

Supplementary information

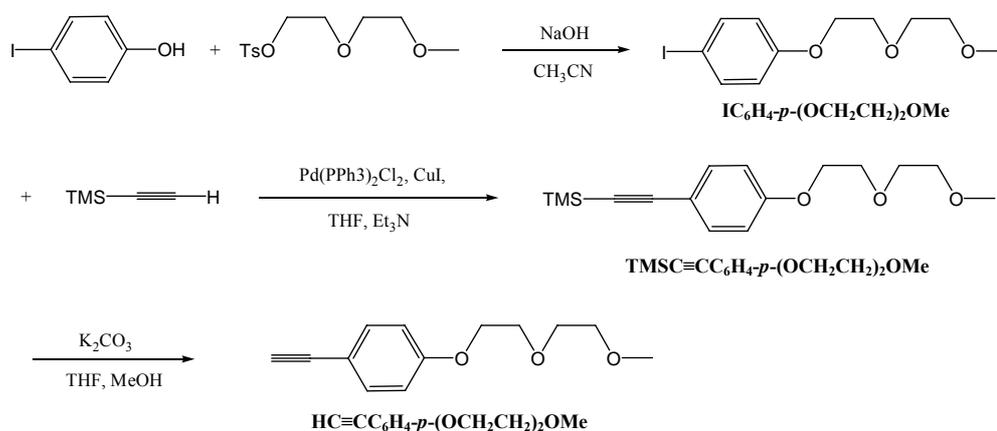
Selective ion probe for Mg^{2+} based on $\text{Au(I)}\cdots\text{Au(I)}$ interactions in tripodal alkynylgold(I) complex with oligoether pendants

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Experimental Procedure:

(1) Ligand synthesis and characterization



$\text{IC}_6\text{H}_4\text{-p-(OCH}_2\text{CH}_2\text{)}_2\text{OMe}$

^1H NMR (CDCl_3 , 400 MHz, relative to Me_4Si): δ 3.39 (3H, s, $-\text{OCH}_3$), 3.58 (2H, t, $J = 4.4$ Hz, $-\text{OCH}_2-$), 3.71 (2H, t, $J = 4.4$ Hz, $-\text{OCH}_2-$), 3.85 (2H, t, $J = 4.7$ Hz, $-\text{OCH}_2-$), 4.11 (2H, t, $J = 4.7$ Hz, $-\text{OCH}_2-$), 6.70 (2H, d, $J = 8.6$ Hz, $-\text{C}_6\text{H}_4-$), 7.54 (2H, d, $J = 8.6$ Hz, $-\text{C}_6\text{H}_4-$). Elemental analysis, Anal. Found (%): C, 40.92; H, 4.62. Calcd. For $\text{C}_{11}\text{H}_{15}\text{IO}_3$: C, 41.01; H, 4.69.

TMSC≡CC₆H₄-*p*-(OCH₂CH₂)₂OMe

¹H NMR (CDCl₃, 400 MHz, relative to Me₄Si): δ 0.24 (9H, s, -SiMe₃), 3.39 (3H, s, -OCH₃), 3.59 (2H, t, *J* = 4.6 Hz, -OCH₂-), 3.72 (2H, t, *J* = 4.6 Hz, -OCH₂-), 3.86 (2H, t, *J* = 4.8 Hz, -OCH₂-), 4.14 (2H, t, *J* = 4.8 Hz, -OCH₂-), 6.83 (2H, d, *J* = 8.7 Hz, -C₆H₄-), 7.39 (2H, d, *J* = 8.7 Hz, -C₆H₄-).

Elemental analysis, Anal. Found (%): C, 65.53; H, 8.29. Calcd. For C₁₆H₂₄O₃Si: C, 65.71; H, 8.27.

HC≡CC₆H₄-*p*-(OCH₂CH₂)₂OMe

¹H NMR (CDCl₃, 400 MHz, relative to Me₄Si): δ 2.99 (1H, s, C≡CH), 3.39 (3H, s, -OCH₃), 3.58 (2H, t, *J* = 4.6 Hz, -OCH₂-), 3.71 (2H, t, *J* = 4.6 Hz, -OCH₂-), 3.85 (2H, t, *J* = 4.9 Hz, -OCH₂-), 4.14 (2H, t, *J* = 4.9 Hz, -OCH₂-), 6.85 (2H, d, *J* = 8.7 Hz, -C₆H₄-), 7.41 (2H, d, *J* = 8.7 Hz, -C₆H₄-).

Elemental analysis, Anal. Found (%): C, 70.85; H, 7.39. Calcd. For C₁₃H₁₆O₃: C, 70.89; H, 7.32.

(2) Complexes 1-3 synthesis and characterization

[Au₃(Triphos){C≡CC₆H₄-*p*-(OCH₂CH₂)₂OMe}₃] (1)

To a dichloromethane solution of [Au(C≡C-L)]_∞ (100 mg, 0.24 mmol) was added a solid sample of 1,1,1-tris(diphenylphosphinomethyl)ethane (50 mg, 0.08 mmol) under a nitrogen atmosphere.

After it was stirred for 2 hours, the reaction became clear and the solvent was evaporated under reduced pressure. Recrystallization by layering *n*-hexane onto a concentrated dichloromethane

solution of the product afforded **1** as white crystals. Yield: 82 mg, 53 %. ¹H NMR (CDCl₃, 400

MHz, relative to Me₄Si): δ 0.76 (3H, s, -CH₃), 3.39 (9H, s, -OCH₃), 3.51 (6H, d, *J* = 10.6 Hz, -CH₂P-), 3.57 (6H, t, *J* = 4.7 Hz, -OCH₂-), 3.72 (6H, t, *J* = 4.7 Hz, -OCH₂-), 3.85 (6H, t, *J* = 4.9

Hz, -OCH₂-), 4.13 (6H, t, *J* = 4.9 Hz, -OCH₂-), 6.80 (6H, d, *J* = 8.8 Hz, -C₆H₄-), 7.41 (24H, m,

-PPh₂ and -C₆H₄-), 8.01 (12H, m, -PPh₂). ³¹P NMR (CDCl₃, 202 MHz, relative to 85 % H₃PO₄): δ

27.79. Elemental analysis, Anal. Found (%): C, 51.40; H, 4.55. Calcd. for $C_{80}H_{84}Au_3O_9P_3$: C, 51.29; H, 4.52. FAB-MS m/z 1654 $[M-L]^+$.

$[Au_3(Triphos)(C\equiv CC_6H_4OMe-p)_3]$ (2)

This was prepared according to the procedure for **1** except $[Au(C\equiv CC_6H_4OMe-p)]_\infty$ (80 mg, 0.24 mmol) was used instead of $[Au(C\equiv C-L)]_\infty$. The product was recrystallized from dichloromethane-*n*-hexane to give **2** as yellow crystals. Yield 100 mg, 77 %. 1H NMR ($CDCl_3$, 400 MHz, relative to Me_4Si): δ 0.77(3H, s, - CH_3), 3.51 (6H, d, $J = 10.7$ Hz, - CH_2P -), 3.80 (9H, s, - OCH_3), 6.80 (6H, d, $J = 8.8$ Hz, - C_6H_4 -), 7.42 (24H, m, - PPh_2 and - C_6H_4 -), 8.02 (12H, m, - PPh_2). ^{31}P NMR ($CDCl_3$, 202 MHz, relative to 85 % H_3PO_4): δ 26.65. Elemental analysis, Anal. Found (%): C, 50.53; H, 3.85. Calcd. For $C_{68}H_{60}Au_3O_3P_3$: C, 50.76; H, 3.76.

FAB-MS m/z : 1479 $[M-L]^+$, 1610 $[M]^+$, 1807 $[M+Au]^+$.

$[Au_3(Triphos)(C\equiv CPh)_3]$ (3)

This was prepared according to the procedure for **1** except $[Au(C\equiv CC_6H_4Ph)]_\infty$ (72 mg, 0.24 mmol) was used instead of $[Au(C\equiv C-L)]_\infty$. The product was recrystallized from dichloromethane-*n*-hexane to give **2** as white crystals. Yield 97 mg, 80 %. 1H NMR ($CDCl_3$, 400 MHz, relative to Me_4Si): δ 0.79 (3H, s, - CH_3), 3.52 (6H, d, $J = 10.6$ Hz, - CH_2P -), 7.25 (9H, m, - C_6H_5 -), 7.44 (24H, m, PPh_2 and - C_6H_5 -), 8.01 (12H, m, - PPh_2). ^{31}P NMR ($CDCl_3$, 202 MHz, relative to 85 % H_3PO_4): δ 26.45. Elemental analysis, Anal. Found (%): C, 50.29; H, 3.58. Calcd. For $C_{65}H_{54}Au_3P_3 \cdot H_2O$: C, 50.79; H, 3.67. FAB-MS m/z : 1419 $[M-L]^+$, 1520 $[M]^+$, 1717 $[M+Au]^+$.

X-Ray Crystallography of $\text{Au}_3(\text{Triphos})(\text{C}\equiv\text{CPh})_3$ (**3**)

Crystals of complex **3** for X-ray studies were obtained by layering of *n*-hexane onto a dichloromethane solution of complex **3**. A crystal of dimensions 0.48 mm \times 0.05 mm \times 0.02 mm mounted in a glass capillary was used for data collection at 28 °C on a Bruker Smart CCD 1000 using graphite monochromatized Mo- K_α radiation ($\lambda = 0.71073$ Å). Raw frame data were integrated with SAINT¹ program. Semi-empirical absorption correction with SADABS² was applied.

The structure was solved by direct methods employing SHELXS-97 program³ on PC. Au, P and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97⁴ on PC. There were two formula units in the asymmetric unit. Two water O were also located and their occupancies were set to be 0.5 due to closure. Phenyl rings were constrained to be regular hexagon rings with bond lengths of 1.39 Å. C \equiv C triple bonds were also restrained to be around 1.18(2) Å.

According to the SHELXL-97 program,⁴ all 22320 independent reflections (R_{int} ⁵ equal to 0.0452, 15563 reflections larger than $4\sigma(F_o)$) from a total 67724 reflections were participated in the full-matrix least-square refinement against F^2 . These reflections were in the range $-31 \leq h \leq 35$, $-13 \leq k \leq 17$, $-35 \leq l \leq 35$ with $2\theta_{\text{max}}$ equal to 51.36°.

One crystallographic asymmetric unit consists of two formula units. In the final stage of least-squares refinement, water O atoms were refined isotropically, other non-H atoms were refined anisotropically. H atoms were generated by program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final *R*-indices⁶.

Convergence ($(\Delta/\sigma)_{\text{max}} = 0.001$, av. 0.001) for 1073 variable parameters by full-matrix least-squares

refinement on F^2 reaches to $R_1 = 0.0498$ and $wR_2 = 0.1189$ with a goodness-of-fit of 1.043, the parameters a and b for weighting scheme are 0.0609 and 46.01. The final difference Fourier map shows maximum rest peaks and holes of 1.420 and $-0.970 \text{ e}\text{\AA}^{-3}$ respectively.

All experimental details are given in Table S1 .

¹ SAINT+. SAX area detector integration program. Version 7.34A. Bruker AXS, Inc. Madison, WI.

² G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 2004.

³ SHELXS97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

⁴ SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

$$^5 R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$$

⁶ Since the structure refinements are against F^2 , R -indices based on F^2 are larger than (more than double) those based on F . For comparison with older refinements based on F and an OMIT threshold, a conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is also given (corresponding to Intensity $\geq 2\sigma(I)$). $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, The Goodness of Fit is always based on F^2 : $\text{GooF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

Table S1 Crystal structure determination data for complex **3**·0.5H₂O

Empirical formula	C ₆₅ H ₅₆ Au ₃ O _{0.5} P ₃
Formula weight	1527.90
<i>T</i> , K	301 (2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	<i>a</i> = 29.200(6) Å, <i>α</i> = 90° <i>b</i> = 13.992(2) Å, <i>β</i> = 96.25(2)° <i>c</i> = 28.986(6) Å, <i>γ</i> = 90°
Volume	11772(4) Å ³
<i>Z</i>	8
Density (calculated)	1.724 g cm ⁻³
Absorption coefficient	7.579 mm ⁻¹
<i>F</i> (000)	5848
Crystal size	0.48 mm × 0.05 mm × 0.02 mm
Theta range for data collection	1.65 to 25.68°
Index ranges	-31 ≤ <i>h</i> ≤ 35, -13 ≤ <i>k</i> ≤ 17, -35 ≤ <i>l</i> ≤ 35
Reflections collected	67724
Independent reflections	22320 [<i>R</i> (int) = 0.0452]
Completeness to theta = 25.68°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	22320 / 21 / 1073
Goodness-of-fit on <i>F</i> ²	1.043
Final <i>R</i> indices ^[a] [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0498, <i>wR</i> ₂ = 0.1189
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0830, <i>wR</i> ₂ = 0.1343
Largest diff. peak and hole	1.420 and -0.970 eÅ ⁻³

[a] $R_{\text{int}} = \Sigma |F_o^2 - F_c^2(\text{mean})| / \Sigma [F_o^2]$, $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

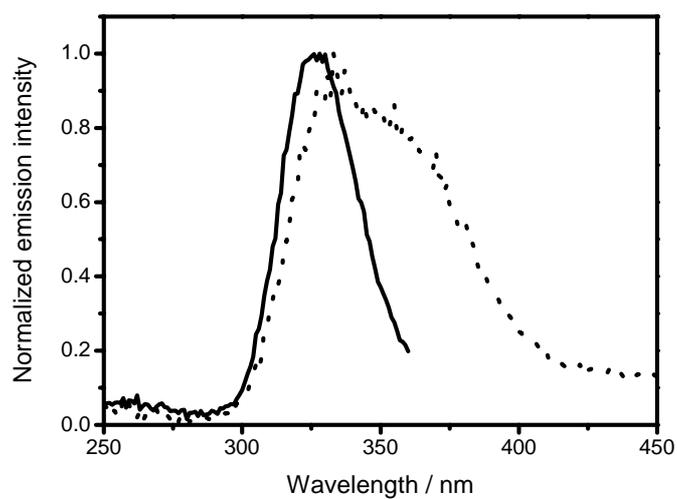


Figure S1 Excitation spectra of **1** (9.13×10^{-5} M) in the absence (—) and in the presence (---) of Mg^{2+} (2.8×10^{-2} M), monitored at 450 nm and 675 nm, respectively

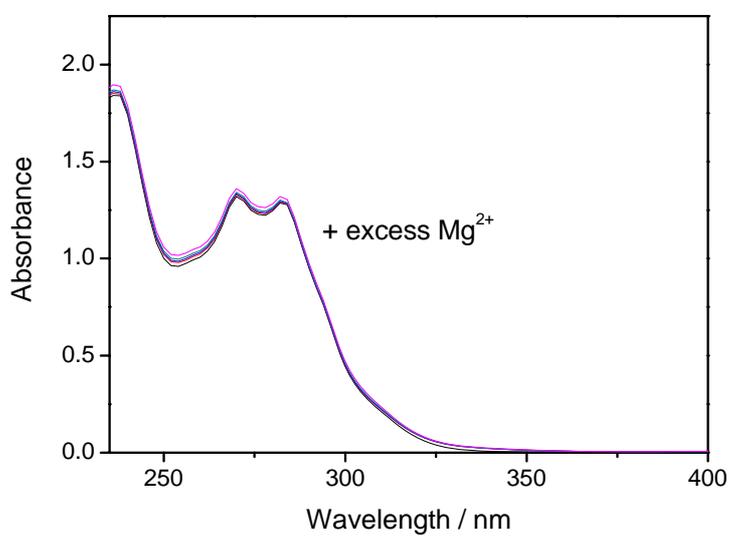


Figure S2 UV-Vis spectral changes of complex **3** (1.8×10^{-5} M) in CH_2Cl_2 -MeOH (1:1 v/v, containing 0.1 M $n\text{Bu}_4\text{NPF}_6$) in the presence of a large excess of $\text{Mg}(\text{ClO}_4)_2$

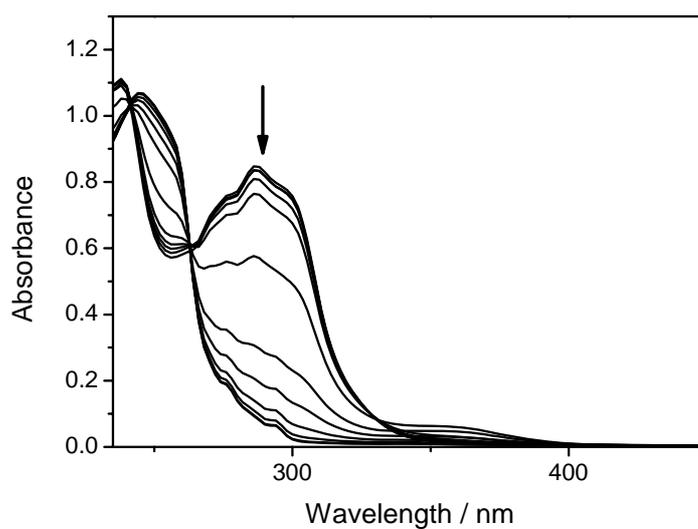


Figure S3 UV-Vis spectral changes of complex **2** (1.4×10^{-5} M) in CH_2Cl_2 -MeOH (1:1 v/v, containing 0.1 M $n\text{Bu}_4\text{NPF}_6$) upon addition of $\text{Mg}(\text{ClO}_4)_2$

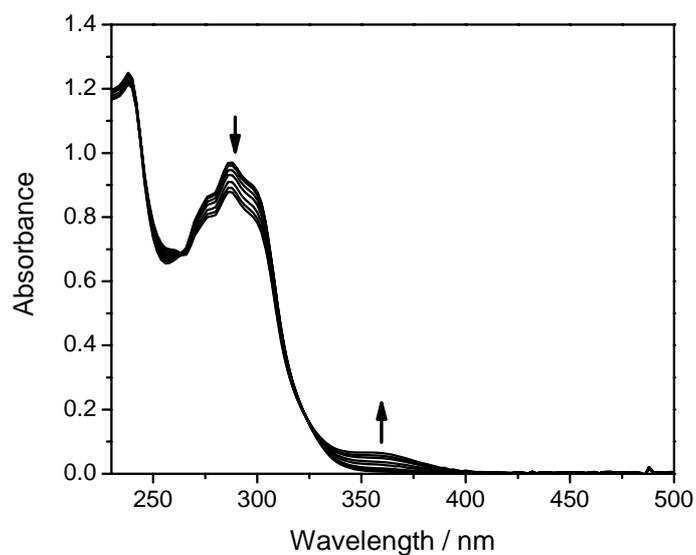


Figure S4 UV-Vis spectral changes of complex **1** (1.5×10^{-5} M) in CH_2Cl_2 -MeOH (1:1 v/v, containing 0.1 M $n\text{Bu}_4\text{NPF}_6$) upon addition of $\text{Ca}(\text{ClO}_4)_2$