Functional Nanomaterials Using Phenolic Chelating Molecules as Colorimetric and Biological Sensors

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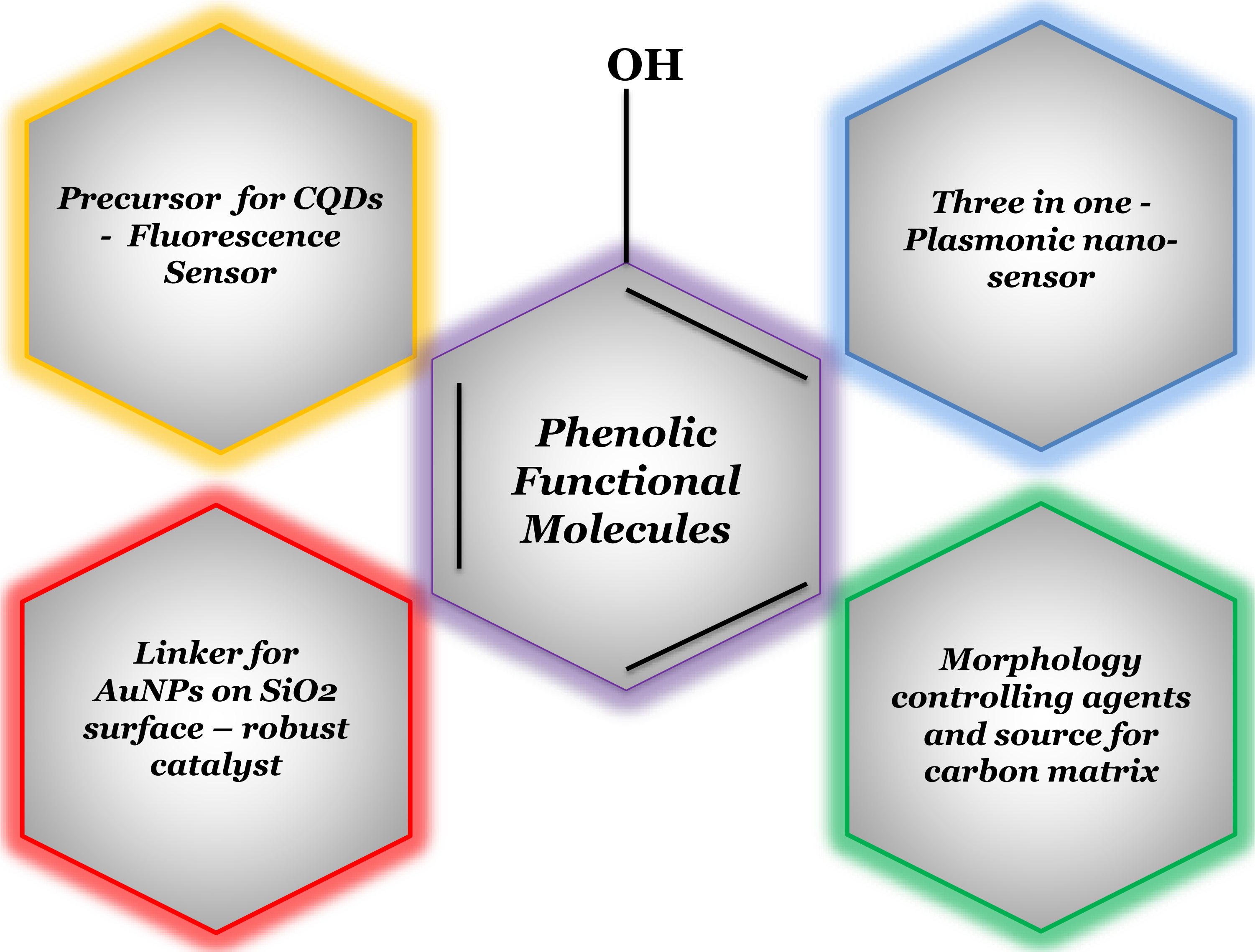
Overview

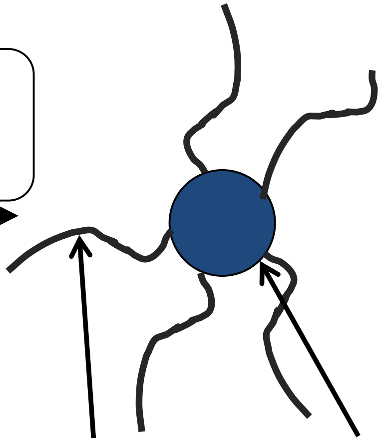

OH
Phenolic Functional Molecules
Precursor for CQDs - Fluorescence Sensor
Three in one - Plasmonic nano-sensor
Linker for AuNPs on SiO2 surface – robust catalyst
Morphology controlling agents and source for carbon matrix

Nanostructured Materials

- Materials which features with at least one of its critical dimensions between 1 nm to 100nm.
- Nanomaterials can be of two types; engineered or non-engineered
- Engineered nanoparticles are intentionally created to meet the specific applications e.g. CNT, Fullerene etc.
- Non-engineered nanoparticles are unintentionally created by nature such as volcanic ash, DNA and protein.

Synthesis of Nanoparticles (Wet Chemical Approach)

Metal precursors + **Stabilizing agents** → **Reducing agents** →



Ag^{+}, Au^{3+}, Cd^{2+}, Cu^{2+} salts

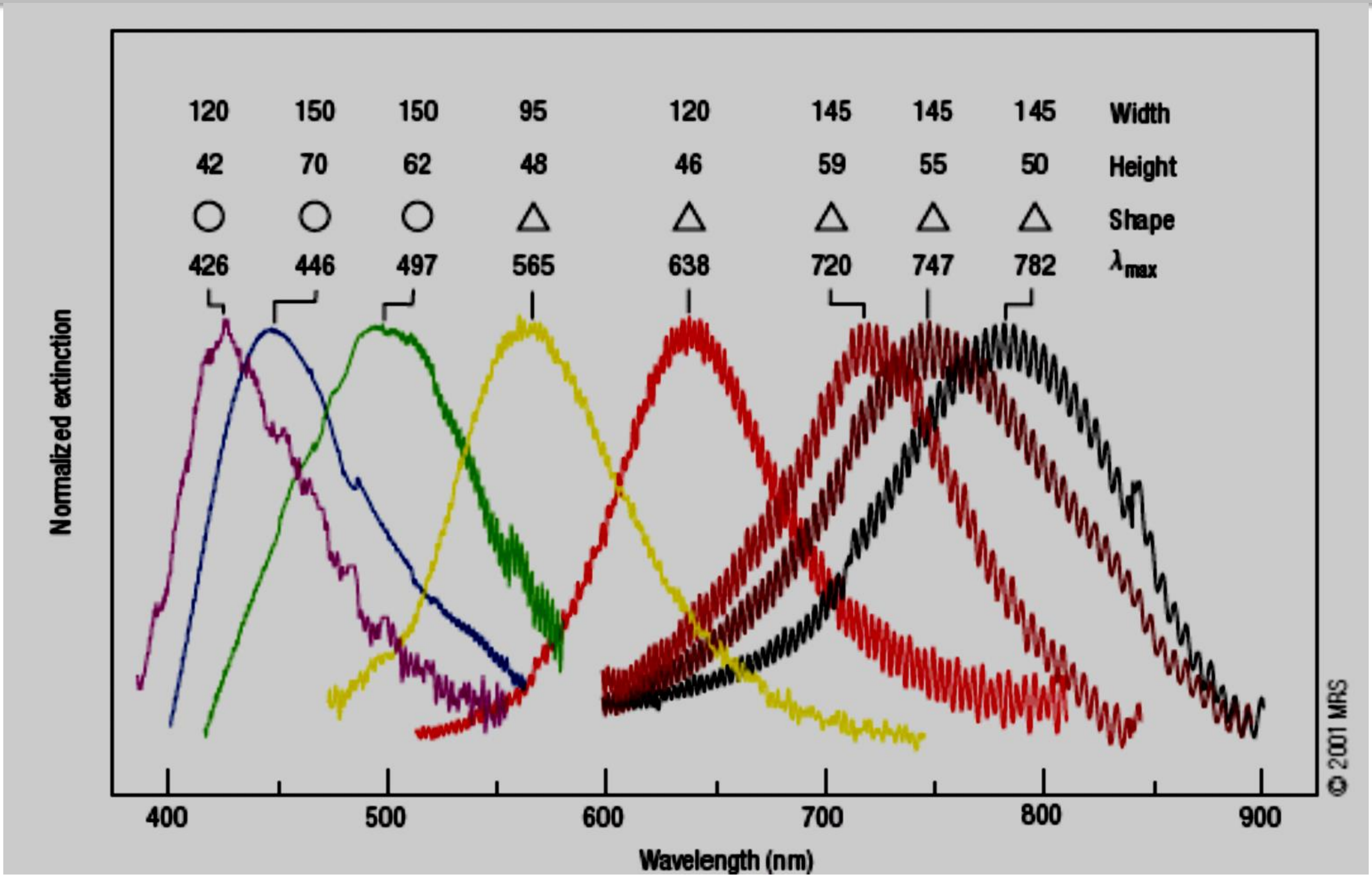
Citrate, CTAB, Polymer (PVA, PVP), etc

NPs

Surface functionality

- Control the size and shape
- Biological activity
- Stability

Size or shape – modulate optical and catalytic property



(Anker et al., Nature Mat. 2008)

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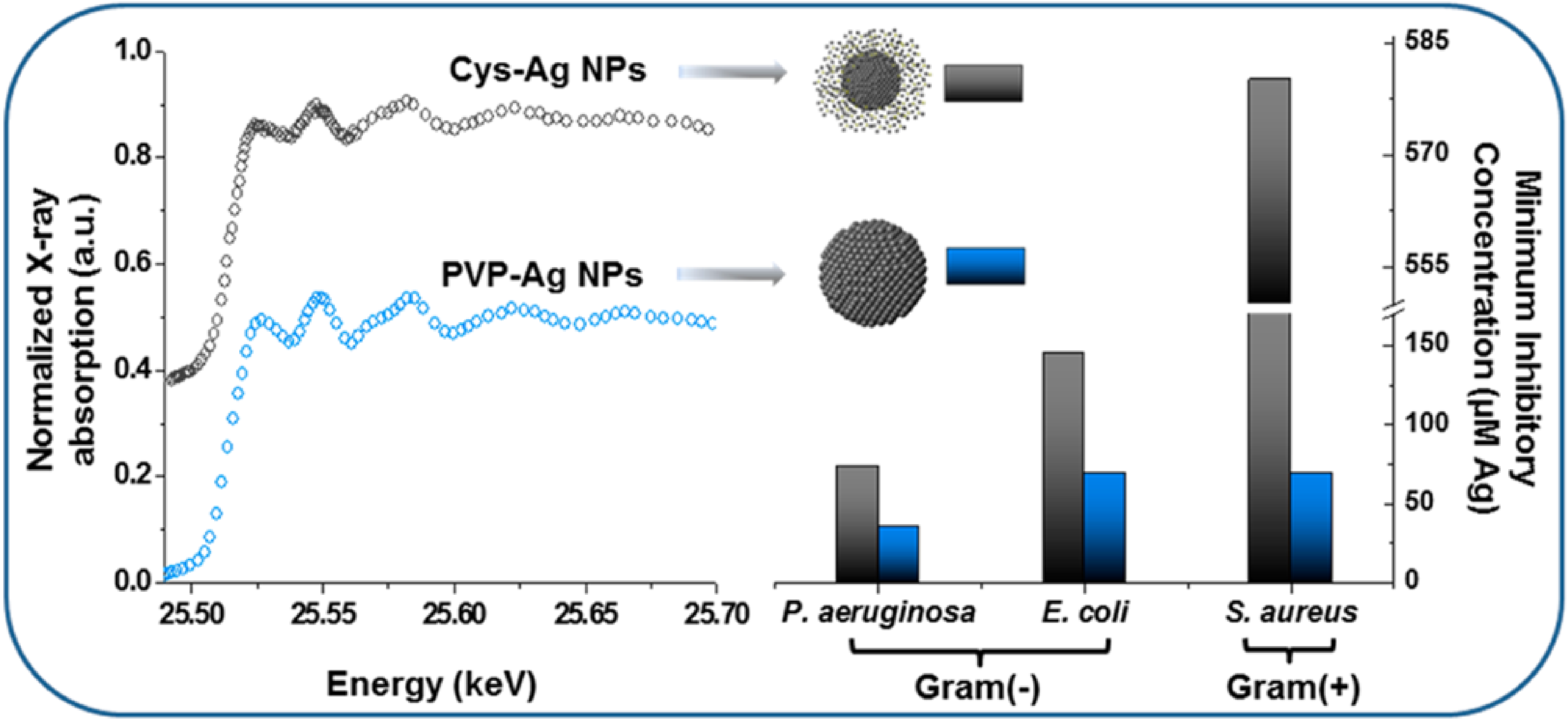
Surface functionality – Cell permeability and interaction with biomolecules



(J. D. Padmos et al. Langmuir, 2015)

Phenolic Functional Molecules

- Redox reagent – Plasmonic NPs (Ag and Au) preparation with surface functionality
- Strong interaction/coordination with metal ions – Surface functionality - Plasmonic Sensor
- Synthetic versatility to modulate the structure – Structure-property studies
- High Water solubility – Biological studies and environmentally benign

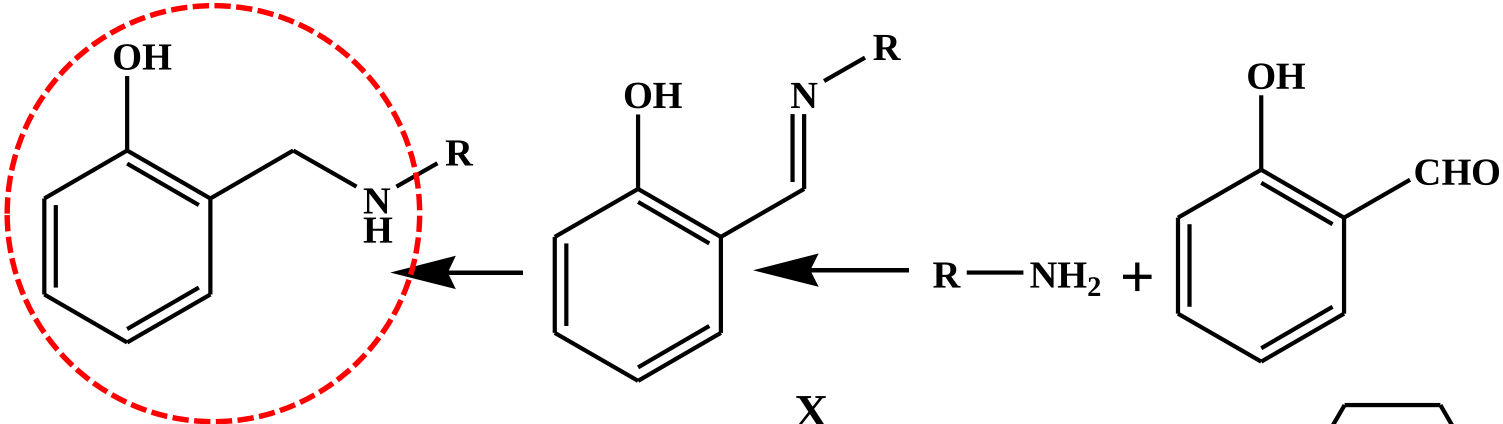
Three in one - Plasmonic nano-sensor

Plasmonic Nano-Sensor

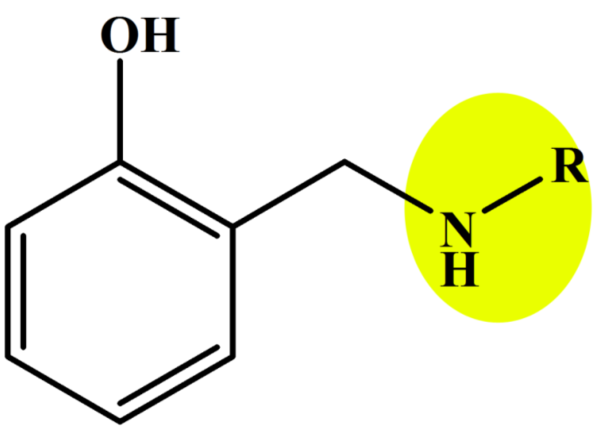
1. Multi-functional role in plasmonic nanosensors

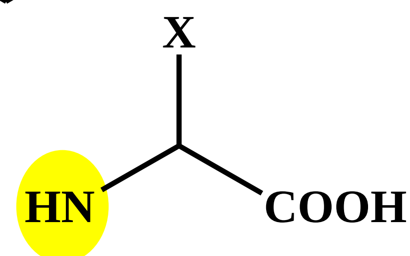
- ❑ Used as reducing, stabilizing and surface functionalizing agents
- ❑ Surface functionality used for selective sensing of metal cations and anions
- ❑ Role of phenolic chelating molecules structure on selectivity of cations/anions

Phenolic Chelating Molecules

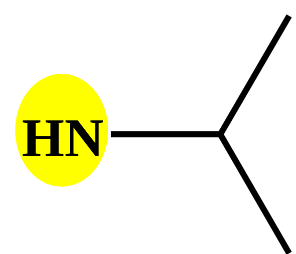


Our Interest

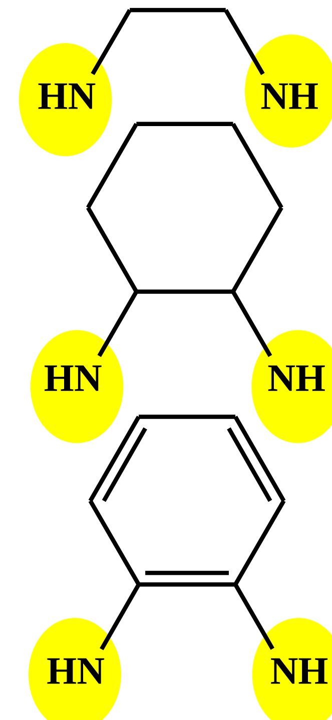




1. Amino acids

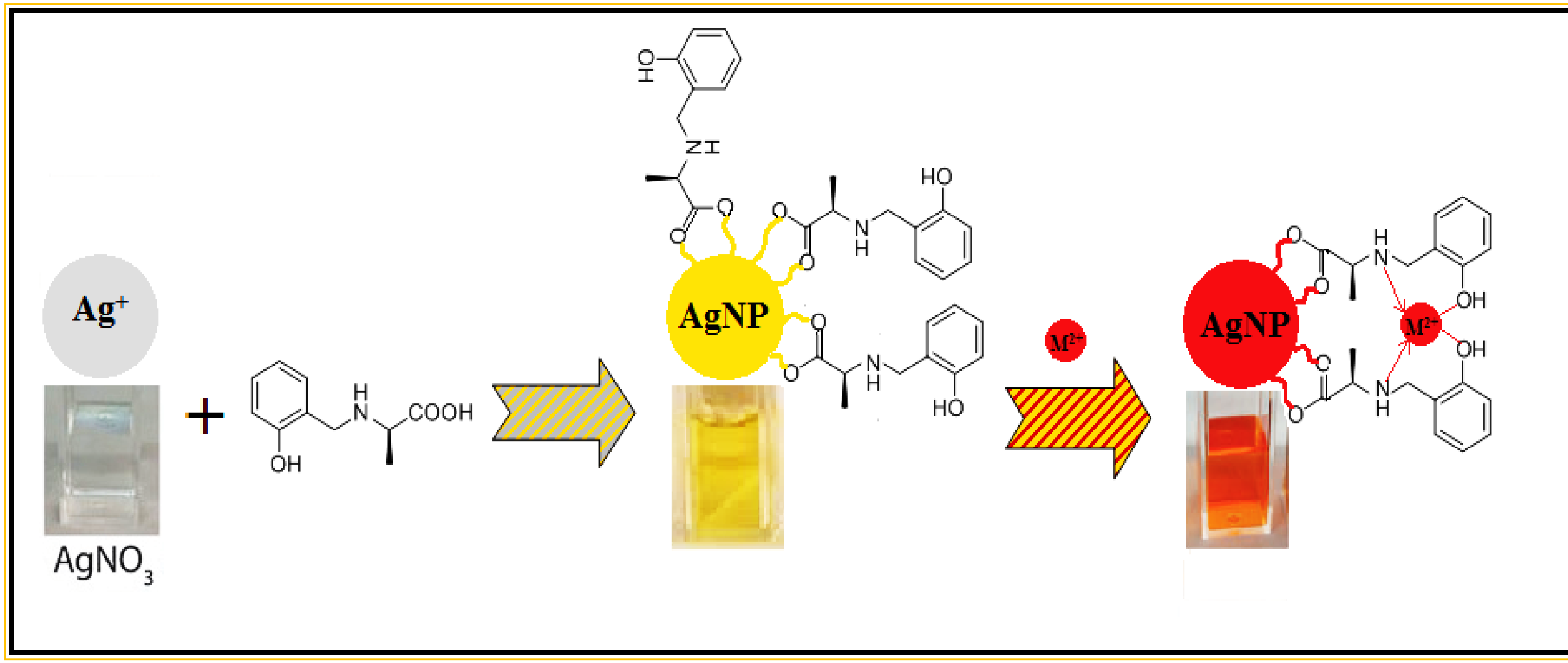


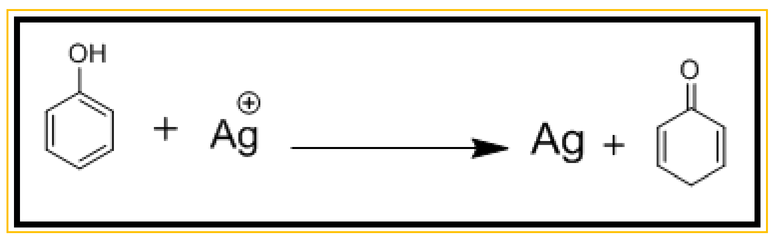
2. Isopropyl amine

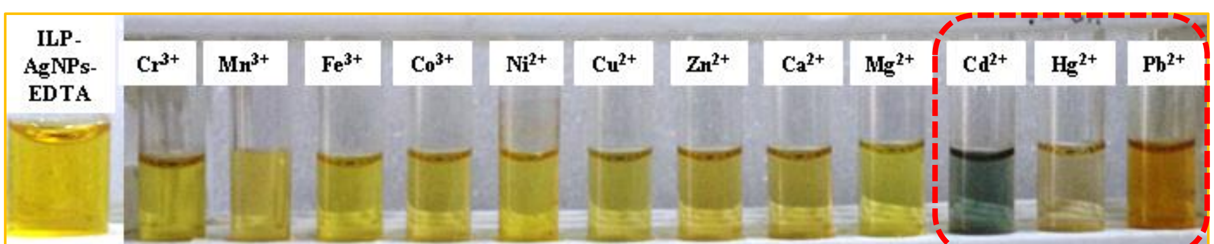


3. Structural flexibility based Diamines

Scheme of AgNPs synthesis with ligand functionality



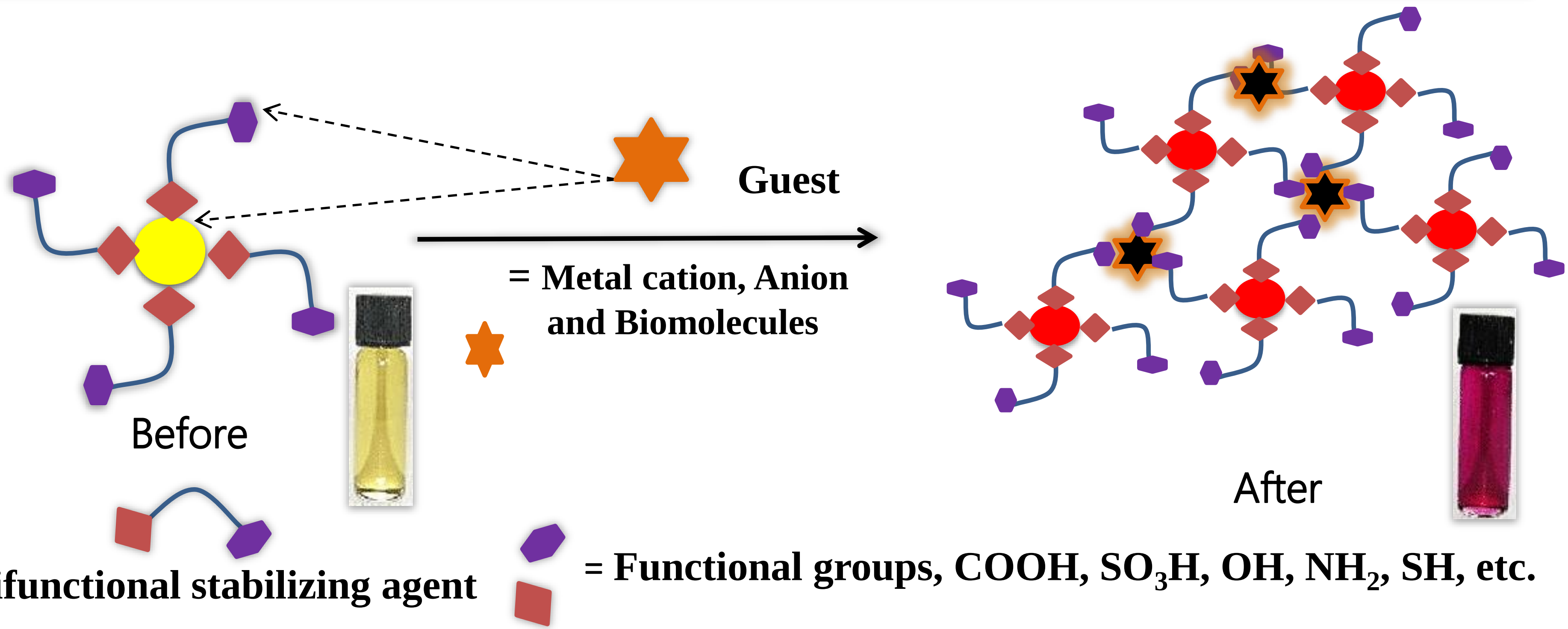




(V. V. Kumar et al. SNB, 2014)

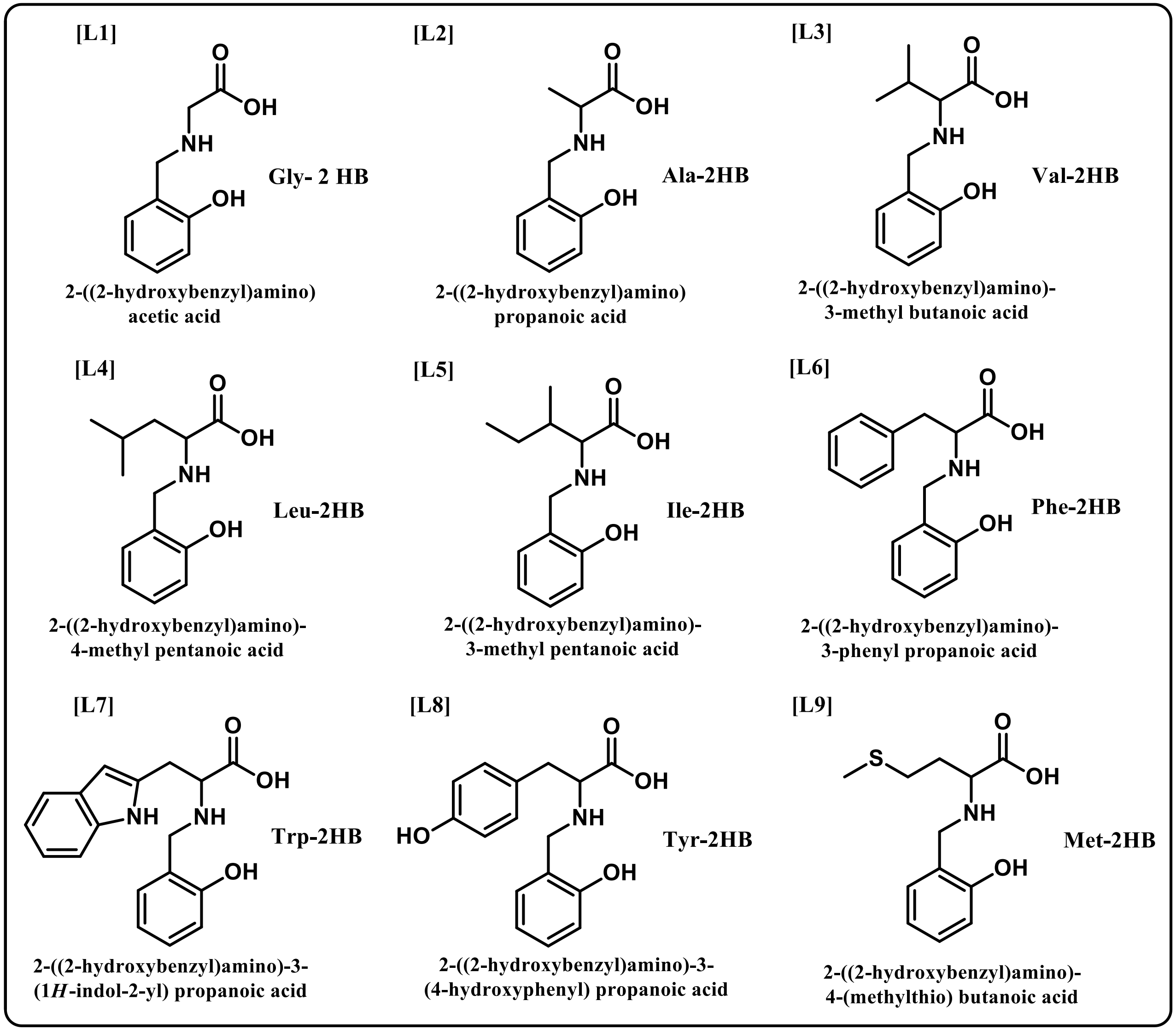
Distance dependent optical properties

- Decrease in size of Ag, AuNPs produce-colour
- Modulation of shape & change in the distance between NPs effects the electronic coupling and change the colour



Tuning of VP- and ILP-AgNPs metal ions sensing

1. Amino acids based phenolic chelating ligands functionalized AgNPs



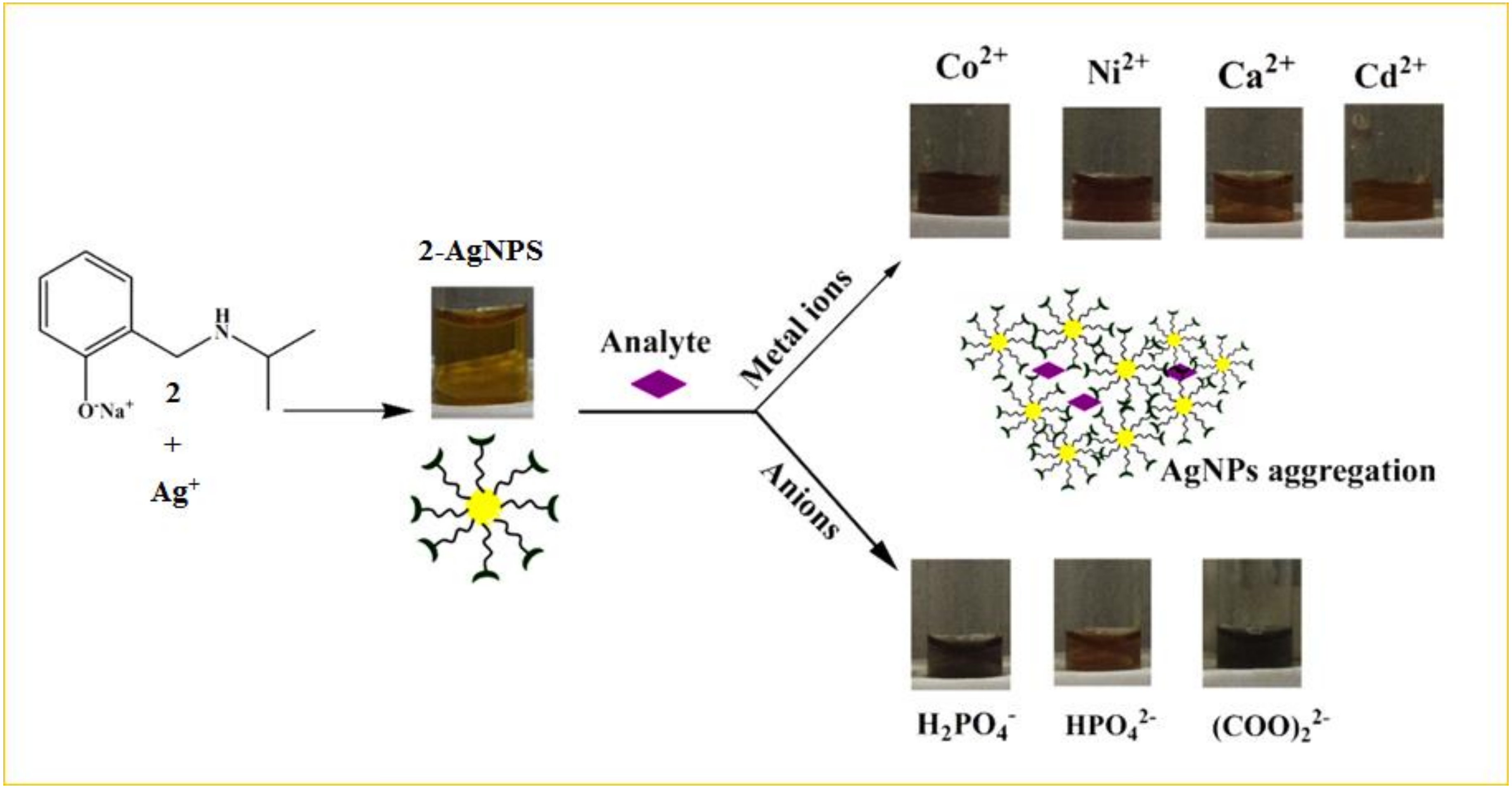
I row: **Gly**-Glycine, **Ala**-Alanine, **Val**-Valine, **Leu**-Leucine **II row**: **Ile**-Isoleucine, **Phe**-Phenylalanine, **Trp**-Tryptophan, **Tyr**-Tyrosine

Compound		Metal cations sensed
VP-AgNPs	VP-AgNPs	Cd^{2+}, Pb^{2+}
	VP-AgNPs-TSC	Cd^{2+}, Pb^{2+}
	VP-AgNPs-PVA	Hg^{2+}
	VP-AgNPs-EDTA	Cd^{2+}, Pb^{2+}
ILP-AgNPs	ILP-AgNPs	Cd^{2+}, Pb^{2+}
	ILP-AgNPs-TSC	Cd^{2+}, Pb^{2+}
	ILP-AgNPs-PVA	Hg^{2+}
	ILP-AgNPs-EDTA	Cd^{2+}, Pb^{2+}, Hg^{2+}
AP-AgNPs	AP-AgNPs	Zn^{2+}, Cd^{2+}, Pb^{2+}
	AP-AgNPs-TSC	Zn^{2+}, Cd^{2+}, Pb^{2+}
	AP-AgNPs-PVA	Hg^{2+}
	AP-AgNPs-EDTA	Cd^{2+}, Pb^{2+}
GP-AgNPs	GP-AgNPs	Pb^{2+}
	GP-AgNPs-TSC	Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Cr^{3+}
	GP-AgNPs-PVA	Hg^{2+}
	GP-AgNPs-EDTA	Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}
LP-AgNPs	LP-AgNPs	Cd^{2+}, Pb^{2+}
	LP-AgNPs-TSC	Cd^{2+}, Pb^{2+}
	LP-AgNPs-PVA	Hg^{2+}
	LP-AgNPs-EDTA	Cd^{2+}, Pb^{2+}
TYP-AgNPs	TYP-AgNPs	Hg^{2+}
	TYP-AgNPs-TSC	Hg^{2+}
	TYP-AgNPs-PVA	Hg^{2+}
	TYP-AgNPs-EDTA	Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}

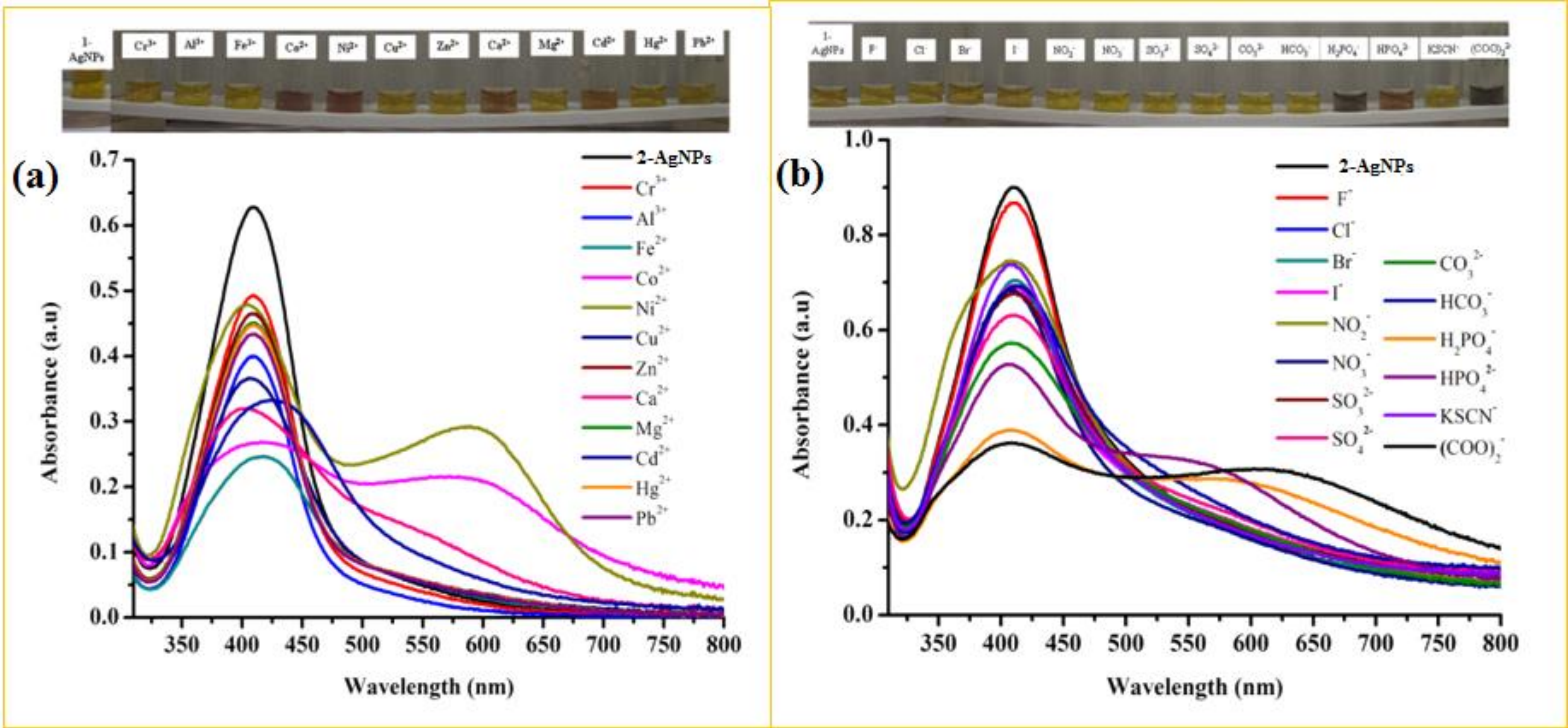
- Amino acid attached phenolic ligands were chosen due to its redox properties
- Phenolic unit reduces silver ions into AgNPs and also provides stability and surface functionality to the NPs
- Phenolic chelating ligands were known to form strong coordination with metal ions
- Coordination expected to produce smaller aggregates of AgNPs that would show different colour due to distance dependent optical properties

Selectivity!!!

2. Isopropyl amine based phenolic chelating ligands functionalized AgNPs



(V. V. Kumar et al. New J Chem., 2015)

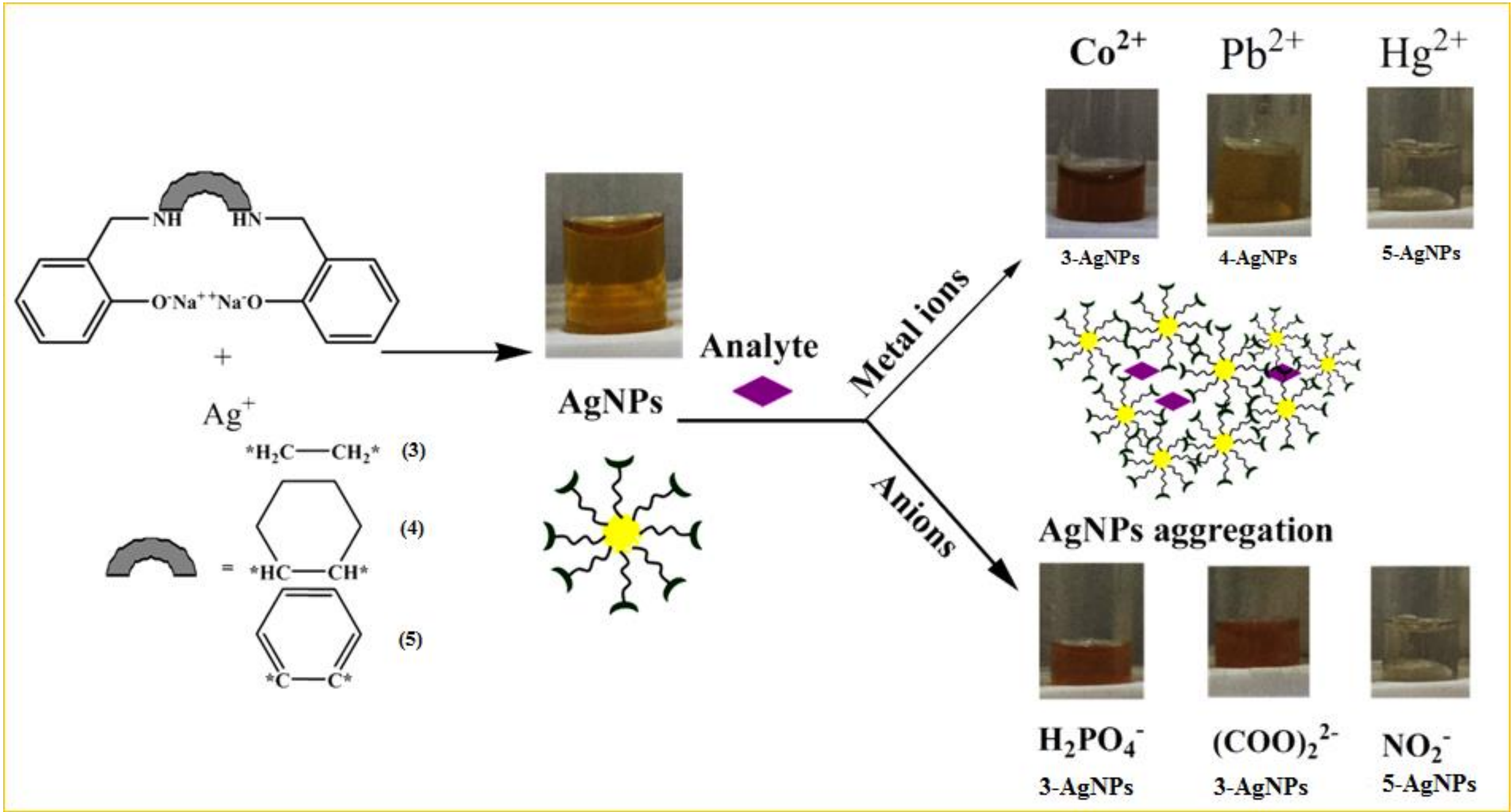


Guest	LOD (µg/ml)	LOQ (µg/ml)
Co^{2+}	85	255
Ni^{2+}	65	195
Ca^{2+}	80	240
Cd^{2+}	210	630

Guest	LOD (µg/ml)	LOQ (µg/ml)
$H_2PO^{-}_4$	130	390
HPO^{2-}_4	145	435
$(COO)^{2-}_2$	160	480

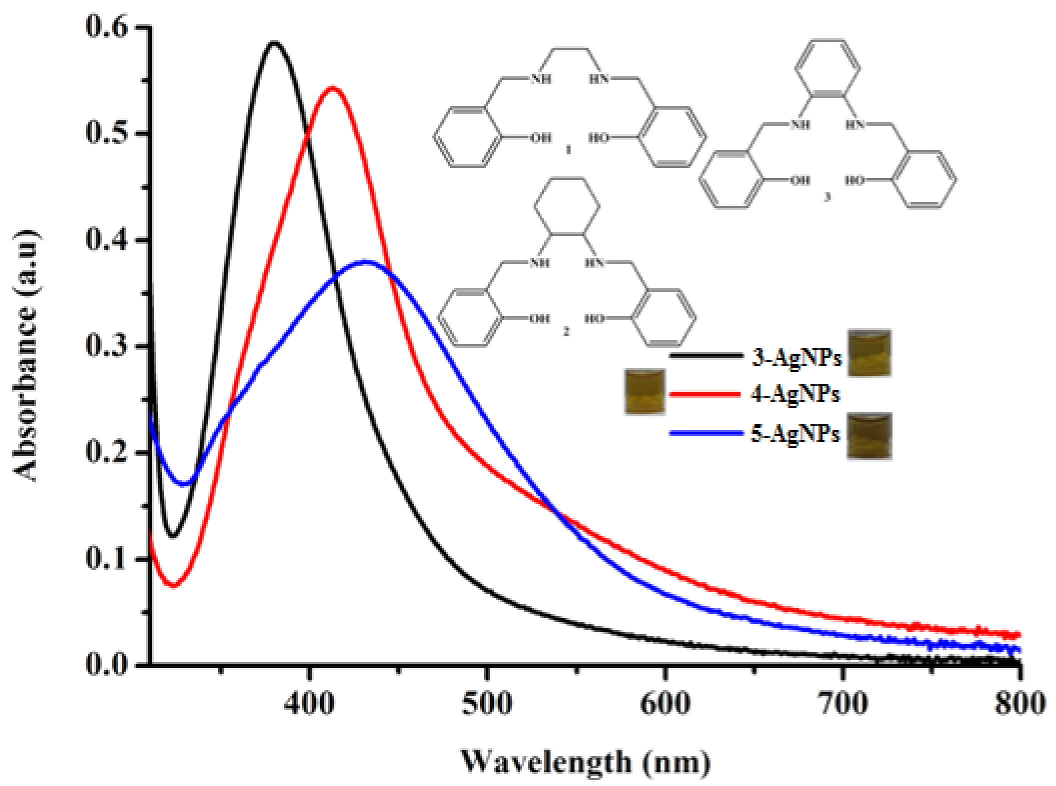
Absorbance spectra of IPA-AgNPs for (a) different metal ions (b) anions with inset digital image (c) LOD and LOQ values for detectable metal ions and anions

3. Role of structural flexibility of phenolic chelating ligands for sensing

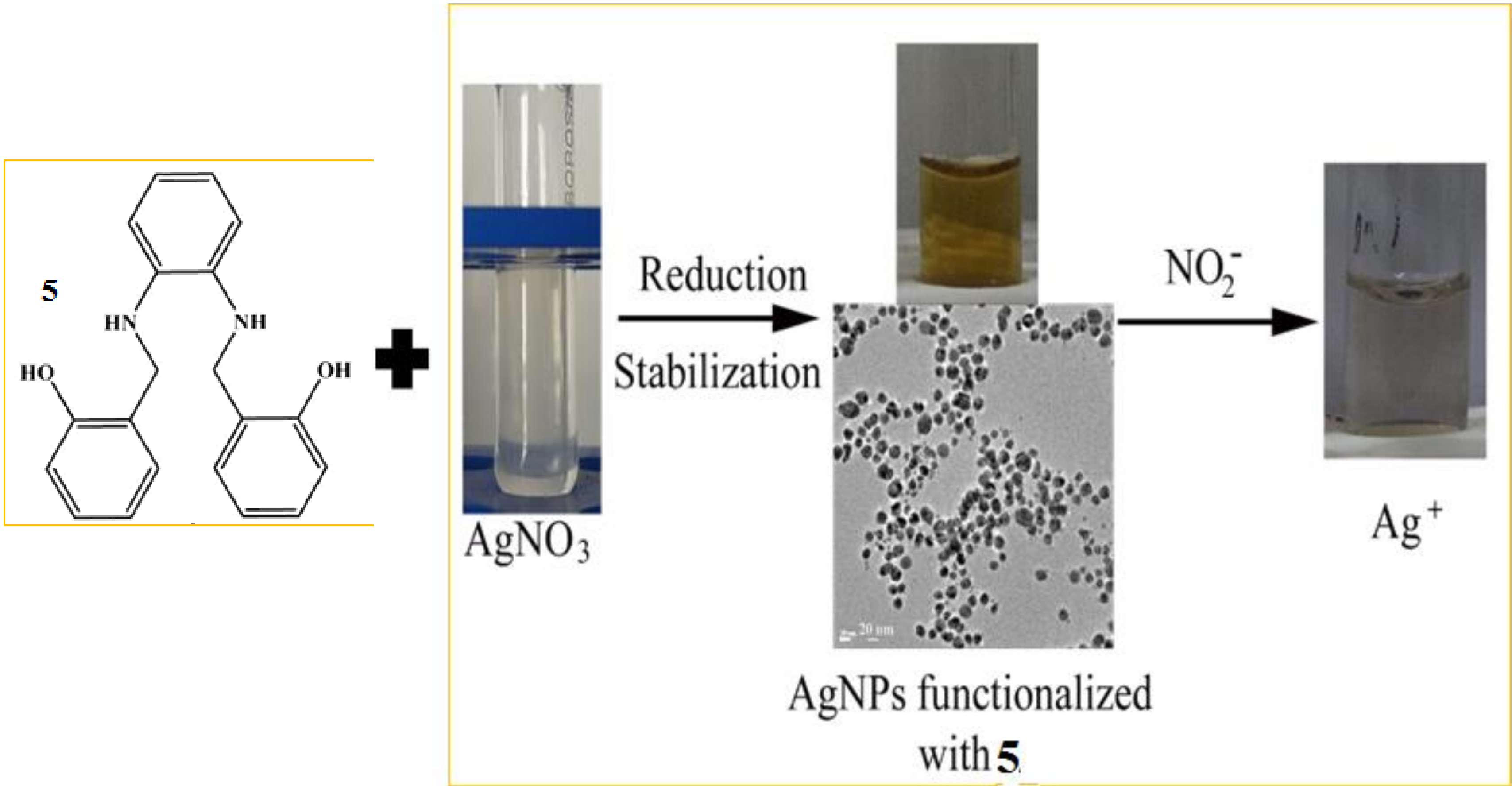


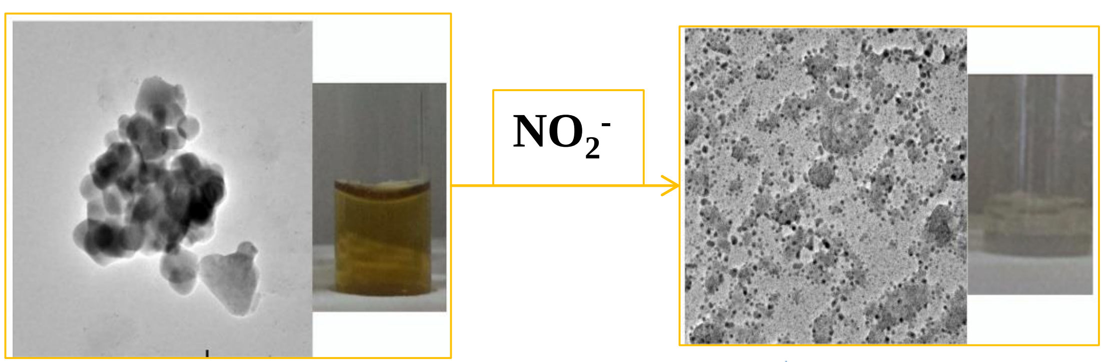
(V. V. Kumar et al. RSC Adv., 2015)

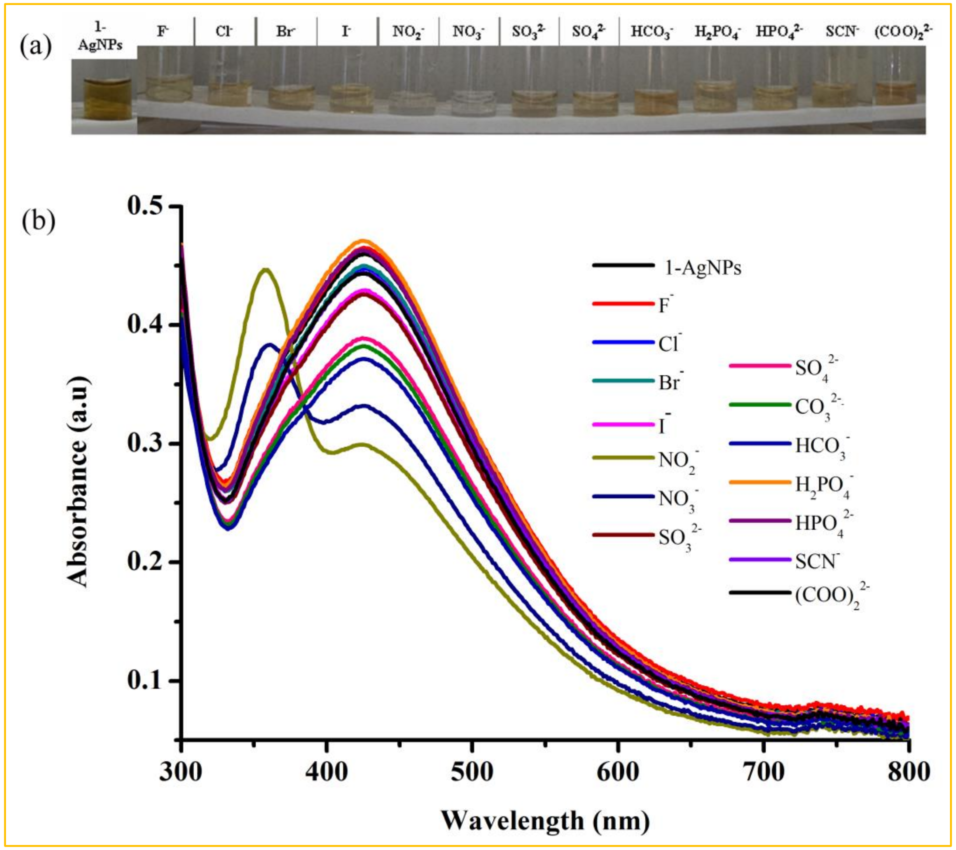
Absorption spectra of AgNPs



Guest	LOD (µg/ml)	LOQ (µg/ml)	Guest	LOD (µg/ml)	LOQ (µg/ml)
Co^{2+}	155	465	$H_2PO^-_4$	275	825
Pb^{2+}	160	480	$(COO)^{2-}_2$	225	675
Hg^{2+}	120	360	NO_2^-	110	330


5
HN
NH
HO
OH
AgNO3
Reduction
Stabilization
20 nm
AgNPs functionalized
with 5
NO2-
Ag+

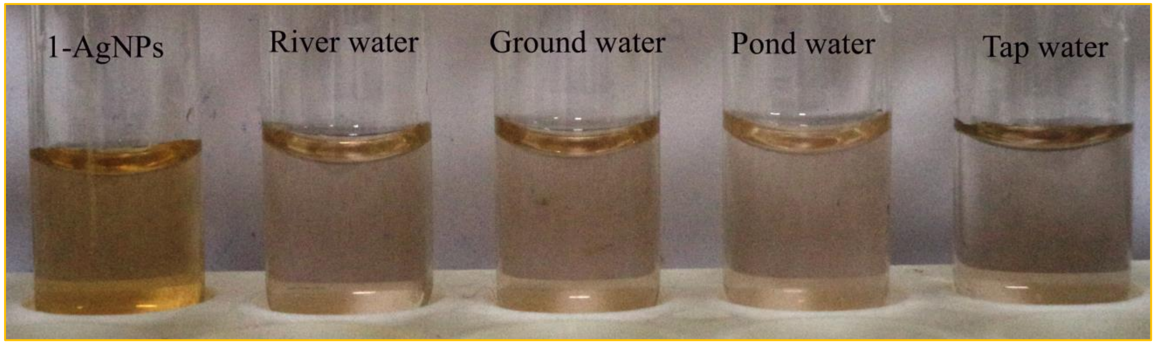

NO2-



Guest	LOD (µg/ml)	LOQ (µg/ml)
NO_2^-	0.100	0.300

(c)

(d)



OPD-AgNPs- (a) inset of digital image for different anions (b) Absorbance spectra (c) LOD and LOQ value for NO_2^- and (d) Real water samples

(V. V. Kumar et al. ACA, 2015)

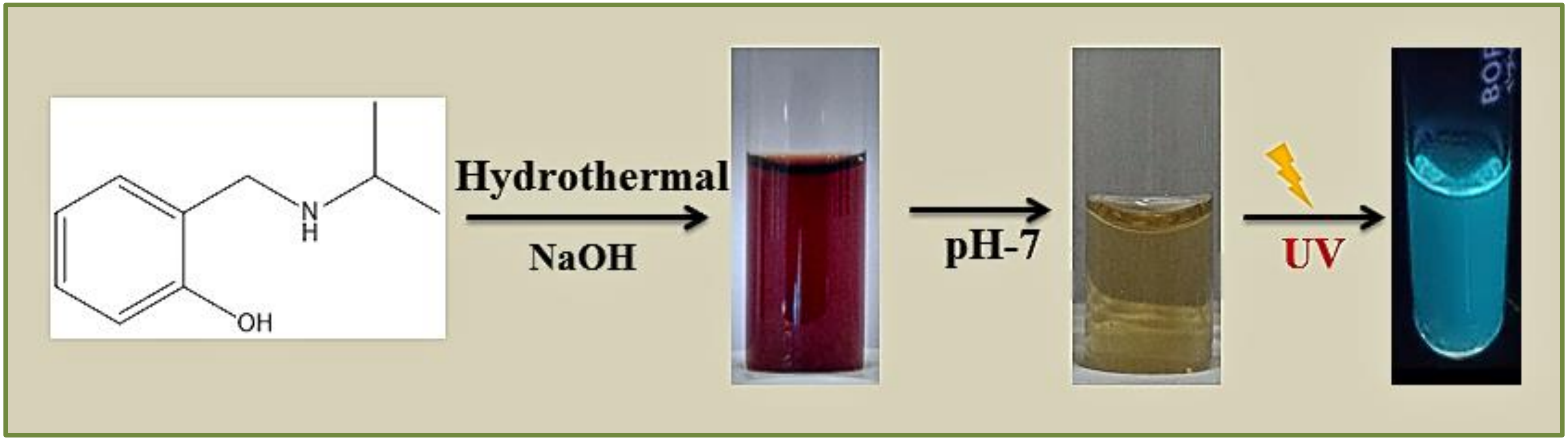
Conclusion

- ✓ Three-in-one role from phenolic chelating molecules
- ✓ Inexpensive and Simple naked-eye detectable probes
- ✓ Tunable sensitivity and selectivity

Precursor for CQDs - Fluorescence Sensor

Precursor for CQD

- C-dots are composed of carbon-core and surface domains
- CQDs characterized by UV-Visible, Fluorescence, XPS and FE-TEM
- Successfully use for selective sensing and potential bio-imaging probes for Zn^{2+}, Pb^{2+}



(V. V. Kumar et al. New J Chem., 2017)

Role of phenolic structure on CQDs formation

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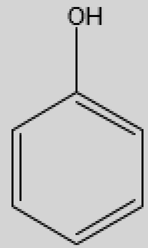
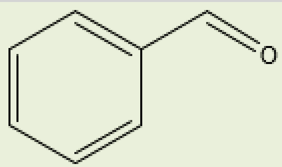
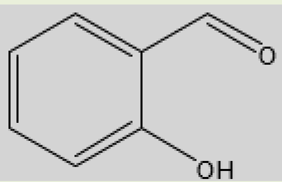
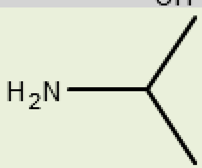
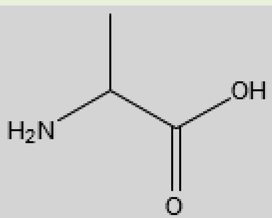
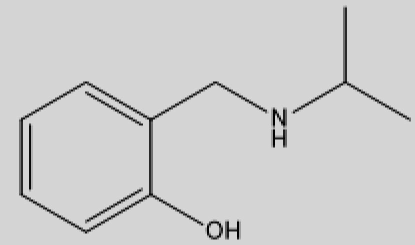
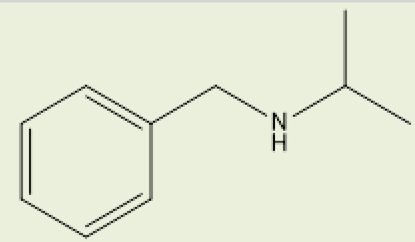
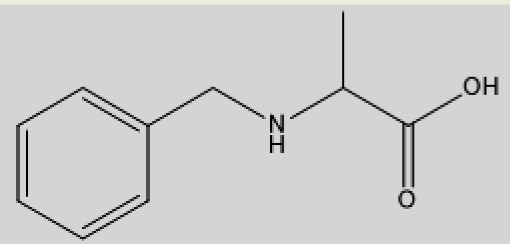
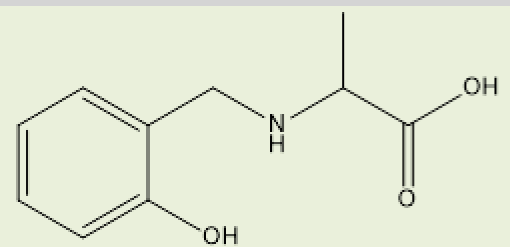
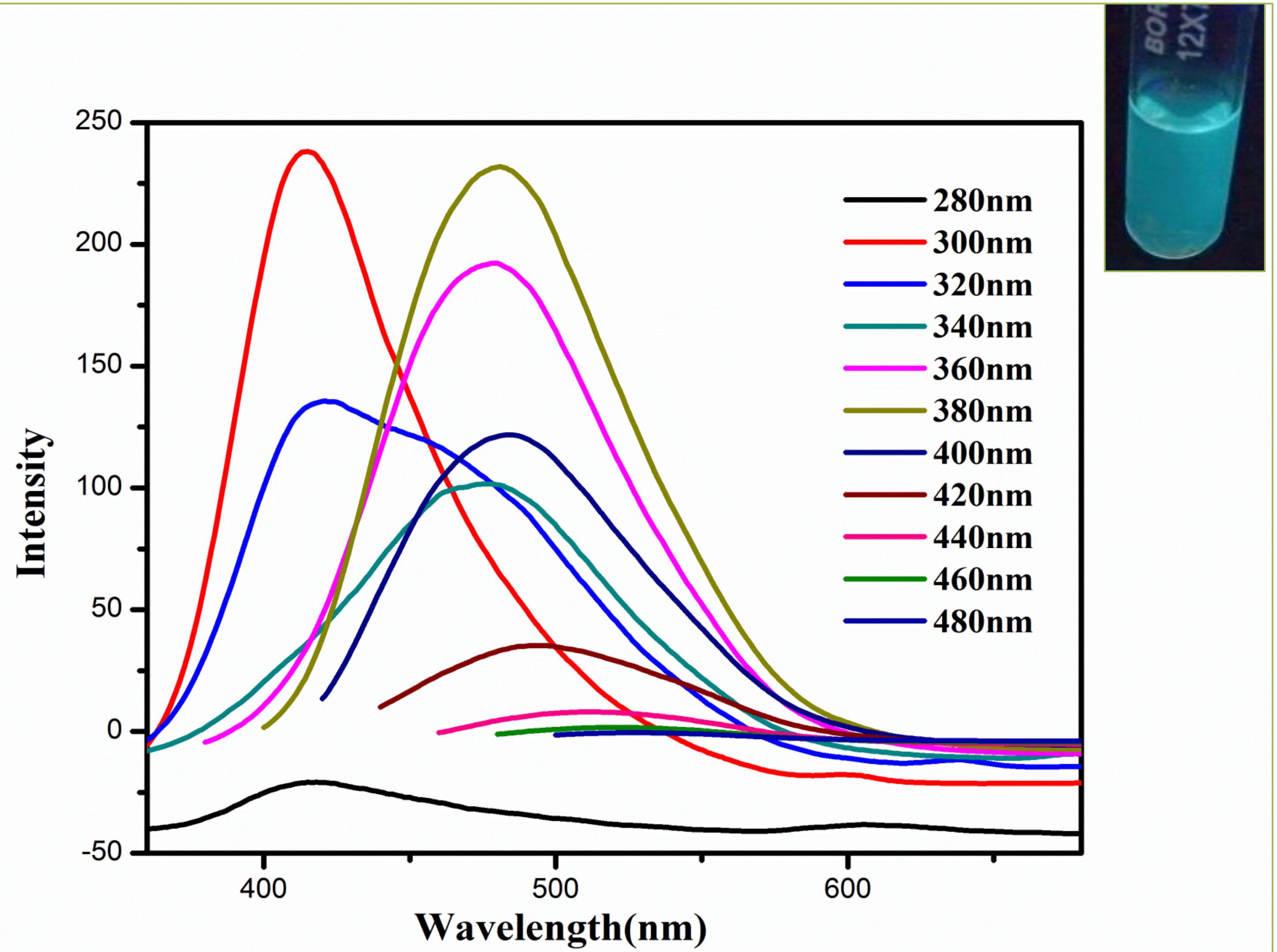
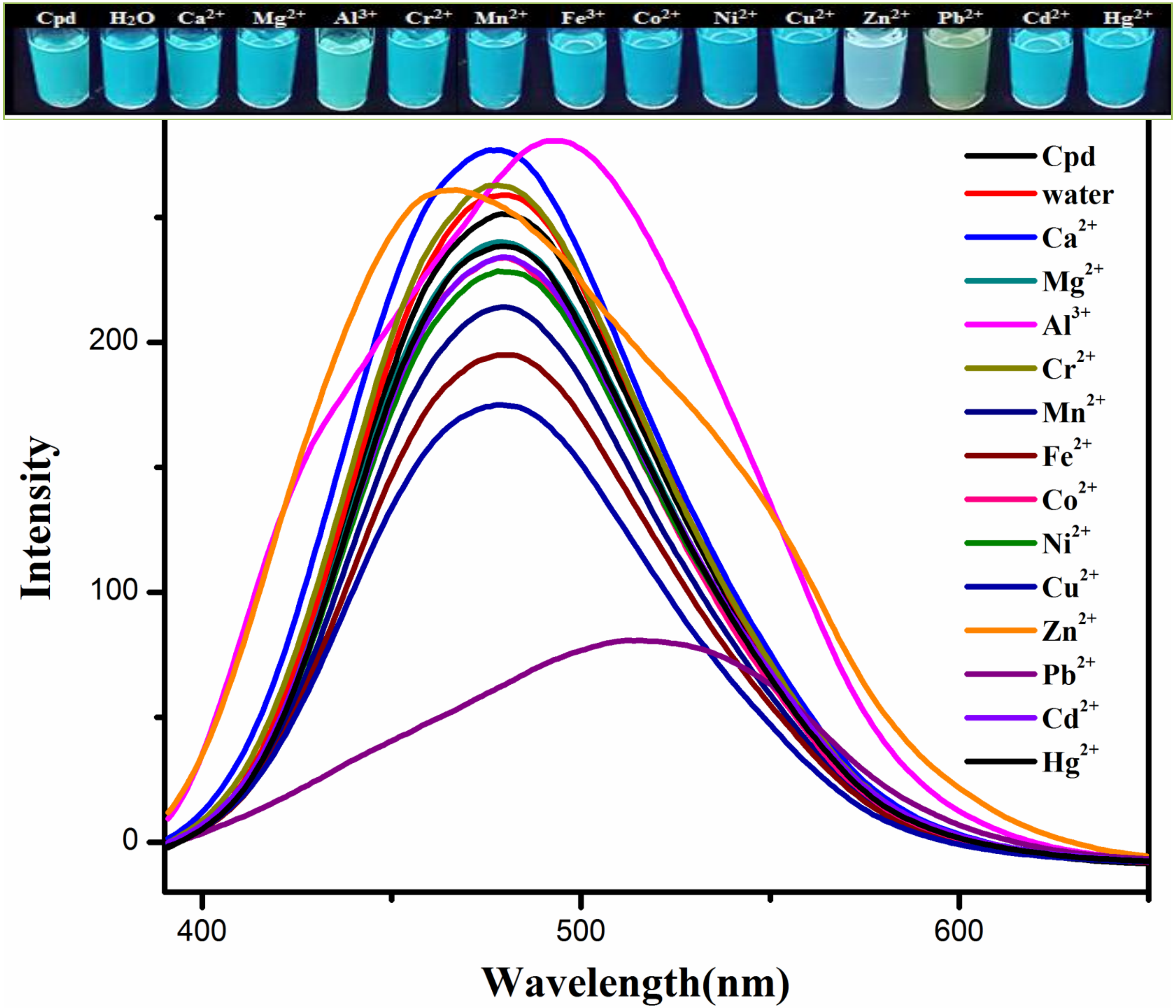
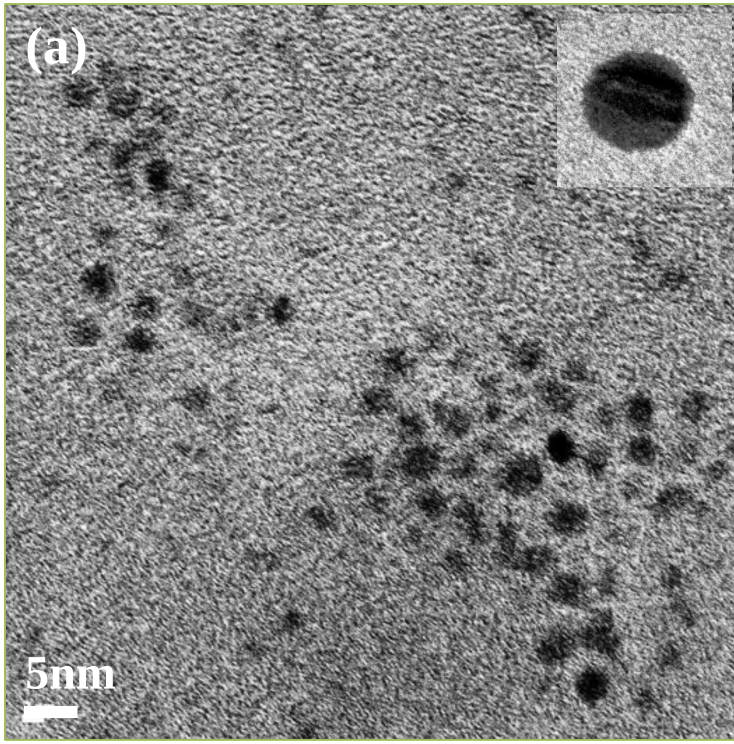
1.		No
2.		No
3.		No
4.		No
5.		No
6.		Yes
7.		No
8.		No
9		Yes

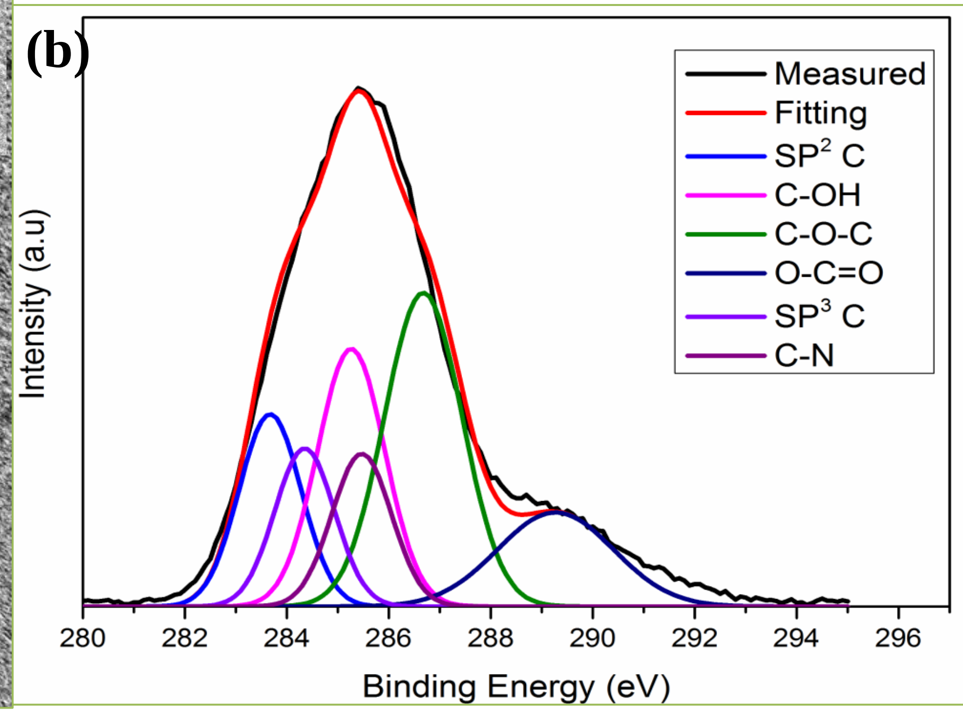


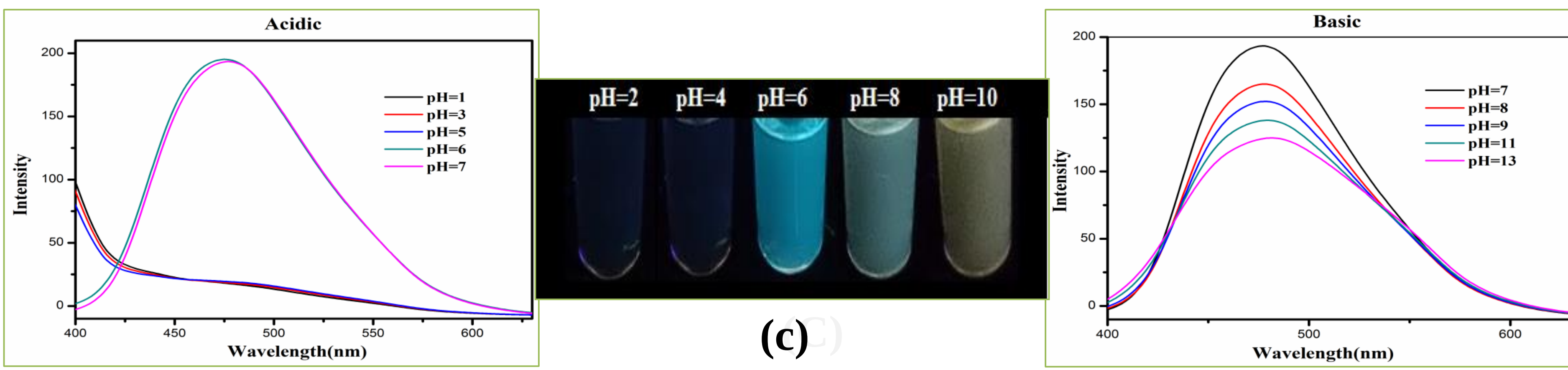
Emission spectra monitored at different excitation wavelengths in the range of 280−480 nm, inset digital images of CQD



(a) Digital images and (b) Emission spectra of CQD excited at 370nm with different metal ions in H_2O.







(a) HR-TEM of CQD and (b) XPS spectra CQD and (c) Digital images of pH tuned studies with its Fluorescence spectra in acidic and basic studies

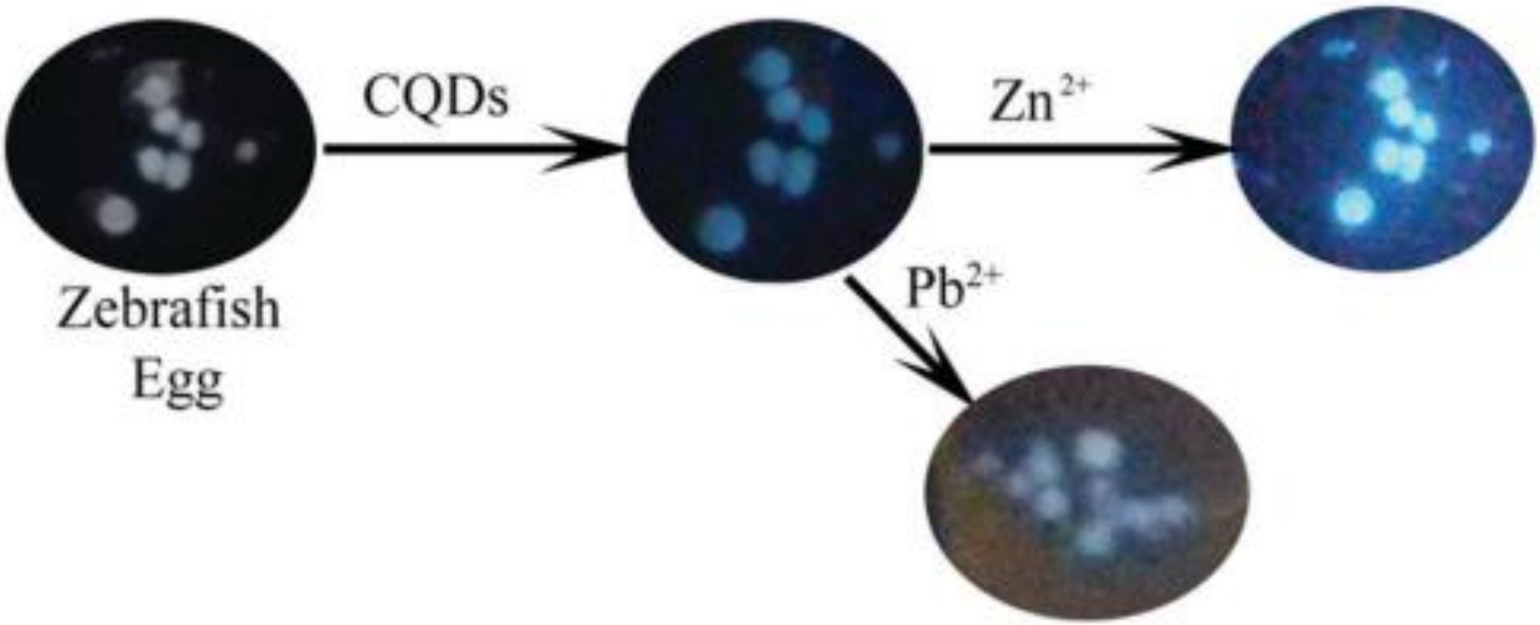


Fig. 8 Biological application of CQD-based fluorescence sensing of Zn^{2+} and Pb^{2+} in zebrafish eggs.

***New J. Chem.*, 2017, 41, 15157**

Table 1 Different CQD fluorescence sensors reported for metal cations

Source for CQDs	Metal ions detected
Pomelo peel	Hg^{2+}
Rose-heart radish	Fe^{3+}
Citric acid	Cu^{2+}
Citric acid/urea/cysteine	Hg^{2+}
Citric acid/cysteine	Cu^{2+}
Valine	Hg^{2+}
Poly(ethylenimine) functionalized CQDs	Cu^{2+}
N-(β-Aminoethyl)-γ-aminopropyl methyldimethoxysilane	Cu^{2+}
Jinhua bergamot	Hg^{2+}, Fe^{3+}
L-Glutamic acid	Fe^{3+}
Sweet potato	Fe^{3+}
Colistin	Fe^{3+}
L-Arginine	Cu^{2+}
Glucose, 1,2-ethylenediamine (EDA) and concentrated phosphoric acid (H_3PO_4)	Cr^{6+}
Biomass	Cr^{6+}
Ocimum sanctum	Pb^{2+}
2-(2-Hydroxybenzylamino)propanoic acid	Zn^{2+}, Pb^{2+}

Conclusion

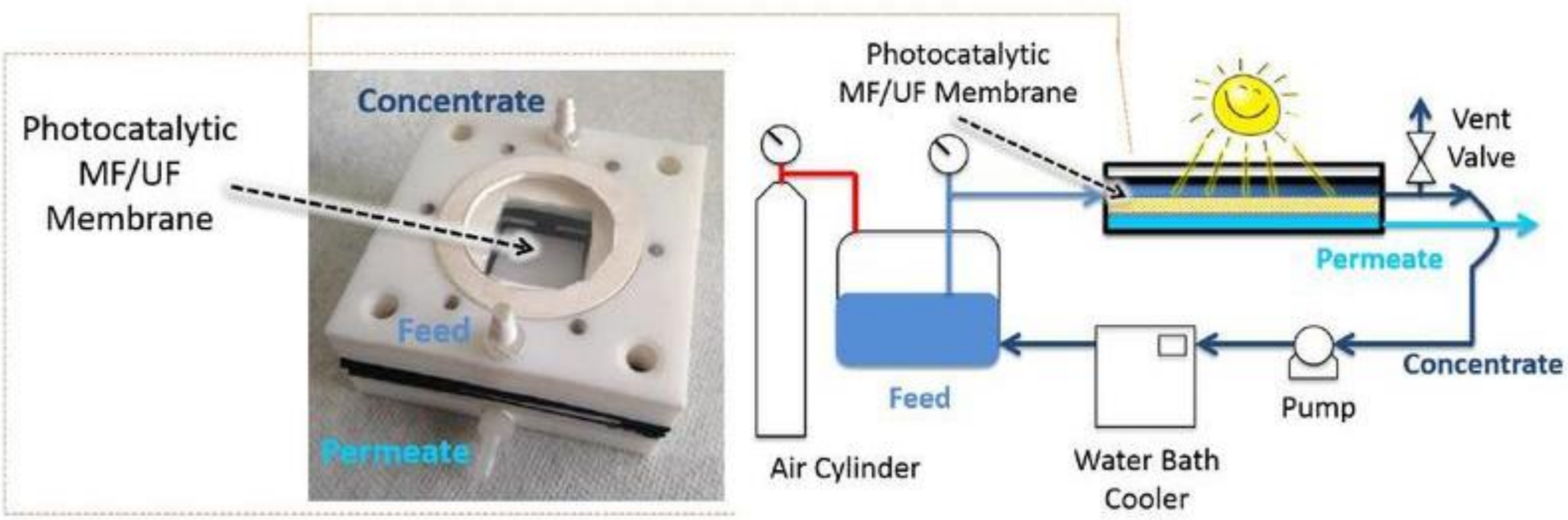
- Fluorescent CQDs were prepared via a hydrothermal reaction using amino acid based phenolic molecule
- Investigated the role of phenolic structure on CQDs formation
- Demonstrated selective metal ions sensing of (Zn^{2+} , Pb^{2+})

Summary

- ✓ Surface engineering for plasmonic nano-sensors
- ✓ Morphology controlling agents in AgNPs
- ✓ Precursor for fluorescent CQDs
- ✓ Over all, the work exploited the versatility of phenolic chelating molecules for fabricating nanomaterials and demonstrated sensing and biological applications.

Present Work @ Water Tech Laboratory

- ❖ Constructing a UVA/visible-light-driven photocatalytic membrane reactor with improved permeability and low energy consumption
- ❖ Develop ceramic/polymer coated membranes and 3D printed membranes by simple spray coating and FDM technologies.



Thank You