Electronic Supporting Information

NHC-Stabilized Au$_{10}$ Nanoclusters and their Conversion to Au$_{25}$ Nanoclusters

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Table of Contents

1 General information ................................................................. 5

1.1 Materials ............................................................................. 5

1.2 Instruments and sample preparation .......................................... 5

1.3 Mass spectrometry ................................................................. 5

1.4 X-ray crystallography ............................................................. 6

1.5 Photoluminescence quantum yield ........................................... 6

1.6 Computational methods ......................................................... 7

2 Synthetic procedures and purification protocols ............................. 8

2.1 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium chloride (1a) ........................................................................ 8

2.2 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium bromide (1b) .......................................................... 8

2.3 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)-[2-$^{13}$C]-benzimidazolium bromide (1b*) ..................................................... 9

2.4 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold chloride (2a) .................................................... 9

2.5 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold bromide (2b) .................................................... 9

2.6 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)-[2-$^{13}$C]-benzimidazolium-ylidene gold bromide (2b*) ................................. 10

2.7 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold iodide (2c) ....................................................... 10

2.8 Isolation of [Au$_{10}$($^{\text{MesCH}_2}$Bim)$_6$Cl$_3$]Cl ([3a]Cl) from reduction of 2a .......................................................... 11

2.9 Isolation of [Au$_{10}$($^{\text{MesCH}_2}$Bim)$_6$Cl$_3$][PF$_6$] ([3a][PF$_6$]) from [3a]Cl .......................................................... 11

2.10 Isolation of [Au$_{10}$($^{\text{MesCH}_2}$Bim)$_6$Br$_3$]Br ([3b]Br) from reduction of 2b .......................................................... 12

2.11 Isolation of [Au$_{10}$($^{\text{MesCH}_2}$Bim)$_6$Br$_3$][PF$_6$] ([3b][PF$_6$]) from [3b]Br ....................................................... 12

Figure S1. Photographs showing the column purification of [3b]Br. ........................................................................ 13

Figure S2. UV–vis absorbance spectra (DCM) showing (A) isolation of crude [3b]Br and (B) purification of [3b]Br by column chromatography followed by anion exchange. ........................................................................ 13

S1
2.12 Isolation of $^{13}$C-labeled $[\text{Au}_{10}^{\text{MesCH}_2} \text{Bimy}]_3 \text{Br}_3 \text{Br}$ ($[3b^*] \text{Br}$) from reduction of $2b^*$ ............................................. 14

Figure S4. Aliphatic (top) and aromatic (bottom) regions of $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra showing the isolation and purification of $[3b^*] \text{Br}$ from reduction of $2b^*$ (top red trace). .......................................................... 15

Figure S5. $^{13}$C $^1$H NMR (151 MHz, CD$_2$Cl$_2$) spectra showing the isolation and purification of $[3b^*] \text{Br}$ from reduction of $2b^*$ (top red trace). .......................................................... 16

2.13 Isolation and crystallization of $[3b] \text{OTf}$ from $[3b] \text{Br}$ ........................................................................... 16

2.14 Reduction of $2c$ and evidence for the formation of $[\text{Au}_{10}^{\text{MesCH}_2} \text{Bimy}]_3 \text{I}$ and $[\text{Au}_{25}^{\text{MesCH}_2} \text{Bimy}]_{10} \text{I}_2$ ................. 16

Figure S6. UV–vis absorbance spectra (DCM) showing the attempted isolation and purification of $[3c] \text{I}$ and $[4c] \text{I}_2$ from the reduction of $2c$ ............................................................................. 17

Figure S7. ESI-MS showing the attempted isolation and purification of $[3c] \text{I}$ and $[4c] \text{I}_2$ from the reduction of $2c$ . ................. 17

Figure S8. Aliphatic (top) and aromatic (bottom) region of $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra showing the attempted isolation and purification of $[3c] \text{I}$ and $[4c] \text{I}_2$ from the reduction of $2c$ (top red trace). .......................................................... 18

2.15 Isolation and crystallization of $[\text{Au}_{25}^{\text{MesCH}_2} \text{Bimy}]_{10} \text{Br}_8 ([5b] \text{B(C}_6\text{F}_5)_4) ([6b] \text{B(C}_6\text{F}_5)_4)$ from conversion of $[3b] \text{Br}$ in EtOH at room temperature .......................................................... 19

2.16 Isolation of $[\text{Au}_{25}^{\text{MesCH}_2} \text{Bimy}]_{10} \text{Br}_7 [[4b] \text{PF}_6$ by conversion of crude $[3b] \text{Br}$ in MeOH at 60 °C .......... 19

Figure S9. UV–vis absorbance spectra (DCM) showing the attempted isolation and purification of $[4b] \text{PF}_6$ from conversion of $[3b] \text{Br}$ in methanol at 60 °C ........................................................................ 20

Figure S10. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra showing the isolation and purification of $[4b] \text{PF}_6$ from conversion of $[3b] \text{Br}$ in methanol at 60 °C ........................................................................ 20

2.17 Isolation of $[\text{Au}_{25}^{\text{MesCH}_2} \text{Bimy}]_{10} \text{Br}_7 [[4b^*] \text{PF}_6$ by conversion of crude $[3b^*] \text{Br}$ in MeOH at 60 °C ............. 21

2.18 Isolation and crystallization of $[\text{Au}_{25}^{\text{MesCH}_2} \text{Bimy}]_{10} \text{Br}_7 [[5b] \text{B(C}_6\text{F}_5)_4]_2 ([6b] \text{B(C}_6\text{F}_5)_4]_2$ from $[4b] \text{PF}_6$ ................. 21

3 Monitoring reaction progress .................................................................................................................. 22

3.1 Monitoring reduction of $2a$, $2b$, or $2c$ ............................................................................................ 22

Figure S11. In situ monitoring of the reduction of (A) $2a$ (X = Cl), (B) $2b$ (X = Br) and (C) $2c$ (X = I) at 2.31 mM in DCM/EtOH (10:3) with NaBH$_4$ by UV–vis absorbance spectroscopy. .......................................................... 22

Figure S12. In situ monitoring of the reduction of (A) $2a$ (X = Cl), (B) $2b$ (X = Br) and (C) $2c$ (X = I) at 2.31 mM in DCM/EtOH (10:3) with NaBH$_4$ by UV–vis absorbance spectroscopy (continued) ........................................................................ 23

Figure S13. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra of aliquots taken from the reduction of $2b$ (top red trace) with NaBH$_4$ over time, showing the aliphatic (top) and aromatic (bottom) regions. .......................................................... 23

Figure S14. ESI-MS of aliquots taken from the reduction of $2b$ with NaBH$_4$ over time ........................................................................ 25

Figure S15. ESI-MS of aliquots taken from the reduction of $2c$ with NaBH$_4$ over time ........................................................................ 25

3.2 Monitoring conversion of $[3b] \text{X}$ clusters .................................................................................. 26

Figure S16. UV–vis spectra of (A) $[3b] \text{Br}$ upon stirring in EtOH for 84 h at room temperature and (B) $[3b] \text{Br}$ upon stirring in various solvents for 48 h at room temperature (insets show the new band at 658 nm attributed to $\text{Au}_{25} \text{Cl}_{25}$ clusters) ........................................................................ 26

Figure S17. UV–vis spectra of aliquots taken from the conversion of (A) $[3b] \text{Br}$ and (B) $[3b^*] \text{PF}_6$ in methanol at 60 °C over time (inset shows the characteristic band of $[4b]^+$ at 658 nm) ........................................................................ 26

Figure S18. UV–vis absorbance at 658 nm plotted over time for aliquots taken from the conversion of $[3b] \text{Br}$ (blue) and $[3b^*] \text{PF}_6$ (red) in methanol at 60 °C ........................................................................ 26

Figure S19. ESI-MS spectra of aliquots taken from the conversion of $[3b] \text{Br}$ in methanol at 60 °C over time ........................................................................ 27

Figure S20. Monitoring conversion of $[3b] \text{PF}_6$ in CD$_2$OD at 60 °C by $^1$H NMR spectroscopy (600 MHz), showing the aliphatic (top) and aromatic (bottom) regions. ........................................................................ 28

Figure S21. Monitoring conversion of $[3b] \text{PF}_6$ in CDCl$_3$ at 60 °C by $^1$H NMR spectroscopy (600 MHz), showing the aliphatic (top) and aromatic (bottom) regions. ........................................................................ 29

Figure S22. Comparison of the $^1$H NMR spectra (CD$_2$Cl$_2$, 600 MHz) of (A) the crude reaction mixture from conversion of $[3b^*] \text{Br}$ in MeOH at 60 °C for 4 days, (B) the crude reaction mixture extracted with pentane/EtO from conversion of $[3b^*] \text{Br}$ in MeOH at 60 °C for 4 days with NaBH$_4$. .......................................................... 29
with added TBAB (10 eq.) in CD$_2$OD at 60 °C for 4.5 hours, (C) [4b][PF$_6$] with added TBAB (10 eq.), and (D) [4b][PF$_6$] alone, showing the aliphatic (top) and aromatic (bottom) regions. .................................................. 30

Figure S23. Comparison of the cluster regions of the $^{13}$C [$^{1}$H] NMR spectra (CD$_2$Cl$_2$, 151 MHz) of (A) the crude reaction mixture from conversion of [3b*]Br in MeOH at 60 °C for 4 days, (B) the crude reaction mixture extracted with pentane/Et$_2$O from conversion of [3b*][PF$_6$] with added TBAB (10 eq.) in CD$_2$OD at 60 °C for 4.5 hours, and (C) [4b*][PF$_6$] alone. ........... 31

4 Characterization data of purified compounds .................................................................................................. 32

4.1 NMR spectra .................................................................................................................................................. 32

Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1a. ........................................................................... 32
Figure S25. $^{13}$C [$^{1}$H] NMR (101 MHz, CDCl$_3$) spectrum of 1a. ................................................................. 32
Figure S26. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1b. ........................................................................... 33
Figure S27. $^{13}$C [$^{1}$H] NMR (101 MHz, CDCl$_3$) spectrum of 1b. ................................................................. 33
Figure S28. $^1$H NMR (600 MHz, CD$_2$OD) spectrum of $^{13}$C-labeled 1b*. .................................................. 34
Figure S29. $^{13}$C [$^{1}$H] NMR (151 MHz, CD$_2$OD) spectrum of $^{13}$C-labeled 1b*. ........................................ 34
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2a. ........................................................................... 35
Figure S31. $^{13}$C [$^{1}$H] NMR (101 MHz, CDCl$_3$) spectrum of 2a. ................................................................. 35
Figure S32. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2b. ........................................................................... 36
Figure S33. $^{13}$C [$^{1}$H] NMR (101 MHz, CDCl$_3$) spectrum of 2b. ................................................................. 36
Figure S34. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of $^{13}$C-labeled 2b*. .................................................. 37
Figure S35. $^{13}$C [$^{1}$H] NMR (151 MHz, CD$_2$Cl$_2$) spectrum of $^{13}$C-labeled 2b*. ........................................ 37
Figure S36. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 2c. ........................................................................... 38
Figure S37. $^{13}$C [$^{1}$H] NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 2c. ................................................................. 38
Figure S38. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) spectrum of [3a][PF$_6$] .............................................................. 39
Figure S39. $^{13}$C [$^{1}$H] NMR (126 MHz, CD$_2$Cl$_2$) spectrum of [3a][PF$_6$]. .................................................. 39
Figure S40. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$] .............................................................. 40
Figure S41. $^{13}$C [$^{1}$H] NMR (176 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$]. .................................................. 40
Figure S42. $^{31}$P [$^{1}$H] NMR (283 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$]. .................................................. 41
Figure S43. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$]. .............................................................. 41
Figure S44. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of $^{13}$C-labeled [3b*][PF$_6$] ........................................... 42
Figure S45. $^{13}$C [$^{1}$H] NMR (151 MHz, CD$_2$Cl$_2$) spectrum of [3b*][PF$_6$] .................................................. 42
Figure S46. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .............................................................. 43
Figure S47. $^{13}$C [$^{1}$H] NMR (151 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 43
Figure S48. $^1$H H COSY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 44
Figure S49. Aromatic region of $^1$H-1H COSY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 44
Figure S50. $^1$H-H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 45
Figure S51. Methyl correlations of $^1$H-H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 45
Figure S52. Methyl-aromatic correlations of $^1$H-H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 46
Figure S53. Aromatic correlations of $^1$H-H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 46
Figure S54. $^{31}$P [$^{1}$H] NMR (162 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .................................................. 47
Figure S55. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$] .............................................................. 47
Figure S56. Assignment of NMR signals for [3b][PF$_6$] and [3b*][PF$_6$] nanoclusters based on 1D NMR and crystallography data. 48
Figure S57. Assignment of NMR signals for [4b][PF$_6$] nanoclusters based on 1D and 2D NMR and crystallography data. 49
Figure S58. Assignment of NMR signals for [4b][PF$_6$] nanoclusters based on 1D and 2D NMR and crystallography data (continued). 50

4.2 Mass spectra .................................................................................................................................................. 51

Figure S59. ESI-MS of [3a][PF$_6$] .............................................................. 51
Figure S60. ESI-MS of [3b*]Br .............................................................. 51

4.3 X-ray crystallography and structural analysis ............................................................................................ 52

Figure S61. ORTEP plot of the core framework of [3b][OTf] with atom numbering scheme. .......................... 52
Figure S62. ORTEP plot of the core framework of [5b][B(C$_6$F$_5$)$_4$] with atom numbering scheme. .......... 53
Figure S63. Two different Au–Br bonding modes at the waist sites in [5b][B(C6F5)4] nanocluster .................................................. 54
Figure S64. ORTEP plot of the core framework of [4b][B(C6F5)4]; with atom numbering scheme ............................................. 55
Figure S65. The packing structures of (A) [3b][OTf], (B) [5b][B(C6F5)4], and (C) [4b][B(C6F5)4] in their single crystals. ........................ 56
Table S1. X-ray crystallographic data for [3b][OTf] ................................................................................................................. 57
Table S2. X-ray crystallographic data for [5b][B(C6F5)4] ............................................................................................................. 58
Table S3. X-ray crystallographic data for [4b][B(C6F5)4] .......................................................................................................... 61
Table S4. Summary of important bond lengths for [3b][OTf] ................................................................................................... 62
Table S5. Summary of important bond lengths for [5b][B(C6F5)4] .......................................................................................... 63
Table S6. Summary of important bond lengths for [4b][B(C6F5)4] .......................................................................................... 64
Table S7. Average bond distances in [3b][OTf] and their comparison to those in [Au2(κ3-PCH2Bimy)2Cl][PF6] nanocluster .......................................................................................................................... 65
Table S8. Average bond distances in [4b][B(C6F5)4] and [5b][B(C6F5)4], and their comparison to those in [Au2(κ3-Bimy)2Br][NO3][Cl] nanocluster ............................................................... 66

4.5 UV–vis absorbance and fluorescence spectra ............................................................................................................................... 67
Figure S66. UV–vis absorbance spectra of 2a, 2b, and 2c in EtOH ................................................................................................. 67
Figure S67. UV–vis absorbance spectra of [3a][PF6] in DCM ........................................................................................................ 67
Figure S68. Emission (excited at 475 nm) and excitation (monitored at 800 nm) spectra of [3b]PF6 in DCM ..................... 68
Figure S69. Emission (excited at 657 nm) and excitation (monitored at 785 nm) spectra of [4b][PF6] in DCM. Inset: emission spectra of [4b][PF6] excited at different wavelengths ........................................... 68
Figure S70. 3D (top) and 2D (bottom) plots for the fluorescence EEM spectra of [3b]PF6 in DCM .................. 69
Figure S71. 3D (top) and 2D (bottom) plots for the fluorescence EEM spectra of [4b][PF6] in DCM ......................... 70
Figure S72. Emission spectra (excited at 360 nm) of [3b]PF6 in DCM and ZnPc standard in pyridine for photoluminescence QY calculations .................................................. 71
Figure S73. Emission spectra (excited at 370 nm) of [4b][PF6] in DCM and ZnPc standard in pyridine for photoluminescence QY calculations .................................................. 71

5 Computational data ........................................................................................................................................................................ 72

5.1 Computational analysis of cluster [3b]+ ............................................................................................................................................ 72
Figure S74. Optimized structure of the gas-phase model of [3b]+ using the PBE exchange-correlational functional .......... 72
Table S9. Experimental and computed (PBE) atom-atom bond lengths in the crystal structure and in the gas-phase model of [3b]+ ........................................................................................................................................................................ 72
Figure S75. Electronic density of states in the gas-phase model of [3b]+ by using the PBE (top) and GLLB-SC (bottom) xc functional .................................................. 73
Table S10. Bader charges for gold atoms and ligands in the gas-phase model of [3b]+ calculated using the GLLB-SC functional .................................................................................................................. 73
Figure S76. Visualisation of frontier orbitals for [3b]+ .................................................................................................................. 74
Figure S77. Dipole transition contribution maps (DTCM) analysis for [3b]+ – Principal axes of moments of inertia .......... 75
Figure S78. DTCM analysis for the lowest-energy peak (2.44 eV, shown in the bottom right panel) in the UV–vis absorbance spectrum of [3b]+ .................................................................................................................. 76
Figure S79. DTCM for peak at E = 3.07 eV ............................................................................................................................................ 77
Figure S80. DTCM for peak at E = 3.54 eV ............................................................................................................................................ 78
Figure S81. DTCM for peak at E = 3.94 eV ............................................................................................................................................ 79
1 General information

1.1 Materials

All reactions and analyses were performed under ambient conditions unless otherwise specified. Benzimidazole, 2,4,6-trimethylbenzyl chloride, potassium hydroxide, potassium carbonate, anhydrous sodium sulfate, chloro(dimethylsulfide)gold(I) (Me₂SAuCl), sodium borohydride (NaBH₄), ammonium hexafluorophosphate (NH₄PF₆), potassium tetrakis(pentafluorophenyl)borate, lithium tetrakis(pentafluorophenyl)borate ethyl etherate, sodium iodide, tetrabutylammonium bromide (TBAB), and sodium trifluoromethanesulfonate (sodium triflate, NaOTf) were purchased from Aldrich, Wako, TCI or Kanto Chemicals. 2,4,6-trimethylbenzyl bromide and [2-¹³C]benzimidazole were synthesized according to literature procedures. Column chromatographic purification of gold clusters was performed with Chromatorex PSQ60AB microbead silica purchased from Fuji Silysia Chemical Ltd. For any other needs, irregular silica SiliaFlash P60 purchased from SiliCycle was used. Spectra/Por regenerated cellulose membrane (12000–14000 g/mol molecular weight cut-off) for purification by dialysis was purchased from SpectrumLabs and soaked in 95% ethanol before use. 0.22 µm PTFE syringe filters were purchased from Fisher. Acetone (Me₂CO), acetonitrile (MeCN), anhydrous diethyl ether (Et₂O), chloroform (CHCl₃), dichloromethane (DCM), ethyl acetate (EtOAc), fluorobenzene, n-hexane, methanol (MeOH), tetrahydrofuran (THF), pentane, and pyridine were purchased from Fisher Scientific, Wako or Kanto Chemicals. 95% and absolute ethanol (EtOH) was purchased from Commercial Alcohols or Wako. All the commercially obtained reagents and solvents were used without further purification.

1.2 Instruments and sample preparation

¹H, ¹³C{¹H} and all 2-D NMR spectra were recorded on Bruker AV400, AV600, AV700 or JEOL ECA-II 600 MHz spectrometers and referenced externally to SiMe₄. All ¹H NMR spectra were referenced to CDCl₃ at 7.26 ppm, CD₂Cl₂ at 5.32 ppm or CD₃OD at 3.31 ppm; all ¹³C NMR spectra were referenced to CDCl₃ at 77.16 ppm, CD₂Cl₂ at 53.84 ppm or CD₃OD at 49.00. All spectra were recorded at room temperature unless otherwise noted. All NMR data was processed and displayed using MestReNova software. In cases of residual solvent contamination of NMR solvents, these contaminants are noted on each spectrum. Other impurities are noted where assignment was possible. Elemental analyses were performed on a Thermo Scientific Flash 2000 CHNS-O analyzer. UV–vis absorbance spectra were recorded using an Agilent Cary 60 or Cary 3500 Multizone UV–vis spectrophotometers, or Shimadzu UV-1800 spectrometer using 1 cm² quartz cuvettes. UV–vis absorbance spectra were recorded at ambient temperature unless otherwise specified. Monitoring reaction progress over time in situ (kinetics experiment) at controlled temperature was performed on Agilent Cary 3500 Multizone UV–vis spectrophotometer using Cary UV Workstation software. Time intervals for recurrent measurements of reaction mixture and temperature of the cuvette compartment are specified for each experiment of this kind. Alternatively, for ex situ measurements, small aliquots were taken from the reaction mixture at given reaction times, diluted with corresponding solvent at room temperature to obtain a 3.0 mL of solution, and their UV–vis absorbance spectra recorded. Excitation, emission, and fluorescence excitation-emission matrix (EEM) data were obtained using the Horiba Duetta Fluorescence and Absorbance Spectrometer, and inner-filter effects and Rayleigh scattering were corrected using EzSpecTM software. Samples for photoluminescence studies (sufficiently dilute to diminish inner-filter effects) were prepared in 1 cm² pathlength quartz fluorescence cuvettes with graded seal tube, sealed with rubber septa, and deoxygenated by purging with argon.

1.3 Mass spectrometry

Electrospray ionization mass spectra (ESI-MS) of small molecules were recorded at Queen’s University using a Thermo Fisher Orbitrap Velos Pro mass spectrometer with a heated-electrospray ionization probe. ESI-MS of clusters were recorded

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at The University of Tokyo using a JEOL JMS-T100LC time-of-flight mass spectrometer. Acetonitrile–dichloromethane (1:1 v/v) dispersions of samples (ca. 0.1 mg/mL) were directly infused at a flow rate of 3.0 mL/h by a syringe pump. Typical parameters used for the measurements were as follows: spray voltage 2.5 kV; ring electrode 45 V; orifice 1 voltage 40 V; orifice 2 voltage 0 V; desolvation temperature 120 °C; cone temperature 80 °C. The spectra were calibrated with respect to [Cs(Csl)]\(^+\) clusters generated from a 99% aqueous methanolic solution of Csl (0.5 mg/mL) under the same parameters, as an external reference. Additional ESI-MS of clusters was recorded at Nagoya University on a Bruker Compact QTOF mass spectrometer. Acetonitrile–dichloromethane (1:1 v/v) dispersions of samples (ca. 0.1 mg/mL) were infused at a flow rate of 180 μL/h by a syringe pump. Parameters were as follows: end plate offset 500 V, capillary 3.6 kV, nebulizer 0.3 Bar, dry gas 3.0 L/min and dry temp 200 °C. The instrument was first calibrated with Agilent Technologies ESI Tuning Mix under the same parameters as an external reference. Theoretical isotope patterns were calculated using enviPat Web 2.4.

1.4 X-ray crystallography

Crystals of appropriate quality for X-ray diffraction studies were covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fibre or a microsampler, and quickly placed in a low-temperature stream of nitrogen.\(^3\) Data for [3b][OTf] were collected at Iowa State University using a Bruker Venture D8 using Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å), with the crystal cooled to -173 °C. Data for [5b][B(C\(_3\)F\(_3\))]\(_4\) were collected at Queen’s University using a Bruker AXS D8 Venture Duo diffractometer using Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å), with the crystal cooled to -100 °C. Data for both crystals were solved using intrinsic phasing (SHELXT)\(^4\) and refined using SHELXL-2018.\(^5\) Data for [4b][B(C\(_3\)F\(_3\))]\(_2\) were collected at University of Tokyo using a Rigaku Varimax dual diffractometer using Cu K\(_\alpha\) radiation with a Pilatus 200K hybrid pixel array detector. The data was corrected for Lorentz polarization, and absorption correction was performed analytically using CrysalisPro software. The initial phases were determined by the direct method using SHELXS-2018, and the structures were refined using SHELXL-2018. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding models. All aromatic rings were treated using rigid constraints to minimize the number of refinement parameters. Since the cluster had a large solvent-accessible void in the lattice (ca. 33%: 26000 Å\(^3\)), solvent molecules and one of the counter anions could not be modeled due to the significant disorder. These disordered electron densities were treated by the SQUEEZE program on the PLATON platform.\(^6\)\(^,\)\(^7\) Moreover, the large void made the molecular packing loose. This weakened the reflections at higher resolution. Therefore, in order to maintain a reasonable ligand structure, the bond lengths and angles of the moiety were restrained using DFIX and DANG commands.

1.5 Photoluminescence quantum yield

Relative photoluminescence quantum yield (\(\Phi_F\)) was determined by the comparative method.\(^8\) According to the method, the fluorescence quantum yield of a sample is related to that of a standard by the following expression:

\[
\Phi_F = \left( \frac{A_{\text{std}}}{A} \right) \left( \frac{F_{\text{std}}}{F} \right) \left( \frac{n}{n_{\text{std}}} \right)^2 \Phi_{F_{\text{std}}}
\]

where \(F\) and \(F_{\text{std}}\) are the areas under the fluorescence emission curves of the sample and the standard, respectively. \(A\) and \(A_{\text{std}}\) are the absorbances of the samples and standard at the excitation wavelengths, respectively. \(n\) and \(n_{\text{std}}\) are the refractive indices of solvents used for the sample and standard, respectively. Zinc phthalocyanine (ZnPc, Acros Organics) solution in freshly distilled pyridine was employed as the standard (\(\Phi_{F_{\text{std}}} = 0.30\)).\(^9\) The refractive indexes of the solvents were taken

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to be \( n_{\text{pyridine}} = 1.5095 \) and \( n_{\text{DCM}} = 1.4242 \) (both at 20 °C).\(^9\) All solutions were filtered using 0.2 μm PTFE syringe filters, diluted to desired \( A \), placed into 1 cm\(^2\) pathlength quartz fluorescence cuvettes with graded seal tube, sealed with rubber septa, and deoxygenated by purging with argon. In several independent measurements, sample and standard solutions were prepared to have equal absorbances at their respective excitation wavelengths after purging. UV–vis absorbance spectra were recorded on an Agilent Cary60 spectrophotometer with the corresponding pure solvents for background correction. Fluorescence emission spectra were recorded for the same solutions on a Horiba Duetta Fluorescence and Absorbance Spectrometer with EzSpecTM software. Both the sample and standard were excited at the same relevant wavelength (indicated for each particular dataset). The spectra were corrected for wavelength-dependent instrument sensitivity. The areas under the fluorescence emission curves were calculated numerically using Origin Pro 2016 software.

1.6 Computational methods

All the properties of [3b] were calculated using density-functional theory (DFT) as in the implementation of the code-package GPAW\(^{11}\) (Grid-based projector-augmented wave method) using a real-space grid. All calculations included scalar-relativistic correlations. The Perdew–Burke–Ernzerhof (PBE)\(^{12}\) and GLLB-SC\(^{13}\) were used as exchange-correlation-functionals. At first, the experimental crystal structure was relaxed with PBE-functional using 0.2 Å grid spacing and 0.05 eVÅ convergence criterion for the maximum forces acting on atoms in the cluster. The electronic structure and HOMO-LUMO gap were analysed for the relaxed structure with both PBE and GLLB-SC functionals. Related to the electronic structure, the Kohn-Sham wavefunctions were projected to spherical harmonic functions centered at the center of mass of the cluster inside a spherical region of 3.5 Å radius to reveal the superatomic nature.\(^14\) Localization of the wavefunctions to Au-, Br-, C- and N-atoms was also investigated in a similar fashion but using the position of each atom as a central point in analysis. Cutoff radii in the latter analysis were selected to be 1.4 Å, 1.2 Å, 0.7 Å and 0.7 Å for Au, Br, C and N respectively. Due to the more realistic HOMO-LUMO gap, all further analyses were conducted only with the GLLB-SC functional. For these analyses grid spacing was set to 0.25 Å. Optical absorbance spectra were calculated using linear-response time-dependent density functional theory Ir-TDDFT,\(^15\) for which the kernel was calculated with PBE whereas GLLBSC was used to describe the wave functions. Eventually, dipole transition contribution maps (DTCM) were probed to check the strongest electron-hole transitions of the individual absorbance peaks by using time-dependent density functional perturbation theory TD-DFPT.\(^16\) DTCM reveals the increasing and decreasing contributions to the induced dipole moment at the selected excitation energy. In this study, DTCM is represented by taking summation over the contributions from three independent directions of the electric field. Directions were determined based on the principal axis of the moments of inertia of the cluster. Local atomic charges were calculated from all electron density using Bader charge analysis.\(^17\)

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2 Synthetic procedures and purification protocols

2.1 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium chloride (1a)

Benzimidazole (0.591 g, 5.0 mmol), ground potassium hydroxide (0.421 g, 7.5 mmol) and acetonitrile (10 mL) were combined in a 50 mL pressure tube charged with a stir bar. The mixture was stirred and heated for 30 min, then 2,4,6-trimethylbenzyl chloride (1.771 g, 10.50 mmol) was added in small portions. The pressure tube was sealed, and the reaction mixture was stirred and heated at 85 °C for 24 hours, and then cooled to room temperature. After cooling, distilled water (50 mL) was added, and this mixture was decanted into a flask charged with DCM (100 mL). The organic layers were separated and combined, dried with anhydrous sodium sulfate and gravity filtered. The yellowish mixture was reduced in vacuo in a rotary evaporator until crystallization of the product occurred, and the yellowish mixture was layered with an excess of pentane and left to crystallize for 1-2 days at -4 °C. White crystals were collected by vacuum filtration, washed with pentane and dried in vacuo to yield the title compound as a white powder (1.887 g, 90 % yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 11.44 (br m, 1H, NC\(_2\)), 7.34 (dd, 2H, \(^3J_{HH} = 6.4\) Hz, \(^4J_{HH} = 3.2\) Hz, ArH\textit{Bimy}), 7.13 (dd, 2H, \(^3J_{HH} = 6.4\) Hz, \(^4J_{HH} = 3.2\) Hz, ArH\textit{Bimy}), 6.91 (s, 4H, ArH\textit{Mes}), 2.29 (s, 12H, ArCH\(_3\)), 2.28 (s, 6H, ArCH\(_3\)). \(^1^3\)C\(^{\text{1H}}\) NMR (CDCl\(_3\), 101 MHz): \(\delta\) 144.4 (NCHN), 139.8, 138.0, 131.8, 130.3, 127.0, 125.3, 113.8 (ArC), 47.7 (NCH\(_2\)Ar), 21.2, 20.3 (ArCH\(_3\)). ESI-MS for \([\text{C}_2\text{H}_3\text{N}_2]^+\): Calculated – 383.2; Observed – 383.2. \textbf{Elemental analysis for }\text{C}_2\text{H}_3\text{ClN}_2\text{O} – \text{Observed (theoretical): }C – 74.34 (74.20); H – 7.56 (7.61); N – 6.31 (6.41).

2.2 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium bromide (1b)

2,4,6-trimethylbenzyl bromide (2.240 g, 10.50 mmol), benzimidazole (0.591 g, 5.0 mmol) and potassium carbonate (2.200 g, 15.90 mmol) were added to a 150 mL pressure tube with acetonitrile (50 mL). The mixture was heated at 85 °C for 20 hours, and then cooled to room temperature. After cooling, distilled water (50 mL) was added, and this mixture was decanted into a flask charged with DCM (100 mL). The organic layer was separated, and the aqueous layer washed with DCM (3 x 30 mL). The organic fractions were combined, dried with anhydrous sodium sulfate and collected by gravity filtration. The volatiles were removed in vacuo, yielding an off-white crude solid, which was redissolved in DCM (10 mL), and precipitated with Et\(_2\)O (250 mL). The resulting white solid was collected by vacuum filtration, and washed with Et\(_2\)O (3 x 20 mL) to yield the title compound as a white powder (1.877 g, 82 % yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 10.96 (s, 1H, NCHN), 7.39 (dd, 2H, \(^3J_{HH} = 6.3\) Hz, \(^4J_{HH} = 3.2\) Hz, ArH\textit{Bimy}), 7.19 (dd, 2H, \(^3J_{HH} = 6.3\) Hz, \(^4J_{HH} = 3.2\) Hz, ArH\textit{Bimy}), 6.93 (s, 4H, ArH\textit{Mes}), 5.86 (s, 4H, NCH\(_2\)Ar), 2.31 (s, 12H, ArCH\(_3\)), 2.30 (s, 6H, ArCH\(_3\)). \(^1^3\)C\(^{\text{1H}}\) NMR (CDCl\(_3\), 101 MHz): \(\delta\) 143.0 (NCHN), 139.9, 138.0, 131.8, 130.3, 127.2, 125.2, 113.9 (ArC), 47.7 (NCH\(_2\)Ar), 21.2 (ArCH\(_3\)), 20.4 (ArCH\(_3\)). ESI-MS for \([\text{C}_2\text{H}_3\text{N}_2]^+\): Calculated – 383.2; Observed – 383.2. \textbf{Elemental analysis for }\text{C}_2\text{H}_3\text{BrN}_2 – \text{Observed (theoretical): }C – 69.44 (69.97); H – 6.72 (6.74); N – 5.85 (6.04).
2.3 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)-[2-\textsuperscript{13}C]-benzimidazolium bromide (1b\textsuperscript{*})

\[ \text{13C-labeled benzimidazolium salt 1b* was synthesized in a similar manner as the corresponding non-labeled compound 1b using [2-\textsuperscript{13}C]benzimidazole; NMR spectroscopic data in CDCl\textsubscript{3} was identical to the non-labeled compound 1b except for increased intensity of the carbene carbon signal as expected. Data collected in CD\textsubscript{3}OD is presented here for comparison. Note that the NCHN proton was not observed in CD\textsubscript{3}OD due to facile exchange with the solvent on the NMR timescale, and difficulties in shimming to this solvent led to broadening of the 1H NMR spectrum. 1H NMR (CDCl\textsubscript{3}, 600 MHz):} \delta 7.78 (br m, 2H, Ar\textsuperscript{C}), 7.67 (br m, 2H, Ar\textsuperscript{H}), 7.00 (br m, 4H, Ar\textsuperscript{N}), 2.30 (br m, 6H, Ar\textsuperscript{CH}) 2.22 (br m, 12H, Ar\textsuperscript{C-H}). \]

\[ \text{13C{\textsuperscript{1}H}] NMR (CDCl\textsubscript{3}, 151 MHz):} \delta 141.3 (Ar\textsuperscript{C}), 140.9 (t, N\textsuperscript{13}CHN), 139.4, 133.5, 130.0, 128.5, 126.5, 114.9 (Ar\textsuperscript{C}), 47.2 (NCH\textsubscript{2}Ar), 21.1 (Ar\textsuperscript{CH}3), 19.7 (Ar\textsuperscript{CH}3). \]

2.4 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold chloride (2a)

\[ \text{The title compound was prepared using modifications to established synthetic procedures for the preparation of NHC gold complexes published by Nolan et al.} \]

\[ \text{Mes} } \text{Cl-} \xrightarrow{\text{(Me_2S)AuCl}} \text{Mes} } \text{Au-Cl} \text{Acetone, 60 °C} \]

\[ \text{The resulting off-white or pale yellow solid was dissolved in DCM (3 mL) and passed through glass wool and a short silica gel plug in a Pasteur pipette or small column to give a colourless filtrate. The column with the yellow by-products adsorbed to the silica was washed with additional portions of DCM (2 x 3 mL), and filtrates were combined. The solvent from the filtrate was washed in vacuo to yield the title gold complex 2a as a white powder (0.273 g, 89 %). 1H NMR (CDCl\textsubscript{3}, 400 MHz):} \delta 7.07 (dd, \textsuperscript{3}J_{\text{HH}} = 6.3 Hz, \textsuperscript{4}J_{\text{HH}} = 3.2 Hz, 2H, ArH\textsuperscript{Bimy}), 6.90 (s, 4H, ArH\textsuperscript{Mes}), 6.82 (dd, \textsuperscript{3}J_{\text{HH}} = 6.3 Hz, \textsuperscript{4}J_{\text{HH}} = 3.2 Hz, 2H, ArH\textsuperscript{Bimy}), 5.82 (s, 4H, NCH\textsubscript{2}Ar), 2.30 (s, 6H, p-ArCH\textsubscript{3}), 2.20 (s, 12H, o-ArCH\textsubscript{3}). 13C{\textsuperscript{1}H}] NMR (CDCl\textsubscript{3}, 101 MHz):} \delta 180.9 (NCN), 138.3, 137.7, 135.3, 130.0, 127.1, 124.4, 112.2 (ArC), 50.0 (NCH\textsubscript{2}Ar), 21.1 (ArCH\textsubscript{3}), 20.9 (ArCH\textsubscript{3}). \]

\[ \text{ESI-MS for} \text{C_{27}H_{30}AuN_2: due to the difficulty of ionizing 2a, high-resolution ESI-MS was not obtained. UV--vis abs (EtOH):} 272.8, 280.0, and 288.8 nm. \]

\[ \text{Elemental analysis for C_{27}H_{30}AuClN_2: Observed (calculated):} \text{C} – 52.28 (52.73); \text{H} – 4.73 (4.92); \text{N} – 4.41 (4.56). \]

2.5 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold bromide (2b)

\[ \text{Mes} } \text{Br-} \xrightarrow{\text{(Me_2S)AuCl}} \text{Mes} } \text{Au-Br} \text{Acetone, 60 °C} \]

\[ \text{Elemental analysis for C_{27}H_{30}AuBrN_2: Observed (calculated):} \text{C} – 52.28 (52.73); \text{H} – 4.73 (4.92); \text{N} – 4.41 (4.56). \]
The title compound was prepared using modifications to established synthetic procedures for the preparation of NHC gold complexes published by Nolan et al.\textsuperscript{18} Me$_2$SAuCl (0.102 g, 0.35 mmol), 1b (0.160 g, 0.35 mmol), and potassium carbonate (0.140 g, 1.01 mmol) were combined with acetone (20 mL) in a 50 mL round-bottom flask fitted with a condenser, and the solution was refluxed under air atmosphere for 20 hours. After cooling, the solution was filtered by gravity filtration, and the volatiles were removed in vacuo. The resulting solid was dissolved in DCM (2 mL) and passed through a silica gel plug in a Pasteur pipette to give a colourless solution. The volatiles were removed in vacuo to yield the title gold complex 2b as a white powder (0.183 g, 79%). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.07 (dd, $^3$J$_{HH}$ = 6.3 Hz, $^4$J$_{HH}$ = 3.1 Hz, 2H, ArH$_{Bimy}$), 6.90 (s, 4H, ArH$_{Mes}$), 6.83 (dd, $^3$J$_{HH}$ = 6.3 Hz, $^5$J$_{HH}$ = 2.0 Hz, ArH$_{Bimy}$), 5.82 (s, 4H, NCH$_2$Ar), 2.30 (s, 6H, p-ArCH$_3$) 2.28 (s, 12H, o-ArCH$_3$). $^{13}$C$^{[1]}$H NMR (CDCl$_3$, 101 MHz): $\delta$ 184.2 (NCH$_2$Ar), 218.2 (C$_2$Mes), 213.0 (C$_2$Bimy), 139.1, 138.1, 133.8, 130.3, 127.8, 124.7, 112.6 (ArC), 49.9 (NCH$_2$Ar), 21.2 (ArCH$_3$), 21.0 (ArCH$_3$). ESI-MS for C$_{27}$H$_{30}$AuBrN$_2$: due to the difficulty of ionizing 2b, high-resolution ESI-MS was not obtained. UV–vis abs (EtOH): 274.0, 280.8, and 289.6 nm. Elemental analysis for C$_{27}$H$_{30}$AuBrN$_2$ – Observed (calculated): C – 48.53 (49.18); H – 4.66 (4.59); N – 3.94 (4.25).

2.6 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)-[2-13C]-benzimidazolium-ylidene gold bromide (2b*)

$^{13}$C-labeled gold complex 2b* was synthesized in a similar manner as the corresponding non-labeled compound 2b using 1b*. NMR spectroscopic data in CDCl$_3$ was identical to the non-labeled compound 1b except for increased intensity of the carbene carbon signal as expected and some coupling to the $^{13}$C-labeled carbon observed. Data collected in CD$_2$Cl$_2$ is presented here for comparison. Note that one ArC is missing due to low intensity. $^1$H NMR (CD$_2$Cl$_2$, 600 MHz): $\delta$ 7.11 (dd, $^3$J$_{HH}$ = 6.2 Hz, $^4$J$_{HH}$ = 3.3 Hz, 2H, ArH$_{Bimy}$), 6.92 (s, 4H, ArH$_{Mes}$), 6.91 (dd, $^3$J$_{HH}$ = 6.2 Hz, $^4$J$_{HH}$ = 3.4 Hz, 2H, ArH$_{Bimy}$), 5.82 (d, 4H, $^3$J$_{HC}$ = 3.4 Hz, NCH$_2$Ar), 2.30 (s, 6H, p-ArCH$_3$) 2.28 (s, 12H, o-ArCH$_3$). $^{13}$C$^{[1]}$H NMR (CD$_2$Cl$_2$, 151 MHz): $\delta$ 184.4 (NCN) 139.2, 138.2, 133.8, 130.2, 124.6, 112.6 (ArC), 49.9 (d, $^2$J$_{CC}$ = 9.0 Hz, NCH$_2$Ar), 21.2 (ArCH$_3$), 21.0 (ArCH$_3$).

2.7 Synthesis of 1,3-di(2,4,6-trimethylbenzyl)benzimidazolium-ylidene gold iodide (2c)

The title compound was prepared using modifications to an established synthetic procedure published by Wu et al.\textsuperscript{19} A vial was charged with complex 2b (0.05313 g, 0.08057 mmol), sodium iodide (0.18753 g, 1.251 mmol) and a stir bar. Acetone (10 mL) was added and the solution was sonicated briefly to make a uniform suspension. The vial was sealed and covered with tape to protect the solution from ambient light, then the mixture was stirred overnight at room temperature (26 h). The solvent was removed in vacuo yielding a beige residue, which was redissolved in DCM and filtered through a silica plug, washing with more DCM. The filtrate was dried in vacuo yielding a beige solid residue, which was washed with DCM-hexane (1:4 v/v; 1 mL) then pentane (2 x 1 mL) and dried in vacuo yielding the title gold complex 2c as a pale beige powder (0.0539 g, 95%). $^1$H NMR (CD$_2$Cl$_2$, 600 MHz): $\delta$ 7.14 (dd, $^3$J$_{HH}$ = 6.1 Hz, $^4$J$_{HH}$ = 3.1 Hz, 2H, ArH$_{Bimy}$), 6.96 (dd, $^3$J$_{HH}$ = 6.1 Hz, $^4$J$_{HH}$ = 3.1 Hz, 2H, ArH$_{Bimy}$), 6.92 (s, 4H, ArH$_{Mes}$), 5.81 (s, 4H, NCH$_2$Ar), 2.30 (s, 6H, p-ArCH$_3$) 2.29 (s, 12H, o-ArCH$_3$). $^{13}$C$^{[1]}$H NMR (CD$_2$Cl$_2$, 151 MHz): $\delta$ 190.2 (NCN), 139.1, 138.1, 133.8, 130.3, 127.8, 124.7, 112.6 (ArC), 49.5

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(NCH₂Ar), 21.2 (ArCH₃), 21.0 (ArCH₃). **ESI-MS for C₇₋₇₃AuN₂:** due to the difficulty of ionizing 2c, high-resolution ESI-MS was not obtained. **UV–vis abs (EtOH):** 284.2 and 293.0 nm. **Elemental analysis for C₇₋₇₃AuN₂ – Observed (calculated):** C – 45.69 (45.91); H – 4.21 (4.28); N – 3.98 (3.97).

### 2.8 Isolation of [Au₁₀(MesCH₂Bimy)₆Cl₃][Cl] (3a)Cl from reduction of 2a

A round bottom flask (100 mL) was charged with a stir bar and 2a (0.0738 g, 0.12 mmol), and DCM (40 mL) was added to dissolve the gold complex. To the stirring solution of gold complex was added a thoroughly sonicated solution of NaBH₄ (0.00454 g, 0.12 mmol) in absolute EtOH (12 mL). The mixture was stirred 20–22 h at room temperature. The orange-brown reaction mixture was evaporated to dryness in vacuo yielding crude clusters along with 2a as pale orange-brown and white residue. Unlike for [3b]Br (*vide infra*), extraction with Et₂O was found not efficient in separating the title clusters from gold complexes 2a and [C{(MesCH₂)Bimy}]₂AuCl, thus the crude cluster mixture was separated by silica gel column chromatography using PSQ60AB silica; 19:1 DCM/MeOH eluent; ~3x6 cm column size. Three coloured bands were collected separately from the column and evaporated to dryness in vacuo as follows: 1) an initial orange-brown band, yielding an orange-brown and white residue (0.0259 g) containing gold complexes 2a and [C{(MesCH₂)Bimy}]₂AuCl along with unknown cluster byproducts; 2) an intermediate beige or light-brown band, which yields a brown residue (0.0086 g) containing a mixture of unidentified cluster species; and 3) a bright orange band, which yields the title cluster [3a]Cl as an orange residue (0.0089 g, 17 % based on Au). To further purify [3a]Cl from traces of 2a, slow re-crystallization from DCM by layering with pentane was employed, yielding dark red-orange crystals (0.0066 g after drying under vacuum) of fairly pure [3a]Cl with only trace impurities by NMR spectroscopy. **1H and 13C{¹H} NMR spectra, as well as ESI-MS for [3a]Cl are identical to [3a][PF₆] (see below). **Elemental analysis for C₁₆₂H₁₈₀Au₁₀Cl₄N₁₂ – Observed (calculated):** C – 44.61 (44.15); H – 3.99 (4.12); N – 3.71 (3.81).

### 2.9 Isolation of [Au₁₀(MesCH₂Bimy)₆Cl₃][PF₆] ([3a][PF₆]) from [3a]Cl

The purity of [3a]Cl isolated from column and re-crystallization can be further improved by anion exchange to the PF₆ salt via the following procedure. [3a]Cl (0.015 g, 0.0034 mmol) was combined with an excess of NH₄PF₆ (0.120 g, 0.736 mmol), 10 mL of MeOH were added, and the mixture was stirred overnight at room temperature. Suspended orange solid was allowed to settle down, and the liquid was decanted. Orange precipitate was dissolved in 2 mL of DCM, and the solution was run through a small column with PSQ60AB silica (~1x5 cm column size), collecting the coloured band separately and pumping that to dryness in vacuo. Pure [3a][PF₆] was obtained as a bright orange residue (0.013 g, 87 %).

**1H NMR (CD₂Cl₂, 500 MHz):** δ 6.99 (br m, 4H, ArH_{Bimy}), 6.92 (br m, 8H, ArH_{Bimy}), 6.61 (br m, 4H, ArH_{Bimy}), 6.56 (s, 8H, ArH_{Mes}), 6.49 (br m, 8H, ArH_{Bimy}), 6.43 (broa s, 16H, ArH_{Mes}), 6.00 (br m, 16H, NCH₂Ar), 5.70 (br m, 8H, NCH₂Ar), 2.20 (br s, 48H, ArCH₃), 2.17 (s, 24H, ArCH₃), 2.12 (s, 12H, ArCH₃), 2.05 (s, 24H, ArCH₃). **13C{¹H} NMR (CD₂Cl₂, 126 MHz):** δ 131.6, 200.9 (NCN), 138.6, 138.5, 137.8, 137.6, 134.6, 133.7, 130.0, 129.9, 127.5, 127.4, 124.6, 124.4, 112.9, 112.7 (ArC), 50.4, 49.4 (NCH₂Ar), 21.9, 21.4, 21.3, 21.1 (ArCH₃). **ESI-MS for [C₁₆₂H₁₈₀Au₁₀Cl₄N₁₂]:** Calculated – 4371.0; Observed − 4371.0. **UV–vis abs (DCM):** 283, 290, ~318, 361, 469, and 498 nm.
2.10 Isolation of \([\text{Au}_{10}^{\text{MesCH}_2\text{Bimy}}]_6\text{Br}_3\text{Br} \) from reduction of \(2b\)

A round bottom flask (50 mL) was charged with a stir bar and \(2b\) (0.0405 g, 0.0614 mmol), and DCM (20 mL) was added to dissolve the gold complex. To the stirring solution of gold complex was added a thoroughly sonicated solution of NaBH\(_4\) (0.00230 g, 0.0608 mmol) in absolute EtOH (6 mL). The mixture was stirred 18–20 h at room temperature. The red-brown coloured reaction mixture was evaporated to dryness in vacuo. According to UV–vis absorbance spectroscopy, NMR and ESI-MS (see the corresponding figures below), at this stage crude reaction mixture contains gold clusters along with large amount of \(2b\) and \([\text{Au}^{\text{MesCH}_2\text{Bimy}}]_6\text{Br}_3\text{Br}\) gold complexes. Initial separation of the clusters was performed by extraction and precipitation, leveraging higher solubility of clusters in Et\(_2\)O compared with gold complexes. Et\(_2\)O (~4 mL) was added to heterogeneous red-brown and beige dry residue, and the mixture was sonicated 5–10 min until a uniform brown suspension was formed. Then the mixture was filtered through a Celite plug, removing a beige or pale brown precipitate and collecting red-brown filtrate. The precipitate was collected separately by washing the Celite plug with DCM and pumping the filtrate to dryness to yield a pale brown coloured residue, identified by UV–vis absorbance and NMR spectroscopy, and ESI-MS as a mixture of majority \([\text{Au}^{\text{MesCH}_2\text{Bimy}}]_6\text{Br}_3\text{Br}\) byproduct and \(2b\) (0.0250 g). The Et\(_2\)O filtrate was dried in vacuo to yield the crude cluster mixture as a red-brown residue (0.0121 g). The crude cluster mixture was purified by silica gel column chromatography (see Figure S1; PSQ60AB silica; 12:1 DCM/MeOH eluent; ~3x10 cm column size). Three coloured bands were collected separately from the column and evaporated to dryness in vacuo as follows: 1) an initial red coloured band, yielding a red residue (0.0057 g) containing mostly the starting complex \(2b\) and unknown byproducts; 2) a second brown band at the front of the main orange coloured cluster band, which yields a brown residue (0.0041 g) containing a mixture of cluster species, including some \(3b\) [Br; and 3) an orange band, which yields the title cluster \(3b\) [Br as an orange residue (0.0077 g, 27 % based on Au). While the cluster obtained from column purification is typically fairly pure, trace contamination of \(2b\) and other impurities can remain. The purity can be improved by precipitation of the cluster from an Et\(_2\)O or DCM solution (~1-2 mg/mL) with pentane or hexane (~4x v/v). Careful removal of the supernatant solution, followed by washing the precipitate with Et\(_2\)O-pentane (1:4 v/v; 1 x 0.5 mL) and pentane (2 x 1 mL) and drying in vacuo typically affords the cluster with only trace impurities by NMR spectroscopy. For the above example, precipitation was carried out with DCM-hexane, yielding pure cluster \(3b\) [Br as a bright orange solid (0.0045 g, 16 % based on Au). \(^1\)H and \(^{13}\)C\({}^1\)H NMR spectra, as well as ESI-MS for \(3b\) [Br are identical to \(3b\) [PF\(_6\)] (see below). For UV–vis absorbance spectra and ESI-MS showing the purification of this cluster see Figures S2-3 below. **Elemental analysis for C\(_{162}\)H\(_{180}\)Au\(_{10}\)Br\(_4\)N\(_{12}\) – Observed (calculated):** C – 42.15 (42.44); H – 4.03 (3.96); N – 3.52 (3.67).

2.11 Isolation of \([\text{Au}_{10}^{\text{MesCH}_2\text{Bimy}}]_6\text{Br}_3\text{Br}[\text{PF}_6] ([3b][\text{PF}_6])\) from \(3b\) [Br]

If necessary, the purity of \(3b\) [Br isolated from column can also be improved by anion exchange to the PF\(_6\) salt via the following procedure. To a solution of column purified \(3b\) [Br (0.0051 g, 0.0011 mmol) in MeOH (~3 mL) was added a solution of excess NH\(_3\)PF\(_6\) (0.0220 g, 0.135 mmol) in MeOH (~2 mL), causing precipitation of an orange solid after a few minutes standing at room temperature. The precipitate was filtered on a Celite plug, washed thoroughly with MeOH to remove excess salts, and redissolved in DCM. The DCM filtrate was evaporated to dryness yielding pure \(3b\) [PF\(_6\)] as a bright orange residue (0.0049 g, 95 %). For UV–vis absorbance spectra and ESI-MS showing the isolation of this cluster see Figures S2-3 below. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 600 MHz): \(\delta \) 6.98 (dd, \(3J_{\text{HH}} = 6.0 \) Hz, \(4J_{\text{HH}} = 3.0 \) Hz, 4H, ArH\(_{\text{Bimy}}\)), 6.93 (dd, \(3J_{\text{HH}} = 6.0 \) Hz, \(4J_{\text{HH}} = 3.0 \) Hz, 8H, ArH\(_{\text{Bimy}}\)), 6.59 (dd, \(3J_{\text{HH}} = 6.0 \) Hz, \(4J_{\text{HH}} = 3.0 \) Hz, 4H, ArH\(_{\text{Bimy}}\)), 6.56 (s, 8H, ArH\(_{\text{Me}}\)), 6.49

S12
(dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.0$ Hz, 8H, ArH$_{Bim}$), 6.43 (br s, 16H, ArH$_{Mes}$), 6.01 (br m, 16H, NCH$_2$Ar), 5.72 (broad s, 8H, NCH$_2$Ar), 2.22 (s, 48H, ArCH$_3$), 2.17 (s, 24H, ArCH$_3$), 2.12 (s, 12H, ArCH$_3$), 2.05 (s, 24H, ArCH$_3$). $^{13}$C$^1$H NMR (CD$_2$Cl$_2$, 176 MHz): $\delta$ 214.9, 200.7 (NCN), 138.6, 138.4, 137.7, 137.6, 134.5, 133.6, 129.9, 129.9, 127.4, 124.4, 124.4, 112.8, 112.7 (ArC), 50.6, 49.7 (NCH$_2$Ar), 21.9, 21.7, 21.1, 21.0 (ArCH$_3$). $^{31}$P$^1$H NMR (CD$_2$Cl$_2$, 283 MHz): $\delta$ -144.5 (sept, $^1J_{PF} = 711$ Hz, PF$_6$). $^{19}$F NMR (CD$_2$Cl$_2$, 376 MHz): $\delta$ -73.5 (d, $^1J_{PF} = 711$ Hz, PF$_6$). ESI-MS for [C$_{162}$H$_{180}$Au$_{10}$Br$_3$N$_{12}$]$:^+$ Calculated – 4504.9; Observed – 4504.9. UV–vis abs (DCM): 283, 291, ~317, 366, 474, and ~505 nm.

Figure S1. Photographs showing the column purification of [3b]Br.

Figure S2. UV–vis absorbance spectra (DCM) showing (A) isolation of crude [3b]Br and (B) purification of [3b]Br by column chromatography followed by anion exchange.
Figure S3. ESI-MS showing the purification of [3b]Br
(A) 200-6000 m/z range normalized to [AuL2]^+ (L = MesCH2Bimy) to illustrate the effect of purification on complex/cluster ratio and (B) 1000-5000 m/z range normalized to the most intense peak to reflect the changes in cluster mixture composition.

2.12 Isolation of 13C-labeled [Au10(MesCH2Bimy)6Br3]Br ([3b*]Br) from reduction of 2b*

13C-labeled cluster [3b*]Br was synthesized from 2b* via the same procedure as non-labeled version 3b. Spectroscopic data are consistent with the non-labeled cluster. The carbon-carbon coupling of the labeled carbene carbons could be distinguished by 13C{1H} NMR spectroscopy as follows. 13C{1H} NMR (CD2Cl2, 176 MHz): δ 215.0 (br t, J = 3 Hz, N13C), 200.7 (br d, J = 3 Hz, N13CN), 140.7 (br d, J = 3 Hz, N13CN). ESI-MS for [13C6C15N12H180Au10Br3]1+: Calculated – 4509.9; Observed – 4509.9. For NMR spectra showing the purification of this cluster see Figures S4-5 below.
Figure S4. Aliphatic (top) and aromatic (bottom) regions of $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra showing the isolation and purification of $[3b^*]$Br from reduction of $2b^*$ (top red trace).
Figure S5. $^{13}$C{1H} NMR (151 MHz, CD$_2$Cl$_2$) spectra showing the isolation and purification of [3b*]Br from reduction of 2b* (top red trace).

2.13 Isolation and crystallization of [3b][OTf] from [3b]Br

For crystallization purposes, [3b]Br was anion exchanged to the triflate (OTf) salt. Crystals suitable for X-ray crystallography were grown from a saturated solution of [3b][OTf] in DCM layered with n-hexane.

2.14 Reduction of 2c and evidence for the formation of [Au$_{10}$($^{\text{MesCH2Bimy}}$)$_6$I$_3$]I and [Au$_{25}$($^{\text{MesCH2Bimy}}$)$_{10}$I$_7$]I$_2$

A round bottom flask (50 mL) was charged with a stir bar and 2c (0.03022 g, 0.04278 mmol), and DCM (10 mL) was added to dissolve the gold complex. The flask was then covered with aluminum foil to avoid excess light exposure. To the stirring solution of gold complex was added a thoroughly sonicated solution of NaBH$_4$ (0.00194 g, 0.0513 mmol) in absolute EtOH (3 mL). Samples of the reaction mixture (0.1 mL) were removed via syringe at 10 minutes, 2 hours and 19 hours and dried in vacuo before analysis by UV–vis and NMR spectroscopy as well as ESI-MS. The remaining reaction mixture at 19 hours was evaporated to dryness in vacuo, then the residue was extracted with Et$_2$O (4 x 1 mL), and the supernatant solution filtered through a Celite plug and evaporated to dryness yielding a red-brown residue (0.0079 g). The precipitate from Et$_2$O was collected separately from the Celite plug via washing with DCM, and pumping the filtrate to dryness yielding purple-brown residue (0.0192 g). The crude Et$_2$O supernatant residue was purified by silica gel column chromatography (PSQ60AB silica; 12:1 DCM/MeOH eluent; ~2x5 cm column size). Two initial coloured bands were collected separately from the column and evaporated to dryness in vacuo as follows: 1) an initial red coloured band, yielding a red-brown residue (0.0053 g) containing a complex mixture of unknown species as well as gold complexes and some [3c]I, and 2) a second brown band, which yielded a brown residue (0.0017 g) containing a mixture of mostly gold complexes and [3c]I (as identified by ESI-MS). A third brown band moved slowly at the top of the column, and was eluted by adding NH$_4$PF$_6$ (~5-10 mg) into the remaining eluent (12:1 DCM/MeOH) and eluting all brown coloured fractions with MeOH. The fractions were evaporated to dryness and the residue redissolved in DCM and filtered through Celite to remove excess salts, followed by drying in vacuo yielding a brown residue, which was washed with pentane (3 x 1 mL) and dried in vacuo (0.0020 g).
Confirmation of the presence of $[\text{Au}_{125}L_{10}I_7]^{2+}$ in this residue was made by ESI-MS, and UV–vis and NMR spectra showed features similar to the bromide analogue $[4b][\text{PF}_6]_2$. For UV–vis and NMR spectra and ESI-MS for this reaction see Figures S6-8 below. Attempts to further purify the fractions containing the Au$_{10}$ or Au$_{25}$ clusters from this reaction were unsuccessful due to their facile decomposition, and therefore full characterization of these clusters was not possible.

ESI-MS for $[\text{C}_{162}\text{H}_{180}\text{Au}_{10}\text{I}_3]\text{N}_{12}$]: Calculated – 4644.8; Observed – 4644.8; for $[\text{C}_{270}\text{H}_{300}\text{Au}_{25}\text{I}_7]\text{N}_{20}$]: Calculated – 4819.0; Observed – 4819.0.

Figure S6. UV–vis absorbance spectra (DCM) showing the attempted isolation and purification of $[3c]I$ and $[4c]I_2$ from the reduction of $2c$.

Figure S7. ESI-MS showing the attempted isolation and purification of $[3c]I$ and $[4c]I_2$ from the reduction of $2c$. (A) 1000-5000 m/z region normalized to the most intense peak to reflect the changes in cluster mixture composition; (B) expanded regions of $[3c]^+ ([\text{Au}_{10}L_6]\text{I}_3]^+$, where $L = \text{MesCH}_{2}\text{Bimy}$) and (C) $[4c]^{2+} ([\text{Au}_{25}L_{10}I_7]^2^+)$. Note that in all column bands a significant amount of $[\text{AuL}_2]^{-}$ was detected.
Figure S8. Aliphatic (top) and aromatic (bottom) region of $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra showing the attempted isolation and purification of [3c]I and [4c]I$_2$ from the reduction of 2c (top red trace).
2.15 Isolation and crystallization of [Au$_{25}$(MesCH$_2$Bimy)$_{10}$Br$_8$][B(C$_6$F$_5$)$_4$] ([5b][B(C$_6$F$_5$)$_4$]) from conversion of [3b]Br in EtOH at room temperature

Cluster [3b]Br (0.0120 g, 0.00262 mmol) was dissolved in EtOH (6 mL) and stirred at room temperature for 7 days. Following this, the sample was filtered through a 0.22 µm PTFE syringe filter, and the filtrate was dialyzed against ~800 mL of 95% EtOH for two days. Next, the EtOH solution was transferred to a 20 mL vial and the solvent removed in vacuo yielding a dark red solid. DCM (5 mL) and K[B(C$_6$F$_5$)$_4$] (5.0 mg, 6.96 µmol) were added to the solid, and the mixture was stirred for 24 hours before being filtered to remove excess K[B(C$_6$F$_5$)$_4$]. The resultant solid was dissolved in fluorobenzene (1 mL), layered with $n$-hexane (3 mL), and allowed to sit at room temperature for 48 hours to afford dark brown-black crystals of [5b][B(C$_6$F$_5$)$_4$] (0.0020 mg, 15 % based on Au). ESI-MS for [C$_{278}$H$_{380}$Au$_{25}$Br$_8$N$_{20}$]+: Calculated – 9388.9; could not be observed experimentally, likely due to facile loss of one bromide ligand on the core during ionization.

2.16 Isolation of [Au$_{25}$(MesCH$_2$Bimy)$_{10}$Br$_7$][PF$_6$], (4b)[PF$_6$]) by conversion of crude [3b]Br in MeOH at 60 °C

Conversion of cluster [3b]Br to cluster [4b][PF$_6$] can be achieved without the need for intermediate purification as follows. To a solution of 2b (0.0424 g, 0.0643 mmol) in EtOH (20 mL) was added a sonicated suspension of NaBH$_4$ (0.00246 g, 0.0650 mmol) in EtOH (6 mL), and the mixture was stirred at room temperature for 24 hours. The mixture was evaporated to dryness in vacuo, then the crude residue was extracted with Et$_2$O (4 x 2 mL). The supernatant solutions were filtered through Celite and evaporated to dryness yielding crude [3b]Br as an orange-brown residue (0.0140 g). This mixture was dissolved in MeOH (5 mL) and transferred to a screw top glass reaction tube (50 mL) charged with a stir bar. The tube was capped with a Teflon lined screw cap and the mixture was heated in a 60 °C oil bath for 5 days after which the colour had changed from orange-brown to dark green with some purple-black gold nanoparticle precipitate and gold(0) plating on the walls of the tube. The mixture was cooled and excess NH$_4$PF$_6$ (~50 mg) was added directly to the solution, and it was stirred a few minutes. The solvent was removed in vacuo and the residue redissolved in DCM and filtered through a Celite plug, removing some purple-black precipitate and excess salts. The resultant dark green-brown crude residue was purified by column chromatography (PSQ60AB silica; 12:1 DCM/MeOH eluent; ~3x10 cm column size). The initial colourless fraction, followed by pale orange fraction, were collected separately and purified by column chromatography (PSQ60AB silica; 12:1 DCM/MeOH eluent; ~3x10 cm column size). The initial colourless fraction, followed by pale orange fraction, were collected separately and evaporated to dryness yielding pale orange residues (0.0022 g and 0.0051 g, respectively), which contained mostly the starting complex 2b and by-product [(MesCH$_2$Bimy)$_2$Au]Br (as judged by NMR spectroscopy; see below). Next, a dark olive-green band containing the title cluster was eluted. The fraction was evaporated to dryness in vacuo, and the residue was washed with pentane (2 x 1 mL) and dried in vacuo yielding cluster [4b][PF$_6$], as a dark olive-green coloured residue (0.0025 g, 10 % based on Au). Typically, the cluster after column contains small impurities (gold complexes or other unidentified by-products) therefore the cluster was purified by precipitation as follows. The column residue was partially dissolved in Et$_2$O (1-2 mL), then DCM was added dropwise to until the cluster just dissolved. The cluster was then precipitated with the addition of pentane (~2x volume). The precipitate was allowed to settle, and the supernatant solution was carefully removed via pipet. The precipitate was washed with pentane (2 x 1 mL) and dried in vacuo yielding pure cluster [4b][PF$_6$]; as a dark olive-green coloured powder (0.0019 g, 8 % based on Au). UV–vis absorbance and NMR spectra tracking the purification of this cluster are shown in Figure S9-10 below.

$^1$H NMR (CD$_2$Cl$_2$, 600 MHz): $\delta$ 7.14 (s, 1H, ArH$_{Mes}$), 6.91 (d, $^3$J$_{HH}$ = 14.8 Hz, 1H, NCH$_2$Ar), 6.88 (t, $^3$J$_{HH}$ = 8.4 Hz, 1H, ArH$_{Bimy}$), 6.80 (s, 1H, ArH$_{Mes}$), 6.78 (t, $^3$J$_{HH}$ = 8.4 Hz, 1H, ArH$_{Bimy}$), 6.76 (s, 1H, ArH$_{Mes}$), 6.56 (d, $^3$J$_{HH}$ = 16.0 Hz, 1H, NCH$_2$Ar), 6.06 (d, 1H, $^3$J$_{HH}$ = 8.4 Hz, ArH$_{Bimy}$), 5.88 (d, 1H, $^3$J$_{HH}$ = 8.4 Hz, ArH$_{Bimy}$), 5.30 (d, $^3$J$_{HH}$ = 14.9 Hz, 1H, NCH$_2$Ar), 4.85 (s, 1H, ArH$_{Mes}$), 4.81 (d, $J$ = 16.0 Hz, 1H, NCH$_2$Ar), 2.55 (s, 3H, MesCH$_3$), 2.26 (s, 3H, MesCH$_3$), 2.25 (s, 3H, ArCH$_2$), 1.88 (s, 3H, ArCH$_3$), 1.68 (s, 3H, ArCH$_2$), 0.77 (s, 3H, ArCH$_3$). $^{13}$C$[^1$H] NMR (CD$_2$Cl$_2$, 151 MHz):
δ 206.7 (NCN), 139.1, 138.3, 137.7, 136.8, 136.3, 133.9, 133.1, 130.5, 130.0, 129.5, 127.8, 126.9, 124.8, 123.9, 113.1, 112.0 (ArC), 52.3, 51.4 (NCHAr), 21.6, 21.0, 20.9, 20.6, 19.7, 18.9 (ArCH₃). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ -139.7 (sept, ¹J_{PF} = 711 Hz, PF₆). ¹⁹F NMR (CD₂Cl₂, 376 MHz): δ -69.8 (d, ¹J_{PF} = 711 Hz, PF₆). ESI-MS for [C₂₋₋H₂₋₋Au₂₋₋Br₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-
2.17 Isolation of \([\text{Au}_{25}^{(\text{MesCH}_2\text{Bimy})_{10}}\text{Br}_7]\)[PF\(_6\)]\(_2\) ([4b*][PF\(_6\)]\(_2\)) by conversion of crude [3b*]Br in MeOH at 60 °C

\[
\begin{align*}
\text{[Au}_{10}^{(\text{MesCH}_2\text{Bimy})_{5}}\text{Br}_3]\text{Br} & \xrightarrow{\text{1) MeOH, 60 °C, 5 d}} [\text{Au}_{25}^{(\text{MesCH}_2\text{Bimy})_{10}}\text{Br}_7]\text{][PF}_6\text{]_2} \\
\text{[3b*]}\text{Br} & \xrightarrow{\text{2) xs NH}_4\text{PF}_6} [\text{4b*][PF}_6\text{]}\text{]}
\end{align*}
\]

\(^{13}\text{C}-\text{labeled cluster [4b*][PF}_6\text{]}\] was synthesized from [3b*]Br via the same procedure as non-labeled version [4b][PF\(_6\)]. Spectroscopic data are consistent with the non-labeled cluster except for higher intensity of the carbene carbon signal as expected.

2.18 Isolation and crystallization of \([\text{Au}_{25}^{(\text{MesCH}_2\text{Bimy})_{10}}\text{Br}_7]\)[B(C\(_6\text{F}_5\))\(_4\)]\(_2\) ([4b][B(C\(_6\text{F}_5\))\(_4\)]\(_2\)) from [4b][PF\(_6\)]\(_2\)

Cluster [4b][PF\(_6\)]\(_2\) (0.0028 g, 2.9x10\(^{-4}\) mmol) was dissolved in MeOH (3 mL) and a solution of excess Li[B(C\(_6\text{F}_5\))\(_4\)][OEt\(_2\)] (0.00269 g, 0.00309 mmol) in MeOH (2 mL) was added. The mixture was stirred at room temperature for 2 hours, then evaporated to dryness in vacuo, redissolved in DCM, filtered through Celite, and evaporated to dryness yielding a dark olive-green residue (0.0035 g). The residue was purified by column chromatography (PSQ60AB silica; 12:1 DCM/MeOH eluent; ~1x5 cm column size). The dark green fractions were collected and evaporated to dryness yielding a dark green residue of [4b][B(C\(_6\text{F}_5\))\(_4\)]\(_2\) (0.0015 g). The residue was redissolved in Et\(_2\)O (~1 mL) and hexane (~1 mL) was added until the solution became cloudy, then Et\(_2\)O was added dropwise to just dissolve the cluster and the solution was syringe filtered and left in a capped vial overnight at room temperature. Overnight, dark green-black cube/block shaped crystals had formed. A portion of these crystals and mother liquor was carefully removed via pipet and analyzed by X-ray crystallography; however, the quality of the data was not suitable for structural analysis. A new batch of crystals suitable for X-ray crystallography was regrown from this material by layering n-hexane onto a DCM solution of the cluster (ca. 5 mg/mL) at leaving the mixture -4 °C for several days. The remaining crystals were carefully washed with pentane (3 x 1 mL) with a few drops of Et\(_2\)O added, then pentane only (3 x 1 mL), followed by drying in vacuo yielding a dark green-black blocky crystalline solid (0.0001 g). Spectroscopic data were consistent with [4b][PF\(_6\)]\(_2\) except for the \(^{19}\text{F}\) NMR spectrum as follows.

\(^{19}\text{F}\) NMR (CD\(_2\)Cl\(_2\), 376 MHz): \(\delta\) -133.1, -163.8 and -167.6 (br m x 3, B(C\(_6\text{F}_5\))\(_4\)).
3 Monitoring reaction progress

3.1 Monitoring reduction of 2a, 2b, or 2c

Figure S11. *In situ* monitoring of the reduction of (A) 2a (X = Cl), (B) 2b (X = Br) and (C) 2c (X = I) at 2.31 mM in DCM/EtOH (10:3) with NaBH₄ by UV–vis absorbance spectroscopy. Spectra were automatically recorded every 30 min for 2.5 days. Note that the noise observed in the spectra recorded at 0 h is related to solution inhomogeneity due to H₂ evolution at early reaction stages.
Figure S12. *In situ* monitoring of the reduction of (A) 2a (X = Cl), (B) 2b (X = Br) and (C) 2c (X = I) at 2.31 mM in DCM/EtOH (10:3) with NaBH₄ by UV–vis absorbance spectroscopy (continued).

The same data as on Figure S11 are grouped in two time periods: initial (left), characterized by growth of intermediate gold species ($\dagger$), and main (right), when formation of Au₁₀ (#) and Au₂₅ (&) clusters was observed.

The following trends can be observed. Intermediate gold species were detected in all reactions (X = Cl, Br, and I), and the initial period was the shortest for X = Cl and the longest for X = I. Au₁₀ cluster forms for all halides. Au₂₅ is detected in significant amounts for X = I, whereas the amount of Au₂₅ formed with X = Br over the same time was small. Au₂₅ clusters were not observed when X = Cl.
Figure S13. ¹H NMR (600 MHz, CD₂Cl₂) spectra of aliquots taken from the reduction of 2b (top red trace) with NaBH₄ over time, showing the aliphatic (top) and aromatic (bottom) regions.
Figure S14.  ESI-MS of aliquots taken from the reduction of 2b with NaBH₄ over time. (A) 1000-6000 m/z region normalized to the most intense peak to reflect the changes in cluster mixture composition; (B) expanded region of [3b]⁺ ([Au₁₀L₆Br₃]⁺, where L = MesCH₂Bimy). Note that ESI-MS reveals several peaks of unidentified gold nanoclusters larger than Au₁₀ (e.g., at m/z 2792.2 or 2514.8), which are present in reaction mixture at early stages only. Such species potentially may be associated with "intermediate gold species" observed in UV–vis absorbance spectra.

Figure S15.  ESI-MS of aliquots taken from the reduction of 2c with NaBH₄ over time. (A) 1500-6000 m/z region normalized to the most intense peak to reflect the changes in cluster mixture composition; expanded regions of (B) [3c]⁺ ([Au₁₀L₆I₃]⁺, where L = MesCH₂Bimy) and (C) [4c]²⁺ ([Au₂₅L₁₈I₂]²⁺).
3.2 Monitoring conversion of [3b]X clusters

Figure S16. UV–vis spectra of (A) [3b]Br upon stirring in EtOH for 84 h at room temperature and (B) [3b]Br upon stirring in various solvents for 48 h at room temperature (insets show the new band at 658 nm attributed to Au$_{25}$ clusters).

Figure S17. UV–vis spectra of aliquots taken from the conversion of (A) [3b]Br and (B) [3b$^*$][PF$_6$] in methanol at 60 °C over time (inset shows the characteristic band of [4b]$^+$ at 658 nm).

Figure S18. UV–vis absorbance at 658 nm plotted over time for aliquots taken from the conversion of [3b]Br (blue) and [3b$^*$][PF$_6$] (red) in methanol at 60 °C.
Figure S19. ESI-MS spectra of aliquots taken from the conversion of [3b]Br in methanol at 60 °C over time.
Figure S20. Monitoring conversion of [3b][PF₆] in CD₃OD at 60 °C by ¹H NMR spectroscopy (600 MHz), showing the aliphatic (top) and aromatic (bottom) regions.
**Figure S21.** Monitoring conversion of [3b][PF₆] in CDCl₃ at 60 °C by ¹H NMR spectroscopy (600 MHz), showing the aliphatic (*top*) and aromatic (*bottom*) regions.
Figure S22. Comparison of the $^1$H NMR spectra (CD$_2$Cl$_2$, 600 MHz) of (A) the crude reaction mixture from conversion of [3b*]Br in MeOH at 60 °C for 4 days, (B) the crude reaction mixture extracted with pentane/Et$_2$O from conversion of [3b*][PF$_6$] with added TBAB (10 eq.) in CD$_3$OD at 60 °C for 4.5 hours, (C) [4b][PF$_6$] with added TBAB (10 eq.), and (D) [4b][PF$_6$] alone, showing the aliphatic (top) and aromatic (bottom) regions.
Figure S23. Comparison of the cluster regions of the $^{13}$C{H} NMR spectra (CD$_2$Cl$_2$, 151 MHz) of (A) the crude reaction mixture from conversion of [3b*]Br in MeOH at 60 °C for 4 days, (B) the crude reaction mixture extracted with pentane/Et$_2$O from conversion of [3b*][PF$_6$] with added TBAB (10 eq.) in CD$_3$OD at 60 °C for 4.5 hours, and (C) [4b*][PF$_6$] alone.
4 Characterization data of purified compounds

4.1 NMR spectra

Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1a.

Figure S25. $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) spectrum of 1a.
Figure S26. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1b.

Figure S27. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 1b.
Figure S28. $^1$H NMR (600 MHz, CD$_3$OD) spectrum of $^{13}$C-labeled $1b^*$. 

Figure S29. $^{13}$C{${^1}$H} NMR (151 MHz, CD$_3$OD) spectrum of $^{13}$C-labeled $1b^*$. 
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2a.

Figure S31. $^{13}$C\{${^1}$H\} NMR (101 MHz, CDCl$_3$) spectrum of 2a.
Figure S32. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2b.

Figure S33. $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) spectrum of 2b.
Figure S34. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of $^{13}$C-labeled 2b$^*$.  

Figure S35. $^{13}$C{$^1$H} NMR (151 MHz, CD$_2$Cl$_2$) spectrum of $^{13}$C-labeled 2b$^*$.  

S37
Figure S36. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 2c.

Figure S37. $^{13}$C{$^1$H} NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 2c.
Figure S38. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) spectrum of [3a][PF$_6$].

Figure S39. $^{13}$C{$^1$H} NMR (126 MHz, CD$_2$Cl$_2$) spectrum of [3a][PF$_6$].
Figure S40. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$].

Figure S41. $^{13}$C{^1}H NMR (176 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$].
Figure S42. $^{31}$P{$^1$H} NMR (283 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$].

Figure S43. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [3b][PF$_6$].
Figure S44. \(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\)) spectrum of \(^{13}\)C-labeled [3b*][PF\(_6\)].

Figure S45. \(^{13}\)C{\(^1\)H} NMR (151 MHz, CD\(_2\)Cl\(_2\)) spectrum of [3b*][PF\(_6\)].
Figure S46. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].

Figure S47. $^{13}$C{$^1$H} NMR (151 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].
Figure S48. $^1$H-$^1$H COSY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$]$_2$.

Figure S49. Aromatic region of $^1$H-$^1$H COSY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$]$_2$. 

S44
Figure S50. $^1$H-$^1$H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].

Figure S51. Methyl correlations of $^1$H-$^1$H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].
Figure S52. Methyl-aromatic correlations of $^1$H-$^1$H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].

Figure S53. Aromatic correlations of $^1$H-$^1$H NOESY NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$].
Figure S54. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$]$_2$.

Figure S55. $^{19}\text{F}$ NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [4b][PF$_6$]$_2$. 
Figure S56. Assignment of NMR signals for [3b][PF₆] and [3b*][PF₆] nanoclusters based on 1D NMR and crystallography data.
Figure S57. Assignment of NMR signals for [4b][PF₆]₂ nanoclusters based on 1D and 2D NMR and crystallography data.
Figure S58. Assignment of NMR signals for [4b][PF_6]_2 nanoclusters based on 1D and 2D NMR and crystallography data (continued).
4.2 Mass spectra

**Figure S59.** ESI-MS of [3a][PF₆].

**Figure S60.** ESI-MS of [3b*]Br.
4.3 X-ray crystallography and structural analysis

Figure S61. ORTEP plot of the core framework of [3b][OTf] with atom numbering scheme. Thermal ellipsoids are drawn on the 50% probability level. Anion and NHC ligands (except carbon atoms directly attached to Au) are omitted for clarity. Colour key: Yellow = Au, Orange = Br, Grey = C. Alternative views: along the pseudo C$_{2v}$ axis (inset, top right) and side view (inset, bottom right).

The structure of [3b]$^+$ can be described as a hexagonal ring of six edge- and face-sharing Au tetrahedra which have a common central gold atom, and overall toroidal topology.
**Figure S62.** ORTEP plot of the core framework of [5b][B(C₆F₅)₄] with atom numbering scheme. Thermal ellipsoids are drawn on the 50% probability level. Anion and NHC ligands (except carbon atoms directly attached to Au) are omitted for clarity. Colour key: Yellow = Au, Orange = Br, Grey = C. Alternative views: from side (top) and from top (bottom).
Figure S63. Two different Au–Br bonding modes at the waist sites in [5b][B(C₆F₅)₄] nanocluster. μ₂-Br-Au (left) and μ₁-Br-Au (right). Colour key: Yellow = Au, Orange = Br.
Figure S64. ORTEP plot of the core framework of $[\text{4b}][\text{B(C}_6\text{F}_5)_4]$ with atom numbering scheme. Thermal ellipsoids are drawn on the 50% probability level. Anions and NHC ligands (except carbon atoms directly attached to Au) are omitted for clarity. Colour key: Yellow = Au, Orange = Br, Grey = C. Alternative views: from side (top) and from top (bottom).
Figure S65. The packing structures of (A) [3b][OTf], (B) [5b][B(C₆F₅)₄], and (C) [4b][B(C₆F₅)₄]₂ in their single crystals. Hydrogen atoms have been omitted for clarity. Colour key: Yellow = Au, Orange = Br, Grey = C, Blue = N, Red = O, Light Pink = B, Light Green = F, Light Orange = S.
**Table S1.** X-ray crystallographic data for [3b][OTf].

| Characteristic                        | Value                                    |
|---------------------------------------|------------------------------------------|
| Empirical formula                     | C₃₄₄H₄₀₄Au₂₀Br₆Cl₄F₆N₂₄O₆S₂               |
| Formula weight                        | 9721.61                                  |
| Temperature                           | 100(2) K                                 |
| Wavelength                            | 0.71073 Å                                |
| Crystal system                        | Orthorhombic                             |
| Space group                           | Pccn                                     |
| Unit cell dimensions                  |                                          |
| a = 40.3926(19) Å, α = 90°             |                                          |
| b = 27.4376(12) Å, β = 90°             |                                          |
| c = 31.0196(14) Å, γ = 90°             |                                          |
| Volume                                | 34378(3) Å³                              |
| Z                                     | 4                                        |
| Density (calculated)                  | 1.878 Mg/m³                              |
| Absorption coefficient                | 9.296 mm⁻¹                               |
| F(000)                                | 18536                                    |
| Crystal size                          | 0.500 x 0.100 x 0.100 mm³                |
| Theta range for data collection       | 2.136 to 27.618°                         |
| Index ranges                          | -34<=h<=52, -35<=k<=35, -31<=l<=40        |
| Reflections collected                 | 320840                                   |
| Independent reflections               | 39700 [R(int) = 0.1530]                  |
| Completeness to theta = 25.242°       | 99.9 %                                   |
| Absorption correction                 | Semi-empirical from equivalents          |
| Max. and min. transmission            | 0.7456 and 0.5443                        |
| Refinement method                     | Full-matrix least-squares on F²          |
| Data / restraints / parameters        | 39700 / 0 / 1853                         |
| Goodness-of-fit on F²                 | 1.018                                    |
| Final R indices [I>2sigma(I)]         | R1 = 0.0533, wR2 = 0.0941                |
| R indices (all data)                  | R1 = 0.1116, wR2 = 0.1108                |
| Extinction coefficient                | n/a                                      |
| Largest diff. peak and hole           | 2.005 and -1.748 e.Å⁻³                   |
Table S2.  X-ray crystallographic data for [5b][B(C₆F₅)₄].

| Property                                           | Value                        |
|----------------------------------------------------|------------------------------|
| Empirical formula                                  | C₂₉₄H₃₀₂Au₂₅Br₈F₂₀N₂₀        |
| Formula weight                                     | 10067.77                     |
| Crystal Color, Habit                               | black-brown plate-like       |
| Crystal dimensions (mm)                            | 0.177 × 0.123 × 0.067        |
| Crystal system                                     | triclinic                    |
| Space group                                        | P₁ [2]                       |
| Unit cell parameters \(a)\ (Å)                    | 19.6290(5)                   |
| Unit cell parameters \(b)\ (Å)                    | 25.1157(7)                   |
| Unit cell parameters \(c)\ (Å)                    | 33.5491(10)                  |
| Unit cell parameters \(α\) (°)                    | 89.4350(10)                  |
| Unit cell parameters \(β\) (°)                    | 83.0503(9)                   |
| Unit cell parameters \(γ\) (°)                    | 89.9484(10)                  |
| Unit cell volume \(V\) (Å³)                       | 16417.3(8)                   |
| \(Z\)                                              | 2                            |
| \(F(000)\)                                         | 9288                         |
| Density \(\rho_{calc}\) (Mg/m³)                   | 2.037                         |
| Absorption coefficient \(μ\) (mm⁻¹)               | 12.152                       |
**Table S2 (continued).** Data Collection and Refinement Conditions for [5b][B(C₆F₅)₄].

| Parameter                                      | Value/Condition                                                                 |
|------------------------------------------------|----------------------------------------------------------------------------------|
| **Diffractometer**                             | Bruker AXS D8 Venture Duo diffractometer                                         |
| **Radiation**                                  | monochromated Mo Kα                                                            |
| **Wavelength (Mo Kα)**                         | 0.71073 Å                                                                      |
| **Temperature**                                | -93(2) °C [180(2) K]                                                           |
| **Scan type**                                  | φ- and ω-scans (0.5º/frame, 10 s exposure/frame, 7 sets)                         |
| **Theta range for data collection**            | 2.224 to 26.427°                                                               |
| **Completeness to theta = 25.242°**            | 99.9%                                                                           |
| **Reflections collected**                      | 725548                                                                          |
| **Index ranges**                               | -24 ≤ h ≤ 24, -31 ≤ k ≤ 31, -42 ≤ l ≤ 42                                      |
| **Independent reflections** [\(F_o^2 \geq 3\sigma(F_o^2)\)] | 67389 \(R_{int} = 0.0689\)^a                                                  |
| **Observed reflections** [\(F_o^2 > 2\sigma(F_o^2)\)] | 51320                                                                          |
| **Absorption correction method**               | multi-scan [SADABS]                                                            |
| **Anomalous Dispersion**                       | For all non-hydrogen atoms                                                      |
| **Structure solution method**                  | Direct methods (SHELXT-2014/5)^b                                               |
| **Refinement method**                          | Full-matrix least-squares on \(F^2\)                                           |
| **Function Minimized**                         | \(\Sigma w(|F_o|^2 - |kF_c|^2)^2\) (k: overall scale factor)                |
| **Weighing scheme, w**                         | \(w = [\sigma(F_o^2) + (0.0264 P)^2 + 39.3662 P]^{-1}\)                       |
| **P-factor**                                   | \(w = [\sigma(F_o^2) + (a P)^2 + (b P)]^{-1}\) \(\text{[Max}(F_o^2,0) + 2 F_c^2]/3\) |
| **Data / restraints / parameters**             | 67389 \(F_o^2 \geq 3\sigma(F_o^2)\) / 0 / 3343                             |
| **Reflection (observed)/parameter ratio**      | 15:1                                                                           |
| **Reflection (data)/parameter ratio**          | 20:1                                                                           |
| **Goodness-of-fit on \(F^2\)**                | 1.034                                                                          |
| **\(GooF = \Sigma[w(F_o^2-F_c^2)^2]/(n - p)\)^{1/2}** | \(n\): number of reflections, \(p\): number of parameters                   |
| **Final R indices**                            |                                                                                   |
| **\(R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o||\) for [\(F_o^2 > 2\sigma(F_o^2)\)]** | 0.0280                                                                         |
| **\(wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2\)^{1/2} [all data]** | 0.0677                                                                         |
| **Max. Shift/Error in Final Cycle**            | 0.004                                                                          |
| **Largest difference peak and hole**           | 1.340 and -1.214 e/Å³                                                           |
| **Transmission factor (min)**                  | 0.4980 [SADABS]^j                                                                |
| **Transmission factor (max)**                  | 0.7454 [SADABS]^j                                                                |

- Obtained from least-squares refinement of 9462 centered reflections with 2.461° < θ < 26.28°.
- \(Z\) is the number of formula units per unit cell. Comparison of \(Z\) with the multiplicity of the general position \(n_a\) of the space group will then require that the asymmetric unit is \(Z/n_a\) times the formula unit. The asymmetric unit is the minimum group of atoms whose positions, together with those generated by the symmetry operations of the space group generate the complete contents of the unit cell.
- Number of reflections after truncation or rejection (before merging).
The criterion for the independent or unique reflections $[F_o^2 \geq -3\sigma(F_o^2)]$ was taken from:

G. M. Sheldrick, *SHELX-2018/3, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany 2018. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.

The criterion for the observed reflections $[F_o^2 > 2\sigma(F_o^2)]$ is equivalent to $[I > 2\sigma(I)]: I$ is proportional to $F_o^2$.

Refinement on $F_o^2$ for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted $R$-factors $wR_2$ and the values for GooF are based on $F_o^2$; conventional $R$-factors $R_1$ are based on $F_o$, with $F_o$ set to zero for negative $F_o^2$. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating $R_1$ and is not relevant to the choice of reflections for refinement. $R$-factors based on $F_o^2$ are statistically about twice as large as those based on $F_o$, and $R$-factors based on ALL data will be even larger.

Standard deviation of an observation of unit weight (goodness-of-fit on $F^2$):

$$\text{GooF} = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{(n - p)} \right\}^{1/2}$$

$n$: number of reflections, $p$: number of parameters

*Bruker SADABS v2016/2: Part of the APEX3 software package v2019.1-0, Bruker AXS Inc.: Madison, WI, 2019. Krause, L.; Herbst-Irmer, R.; Sheldrick G.M.; Stalke D., *J. Appl. Cryst.*, **48** (2015), 3-10.*
Table S3.  X-ray crystallographic data for [4b][B(C6F5)4]2.

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Formula                                       | C306H300Au25B13Br7F30N20     |
| FW (g mol⁻¹)                                  | 10327.39                     |
| Crystal size (mm)                             | 0.261 × 0.022 × 0.022        |
| Crystal system                                | Monoclinic                   |
| Space group, Z                                | P2₁/c, 8                     |
| a (Å)                                        | 38.7941(6)                   |
| b (Å)                                        | 65.5532(6)                   |
| c (Å)                                        | 31.3032(3)                   |
| β (°)                                         | 94.4289(11)                  |
| V (Å³)                                       | 79368.6(16)                  |
| T (K)                                        | 93(2)                        |
| ρcalc (g cm⁻³)                                | 1.729                        |
| μ (mm⁻¹)                                      | 18.178                       |
| θ range (°)                                   | 1.955 – 67.684               |
| Measured reflections                          | 359433                       |
| Unique reflections                            | 144181 (Rint = 0.1084)       |
| Data/restraints/parameters                    | 144181/11108/6148            |
| R₁, R₂ indices [I > 2σ(I)]                    | R₁ = 0.0652, wR₂ = 0.1531    |
| R₁, R₂ indices [all data]                     | R₁ = 0.1658, wR₂ = 0.1948    |
| Goodness-of-fit on F²                          | 0.907                        |

\[^a\] R₁ = \Sigma(\mid F_o \mid - \mid F_c \mid)/\Sigma F_o. \[^b\] wR₂ = [\Sigma w(\sigma^2 - \bar{\sigma}^2)²]/[\Sigma w(\sigma^2)²]^{1/2}, w = 1/[\sigma^2(F_o^2) + (aσ)^2 + bσ], where p = [max(F_o, 0) + 2F_c^2]/3.
Table S4. Summary of important bond lengths for [3b][OTf].

| Atom 1 | Atom 2 | Length, Å |
|--------|--------|-----------|
| Au1    | Au2    | 2.679(1)  |
| Au1    | Au3    | 2.7300(9) |
| Au1    | Au4    | 2.7020(8) |
| Au1    | Au5    | 2.697(1)  |
| Au1    | Au6    | 2.7382(9) |
| Au1    | Au7    | 2.6271(9) |
| Au1    | Au8    | 2.7348(8) |
| Au1    | Au9    | 2.6873(9) |
| Au1    | Au10   | 2.709(1)  |
| Au2    | Au3    | 2.664(1)  |
| Au2    | Au4    | 2.883(1)  |
| Au2    | Au10   | 2.8788(8) |
| Au2    | Br1    | 2.416(1)  |
| Au3    | Au4    | 2.8085(9) |
| Au3    | Au10   | 2.7954(9) |
| Au3    | Br3    | 2.420(1)  |
| Au4    | Au5    | 2.852(1)  |
| Au4    | Au6    | 2.8891(9) |
| Au4    | C82    | 2.040(8)  |
| Au5    | Au6    | 2.695(1)  |
| Au5    | Au7    | 2.8477(9) |
| Au5    | Cl09   | 2.028(8)  |
| Au6    | Au7    | 2.9273(8) |
| Au6    | C1     | 2.041(9)  |
| Au7    | Au8    | 2.8877(9) |
| Au7    | Au9    | 2.936(1)  |
| Au7    | Br2    | 2.427(1)  |
| Au8    | Au9    | 2.710(1)  |
| Au8    | Au10   | 2.876(1)  |
| Au8    | Cl36   | 2.026(9)  |
| Au9    | Au10   | 2.8339(9) |
| Au9    | C28    | 2.030(9)  |
| Au10   | C55    | 2.031(9)  |
Table S5. Summary of important bond lengths for [5b][B(C₆F₅)₄].

| Atom 1 | Atom 2 | Length, Å |
|--------|--------|-----------|
| Au1    | Au2    | 2.9773(6) |
| Au1    | Au3    | 2.9459(8) |
| Au1    | Au4    | 2.9408(7) |
| Au1    | Au5    | 2.9517(8) |
| Au1    | Au6    | 2.9592(9) |
| Au1    | Au7    | 2.7128(7) |
| Au1    | Br1    | 2.4718(9) |
| Au2    | Au3    | 2.9104(8) |
| Au2    | Au6    | 2.8935(8) |
| Au2    | Au7    | 2.7313(6) |
| Au2    | Au8    | 2.9343(8) |
| Au2    | Au9    | 2.9419(8) |
| Au2    | C1     | 2.045(7)  |
| Au3    | Au4    | 2.9427(6) |
| Au3    | Au7    | 2.7109(9) |
| Au3    | Au9    | 2.8687(7) |
| Au3    | Au10   | 2.8810(7) |
| Au3    | C28    | 2.026(6)  |
| Au4    | Au5    | 2.920(1)  |
| Au4    | Au7    | 2.7604(7) |
| Au4    | Au10   | 2.9417(7) |
| Au4    | Au11   | 2.8415(8) |
| Au4    | C55    | 2.045(6)  |
| Au5    | Au6    | 2.9776(6) |
| Au5    | Au7    | 2.7363(7) |
| Au5    | Au1    | 2.8574(8) |
| Au5    | Au12   | 2.8827(7) |
| Au5    | C82    | 2.024(6)  |
| Au6    | Au7    | 2.7271(9) |
| Au6    | Au8    | 2.8490(7) |
| Au6    | Au12   | 2.9731(7) |
| Au6    | C109   | 2.034(6)  |
| Au7    | Au8    | 2.7718(7) |
| Au7    | Au9    | 2.7921(7) |
| Au7    | Au10   | 2.8557(9) |
| Au7    | Au11   | 2.7768(6) |
| Au7    | Au12   | 2.7731(9) |
| Au7    | Au13   | 2.7965(7) |
| Au8    | Au9    | 2.961(1)  |
| Au8    | Au12   | 2.8471(6) |
| Au8    | Au13   | 2.8635(7) |
| Au8    | Au14   | 3.0369(7) |
| Au8    | Br2    | 2.5767(8) |
| Au9    | Au10   | 2.8483(6) |
| Au9    | Au13   | 2.7915(8) |
| Au9    | Au15   | 3.0119(7) |
| Au9    | Br3    | 2.5794(7) |
| Au10   | Au1    | 2.9165(8) |
| Au10   | Au3    | 2.8593(9) |
| Au10   | Au6    | 2.9388(7) |
| Au10   | Br6    | 2.4609(9) |
| Au11   | Au12   | 2.8469(8) |
| Au11   | Au13   | 2.8923(6) |
| Au11   | Au17   | 3.0179(7) |
| Au11   | Br5    | 2.5316(8) |
| Au12   | Au13   | 2.8666(8) |
| Au12   | Au18   | 3.0474(7) |
| Au12   | Br4    | 2.560(1)  |
| Au13   | Au14   | 2.8884(8) |
| Au13   | Au15   | 2.8865(6) |
| Au13   | Au16   | 2.8492(9) |
| Au13   | Au17   | 2.7788(7) |
| Au13   | Au18   | 2.8724(8) |
| Au13   | Au19   | 2.7943(7) |
| Au14   | Au15   | 2.8239(9) |
| Au14   | Au18   | 2.8340(6) |
| Au14   | Au19   | 2.7830(8) |
| Au14   | Au20   | 2.9618(7) |
| Au14   | Au21   | 2.8625(7) |
| Au14   | Br2    | 2.5516(9) |
| Au15   | Au16   | 2.9265(7) |
| Au15   | Au19   | 2.7880(7) |
| Au15   | Au21   | 2.8771(8) |
| Au15   | Au22   | 2.8308(8) |
| Au15   | Br3    | 2.5405(8) |
| Au16   | Au17   | 2.8615(7) |
| Au16   | Au19   | 2.8414(9) |
| Au16   | Au22   | 2.9322(6) |
| Au16   | Br7    | 2.455(1)  |
| Au17   | Au18   | 2.9831(9) |
| Au17   | Au19   | 2.8019(6) |
| Au17   | Au23   | 2.8692(7) |
| Au17   | Au24   | 2.9214(8) |
| Au17   | Br5    | 2.5750(7) |
| Au18   | Au19   | 2.7660(8) |
| Au18   | Au20   | 2.8475(7) |
| Au18   | Au24   | 2.8923(8) |
| Au18   | Br4    | 2.565(1)  |
| Au19   | Au20   | 2.7484(9) |
| Au19   | Au21   | 2.7438(6) |
| Au19   | Au22   | 2.7454(8) |
| Au19   | Au23   | 2.7329(8) |
| Au19   | Au24   | 2.7205(7) |
| Au19   | Au25   | 2.9351(7) |
| Au20   | Au21   | 2.9296(7) |
| Au20   | Au25   | 2.9913(9) |
| Au20   | C136   | 2.043(6)  |
| Au21   | Au22   | 2.9050(9) |
| Au21   | Au25   | 2.9960(7) |
| Au21   | C163   | 2.040(6)  |
| Au22   | Au23   | 3.018(6)  |
| Au22   | Au25   | 2.9456(8) |
| Au22   | C190   | 2.042(6)  |
| Au23   | Au24   | 2.9359(9) |
| Au23   | Au25   | 2.9318(8) |
| Au23   | C217   | 2.038(6)  |
| Au24   | Au25   | 2.9772(6) |
| Au24   | C244   | 2.039(6)  |
| Au25   | Br8    | 2.4706(9) |
Table S6. Summary of important bond lengths for [4b][B(C$_6$F$_5$)$_4$].

| Atom1  | Atom2  | Length  |
|--------|--------|---------|
| Au1    | Au2    | 2.854(1) |
| Au1    | Au3    | 2.8235(9) |
| Au1    | Au4    | 2.853(1)  |
| Au1    | Au9    | 2.8289(9) |
| Au1    | Au10   | 2.858(2)  |
| Au1    | Au11   | 2.852(2)  |
| Au1    | Au12   | 2.856(1)  |
| Au1    | Au16   | 2.862(1)  |
| Au1    | Au18   | 2.860(2)  |
| Au1    | Au19   | 2.869(1)  |
| Au1    | Au20   | 2.863(1)  |
| Au1    | Au23   | 2.853(1)  |
| Au1    | Au24   | 2.772(1)  |
| Au1    | Au25   | 2.777(1)  |
| Au9    | Au12   | 2.775(1)  |
| Au9    | Au14   | 2.716(2)  |
| Au9    | Au15   | 2.725(1)  |
| Au9    | Au16   | 2.772(1)  |
| Au9    | Au17   | 2.733(1)  |
| Au9    | Au18   | 2.766(2)  |
| Au9    | Au20   | 2.772(1)  |
| Au9    | Au24   | 2.7144(9) |
| Au9    | Au25   | 2.725(1)  |
| Au10   | Au19   | 2.871(1)  |
| Au10   | Au21   | 2.9090(9) |
| Au10   | Br7    | 2.565(2)  |
| Au11   | Au13   | 2.8596(9) |
| Au11   | Au18   | 2.772(1)  |
| Au11   | Au23   | 2.867(1)  |
| Au12   | Au14   | 2.9090(1) |
| Au12   | Au19   | 3.0049(9) |
| Au12   | Au20   | 2.860(2)  |
| Au12   | Au25   | 2.867(1)  |
| Au12   | Br6    | 2.564(2)  |
| Au13   | Au22   | 2.912(2)  |
| Au13   | Au23   | 2.934(1)  |
| Au13   | Au25   | 2.927(1)  |
| Au13   | C5     | 2.07(2)   |
| Au14   | Au17   | 2.914(1)  |
| Au14   | Au24   | 2.944(2)  |
| Au14   | Au25   | 2.9090(9) |
| Au14   | C7     | 2.06(2)   |
| Au15   | Au16   | 2.933(1)  |
| Au15   | Au17   | 2.905(2)  |
| Au15   | Au18   | 2.8732(9) |
| Au15   | Au24   | 2.930(1)  |
| Au15   | C9     | 2.06(2)   |
| Au16   | Au17   | 2.868(1)  |
| Au16   | Au18   | 2.856(1)  |
| Au16   | Br3    | 2.559(2)  |
| Au17   | Au24   | 2.937(1)  |
| Au17   | C8     | 2.01(2)   |
| Au18   | Au20   | 2.866(1)  |
| Au18   | Br4    | 2.554(2)  |
| Au19   | Au21   | 2.842(1)  |
| Au19   | Au22   | 2.937(1)  |
| Au19   | Au23   | 2.857(2)  |
| Au19   | Br6    | 2.574(2)  |
| Au20   | Au23   | 3.0361(9) |
| Au20   | Au25   | 2.924(1)  |
| Au20   | Br5    | 2.566(2)  |
| Au21   | Au22   | 2.941(2)  |
| Au21   | C3     | 2.07(2)   |
| Au22   | Au23   | 2.854(1)  |
| Au22   | C4     | 2.04(2)   |
| Au23   | Br5    | 2.570(2)  |
| Au24   | Au25   | 2.930(1)  |
| Au24   | Br1    | 2.452(2)  |
| Au25   | C6     | 2.02(2)   |
Table S7. Average bond distances in [3b][OTf] and their comparison to those in [Au\textsubscript{13}(\text{PhCH\textsubscript{2}Bimy})\textsubscript{9}Cl\textsubscript{3}][PF\textsubscript{6}]\textsubscript{2} nanocluster. Bonds are referenced according to the scheme below.

| Bond description                      | Bond labeling                  | Average bond length, Å | [3b]\textsuperscript{+} | [Au\textsubscript{13}]\textsuperscript{2+} |
|---------------------------------------|--------------------------------|------------------------|--------------------------|------------------------------------------|
| metal core, radial                    | Au\textsubscript{a} – Au\textsubscript{c} | 2.679                  | 2.740                    |
| metal core, radial                    | Au\textsubscript{b} – Au\textsubscript{c} | 2.711                  | 2.778                    |
| metal core, all radial bonds          | Au\textsubscript{a} – Au\textsubscript{c} and Au\textsubscript{b} – Au\textsubscript{c} | 2.700                  | 2.768                    |
| metal core, peripheral                | Au\textsubscript{a} – Au\textsubscript{a} | 2.664                  | –                        |
| metal core, peripheral                | Au\textsubscript{a} – Au\textsubscript{b} | 2.871                  | 2.895                    |
| metal core, peripheral                | Au\textsubscript{b} – Au\textsubscript{b} | 2.809                  | 2.926                    |
| metal core, all peripheral bonds      | Au\textsubscript{a} – Au\textsubscript{a}, Au\textsubscript{a} – Au\textsubscript{b}, and Au\textsubscript{b} – Au\textsubscript{b} | 2.832                  | 2.910                    |
| metal-to-ligand                       | Au\textsubscript{a} – X          | 2.421                  | 2.353                    |
| metal-to-ligand                       | Au\textsubscript{b} – C\textsubscript{NHC} | 2.034                  | 2.055                    |

For [Au\textsubscript{13}(\text{PhCH\textsubscript{2}Bimy})\textsubscript{9}Cl\textsubscript{3}]\textsuperscript{2+} nanoclusters,\textsuperscript{20} calculations were made using deposited data CCDC1886732.

\textsuperscript{20} M. R. Narouz, S. Takano, P. A. Lummis, T. I. Levchenko, A. Nazemi, S. Kaappa, S. Malola, G. Yousefizadeh, L. A. Calhoun, K. G. Stamplecoskie, H. Häkkinen, T. Tsukuda, C. M. Crudden, \textit{J. Am. Chem. Soc.} \textbf{2019}, \textit{141} (38), 14997.
Table S8. Average bond distances in [4b][B(C$_6$F$_5$)$_4$]$_2$ and [5b][B(C$_6$F$_5$)$_4$], and their comparison to those in [Au$_{25}$($^{i}$PrBimy)$_{10}$Br$_7$][NO$_3$][Cl] nanocluster. Bonds are referenced according to the scheme below.

| Bond description                     | Bond labeling | Average bond length, Å |
|--------------------------------------|---------------|------------------------|
| metal core, radial                   | Au$_a$ – Au$_c$ | 2.711 2.708 2.728 |
| metal core, radial                   | Au$_b$ – Au$_c$ | 2.729 2.736 2.730 |
| metal core, radial                   | Au$_c$ – Au$_d$ | 2.772 2.795 2.780 |
| metal core, pivotal                  | Au$_c$ – Au$_e$ | 2.826 2.796 2.808 |
| metal core, peripheral               | Au$_a$ – Au$_b$ | 2.940 2.962 2.940 |
| metal core, peripheral               | Au$_b$ – Au$_d$ | 2.893 2.892 2.898 |
| metal core, waist                    | Au$_d$ – Au$_e$ | 2.859 2.855 2.865 |
| metal core, icosahedron-             | Au$_d$ – Au$_d'$ | 3.033 3.011 2.979 |
| icosahedron'                         |               |                        |
| metal-to-ligand, vertexes            | Au$_a$ – ($\mu_1$-Br) | 2.456 2.472 2.439 |
| metal-to-ligand, waist               | Au$_d$ – ($\mu_2$-Br) | 2.565 2.560 2.564 |
| metal-to-ligand, waist               | Au$_a$ – ($\mu_1$-Br) | – 2.458 – |
| metal-to-ligand                      | Au$_b$ – C$_{NH}$ | 2.053 2.039 2.063 |

For [Au$_{25}$($^{i}$PrBimy)$_{10}$Br$_7$]$^{2+}$ nanoclusters, calculations were made using deposited data CCDC1916156. The following general trends can be observed: average radial Au–Au bonds are shorter than average peripheral; Au–Au bonds within icosahedron are shorter than those between the two icosahedra; average Au–Br terminal bonds are shorter than Au–Br bridging ones.

21. H. Shen, G. Deng, S. Kaappa, T. Tan, Y.-Z. Han, S. Malola, S.-C. Lin, B. K. Teo, H. Häkkinen, N. Zheng, Angew. Chem. 2019, 131 (49), 17895.

S66
4.5 UV–vis absorbance and fluorescence spectra

Figure S66. UV–vis absorbance spectra of 2a, 2b, and 2c in EtOH.

Figure S67. UV–vis absorbance spectrum of [3a][PF₆] in DCM.
Figure S68. Emission (excited at 475 nm) and excitation (monitored at 800 nm) spectra of \([3b]\text{PF}_6\) in DCM. Note that the weak emission of \([3b]\text{PF}_6\) and low stability of this cluster under irradiation complicate obtaining its excitation spectra.

Figure S69. Emission (excited at 657 nm) and excitation (monitored at 785 nm) spectra of \([4b]\text{[PF}_6\text{]}_2\) in DCM. Inset: emission spectra of \([4b]\text{[PF}_6\text{]}_2\) excited at different wavelengths.
Figure S70. 3D (top) and 2D (bottom) plots for the fluorescence EEM spectra of [3b]PF$_6$ in DCM.
Figure S71. 3D (top) and 2D (bottom) plots for the fluorescence EEM spectra of $[4b][\text{PF}_6]_2$ in DCM.
Figure S72. Emission spectra (excited at 360 nm) of [3b]PF₆ in DCM and ZnPc standard in pyridine for photoluminescence QY calculations.

Figure S73. Emission spectra (excited at 370 nm) of [4b][PF₆]₂ in DCM and ZnPc standard in pyridine for photoluminescence QY calculations.
5 Computational data

5.1 Computational analysis of cluster $[3b]^+$

![Optimized structure of the gas-phase model of $[3b]^+$ using the PBE exchange-correlational functional.](image)

**Figure S74.** Optimized structure of the gas-phase model of $[3b]^+$ using the PBE exchange-correlational functional.

**Table S9.** Experimental and computed (PBE) atom-atom bond lengths in the crystal structure and in the gas-phase model of $[3b]^+$.

Atom indexing is shown in Figure S58.

| Bond         | Exp.  | Calc. |
|--------------|-------|-------|
| Au(1)-Au(2)  | 2.679 | 2.749 |
| Au(1)-Au(3)  | 2.730 | 2.768 |
| Au(1)-Au(4)  | 2.702 | 2.790 |
| Au(1)-Au(5)  | 2.697 | 2.828 |
| Au(1)-Au(6)  | 2.738 | 2.868 |
| Au(1)-Au(7)  | 2.627 | 2.676 |
| Au(1)-Au(8)  | 2.735 | 2.835 |
| Au(1)-Au(9)  | 2.687 | 2.826 |
| Au(1)-Au(10)| 2.709 | 2.799 |
| Au(2)-Au(3)  | 2.664 | 2.714 |
| Au(2)-Au(4)  | 2.883 | 3.043 |

| Bond         | Exp.  | Calc. |
|--------------|-------|-------|
| Au(2)-Au(10)| 2.879 | 2.973 |
| Au(2)-Br(1) | 2.416 | 2.471 |
| Au(3)-Au(4) | 2.809 | 2.945 |
| Au(3)-Au(10)| 2.795 | 2.887 |
| Au(3)-Br(3) | 2.420 | 2.481 |
| Au(4)-Au(5) | 2.852 | 2.933 |
| Au(4)-Au(6) | 2.889 | 2.967 |
| Au(4)-C(82) | 2.041 | 2.092 |
| Au(5)-Au(6) | 2.695 | 2.776 |
| Au(5)-Au(7) | 2.848 | 2.908 |
| Au(5)-C(109)| 2.029 | 2.076 |

| Bond         | Exp.  | Calc. |
|--------------|-------|-------|
| Au(6)-Au(7) | 2.927 | 3.015 |
| Au(6)-C(1)  | 2.042 | 2.087 |
| Au(7)-Au(8) | 2.888 | 2.959 |
| Au(7)-Au(9) | 2.936 | 2.984 |
| Au(7)-Br(2) | 2.427 | 2.484 |
| Au(8)-Au(9) | 2.710 | 2.745 |
| Au(8)-Au(10)| 2.876 | 2.947 |
| Au(8)-C(136)| 2.027 | 2.063 |
| Au(9)-Au(10)| 2.834 | 2.921 |
| Au(9)-C(28) | 2.031 | 2.068 |
| Au(10)-C(55)| 2.032 | 2.072 |
Figure S75. Electronic density of states in the gas-phase model of [3b]$^+$ by using the PBE (top) and GLLB-SC (bottom) xc functional. Color coding shows the projection of the orbitals into spherical symmetry about the c.o.m of the cluster. The projection is done in a sphere of radius 3.5 Å. The grey area labeled as “out” denotes that part of the electron density that is either outside this radius (in the ligands) or cannot be spanned by the angular momentum components up to J symmetry.

Table S10. Bader charges for gold atoms and ligands in the gas-phase model of [3b]$^+$ calculated using the GLLB-SC functional.

| Atom group | N | Total Q (e) | Q/N (e) |
|------------|---|-------------|---------|
| Au-center  | 1 | -0.084      | -0.084  |
| Au-Br      | 3 | -0.086      | -0.028  |
| Au-C       | 6 | -0.067      | -0.011  |
| Br         | 3 | -1.465      | -0.488  |
| NHC        | 6 | 2.703       | 0.45    |
Figure S76. Visualisation of frontier orbitals for [3b]$^+$. 

HOMO-1

HOMO

LUMO

LUMO+1
Figure S77. Dipole transition contribution maps (DTCM) analysis for [3b]+ – Principal axes of moments of inertia.
Figure S78. DTCM analysis for the lowest-energy peak (2.44 eV, shown in the bottom right panel) in the UV–vis absorbance spectrum of [3b]+.

Bottom left panel shows the occupied electron states and the vertical panel on the right shows the empty states. Red/blue areas in the map denote constructive/destructive contributions of the electron-hole transitions to the total transition dipole. Along the dashed line, the hole-electron orbital energy difference matches the peak energy. The occupied and empty electron states are decomposed by the elemental weights as shown in the color coding.
Figure S79. DTCM for peak at $E = 3.07$ eV.
Figure S80. DTCM for peak at $E = 3.54$ eV.
Figure S81. DTCM for peak at $E = 3.94$ eV.