

Mini-Review

How to Solve a Common Problem of Organic Luminescent Materials: Concentration Quenching of Luminescence

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Abstract: Concentration quenching is a common problem in organic luminescent materials, significantly reducing the efficiency of luminescent devices and luminescence-based tools. Although the mechanism of this phenomenon has been studied for a long time, it remains still not yet fully understood. It is a great challenge to find the most efficient ways to diminish or to overcome concentration quenching. This mini-review examines the progress made in biological and optoelectronic research to address this problem, mainly over the last decade. All known mechanisms of concentration quenching (except for light reabsorption and energy migration) are based on intermolecular interactions. Thus, to prevent or diminish concentration quenching of luminescence in organic molecules, one can only remove or reduce short-range interactions between the emitting molecules. Internal (adjusting the mutual orientation of the emitting molecules, designing molecules with bulky side chains, and sterically wrapping additional molecular parts, which results in the increasing the distance between molecules) and external (host-guest systems which isolate emitting molecules by means of creating a shielding barrier between them) tools for minimizing concentration quenching are considered. Shielding barriers can be obtained by doping and encapsulating molecules. Organic, metal-organic, and inorganic cages, organic, metal-organic, and inorganic frameworks, polymeric and inorganic nanoporous materials, as well as carbon and other nanomaterials, are being successfully developed for dye encapsulation. All the proposed tools have resulted in diminishing concentration quenching. However, for further progress in overcoming of concentration quenching, a series of new proposed approaches such as the synthesis of new sterically wrapped and Aggregation-Induced Emission (AIE) molecules, hyperfluorescent structures, and the embedding of luminescent molecules into organic, metal-organic, inorganic, and carbon-based cages as well as covalent organic and metal-organic frameworks are considered to be the most prospective, because they make it possible to apply the highest concentrations without essential luminescence quenching.

Keywords: dye phosphors, luminescence, quenching, prevention

1. Introduction

Among the huge variety of organic molecules, many of them are luminescent (emitting light) upon excitation. Fluorescent dyes, which represent one of the main groups of luminescent materials, have promising properties, including broad absorption and emission bands, a large absorption coefficient, high quantum efficiency, and short fluorescence lifetime (typically less than 10 ns). They are the focus of intense investigations in the field of organic electronics due

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to their wide applications in electroluminescent devices, sensors, transistors, and other semiconductor devices [1]. In addition, the luminescent ability of organic luminescent compounds finds wide application in biological imaging and sensing [2]. Fluorescence is often used to detect molecular recognition in sensors, which play an important role in biology and chemistry [3].

When a molecule absorbs light in the visible or ultraviolet range of the spectrum, it is excited from the electronic ground state to higher states, followed by a quick relaxation to the lowest excited state. After fast relaxation, it can return to the ground state by releasing the absorbed energy in the form of heat and light radiation in the visible or near-infrared spectral range. It can also turn to the triplet state and dissipate through heat (typically) or light emission. The emitted light is called fluorescence or phosphorescence when the excited state is a singlet or triplet state, respectively. The quantum yield of luminescence, as a characteristic important for practical applications, is determined by the internal properties of the emitting molecule (energy conversion pathways) and the surrounding environment, which is capable of quenching the luminescence. The dye molecule is luminescent when the radiative pathway can compete with the nonradiative one.

The emission of light from the excited state of a molecule can be quenched by interaction with another molecule. Known interactions include dipole-dipole, polarization, donor-acceptor, electrostatic, and others (see any chemistry textbook; an interesting review can be found in [4]). Many atoms and molecules can strongly interact with a light-emitting molecule. When dye luminescence is measured at ambient conditions, adsorbed molecules of oxygen [5] and water [6] from the atmosphere can easily quench luminescence and decrease the stability of the emitting molecule. Note that the substitution of the external hydrogen atoms with fluorine was found to reduce oxygen quenching [5]. However, it was observed that an increase in the concentration of the emitting molecules leads to a decrease in the quantum yield of luminescence [7]. This means that luminescence quenching can be caused by interactions between the same molecules located close to each other. This phenomenon is called concentration quenching [7].

Concentration quenching is an old and general problem in luminescent systems, strongly decreasing the efficiency of luminescent devices and tools. That is why it remains a great challenge to design organic luminescent molecules with strong emission in both concentrated solutions and the solid state, or to find the most efficient ways to overcome this problem. It is very important in optoelectronics as a limiting factor in the realization of efficient devices. Beyond optoelectronics, these questions are widely studied in biology and medicine [8], where this phenomenon decreases the efficiency of fluorescence bioimaging and photo-mediated therapy. Thus, developing facile strategies to overcome the above-mentioned issues is highly desirable. It is of great interest to bring together information on these questions available in the studies in biology and opto-electronics, because the nature of the studied phenomena is the same. This information obtained in biological studies will be useful in electronics and vice versa. However, in electronics, we also have to take into account the limitations imposed by electrical excitation or charge transporting in their architectures. There are numerous reviews devoted to several tools for reducing concentration quenching, but no review (to our knowledge) that presents the complete picture and progress of these studies. The proposed mini review explores the progress made in the field of concentration quenching and the tools developed to solve this problem.

2. The origins of concentration quenching of dye luminescence and methods for its elimination

Concentration quenching has been studied for a long time, along with the studies on luminescence. However, its mechanism is not yet fully understood. High concentrations bring fluorophore molecules closer together. It is supposed that in this case, the probability of energy [7] or charge [9] transfer is increased. Fluorophore molecules can form non-fluorescent complexes or aggregates [10]. The intensity of emitting light also decreases due to light reabsorption owing to the Stokes shift between absorption and luminescence spectra, as well as trapping of light on impurity molecules (even very clean commercial substances contain at least 0.001% admixtures, typically they contain much more impurities) or trapping at the same molecules during energy migration [11]. It can be supposed that different mutual arrangements of molecules in disordered systems can reduce the energy migration distance. However, there are non-luminescent molecules with twisted or propeller-like configurations that become emissive when aggregated [12] owing to the restriction of intramolecular

motions that prevent π - π stacking and possible intramolecular proton transfer, which results in blocking the non-radiative decay pathways. This phenomenon is called Aggregation-Induced Emission (AIE) [12]. Unfortunately, the number of such molecules is very limited. Experimental and theoretical studies of the nature of concentration quenching continue to date [11] to find a unified understanding of this phenomenon and search for effective ways to eliminate it. In general, the magnitude of the concentration quenching effect depends on the type of molecule, and this issue has to be studied on an individual basis. Thus, for every molecule, all the types of quenching interactions are different, making it difficult to understand the full nature of the quenching process. In any case, luminescence quenching is caused by close intermolecular interactions. The proximity of molecules at high concentrations facilitates the quenching processes, causing excited states to deactivate before they can emit light. It should be noted that, except for the above static quenching processes, there is a so-called dynamic quenching caused by collisions between molecules.

As it was shown above, commonly, all mechanisms of concentration quenching (except for light reabsorption and energy migration) are based on intermolecular interactions. Thus, to prevent or diminish concentration quenching of luminescence in organic molecules, one can only remove or reduce short-range interactions between the emitting molecules. In general, intermolecular interactions can be removed by a screen of some kind between the molecules (Figure 1). Numerous methods, more or less successful, have been developed to address this problem. For a brief overview, we will consider the most interesting methods for minimizing concentration quenching described in the literature to find the most effective solution to this problem. Commonly, internal (or molecule-related) and external tools for preventing or diminishing the concentration quenching of luminescence in luminescent organics are used. Internal tools are based on manipulations with emitting molecules, while external tools are based on building special isolating screens between the emitting molecules. The best results can be achieved by combining different tools (see, for example, [13]).

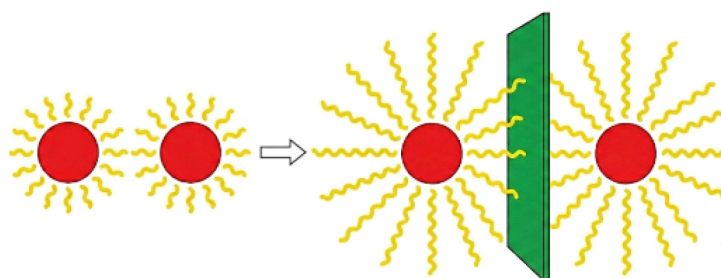


Figure 1. Shielding of various natures can eliminate or reduce intermolecular interactions, increasing the efficiency of luminescence

3. Internal tools to escape concentration quenching

3.1 Design of molecular arrangement

Manipulations with molecular design can be physical or chemical. Organic molecules are not typically spherical, and different molecular parts can contain groups with various properties. Thus, the type and power of interaction of molecules contacting each other with different molecular parts are also different. As a result, the packing configuration of the emissive molecules has a strong impact on optical and charge-transporting properties and, therefore, on device performance [14]. One of the tools to adjust the molecules' packing was found to be the thermo-vacuum deposition rate [15]. Being evaporated from the heated source, molecules are freely moving and colliding with each other in the flux of the molecular beam, and reach a target substrate at different angles. At low deposition rates, molecules move slowly and tend to occupy energetically more favorable positions near neighboring molecules previously attached to the substrate. As a result, the obtained film is more densely packed due to significant aggregation. With a high evaporation rate, the molecules are deposited more chaotically, forming a more porous film. The annealing of such films typically results in the formation of more ordered films. Thus, the film morphology and optical properties (absorption and luminescence spectra) strongly depend on the thermo-vacuum deposition rate [15]. Good results in diminishing concentration quenching have

been obtained with a new type of molecule with an asymmetrical distribution of charge attached to proteins [16]. Such molecules are used as a probe for *in vivo* imaging. The asymmetry leads to the repulsion of the fluorophores from each other, breaking the coupling between the individual dyes. This asymmetrical distribution prevents the chromophores from π -stacking, minimizing the energy transfer between the molecules and, therefore, fluorescence quenching [16]. Such a self-organization strategy for organizing dyes is used for electrostatically driven ion pair formation between charged dyes and various counterions, similar to any surfactants. Large counterions also partially act as spacers between cationic organic dyes and thereby reduce concentration quenching. This strategy is widely applied for cationic dyes paired with the large counterion [17]. Thus, to minimize the concentration quenching, one can adjust the mutual orientation of the emitting molecules (Figure 2a). This approach will result in the significant decrease of luminescence quenching.

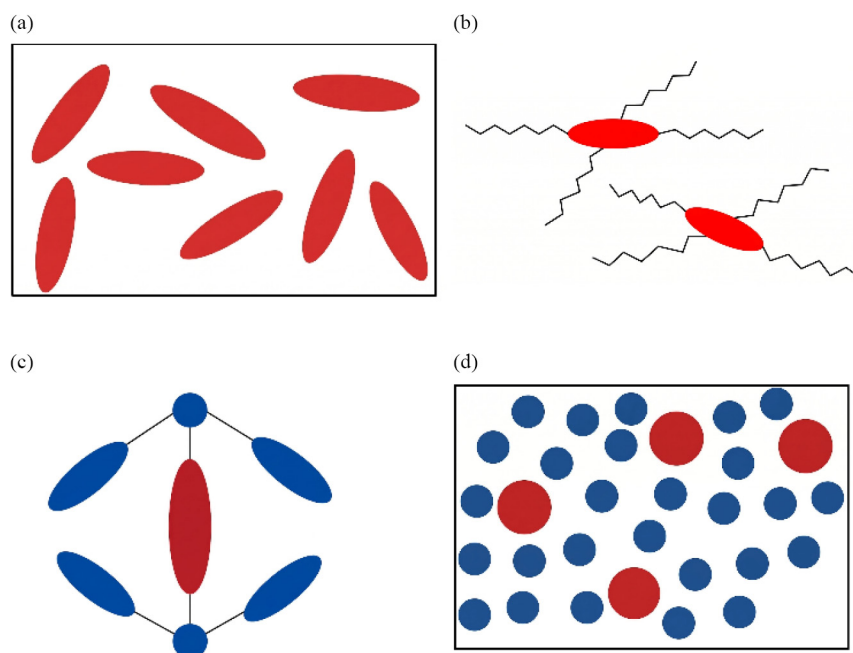


Figure 2. Schematic samples of methods to diminish concentration quenching: adjusting the mutual orientation of the emitting molecules (a), molecules with bulky tails (b), molecules with wrapping parts (c), doped structures (d). Luminescent molecules and luminescent cores are marked in red; surrounding molecules and inactive molecular parts are marked in blue

3.2 Design of molecular structure

To reduce concentration quenching, chemical manipulations with dye molecules are used, such as increasing the volume of the molecule by grafting optically neutral substituents to the emitting molecule, which increases the distance between the emitting cores. One commonly used and rather efficient method to diminish concentration quenching is the attachment of bulky side chains or substituents to the emissive molecules, which increases intermolecular distances and inhibits interchromophore interactions. For this purpose, various alkyl derivatives are used [18] (see Figure 2b and Figure 3b). They maintain some distance between molecules or form a partial “cage” to inhibit interactions at higher concentrations. Absorption and luminescence spectra show that even one hexyloxy group in the side chain of dibenzoxazolylbiphenyl molecule decreases molecular aggregation [19]. A thin film made from this material is more porous than a film consisting of the same molecules without this side chain, as evidenced by stronger quenching of luminescence by both intermolecular interactions and penetrated oxygen. This strategy is very similar to that used for semiconductor polymers [1], which increase the solubility of these organic substances in various solvents for thin-film deposition from solutions.

The further development of this strategy is the creation of bulky emitters where the emitting core of the molecule can be wrapped by another bulky part of the molecule [13, 20], forming a stereo structure (Figure 2c, Figure 3c). The partial shielding of neighboring molecules by wrapping molecular parts more efficiently isolates the emission core, minimizing any short-range interactions and improving performance at higher concentrations. Thermally Activated Delayed Fluorescence (TADF) and multi-resonance TADF molecules containing molecular parts wrapping the emitting core (Figure 2c), as well as molecules containing AIE-active substituents (Figure 3d), can also be related to this approach [21–23]. The concept of “sterically-wrapped multi-resonance TADF fluorophores” gives the possibility to increase guest concentration up to 20% and higher [24]. For this purpose, even inorganic bulky substituents, such as Polyhedral Oligomeric Silsesquioxane (POSS), have been applied [25]. POSS molecules have a rigid, cage-like structure made of silicon and oxygen and an outer layer of organic functional groups. They are considered some of the smallest possible discrete silica particles. The bulky structure of POSS can disturb intermolecular interactions in organic fluorophores, thereby avoiding concentration quenching. In general, the addition of a small amount of any non-interacting bulk molecules to fluorophores to disrupt intermolecular interactions can also serve this purpose.

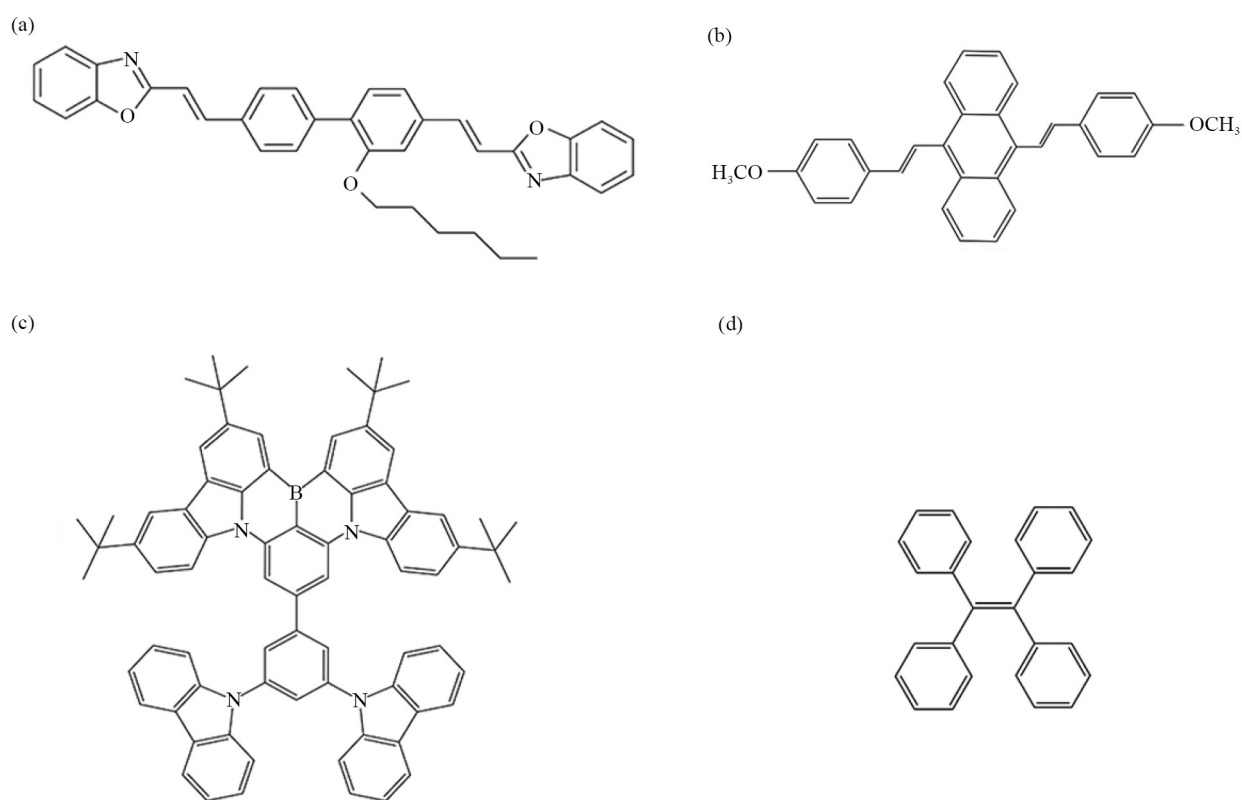


Figure 3. Simple examples of molecular design tools to diminish concentration quenching: molecules with a long aliphatic chain (a), molecules with a bulky chain (b), molecules with wrapped molecular part (c), AIE molecules (d)

4. External tools to overcome concentration quenching

A variety of external tools for preventing concentration quenching have also been widely developed. They are based on the isolation of emitting molecules by means of creating an external shielding barrier between them. This shielding can be organic, inorganic, or hybrid.

4.1 Doping

A common and widely used strategy is to dope the guest molecules into the host matrix. This involves the dissolution of the emitting molecules in a solid host matrix, similar to a liquid solvent. This host-guest material can be easily obtained by mixing corresponding solutions or co-evaporating corresponding substances in the required proportion. The typical guest concentration is several percent. In this case, every guest molecule is surrounded by many host molecules (Figure 2d). The host molecules can serve as a shield, preventing the interaction between the emitting guest molecules. A host matrix has to be non-absorbing of luminescence emission and must not quench the guest luminescence. Good examples are the dissolution of emitting molecules in Polymethyl Methacrylate (PMMA) [26] or other polymers. Emitters for Organic Light Emitting Diodes (OLED) emitters are typically embedded at low concentrations (not more than several percent) in a host matrix to suppress emission quenching [1]. However, this tool does not allow for achieving high concentrations, and low concentration results in lower brightness and efficiency of OLEDs. However, a polymer matrix consisting of π -conjugated polymers with covalently attached side chains allows for much higher dye loading because the backbones are kept from strong interaction [27]. It is beneficial if host molecules absorb light and transfer energy to luminescent molecules [28]. The development of this approach has led to the creation of a very efficient next-generation hyperfluorescent OLED [28], which combines a TADF sensitizer with a fluorescent emitter to convert triplet excitons into light radiation.

4.2 Encapsulation

To overcome intermolecular interactions more efficiently, every molecule needs to be placed into a hollow sphere with inert thin walls, where this inert shell can isolate the luminescent core. As a result, high dye concentrations can be easily applied without a significant decrease in luminescence intensity. In the last decade, different core-shell nanostructures have been intensively developed. Luminescent organic molecules can be embedded into such hollow nanomaterials. Various nanomaterials can be used for this purpose. This strategy allows precise control of the contents, packaging, and the prevention of intermolecular interactions, thereby avoiding concentration quenching. The encapsulation of luminescing organic molecules into such porous nanostructures can be achieved by tuning the pore size, shape, and surface chemistry of the material to match the properties of the guest molecule. Individual core-shell nanoparticles and porous frameworks are developed. The important requirements for dye encapsulation into porous materials are the simplicity of encapsulation, stability, and the absence of quenching interactions. Depending on the structure of the host, luminescent organic molecules can be embedded into it through available holes or during the synthesis of the host particles. The rigid matrix of the cage prevents the aggregation distance of dyes and avoids the generation of excimers and exciplexes. Cavities of cages can effectively bind guest molecules by multiple noncovalent interactions. These interactions can be weak, such as van der Waals forces and hydrogen bonds, or stronger, such as electrostatic interactions. In the case of the absence of dye-cage interactions, physical entrapment can be used. It is noted that molecular encapsulation is widely observed in Nature (several examples are listed in [10]). Ideally, one cage can accommodate one molecule. However, for molecules with large energy migration distances, it is possible to accommodate several molecules in one cage.

4.2.1 Organic cages

It is attractive to fill various organic cages with organic fluorophores. One type of such materials, Cyclodextrins (CDs), has been known for several decades, since extensive research on dye lasers [29] and even earlier. They are stable, inexpensive, negligibly toxic, and easily modified, so they are constantly finding new applications. CDs are used widely in the food and pharmaceutical industries [29]. Cyclodextrin is a kind of cyclic polysaccharide of D-galactose connected by 1,4-glycosidic bonds, with a truncated cone-like porous structure (Figure 4a). α -CD (contains six glucopyranose units), β -CD (seven glucopyranose units), and γ -CD (eight glucopyranose units) differ in their cavity top and bottom diameters, which are 4.7 Å and 5.3 Å, 6.0 Å and 6.5 Å, and 7.5 Å and 8.3 Å, respectively [30] with the same height of approximately 8.0 Å. Such a structure with an open cone bottom possesses easy molecule encapsulation in CD cavities. CDs are hydrophobic inside the cavities and hydrophilic outside them. These cyclodextrins and their derivatives can encapsulate a wide range of hydrophobic single molecules of varying polarity and average sizes, or fragments of larger

molecules, corresponding to the degree of compatibility between the guest molecule and the host cavity, through non-covalent interactions with the cavity, forming water-soluble host-guest complexes. These complexes can also be dissolved in some organic and special solvents [31]. This encapsulation reduces the interaction between the dye and quencher molecules, which can be particularly effective against both static and dynamic quenching.

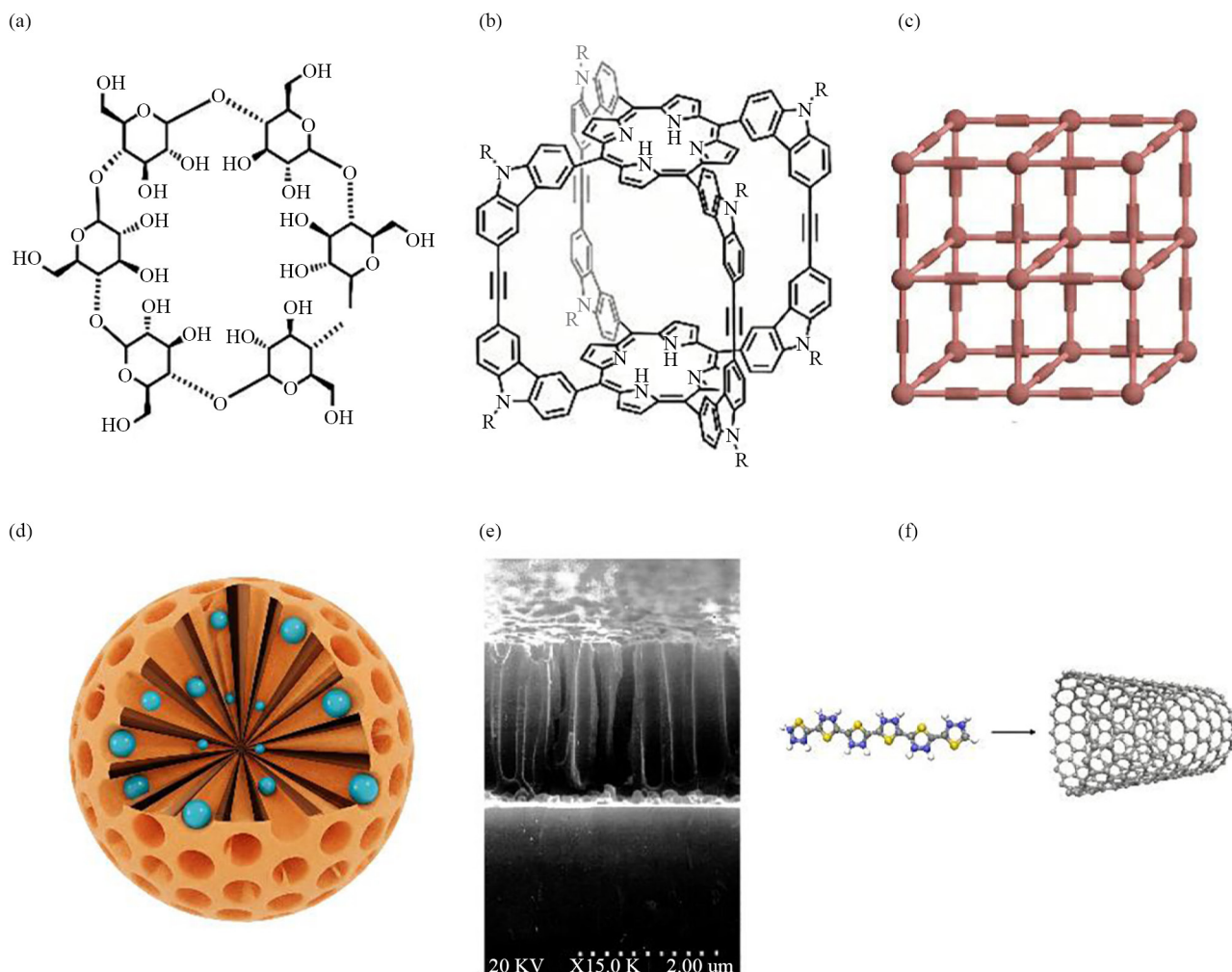


Figure 4. Examples of external tools to diminish concentration quenching: CD [27] (a), organic cage [32] (b), Covalent Organic Frameworks (COF) and Metal-Organic Framework (MOF) [33] (c), silica nanoparticles (green spots represent embedded molecules) [34] (d), porous alumina (e), carbon nanotube [35] (f)

A variety of studies using different fluorescent dyes incorporated into the CD cavity have demonstrated substantial enhancements in fluorescence intensity, quantum yield and luminescence decay at high concentrations [36, 37]. Even partial incorporation of the fluorophore molecule can inhibit concentration quenching [38]. Phosphorescent molecules in the CD cage exhibit blue emission and increased quantum yield [38]. Using dye-containing CDs instead of pure dyes in dye-sensitised solar cells has increased efficiency and open-circuit voltage [39]. Introducing an additional CD polymer layer between the hole-transporting and hole-emitting layers of an organic light-emitting device suppresses self-association, increases efficiency and enables light emission at lower voltages [40], due to molecules penetrating the CD pores. The modest results observed in this system are due to the low conductivity of CDs. Similar organic host systems, such as rotaxanes, calixarenes, cucurbit[n]urils, micelles and polymers, are also used to encapsulate larger guest molecules [36, 41–43]. The first example of a white-emitting binary polymer blend incorporating threaded molecular wires was

presented using organic-soluble polyrotaxanes [44]. It was demonstrated that energy transfer between polymeric species with resonant electronic transitions could be successfully controlled by supramolecular encapsulation.

The systems described in review [32] demonstrate the broad scope of this field, enabling the creation of molecular structures with cavities of various sizes (Figure 4b). Considered are supramolecular structures for encapsulation, such as carcerands, cryptands, cavitands, capsules and cages. The majority of organic cages are insoluble in water due to their hydrophobic nature. Polyaromatic cages are ideal for encapsulating bulky luminescent dyes. They are also attractive for optoelectronic applications due to their electrical conductivity. The structure of the cages formed by fluorophores prevents them from aggregating. As a result, organic cages composed of luminescent components can exhibit bright luminescence [45], which can either broaden the luminescence spectrum or enhance the emission efficiency of guest molecules through energy transfer.

4.2.2 Covalent Organic Frameworks (COF)

In general, porous molecular materials containing cavities or pore networks are created by self-assembly of discrete molecules. Covalently connected organic cages can form COF. These materials are crystalline porous organic polymers composed of two different organic monomers interconnected via covalent bonds (Figure 4c), with highly ordered layer structures, unique functionalities, and outstanding structural stability [33]. A variety of such porous organic polymers are constantly being developed [46]. A wide range of source materials allows the formation of uniform 2D/3D pores of various sizes, capable of incorporating luminescent organic dyes. The differing bonding modes significantly influence the chemical structure, physical properties, and electronic characteristics of COF materials. Key parameters such as conductivity and band gap can be tuned by varying bond types and molecular structures, providing a wide choice of materials for creating high-performance OLEDs [47] and other electronic devices [48].

4.2.3 Metal-organic cages and frameworks

Metal-organic cages and ordered frameworks based on such cages are hybrid organo-inorganic coordination materials. They have attracted the enormous attention of scientists, and their discovery was awarded the 2025 Nobel Prize in Chemistry. The principles of their formation are similar to those of the formation of covalent organic frameworks. Metal-Organic Frameworks (MOFs) and covalent organic frameworks are the two most prominent classes of porous crystalline materials known for their high surface areas and tunable structures, for wide practical applications. MOFs represent 2D or 3D micro/nanosized highly ordered structures (Figure 4c) formed by the connection of metal ions or clusters with organic ligands [49]. MOFs differ in the type of metal or organic ligand. Commonly, there are five types of MOF structures [50]. The synthesis methods of MOFs are quite simple and reliable [48]. They are a good host matrix for the inclusion of various molecules, particularly organic fluorophores [51].

There are three main methods for encapsulating organic dyes in MOFs [51], each with its own advantages and disadvantages. The first method is a two-step synthesis, in which the pristine MOF is first synthesized and then immersed in a solution of fluorescent dyes. However, the aperture size mismatch between MOFs and organic dyes not only limits the choice of dyes but also leads to guest leakage, which hinders the widespread application of this approach. The second method is the one-step encapsulation, where dyes are introduced during crystal formation. However, more factors, including pore size, pore windows, and MOF structure, should be considered to introduce the desired organic dyes. The third method involves the use of fluorescent linkers incorporated in the frame of MOFs. Unfortunately, the steric hindrance caused by bulky ligands often reduces the yield of MOFs' fluorescence. The dimensions, shape, and properties of the cavities depend on the type of ligands. Typically, MOFs have pore sizes less than 2 nm, although some organic linkers have pore diameters of up to 50 nm or more. The conductivity of MOFs is highly dependent on the components used and the type of MOF structure [52]. Studies on dye-doped MOF structures have developed rapidly in the last decade. Two-dimensional and flat three-dimensional frameworks with embedded dyes are attractive for electronic devices, since they form high-quality films with uniformly distributed dyes. These hybrid materials already have a wide range of various applications [47], particularly in a series of electronic devices [52, 53]. MOFs can provide luminescence in groups, and charge transfer between metals and ligands can induce specific luminescence [54]. By using a combination of MOF matrix

and dye emission, white emission can be obtained by incorporating several dyes into MOF pores of about 1 nm in size [55]. An interesting MOF is formed from γ -CDs, linked by potassium ions [56]. The hydrophilic external surfaces of 6 γ -CDs form a void with a cross dimension of 16.9 Å. This dimension is larger than the dimensions of the γ -CDs cavity, allowing for the complete inclusion of larger molecules. As a result, the increase in luminescence intensity for several molecules is higher than for γ -CD-dye systems. Such CD-based MOFs and MOFs with incorporated organic molecules were prepared easily using a standard diffusion method [57]. Metal-aromatic coordination systems for dye encapsulation have become very attractive in recent years [58], partly for applications in electronics [59].

4.2.4 Inorganic cages

Transparent inert inorganic materials can also create a screen between interacting organic molecules and prevent concentration quenching by means of their isolation. Inorganic hollow nanoparticles are attractive for incorporating organic fluorophore molecules to reduce concentration quenching.

Silica nanoparticles (SiO_2) are the most widely used porous particles to protect organic molecules from aggregation [34]. Here, we consider only porous silica nanoparticles. Mesoporous silica nanoparticles (Figure 4d) have well-defined pores with tunable sizes and shapes, large surface areas, good biocompatibility, nontoxicity, hydrophilicity, optical transparency, and ease of functionalization [34]. In recent years, these nanoparticles have attracted much attention because their pores can encapsulate various organic luminophores, and such luminescent materials have found wide applications in nanomedicine, biotechnology, pharmaceuticals, catalysis, and environmental sciences [34]. Depending on the pore size and pore surface area of the silica, and the size and structure of the guest molecules, they can be incorporated through physical entrapment or covalent attachment as a monomer or aggregate. Positively charged dyes are well-suited for physical embedding into the negatively charged silica network, but covalent linking is preferred [60] because it minimizes dye leakage from the nanoparticle over time. The number of dye molecules in a silica nanoparticle varies significantly depending on particle size, dye concentration, and synthesis method. Silica nanoparticles with embedded organic fluorophores can be easily synthesized using silanes based on the reverse microemulsion process and other methods [61]. All these methods lead to the synthesis of silica nanoparticles with a well-ordered periodic mesoporous structure. Typical external dimensions of these nanoparticles are 30-100 nm. These dimensions are well-suited for medical applications, but for electronics, they seem too large and require additional measures to reduce concentration quenching. Electrochemiluminescence has been observed with dye-doped silica nanoparticles of 22 nm in diameter [62]. Authors [63] synthesized encapsulated silica nanoparticles with average diameters of 4.5 nm and 3.5 nm. However, even nanoparticles with such small dimensions can contain many, or at least a few, molecules. Thus, one needs to diminish the interaction between molecules. To prevent π -stacking of flat perylene molecules, some amount of cholecalciferol has been added. The amide linkage between the carboxylic group of the dyes and the amino group of silanes prevents dye aggregation and increases the stability of this system [64]. An additional protective layer of titanium dioxide over the encapsulated molecules in silicon nanoparticles helps to increase stability and prevent leakage of dye molecules [65].

Inorganic materials can form 2D/3D frameworks that can be used for the embedding of luminescent organic dyes. Typical examples are crystalline aluminosilicate minerals with a microporous structure, such as zeolites [66]. There are many inorganic porous materials, such as porous silica glasses [67], which have long, disordered pores. Aluminum oxide [68] (Figure 4e) and several other metal oxide films with pores of various diameters can easily be obtained using an anodizing process followed by the introduction of a dye. The one-dimensional structure facilitates a reduction in intermolecular distances (except in one dimension), which can reduce aggregation-induced quenching. Furthermore, the potential energy transfer from the matrix can enhance the luminescence intensity of the guest molecules.

4.2.5 Carbon nanomaterials

Another type of nanomaterial, such as carbon nanomaterials, is also being explored for encapsulating luminescent organic dyes. They exhibit electrical conductivity, which allows them to overcome the conductivity limitations of many cage-based systems. It is a known problem that deposition of luminescent molecules on different conducting surfaces typically results in strong luminescence quenching [69]. However, the luminescence of the linear sexithiophene

molecule inserted into a single-wall Carbon Nanotube (CNT) was not quenched [35] (Figure 4f). But the luminescence of molecules placed on the external CNT surface is strongly quenched [70]. The only exception to the quenching of organic luminescence on the nanocarbon surface is the organic europium complex [71], where the absence of luminescence quenching is observed due to an intrinsic property of this complex. Graphene oxide can host europium complexes across its entire surface by simply grafting onto multiple oxygen-containing sites [35]. Cages for luminescent molecules made from very thin carbon nanomaterials can be very effective in preventing concentration quenching and can achieve the highest concentrations. Attempts have been made to use carbon dots [72] and graphene [73] to encapsulate dyes, with the dye molecules wrapped in graphene nanosheets. It was observed that carbon dots not only suppress the luminescence of the dye but also can enhance the unusual luminescence from higher levels due to the strong interaction between the quantum dot and the dye molecule [74]. It is also possible to sandwich individual dye molecules between two graphene or carbon dot nanosheets. Fullerene has a close-caged structure with a hollow cavity, which seems ideal for our purpose. However, to encapsulate the molecule, its cavity must be opened [75]. The use of carbon nanomaterials for dye encapsulation has not yet been sufficiently studied. Carbon dots and some graphenes exhibit photoluminescence, which should also be taken into account. It should be noted that the physical attachment of dye molecules in porous nanomaterials requires additional steps to keep the luminescent molecules within the pores.

5. Conclusions

Thus, the strategies to minimize concentration quenching are constantly developing. This mini-review examines the progress made mainly over the past decade in biological and optoelectronic studies aimed at addressing this problem. All mechanisms of concentration quenching (except for light reabsorption) are based on intermolecular interactions. Thus, to prevent or diminish concentration quenching of luminescence in organic molecules, one can only remove or reduce short-range interactions between the emitting molecules. A wide range of different methods has been proposed in the literature to reduce concentration quenching. Internal (adjusting the mutual orientation of the emitting molecules, designing molecules with bulky side chains to increase the distance between molecules, and sterically wrapping with additional molecular parts, thereby shielding the emitting cores) and external (host-guest systems that isolate emitting molecules by means of creating a shielding barrier between them) tools for minimizing concentration quenching are considered. Shielding barriers can be obtained by doping and encapsulating molecules. For encapsulation, core-shell organic nanoparticles (cyclodextrins, various cages of aromatic compounds) and inorganic nanoparticles with a core-shell structure (mesoporous silica nanoparticles), porous organic, metal-organic and inorganic cages and frameworks, as well as carbon and other nanomaterials, are being developed. All the proposed methods have resulted in diminishing concentration quenching, though each of these methods has both advantages and disadvantages. For further progress in overcoming of concentration quenching, a series of new proposed approaches such as the synthesis of new sterically wrapped and AIE molecules, hyperfluorescent structures, and embedding of luminescent molecules into organic, metal-organic, inorganic, and carbon-based cages as well as covalent organic and metal-organic frameworks are considered to be the most prospective, because they make it possible to apply the highest concentrations without essential luminescence quenching. Mixed strategies can further improve the luminescence efficiency. Note that many of these strategies can also be applied to inorganic luminescent species. The information about concentration quenching in organic dyes, obtained in biological studies, will be useful in electronics and vice versa. Although the use of external methods to prevent concentration quenching in electronics is modest, wider application of these methods will be very efficient. Conversely, the application of some internal methods to combat concentration quenching in biology will be attractive.

Conflicts of interest

The author declares no conflicts of interest.

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