UNIVERSITAS BRAWIJAYA

IC2MS 2017

INTERNATIONAL CONFERENCE
ON CHEMISTRY AND MATERIAL SCIENCE

CERTIFICATE

OF PARTICIPATION

this is to certify that

Hendrik Oktendy Lintang

participated as a

PRESENTER

In INTERNATIONAL CONFERENCE ON CHEMISTRY AND MATERIAL SCIENCE (IC2MS)

held on 4-5 November 2017 in Malang, Indonesia, organized by Brawijaya University

KEMENTERIAN RISET, TEKNOLOGI DAN PENDIDIKAN TINGGI
UNIVERSITAS BRAWIJAYA
FAKULTAS MIPA

Adi Susilo, Ph.D.
Dean of Faculty of Science

IC2MS 2017

Anna Safitri, Ph.D.
The IC2MS Chair

UNIVERSITAS
MA CHUNG

LETTER OF ASSIGNMENT

No: 346/MACHUNG/ST/X/2017

The Rector of Universitas Ma Chung hereby assigns:

Name	:	Dr. Eng. Hendrik Oktendy Lintang, S.Si., M.Eng.
Employee's Number	:	20160017
Position	:	Principal Investigator PUI MRCPP

to participate in the **International Conference on Chemistry and Material Science (IC2MS) 2017 as Oral Presenter** with abstract entitled "**Trinuclear Group 11 Pyrazolate Complexes with Supramolecular Assembly for Phosphorescent Chemosensors of Benzene Vapors**" organized by Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Brawijaya University which is held on 4-5 November 2017 in Ijen Suites Resort & Convention Hotel, Malang.

He has to submit an official report when returns to work.

Please be informed.

Malang, 31 October 2017
Rector,

MA CHUNG

Dr. Chatief Kunjaya

Acknowledged by,

KEMENTERIAN RISET, TEKNOLOGI DAN PENDIDIKAN TINGGI
UNIVERSITAS BRAWIJAYA
FAKULTAS MIPA
JURUSAN KIMIA

(Name)

CC:
1. Vice Rectors
2. Ma Chung Research Center for Photosynthetic Pigments (MRCPP)
3. Human Resource Management

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http://www.machung.ac.id

International Conference on Chemistry and Materials Science
IC2MS 2017
4-5 November 2017, Malang, INDONESIA

INO/O-003

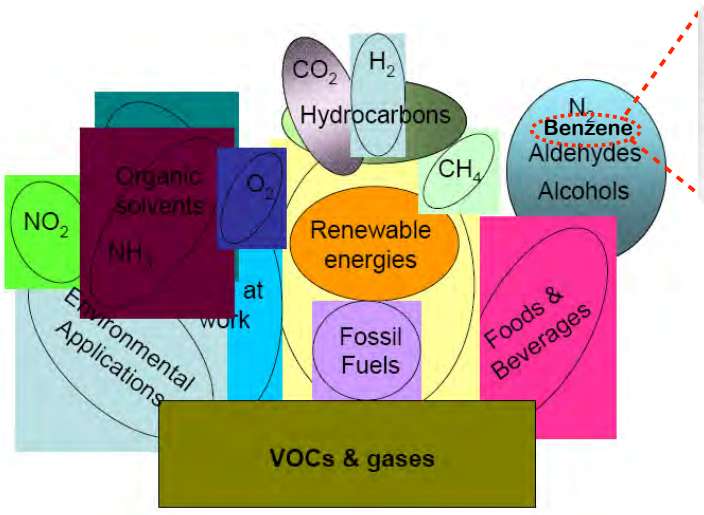
Trinuclear Group 11 Pyrazolate Complexes with Supramolecular Assembly for Phosphorescent Chemosensors of Benzene Vapors

Hendrik. O. LINTANG,[1,2,3]
Nur Fatiha Ghazalli[4,5] and Leny Yuliati[1,2,3]

[1]Ma Chung Research Center for Photosynthetic Pigments (MRCPP), [2]Department of Chemistry, Faculty of Science and Technology Universities Ma Chung, Indonesia
[3]Centre for Sustainable Nanomaterials, Universiti Teknologi Malaysia, Malaysia
[4]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Malaysia
[5]Department of Chemistry, Faculty of Science, Universiti Malaysia Terengganu, Malaysia

Volatile Organic Compounds (VOCs)

VOCs are commonly used as ingredients in household products or in industrial processes where they normally get vaporize at room temperature as toxic and organic vapors as well as non-organic vapor



Flammable Carcinogen Irritation

Elosua, C, *et al*., *Sensors* **2006**, *6*, 1440

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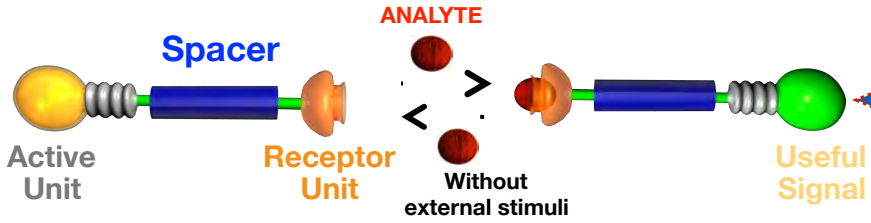
Luminescent Chemosensors

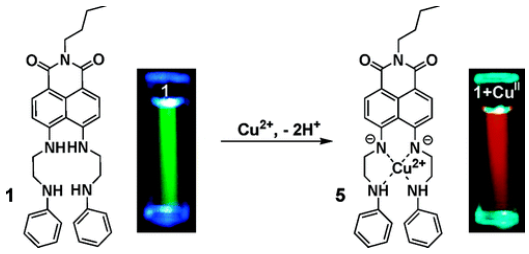
Chemical sensors (chemosensors) are a molecule, when receptor unit interact with analytes, it transforms specific information through spacer to the active unit to give analytical useful signals



Changes in Properties
- Absorption
- Permittivity
- Swelling
- Mass
- Refractive index
- Thermal resistivity
- Luminescence

Example of Luminescent Chemosensors

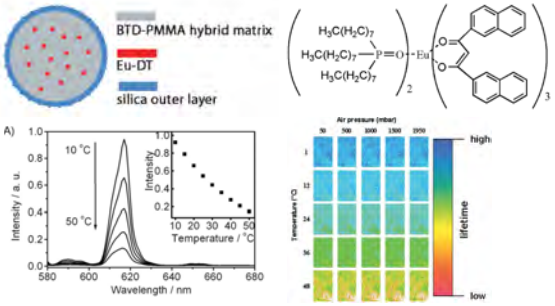
1. Metal Ion Sensors



Naphthalimide Chemosensor

Xu, Z., *et al*., *Organic Letters* **2005**, *7*, 3029

2. Temperature Sensors

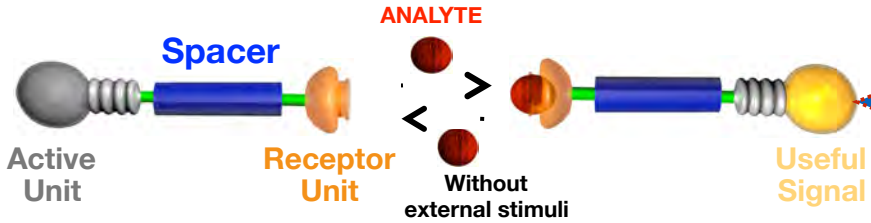


Eu Complex Chemosensor

Peng, H., *et al*., *Advanced Materias* **2010**, 22, 716

Luminescent Chemosensors

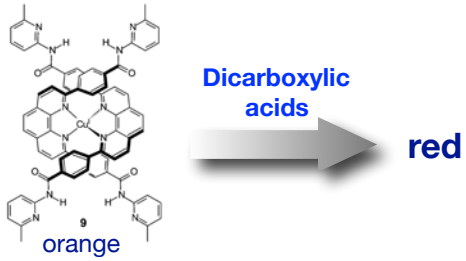
Chemical sensors (chemosensors) are a molecule, when receptor unit interact with analytes, transform specific information through spacer to the active unit to give analytical useful signals



Changes in Properties
- Absorption
- Permittivity
- Swelling
- Mass
- Refractive index
- Thermal resistivity
- Luminescence

Example of Luminescent Chemosensors

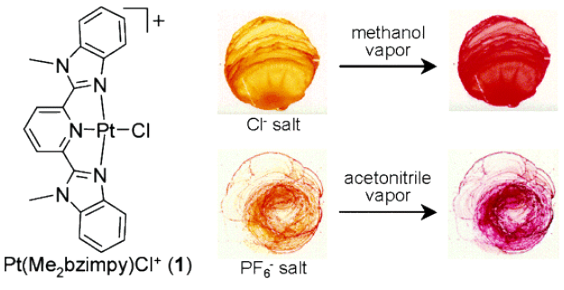
3. Molecular Sensors



Cu Complex Chemosensor

Goodman, M.S., *Journal of the American Chemical Society* **1995**, *117*, 8447

4. Vapor Sensors

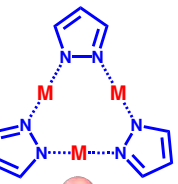


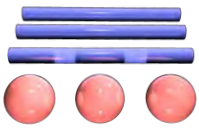
Pt Complex Salt Chemosensor

Grove, L.J., *et al*., *Journal of the American Chemical Society* **2004**, *126*, 1594

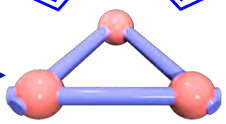
Phosphorescent Group 11 Metal Complexes

Group 11
Metal Complexes

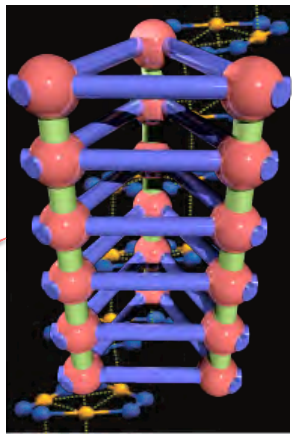




Coordination



Self-Assembly



Cu(I)
Ag(I)
Au(I)
Ligands

Complexes

1D Phosphorescent Compounds

Supramolecular Columnar Assembly with *Chair-Like Coordination*

- Longer Lifetime
- High Luminescent Quantum Yield
- Phosphorescent Properties at Room Temperature
- Cheaper than Platinum Complexes
- Highly Sensitive to External Stimuli

Yam, V. W.-W. and Lo, K. K.-M. *Chemical Society Reviews* **1999**, *28*, 323.

Ford, P. C., Cariati, E. and Bourassa, J., *Chemical Reviews* **1999**, *99*, 3625.

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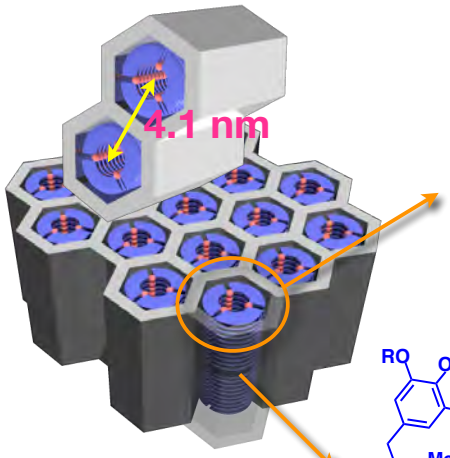
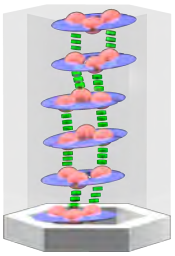
Discotic Columanr Assembly of Gold Complex in the Channels of Mesoporous Silica Nanocomposites

Lintang, H. O., *et al*., *Angewandte Chemie International Edition* **2010**, *49*, 4241

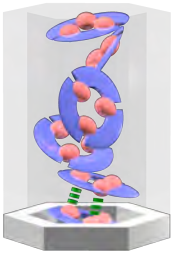




140 °C

Heating

Cooling



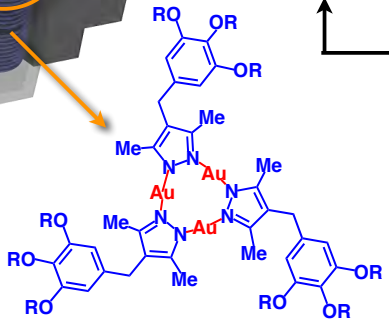
Au(I)-Au(I)
Metallophilic
Interaction

20 °C

20 °C

Standing

Perfect Self-Repairing in 5 h

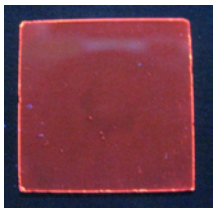


Complex Amphiphile

Room Light

Transparent

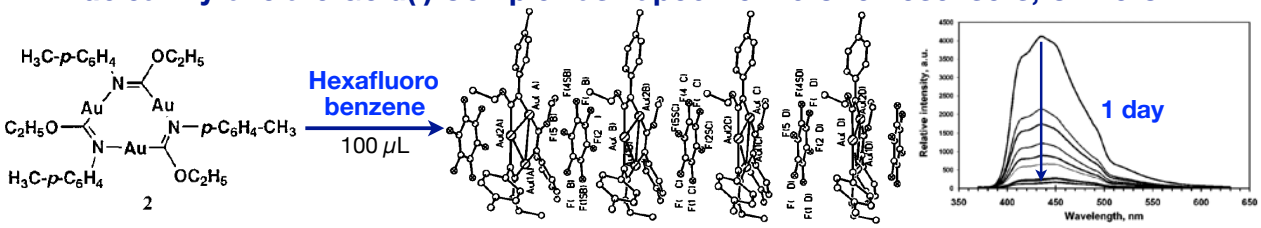
λ_{ext} = 254 nm



Red

Group 11 Pyrazolate Complexes as Chemosensors

1. Trinuclear Pyrazolate Gold(I) Complex as Vapochromic Chemosensors; ON to OFF



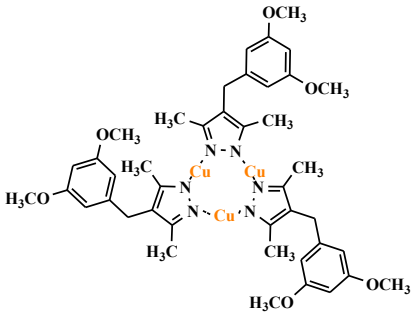
2

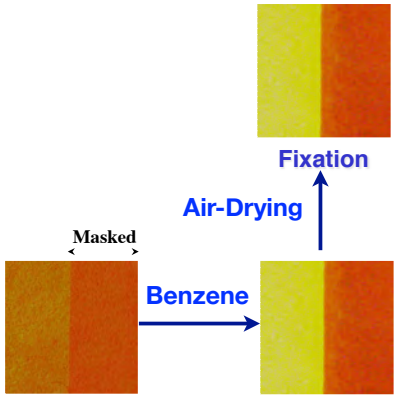
Reusability: Irreversible

Response time: 1 day

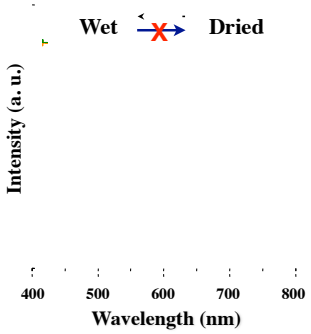
All Chemosensors Showed Irreversible Changes in the Emission

2. Trinuclear Pyrazolate Copper(I) Complex as Vapochromic Chemosensors: SHIFTING





Reusability: Irreversible



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Kishimura, A., *PhD Thesis, The University of Tokyo* **2005**

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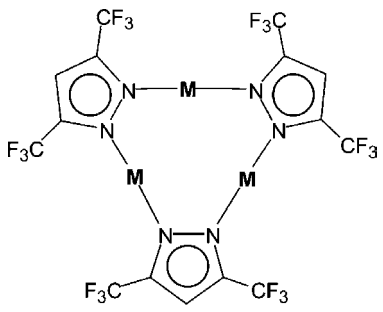
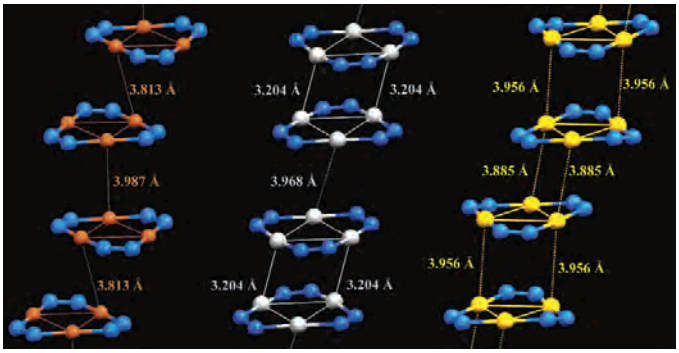
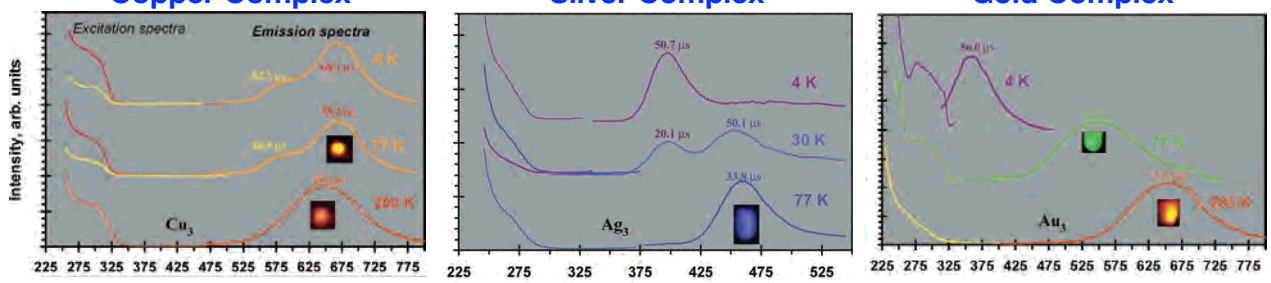
Group 11 Pyrazolate Complexes

Effect of Group 11 Metal Ions on Distance of Metal-Metal Interactions; Difference of Phosphorescent Properties





Copper Complex | **Silver Complex** | **Gold Complex**



Omary, M. A., *et al*., *Inorganic Chemistry* **2005**, *44*, 8200

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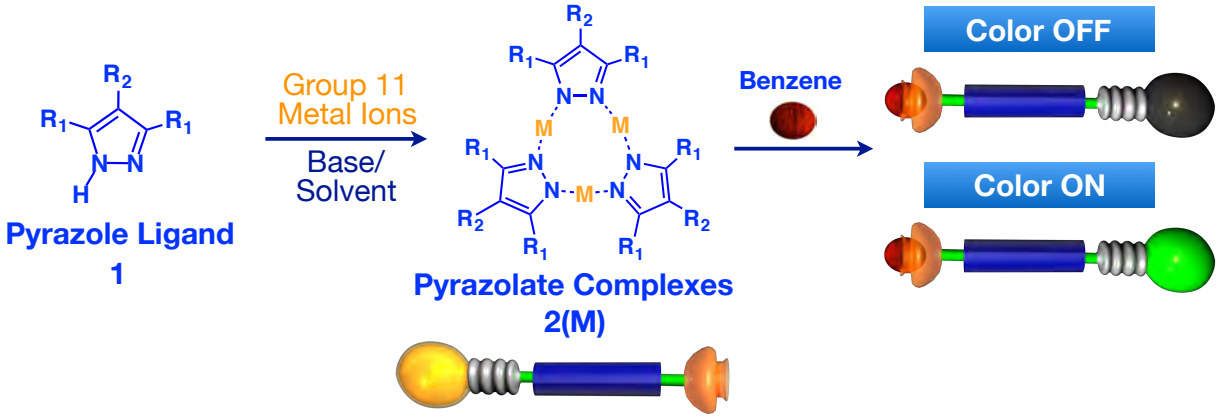
Research Objectives

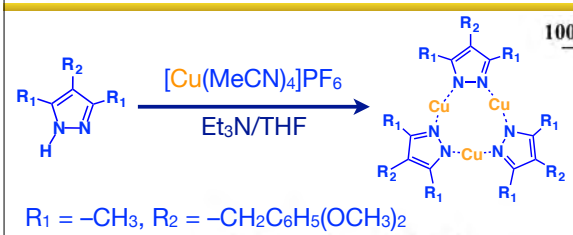
Effect of Group 11 Metal Ions with Pyrazolate Complexes on Vapochromic Chemosensors of Benzene Vapors



Group 11 Metal Ions: Cu. Ag and Au

- Synthesis of Group 11 Pyrazolate Complexes
- Phosphorescent Properties of Group 11 Pyrazolate Complexes
- Sensing Capability of Group 11 Pyrazolate Complexes

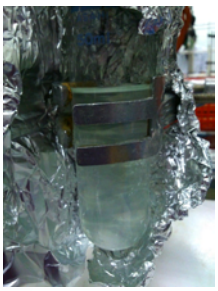
Synthesis of Copper(I) Pyrazolate Complexes



$R_1 = -CH_3$, $R_2 = -CH_2C_6H_5(OCH_3)_2$

100 mL Schlenk (1st STAGE)

- Vacuum
- Changed air with N_2 gas
- Dry THF
- pyrazole ligand
- Degassed (3 times)
- Poured ($[Cu(MeCN)_4]PF_6$ 1 equi.
- Mix 5 minute under N_2
- Triethylamine 2 equi.
- Stirred overnight at room temperature
- Remove THF by trapping
- Dissolve with dry CH_2Cl_2



200 mL Schlenk (2nd STAGE)

- Vacuum
- Changed air with N_2 gas
- Dry methanol

Transfer with cannula

- In-Situ recrystallization with CH_2Cl_2 to dry methanol (except for 2_C uisng dry hexane)
- In-Situ Filtration with cannula and filter paper
- Collected, Dry-off, and Flow N_2 gas

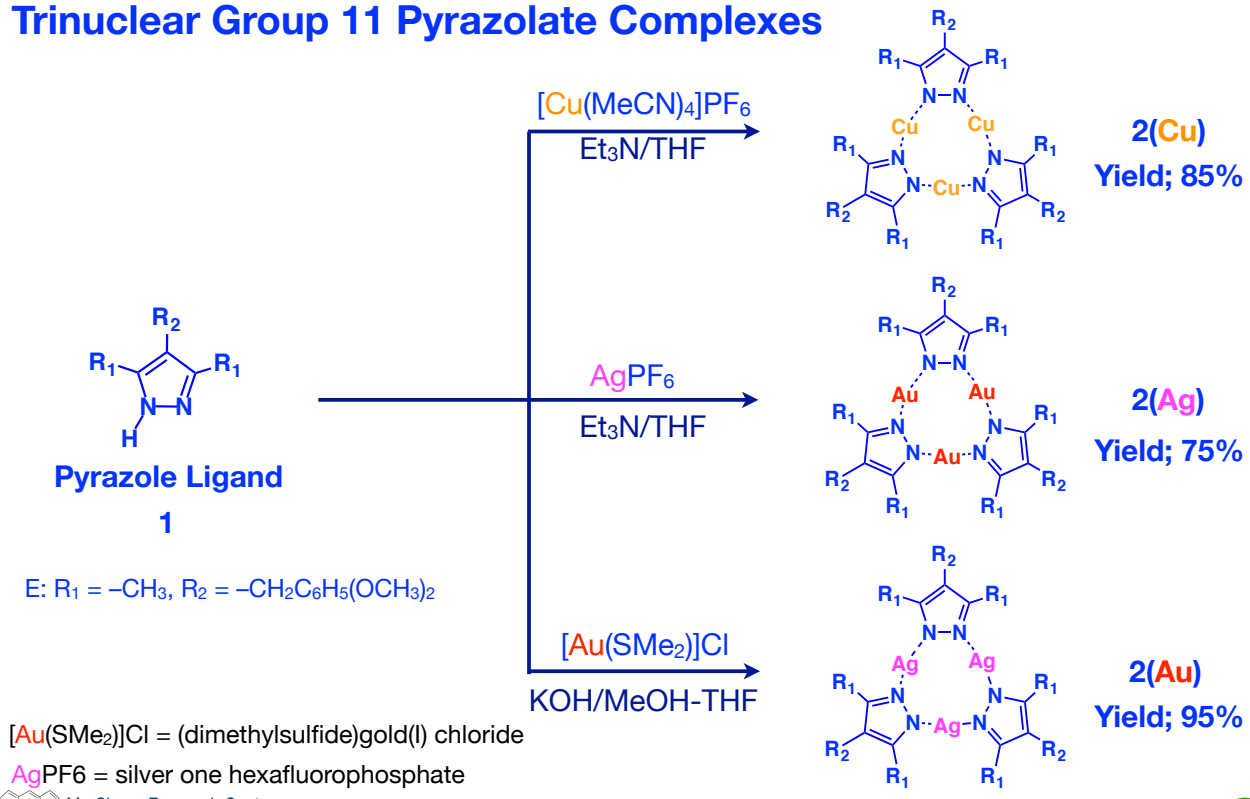
Product Copper(I) Complexes

Solid Powder

$[Cu(MeCN)_4]PF_6$ =
tetrakis(acetonitrile)copper(I) hexafluorophosphate

Synthesis of Group 11 Pyrazolate Complexes

Trinuclear Group 11 Pyrazolate Complexes



[Au(SMe2)]Cl = (dimethylsulfide)gold(I) chloride

AgPF6 = silver one hexafluorophosphate

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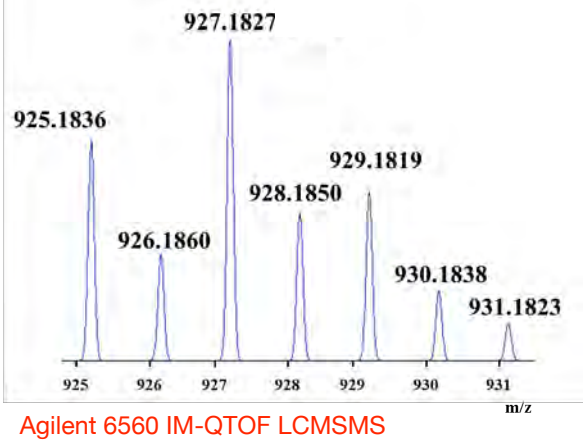
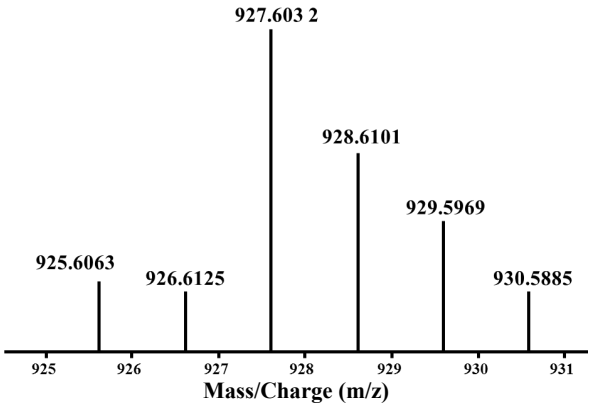
Mass Spectrum of Copper(I) Pyrazolate Complexes

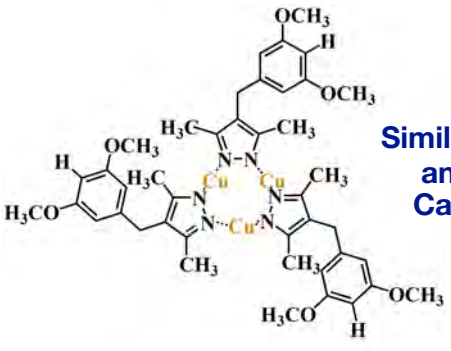
Calculation
[M+H+] = 927.1827 Da



Observation
[M+Na+] = 927.6032 Da



Agilent 6560 IM-QTOF LCMSMS



Similar Monoisotope Patterns and Mass Value (m/z) of Calculated and Observed Copper Complexes

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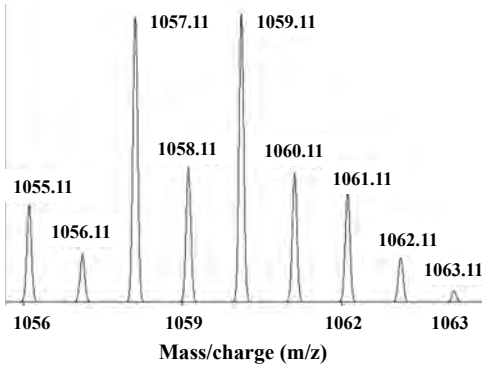
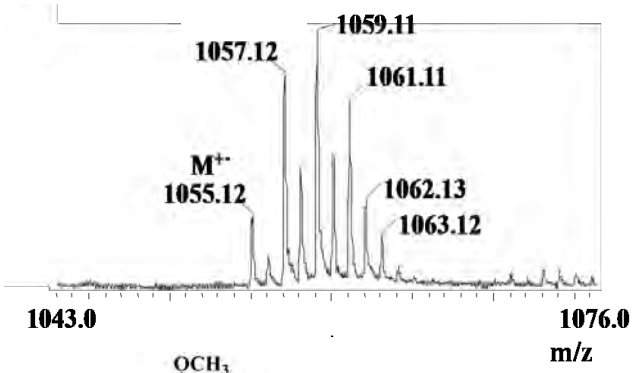
for Photosynthetic Pigments

Mass Spectrum of Silver(I) Pyrazolate Complexes

Calculation
[M+H⁺] = 1057.11 Da



Observation
[M+Na⁺] = 1057.12 Da

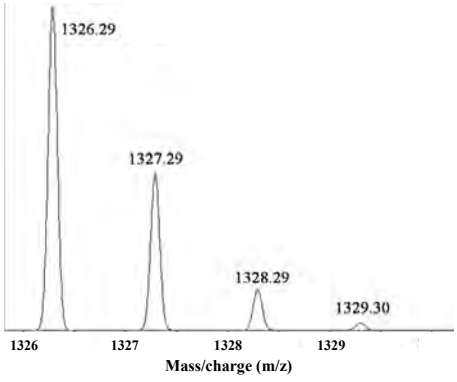


Agilent 6560 IM-QTOF LCMSMS

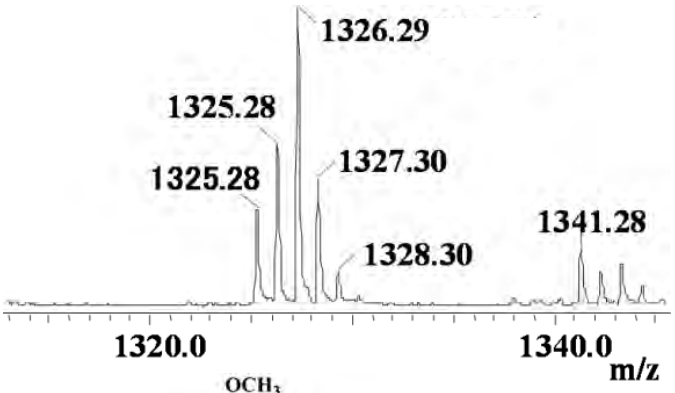
Similar Monoisotope Patterns and Mass Value (m/z) of Calculated and Observed Silver Complexes

Mass Spectrum of Gold(I) Pyrazolate Complexes

Calculation
[M+H⁺] = 1326.28 Da



Observation
[M+Na⁺] = 1326.29 Da



Agilent 6560 IM-QTOF LCMSMS

Similar Monoisotope Patterns and Mass Value (m/z) of Calculated and Observed Gold Complexes

Phosphorescent Properties of Group 11 Complexes

Green to Red Emission of Trinuclear Group 11 Pyrazolate Complexes

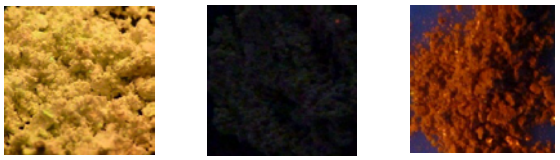
Photograph Images under Daylight

2(Cu) | 2(Ag) | 2(Au)

greenish-white | brownish | white

Photograph Images under λ_{ext} = 254 nm

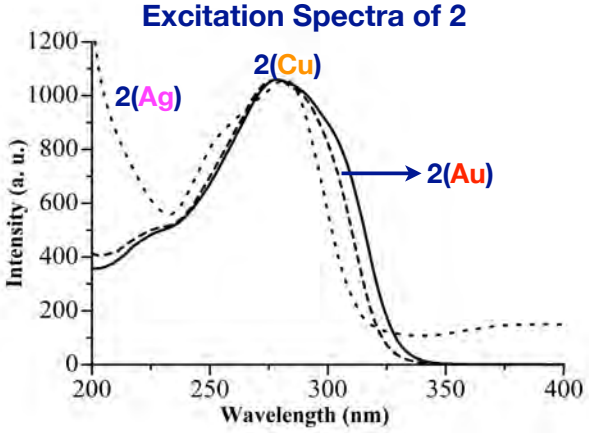
2(Cu) | 2(Ag) | 2(Au)



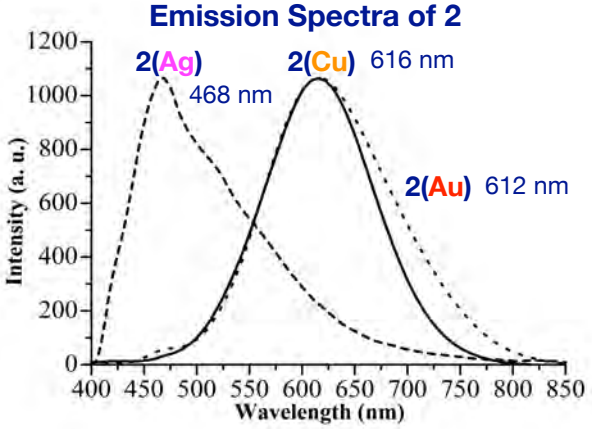
orange | dark-green | reddish

λ_{em} = 616 nm | λ_{em} = 468 nm | λ_{em} = 612 nm

Excitation Spectra of 2



Emission Spectra of 2



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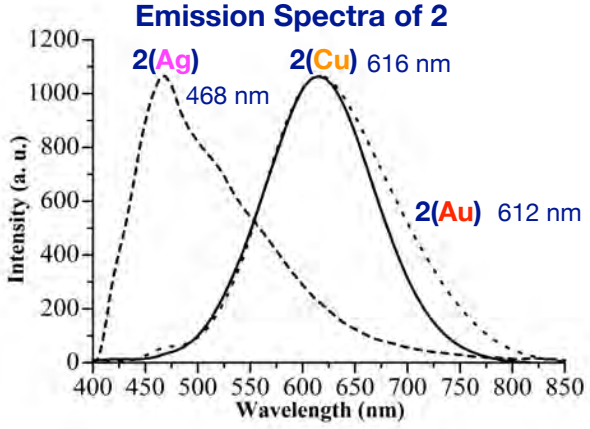
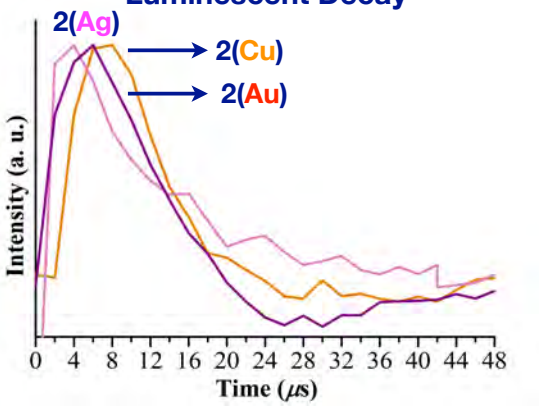
Phosphorescent Properties of Pyrazolate Complexes

Characteristics of Large Stokes Shifts and Microsecond Lifetimes

Emission Spectra of 2



Luminescent Decay



Complexes	Excitation (nm)	Emission (nm)	Stokes Shift (Δλ)	Lifetime (μs)
2_E(Cu)	278	616	338	8.2 ± 1.8
2_E(Ag)	284	468	184	7.8 ± 0.7
2_E(Au)	280	612	332	8.8 ± 0.7

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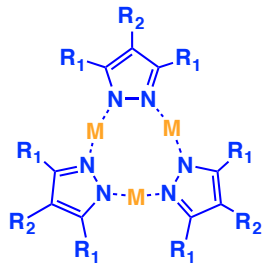
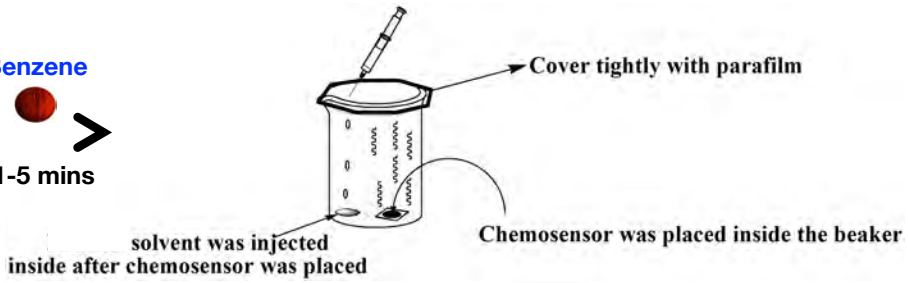
Vapochromic Chemosensors of Alcohol Derivatives



Benzene

1-5 mins



Pyrazolate Complexes

2

$R_1 = -CH_3$, $R_2 = -CH_2C_6H_5(OCH_3)_2$

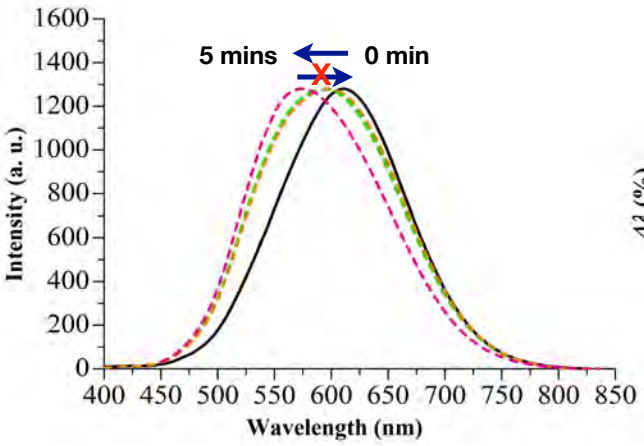
M = Cu, Ag and Au

Sensing Capability

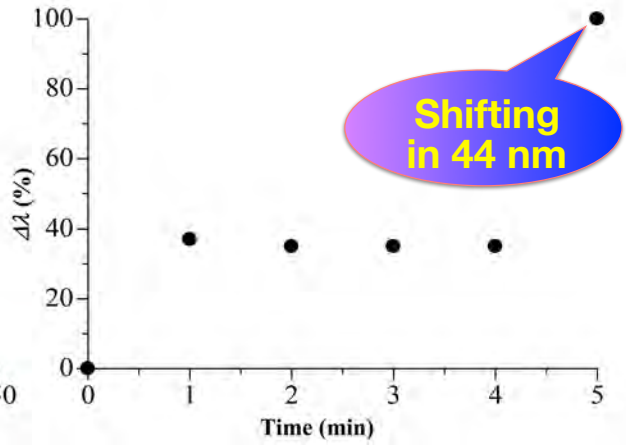
1. **Emission Changes**
2. **Color Changes**

Sensing Capability of Chemosensor 2(Cu)

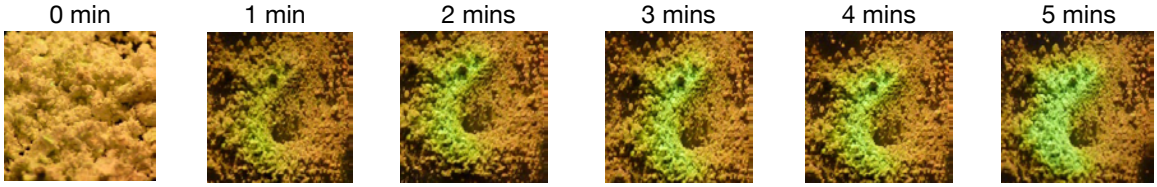
Emission Spectral Changes (λ_{ext} = 278 nm)



Sensing Capability (λ_{em} = 616 nm)



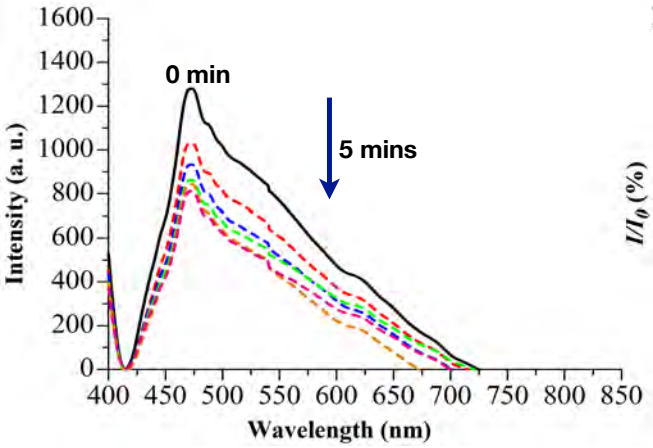
Photograph Images under λ_{ext} = 254 nm



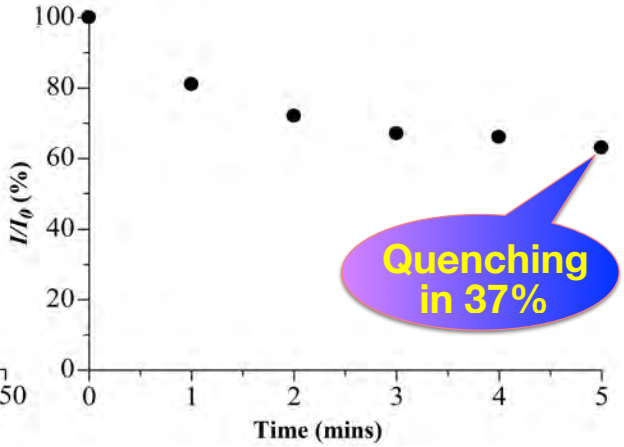
Color changes from orange to green-orange in 5 minutes

Sensing Capability of Chemosensor 2(Ag)

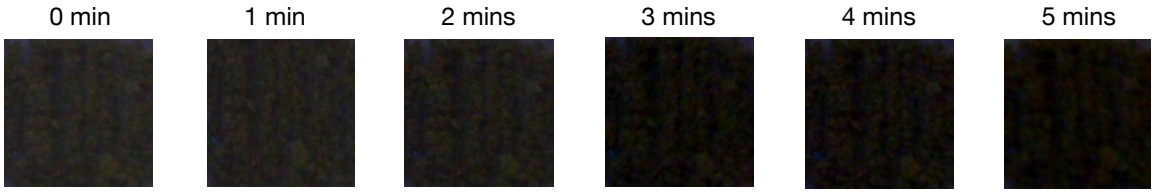
Emission Spectral Changes (λ_{ext} = 284 nm)



Sensing Capability (λ_{em} = 468 nm)



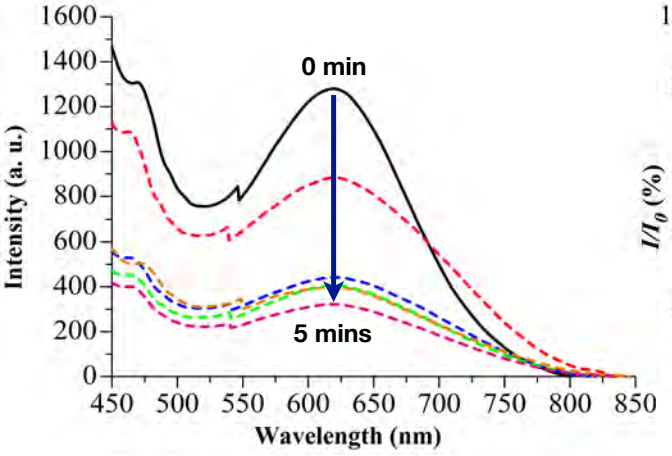
Photograph Images under λ_{ext} = 254 nm



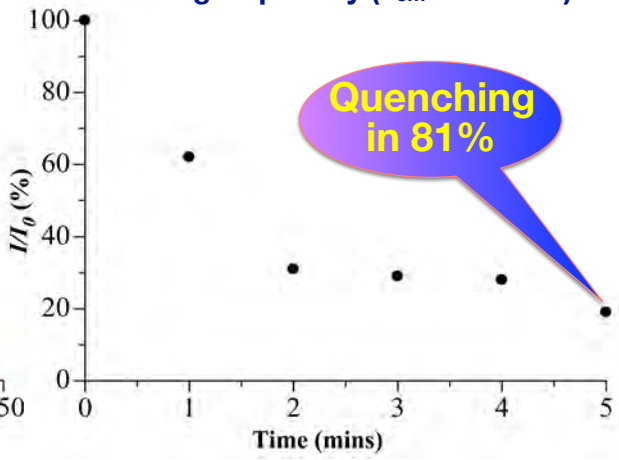
Color changes from dark green to less emissive in 5 minutes

Sensing Capability of Chemosensor 2(Au)

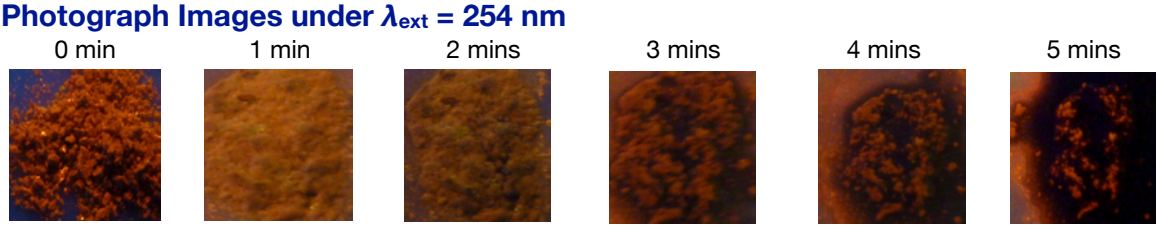
Emission Spectral Changes (λ_{ext} = 280 nm)



Sensing Capability (λ_{em} = 612 nm)



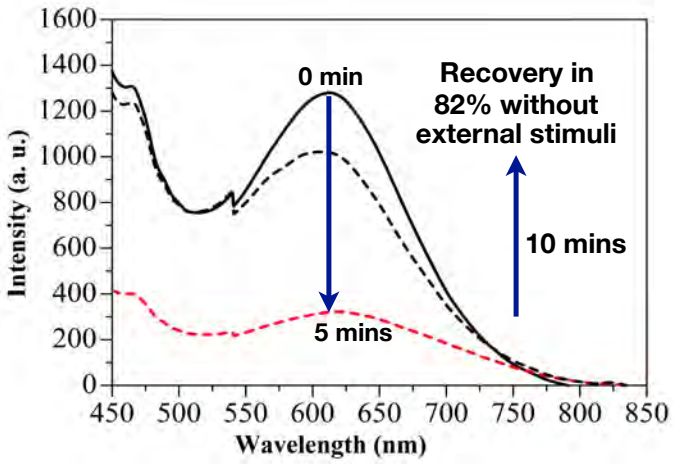
Photograph Images under λ_{ext} = 254 nm



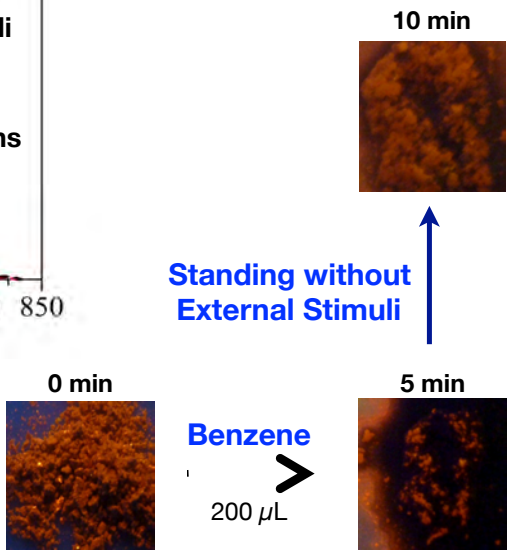
Color changes from reddish to less emissive in 5 minutes

Reusability Testing of Chemosensor 2(Au)

Emission Spectral Changes (λ_{ext} = 280 nm, λ_{em} = 570 nm)

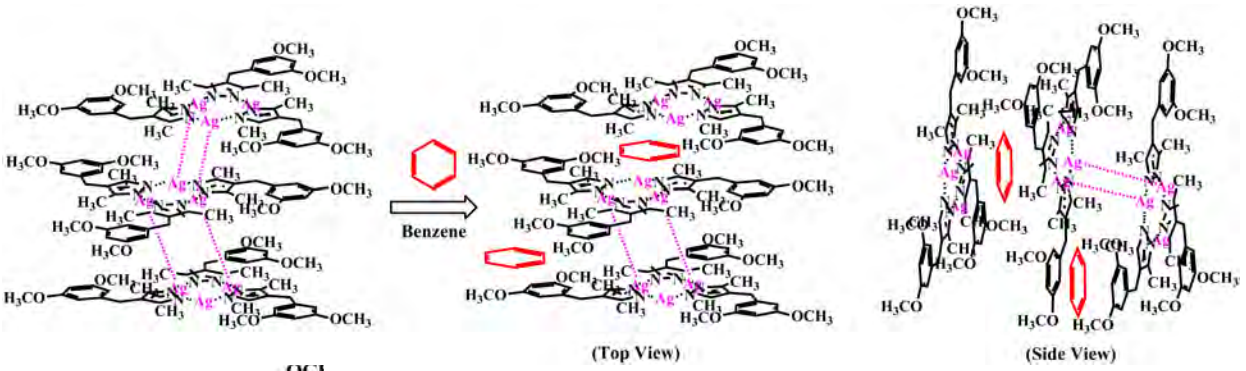


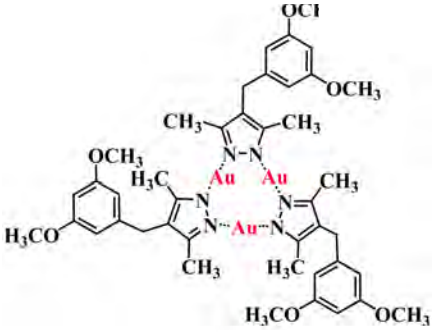
Photograph Images under λ_{ext} = 254 nm



Recovery of reddish without esternal stimuli compared to the original color

Proposed Mechanism for 2E(Cu)





2(Au)

Short distance of Au(I)–Au(I) interactions tends to encourage the diffusion of benzene vapors to Au-Au interaction for removing the light-emitting capability and to benzyl ring for formation of weak π–π interactions

Conclusions

1. Successful synthesis of trinuclear pyrazolate complexes with different Group 11 metal ions at the pyrazole rings as a powder with different color appearances under daylight in high yield.

2. Successful characterization of phosphorescent properties of trinuclear group 11 pyrazolate complexes as orange, dark green and reddish emission with lifetime at microsecond and large Stokes shifts.

3. Successful investigation of sensing capability of trinuclear group 11 pyrazolate complexes with chemosensors 2(Au) as the best chemosensor for detection of benzene with quenching of emission intensity in 81%.

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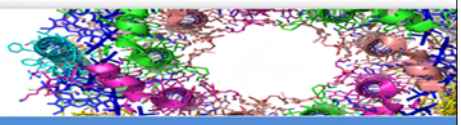
Ma Chung Research Center for Photosynthetic Pigments
CAPTURING THE SUN coloring the world



NAT Chrom

MOLECULAR PHOTOCHEMOSTRY RESEARCH GROUP

THANK YOU.....

- **Doctoral Students (7):**
  - Juan Matmin (Completed PhD)
  - Norsahika Mohd Basir (Completed PhD)
  - Nur Fatiha Ghazalli (D3)
  - Mohamad Azani (D3)
  - Nurliana Roslan (D3)
  - Abdul Hamid Umar (D3)
  - Nurul Husna Sabran (D2)
- **Master Students (1):**
  - Goh Cheow Kit (M2)

Picture with PhD Students