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CO_2 Reduction

Anchoring of Metal Complexes on Au_{25} Nanocluster for Enhanced Photocoupled Electrocatalytic CO_2 Reduction

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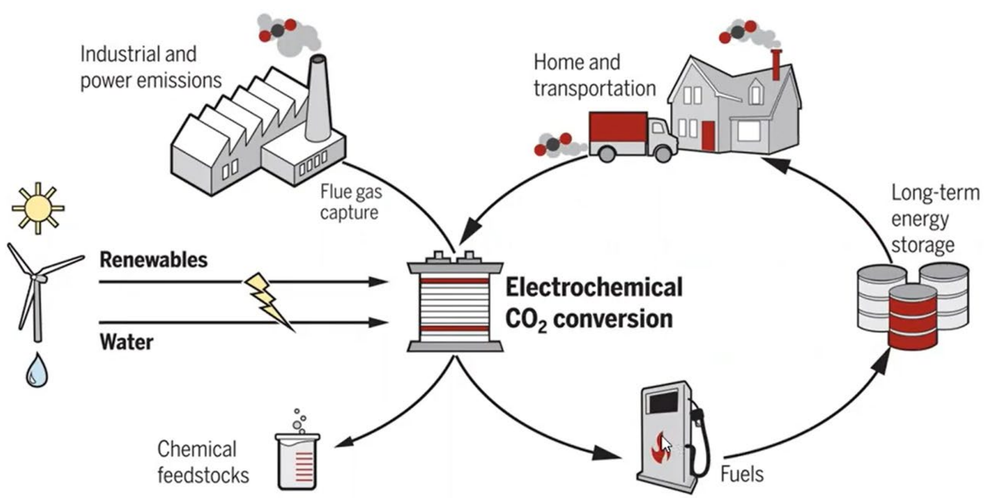

De Luna et al., *Science* 2019, *364*, eaav3506

Anagha Jose
20-07-24

Background

Stable Dioxin-Linked Metallophthalocyanine Covalent Organic Frameworks (COFs) as Photo-Coupled Electrocatalysts for CO_2 Reduction

Meng Lu, Mi Zhang, Prof. Chun-Guang Liu, Dr. Jiang Liu, Lin-Jie Shang, Min Wang, Jia-Nan Chang, Prof. Shun-Li Li, Prof. Ya-Qian Lan

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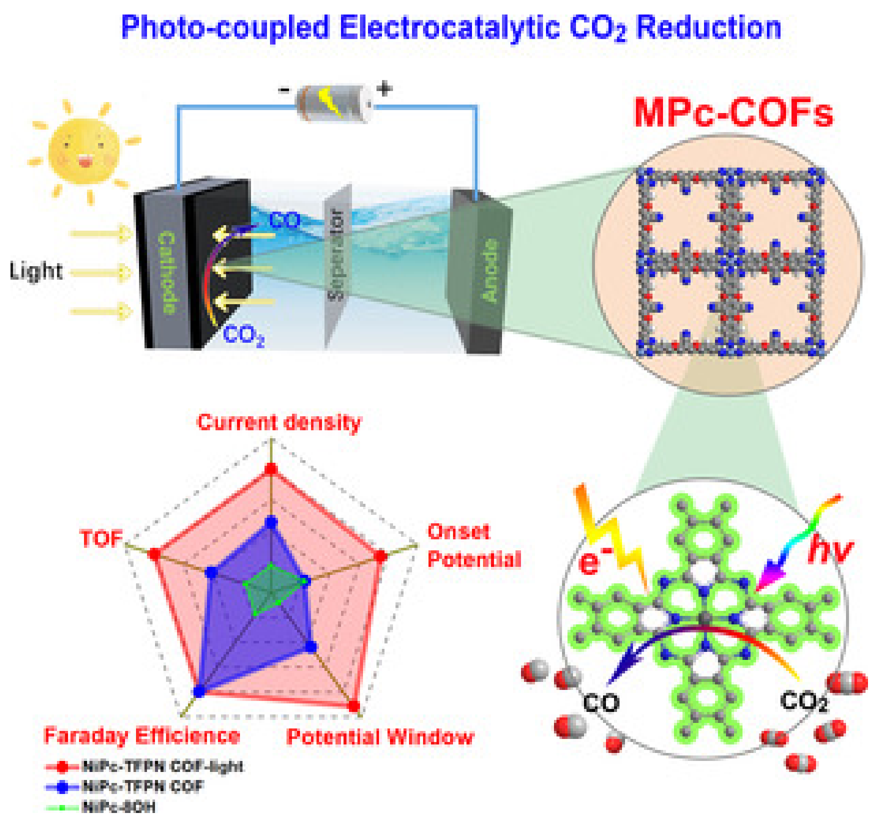

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Engineering ligand chemistry on Au_{25} nanoclusters: from unique ligand addition to precisely controllable ligand exchange†

Jiangtao Zhao,[a] Abolfazl Ziarati, *[a] Arnulf Rosspeintner, [a] Yanan Wang[b] and Thomas Bürgi *[a]

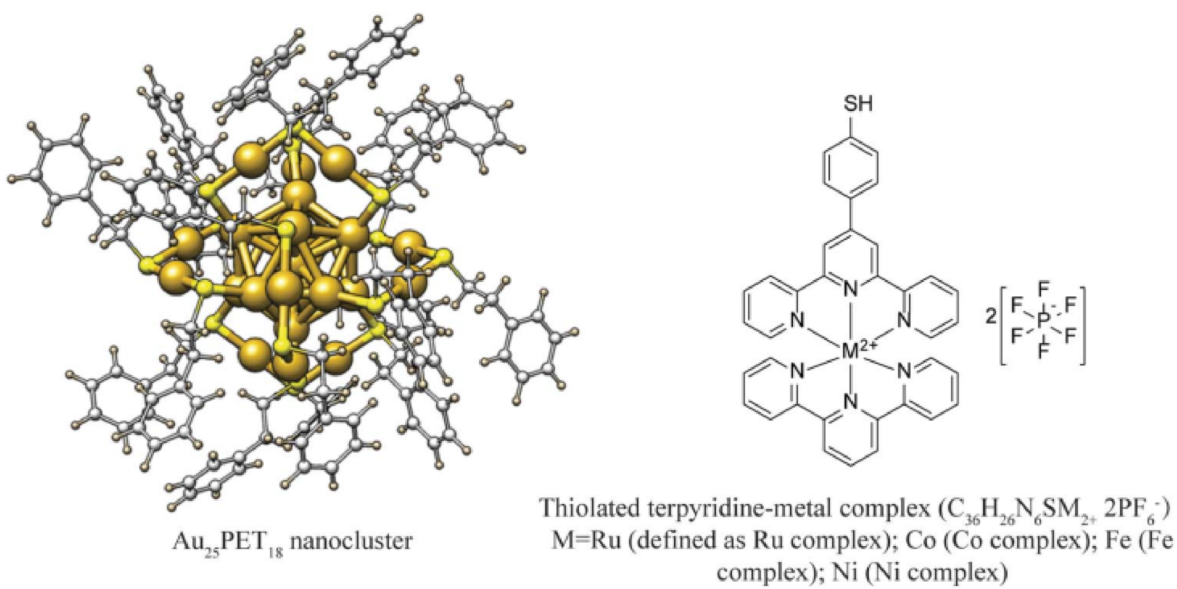
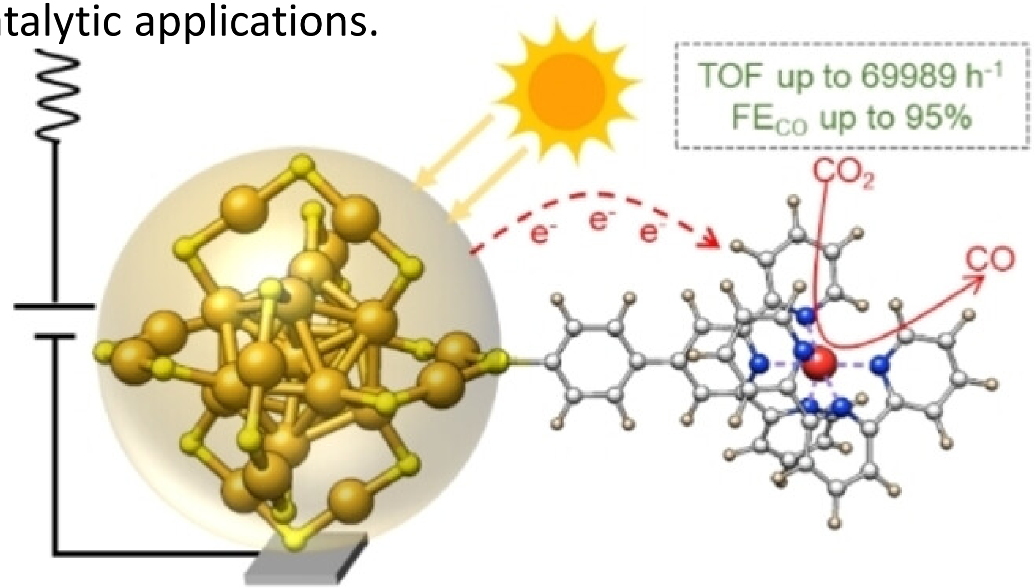


Fig. 1 Schematic diagram of $Au_{25}PET_{18}$ NC and thiolated terpyridine-metal complex (counter ions: $2PF_6^-$).

Why this paper

This work provides a new strategy for designing active and stable NCs for different photo/electrocatalytic applications.



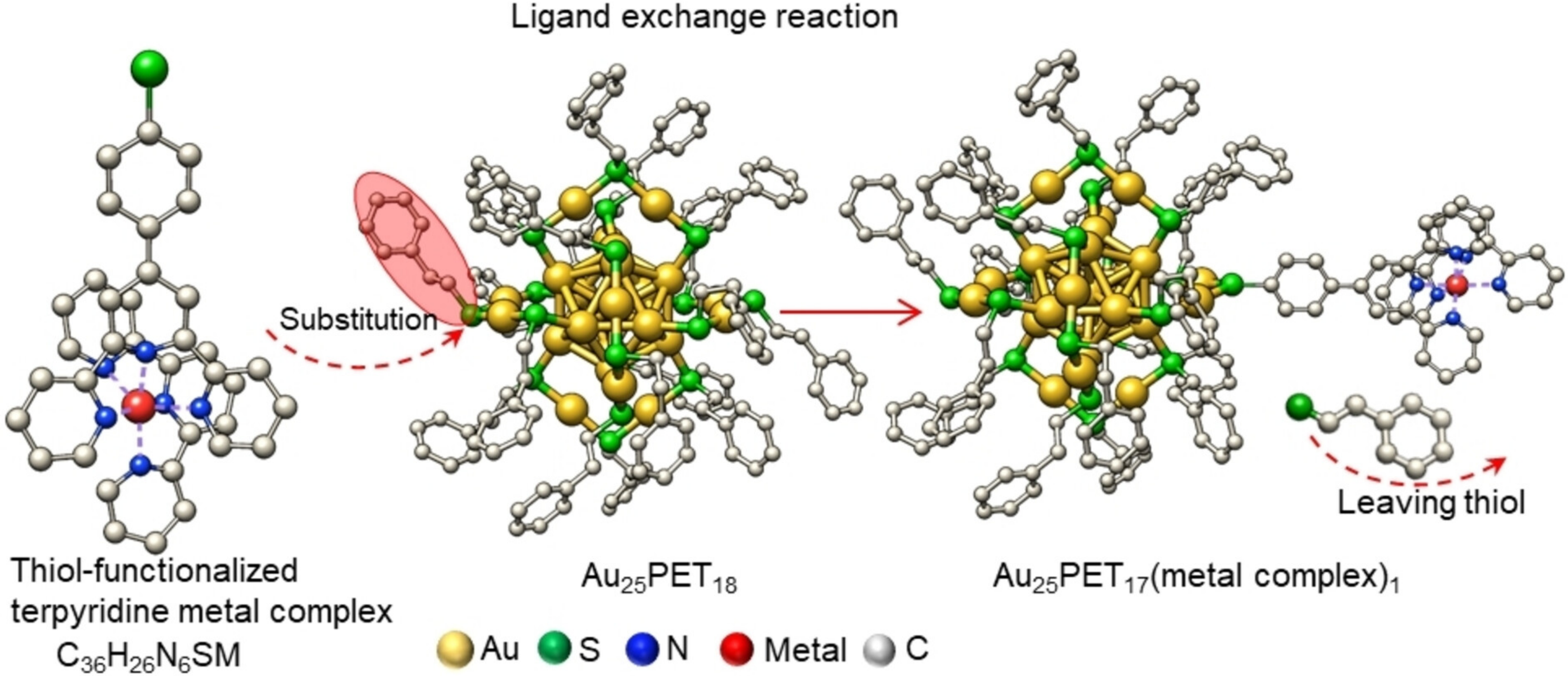
- Atomically precise Au nanoclusters (NCs) with discrete energy levels can be used as photosensitizers for CO_2 reduction.
- However, tight ligand capping of Au NCs hinders CO_2 adsorption on its active sites.
- Here, a new hybrid material is obtained by anchoring of thiol functionalized terpyridine metal complexes (metal=Ru, Ni, Fe, Co) on Au NCs by ligand exchange reactions (LERs).

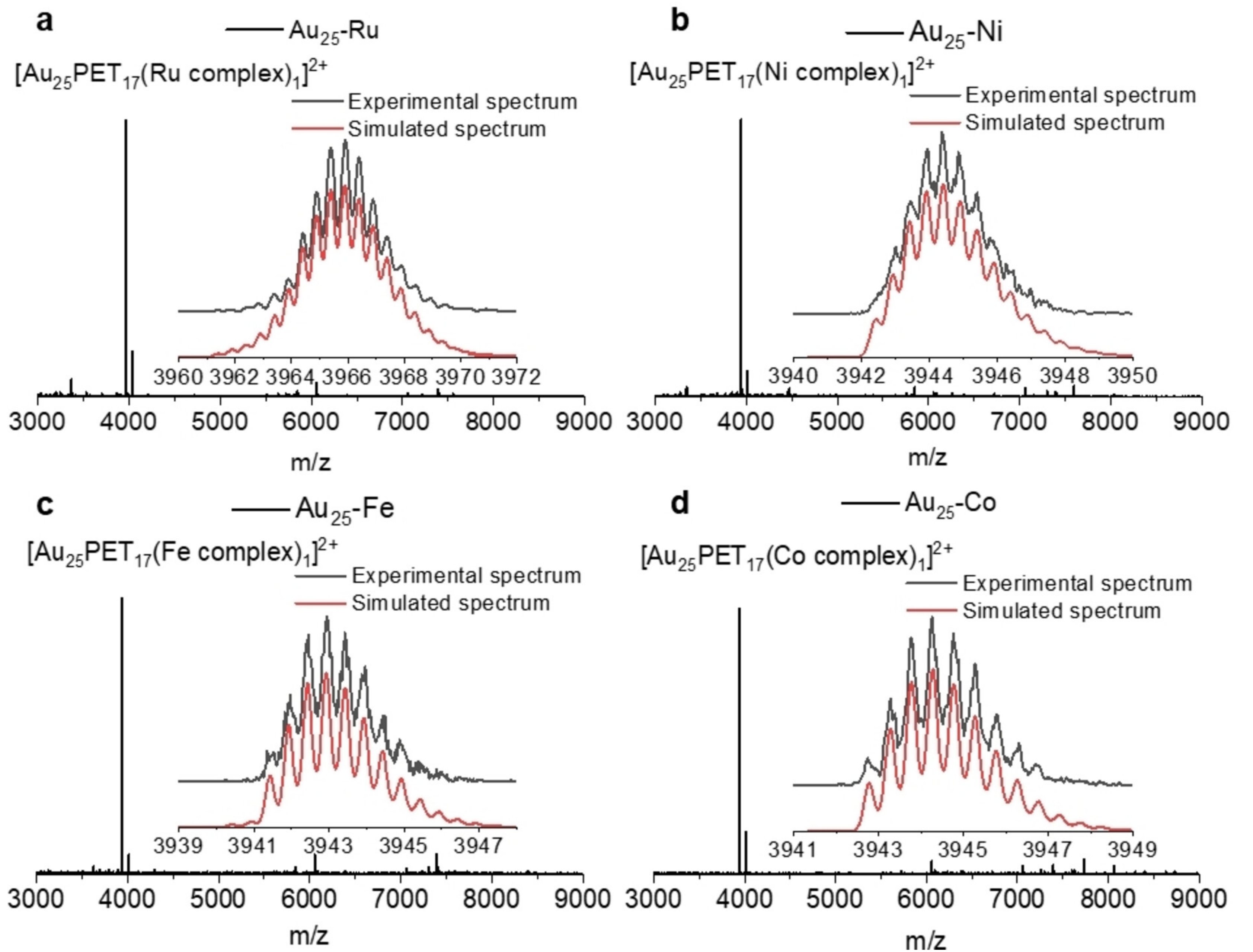
Introduction

- In this work, a series of metal complexes are grafted on the atomically precise Au_{25} NC to construct Au_{25}−M (M=Fe, Ni, Ru, Co) catalysts.
- For electrocatalytic CO_2 reduction (ECR), benefitting from the advantages of a single atom as the active site, Au_{25}−Ru and Au_{25}−Ni exhibit remarkable activity and selectivity for CO_2 to CO conversion.
- The anchoring of Ru and Ni complexes on Au_{25} NC (Au_{25}−Ru and Au_{25}−Ni) leads to adequate CO_2 to CO conversion for photocoupled electrocatalytic CO_2 reduction (PECR) in terms of **high selectivity**, with Faradaic efficiency of CO (FE_{CO}) exceeding 90 % in a wide potential range, **remarkable activity** (CO production rate up to two times higher than that for pristine $Au_{25}PET_{18}$) and extremely large turnover frequencies (TOFs, 63012 h^{-1} at −0.97 V for Au_{25}−Ru and 69989 h^{-1} at −1.07 V vs. RHE for Au_{25}−Ni).
- Moreover, PECR stability test indicates the **excellent long-term stability** of the modified NCs in contrast with pristine Au NCs.

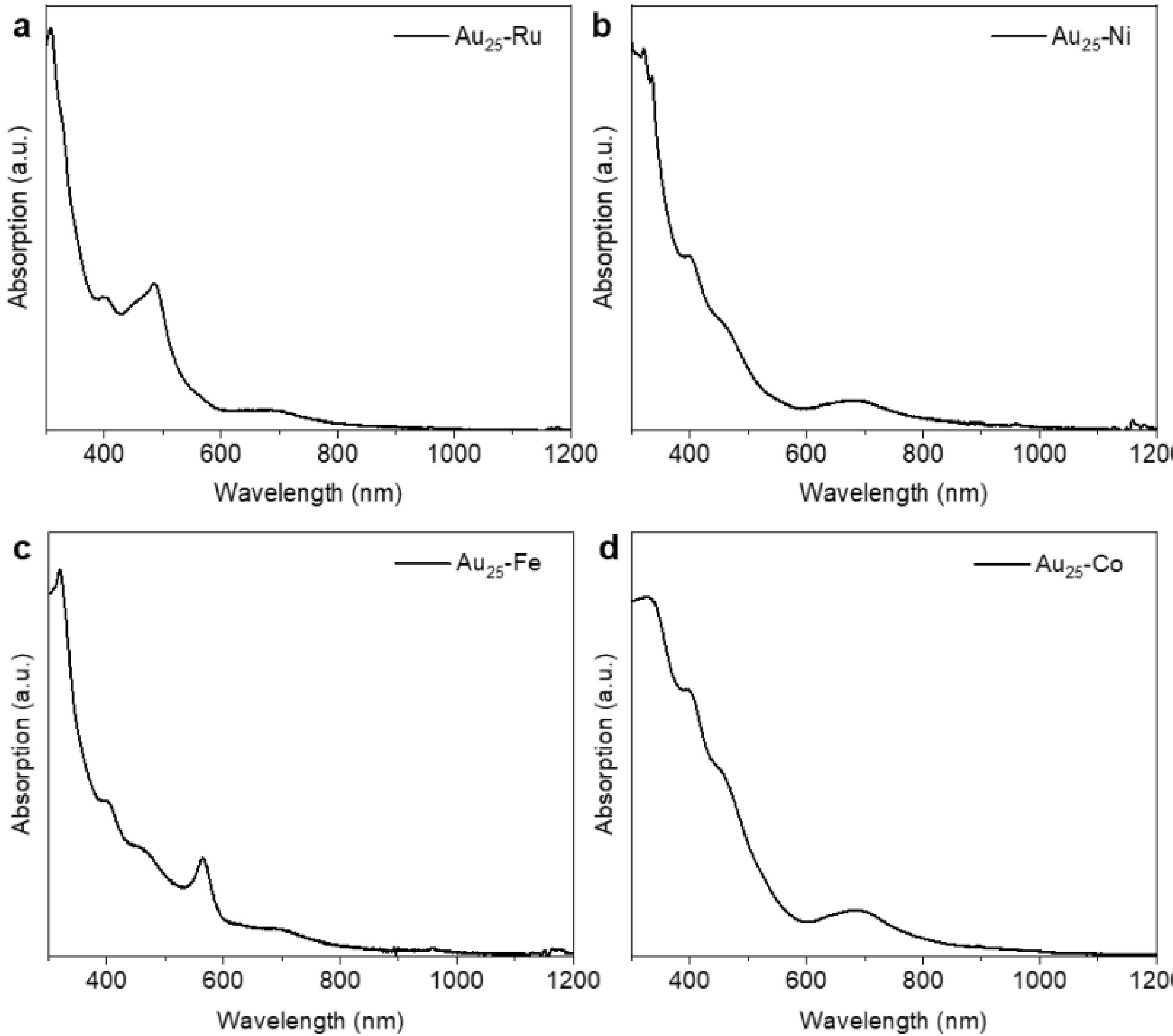
- The present approach **offers a novel strategy to enhance PECR activity and selectivity, as well as to improve the stability** of Au NCs under light illumination, which paves the way for highly active and stable Au NCs catalysts.

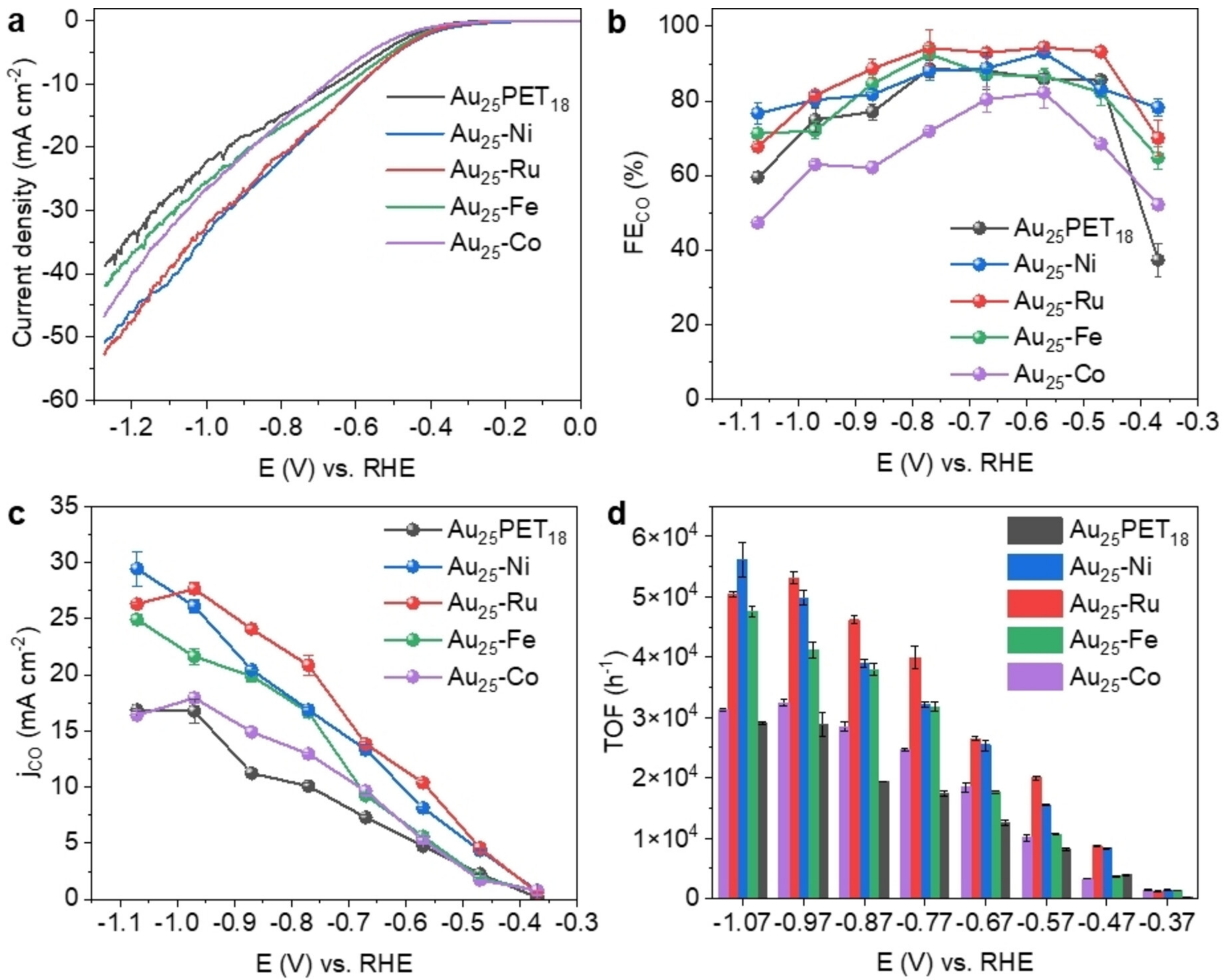
Results and Discussion





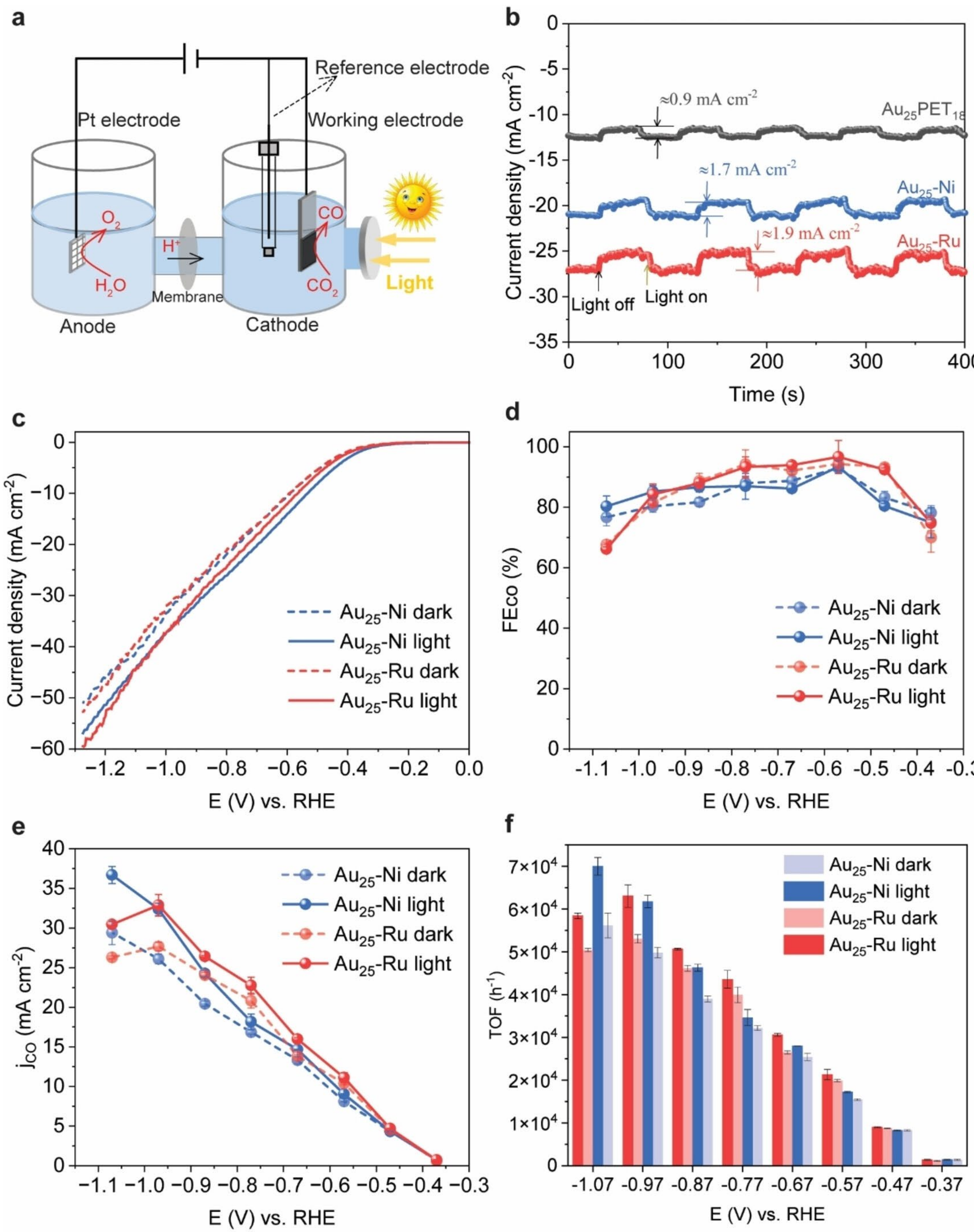
a
Au25-Ru
[Au25PET17(Ru complex)1]2+
Experimental spectrum
Simulated spectrum
3960 3962 3964 3966 3968 3970 3972
3000 4000 5000 6000 7000 8000 9000
m/z
b
Au25-Ni
[Au25PET17(Ni complex)1]2+
Experimental spectrum
Simulated spectrum
3940 3942 3944 3946 3948 3950
3000 4000 5000 6000 7000 8000 9000
m/z
c
Au25-Fe
[Au25PET17(Fe complex)1]2+
Experimental spectrum
Simulated spectrum
3939 3941 3943 3945 3947
3000 4000 5000 6000 7000 8000 9000
m/z
d
Au25-Co
[Au25PET17(Co complex)1]2+
Experimental spectrum
Simulated spectrum
3941 3943 3945 3947 3949
3000 4000 5000 6000 7000 8000 9000
m/z


a
Au25-Ru
b
Au25-Ni
c
Au25-Fe
d
Au25-Co
Absorption (a.u.)
Wavelength (nm)
400
600
800
1000
1200

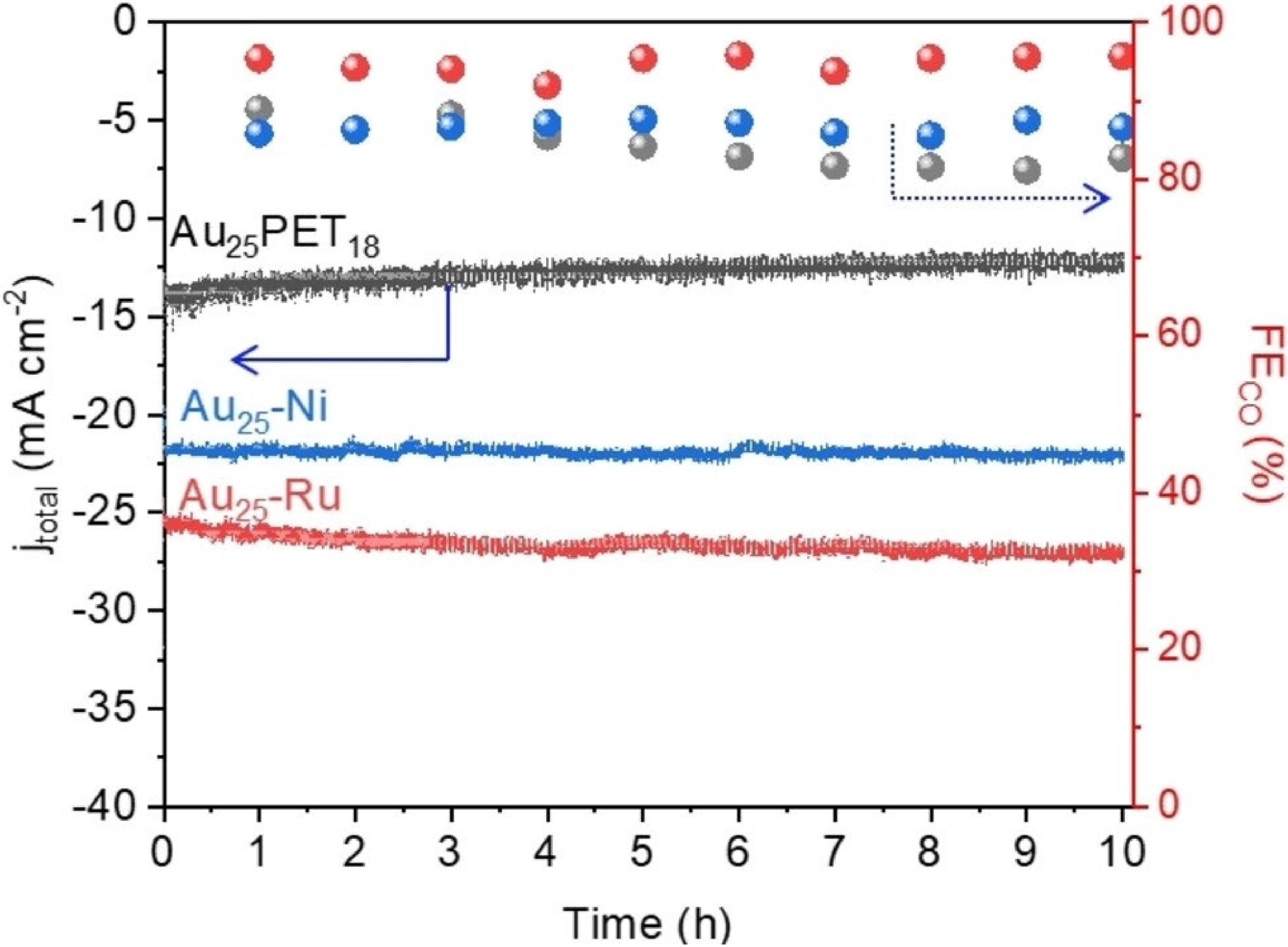


a
b
c
d
Current density (mA cm-2)
E (V) vs. RHE
FECO (%)
jCO (mA cm-2)
TOF (h-1)
Au25PET18
Au25-Ni
Au25-Ru
Au25-Fe
Au25-Co

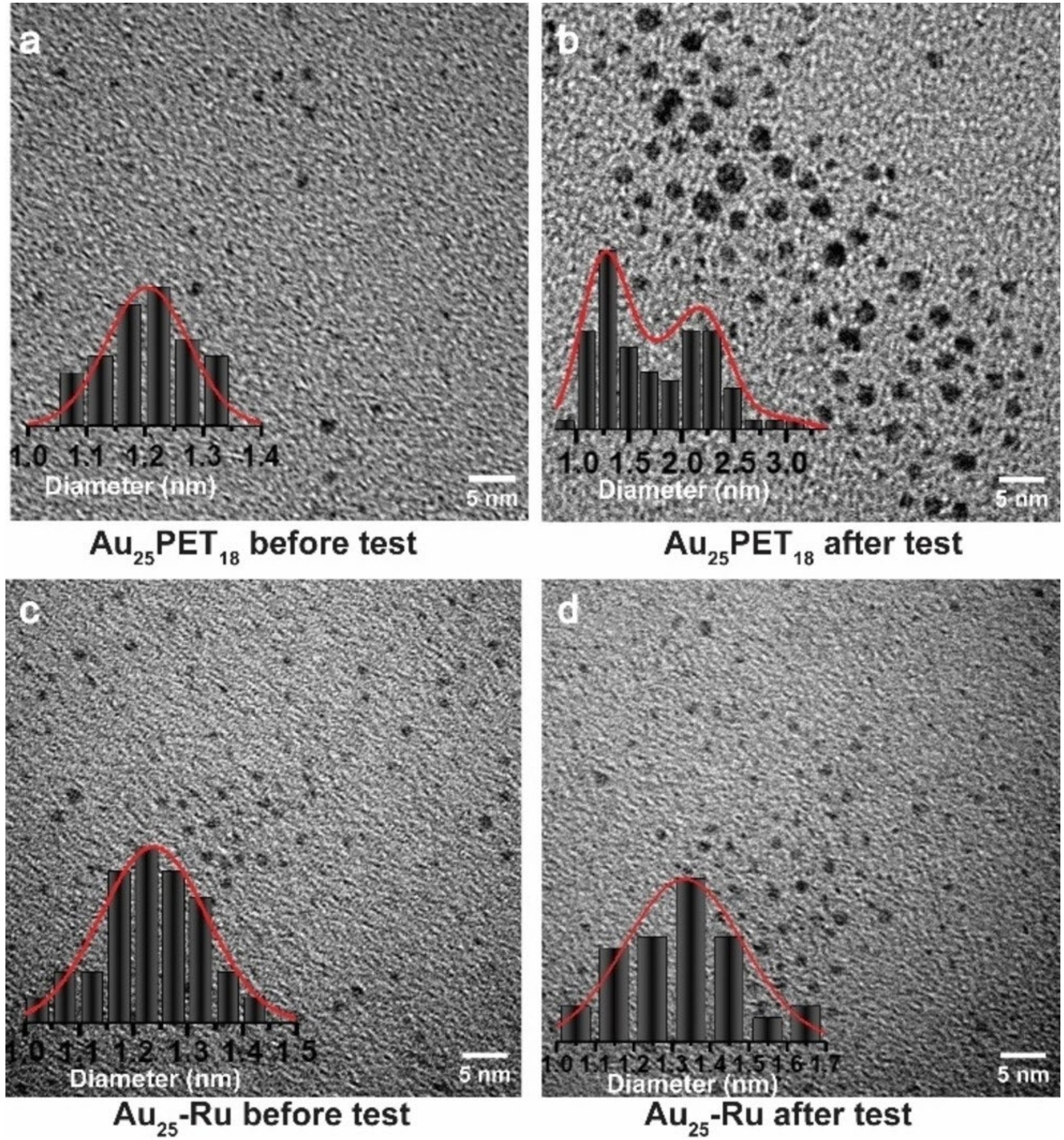
Catalysts	Potential vs. RHE (V)	CO partial current density (mA/cm^2)	TOF (h^{-1})	ref
$Au_{25}PET_{18}$	-0.97	18		[4]
Au_{25} rod	-0.97	14		[5]
Au_{55}	-0.9	18		[6]
Au_{28}	-0.87	9	1731	[7]
Au_{44}	-0.9	5		[8]
Au_{47}	-0.9	8		[8]
Au_{28}-C	-1.0	4	43200	[9]
Au_{11}	-0.9	4.5	600	[10]
$Au_{22}H_3$	-0.9	10	1100	[10]
Au_{23}	-0.97	25	15	[11]
HNTM-Au-SA	-1.0	6	37000	[12]
Au nanoparticles	-1.0	5		[13]
Au_{25}-Ru	-0.97	27.7	53044	This work
Au_{25}-Ni	-1.07	29.4	56138	



a
Reference electrode
Pt electrode
Working electrode
O_2
H_2O
H^+
CO
CO_2
Light
Membrane
Anode
Cathode
b
≈0.9 mA cm^{-2}
$Au_{25}PET_{18}$
≈1.7 mA cm^{-2}
Au_{25}-Ni
≈1.9 mA cm^{-2}
Au_{25}-Ru
Light off
Light on
Current density (mA cm^{-2})
Time (s)
c
Current density (mA cm^{-2})
Au_{25}-Ni dark
Au_{25}-Ni light
Au_{25}-Ru dark
Au_{25}-Ru light
E (V) vs. RHE
d
FE_{CO} (%)
Au_{25}-Ni dark
Au_{25}-Ni light
Au_{25}-Ru dark
Au_{25}-Ru light
E (V) vs. RHE
e
j_{CO} (mA cm^{-2})
Au_{25}-Ni dark
Au_{25}-Ni light
Au_{25}-Ru dark
Au_{25}-Ru light
E (V) vs. RHE
f
TOF (h^{-1})
Au_{25}-Ni dark
Au_{25}-Ni light
Au_{25}-Ru dark
Au_{25}-Ru light
E (V) vs. RHE



Au25PET18
Au25-Ni
Au25-Ru
jtotal (mA cm-2)
FECO (%)
Time (h)
0
-5
-10
-15
-20
-25
-30
-35
-40
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10


a
1.0 1.1 1.2 1.3 1.4
Diameter (nm)
5 nm
Au25PET18 before test
b
1.0 1.5 2.0 2.5 3.0
Diameter (nm)
5 nm
Au25PET18 after test
c
1.0 1.1 1.2 1.3 1.4 1.5
Diameter (nm)
5 nm
Au25-Ru before test
d
1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7
Diameter (nm)
5 nm
Au25-Ru after test

Conclusions

- In this work, we designed catalysts to promote the CO2 reduction activity via anchoring metal complexes into the ligand shell of Au25 NC by ligand exchange reaction. For ECR, the results show that Au_{25}–Ru and Au_{25}–Ni, exhibit superior activity and selectivity compared to Au_{25}–Co, Au_{25}–Fe and pristine Au_{25}.
- With the assistance of light field, both j_{CO} and TOF for Au_{25}–Ru and Au_{25}–Ni were further improved compared to dark condition in a wide potential range implying higher performance for PECR. The above results suggest that the anchoring of Ru and Ni complexes on Au_{25} NC improves both ECR activity and selectivity, since the metal complexes could provide more active sites and a more efficient electron-transfer pathway.
- Moreover, the external light irradiation on Au_{25}-based catalysts could further enhance the electron transfer to absorbed CO_2. Importantly, Au_{25}–Ru and Au_{25}–Ni show higher catalytic stability compared with pristine $Au_{25}PET_{18}$ possibly due to removing the excitation from the Au NC.

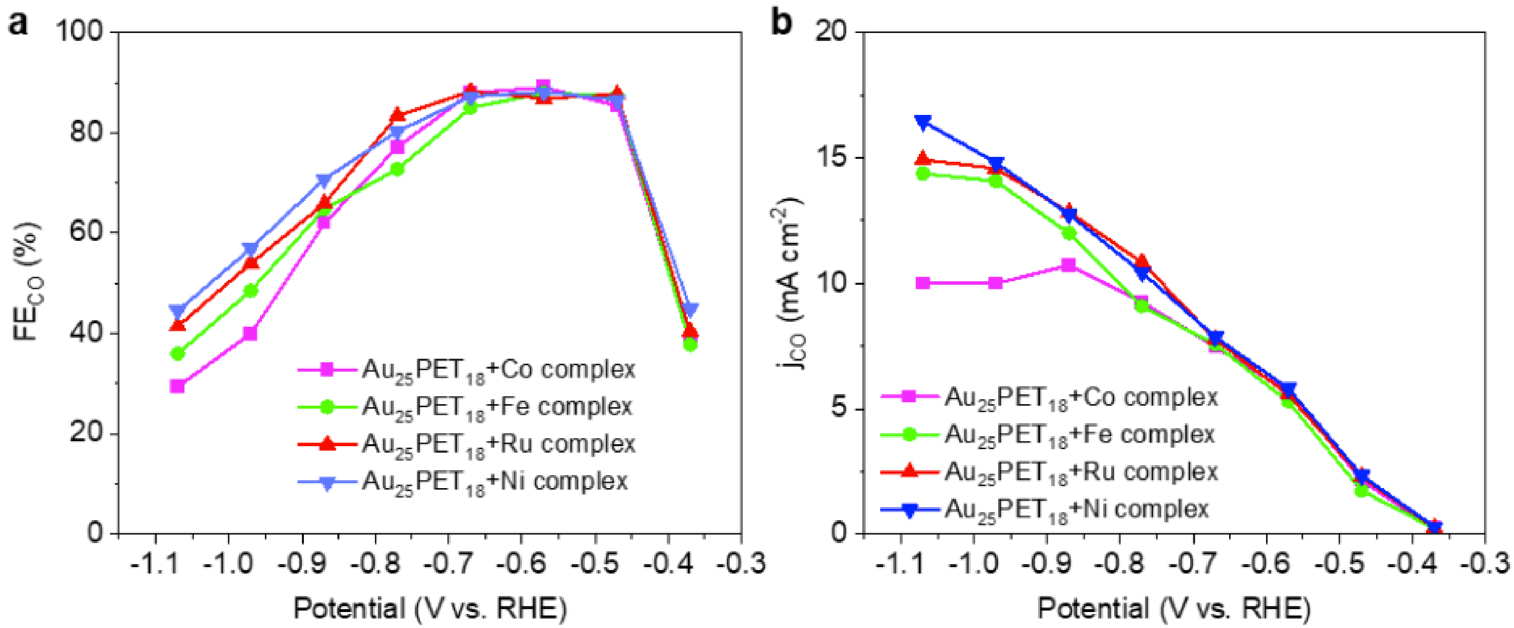


Figure S16. (a) FECO and (b) CO partial current density at different potentials for the physical mixture of $Au_{25}PET_{18}$ and metal complexes under dark condition.

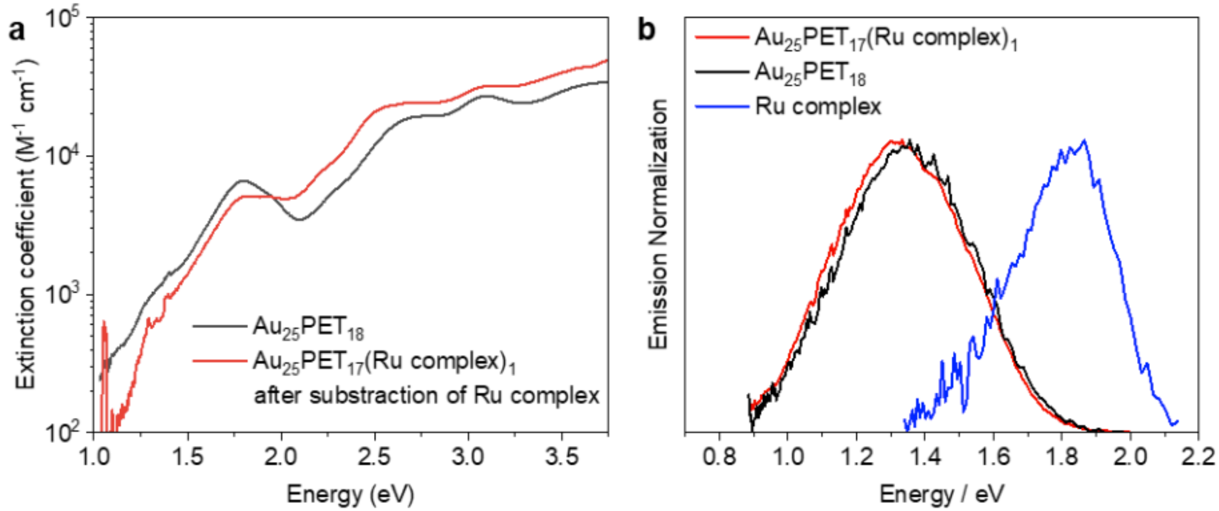


Figure S8. (a) The comparison of spectral extinction coefficient after subtraction of the Ru complex for $Au_{25}PET_{17}$(Ru complex)$_1$ and $Au_{25}PET_{18}$. (b) Emission spectra after normalization for $Au_{25}PET_{18}$, $Au_{25}PET_{17}$(Ru complex)$_1$ and Ru complex.

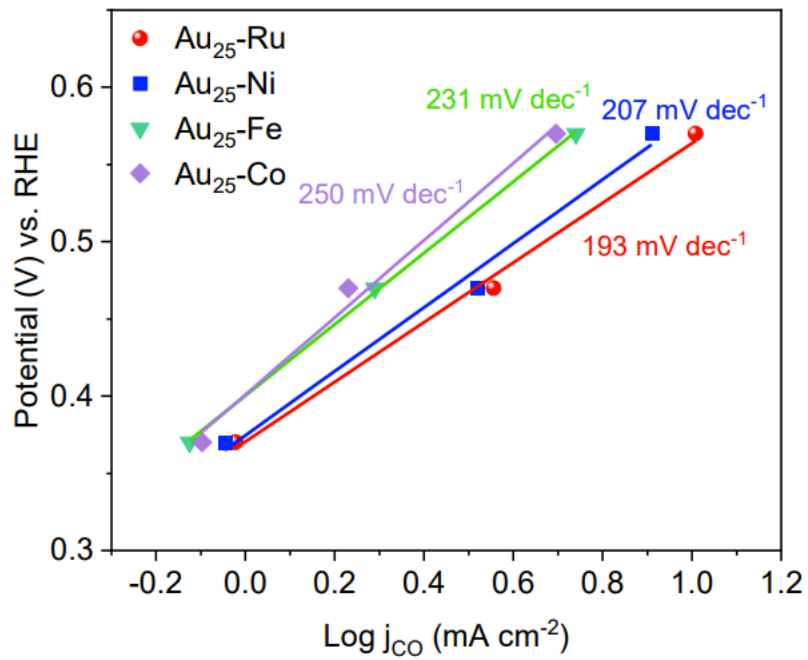
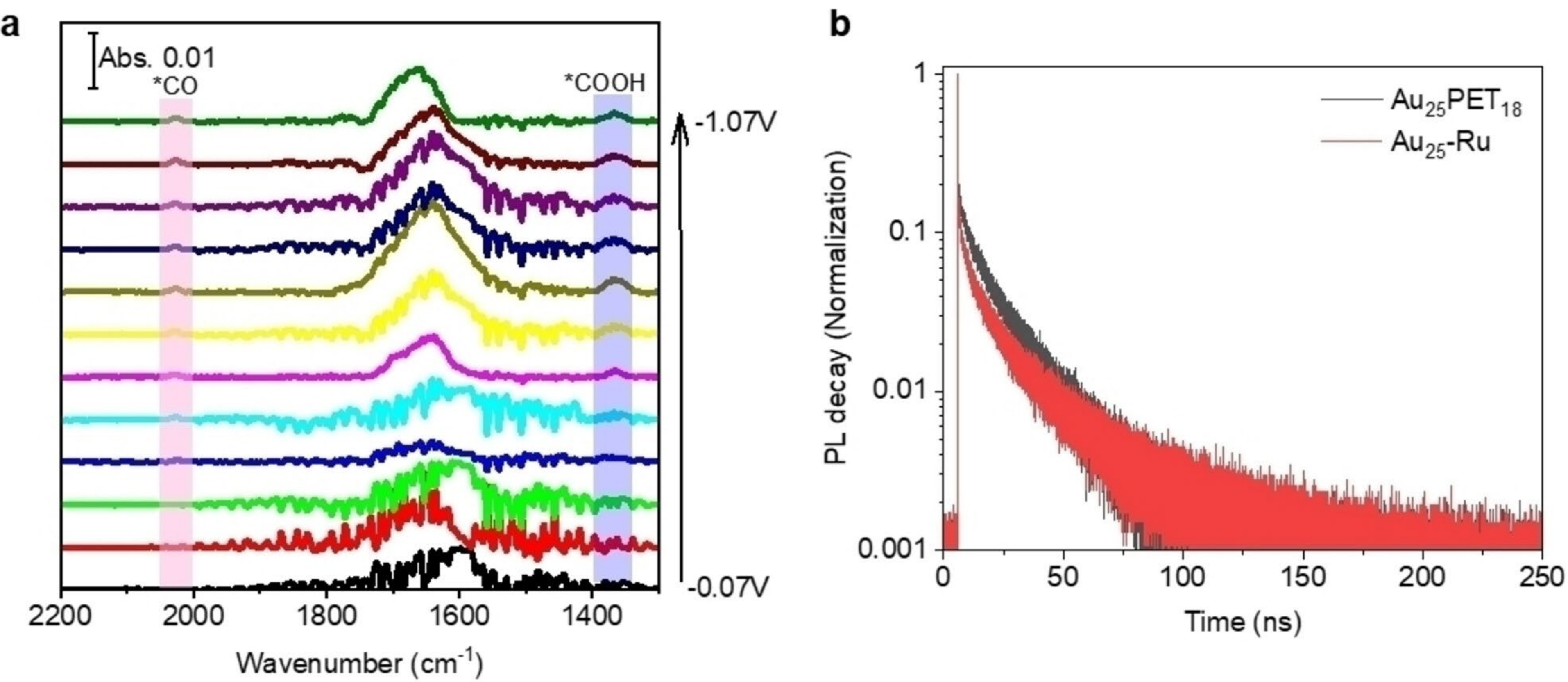
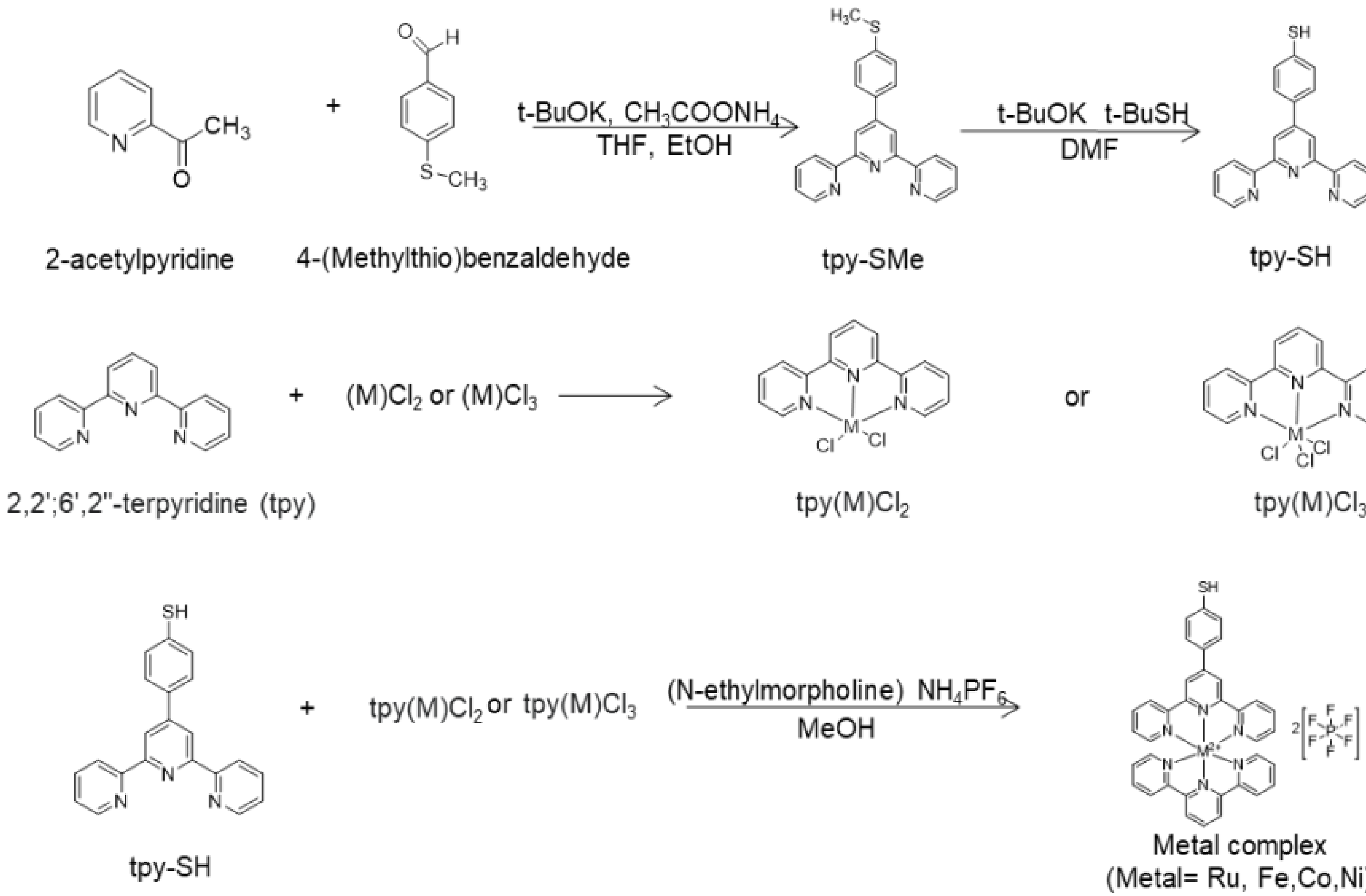


Figure S12. Tafel plots of Au_{25}-Ru, Au_{25}-Ni, Au_{25}Fe and Au_{25}-Co under dark condition.


a
Abs. 0.01
*CO
*COOH
-1.07V
-0.07V
2200
2000
1800
1600
1400
Wavenumber (cm-1)
b
Au25PET18
Au25-Ru
PL decay (Normalization)
1
0.1
0.01
0.001
0
50
100
150
200
250
Time (ns)

Synthesis of and metal complex (Metal= Ru, Fe, Co, Ni)



Scheme S1. Synthesis procedure of metal complex