</tr>
<tr>
<td>Cu−Nmetr (Å)</td>
<td>1.867</td>
</tr>
<tr>
<td>Cu−O (Å)</td>
<td>1.872</td>
</tr>
<tr>
<td>Cu−OT (Å)</td>
<td>2.039-2.074</td>
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<tr>
<td>Cu−Nquad (Å)</td>
<td>2.004-2.009</td>
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<td>2.050-2.058</td>
<td>2.063-2.205</td>
</tr>
<tr>
<td>2.036 (CuIII), 1.885 (CuII)</td>
<td>1.880 (CuIII), 2.666 (CuII)</td>
</tr>
<tr>
<td>2.266 (CuIII), 2.630 (CuII)</td>
<td>2.017-2.019 (CuIII)</td>
</tr>
<tr>
<td>2.048-2.130 (CuII)</td>
<td></td>
</tr>
<tr>
<td>Adduct name</td>
<td>Compound</td>
</tr>
<tr>
<td>-------------</td>
<td>----------</td>
</tr>
<tr>
<td>[DBEDCu(x-DBDI)]CuDBED</td>
<td>1823010</td>
</tr>
<tr>
<td>[TEEDCu(x-OH)]CuTEED</td>
<td>1830574</td>
</tr>
</tbody>
</table>

Table S2. X-ray crystallographic data for other complexes
4. DFT details

The theoretical electronic spectra of the analogous para-substituted arylnitroso complexes **DBED-Z** and (Z = NMe₂, Br, H, NO₂) were predicted using TD-DFT calculations. All calculations were performed on Gaussian 09¹ using the GGA pure DFT functional BP86 with the triple-zeta polarized Ahlrich basis set Def2TZVP. Geometry optimizations were carried out from x-ray crystal structures using the ultrafine integration grid, tight SCF convergence criteria, and Polarized Continuum Model (PCM) solvent corrections for tetrahydrofuran (ε = 7.6), which was the solvent used to record the compounds’ experimental UV-Vis spectra. Using the geometries optimized under implicit solvation, 40 singlet excited states were calculated for each compound using TD-DFT at the same level of theory. Theoretical fits of the UV-Vis spectra were plotted based on the 40 calculated excited states, and Electron Density Difference (EDD) plots were generated for each transition associated with the most intense predicted excited state in the visible range, not including de-excitations or excitations with small or negative CI expansion coefficients.

A sample input section for each type of calculation is provided below:

**Geometry Optimization:**

```
# bp86/Def2TZVP opt nosymm int=grid=ultrafine
scf=tight scrf=(solvent=tetrahydrofuran)

gallery optimization with implicit solvation
```

**Excited State Calculation:**

```
# td=(nstates=40) bp86/def2TZVP nosymm int=grid=ultrafine scf=tight

geom=check TDDFT without scrf=solvent=thf
```

4.1. DBED-NMe2

Table S3. Transitions involved in the 507.61 nm peak (excited state #2) for DBED-NMe2.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals Involved</th>
<th>CI expansion Coefficient</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>101 → 104</td>
<td>HOMO-2 → LUMO</td>
<td>0.12349</td>
<td>MLCT</td>
</tr>
<tr>
<td>102 → 104</td>
<td>HOMO-1 → LUMO</td>
<td>0.68949</td>
<td>MLCT</td>
</tr>
<tr>
<td>102 ← 104</td>
<td>HOMO-1 ← LUMO</td>
<td>-0.12183</td>
<td></td>
</tr>
</tbody>
</table>

Figure S13. Calculated UV-vis spectrum for DBED-NMe2.

Figure S14. EDD plot of absolute value of 104-101 (left) and 140-102 (right) for DBED-NMe2. Purple = (+), yellow = (-).
4.2. DBED-H

Figure S15. Calculated UV-vis spectrum for DBED-H.

Table S4. Transitions involved in the 491.31 nm peak (excited state #2) for DBED-H.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals Involved</th>
<th>CI expansion Coefficient</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>83 → 92</td>
<td>HOMO-8 → LUMO</td>
<td>0.11167</td>
<td></td>
</tr>
<tr>
<td>85 → 92</td>
<td>HOMO-6 → LUMO</td>
<td>0.10364</td>
<td></td>
</tr>
<tr>
<td>89 → 92</td>
<td>HOMO-2 → LUMO</td>
<td>-0.15051</td>
<td></td>
</tr>
<tr>
<td>90 → 92</td>
<td>HOMO-1 → LUMO</td>
<td><strong>0.67080</strong></td>
<td>MLCT</td>
</tr>
<tr>
<td>90 ← 92</td>
<td>HOMO-1 ← LUMO</td>
<td>-0.13135</td>
<td></td>
</tr>
</tbody>
</table>

Figure S16. EDD plot of absolute value of 92-90 for DBED-H. Purple = (+), yellow = (-).
4.3. DBED-Br

![UV-Vis Spectrum](image)

Figure S17. Calculated UV-vis spectrum for DBED-Br.

Table S5. Transitions involved in the 512.53 nm peak (excited state #2) for DBED-Br.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals Involved</th>
<th>CI expansion Coefficient</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>106 → 109</td>
<td>HOMO-2 → LUMO</td>
<td>0.15535</td>
<td>LMCT</td>
</tr>
<tr>
<td>107 → 109</td>
<td>HOMO-1 → LUMO</td>
<td>0.67634</td>
<td>MLCT</td>
</tr>
<tr>
<td>107 ← 109</td>
<td>HOMO-1 ← LUMO</td>
<td>-0.12520</td>
<td></td>
</tr>
</tbody>
</table>

Interestingly, DBED-Br is an exception to the MLCT assignment, compared with the other species. Its most intense visible excited state includes important contribution from both MLCT and LMCT component transitions, with the second most important contributor identified by EDD plots as an LMCT from HOMO-2 → LUMO (see below).

![EDD Plot](image)

Figure S18. EDD plot of absolute value of 109-106 (left) and 109-107 for DBED-Br (right). Purple = (+), yellow = (-).
4.4. DBED-NO₂

Figure S19. Calculated UV-vis spectrum for DBED-NO₂.

Table S6. Transitions involved in the 531.58 nm peak (excited state #2) for DBED-NO₂.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals Involved</th>
<th>CI expansion Coefficient</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>99 → 103</td>
<td>HOMO-3 → LUMO</td>
<td>-0.11235</td>
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</tr>
<tr>
<td>101 → 103</td>
<td>HOMO-1 → LUMO</td>
<td>0.66326</td>
<td>MLCT</td>
</tr>
<tr>
<td>101 → 104</td>
<td>HOMO-1 → LUMO+1</td>
<td>0.17260</td>
<td>MLCT</td>
</tr>
<tr>
<td>101 ← 103</td>
<td>HOMO-1 ← LUMO</td>
<td>-0.13253</td>
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</tr>
</tbody>
</table>

Figure S20. EDD plot of absolute value of 103-101 (left) and 104-101 (right) for DBED-NO₂. Purple = (+), yellow = (-).
5. Reference