Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## Chiral metal nanoparticles encapsulated by chiral phosphine cavitand with tetrakis-BINAP moiety: their remarkable stability toward ligand exchange and thermal racemization

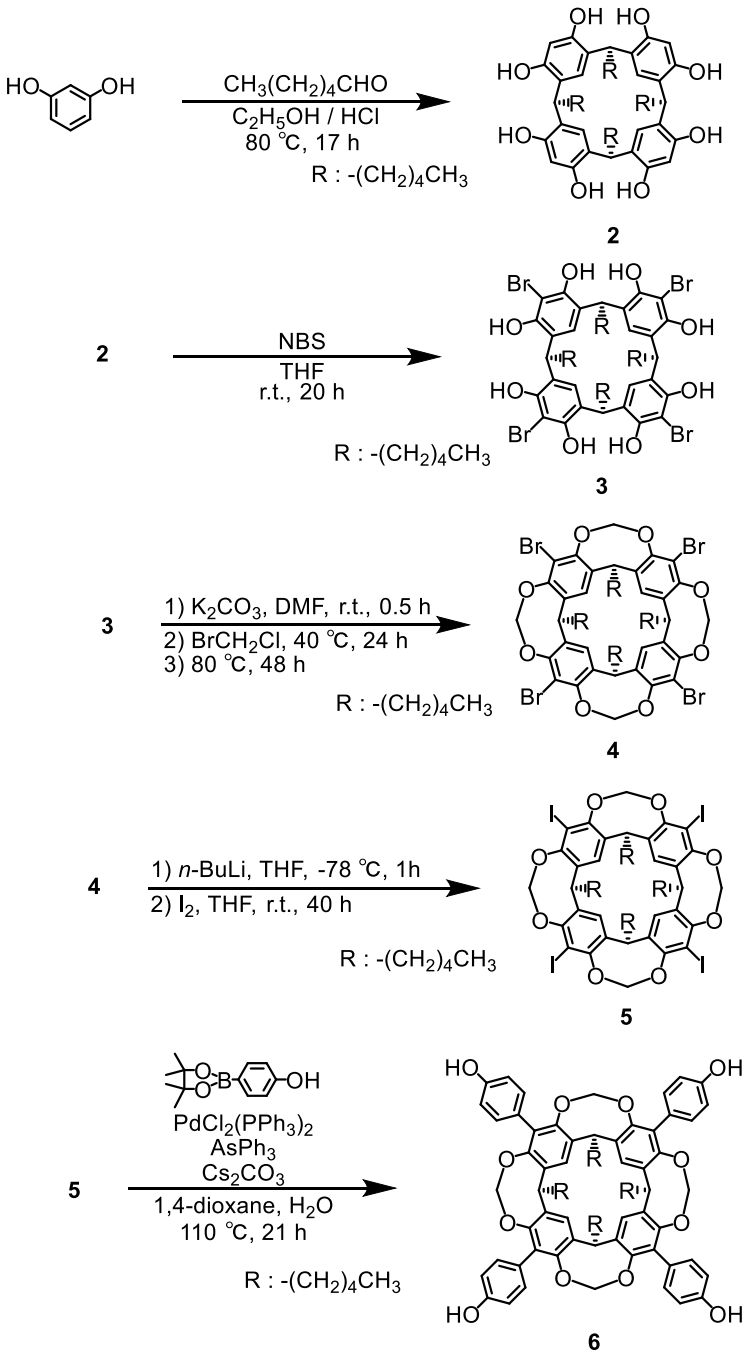
Ryo Nishimura, Ryo Yasutake, Shota Yamada, Koji Sawai, Kazuki Noura, Tsukasa Nakahodo and Hisashi Fujihara*

*Department of Applied Chemistry, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan*

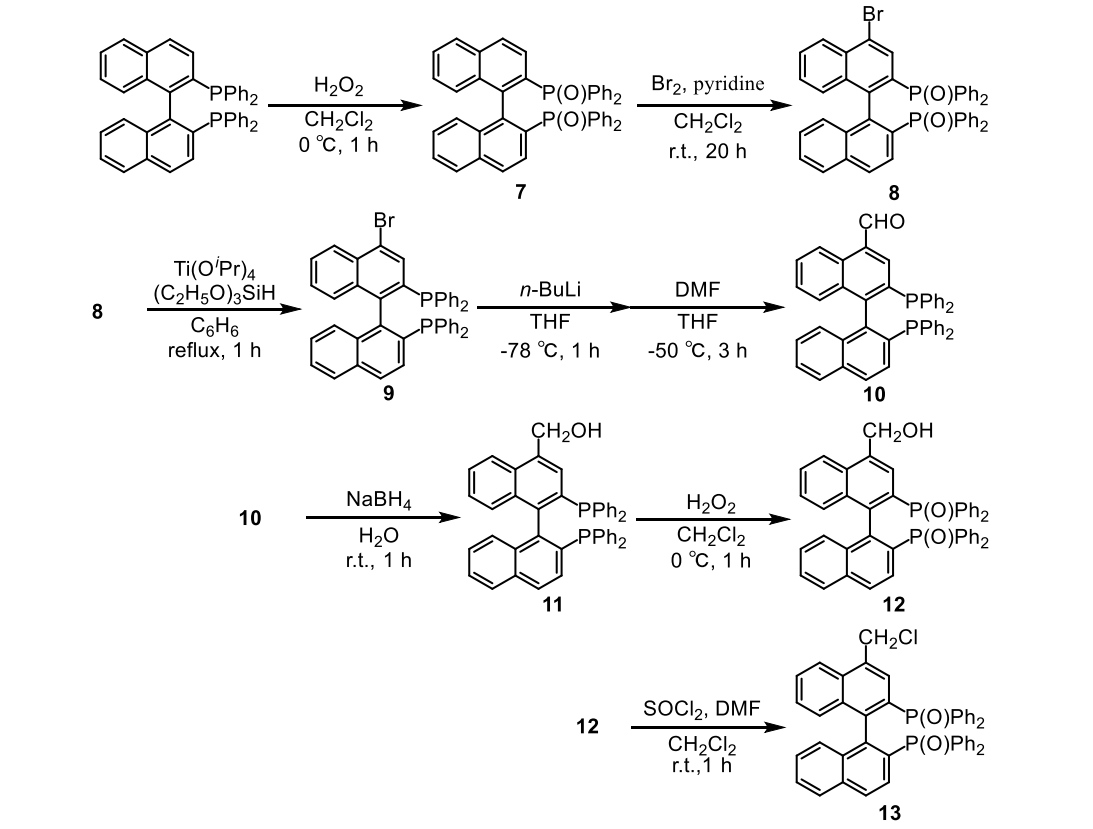
1) Synthesis of **1** and **1**-P=O.
2) Synthesis of metal nanoparticles (NPs).
3) Figures S1-S10.

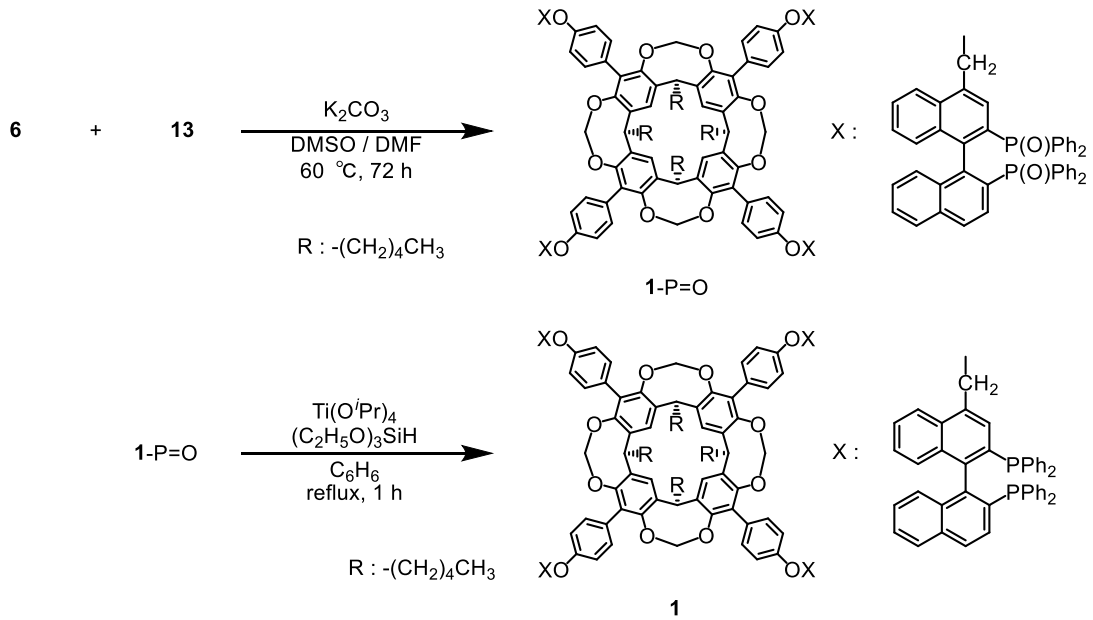
**(1) Synthesis of 1 and 1-P=O.**

Phosphine **1** and the corresponding phosphine-oxide **1**-P=O were synthesized according to Schemes S1 and S2.




**Scheme S1**


PPh2
PPh2
H2O2
CH2Cl2
0 ℃, 1 h
P(O)Ph2
P(O)Ph2
7
Br2, pyridine
CH2Cl2
r.t., 20 h
Br
8
Ti(OiPr)4
(C2H5O)3SiH
C6H6
reflux, 1 h
9
n-BuLi
THF
-78 ℃, 1 h
DMF
THF
-50 ℃, 3 h
CHO
10
NaBH4
H2O
r.t., 1 h
CH2OH
11
12
SOCl2, DMF
CH2Cl2
r.t.,1 h
CH2Cl
13


6
13
K2CO3
DMSO / DMF
60 ℃, 72 h
R : -(CH2)4CH3
XO
OX
R
R'
X :
CH2
P(O)Ph2
1-P=O
Ti(OiPr)4
(C2H5O)3SiH
C6H6
reflux, 1 h
PPh2
1

**Scheme S2**

**6**: FT-IR ($cm^{-1}$, KBr) 3448 (O-H); $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 0.90 (t, 12H, -$CH_3$), 1.29-1.45 (m, 24H, -(C$H_2$)$_3$-$CH_3$), 2.45 (m, 8H, -C$H_2$-($CH_2$)$_3$-$CH_3$), 4.24 (d, 4H, -OC$H_2$O-), 4.66 (t, 4H, -C*H*-), 5.17 (d, 4H, -OC$H_2$O-), 6.68 (d, 8H, Ar-H), 6.84 (d, 8H, Ar-H), 7.70 (s, 4H, Ar-H); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 14.0 (-($CH_2$)$_4$-*C*$H_3$), 22.3, 27.4, 29.6, 31.5 (-(*C*$H_2$)$_4$-$CH_3$), 37.2 (-*C*H-), 99.7 (-O*C*$H_2$O-), 114.6, 120.9, 123.6, 129.0, 131.1, 138.0, 152.0, 156.2 (Ar); MS (FAB) *m/z* 1186 ($MH^+$).

**13**: FT-IR ($cm^{-1}$, KBr) 1437 (P-Ph), 1199 (P=O); $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 4.82, (d, 1H, -C$H_2$-Cl), 5.19 (d, 1H, -C$H_2$-Cl), 6.79-6.87 (m, 4H, Ar-H), 7.22-7.48 (m, 20H, Ar-H), 7.65-7.72 (m, 4H, Ar-H), 7.79-7.86 (m, 2H, Ar-H), 8.11 (d, 1H, Ar-H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 44.7 ($CH_2Cl$), 123.4, 125.9, 127.1, 127.2, 127.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 129.5, 129.7, 130.9, 131.0, 131.2, 131.3, 131.8, 131.9, 132.0, 132.4, 132.5, 133.8, 134.0, 134.7, 134.9 (Ar); MS (FAB) *m/z* 703 ($M^+$).

**1**-P=O: FT-IR ($cm^{-1}$, KBr) 1437 (P-Ph), 1207 (P=O); $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 12H, -$CH_3$), 1.42-1.49 (m, 24H, -(*C*$H_2$)$_3$-$CH_3$), 2.37 (m, 8H, -C$H_2$-($CH_2$)$_3$-$CH_3$), 4.33 (d, 4H, -OC$H_2$O-), 4.90 (t, 4H, -C*H*-($CH_2$)$_4$-), 5.21 (d, 4H, -C$H_2$O-), 5.37 (d, 4H, -OC$H_2$O-), 5.55 (d, 4H, -C$H_2$O-), 6.75-7.99 (m, Ar-H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 14.2 (-$CH_3$), 22.7, 27.7, 30.5, 32.1, 37.2, 68.8 (-*C*$H_2$-), 100.7 (-O*C*$H_2$O-), 114.2, 119.6, 123.6, 125.8, 126.5, 127.2, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.8, 130.0, 130.8, 131.0, 131.2, 131.3, 131.8, 131.9, 132.0, 132.2, 132.3, 132.4, 132.5, 133.1, 133.2, 133.3, 133.5, 133.7, 133.8, 133.9, 134.6, 134.8, 148.9, 152.8, 154.2, 157.8 (Ar); $^{31}$P-NMR (202 MHz, $CDCl_3$) δ 28.6, 29.2 [$^{31}$P-NMR of the phosphine-oxide of BINAP ($CDCl_3$) δ 28.9]; MS (FAB) *m/z* 3852 ($M^+$).

**1**: FT-IR ($cm^{-1}$, KBr) 1433 (P-Ph); $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 12H, -$CH_3$), 1.38-1.47 (m, 24H, -(C$H_2$)$_3$-$CH_3$), 2.35 (m, 8H, -C$H_2$-($CH_2$)$_3$-$CH_3$), 4.30 (d, 4H, -OC$H_2$O-), 4.88 (t, 4H, -C*H*-), 5.29 (d, 4H, -C$H_2$O-), 5.34 (d, 4H, -OC$H_2$O-), 5.46 (d, 4H, -C$H_2$O-), 6.60-8.09 (m, Ar-H); $^{31}$P-NMR (202 MHz, $CDCl_3$) δ -15.0, -14.9 [$^{31}$P-NMR of the phosphine of BINAP ($CDCl_3$) δ -14.9].

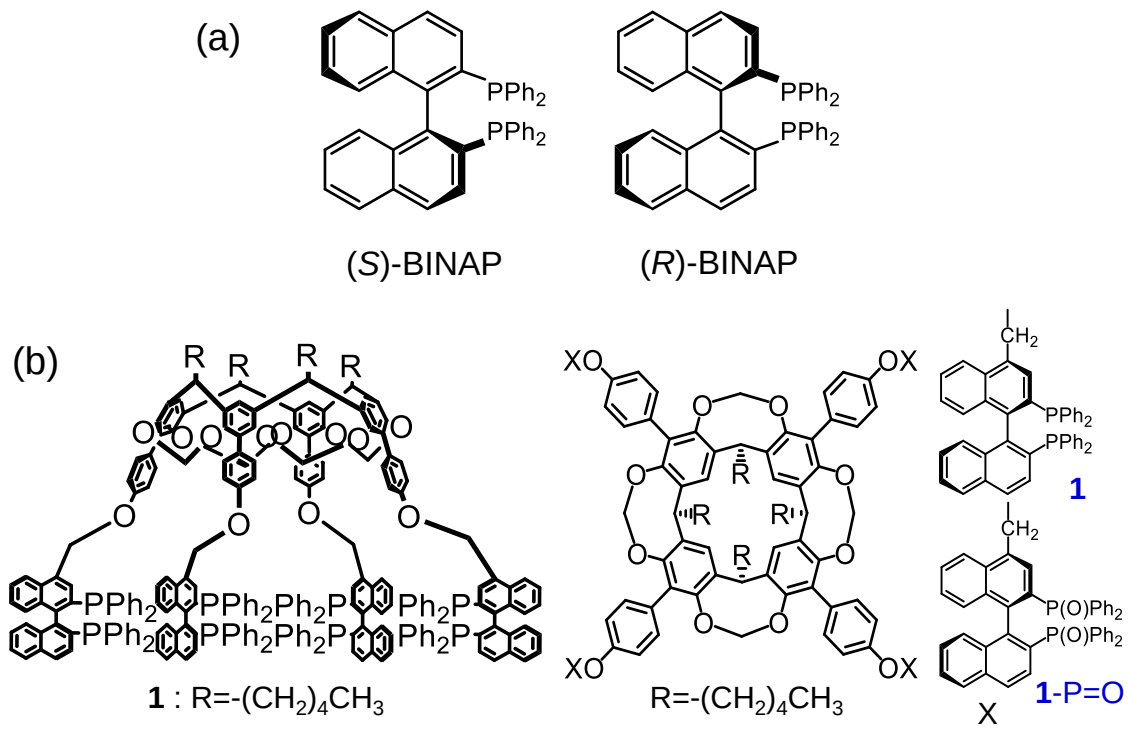



***Chart S1***. Structures of (*R*)-BINAP, (*S*)-BINAP, **1** and **1**-P=O.

**(2) Synthesis of chiral metal NPs**.

The chiral phosphine cavitand **1**-protected gold NPs were prepared as follows. To a vigorously stirred solution of $HAuCl_4 \cdot 4H_2O$ (16 mg, 0.04 mmol) in 7 mL of deionized water under an argon atmosphere was added the chiral phosphine **1** (120 mg, 0.032 mmol) in 30 mL of THF. A solution of $NaBH_4$ (16 mg, 0.43 mmol) in 6 mL of deionized water was added at 0 $^oC$, and the resulting mixture was stirred for 1 h at room temperature under an argon atmosphere. After the reaction, the filtrate was evaporated in vacuo to yield the chiral phosphine cavitand **1**-protected gold NPs (**1**-Au NPs). Purification (dichloromethane-*n*-hexane) of the **1**-Au NPs was repeated until no free phosphine remained, as detected by TLC, $^1H$ and $^{13}C$ NMR spectroscopies. The X-ray photoelectron spectroscopy (XPS) spectrum of the **1**-Au NPs showed the Au 4f binding energies at 84.2 and 87.9 eV, corresponding to the $Au^0$ state. There was a feature at

285 eV due to C 1s and 132 eV due to P 2p. The **1**-Au NPs are remarkably stable both in solution, as well as in the solid state. The number of gold atoms and the ligand in the **1**-protected Au NPs is roughly estimated to be ~21 for gold atoms and ~9 for the ligand. A detailed characterization is currently in progress. The other metal (Ru, Rh, Pd, Ag, and Pt) NPs were prepared by similar methods.

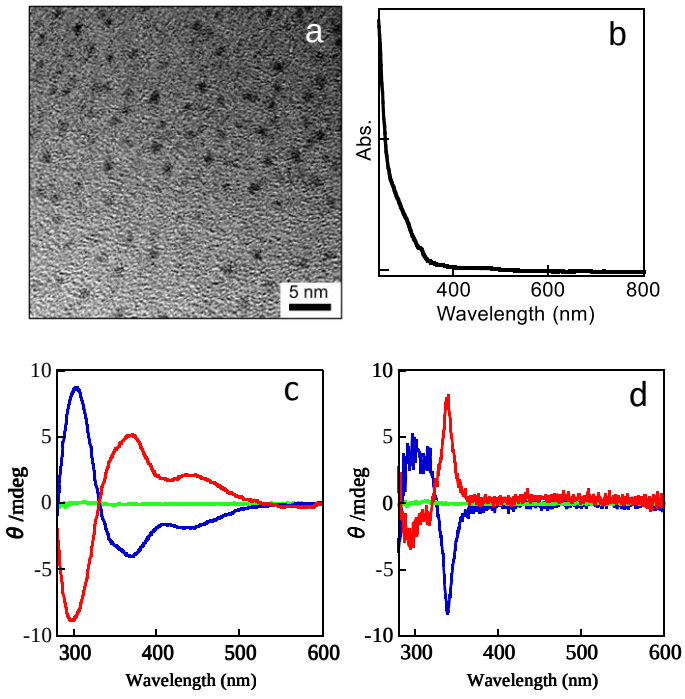



***Figure S1***. a) TEM image of **1**-Au NPs, b) UV-vis spectrum of **1**-Au NPs in $CH_2Cl_2$, c) CD spectrum of **1**-Au NPs in $CHCl_3$, and d) CD spectrum of **1** in $CHCl_3$.

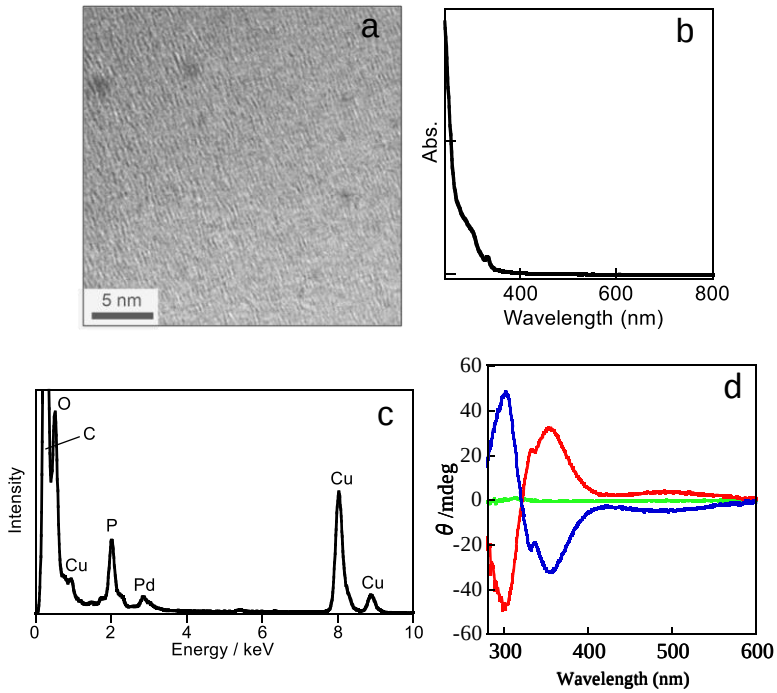



***Figure S2***. **1**-Pd NPs: a) TEM image, b) UV-vis spectrum in $CH_2Cl_2$, c) EDX spectrum. Cu peaks are from the supporting copper grid, and d) CD spectra in $CHCl_3$.

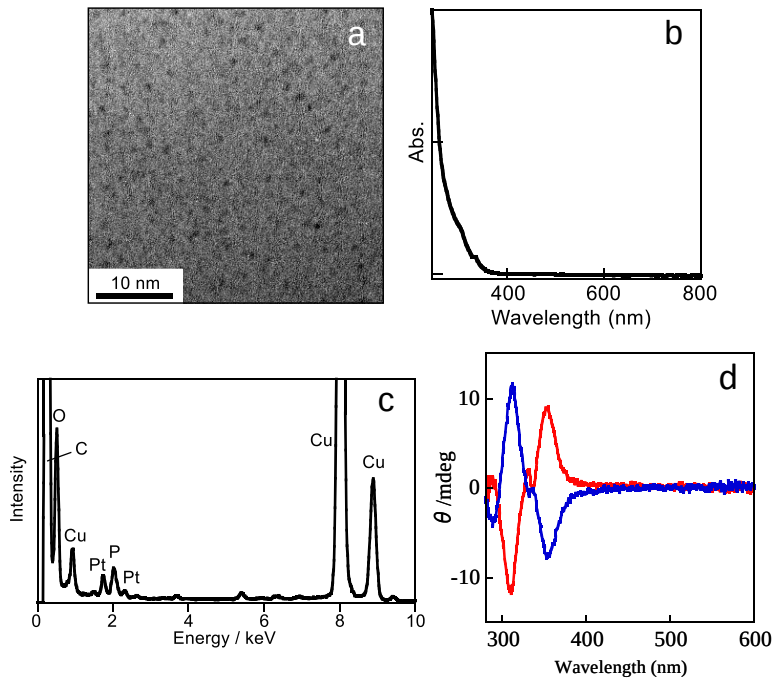



***Figure S3***. **1**-Pt NPs: a) TEM image, b) UV-vis spectrum in $CH_2Cl_2$, c) EDX spectrum. Cu peaks are from the supporting copper grid, and d) CD spectra in $CHCl_3$.

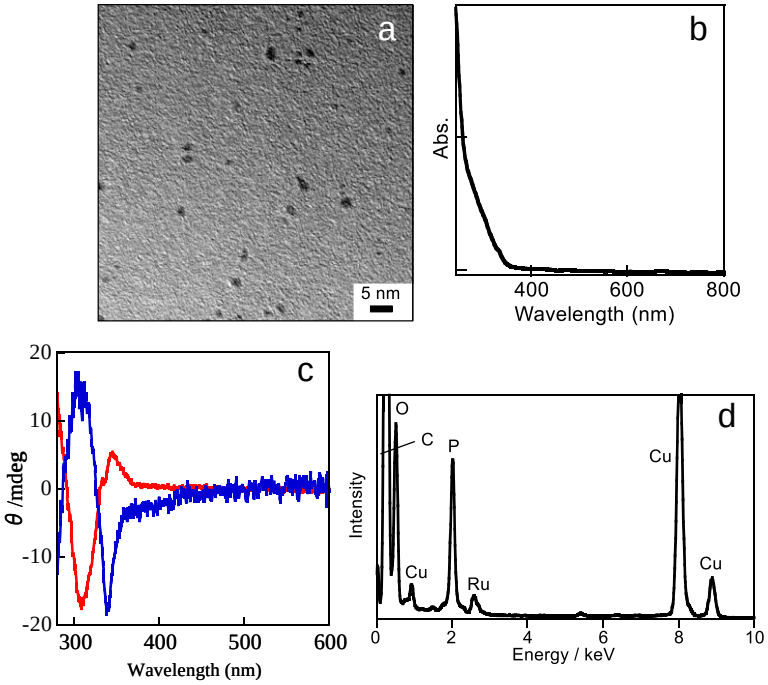



***Figure S4***. **1**-Ru NPs: a) TEM image, b) UV-vis spectrum in $CH_2Cl_2$, c) CD spectra in $CHCl_3$, and d) EDX spectrum. Cu peaks are from the supporting copper grid.

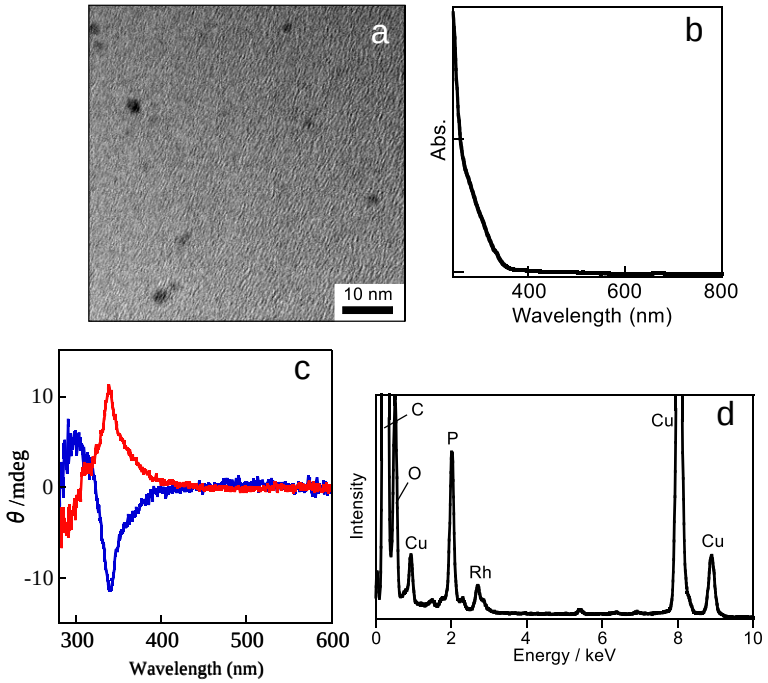



***Figure S5***. **1**-Rh NPs: a) TEM image, b) UV-vis spectrum in $CH_2Cl_2$, c) CD spectra in $CHCl_3$, and d) EDX spectrum. Cu peaks are from the supporting copper grid.

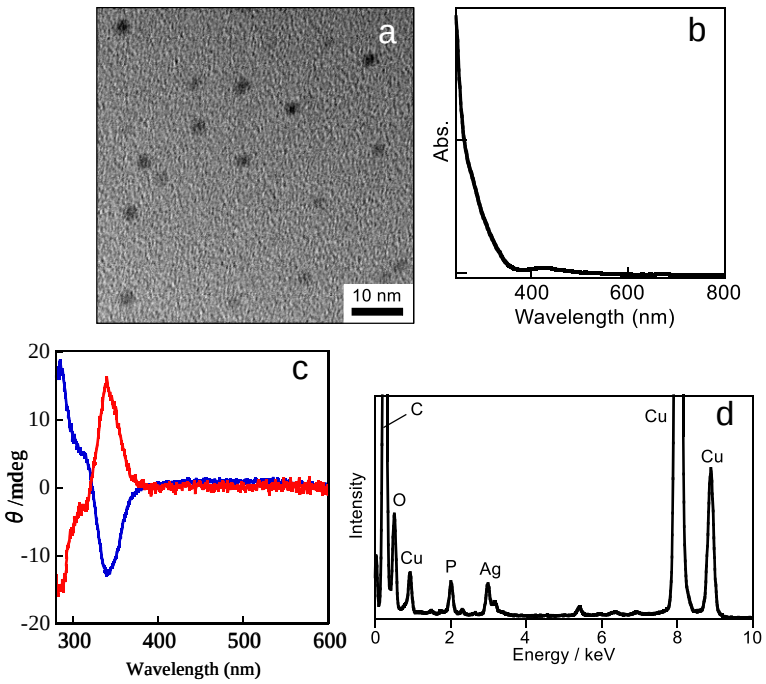



***Figure S6***. **1**-Ag NPs: a) TEM image, b) UV-vis spectrum in $CH_2Cl_2$, c) CD spectra in $CHCl_3$, and d) EDX spectrum. Cu peaks are from the supporting copper grid.

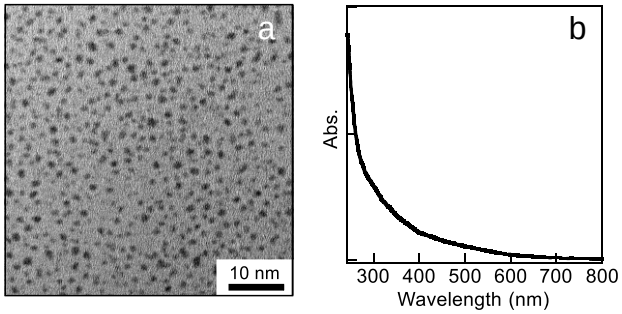



***Figure S7***. $Ph_3P$-Au NPs: a) TEM image (scale bar = 10 nm) and b) UV-vis spectrum ($CH_2Cl_2$).

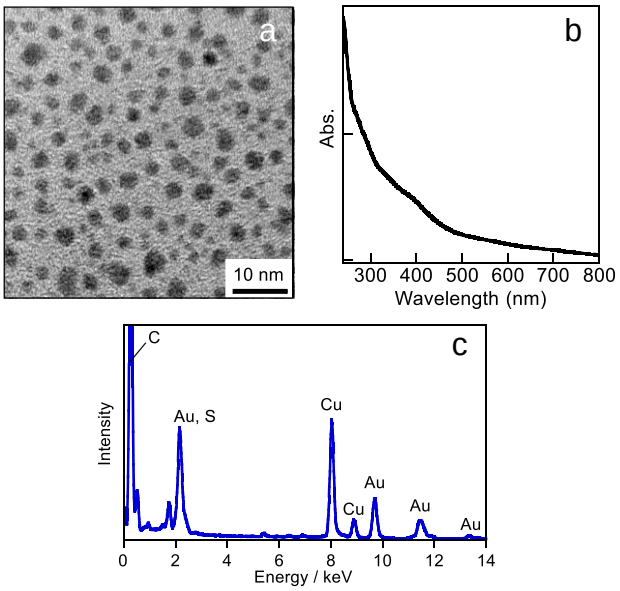



***Figure S8***. *RS-AuNP* formed from the ligand exchange of $Ph_3P$-Au NPs with octanethiol: a) TEM image (scale bar = 10 nm), b) UV-vis spectrum ($CH_2Cl_2$), and c) EDX spectrum. Cu peaks are from the supporting copper grid.

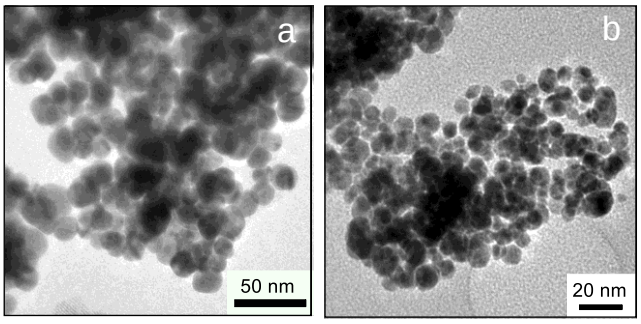



***Figure S9***. TEM images of a): $Ph_3P$-Au NPs after heating (1 h) [scale bar = 50 nm] and b): BINAP-Au NPs after heating (24 h) [scale bar = 20 nm].

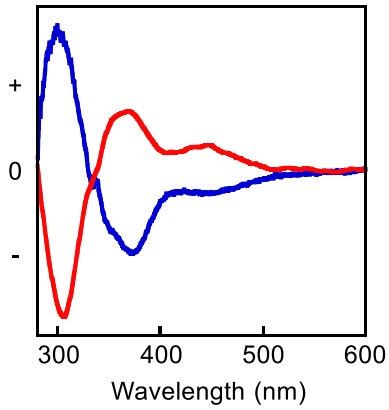



***Figure S10***. CD spectra ($CHCl_3$) of (*R*)-**1**-Au NPs (red line) and (*S*)-**1**-Au NPs (blue line) after heating (24 h).