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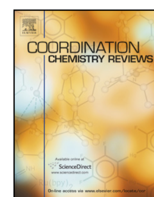

Review

Two-photon luminescent metal complexes for bioimaging and cancer phototherapy

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ABSTRACT

Possessing important advantages over conventional one-photon excited emission such as great depth discrimination and reduced photo-damage, two-photon excited emission (TPE) materials has attracted increasing attention and been applied in various research areas. These applications have generated a demand for new two-photon dyes. In recent years, metal complexes with TPE property have been widely studied due to their attractive photophysical properties, especially for bioimaging and therapeutic agent applications. In this review, we first summarize the recent developments regarding metal complexes as two-photon dyes for cell organelles, cations, anions, gas molecules and biomolecules. The applications of two-photon therapeutic agents are also summarized.

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1. Introduction

As the simplest nonlinear optical phenomenon, two-photon absorbance (TPA) has attracted a great deal of interest in the past few decades, at both the theoretical and experimental levels [1]. TPA has been applied in various research areas, such as three-dimensional data storage [2–5], up-converted lasing, optical power limiting [6–8], materials micro-fabrication [9,10], photodynamic therapy (PDT) [11–14] and especially fluorescence microscopy [15–20]. Fluorescence microscopy has become an essential tool in biology and biomedical sciences and offers a visualization approach to understand life (bioimaging). Since the advent of two-photon fluorescence microscopy (TPM) in 1990 by Webb and co-workers [21], great progress has been made in hardware systems; hence, a wide range of bioimaging studies have been carried out by numerous researchers. Imaging and analysis of the dynamic processes in living cells and tissues are the most common applications of TPM: tracking organelle (mitochondria, lysosomes, vacuoles, etc.) dynamics, visualizing drug delivery, imaging cancer and neural tissue, studying the vasculature, heart, eye and brain, and detecting small molecules among others [22–32].

Most of these applications are dependent upon the availability of probes with a large two-photon absorption or an excellent two-photon excited emission (TPE). Therefore, there is now a great demand for the design and synthesis of efficient two-photon dyes. This field has been comprehensively reviewed [33–35]. However, all of these reviews focus on only organic compounds. Metal complexes possess various advantages over organic compounds [36–40], and applications of the former as two-photon dyes have been developing rapidly. Here, we provide an overview of two-photon luminescent metal complexes applied as bioimaging dyes and cancer therapeutic agents.

2. Theory of TPA and TPE

The theory of TPA was first proposed by Maria Goeppert-Mayer, the Nobel Prize winner in Physics in 1963 [33]. In her 1931 doctoral thesis, she postulated that a single molecule might be able to simultaneously absorb two photons and be excited from the electronic ground state to an excited state [41]. The TPA process was first demonstrated experimentally by Kaiser and Garret in 1961 [42].

The TPA cross-section (δ) is an important parameter in the TPA phenomenon that reflects the molecular ability of TPA. Two-photon excited emission (TPE) is one of the main techniques for measuring TPA cross-sections [43]. A molecule re-emits light after absorbing energy from a single photon and be excited from the electronic ground state (S_0) to an excited state (S_n), which is known as one-photon emission (OPE). In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation (Stokes shift). Similar to this familiar one-photon emission, the electron in the molecule jumps from S_0 to S_n and then falls back to the ground state, which is involved in TPE. The major difference is that the TPE process is excited by two photons within an unimaginably brief period of time (10^{-18} s), each of which contributes one half of the total energy required to induce emission (Fig. 1) [44]. Therefore, the re-emitted light is shorter than the exciting light in wavelength. For example, in OPE mode, Rhodamine B can be excited by a single green photon ($\lambda = 488$ nm) and then re-emits a photon of orange light ($\lambda = 580$ nm). The same orange emission light can be observed when Rhodamine B is excited by two photons of near-infrared light ($\lambda \approx 900$ nm), each of which has approximately half the energy of the one-photon green excitation light. Using the assumptions equivalent to those of the Lambert-Beer law for one-photon absorbance, the TPA cross-section δ can be calculated from Equation (1):

$$\delta = \frac{h\nu}{N_0} = \frac{10^3 h\nu\beta}{N_A C} \quad (1)$$

where δ is typically reported in Goeppert-Mayer units (GM, 1 GM = 10^{-50} cm^4 s photons^{-1} molecule^{-1}), N_0 is the number density of absorption centers, N_A is the Avogadro constant, C represents the solute molar concentration, and β is the value of the two-photon absorption coefficient, which is determined by fitting the experimental results with self-compiled programs [43].

The TPA cross-section δ coupled with the fluorescence quantum yield (Φ), named the TPA action cross-section, is another parameter for characterizing TPA molecules commonly used in the past decade. However, the impact of photostability is not considered by this TPA action cross-section [34]. Photostability is one of the most important criteria for developing fluorescent imaging agents [45]. Poor photostability will significantly limit the applications of a fluorescent probe. Thus, Belfield and coworkers [46] defined a new figure of merit (F_M) to estimate the potential of a TPA fluorescent probe (Equation 2):

$$F_M = \frac{\delta \Phi_f}{\Phi_d} \quad (2)$$

where δ is the TPA cross-section, Φ_f is the fluorescence quantum yield, and Φ_d is the photodecomposition quantum yield [34]. The incorporation of the photo-decomposition quantum yield in F_M provides a more accurate method to value and compare the potential of TPA fluorescent probes.

3. Advantages of TPA and TPE

As mentioned above, fluorescence microscopy has become an essential tool in biology and the biomedical sciences because it offers a visualization approach to understand life. However, important challenges arise when attempting to visualize fluorescently labeled cells deep within living tissues [44]. One-photon confocal microscopy (OPM), developed in 1980s, provides a partial solution to this and works well for many applications [47–50]. However, the excitation source of the most striking examples of OPM is the single

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