Highly photoluminescent copper carbene complexes based on prompt rather than delayed fluorescence

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Synthesis of Complexes

**General Considerations.** Unless stated otherwise all reactions were carried out in air. Solvents were distilled and dried as required. Sodium tert-butoxide and carbazole were purchased and used as received. $^{\text{Ad}}$CAAC$^{51}$ and $(^{\text{Ad}}L)$AuX (X = Cl, Br, I)$^{52}$ were obtained according to a literature procedure. $^1$H, $^{13}$C{$^1$H} and $^{19}$F NMR spectra were recorded using a Bruker Avance DPX-300 MHz NMR spectrometer. $^1$H NMR spectra (300.13 MHz) and $^{13}$C{$^1$H} (75.47 MHz) were referenced to CD$_2$Cl$_2$ at δ 5.32 ($^{13}$C, δ 53.84), C$_6$D$_6$ at δ 7.16 ($^{13}$C, δ 128.4), C$_6$D$_5$Cl at δ 7.26 ($^{13}$C 77.16), or C$_6$D$_5$Br at δ 7.30 for the most downfield signal ($^{13}$C, δ 122.5) ppm. UV-visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Photoluminescence measurements were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer with a solids mount attachment where appropriate. Time resolved fluorescence data for $^{\text{Ad}}$CAAC were collected on a TCSPC Fluorolog Horiba Jobin Yvon spectrofluorimeter using Horiba Jobin Yvon DataStation v2.4 software. A NanoLED of 370 nm was used as excitation source. The collected data were analysed using a Horiba Jobin Yvon DAS6 v6.3 software. All electrochemical experiments were performed using an Autolab PGSTAT 302N computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration consisting of either a glassy carbon macrodisk working electrode (GCE) (diameter of 3 mm; BASi, Indiana, USA) combined with a Pt wire counter electrode (99.99 %; GoodFellow, Cambridge, UK) and an Ag wire pseudoreference electrode (99.99 %; GoodFellow, Cambridge, UK). The GCE was polished between experiments using alumina slurry (0.3 μm), rinsed in distilled water and subjected to brief ultrasonication to remove any adhered alumina microparticles. The metal electrodes were then dried in an oven at 100 °C to remove any residual traces of water, the GCE was left to air dry and residual traces of water were removed under vacuum. The Ag wire pseudoreference electrodes were calibrated to the ferrocene/ferrocenium couple in MeCN at the end of each run to allow for any drift in potential, following IUPAC recommendations.$^{53}$ All electrochemical measurements were performed at ambient temperatures under an inert Ar atmosphere in MeCN containing the complex under study (0.14 mM) and [n-Bu$_4$N][PF$_6$] as supporting electrolyte (0.13 mM). Data were recorded with Autolab NOVA software (v. 1.11). Elemental analyses were performed by the London Metropolitan University. Thermogravimetric analysis (TGA) was performed using a METTLER-TOLEDO TGA-1. The solid sample (approx. 7 mg) was placed in a 70 μL platinum pan and measurements were taken while heating of the sample from 50 °C to 600 °C under nitrogen atmosphere. The background measurement was performed during heating the empty pan over the same temperature range.
Synthesis of \(^{(Ad)L}CuCl\). An oven-dried 100-mL Schlenk flask was equipped with a stirring bar and charged with \(^{(Ad)L}\) (1.58 g, 4.2 mmol) and CuCl (0.42 g, 4.2 mmol) under an argon atmosphere. Anhydrous THF (20 mL) was added, and the resulting suspension was stirred overnight. The solvent was removed, the residue dissolved in CH\(_2\)Cl\(_2\) and filtered through a short pad of silica (1.5 cm). The colorless filtrate was concentrated and hexane was added to precipitate the copper complex, solvents were decanted and the residue dried in vacuum to give a white solid. Yield: 1.86 g (3.9 mmol, 93%).

\[^{1}\H\text{NMR}\ (300\ MHz, CDCl\(_3\)) \delta 7.46\ (t, J = 7.2 Hz, 1H, aryl), 7.30\ (d, J = 7.2 Hz, 2H, aryl) 3.52\ (d, J = 11.4 Hz, 2H, CHMe\(_2\)) 2.81\ (sept, J = 6.6 Hz, 2H, CHMe\(_2\)) 2.23-1.78\ (m, 14H, adamantyl CH and CH\(_2\)), 1.33 (s, 6H, CMe\(_2\)) 1.30 (d, J = 6.6 Hz, 6H, CHMe\(_2\)) 1.29 (d, J = 6.6 Hz, 6H, CHMe\(_2\)). \[^{13}\C\text{NMR}\ (75\ MHz, CDCl\(_3\)) \delta 253.0\ (C\ carbene), 145.4\ (\alpha-C), 135.8\ (ipso-C), 129.9\ (p-CH), 125.1\ (m-CH), 78.9\ (C\(_q\)), 64.9\ (C\(_q\)), 48.1\ (CH\(_2\)), 38.9\ (CH\(_2\)), 37.5\ (CH), 36.2\ (CH\(_2\)), 34.5\ (CH\(_2\)), 29.54\ (CH), 29.40, 28.4, 27.6, 27.0, 22.6\ (CH\(_3\)). Anal. Calcd. for C\(_{27}\)H\(_{39}\)NCuCl (476.60): C, 68.04; H, 8.25; N, 2.94. Found: C, 67.91; H, 8.35; N, 3.07.

Synthesis of \(^{(Ad)L}CuBr\). Prepared as described for \(^{(Ad)L}CuCl\) from 217 mg (0.58 mmol) of \(^{(Ad)L}\) and 82.5 mg (0.58 mmol) of CuBr as a white solid. Yield: 0.193 g (0.37 mmol, 64%).

\[^{1}\H\text{NMR}\ (300\ MHz, CDCl\(_3\)) \delta 7.40\ (t, J = 7.2 Hz, 1H, aryl), 7.25\ (d, J = 7.2 Hz, 2H, aryl) 3.57\ (d, J = 12.6 Hz, 2H, CHMe\(_2\)) 2.79\ (sept, J = 6.6 Hz, 2H, CHMe\(_2\)) 2.22-1.77\ (m, 14H, adamantyl CH, CH\(_2\)), 1.34 (s, 6H, CHMe\(_2\)) 1.32 (d, J = 6.6 Hz, 6H, CHMe\(_2\)) 1.29 (d, J = 6.6 Hz, 6H, CHMe\(_2\)). \[^{13}\C\text{NMR}\ (75\ MHz, CDCl\(_3\)) \delta 253.3\ (C\ carbene), 144.9\ (\alpha-C), 135.2\ (ipso-C), 129.9\ (p-CH), 124.9\ (m-CH), 78.5\ (C\(_q\)), 64.8\ (C\(_q\)), 48.1\ (CH\(_2\)), 38.7\ (CH\(_2\)), 37.3\ (CH), 36.0\ (CH\(_2\)), 34.4\ (CH\(_2\)), 29.5\ (CH), 29.2, 27.8, 27.23, 27.20, 22.7\ (CH\(_3\)). Anal. Calcd. for C\(_{27}\)H\(_{39}\)NCuBr (521.05): C, 62.24; H, 7.54; N, 2.69. Found: C, 62.15; H, 7.68; N, 2.75.

Synthesis of \(^{(Ad)L}CuI\). Prepared as described for \(^{(Ad)L}CuCl\) from 199 mg (0.53 mmol) of \(^{(Ad)L}\) and 100 mg (0.53 mmol) of CuI as a white solid. Yield: 0.170 g (0.30 mmol, 56%).

\[^{1}\H\text{NMR}\ (300\ MHz, CDCl\(_3\)) \delta 7.41\ (t, J = 7.5 Hz, 1H, aryl), 7.26\ (d, J = 7.5 Hz, 2H, aryl) 3.59\ (d, J = 12.6 Hz, 2H, CHMe\(_2\)) 2.79\ (sept, J = 6.6 Hz, 2H, CHMe\(_2\)) 2.23-1.79\ (m, 14H, adamantyl CH, CH\(_2\)), 1.36 (s, 6H, CMe\(_2\)) 1.35 (d, J = 6.6 Hz, 6H, CHMe\(_2\)) 1.29 (d, J = 6.6 Hz, 6H, CHMe\(_2\)). \[^{13}\C\text{NMR}\ (75\ MHz, CDCl\(_3\)) \delta 254.1\ (C\ carbene), 145.0\ (\alpha-C), 135.2\ (ipso-C), 129.8\ (p-CH), 124.9\ (m-CH), 78.6\ (C\(_q\)), 65.0\ (C\(_q\)), 48.2\ (CH\(_2\)), 38.8\ (CH\(_2\)), 37.4\ (CH), 36.0\ (CH\(_2\)), 34.4\ (CH\(_2\)), 29.5\ (CH), 29.2, 27.9, 27.4, 27.2, 22.9\ (CH\(_3\)). Anal. Calcd. for C\(_{27}\)H\(_{39}\)NCuI (568.05): C, 57.09; H, 6.92; N, 2.47. Found: C, 57.50; H, 7.09; N, 2.68.
Table S1. Decomposition temperature ($T_d$, °C) and melting point ($T_m$, °C) for complexes 1/2 a-f obtained by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

|     | $T_d/T_m$  |     | $T_d/T_m$ |
|-----|------------|-----|-----------|
| 1a  | 328/280    | 2a  | 345/305   |
| 1b  | 319/276    | 2b  | 323/300   |
| 1c  | 313/273    | 2c  | 309/303   |

Figure S1. Left: UV-vis spectrum of $^\text{Ad}$CAAC in THF solution. Right: Emission spectrum of $^\text{Ad}$CAAC in the solid state (excitation at $\lambda_{ex} = 365$ nm).
**Figure S2.** Left: UV-vis spectra of THF solutions of \((\text{AdL})\text{CuX}\) (X = Cl, Br, I). Right: Emission spectra of \((\text{AdL})\text{CuX}\) (X = Cl, Br, I) in the solid state (excited at \(\lambda_{ex} = 365\) nm).

**Figure S3.** Left: UV-vis spectra of THF solutions of \((\text{AdL})\text{AuX}\) (X = Cl, Br, I). Right: Emission spectra of \((\text{AdL})\text{AuX}\) (X = Cl, Br, I) in the solid state (excited at \(\lambda_{ex} = 365\) nm).
|   | HOMO | LUMO |
|---|------|------|
| 1a | ![Image](image1.png) | ![Image](image2.png) |
| 1b | ![Image](image3.png) | ![Image](image4.png) |
| 1c | ![Image](image5.png) | ![Image](image6.png) |
| 2a | ![Image](image7.png) | ![Image](image8.png) |
| 2b | ![Image](image9.png) | ![Image](image10.png) |
| 2c | ![Image](image11.png) | ![Image](image12.png) |

**Figure S4.** Representations of the HOMOs and LUMOs of the halide complexes (L^*M)MX (M = Cu, Au; X = Cl, Br, I).
Figure S5. Optimized calculated geometries of the $S_0$, $S_1$ and $T_1$ states of the halide complexes ($^{\text{Ad}}L$)MX ($M = \text{Cu, Au}; X = \text{Cl, Br, I}$).
Figure S6. Highest singly-occupied molecular orbitals of 1a - 1c.

Table S2. Selected structural parameters of the optimized ground and excited state geometries of copper and gold halides

|       | M–C |       | M–X |       | C-M-X | Exper.[°] | C–M–X calc. | C6–N–C–M |
|-------|-----|-------|-----|-------|-------|-----------|-------------|----------|
|       | S₀  | S₁    | S₀  | S₁    |       |           |             |          |
| 1a    | 1.894 | 1.851 | 1.890 | 2.111 | 2.141 | 2.129 | 175.33(5) | 179.7 | 175.8 | 176.2 | 0.6 | 4.3 | 3.0 |
| 1b    | 1.902 | 1.863 | 1.890 | 2.248 | 2.267 | 2.264 | 177.59(11) | 179.6 | 156.0 | 168.0 | 1.1 | 31.0 | 12.8 |
| 1c    | 1.913 | 1.873 | 1.914 | 2.426 | 2.442 | 2.439 | 178.52(5) | 179.2 | 144.5 | 154.2 | 0.6 | 28.5 | 4.0 |
| 2a    | 1.989 | 1.998 | 1.997 | 2.277 | 2.288 | 2.288 | 179.7 | 153.5 | 159.2 | 0.5 | 13.1 | 7.9 |
| 2b    | 1.998 | 2.004 | 1.998 | 2.405 | 2.418 | 2.411 | 178.60(10) | 179.8 | 145.2 | 156.2 | 1.5 | 48.9 | 9.1 |
| 2c    | 2.014 | 2.013 | 2.013 | 2.571 | 2.586 | 2.583 | 179.15(9) | 179.8 | 141.1 | 153.4 | 1.6 | 46.2 | 33.2 |

Figure S7. Photoluminescence spectra of 1a at 4 K to 300 K for the 420-700 nm emission edge. No significant shift is observed, indicating a minimal contribution from phosphorescence.
Figure S8. Photoluminescence decay lifetimes of 1a and 2a at various emission wavelengths measured using time-correlated single photon counting (TCSPC) as a function of temperature. All decays are temperature-independent within error.
Figure S9. Comparison of emission spectra for (AdL)CuCl in solid state ($\lambda_{ex} = 365$ nm) and in various solvents (the small peaks near 400 nm are due to Raman scattering).

Table S3. Photophysical properties of (AdL)MX complexes in aerated CH$_2$Cl$_2$ solution.

| Complex | $\lambda_{em}$ ($\lambda_{exc}$), nm | Lifetime (ns)$^a$ |
|---------|-------------------------------------|------------------|
| 1a      | 456 (290–390)                      | 6 (3%), 160 (97%)|
| 1b      | 453 (300–375)                      | 10 (28%), 72 (72%)|
| 1c      | 445 (290–380)                      | 38 (72%), 146 (28%)|
| 2a      | 480 (300–375)                      | 5 (53%), 25 (47%)|
| 2b      | 513 (280–380)                      | 4 (23%), 33 (77%)|
| 2c      | 544 (290–360)                      | 7 (3%), 175 (97%)|

$^a$ Lifetimes are measured at maximum of $\lambda_{em}$ and are limited by the instrument response (2 ns)
Table S4. Binding energies and M–O distances of the S₀ and T₁ states of the THF-coordinated halide complexes (L⁻)MX (M = Cu, Au; X = Cl, Br, I).

| Complex | Binding energy (kJ mol⁻¹) | M–O (Å) |
|---------|--------------------------|---------|
| 1a (T₁) | −46.5                    | 2.174   |
| 1b (T₁) | −45.7                    | 2.164   |
| 1c (S₀) | −9.2                     | 2.387   |
| 1c (T₁) | −43.6                    | 2.176   |
| 2a (T₁) | −21.3                    | 2.382   |
| 2b (T₁) | −20.8                    | 2.486   |
| 2c (T₁) | −20.5                    | 2.443   |

Figure S10. Optimized calculated geometries of the S₀ (Cu-O 2.387) and T₁ (Cu-O 2.176) states of the THF-coordinated halide complex (L⁻)CuI (Cu-O distances: S₀: 2.387 Å; T₁: 2.176 Å). Hydrogens are omitted for clarity.

Table S5. Formal electrode potentials (E₁/₂ for irreversible and for partially reversible processes (*), V, vs. FeCp₂), onset potentials (E, V, vs. FeCp₂), E_HOMO/E_LUMO (eV) and band gap values (ΔE, eV) for the redox changes exhibited by 1 and 2 in MeCN solution.ᵃ

| Complex | Reduction | Oxidation | E_HOMO | ΔE |
|---------|-----------|-----------|--------|----|
| E_M(II)/M(0) | E_onset red | E₁st | E_onset ox | E₂nd | eV |
| 1a      | −2.65     | −2.60     | −2.79  | +0.67 | +0.59 | − | −5.98 | 3.19 |
| 1b      | −2.66     | −2.61     | −2.78  | +0.58 | +0.49 | − | −5.88 | 3.10 |
| 1c      | −2.56     | −2.45     | −2.94  | +0.17 | +0.11 | +0.76 | −5.50 | 2.56 |
| 2a      | −2.57     | −2.52     | −2.87  | +1.46 | +1.34 | − | −6.73 | 3.86 |
|    | 2b  | 2c  |
|----|-----|-----|
| 2b | -2.67* | -2.57 | -2.82 | +1.43 | +1.37 | – | -6.76 | 3.94 |
| 2c | -2.59* | -2.50 | -2.89 | +0.86 | +0.79 | – | -6.18 | 3.29 |

*Recorded using a glassy carbon electrode, concentration 0.14 mM, supporting electrolyte [n-Bu₄N][PF₆] (0.13 M), measured at 0.1 V s⁻¹.

Cryogenic and time-resolved PL measurements.

For PL measurements, the samples (spin-cast films on quartz substrates) were photoexcited using a 407 nm pulsed laser with pulse width <200 ps. The time-integrated PL spectra were measured with a spectrograph (SpectraPro 2500i, Princeton Instruments) coupled with a thermo-electronically cooled CCD camera (PIXIS 100-F, Princeton Instruments). A time-correlated single photon counting (TCSPC) setup (Lifespec-ps, Edinburgh Instruments) was used to measure the PL kinetics. The cooling of the sample was provided by a liquid helium cryostat.

X-Ray Crystallography.

Crystals suitable for X-ray study for copper complexes were obtained by layering of CH₂Cl₂ solutions with hexanes, while gold complexes were crystallized by slow evaporation of benzene solutions. Crystals were mounted in oil on glass fibers and fixed on the diffractometer in a cold nitrogen stream. Data were collected on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 140 K. Data were processed using the CrystAlisPro-CCD and –RED software. The principal crystallographic data and refinement parameters are listed in Table S1. The complexes (L⁻⁻)CuX (X = Cl, Br, and I) crystallized with two independent molecules in the unit cell. The structures were solved by direct methods and refined by the full-matrix least-squares against F² in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in “riding” model with the U(eq)(H) parameters equal to 1.2 U(eq)(Cᵢ), for methyl groups equal to 1.5 U(eq)(Cᵢ), where U(Cᵢ) and U(Cᵢ) are respectively the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software.
Figure S11. Crystal structure of independent molecules A for \((^{\text{Ad}}L)\text{CuCl} / (^{\text{Ad}}L)\text{CuBr} / (^{\text{Ad}}L)\text{CuI}\). Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1A–C1A 1.883(2) / 1.893(4) / 1.9059(17), Cu1A–Hal1A 2.1099(5) / 2.2176(6) / 2.4224(2), C1A–C2A 1.530(2) / 1.523(5) / 1.525(2), C1A–N1A 1.305(2) / 1.301(5) / 1.305(2), C1A–Cu1A–Hal1A 175.33(5) / 177.59(11) / 178.52(5)

Table S6. Summary of crystallographic data and structure refinement.

|                        | \((^{\text{Ad}}L)\text{CuCl}\) | \((^{\text{Ad}}L)\text{CuBr}\) | \((^{\text{Ad}}L)\text{CuI}\) |
|------------------------|---------------------------------|---------------------------------|---------------------------------|
| Empirical formula      | \(\text{C}_{27}\text{H}_{39}\text{ClCuN}\) | \(\text{C}_{27}\text{H}_{39}\text{BrCuN}\) | \(2\text{C}_{27}\text{H}_{39}\text{CuIN\cdotCH}_{2}\text{Cl}_{2}\) |
| Molecular weight       | 476.58                          | 521.04                          | 1220.99                         |
| Crystal system         | Monoclinic                      | Monoclinic                      | Triclinic                       |
| Space group            | \(P2_1/c\)                      | \(P2_1/c\)                      | \(P-1\)                         |
| Crystal colour, habit  | colorless/block                 | colorless/block                 | colorless/block                 |
| Crystal size (mm)      | 0.48×0.45×0.29                  | 0.48×0.39×0.36                  | 0.33×0.28×0.13                  |
| \(a\) (Å)              | 15.9209(1)                      | 16.0878(2)                      | 11.1918(2)                      |
| \(b\) (Å)              | 19.4144(2)                      | 19.4137(3)                      | 11.9685(2)                      |
| \(c\) (Å)              | 16.2447(2)                      | 16.2912(3)                      | 20.7901(4)                      |
| \(\alpha\) (°)         | 90                              | 90                              | 101.520(2)                      |
| \(\beta\) (°)          | 103.631(1)                      | 103.540(2)                      | 94.798(1)                       |
| \(\gamma\) (°)         | 90                              | 90                              | 94.419(1)                       |
| \(V(\text{Å}^3)\)      | 4879.72(8)                      | 4946.71(13)                     | 2706.59(8)                      |
| \(Z\)                  | 8                               | 8                               | 2                               |
| \(D_{\text{calc}}(\text{g cm}^{-3})\) | 1.297                          | 1.399                          | 1.498                          |
| \(2\theta_{\text{max}}\) (°) | 28.00                          | 27.00                          | 28.00                          |
| Abs. coeff., \(\mu(\text{Mo-K}\alpha)\) (cm\(^{-1}\)) | 1.018                          | 2.512                          | 2.061                          |
| \(T_{\text{max}}/T_{\text{min}}\) | 0.7566/0.6406                   | 0.4649/0.3785                   | 0.7754/0.5495                   |
| Number of collected    | 80046                           | 71950                           | 47637                           |
### Number of independent reflections

|          | 11765 | 10788 | 13045 |
|----------|-------|-------|-------|

### Number of observed reflections ($I > 2\sigma(I)$)

|          | 9821  | 8881  | 11265 |
|----------|-------|-------|-------|

### $\hat{R}_{int}$

|          | 0.0411 | 0.0411 | 0.0227 |
|----------|--------|--------|--------|

### Number of parameters

|          | 553    | 553    | 580    |
|----------|--------|--------|--------|

### $R_1$ (on $F$ for observed reflections)

|          | 0.0411 | 0.0411 | 0.0227 |
|----------|--------|--------|--------|

### $wR_2$ (on $F^2$ for all reflections)

|          | 0.0838 | 0.1574 | 0.0574 |
|----------|--------|--------|--------|

### Weighting scheme

|          | $A$ | $B$ | F(000) | Goodness-of-fit | $\Delta\rho_{max}/\Delta\rho_{max}$ (e Å$^{-3}$) |
|----------|-----|-----|--------|----------------|-------------------------------------------|
|          | 0.04| 0.08| 2032   | 0.994          | 0.820/-0.272                              |
|          |     |     |        |                | 1.278/-1.861                             |
|          |     |     |        |                | 0.826/-0.624                             |

### Table S7. Intermolecular C–H···Hal (Hal = Cl, Br, I) hydrogen bonds (Å, °) found for 1/2 a-c.

| Compound | D–H···A | d(D–H) | d(H···A) | $\Delta^*$ | d(D···A) | DHA [°] |
|----------|---------|--------|---------|-----------|---------|---------|
| 1a       | C17B–H17B$^3$···Cl1A | 1.00   | 2.91    | –0.04     | 3.596(2)| 128     |
| 1b       | C8A–H8A···Br1A$^b$   | 1.00   | 3.03    | –0.02     | 3.034(3)| 148     |
|          | C17B–H17B$^c$···Br1B | 1.00   | 2.94    | –0.11     | 3.627(5)| 128     |
| 1c·CH$_2$Cl$_2$ | C9A–H9A$^d$···I1B | 1.00   | 3.06    | –0.12     | 3.850(2)| 144     |
| 2a       | C22A–H24A$^c$···Cl1$^{**}$ | 1.00   | 2.90    | –0.03     | 3.592(4)| 128     |
| 2b       | C9A–H9A$^f$···Br1B  | 1.00   | 2.98    | –0.07     | 3.760(2)| 142     |
| 2c       | none     | –      | –       | –         | –       | –       |

* Difference between spherical van der Waals radii of H atom and halides proposed by Bondi (A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451; R.S. Rowland, R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384–7391)

** G.D. Frey, R.D. Dewhurst, S. Kousar, B. Donnadieu, G. Bertrand, *J. Organomet. Chem.*, 2008, **693**, 1674.

Symmetry transformations used to generate equivalent atoms: $^a$ = $1 + x$, $y$, $1 + z$; $^b$ = $2 - x$, $1 - y$, $2 - z$; $^c$ = $1 - x$, $1 - y$, $2 - z$; $^d$ = $x$, $1 + y$, $z$; $^e$ = $x$, $3/2 - y$, $1/2 + z$; $^f$ = $x$, $-1 + y$, $z$.
Computational details

The ground states were fully optimized by the hybrid density functional PBE0\textsuperscript{56} method in combination with def2-TZVP basis set of Ahlrichs and coworkers.\textsuperscript{57} Relativistic effective core potentials of 28 and 60 electrons were used to describe the core electrons of I and Au, respectively.\textsuperscript{58} The excited states were studied similarly by time-dependent DFT.\textsuperscript{59} The methods and basis sets have been previously employed with success in studies of luminescent Cu- and Au-complexes.\textsuperscript{60} All calculations were carried out by Gaussian 09.\textsuperscript{61}

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