Unsupported Au(I)···Cu(I) interactions: influence of nitrile ligands and aurophilicity on the structure and luminescence.

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ELECTRONIC SUPPLEMENTARY INFORMATION

Figure S1. Phase and modulation data for complex [AuCu(C$_6$F$_5$)$_2$(N≡CPh)$_2$]$_2$ (**2**) recorded at different frequencies in solid state at room temperature
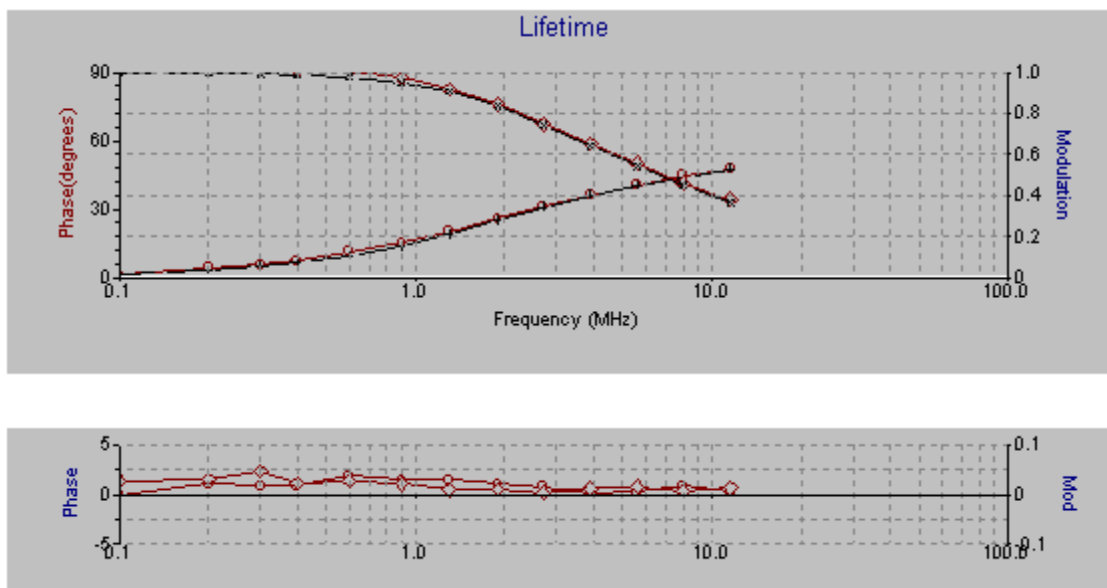
Figure S2. Molecular orbitals involved in the theoretical excitations for complex **2**.

325a LUMO+6

323a LUMO+4

322a LUMO+3

320a LUMO+1

319a LUMO

$\triangle$ = 3.030 eV

318a HOMO

317a HOMO-1
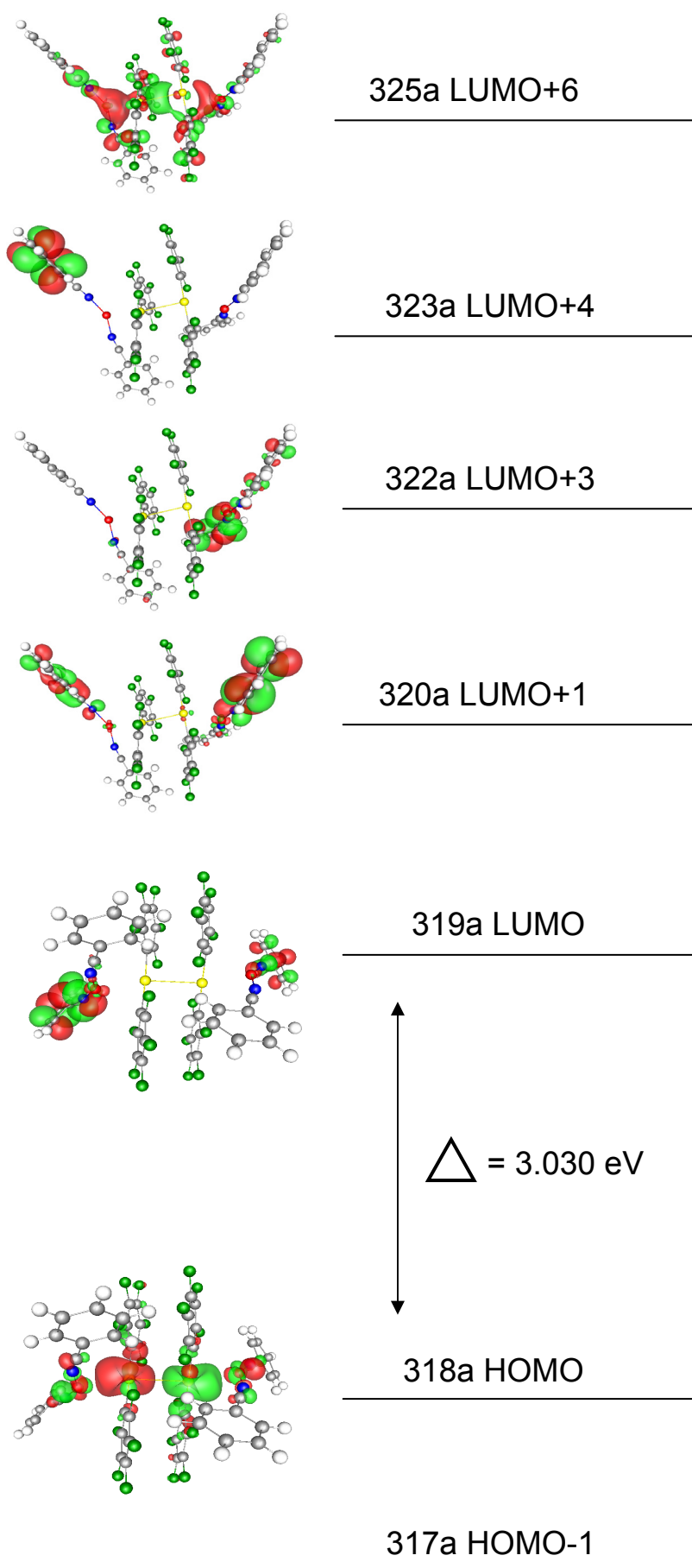
MOST IMPORTANT SINGLET EXCITATIONS FOR COMPLEX 2
1 singlet a excitation
Excitation energy / eV: 2.570561103936059
Excitation energy / nm: 482.3236600624778

Oscillator strength:
    mixed representation: 0.6808400617238028E-01

 Dominant contributions:
occ. orbital energy / eV   virt. orbital energy / eV |coeff.|^2*100
   318 a   -5.23   319 a   -2.20   95.9

2 singlet a excitation
Excitation energy / eV: 2.637679549127771
Excitation energy / nm: 470.0504428123861

Oscillator strength:
    mixed representation: 0.1097800516171850

 Dominant contributions:
occ. orbital energy / eV   virt. orbital energy / eV |coeff.|^2*100
   318 a   -5.23   320 a   -2.16   95.3

4 singlet a excitation
Excitation energy / eV: 2.867950581709468
Excitation energy / nm: 432.3095551129280

 Oscillator strength:
    mixed representation: 0.2176986889319306E-01

 Dominant contributions:
occ. orbital energy / eV   virt. orbital energy / eV |coeff.|^2*100
   318 a   -5.23   322 a   -1.85   97.2

11 singlet a excitation
Excitation energy / eV: 3.285136179811383
Excitation energy / nm: 377.4097547870509

 Oscillator strength:
    mixed representation: 0.1075028324213863E-01

 Dominant contributions:
occ. orbital energy / eV   virt. orbital energy / eV |coeff.|^2*100
   315 a   -5.84   320 a   -2.16   90.2

17 singlet a excitation
Excitation energy / eV: 3.499534458819486
Excitation energy / nm: 354.2878216101136

 Oscillator strength:
    mixed representation: 0.2083390723691779E-01

 Dominant contributions:

occ. orbital energy / eV   virt. orbital energy / eV |coeff.|^2*100
   313 a   -6.19   320 a   -2.16   49.9
   312 a   -6.23   319 a   -2.20   16.6
   313 a   -6.19   319 a   -2.20   14.2

18 singlet a excitation
Excitation energy / eV: 3.508564796640119
xcitation energy / nm: 353.3759562462646

 Oscillator strength:
    mixed representation: 0.2685116268890082E-01

 Dominant contributions:
occ. orbital   nergy / eV   virt. orbital   energy / eV |coeff.|^2*100
    312 a   -6.23   319 a   -2.20   52.9
    312 a   -6.23   320 a   -2.16   16.5
    313 a   -6.19   319 a   -2.20   10.2

25 singlet a excitation
Excitation energy / eV: 3.672948486701009
Excitation energy / nm: 337.5605306074664

 Oscillator strength:
    mixed representation: 0.5069757280015828E-01

 Dominant contributions:

occ. orbital energy / eV   virt. orbital   energy / eV |coeff.|^2*100
    318 a   -5.23   323 a   -1.19   88.4
    318 a   -5.23   325 a   -0.96   9.9

27 singlet a excitation
Excitation energy / eV: 3.696245980012412
Excitation energy / nm: 335.4328815693484

 Oscillator strength:
    mixed representation: 0.2966461032832548

 Dominant contributions:
occ. orbital energy / eV   virt. orbital   energy / eV |coeff.|^2*100
    318 a   -5.23   325 a   -0.96   78.4
    318 a   -5.23   323 a   -1.19   10.7

28 singlet a excitation
Excitation energy / eV: 3.715930681121008
Excitation energy / nm: 333.6559657487077

 Oscillator strength:
    mixed representation: 0.1524076366151150E-01

 Dominant contributions:
occ. orbital energy / eV   virt. orbital   energy / eV |coeff.|^2*100
    312 a   -6.23   320 a   -2.16   41.7
    312 a   -6.23   321 a   -1.89   24.7

Structural optimisation of model system [AuCu(C₆F₅)₂(N≡CH)₂] at DFT level.

The optimization was performed using the Gaussian 03 package program.[1] The molecular geometry of model system [AuCu(C₆F₅)₂(N≡CH)₂] (Cs symmetry) was optimized at DFT level of theory using the B3LYP functional.(Figure S3) The following basis set combination was employed: for the metals, the 19-VE pseudopotentials from Stuttgart and the corresponding basis sets[2] augmented with two f polarization functions were used.[3] The atoms C, F and N were treated by Stuttgart pseudopotentials,[4] including only the valence electrons for each atom. For these atoms double-zeta basis sets of reference 4 were used, augmented by d-type polarization functions.[5] For the H atom, a double-zeta, plus a p-type polarization function was used.[6] The results are given in Table S1.

Figure S3. Optimized a simplified model system [AuCu(C₆F₅)₂(N≡CH)₂] at DFT-B3LYP level of theory and using a C$_s$ symmetry.
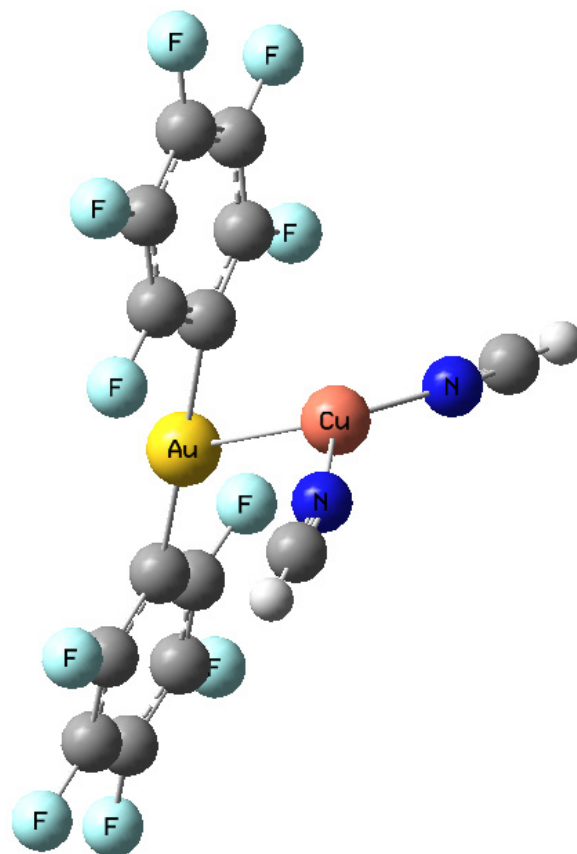
Table S1. Selected structural parameters (distances in Å and angles in deg) for complexes **1-3** and the optimised model system [AuCu(C_6F_5)$_2$(N≡CH)$_2$] (C$_s$ symmetry)

	Complex 1	Complex 2	Complex 3	[AuCu(C₆F₅)₂(N≡CH)₂]
Au-Cu	2.93	2.61, 2,62	2.67	2.60
Au-C	2.04, 2.03	2.07, 2.06	2.05, 2.03	2.12, 2.06
Cu-N	1.92, 1.86	1.87, 1.87	1.87, 1.87	1.95, 1.95
Cu⋯C$_{ipso}$	2.89, 4.11	2.72, 3.77	2.64, 3.98	2.24, 4.15
C-Au-C	179.0	176.8	176.1	178.9
N-Cu-N	151.3	155.2	155.9	130.9
C$_{ipso}$-Au-Cu	110.5, 68.8	107.0, 70.0	114.8, 66.4	125.6, 55.5

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