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Review

Fluorescent/luminescent detection of natural amino acids by organometallic systems

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Contents

Abbreviations: AAs, amino acids; GSH, glutathione; NPs, nanoparticles; Tpy, terpyridine; Trp, tryptophan; His, histidine; Ala, alanine; Asp, aspartic acid; Cys, cysteine; ICT, intramolecular charge-transfer; THF, tetrahydrofuran; PBS, phosphate-buffered saline; PET, photoinduced electron transfer; MLCT, metal-to-ligand charge transfer; DMSO, dimethyl sulfoxide; rGO, reduced graphene oxide; acac, acetylacetone; FRET, fluorescence resonance energy transfer; PL, photoluminescence; DNBS, 2,4-dinitrobenzenesulfonyl; NIR, near infrared; ssDNA, single-stranded DNA; C, cytosine; QDs, quantum dots; BSA, bovine serum albumin; IDA, indicator-displacement assay; Tyr, tyrosine; MPA, mercapto propionic acid; GNRs, gold nanorods; Met, methionine; Gly, glycine; MeOH, methanol; HEPES, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; Hcy, homocysteine; ET, electron transfer; NCs, nanoclusters; Phen, 1,10-Phenanthroline; Phe, phenylalanine; Val, valine; Pro, proline; Glu, glutamic acid; Arg, arginine; LOD, limit of detection; LMCT, ligand-to-metal charge transfer; DMF, dimethylformamide; BINOL, 1,1′-bi-naphthol; IFE, fluorescence inner filter effect; T, thymine; pba, 4-(2-pyridyl)benzaldehyde; bpy, 2,2′-bipyridine; Ser, serine; ECL, electrochemiluminescence; G, guanine; NEM, N-ethylmaleimide; dsDNA, double-stranded DNA; Cit, sodium citrate; MAA, mercaptoacetic acid; HSA, human serum albumin; Thr, threonine; DA, dopamine; Leu, leucine; Asn, asparagine; Ile, isoleucine; Lys, lysine; Gln, glutamine.

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ABSTRACT

In comparison with other detection technologies, fluorescence/luminescence technology has become a powerful tool owing to its advantageous features including simplicity, low cost, high sensitivity, quick response time, easy sample preparation, noninvasive and nondestructive nature, etc. Due to the important roles played by 20 natural amino acids in living systems, this review focuses on recent contributions (from the year 2000 until July 2014) regarding the development of fluorescent/luminescent chemosensors and chemodosimeters to detect specific AAs, as well as chiral recognition to discriminate AA enantiomers (i.e., D and L), and pattern recognition to distinguish a range of AAs simultaneously based on fluorescent/luminescent organometallic systems, which include organic–metal complexes and hybrid organic–metal nanoparticles/nanoclusters.

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1. Introduction

Amino acids (AAs) are important components in a range of chemical and biological systems. They combine to yield proteins, enzymes, structural elements and many other molecules with biological activity. Their role as building blocks in living systems, along with the discovery that the concentration of free AAs is closely related to the metabolism of peptides and proteins in life and various physiological processes, has prompted increasing interest in their detection in various fields, such as chemistry, biochemistry and clinical chemistry [1–4]. In view of the role played by the 20 natural AAs in daily life [5–17], the development of techniques for sensing and monitoring natural AAs is important in the diagnosis and treatment of diseases.

Among the different methods applied to the detection of AAs, fluorescence/luminescence spectroscopic techniques, have drawn substantial interest from researchers owing to their advantageous features including simplicity, low cost, high sensitivity, quick response time, easy sample preparation, noninvasive and nondestructive nature, real-time analysis, and diverse signal output modes. Natural AAs exhibit similar properties because of the special arrangement of their carboxyl and amino groups. The key requirement of fluorescent/luminescent approaches to selective and discriminative detection of target AAs are fluorescent/luminescent probes that have the ability to differentially interact with the target AAs in a manner that gives rise to different optical signal outputs. Chemosensors that rely on the coordination are not as selective as preferred because of their relatively low selectivity and the structural similarity of natural AAs [18]. Therefore, the achievement of a selective AA recognition represents a challenge [19–21], a combination of stronger binding sites in a recognition system is an important factor in designing effective AA receptors. However, selective detection of a specific AA without interference from other AAs is difficult. As far as selectivity is concerned, chemodosimeters provide an ideal way to design fluorescent/luminescent probes, in which a significant chemical transformation involving the breaking or formation of several covalent bonds was induced by a specific natural AA. Currently, organic-metal based fluorescent/luminescent probes are extensively used as one of the most successful strategies [22] for detecting AAs, which however have not been systematically summarized to our knowledge.

Although studies on the use of chemosensors for the detection of AAs have been reviewed by Zhou and Yoon [21], a large number of important studies on natural AA sensing based on organometallic systems were not discussed in their review. Therefore, we focus particular attention to review the literature from 2000 to July 2014, covering the fluorescent/luminescent probing of 20 natural AAs by organometallic systems. Other AAs such as homocysteine (Hcy) and glutathione (GSH), as well as derivatives of AAs, were not included in this review. This review provides a reference for those who are interested in this growing and exciting research field.

2. Detection mechanisms

2.1. Binding site-signaling subunit approach

In the binding site-signaling subunits approach [23–25], the "binding site" part (receptor) and "signaling subunit" part (indicator) are linked through a covalent bond, and the interaction of the analytes (such as AAs) with the binding site alters the electronic properties of the signaling subunit, resulting in sensing of the target analytes via color, absorption or emission modulation. The binding between the receptor and analyte is typically labile and reversible, and involves different interactions, including electronic interactions, hydrogen bonding and metal-ligand interactions, etc.

2.2. Displacement approach

The displacement approach [26] uses binding sites and signaling subunits to form a molecular ensemble through non-covalent interactions. Upon the addition of a specific amino acid (AA), the indicators are replaced, resulting in a change in their optical properties. This type of supramolecular approach toward sensing is very simple to implement. Furthermore, the sensitivity and selectivity of the assay can be modulated by varying the receptor-indicator ratio or sensing conditions (e.g. pH).

2.3. Chemodosimeter approach

Chemodosimeters [27] are molecular devices that interact with their analytes and yield physically measurable signals in an irreversible manner. Conventional chemodosimeters are generally molecular assemblies of receptor and signaling units. In contrast to chemosensors, which respond to the real-time concentration of their analytes, chemodosimeters respond to their analytes in a cumulative manner. Compared with chemosensors, chemodosimeters have advantages in terms of selectivity and sensitivity, and their cumulative effect plays an important role in the detection of analytes [28].

3. The advantages of metal and organic combination

For detecting AAs, metal ions can play an important role [29]: (1) they can represent the active site for interacting with AAs [30]. They serve as binding sites in the development of AA probes. An obvious requirement for an organic-metal combined system to serve as a binding site is its stability. (2) The interaction between a metal center and AAs is often a convenient route for achieving strong binding [26]. In this case, AAs can capture metals from organometallic systems and the organic part can be displaced by the AAs. (3) Metal ions can also be used profitably as structural elements for assisting AAs binding without exerting any a direct interaction with AAs [31,32].

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