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Aggregation induced luminescence of metal complexes: advances and applications

Andrea Fermi, ^{a*} Paola Ceroni ^a and Inamur Rahaman Laskar ^b

The materials science community has witnessed a remarkable development in the design and synthesis of luminescent materials, with a constantly growing body of literature over the last 20 years. Both organic and inorganic compounds showing aggregation induced emission (AIE) – *i.e.* the phenomenon that leads materials to display intense luminescence in aggregated phases, and weak emission in solution – are by now the target of consolidated and well-established branches of chemistry and materials sciences. Recent advances in the analysis of structure related photophysical properties of AIE-active metal complexes have prompted investigations towards their application in disparate areas, disclosing the fundamental role of their rational design and chemical modifications in the tunability of their properties.^{1–3}

Thanks to the rich interplay between the electronic states of metal ions and ligands and due to the presence of heavier transition metal centers able to promote spin–orbit coupling, these compounds show intriguing photophysical features and often display phosphorescence ensuring long luminescence lifetimes and large Stokes shifts, making these compounds attractive for tailored applications such as chemosensing and

stimuli-responsive materials, bioimaging probes or optoelectronic devices.

In this collection, we are pleased to present recent advances in the development of AIE-active materials based on metal complexes, with contributions by prominent researchers.

First-row transition metal complexes showing AIE effects are reported by Bortoluzzi, Ferraro and Castro, showing the solid phase luminescence of a class of naphthylphosphonic diamide Mn(II) complexes (<https://doi.org/10.1039/D1DT00123J>). Lian, Zhang and co-workers describe the use of a family of Mn(II) complexes with three AIE active carbazole-terpyridine ligands for applications in photodynamic therapy (PDT) (<https://doi.org/10.1039/D2DT02410A>). Taking advantage of the inherent antibacterial property of Cu(I) complexes, Yuan and co-workers report a series of AIE active polymer-stabilized luminescent phosphors for analogous applications (<https://doi.org/10.1039/D3DT00333G>). Li, Tang *et al.* also report the use of Cu(I) for the construction of a luminescent metal–organic framework (MOF) with highly flexible pyrazine derivatives as ligands (<https://doi.org/10.1039/D2DT03382H>). Shova, Cazacu and co-workers report the use of solid-state emissive first-row transition metal complexes with salen ligands for application in optical devices and liquid crystals (<https://doi.org/10.1039/D1DT01980E>).

Gabr and Pigge report the formation of a Co(II) complex with a tetraphenylethene derivative and its use as a turn-on probe for cyanide anion detection

(<https://doi.org/10.1039/C7DT04242F>).

The tetraphenylethene motif has also been employed by Fumoto, Tanaka and Ooyama, who describe the photophysical properties of a Zn(II) complex in the solid phase (<https://doi.org/10.1039/D2DT03525A>). With a similar approach, a team lead by Zheng develop a class of AIE active mechano-responsive materials based on Zn(II) complex-luminescence in the solid phase (<https://doi.org/10.1039/D2DT02435G>).

Xu and co-workers show that a pyridine decorated tetraphenylethene ligand was rigidified on coordinating Ag(I), leading to an induced aggregation able to turn-on the luminescence (<https://doi.org/10.1039/C9DT03985F>). The linear coordination of Au(I) is exploited by Moro *et al.* to develop a phosphorescent complex for the sensing of nucleotides in aqueous media (<https://doi.org/10.1039/C9DT04162A>).

Several examples of solid phase luminescence are reported for tricarbonylrhenium(I) complexes by Fery-Forgues *et al.* (<https://doi.org/10.1039/D2DT03573A>; <https://doi.org/10.1039/C9DT02786F>), highlighting the influence of steric hindrance in ligands, isomerism and intramolecular π – π stacking. Re(I) AIE-active complexes are described by Thanasekaran, Lu and co-workers (<https://doi.org/10.1039/D2DT03408E>) as luminescent sensors for nitroaromatics and antibiotics.

Dong, Cao and co-workers show the stimuli-responsive emission of a metal-lacage obtained from the complexation of Pd(II) and a tetraphenylethene

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derivative (<https://doi.org/10.1039/D0DT00469C>). The structural and phosphorescence properties of a class Pd(II) and Pt(II) complexes are described by Zou, Lu *et al.*, emphasizing the role of lipophilic counterions for their aggregation in non-polar solvents (<https://doi.org/10.1039/D2DT03415H>).

Platinum is still one of the most popular metals used in AIE-active materials, which finds wide applications such as in photodynamic therapy (Li, Yin *et al.*, <https://doi.org/10.1039/D2DT03855B>), electroluminescence devices (Zhou and co-workers, <https://doi.org/10.1039/D3DT00238A>), chemoresponsive materials (Shinozaki *et al.*, <https://doi.org/10.1039/D2DT02360A>) and circularly-polarized luminescence (Xiang *et al.*, <https://doi.org/10.1039/C8DT03615B>).

Ir(III)-based AIE metal complexes are also increasing in popularity, with wide and diverse applications in chemo-detection (Sasmal *et al.*, <https://doi.org/10.1039/D3DT00628J>; Liu *et al.*, <https://doi.org/10.1039/D2DT03537E>; Khatua

and co-workers, <https://doi.org/10.1039/C8DT02099J>), photodynamic therapy (Li, Bian, Zhu, Bryce and co-workers, <https://doi.org/10.1039/D2DT03809A>; Chang, Li, Zhu, Bryce *et al.*, <https://doi.org/10.1039/D2DT02960J>; Liang, Mao, Shan, Li *et al.*, <https://doi.org/10.1039/D2DT03404B>) and aqueous media pH-sensing (Fujihara *et al.*, <https://doi.org/10.1039/C8DT04861D>). Water-soluble dinuclear Ir(III)-Pt(II) complexes for AIE-driven imaging in bacterial cells are described by Mallick, Gupta *et al.* (<https://doi.org/10.1039/D2DT03390A>).

Among the most popular entities in photophysics, Ru(II) complexes can also show aggregation-dependent emission, as Khatua *et al.* report (<https://doi.org/10.1039/D2DT03469G>).

Usually overlooked compared to d-block metal cations, lanthanides such as Tb(III) can also show efficient AIE effects as Kitagawa, Hasegawa and co-workers report, displaying the role of ligand-ligand charge transfer on the obtained photophysical properties (<https://doi.org/10.1039/D0DT00094A>).

Overall, we have been delighted to participate in this collection that shows the wide range and vitality of current research in this area, while also suggesting that there is more potential for future developments and discoveries.

We are thankful to all researchers who participated, for their fruitful contributions and we would also like to express our gratitude to Dr Samantha Apps, Dr Kate Tustain and all the members of the Editorial Office involved at *Dalton Transactions*, for their valuable support during the preparation of this Spotlight Collection.

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