Aggregation Induced Emission: Optical and Morphological Insights

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Aggregation Induced Emission

Self Quenching is Not Always Momentous

Ru-arene
Chem. Soc. Rev. 43, 707-733, 2014

Metal-dipyrrins
Dalton Trans. 45, 7163-7177, 2016
Inorg. Chem. 54, 2500 -2511, 2015
Inorg. Chem. 54, 2500 –2500, 2015

Metallacycles
Dalton Trans., 44, 17152-17165, 2015
Organometallics. 34, 4491–4506, 2015.

AIE
J. Phys. Chem. C (under review)

Chemosensors
Dalton Trans. 44, 7118-7122, 2015

Gelators
Chem. Commun. 50, 10086–10089, 2014
Chem. Commun. 50, 8144-8147, 2014
Chem. Commun. 50, 1675-1677, 2014
Luminscent materials have become indispensable in our daily life. In one or other way society’s convenience and welfare depends on it. We can see it in the form of lamps, traffic lights, computer screens, cell phones, labels of different items, airport security check devices, medical applications and many more.

Particularly, photoluminescence has created a revolution in many scientific innovations and technological developments.
LED lamps of different color

Traffic Lights

Airport Security Check

Biomedical

Mobiles
Suppression of unfavourable intermolecular processes by introducing peripheral bulky substituents or intricate chemical structures.
Aggregation induced emission (AIE)

**Perylene**
- Emissive
- \(\pi-\pi\) stacking interaction
- Aggregation-caused quenching (ACQ)
- Nonemissive (off)

**HPS**
- Nonemissive
- Restriction of intramolecular rotation (RIR)
- Aggregation-induced emission (AIE)
- Emissive (on)

*Chem. Commun.*, 1740-1741, 2001
Tetraphenylethylene (TPE)

9-vinylanthracene

Triphenylamine (TPA)

Carbazoles

Polymeric compounds

Hydrogen bonded compounds

Cyanide containing systems

Ar = Ph, 4-MeOPh, 3-pyridinyl, 3-HOPh, 3-MeOPh, 3-BrPh

Ar = Ph, 4-MePh, 4-MeOPh, 4-Me2NPh, 4-HOPh

Ar = 4-CNPh, 4-C6H4CN, 4-C6H4-NC
AIE mechanisms involve restriction of intramolecular rotation (RIR), conformational planarization, E/Z isomerization, excimer/J-aggregate formation, twisted intramolecular charge transfer (TICT), excited state intramolecular proton transfer (ESIPT), and conical intersection.
**Applications of AIE**

Fluorescent bio-/chemosensors. To detect ionic species (Hg$^{2+}$, Ag$^{+}$, CN$^{-}$), bio-molecules (protein, heparin, ATP and DNA), gases (CO$_2$), explosives (TNT, picric acid), as well as for nuclease activity assay.

(A) Lactic acid, B-Ag$^{+}$, C-Hg$^{2+}$

Latent finger printing recognition

Viscosity Sensor

RSC Adv., 5, 87306–87310, 2015


Peptide sensor

Targeting Sequence AP2H

DNA sensor

TPE conjugated with a peptide IHGHHIISVG specifically binds to LAPTM4B


RSC Adv., 5, 28332–28337, 2015
Dual color cell imaging probes

Probe for cellular apoptosis

Serves as an efficient apoptotic marker

Fluorescent nanoparticles


ACS Appl. Mater. Interfaces, 7, 4875-4882, 2015

Mechanochromic AIEgens

Mechano

AIEgens

Mechanical grinding
Thermal Annealing

Writing–erasing process
(Security ink)

AIE materials in LED

Metal based AIE active systems displaying good aggregation-induced phosphorescence emission (AIPE) in CH₂Cl₂/hexane (1/90) via RIR
Unique photophysical properties: strong absorption, sharp fluorescence bands, high quantum yield, large two-photon cross-sections, insensitive to polarity and pH, stable under physiological conditions. Structural modifications tuning their fluorescence characteristics.
Our Aim

AIE: Optical & Morphological insights

Simplified and less restricted approach

Steric Hindrance

Asymmetry
- Photonics of AIE luminogens well known, information relating to aggregates and their morphology is still lacking.
- Developing an approach without conventional decorated luminophores has been challenging.
- Functionalized quinolines are highly emissive in solution as well as in solid state with high quantum yield, good electron transport, and excited state intra-molecular proton transfer (ESIPT).

**Chem. Commun., 2015, 51, 9125-9128**
Decrease in absorbance along with a level-off tail in the visible spectral region.

- Colour of the solution also turned red from yellow.
- It may be attributed to an increase in π-π interactions, thereby, creation of the nanoaggregates.
Discrete Emission Behavior of AIEgens

- Emission band corresponding to quinoline unit gradually disappeared.
- Red shift upon aggregation, a frequently observed feature in AIE systems.
- Multiple emission bands upon aggregation may arise due to presence of both monomeric and aggregated state in solution.
- Substituent effect.
BQ1 and BQ2 -nano-ball aggregates of uniform size with average diameter of 220 and 150 nm.

BQ3 formed a highly reticulated network of ~300 nm thick fibrous nanoaggregate.

Aggregate size in BO2 is smaller as compared to BQ1.
BQ3 forms a typical J-aggregate with both p-p and C-H...p interactions along the long molecular axis. Herring-bone mode and double helical structure with alternate BF$_2$ and -OMe on side with hydrophobic quinoline in centre.
Live cell imaging

DL cells were incubated with BQ1-BQ3 for 2 h and co-stained with Hoechst 33342 to identify nuclear region of the cells.

- Dichromic (green and red) fluorescence under blue or green excitation due to presence of both monomeric and aggregated species.
- Green emission was weakest in BQ3 while BQ1 displayed faint red emission.
One-dimensional (1D) nanostructures play a significant role in construction of high performance optoelectronic devices such as field-effect transistors (FETs), organic light emitting diodes (OLEDs), organic light emitting transistors (OLETs) and solar cells.

Along with conventional symmetrical D-A systems, current research has also been riffling through asymmetric D-A molecules. Presence of more than one D/A unit with competitive strength unleash interesting aspects of push-pull mechanism which may enable adjustments in the molecular structure and desired optoelectronic properties.

We intended to device an asymmetric D-A architecture to control AIE as a function of acceptor strength. Our prime concern was to set up a morphological trademark for achieving 1D nanostructures with AIE characteristics.
Aggregation induced emission

$A' = \text{pyridyl, PM2 and } A' = \text{pyrimidyl, PM3}$

PM2

PM3

525 564 580

$\sim 8$ and $\sim 2.5$ times emission enhancement for PM2 and PM3
Solvatochromic behavior

Change in solvent polarity from extremely non-polar to polar, a red shift of 20 and 40 nm occurred for PM2 and PM3. The emission intensity of PM2 and PM3 diminished in polar solvents.

A’ = pyridyl, PM2 and A’ = pyrimidyl, PM3
Mechanism of Aggregation (TICT vs RIR)

- 30 and 32 nm blue shift in THF/Hexane mixture.
- Competitive TICT and RIR (profound substituent effect)

![Graphs showing intensity vs. wavelength with annotations](image)

- $\tau_{av}$ value -2.66 and 4.85 ns for PM2 at $f_w$ 90 and 100%, respectively.
- $\tau_{av}$ value for PM3 - a bit lower that is 2.59 and 3.29 ns at $f_w$ 90% and 100% respectively

$A' = \text{pyridyl}, \text{PM2} \text{ and } A' = \text{pyrimidyl}, \text{PM3}$
Red shift in emission maxima of PM2 and PM3, from solution to crystalline fibres through aggregates, is 95 and 106 nm respectively

\[ A' = \text{pyridyl}, \text{PM2 and} \ A' = \text{pyrimidyl}, \text{PM3} \]
1D nanoaggregates of different morphology.

PM3 displayed more than one hierarchal assembly.

Twisted ribbons braid together to form helical fibres.

Fluorescence microscopic images for both PM2 and PM3 displayed a dichromic fluorescence under blue or green excitation.
Applicative Aspects of AIEgen

Viscosity Probe

BQN1

BQN2 loaded BSA nanoparticle

40% 50% 60% 70% 80% 90% 100%

Apoptotic Marking

J Phys. Chem. C (Under review)

Live Cell imaging
Currently we are interested in restricting intramolecular rotation by aggregation and supplementing the complexes with long alkyl chain to achieve micelles and vesicles in aqueous solution, which could eventually lead to emission enhancement. In this direction, we have chosen zinc and cyclometalated iridium complexes as these are being widely used in molecular recognition, fluorescent sensors, photonic, optoelectronic and biological fields.
Conclusions

Optical and Morphological Control in AIEgens

Asymmetry induced AIE in D-A molecules

Applicative aspects of AIEgens in Biology

Annexin V         BQNI        Merge        Phase contrast

Control Cells

Dead Dying Cells

Apoptotic marking in cancer cells

Live cell imaging of AIEgen loaded BSA nanoparticle
My group...
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Thank You