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Original Paper

Fluorescent Probes Based on Metal and Aggregation-Induced Emission Organic Molecule Complexes for Bioimaging and Sensing Applications

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Abstract

Metal-Organic Coordination polymer (MOCPs) is an emerging class of inorganic-organic porous hybrid materials with infinite coordination polymers (CPs) or metal-organic backbones (MOFs) formed by the interaction between metal ions and organic ligands and ligand functional groups. The molecular structure of the organic ligands composing MOCPs is rich in variation, while inorganic metal ions generally have good photoelectromagnetic properties. Therefore, MOCPs have diverse structural variations, adjustable pore size, high stability and controllable synthesis, and have received wide attention in gas storage, multiphase catalysis, chemical sensing and biological applications. Fluorescence properties are one of the most widely used techniques for bioimaging and sensing detection. However, conventional luminescent groups are usually affected by aggregation-induced quenching (ACQ) effects. Aggregation-induced luminescence molecules (AIEs) based on metal-organic coordination polymers combine the advantages of organic AIEs and transition metal centers to improve photophysical properties and therapeutic effects.

1. Aggregation-Induced Emission (AIE)

1.1 Introduction to Aggregation-Induced Emission

The concept of aggregation-induced emission (AIE) was first proposed by Dr. Ben-Zhong Tang in 2001 (Luo et al., 2001). Since some solid molecules can also emit bright fluorescence in the dark environment, this phenomenon of fluorescence enhancement in the aggregated state is called AIE effect. Traditionally, some fluorescent groups in the solution state, such as rhodamine and coumarin, show strong fluorescence in the non-aggregated state, but when the concentration of these molecules becomes high or aggregation occurs, the fluorescence intensity of the molecules decreases or is directly burst, and the phenomenon exhibited by these molecules is called the aggregation-caused quenching (ACQ) effect. The excited states of aggregates of these molecules typically decay or relax back to the ground state as nonradiative channels, leading to the luminescence quenching of the luminescent groups. AIE molecules in contrast in the non-aggregated solution state, due to the existence of some AIE molecules can be free to move the structure, the molecular excited state is usually non-radiative channel decay or relaxation back to the ground state, the energy is dissipated almost no fluorescence, but in the aggregated state within the molecule movement is restricted, then the molecular excited state will be released in the form of radiation leap energy, making the molecule emit obvious fluorescence. Because the environment in the organism is mainly in the solution state, the AIE molecules entering the organism will fluoresce by aggregation in a specific microenvironment (Wang et al., 2013). AIE molecules also have the advantages of simple design and preparation, easy introduction of functional groups, and high luminescence intensity, so AIE effect-based fluorescent probes have good prospects for life science applications (Liang et al., 2014; Biju, 2014). In addition, the AIE-based fluorescent probes can be used for chemical sensing, bioimaging and drug transport (Yuan et al., 2015b; Xue et al., 2014; Mei et al., 2015).

1.2 Aggregation-Induced Emission Mechanism

Elucidating the underlying mechanisms of the AIE phenomenon is important for exploring the fundamental principles of photophysics, but equally important, it can also be used to guide the design of new fluorescent molecules, explore practical applications, and promote technological innovation. Since the creation of the AIE concept in 2001, researchers have been exploring the real mechanisms responsible for the AIE phenomenon.. Firstly, based on the study of a common AIE molecule, hexaphenylsilole (HPS) (see Figure 1 for the molecular structure) (Leung et al., 2014), an restriction of intramolecular rotation (RIR) mechanism was proposed. In a close study of the HPS molecular structure, it was found that an HPS molecule is composed of a core of thiazole with six benzene rings attached to it by single bonds, and the large torsion angle between the thiazole as the core and the benzene rings surrounding it gives the HPS molecule a propeller-type flexible conformation. In the solid state, the large spatial repulsion between benzene rings makes it difficult for HPS molecules to stack in a face-to-face manner, and there is almost no π-π interaction between benzene rings of adjacent molecules, but the C-H···π non-covalent interaction between adjacent molecules makes HPS molecules aggregate and limits the free rotation of benzene rings. The non-radiative leap of HPS molecules in the aggregated state is therefore suppressed, and bright fluorescence can be produced. In addition to HPS molecules, substituted styrene molecules can also summarize the same luminescence mechanism, this intra-molecular group rotation is restricted in the way of RIR mechanism. However, the RIR mechanism does not apply to explain all AIE luminescence phenomena. In the structure of another common AIE molecule, bis-dibenzocycloheptane (THBA) (see Figure 1 for the molecular structure) (Viglianti et al., 2017), the symmetric aromatic ring structure in the molecule is held in place by a double bond that cannot rotate freely, but at this point the THBA molecule still has AIE properties, and a new mechanism is clearly needed to explain the luminescence of THBA. Because THBA molecules cannot dissipate energy by intra-molecular rotation, vibrational motion is the main way of energy consumption. Therefore, to explain the AIE phenomenon of THBA-like fluorescent molecules, the team of academician Ben-Zhong Tang also proposed the mechanism of restriction of intramolecular vibration (RIV). By combining RIR and RIV, it can be further summarized as the restriction of intramolecular motion (RIM) mechanism (Yao et al., 2014). Within a molecule there may be both groups that undergo rotational and vibrational motions, when the luminescence of the molecule is not determined by one of the RIR and RIV mechanisms alone, but both together produce the AIE effect.

Figure 1. HPS Molecular Formula and Ball-and-stick Model (Leung et al., 2014)

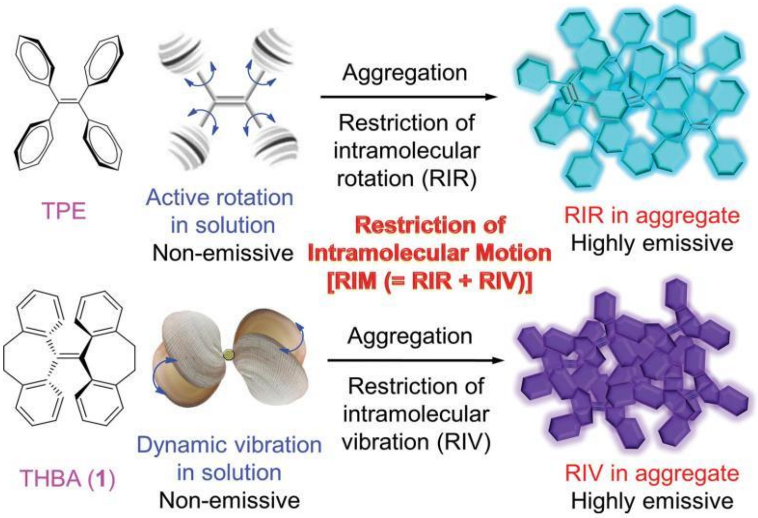

Figure 2. AIE Phenomenon Occurs in TPE due to RIR Mechanism; THBA in the Figure Below Shows the Existence of AIE Phenomenon due to RIV Mechanism (Viglianti et al., 2017)

2. Metal Organic Frameworks (MOFs)

2.1 Introduction to Metal Organic Frameworks (MOFs) Materials

Metal-Organic Frameworks (MOFs) are an interesting class of crystalline porous materials that have received a great deal of attention from researchers and institutions in the past two decades. The first use of MOFs in 1995 (Yaghi & Li, 1995; Chan et al., 2012), since then, thousands of new MOFs with different sizes, shapes and structures have been reported (Li et al., 2012; Li et al., 2016). Since MOFs are self-assembled from metal ions or clusters and organic linkers through coordination bonds (Figure 3), they are highly designable and a wide range of possible structures exist. For example, MOFs can be designed to have large porosity (Furukawa et al., 2010) and a high specific surface area (Farha et al., 2012). It can reach 90% free volume and 7000 m^2/g, respectively. In addition, the versatility of MOFs is fundamentally determined by their diverse structural and chemical properties, biocompatibility and biodegradability. Researchers have developed a large number of potential applications for MOFs, including gas storage and release (Mason et al., 2014), chemical separation (Li et al., 2012), catalysis (Lee et al., 2009), chemical separation (Li et al., 2012), catalysis (Lee et al., 2009), sensing and imaging (Deng et al., 2017; Shustova et al., 2012), drug delivery (Horcajada et al., 2006), drug delivery (Horcajada et al., 2006), removal of toxic substances (Mason et al., 2014; Howarth et al., 2015) etc. Currently, new MOFs materials with good stability are designed and synthesized based on different needs (Dong et al., 2020). The design and synthesis of new MOFs with good stability based on different needs (Dong et al., 2020) has become the focus of researchers to fully utilize their unique properties.

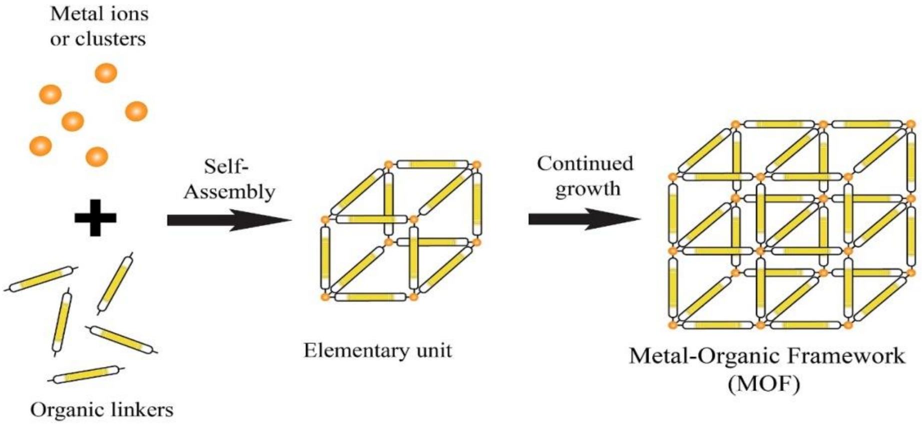

Figure 3. Simplified Representation of Metal Organic Framework (MOF), Consisting of Metal Ions or Cluster Nodes and Organic Linkers

2.2 Synthesis of MOFs

In 1995, Omar M. Yaghi and Hailian Li (Yaghi & Li, 1995) synthesized a crystalline material with a three-dimensional frame structure by solvothermal method using copper nitrate and 4,4 '-combo of methazas. The term "Metal OrganicFrameworks (MOF)" has been proposed to describe their composition and structural characteristics. Since then, these materials, which are formed by coordination and can be extended indefinitely at least in one dimension, have a fixed scientific name, laying the foundation for the subsequent development of these materials. With the continuous development of MOFs materials, some new synthetic methods such as grinding, ultrasonics, electrochemistry (Li et al., 2018; Dai et al., 2021; Stock & Biswas, 2012) have also emerged one after another, but currently the solvothermal method used by Omar M. Yaghi is still the mainstream method for the synthesis of MOFs materials.

MOFs are a class of solid crystalline materials that link metal ions (or metal clusters) and organic ligands through coordination interactions. The selection of metals with coordination orbitals and atoms that can provide lone pairs of electrons is crucial for the successful synthesis of MOFs materials. In general, divalent (e.g., Zn^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}), trivalent (e.g., Fe^{3+}, $A1^{3+}$, Cr^{3+} and most rare earth ions) and tetravalent metal ions (e.g., Zr^{4+}, Ti^{4+}, Ce^{4+}) are often selected as nodes for coordination; ligands are also important factors for the structure, space, and synthesis conditions of MOFs during the construction of coordination bonds and the formation of framework structures, based on groups containing heteroatoms (N, O Based on the nature of heteroatom (N, O) containing groups that can usually be coordinated with metals, ligands containing cobordic acid, N heterocyclic, phosphoric acid and other groups are often chosen as linkage points for the construction of MOFs. In order to form spatially extensible structures, the number of these groups should be at least greater than two, and the complexity of their spatial structures will increase with the increase of the number of coordination groups, and their topology will change (Natarajan & Mahata, 2009). In addition, the backbone of the ligand usually contains a benzene ring structure to enhance its rigidity. In the process of synthesizing MOFs, in order to "customize" the structure of MOFs, direct (one-step) and indirect (multi-step) synthesis methods can be used, depending on the number of synthesis steps.

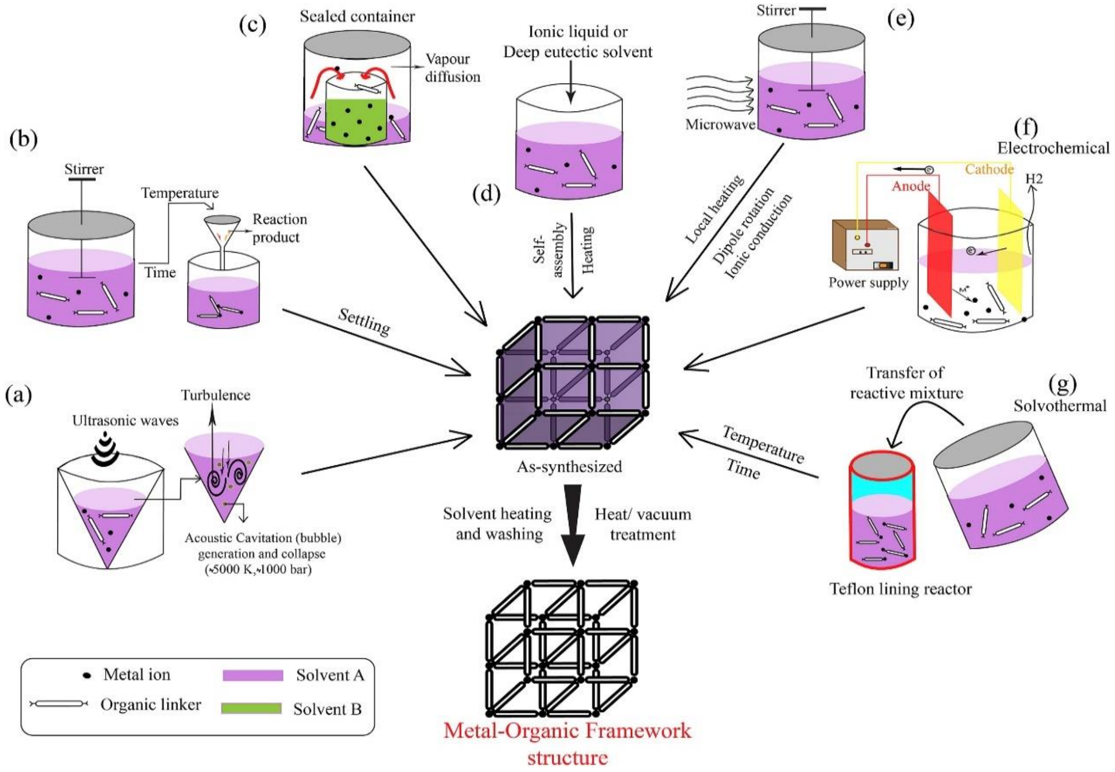

Figure 4. Synthesis of Metal-organic Skeletal Compounds (Sharanyakanth & Radhakrishnan, 2020)

2.2.1 Direct Synthesis

For coordination metal ions as described above, the desired target MOFs materials can be synthesized directly by heating reactions in solvent if suitable ligands are selected for coordination with them (Kalmutzki et al., 2018; Guillerm et al., 2014) The group of Omar M. Yaghi (Li et al., 1999) in 1999, MOF-5 was successfully synthesized using zinc nitrate as a metal salt, and its crystal structure contains Zn_4O secondary building unit (SBU). On this basis, the group of Omar M. Yaghi (Deng et al., 2012) The researchers have also explored the synthesis of MOFs containing Zn_4O structure with the same topology (Isoreticular Metal Organic Framework (IRMOF)) by fixing Zn metal salts and using different functionalized terephthalic acid or rigid ligands of different lengths of para-dicarboxylic acid. Taking Cr as an example, Ferey's research group (Serre et al., 2002) synthesized Cr-based MIL-53 (Materials of the Institute Lavoisier, MIL) in 2002, using terphenyl acid as a ligand. Its pore size can be regulated by hydration and dehydration. Subsequently, the research group directly synthesized MIL-100 (Horcajada et al., 2007) and MIL-101 (Ferey et al., 2005). with Fe and Cr as the metal center, respectively, and added hydrofluoric acid in the synthesis process, which believed that fluoride ions could induce crystal formation UiO-66 was used as a representative of the tetravalent metal Zr-based MOFs (Cavka et al., 2008; Zou & Liu, 2019), with $Zr_6O_4(OH)_4$ as SBU, coordination with terephthalic acid forms a topology with a face centered cubic (FCC) lattice. In addition, the temperature required for the synthesis of metal-based MOFs differs for different valence states (Cheetham et al., 2018; Devic & Serre, 2014), generally higher temperatures (> 100 ℃) are required for higher valence state metals (> 3+). For the synthesis of MOFs by solvothermal method, the solvent selection range is relatively wide, usually N,N '-dimethylformamide (DMF),N,N' -dimethylacetamide (DMAc),N,N '-diethylformamide (DEF) and other solvents with good solubility and high temperature stability are the preferred solvents, and mixed solvent systems can also be selected to improve the solubility (Howarth et al., 2017).

2.2.2 Indirect Synthesis Method

In the actual synthesis process, the target MOFs may not be synthesized in one step due to factors such as reaction conditions, spatial site resistance, and the nature of the substance itself. In such cases, indirect synthesis methods are usually chosen to achieve the customization of functional materials of MOFs (Cui et al., 2019; Yuan et al., 2015a). This method first uses a direct method to synthesize MOFs that can be remodeled, and on this basis, the products are further reacted by chemical modification (Yin et al., 2019). Based on the structural characteristics of MOFs, post-modification can usually be performed by covalent post-modification for ligands or ligand-exchange post-modification for metals and ligands.

The covalent post-modification is generally based on some common chemical reactions, and the reaction process should avoid MOF structure destruction. Therefore, mild and high conversion rate reactions during the modification process are often favored by the researchers. Limited by the poor thermal stability of the anatase skeleton, the group of Hongcai research group used a stepwise synthesis strategy to reserve an aldehyde reaction site in the skeleton of the synthesized MOF, and used this site to react with 1,2,3,3-tetramethyl-3H-iodinated indole salt to remodify the MOF. The cyanine was "installed" into the MOFs material, so as to realize the identification of cyanine (Li et al., 2020) (Figure 4). Yujun Zhao's group (Wang et al., 2019) The reaction of MOFs with salicylaldehyde and 2-bis(diphenylphosphino)benzaldehyde was based on the synthesis of MIL-101-NH_2 using the Schiff base reaction, which provided ligand sites for the subsequent functionalization of ruthenium trichloride. The "click chemistry" reaction can also be applied to the covalent post-modification of MOFs due to its high reaction selectivity. (Goto et al., 2008) The crystals of the synthesized MOFs were immersed in a solution containing catalyst and terminal alkynes at 80 ℃ for a period of time to obtain MOFs modified with different functional groups, taking advantage of the "click reaction" between azide and alkyne to form a five-membered ring. The results show that the modified MOFs still have a good crystalline shape.

3. Current Status of Domestic and International Research on Metal-organic Coordination Polymers

The development and utilization of functional luminescent materials directly affects people's quality of life. As a kind of functional luminescent materials, metal-organic complex materials have attracted widespread attention in academia due to their unique optical properties. Currently, research on the use of metal-organic complexes as molecular fluorescent probes is flourishing. As a fluorescent probe, when metal-organic complexes are subjected to external influences or internal structural changes, they are output as fluorescent signals, which have the advantages of high sensitivity, good selectivity, low detection limit and fast response time, and can effectively improve the simplicity and intuitiveness of signal capture, and are widely used in the field of fluorescence identification of various substances. In conclusion, because metal-organic complex materials are constructed from inorganic metal ions and organic components, they have unique luminescence properties and a wide range of applications.

3.1 Bioimaging

Chemical fluorescent probes have the advantages of simple testing, good selectivity, high sensitivity and convenient use, and can be used as a medium to detect and analyze substances in organisms. Due to the high sensitivity of the application of fluorescent probes in living organisms, the identification of trace amounts of substances in living organisms can be achieved, and a highly selective response can be achieved by modifying the fluorescent probes to exclude the interference of other substances. At the same time, the use of fluorescent probes does not require complicated steps, testing is convenient and fast, and without damaging biological samples, which helps researchers gain insight into the synthesis, localization, and biological roles of biomolecules in complex living systems, and is of great value in studying the physiological functions of important species within the living body. The development of fluorescent probes has simultaneously contributed to the progress of research in cell biology and medical diagnostics. In the past decades, various types of fluorescent probes have been synthesized and applied in bioimaging.

Bioscopy can provide critical information for understanding various physiological and pathological processes, which is important for cancer screening and treatment, stem cell transplantation, etc. Many AIEs have strong resistance to photobleaching, high fluorescence quantum yields in the aggregated state, and good biocompatibility or low toxicity. These properties make them promising as biomaterials (Hu et al., 2014; Wang et al., 2010). Recently, many new AIE molecules have been designed and used to develop specific regions in cells. The design, photophysical properties and biological applications of existing probes allow localization imaging studies of mitochondria, lysosomes, nucleus, Golgi apparatus and endoplasmic reticulum, respectively (Zhu et al., 2014; Peng et al., 2011; Zhang et al., 2014).

Intracellular pH (pH_i) is a fundamental factor controlling cellular behavior, such as cell division, apoptosis, ion transport, enzyme activity, and protein degradation. Tang's group (Chen et al., 2013) reported a pH-sensitive fluorophore, tetraphenylethen-cyanine (TPE-Cy), for pH_i detection and tracking. It is biocompatible and cell-permeable. It enters cells by diffusion and is sensitive to the entire physiological range of pH_i, being strongly red and blue emitting in acidic and alkaline, respectively. The red fluorescence of TPE-Cy varies with pH from strong to moderate between pH 5 -7 and from weak to absent between pH 7- 10. The usefulness of TPE-Cy for pH_i development and monitoring was also demonstrated using confocal microscopy and ratiometric analysis. In addition, Liu et al. achieved two-color biomarkers using nanoprobes based on two AIE dyes (Li et al., 2013).

3.2 Chemical Sensors

The sensing and detection of some metal ions in the environment is important for ecosystems. Some transition metal cations, such as Cu^{2+}, Fe^{3+} and Fe^{2+}, are essential in life processes, and the excess or deficiency of these metal cations during metabolism can lead to cause various diseases. Luminous metal organic complexes can also be used for the detection of metal ions. Du's group constructed Eu@UiO-MOFs for the efficient detection of Cd^{2+} with detection limits up to 5.67×10^{-7} M (114 ppb). Copper ion (Cu^{2+}) is a typical micronutrient that has an important role in living systems. However, due to the frequent human activities, copper pollution in the ecosystem is becoming more and more serious, and long-term exposure to copper can lead to human toxicity. Liu's group prepared and synthesized ZIF-8@Rhodamine B for the detection of Cu^{2+} with a detection limit up to 22.8 nM.

4. Conclusion and Future Outlook

In summary, metal-organic complexes have received increasing attention from scientists as a functional luminescent material with both inorganic and organic luminescent platforms. Currently, research on metal-organic complexes is not only limited to gas storage, separation and catalysis applications, but also the research on using metal-organic complexes as molecular fluorescent sensing materials is flourishing. As an emerging fluorescent sensing material, metal-organic complexes are output as fluorescent signals when they are subjected to external influences or internal structural changes, and have the advantages of high sensitivity, good selectivity, low detection limit and fast response, which can effectively improve the simplicity and intuitiveness of signal capture and are widely used in the field of fluorescence identification of various substances. However, the research of metal-organic complexes as fluorescent sensing materials for identification of substances is relatively single, and the identification mechanism is not explored deeply enough, mostly with the help of environmentally unfriendly organic solvents as the medium, and less research in aqueous solutions or low-toxic ethanol solutions, and the synthesis process is limited in yield, which greatly limits the scope of its practical application.

Once a more complete understanding of the cellular behavior of metal-organic compounds is achieved, it is likely that metal-organic compounds will replace organic matter as biological probes in the near future, especially in applications where both their photophysical and biological properties can be exploited. Metal-organic compounds also offer great advantages over other drugs for combined imaging and therapy, providing a broad scope for metal-organic chemists to explore this relatively new field.

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