# Electronic Supplementary Information

## Calixarene-based alkynyl-bridged gold(I) isocyanide and phosphine complexes as building motif for the construction of chemosensors and supramolecular architecture

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## X-ray Crystallography

A yellow crystal of dimensions 0.30 x 0.15 x 0.05 mm mounted in a glass capillary was used for data collection at 28°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized *Mo-Ka* radiation (A = 0.71073 Å). Data collection was made with 2° oscillation step of φ, 15 minutes exposure time and scanner distance at 120 mm. 90 images were collected. Gold and phosphorus atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were located by Fourier map after successful refinement by full-matrix least-squares using program SHELXL-97[1] on PC. One of the two phenyl rings on P(2) was disordered. The phenyl rings on P(2) were restrained to the normal phenyl rings. Two of the four tertiary butyl groups were disordered and each into two sets of positions. For convergence, restraints for similar C-C bond lengths and related distances were applied for the disordered tert-butyl groups. Four $CH_2CI_2$ solvent molecules were located. For convergence, similar C-Cl bond lengths were applied within each solvent molecule. According to the SHELXL-97 program,[1] all 7816 independent reflections ($R_{int}^{97}$ = 0.0464, 4418 reflections larger than $4\sigma(F_0)$) from a total 12453 reflections were participated in the full-matrix least squares refinement against $F^2$. These reflections were in the range $-13 \le h \le 13$, $-14 \le k \le 13$, $-34 \le l \le 32$ with $2\theta_{max}$ equal to 50.60°. One crystallographic asymmetric unit consists of one half of the formula unit, including four $CH_2Cl_2$ solvent molecules (eight solvent molecules in one formula unit!). In the final stage of least-squares refinement, only Au and P atoms were refined anisotropically and the other non-H atoms isotropically. H atoms were generated by program SHELXL-97.[1] 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-indices. $(\Delta/\sigma)_{max}$ = 0.001, av. 0.001 for 421 variable parameters by full-matrix least-squares refinement on $F^2$ reaches to $R_1$ =

0.0751 and $wR_2 = 0.2182$ with a goodness-of-fit of 0.970，the parameters a and *b* for weighting scheme are 0.1587 and 0.0. The final difference Fourier map shows maximum rest peaks and holes of 1.567 and −1.045 $eA^{-3}$, respectively

**Table S1** Crystal and structure determination data for complex **5**

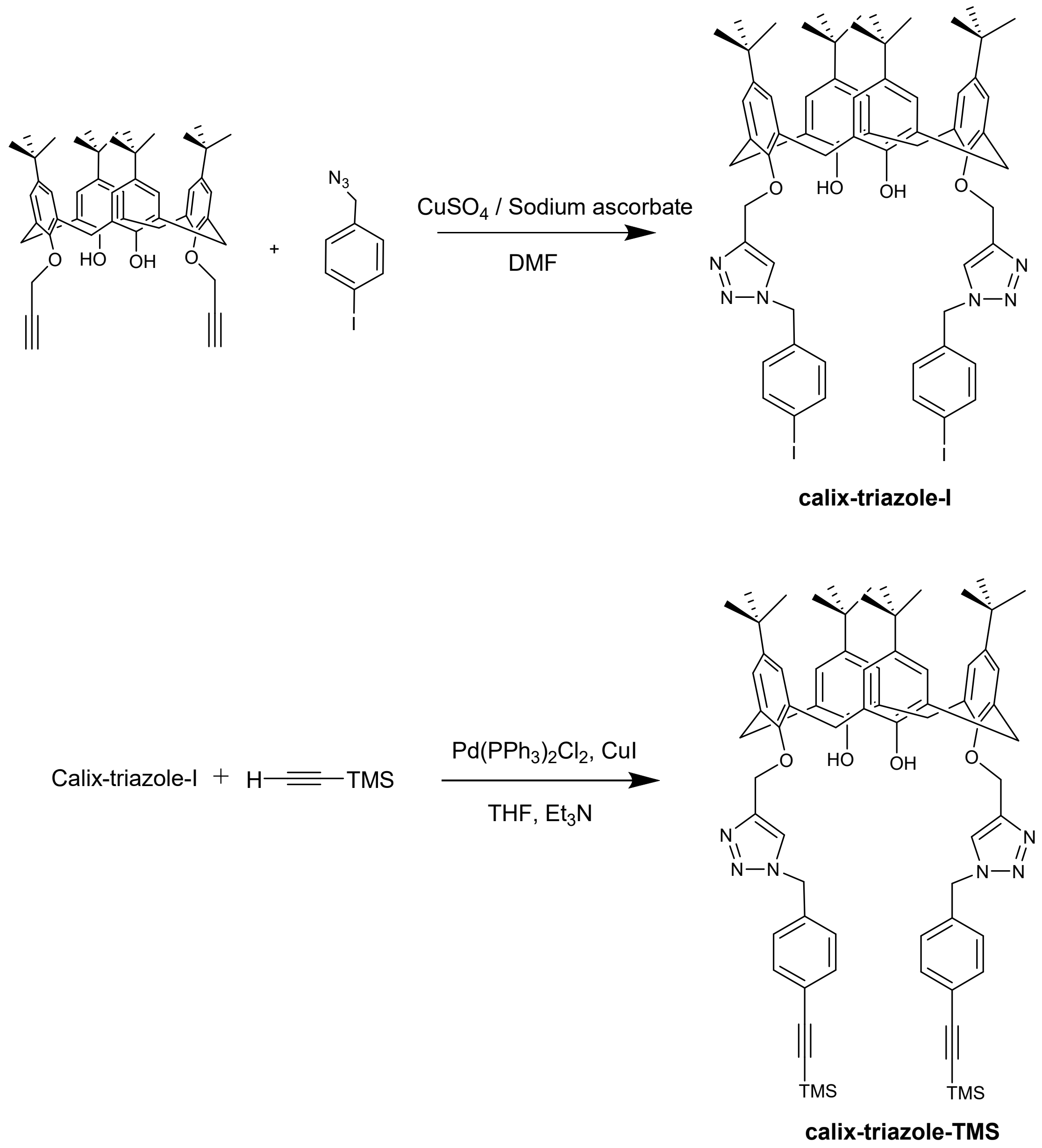
| | |
|---|---|
| Empirical formula | $C_{154}H_{162}Au_4O_8P_4\cdot8CH_2Cl_2$ |
| Formula weight | 3727.96 |
| Temperature | 301(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Trigonal |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a$ = 12.983(3) Å $\alpha$ = 81.31(3)° |
| | $b$ = 13.401(3) Å $\beta$ = 77.62(3)° |
| | $c$ = 29.220(6) Å $\gamma$ = 61.97(3)° |
| Volume | 4375.7(15) Å$^3$ |
| Z | 1 |
| Density (calculated) | 1.415 g cm$^{-3}$ |
| Absorption coefficient | 36.73 cm$^{-1}$ |
| $F$(000) | 1858 |
| Crystal size | 0.30 mm × 0.15 mm × 0.05 mm |
| Index ranges | $-13 \le h \le 13$, $-14 \le k \le 13$, $-34 \le l \le 32$ |
| Reflections collected | 12453 |
| Independent reflections | 4042 [$R_{\text{int}}$ = 0.0883] |
| Goodness-of-fit on $F^2$ | 0.970 |
| Final $R$ indices [$I > 2\sigma(I)$][a] | $R_1$ = 0.0751, $wR_2$ = 0.2182 |
| Largest diff. peak and hole | 1.567 and −1.045 eA$^{-3}$ |

[a] $w = 1/[\sigma^2(F_o^2) + (0.1587P)^2]$, where $P$ is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

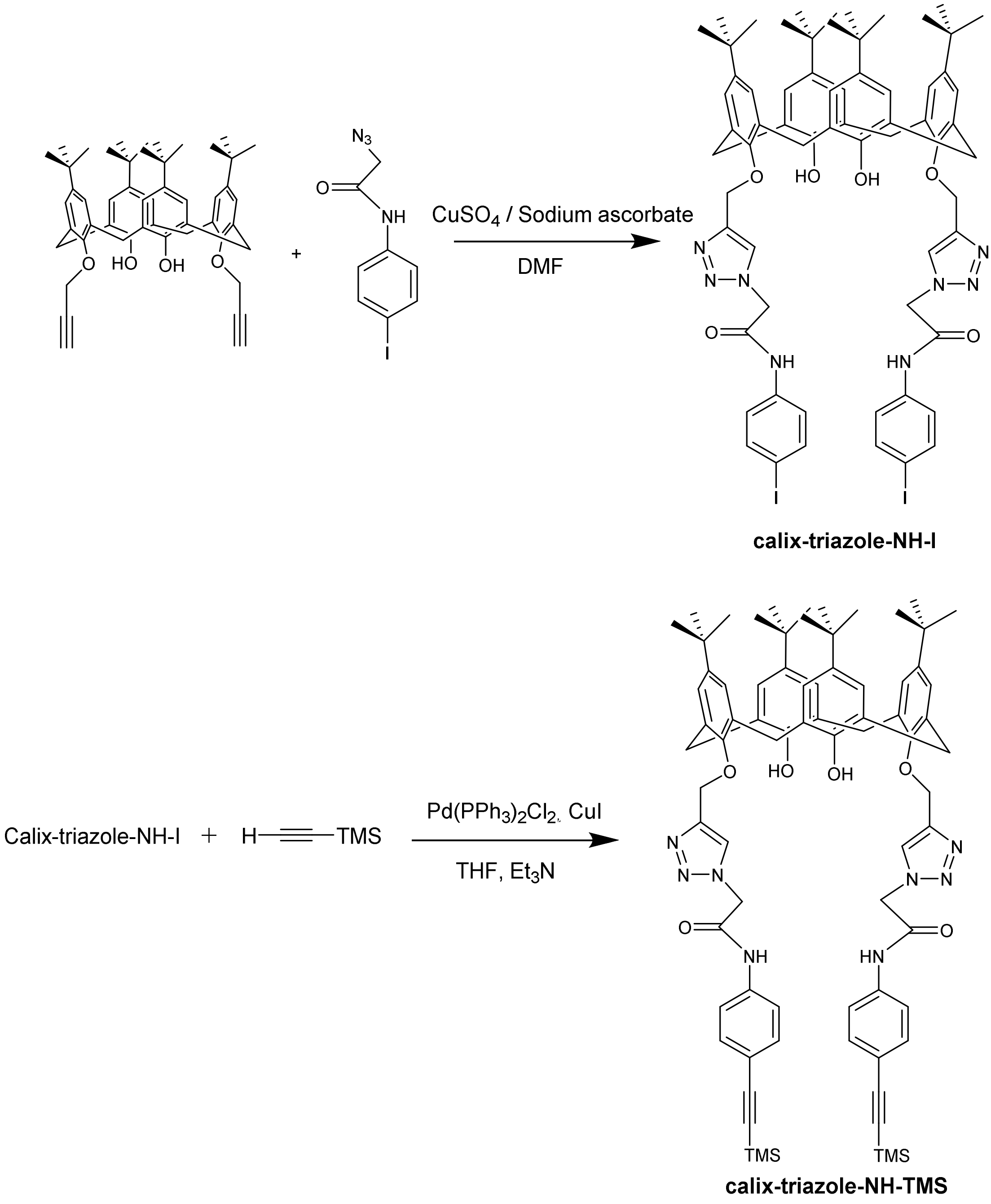
**Table S2** Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **5**

| Bond lengths (Å) | | | |
|---|---|---|---|
| Au(1)–P(1) | 2.274(6) | Au(2)–P(2) | 2.275(5) |
| Au(1)–C(28) | 2.02(2) | Au(2)–C(60) | 2.06(2) |
| C(28)–C(29) | 1.18(3) | C(60)–Au(61) | 1.15(3) |
| Au(1)···Au(2) | 3.0064(17) | | |

| Bond angles (°) | | | |
|---|---|---|---|
| P(1)–Au(1)–C(28) | 174.1(6) | P(2)–Au(2)–C(60) | 172.9 |
| Au(1)–C(28)–C(29) | 172(2) | Au(2)–C(60)–C(61) | 175(2) |
| C(28)–C(29)–C(30) | 176(2) | C(60)–C(61)–C(62) | 172(2) |



**Scheme S1**. Synthetic route of triazole-containing ligands, calix[4]arene-(OCH$_2$-triazolyl-CH$_2$-C$_6$H$_4$C≡CTMS)$_2$



**Scheme S2**. Synthetic route of triazole-containing ligands, calix[4]arene-(OCH$_2$-triazolyl-CH$_2$CONH-C$_6$H$_4$C≡CTMS)$_2$

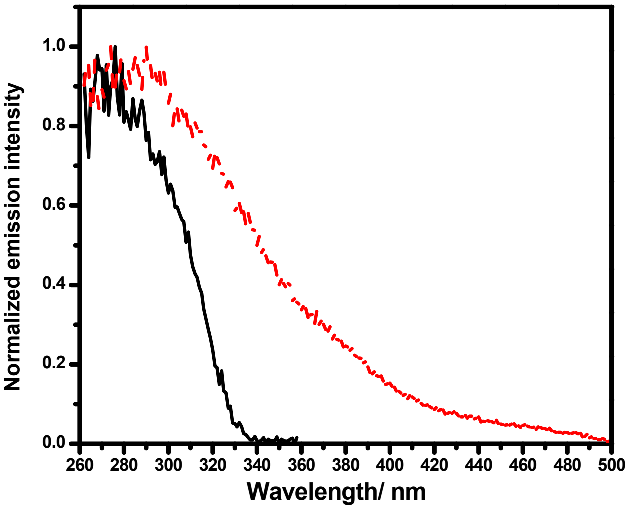


**Figure S1** Excitation spectra of **1** (1.29 ×10$^{-5}$ M) in the absence (—— ) and in the presence (----) of Zn$^{2+}$ (1.29 ×10$^{-3}$ M) monitored at 476 nm and 630 nm, respectively

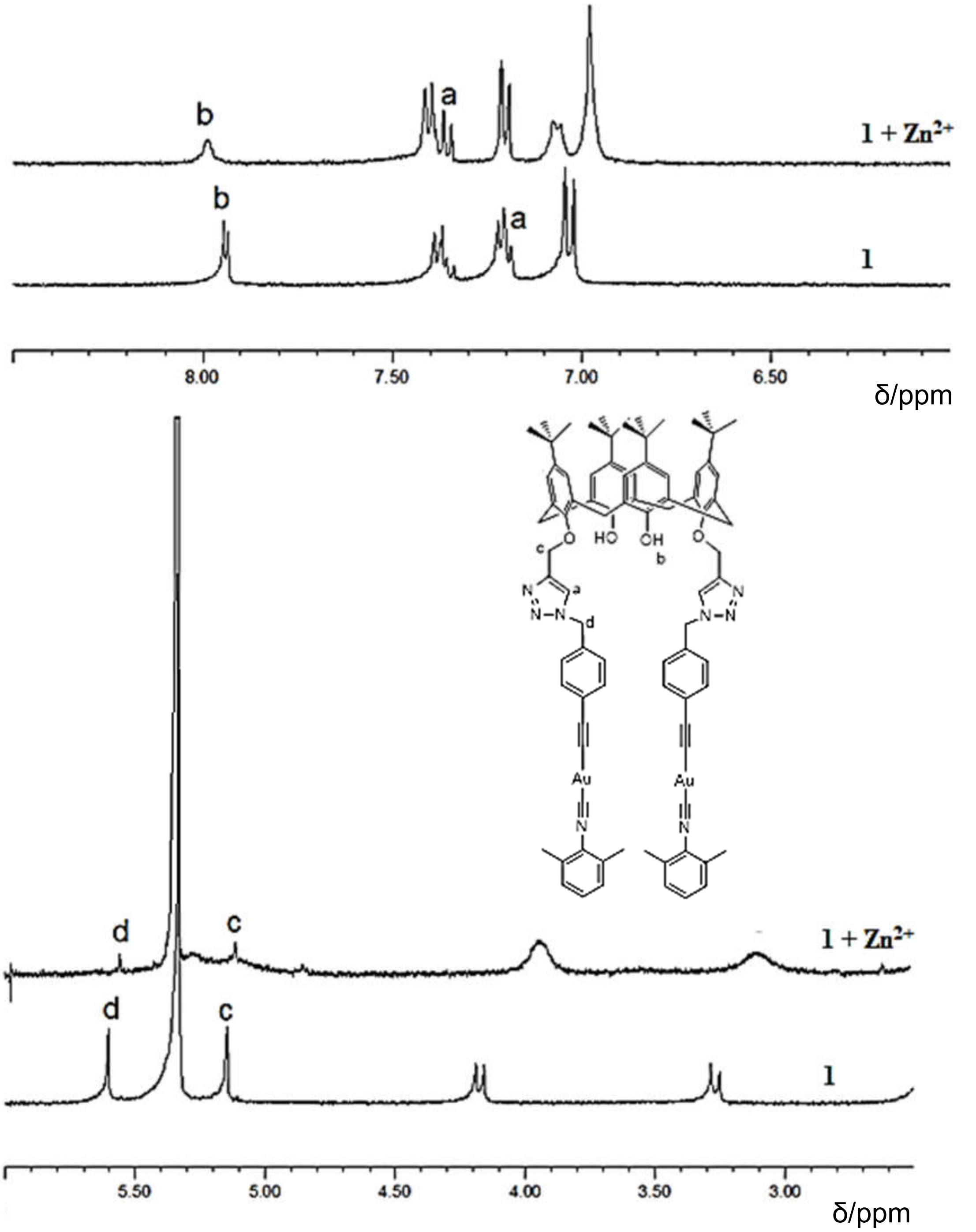


**Figure S2** $^1$H NMR spectral changes of **1** (1.26 mM) upon addition of 5 equiv of $Zn^{2+}$ in $CD_2Cl_2$-$CD_3CN$ (1:1 v/v)

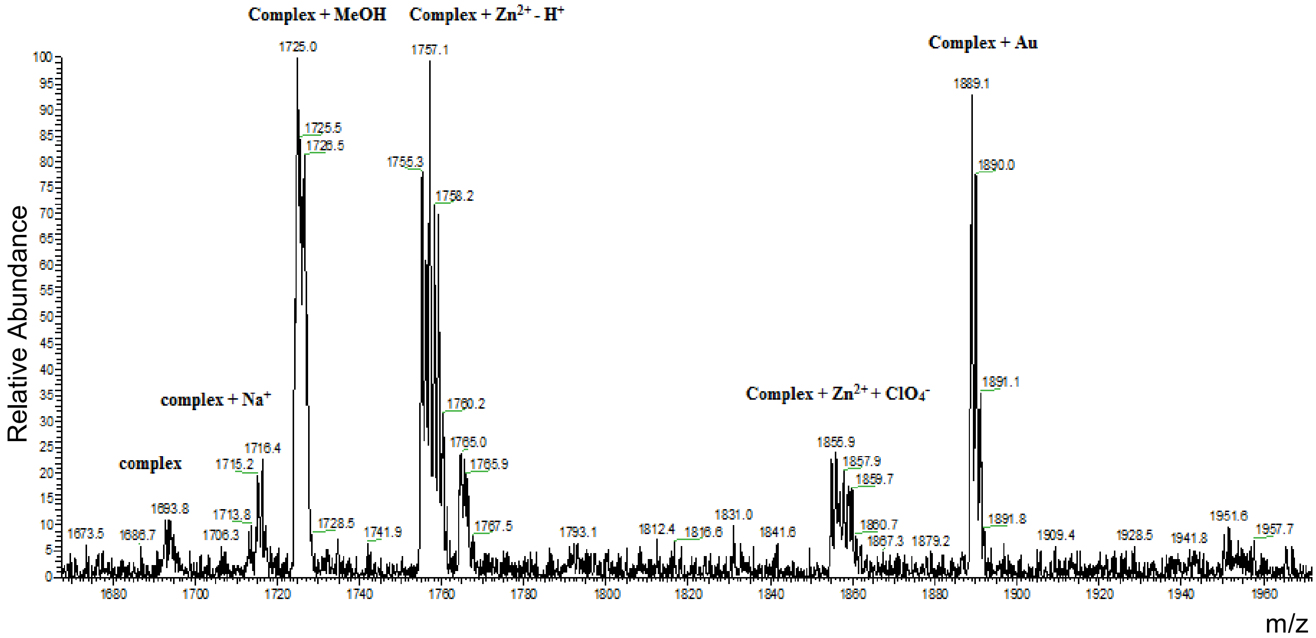


**Figure S3** Positive ESI-mass spectrum of a $CH_2Cl_2$ solution of complex **1** and 1 equiv. of $Zn^{2+}$

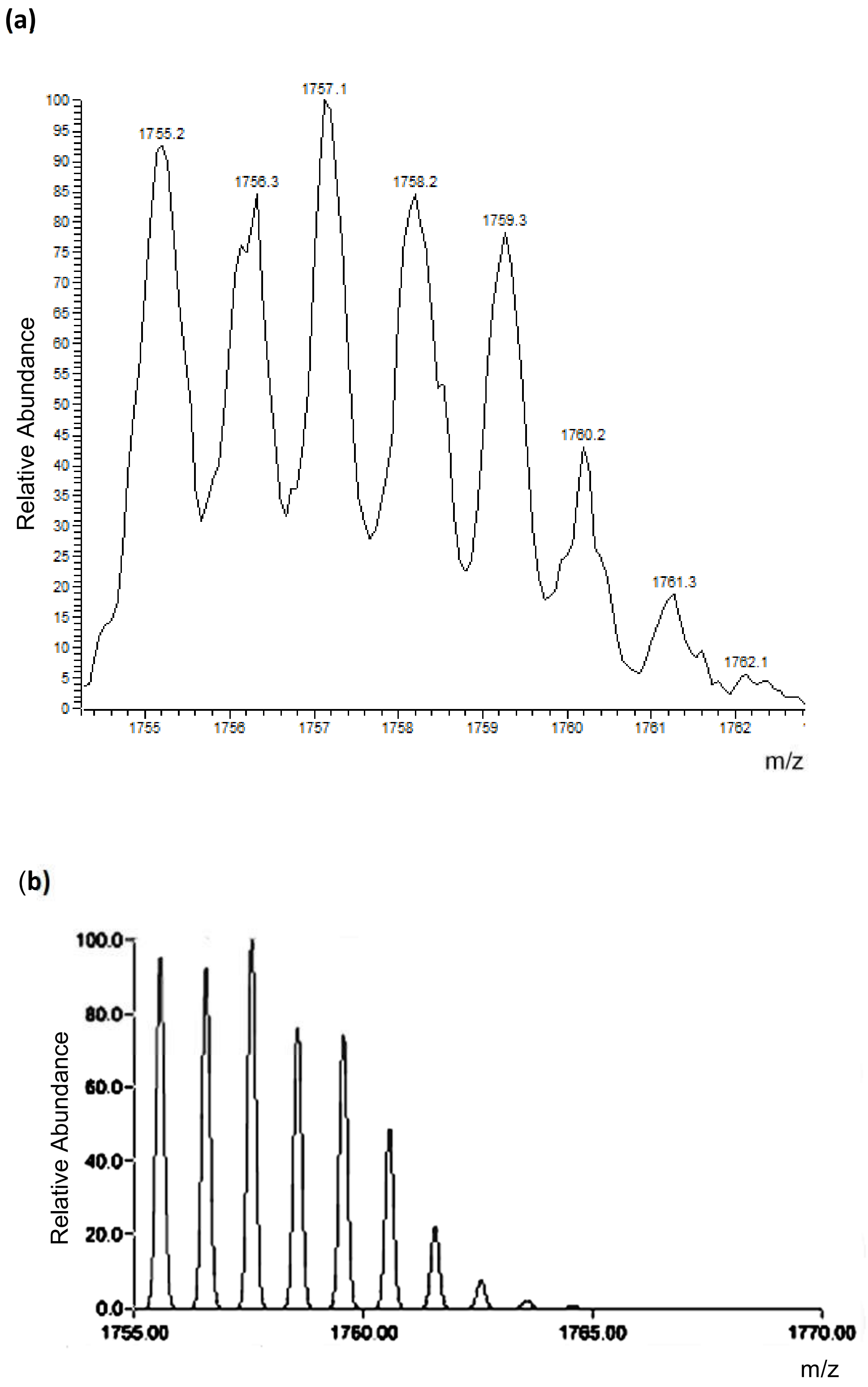


**Figure S4** Expanded ion clusters of (a) $[\mathbf{1}\cdot\mathrm{Zn}^{2+}–\mathrm{H}^{+}]^{+}$ at m/z 1757 from the positive ESI-mass spectrum and (b) simulated isotope pattern for $[\mathbf{1}\cdot\mathrm{Zn}^{2+}–\mathrm{H}^{+}]^{+}$

## References

1. SHELXL-97 / SHELXS-97, Sheldrick GM (1997) SHELX97 *Programs for Crystal Structure Analysis (Release 97-2)*. University of Göttingen, Germany.