The Role of Polyhedral Oligomeric Silsesquioxanes in Optical Applications

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The popularity of polyhedral oligomeric silsesquioxanes (POSS) for use in hybrid organic–inorganic materials and devices has grown in the past two decades due to desirable properties such as good thermal stability and biocompatibility, as well as their potential to be functionalized for a wide range of applications, from polymer composites to optoelectronics. Herein, the role of POSS for photonic applications, including sensing, bioimaging, and optoelectronic devices, is summarized. Functionalized POSS building blocks commonly incorporated with luminescent materials are identified, and areas of potential growth within the field are discussed. The addition of POSS to light-emitting materials is widely shown to prevent aggregation in organic lumophores and inorganic nanocrystals, leading to reduced photoluminescence quenching. The POSS unit is also capable of acting as a passivating agent for nanocrystals and thin films, improving the emission quantum yields of photoluminescent materials and devices. POSS therefore offers the potential to enhance both the functional and photonic properties of cutting-edge hybrid technologies.

1. Introduction

The use of organic–inorganic hybrid materials in photonic applications has grown rapidly over the past two decades.\cite{1,2} Benefits of the organic component, such as low-cost solution processability, can be combined with the advantages of inorganic materials, such as thermal stability, to create effective light-emitting materials suitable for a range of applications, including optoelectronics, sensors, catalysts, and imaging.\cite{1-5} Polyhedral oligomeric silsesquioxanes (POSS) are one class of hybrid materials being investigated for use in light-emitting applications. Being both biocompatible and thermally stable, POSS has been shown to enhance the properties of both organic lumophores and inorganic nanocrystals by inhibiting aggregation and thus preventing aggregation-caused quenching (ACQ) of photoluminescence (PL).\cite{6-9} POSS has also shown promise as a passivating agent and spacer molecule in optoelectronic devices, leading to increased efficiencies and stabilities.\cite{10}

The nanometer-sized inorganic core of POSS is composed of bridging Si and O atoms, which adopt a cage-like structure with organic functional groups attached to each vertex (Figure 1a). This rigid unit is represented by the general formula \((\text{RSiO}_3)_n\), where \(n = 8\). It is also common for \(n\) to be 6 or 10, although these structures are generally referred to as oligomeric silsesquioxanes.\cite{11} The first oligomeric silsesquioxane was reported by Scott;\cite{12} however, the properties and applications of these materials were not widely investigated until the mid-1990s with increased investigation into POSS in the early 2000s (Figure 1b). A wide range of functionalized POSS products are now available to purchase through Hybrid Plastics, expanding the availability of these materials (Hybrid Plastics Home Page. http://www.hybridplastics.com), although synthesis of POSS derivatives is an active area of research and detailed reviews of synthetic routes to POSS are available in the literature.\cite{11,13}

The inert, rigid, thermally stable and nontoxic inorganic core of POSS has resulted in these materials being investigated for many applications including, but not limited to, polymer composites, nanocomposites, catalytic supports, biomedical applications, optoelectronic materials, and soft gel materials.\cite{10,14-19} The variety of applications stems from the ability of POSS to be functionalized using a wide range of organic groups, which can be covalently attached at any one of the eight R-sites on the POSS vertices (Figure 1a). This subsequently affects the functionality of the POSS compound by altering properties such as the solubility, thermal stability, and emission properties.\cite{11,13,20,21}

This Review focuses on the use of POSS in light-emitting materials, outlining the specific role of POSS in the various applications, as well as developments in key areas. While POSS does not normally contribute to the emission process, it can significantly affect the properties of photonic materials and devices. We begin by summarizing the intrinsic properties of the standard POSS unit, where hydrogen occupies each of the R-sites shown in Figure 1a, a structure referred to as POSS-T8. The structural properties are outlined before we move on to discussing the functionalization of POSS, using lumophores as well as polymers. The electronic band structures of POSS functionalized with simple lumophores are then presented, as calculated...
through density functional theory (DFT). We then expand into work demonstrating applications of POSS as photoluminescent materials, in both solution and solid-state forms, with the use of POSS in ion sensing, bioimaging, and photodynamic therapy (PDT) explored. POSS for use in photocatalysis is then described before we discuss the use of POSS in optoelectronic devices, including a wide range of solar cells and light-emitting devices. Finally, the key benefits of POSS containing light-emitting materials are summarized and potential areas of growth are identified.

1.1. Intrinsic Properties of POSS

The intrinsic properties of POSS, as well as the effect of different functional groups at any of the eight R-sites, has been widely studied \([11,12,17,18,30,31]\). A key property of POSS is that the inorganic core rarely changes on addition of one or multiple organic groups; the rigid Si–O cage-like structure with a diameter of \(\approx 0.45 \text{ nm}\) is maintained \([22,24,25]\).

When hydrogen occupies each R-site on POSS \((R_n = H\) in Figure 1a), the compound is denoted by the formula \(\text{H}_n\text{SiO}_{12}\) and the structure is commonly referred to as POSS-T8 \([22]\). This originates from the nomenclature for siloxane polymers, where a silicon atom bonded to three oxygens is denoted by the letter T and, as there are eight of these bonds in POSS, this is subsequently written as \(T_8\) \([26]\). POSS-T8 is the simplest POSS structure and is also occasionally referred to as an octasilsesquioxane in the literature \([26]\). The structure of POSS-T8 has been investigated experimentally via X-ray and neutron powder diffraction (NPD) \([22,27]\), as well as theoretically via DFT calculations \([25,28,29]\). The key structural features determined from experimental and theoretical studies are shown in Table 1.

The packing of POSS units is highly dependent on the functional groups attached to the R-sites; however, POSS cores functionalized with short-chain alkyl groups have shown hexagonal packing \([22,26]\). The R-groups inhibit close packing \([22]\) and this property, along with the Si–O core being virtually unaffected by functionalization, has led to POSS often being used as a spacer molecule in polymers \([14]\) and as a key component to prevent the aggregation of organic molecules and nanocrystals \([25,31–33]\). As we progress through this Review, we will see that these two features are frequently exploited to tune the optical properties of POSS-based materials.

1.2. Functionalization of POSS

POSS is an excellent building block to construct composite materials due to its well-established structure and range of available functional sites. Although the silica-based core is inert, incorporation of POSS into different materials can be achieved through functionalization of the organic pendant R groups. This approach has been exploited widely to produce POSS–polymer composites that exhibit improved mechanical and thermal properties \([34–36]\) including an increase in fire retardancy \([37]\). Figure 2 shows the wealth of network structures that can be envisaged following the incorporation of POSS nanocages into polymeric materials, either as blends, through copolymerization or as pendant groups \([38]\). This approach improves the solubility and processability of the POSS, opening up various potential routes for application \([38,39]\). The R groups can also be modified to introduce one or more reactive and/or functional groups into the structure. The properties can therefore be easily tuned during synthesis \([5,23]\) for example, through use of “click” chemistry \([40]\). A large range of functionalities are available including aliphatic \([38]\), aromatic \([40,41,42]\) and ionic groups \([43,44]\) with a range of the commonly used commercially available POSS functionalities including amino-, mercapto-, or polymerizable acryl- and methacryl-groups (Figure 3). While aliphatic structures tend to be used as synthetic precursors or as polymer composite additives, conjugated aromatic structures have a direct use in optical devices, and ionic structures have also been used to create ionic liquids or water-soluble POSS materials. As shown in Table 2, a wide range of POSS precursors and products have been reported in the literature for different potential photonic applications.

1.3. Theoretical Prediction of POSS Properties

As discussed, functionalization at one or more of the cage vertices can be used to introduce optical (or other) functionality into the POSS material. In most cases, the optical properties will arise...
directly from this introduced functionality and theoretical calculations such as those carried out using DFT and time-dependent DFT (TDDFT) can provide valuable insight into the expected optical properties for a given introduced functionality. This can provide a means of fine tuning the response for potential applications in photovoltaics (PV) or other optical devices.\[24,25\]

The power of this approach was demonstrated by Zhen et al. who investigated the properties of the POSS-T8 unit and derivatives functionalized using an electron-withdrawing group (4-cyanophenyl (Cy)), an electron-donating group (4-carbazole-phenyl (Car)), as well as inserting a N\textsubscript{2} molecule into the POSS cage (Figure 4a).\[25\] In line with experimental observations, the POSS core was found to be rigid, with the body diagonal between Si atoms in POSS-T8 calculated to be 5.473 Å and only varying by 2.7% on the addition of organic functional groups. This rigidity is useful to prevent the aggregation of planar aromatic R groups, which are commonly found in organic aromatic lumophores. Such lumophores show a tendency to aggregate through \(\pi-\pi\) stacking interactions, resulting in ACQ of the PL due to the introduction of nonradiative decay routes. We will see later that the attachment of organic lumophores to the rigid POSS cage can be successfully used to inhibit aggregation, thereby preventing PL quenching. Returning to the study in question, the calculations also showed that the highest occupied molecular orbital (HOMO) of the functionalized POSS unit can be tuned by addition of an electron-donating group, whereas the lowest unoccupied molecular orbital (LUMO) can be tuned by functionalization with an electron-withdrawing group (Figure 4a,b)). Finally, by investigating the insertion of a N\textsubscript{2} molecule, it was determined that the chemical environment inside the POSS cage is not significantly altered by functionalization with organic molecules at the vertices.\[25\]

The combination of computational and experimental studies can provide powerful insight into the design of POSS-based photoactive materials. For example, Philips et al. carried out ab initio calculations based on DFT to calculate the excitation energies of various POSS derivatives functionalized with photocative substituents, including ethylene, styrene, and vinylstilbene. Three

| Symmetry  | Si–O bond lengths [Å] | Si–O–Si bond angles [°] | O–Si–O bond angles [°] |
|----------|-----------------------|--------------------------|------------------------|
| Class: Trigonal | NPD:27 1.623–1.626 | NPD:27 147.25–247.45 | NPD:27 109.14–109.53 |
| Space group: | DFT:25 1.643–1.644 | DFT:25 146.1–149.3 | DFT:25 109.5–109.8 |
| Lattice Parameters: \(a = 9.053 (1) \text{ Å}\) | \(c = 15.149 (1) \text{ Å}\) | | |

Figure 2. Schematic representation of potential polymer/POSS architectures. Nonfunctional POSS can be blended into a free or cross-linked polymer network. Monofunctional POSS can be covalently bound to polymers as terminal groups on pendant side chains or as endcap groups. Difunctional POSS can form the basis of repeat units for linear polymers, whereas polyfunctional POSS may be used as precursors for star/dendritic structures or polymeric networks. Adapted with permission.\[38\] Copyright 2011, Elsevier.
DFT methods (B3LYP, BNL, LR-CωPBEh) were used and results compared with experimentally observed absorption energies in monofunctionalized POSS with styrene and vinylstilbene (Figure 4c,d). It was found that functionalization decreased the calculated and measured absorption energies, with the excitons shown to be localized on the photoactive ligands, therefore demonstrating no charge transfer between the functional group and the core POSS molecule. It should be noted that the exclusion of polarization functions in the B3LYP method resulted in a significant underestimation of these excitation energies.[24]

In another study, computational methods were combined with steady-state and time-resolved PL measurements to investigate POSS-based dendritic molecules.[45] It was determined that the linking of bulky groups (4-vinylbiphenyl) to the POSS vertices via rigid vinyl-bridging molecules reduced intramolecular rotations, enhancing radiative recombination and so increasing the PL efficiency. This demonstrates that the bridging molecule as well as the photoactive functional group could be used to tune the photophysical properties of POSS-based luminescent materials.[45] These computational studies provide insight into the behavior of ground and excited electronic states when POSS is functionalized with photoactive species, therefore aiding our understanding of the applications of POSS in light-emitting materials.

2. Applications of POSS as Photoluminescent Materials

In the previous sections, we saw that light-emitting species (“lumophores”) can be introduced onto POSS through functionalization of one or more of the vertices and that the POSS unit can itself improve the optical properties of the resultant material, predominantly by preventing aggregation of the active species. These features have resulted in a significant increase in the use of POSS structures in light-emitting systems in recent years and considerable effort has been dedicated to the synthesis and characterization of fluorescent POSS materials—the specific details are beyond the scope of this Review and the interested reader is directed to the literature.[46]

The PL of the functionalized POSS is largely determined by the specific characteristics of the appended lumophore. Organic aromatic lumophores such as anthracene or pyrene commonly used as their dimeric emission are well understood and can be used to provide insight into the extent of aggregation.[47–50] Increasingly, novel light emitters such as carbon dots (CDs)[51–54] and aggregation-induced emitters (AIEgens)[55–58] have also attracted attention, opening up new avenues of research. In the following sections, we will consider how the unique properties of different photoluminescent POSS materials can be used in a variety of applications, both in solid materials and in solution, paying particular attention to the additional functionality imparted by the POSS unit.

2.1. Fluorescence Sensing

Fluorescent chemical sensors are devices that convert chemical information, such as the presence or concentration of an analyte, into a fluorescence signal, offering the advantages of high sensitivity, low cost, and fast signal response.[59] The ability of POSS to reduce or conversely induce the aggregation of appended lumophores has been exploited widely to develop fluorescent sensors based on this response for a variety of analytes including anions,[7,48,50,60,61] metal cations,[57,62] organic compounds.[63]
This structural change results in lumophore aggrega-
tion, causing quenching of the fluorescence response. Sun and coworkers. Prevents aggregation Synthesized [6]

In this fi

Moreover, in solid-state probes, the POSS unit may be used to control the 3D structure of the bulk material, increasing the internal porosity and thus sensitivity of the resultant sensor.\textsuperscript{[49,56,64–66]}

Photoluminescent POSS materials have attracted significant attention for use as fluoride sensors, as the fluoride anion triggers Si–O bond cleavage leading to degradation of the POSS cage.\textsuperscript{[67]} This structural change results in lumophore aggregation, leading to ACQ and/or spectral red shifts of the emission.\textsuperscript{[60,68]}

Du et al. used an ACQ-sensitive perylene diimide (PDI) dye for the sensing of fluoride ions in a POSS–PDI–polymer system.\textsuperscript{[60]} Here, the dye was functionalized with a monofunctional POSS core and an amphiphilic polymer on either imide group. The linear structure resulted in the formation of micelle-like nanoparticles (NPs) with POSS cores. In the presence of fluoride ions, the POSS cores are hydrolyzed, leading to aggregation of the PDI units, detected as a fast and selective decrease in fluorescence intensity, reaching a detection limit of 10 μM. Another example of a fluoride sensor is based on an S-annulated PDI with a POSS dumbbell structure reported by Jiang and coworkers.\textsuperscript{[7]}

In the absence of fluoride anions, the POSS cores reduced ACQ of the PDI chromophores, leading to an increase in the PL quantum yield (PLQY) from 38% to 100% in solution and 0.7% to 17.5% in the solid state. When the POSS–PDI was exposed to ten equivalents of fluoride ions, the anion induced Si–O bond cleavage, resulting in significant ACQ and a red shift in the emission spectrum. This was shown to be a highly fast and selective ratiometric probe, with no competition from oxygen-based anions. While the previous examples use an “on–off” response, Sun et al. recently developed an analogous “off–on” fluoride sensor based on a PDI-functionalized amino-POSS network.\textsuperscript{[63]}

Table 2. Examples of POSS in photonic applications in the literature. The role and source of the POSS unit is emphasized. See Figure 3 for common POSS unit structures.

| POSS (abbreviation) | Photoactive component\textsuperscript{a} | Applications | POSS role | Source | Ref. |
|---------------------|---------------------------------|--------------|-----------|--------|-----|
| Octa-benzoic acid-POSS (OBA-POSS) | Tb\textsuperscript{3+} ions | Optoelectronic devices, sensing | Prevents aggregation | Synthesized | [6] |
| Monobenzoic acid-POSS (MBA-POSS) | Tb\textsuperscript{3+} ions | Optoelectronic devices, sensing | Prevents aggregation | Synthesized | [6] |
| Aminopropylisobutyl POSS (AM-POSS/POSS-NH\textsubscript{2}) | PDI | Organic electronics | Affects packing structure | Purchased | [125] |
| Aminopropylisobutyl POSS (AM-POSS/POSS-NH\textsubscript{2}) | S-heterocyclic annulated perylene diimide | Colorimetric chemo sensor | Prevents aggregation | Purchased | [7] |
| Aminopropylisobutyl POSS (AM-POSS/POSS-NH\textsubscript{2}) | PNI-PAM and TPE | Variable temperature fluorescence imaging | Encapsulant | Purchased | [126] |
| Octaphenyl POSS (Ph-POSS) | P3HT | Organic electronics, photovoltaics | Affects packing structure | Purchased/ synthesized | [94] |
| Octaphenyl POSS (Ph-POSS) | P3HT and PCBM | Organic electronics, photovoltaics | Affects packing structure and improved film morphology | Purchased | [31] |
| Octavinyll POSS (OV-POSS) | Porphyrin dye through thiol crosslinker | Explosives/nitroaromatic sensing | Lumophore stabilizer and porosity enhancer | Purchased | [64] |
| Octavinyll POSS (OV-POSS) | Porphyrin and oligo(p-phenylenevinylene groups) | PDT/generation of reactive oxygen species | Prevents aggregation | Purchased | [88] |
| Octa-aminopropyl POSS hydrochloride (OAP-POSS) | Triphenylamine (TPA(COOH)\textsubscript{2}) | Fatty acid sensing | Hydrophobic molecular recognition | Synthesized | [70] |
| Octa-(3-aminopropyl) POSS hydrochloride (OAP-POSS) | CDs | Multicolor cell imaging | Passivator | Synthesized | [51] |
| Octa-aminopropyl POSS (OA-POSS) | CdTe QDs | Optoelectronics | Surface passivator | Purchased | [8] |
| Octakis(dimethylsilyloxy)-POSS (Ot-POSS) | Pyrene recognition unit and pyrene | Optoelectronics | Prevents aggregation | Purchased | [121] |
| Mercaptopropyl-isobutyl POSS (POSS-SH) | TPE | Optoelectronics, imaging | Controlling spacing and aggregation | Purchased | [55] |
| Hydride-monofunctional isobutyl-POSS (Si-H/Bu-POSS) | Perylene dimers | Sensing | Affects packing structure | Synthesized | [47] |
| Mono(acryloisobutyl) POSS (A-POSS) | TPE-based polymers | Explosives/nitroaromatic sensing | Porosity enhancer | Purchased | [56] |
| Monomaleimide isobutyl POSS (MI-POSS) | Porphyrin-containing monomers | PDT/generation of reactive oxygen species | Prevents aggregation | Purchased | [87] |

\textsuperscript{a}Definition of acronyms. PDI—perylen-3,4,9,10-tetracarboxylic dianhydride; P3HT—poly(3-hexylthiophene); PCBM—phenyl-C61-butyric acid methyl ester; PNI-PAM—poly(N-isopropylacrylamide); TPE—tetrphenylethene; QD—quantum dot; CD—carbon dot.

and nitroaromatic vapors.\textsuperscript{[47,49,56,64]} Moreover, in solid-state probes, the POSS unit may be used to control the 3D structure of the bulk material, increasing the internal porosity and thus sensitivity of the resultant sensor.\textsuperscript{[49,56,64–66]}

Photoluminescent POSS materials have attracted significant attention for use as fluoride sensors, as the fluoride anion triggers Si–O bond cleavage leading to degradation of the POSS cage.\textsuperscript{[67]} This structural change results in lumophore aggregation, leading to ACQ and/or spectral red shifts of the emission.\textsuperscript{[60,68]} Here, the dye was functionalized with a monofunctional POSS core and an amphiphilic polymer on either imide group. The linear structure resulted in the formation of micelle-like nanoparticles (NPs) with POSS cores. In the presence of fluoride ions, the POSS cores are hydrolyzed, leading to aggregation of the PDI units, detected as a fast and selective decrease in fluorescence intensity, reaching a detection limit of 10 μM. Another example of a fluoride sensor is based on an S-annulated PDI with a POSS dumbbell structure reported by Jiang and coworkers.\textsuperscript{[7]} In the absence of fluoride anions, the POSS cores reduced ACQ of the PDI chromophores, leading to an increase in the PL quantum yield (PLQY) from 38% to 100% in solution and 0.7% to 17.5% in the solid state. When the POSS–PDI was exposed to ten equivalents of fluoride ions, the anion induced Si–O bond cleavage, resulting in significant ACQ and a red shift in the emission spectrum. This was shown to be a highly fast and selective ratiometric probe, with no competition from oxygen-based anions. While the previous examples use an “on–off” response, Sun et al. recently developed an analogous “off–on” fluoride sensor based on a PDI-functionalized amino-POSS network.\textsuperscript{[63]} In this case, in the absence of fluoride ions, significant fluorescence quenching was observed, which was ascribed to photoinduced
electron transfer from the unreacted amino groups on the POSS cage to the PDI lumophore. It should be noted that although the addition of POSS has been seen to alter the HOMO and LUMO energies, research is still ongoing to determine the role of the POSS cage in charge transfer states. "Ligand-to-silsesquioxane" charge transfer has been proposed before, especially for electron-donating groups such as the amino group in this study, but this rare phenomenon has been theoretically disproven in favor of the more prominent "ligand-to-ligand" charge transfer process. Upon exposure to fluoride ions, the PDI-functionalized amino-POSS network exhibited a 41-fold increase in fluorescence intensity, with high selectivity for fluoride ions (Figure 5).

Although significant focus has been placed on the sensing of fluoride ions, POSS cores can also be used to detect other anions. For example, Chanmungkalakul et al. investigated dianthracene-functionalized POSS cores as fluorescent probes for a series of anions in different solvents. In this case, the POSS core is not only used for anion detection, but also to template the placement of the anthracene lumophores, such that the two photoluminescent units are kept at a short distance. In the absence of anions, this results in simple excimer emission. The incorporation of anions such as $F^-$, $CN^-$, or $OH^-$ disrupts the lumophore stacking, increasing molecular emission and reducing excimer emission (Figure 6). The detection limits varied in different solvents, but in all cases fluoride showed the lowest detection limit, with the lowest value of 1.001 ppb in a 6.0 μM solution of the probe in dimethyl sulfoxide (DMSO). Notably, the study showed that the emission wavelength could be used to determine the position of the anion, with fluoride being the only anion able to undergo encapsulation into the POSS core. Finally, efficient colorimetric sensing of anions such as $F^-$, $CN^-$, and $OH^-$ was demonstrated, which could be detected by the naked eye due to an anion-triggered charge transfer process. Although the authors obtained optical responses to $F^-$, $CN^-$, or $OH^-$ anions, they acknowledged that their system was not capable of differentiating these in a multiple-anion solution due to the higher binding strength of fluoride.

In another example, Chujo and coworkers successfully exploited the ability of POSS to form hydrophobic pockets for the detection of cis- and trans-fatty acids. Here the reaction of an octa-amino-functional POSS with a bifunctional triphenylamine derivative resulted in a luminescent network. While the proposed network is water soluble, the hydrophobic POSS cubes are able to discriminate between cis- and trans-fatty acids in a ratiometric manner due to the different degrees of hydrophobic molecular recognition. In the presence of these hydrophobic
analytes, the triphenylamine lumophores were observed to aggregate, generating a fluorescence response which, although small, was different for each isomer. This study illustrates how POSS cores have the potential for direct molecular recognition without the need for any other sensing functional groups, particularly through the use of POSS micelles or hydrophobic pockets.

The examples discussed so far have shown the ability of POSS to alter the optical properties of appended lumophores and act as recognition sites. POSS can also be used to alter the porosity of photoluminescent materials, leading to improved sensitivity and response times when used as an optical probe. Bai et al. used spin-coated films of pyrene-monofunctionalized POSS for the sensing of a series of nitroaromatic compounds, which are commonly used as analogues for explosives. In this work, the POSS cages induced the controlled formation of pyrene excimers, as well as a porous structure. They compared films

Figure 5. A PDI-functionalized amino-POSS network sensor that shows high selectivity for fluoride anions. a) Absorption spectra of PDI–POSS sensor (0.12 g L\(^{-1}\)) in H\(_2\)O:DMSO (98:2, v/v) with different anions (0.4 mM). b) Selectivity of the probe to different anions, showing high selectivity for fluoride anions and 41-fold increase in fluorescence intensity. The inset shows the corresponding PL spectra of the sensor in the presence of each analyte. c) Photograph of the PDI–POSS sensor solutions in the presence of different anions under UV light irradiation, showing a clear preference for fluoride sensing. Reproduced with permission. Copyright 2020, American Chemical Society.

Figure 6. An anthracene-functionalized POSS core as a fluorescent probe for anions. The proposed anion-sensing mechanism is illustrated, showing different degrees of anion–sensor interaction, leading to anions being detected at different positions of the cage. The different degrees of interaction lead to structural changes in the cage, resulting in the separation of the anthracene units such that a variation in the fluorescence emission of the probe from excimer to molecular emission is obtained. Reproduced with permission. Copyright 2018, Royal Society of Chemistry.
composed of covalently linked POSS–pyrene systems with films containing only pyrene, as well as films of POSS/pyrene blends. It was observed that the tight packing of pyrene reduces the porosity in the two latter systems, with porosity-enhanced diffusion being strongest in the covalently linked network. The increased diffusion rates resulted in very fast fluorescence quenching—60% in 10 s for a 4.5 nm-thick film. Furthermore, while the blended film reached a saturation point of 85% after 5 min, the covalent POSS–pyrene film obtained a high quenching of 93% after a mere 60 s. However, it was noted that the quenching efficiency was significantly affected by the film thickness, with only a 30% quenching obtained after 10 s for a 21 nm POSS–pyrene film.

In an alternative approach, Lu et al. demonstrated that the number of available sensing sites could be increased by crystalizing bispyrenyl-POSS molecules on top of nonfunctional POSS, such that the pyrene detection sites were exposed on the surface of the material.[47] This surface enrichment was used together with microtemplating of grid-like structures to minimize the dependence on diffusion rates, as well as the amount of material required. A fluorescence quenching between 15 and 30% was obtained after 30 min of exposure to nitrobenzene vapor, which is significantly lower than previous examples, even with longer exposure times.

In a further example of a nitroaromatic sensor, Zhang and coworkers used “click” chemistry to generate a crosslinked POSS–porphyrin network system that was grafted to the surface of a U-shaped optical fiber via photopolymerization.[64] The optical fiber enables efficient channeling of the excitation and emission light to the POSS–porphyrin material (Figure 7). In this case, POSS functionalization was shown to stabilize the porphyrin lumophores, reducing ACQ losses and increasing photostability. The system showed good recovery after exposure to nitroaromatic vapors, with minimal changes to the recovered fluorescence intensity after four cycles. This was attributed in part to the covalent nature of the POSS–porphyrin material. Interestingly, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption experiments showed the active material was composed of a hierarchically structured macro- and nanoporous network (Figure 7), which enhanced analyte diffusion and resulted in a faster response to 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), with quenching efficiencies of around 37% after 30 s and above 60% after 5 min.

Hybrid porous polymers (HPPs) have also been investigated as potential fluorescent sensor materials due to their high porosity, high surface area, and tunable fluorescence properties. In the work by Wang et al.,[65] a series of highly porous POSS-triphenylamine (TPA) networks were investigated as nitroaromatic sensors. Their experiments were conducted in THF and showed high PL quenching in the presence of nitroaromatic species, especially TNT, where detection limits below 1 ppm and a Stern–Volmer constant of 5208 M\(^{-1}\) was obtained. A POSS-spirobifluorene-based HPP later developed by the same group showed further improved fluorescence quenching efficiency in the presence of nitroaromatic analyte solutions, with increased Stern–Volmer constants reaching 16 344 M\(^{-1}\) for TNT.[66]

In the examples described so far, the ACQ of appended organic lumophores is used to register the sensor response. However, there exists a class of lumophores whose PL properties can be switched on following aggregation. These “AIEgens” are non- or poorly emissive when well solvated due to effective non-radiative relaxation of excited states through intramolecular motion such as rotations.[71] This mechanism is inhibited upon molecular aggregation, resulting in the activation of radiative pathways and a significant increase in the PL intensity.[71] The combination of AIEgens with the rigid POSS unit has been shown to enhance the AIE response, resulting in increased PLQYs when compared with pure AIE molecules.[55] The increase in PLQY can be explained by the rigidity of the

Figure 7. Working principle of a U-bent POSS–porphyrin probe for nitroaromatic vapors. a) A 365 nm laser is transmitted through the optical fiber to induce photopolymerization on the surface of the probe. b) Schematic drawing of the POSS–porphyrin network showing its nano- and macroporosity. c) SEM image of the U-bent probe demonstrating its macroporous structure. d) Fluorescence sensing mechanism through the U-bent optical fiber. Upon exposure to nitroaromatic vapors, the porous probe is observed to undergo fluorescence quenching. Adapted with permission.[64] Copyright 2015, American Chemical Society.
POSS core, which can restrict the intramolecular rotations of attached AIEgen units.\textsuperscript{[54]} It is also postulated that the presence of POSS can control the size of organic AIEgen aggregates, leading to the formation of nanoaggregates which result in improved PLQYs.\textsuperscript{[72]}

It has been shown that the AIE response can also be modulated through the use of a flexible organic spacer between POSS and the archetypal AIEgen tetraphenylethene (TPE) in a monofunctional endcap I-type system to control the nanostructural self-assembly of the composite.\textsuperscript{[55]} Short spacers (less than eight atoms) suppressed AIE emission as the formation of lamellar structures restricted aggregation of the TPE chromophores, whereas longer spacers achieved larger PLQYs and exhibited characteristic AIE behavior in THF/H\textsubscript{2}O mixtures, reaching maximum emission with the addition of 90% water.

The AIE response has also been exploited to develop sensors to detect explosive vapors. Zhou et al. reported an AIE sensor based on a copolymer of TPE-acrylate and mono(acryloisobutyl) POSS (A-POSS), with both the TPE and the POSS pendant from the acrylate polymer chain, which, upon free-radical polymerization and electrospinning, yielded porous copolymer films.\textsuperscript{[56]} This example exploits the increased porosity obtained through the use of POSS to facilitate the diffusion of the analytes and increase the sensitivity of the system, while reducing the effect of film thickness on the performance of the device. The nanostructured, electrospun films demonstrated fluorescence quenching when exposed to nitroaromatic vapors, with the best performing device exhibiting fluorescence quenching of 90% in 4 min for DNT and 26% in 4.0 min for TNT, with excellent signal recovery after five cycles. Notably, the sensor film showed high sensitivity to explosive vapors with a film thickness as high as 560 nm, when thicknesses of 25 nm usually set the upper limit for vapor detection using dense films.\textsuperscript{[56,73,74]}

This work was subsequently developed to synthesize POSS-TPE hydrogen-bonded organic frameworks (HOFs) for metal-ion sensing (Figure 8).\textsuperscript{[57]} The POSS-TPE HOF formed photoluminescent NPs in organic solvents and exhibited highly efficient emission quenching (97%) in DMSO when exposed to Cu\textsuperscript{2+} ions (1 × 10\textsuperscript{-3} M). The Cu\textsuperscript{2+} ions were able to disrupt the hydrogen bonding in the POSS-TPE HOF framework, leading to a change in structure and so altering the conformation of the TPE components. This led to the formation of additional, nonradiative pathways and thus PL quenching. Removal of the Cu\textsuperscript{2+} ions by CN\textsuperscript{-} led to the recovery of the HOF framework and so to recovery of the emission. An AIE-POSS sensor for metal ions has also been reported by Xiang et al.\textsuperscript{[72]} who prepared a dendritic AIE active system by attaching TPE to each corner of the POSS core. This system exhibited very good thermal stability and high PLQYs (Figure 9). The blue emission was found to be quenched by the presence of picric acid (PA) and Ru\textsuperscript{4+} ions, leading to potential applications as explosive and metal-ion sensors.

2.2. Fluorescence Bioimaging

In the previous section, we saw that molecular design can be used to obtain POSS-based systems that exhibit enhanced photophysical properties, as well as novel structures using the POSS as a templating molecule to create 3D bulk structures, to create networks, or for the use of hydrophobic pockets. In addition, POSS shows low toxicity and excellent biocompatibility.\textsuperscript{[75,76]} These combined features have triggered an interest in the application of POSS structures in areas such as bioimaging\textsuperscript{[77–79]} and nanomedicine.\textsuperscript{[80]}

Li et al. exploited the improved optical performance and cage-like structure of POSS for the detection of HER2-positive cancer cells.\textsuperscript{[79]} In this study, POSS cages were functionalized with a polyfluorene-based conjugated polymer, which showed increased PLQY and improved stability due to reduced aggregation. The POSS unit also functioned as a template to obtain hyperbranched star-like structures, which were subsequently encapsulated by poly(lactic-co-glycolic acid) to form NPs. These NPs were then introduced with Trastuzumab to increase cellular recognition and uptake, which allowed the NPs to discriminate SKBR-3 breast cancer cells from NIH/3T3 fibroblast cells and MCF-7 breast cancer cells with excellent biocompatibility (Figure 10).

While POSS structures can reduce dye aggregation, their potential to be amphiphilic allows them to aggregate and form micelles in solution.\textsuperscript{[81]} Li et al. used POSS-generated micelles for fluorescence bioimaging through the use of a
Figure 9. A dendritic TPE-POSS that shows aggregation-induced emission. a) Synthetic route to target structures. b) Emission spectra and intensities \( (I/I_0) \) of POSS2 (A, C) and POSS4 (B, D) in THF–H\(_2\)O mixtures. The insets show photographs of the emission in pure THF and 1:9 THF–H\(_2\)O mixtures under UV light. \( I_0 \) implies the emission intensity in pure THF. Adapted with permission. Copyright 2015, RSC Publishing.
POSS-end-capped poly(N-isopropylacrylamide) (PNIPAM) temperature-responsive polymer. As PNIPAM is water soluble under the lower critical solution temperature (LCST) and the POSS cages are hydrophobic, the linear POSS–PNIPAM system formed micelles in water. These were used to encapsulate the AIEgen TPE, whose aggregation and thus emission increased upon the coil-to-globule transition of PNIPAM at the biological temperature of 37 ºC, at which the PL intensity achieved its maximum.

2.3. Photodynamic Therapy

PDT is a photoactivated cell or cancer treatment in which a photosensitizer generates cytotoxic species, such as singlet oxygen or other reactive oxygen species, upon activation with light.[82] Localization and irradiation of the photosensitizer at the target area results in increased sensitivity and spatial selectivity. Typical photosensitizers are porphyrins and their derivatives or phthalocyanines or anthraquinones, among others,[83] and can often also be used for bioimaging due to their fluorescence properties.[82] In the context of this application, POSS has been used in an attempt to reduce the inherent aggregation of porphyrin-type photosensitizers in aqueous environments, which hinders their photoactivity. The work by Zhang et al. used a diblock polymer containing coumarin units and POSS pendant groups to generate hollow polymeric capsules for PDT (Figure 11).[84] In this case, the POSS fragments were not used to improve the optical properties of the material but instead to template the formation of POSS-centered micelles, with the POSS fragments later etched to obtain hollow capsules. This is an excellent example of the use of POSS units to template the formation of larger structures. The resulting hollow core was then able to efficiently encapsulate porphyrin photosensitizers and subsequently release them at a cellular pH of 5.5, with excellent cell internalization and singlet-oxygen generation observed.

In separate studies, Zhu et al.[85] and Chen et al.[86] both reported a biodegradable porphyrin–POSS–PEG system for use as a PDT photosensitizer, with chlorin e6 (Ce6) or 5,10,15,20-tetra(m-hydroxyphenyl)porphyrin (m-THPP) photosensitizers, respectively. In both cases, while the porphyrin unit acted as the photosensitizer, the POSS fragments fulfilled multiple functions including reducing the ACQ, increasing the rate of singlet-oxygen generation, and providing new reactive sites for the functionalization of the PEG unit, which enhanced water solubility of the system. In the first example, after cross linking the Ce6 and OA-POSS to generate POSS-Ce6 NPs, the PEG units were attached to unreacted amino groups to coat the surface of the NPs. In the second example, the structure consisted of an m-THPP porphyrin core functionalized with four POSS cages; the seven remaining unreacted sites per POSS unit were attached to PEG fragments to generate a dendritic macromolecule, with the POSS adopting a star-like structure. Both systems displayed excellent intracellular uptake, low cytotoxicity in the dark, and improved PDT efficiency under light irradiation. In both cases, in vivo studies showed excellent reduction in tumor volume and no obvious inherent toxicity or tissue damage of the porphyrin–POSS–PEG systems.

Jin et al. also investigated the potential for PDT of an alternating copolymer of maleimide isobutyl and 4-vinylbenzyl-
terminated tetraphenylporphyrin, which was then further poly-
merized with oligo(ethylene glycol) methyl ether methacrylate
to generate an amphiphilic block copolymer (P(MIPOSS-alt-
VBTPP)-b-POEGMA), containing alternating pendant POSS
and porphyrin groups (Figure 12). In this case, the POSS frag-
ments were no longer used as building blocks due to their mul-
tiple functional sites but were instead used as bulky substituents
on the polymer backbone to reduce the aggregation and stacking
of porphyrin photosensitizers. This effect, together with the cova-
lent attachment of the photosensitizers and the amphiphilic
nature of the polymer, resulted in an enhanced singlet-oxygen
yield, controlled loading of the photosensitizers, and high
biocompatibility and cellular uptake. In vitro studies showed that
the addition of POSS did not increase cell toxicity in the dark, but
a significant increase in toxicity upon irradiation was observed,
demonstrating the improved ability of the POSS system. In vivo
investigations also proved the POSS-containing polymer had an
increased PDT potential, with the tumors being almost
completely eradicated.

The generation of reactive oxygen species has also been inves-
tigated through the use of conjugated oligo- or poly-electrolytes.
Chen et al. reported an energy transfer system based on a cationic
conjugated oligo-electrolyte donor and porphyrin acceptor for use
in photodynamic antimicrobial chemotherapy (Figure 13). In
this system, each porphyrin unit was functionalized with four POSS
cages, which contained seven additional (oligo (p-phenylenevinylene) (OPVE) electrolyte donor groups, creating
a large macromolecule with a porphyrin acceptor center and a
POSS star-like structure. In this example, the POSS was used
to reduce the aggregation of the porphyrin sites but also to act
as a highly functionalizable bridging group, which increased
the local concentration of oligo-electrolyte groups, thus enhancing
the solubility. This also has a templating effect, which brings the
donor and acceptor in close proximity, within the Förster
resonance energy transfer (FRET) distance, enhancing the
energy transfer efficiency. The efficiency of singlet-oxygen gen-
eration in this system was four times higher than that observed
for the corresponding porphyrin control. Moreover, in antibacte-
rial studies, it was observed that the cationic groups on the oli-
go-electrolyte, which contribute to the antibacterial activity,
caused the POSS–porphyrin–oligoelectrolyte macromolecule to accumulate on the bacterial membrane. Due to the enhanced singlet-oxygen generation and antibacterial properties of the oligoelectrolyte, the system was observed to destroy E. coli and S. aureus bacteria with an impressive 99.9% efficiency.

2.4. POSS as Photocatalysts

Photocatalysis involves the use of light energy to drive chemical reactions that are difficult, or even impossible, to conduct in the dark. Usually this involves the addition of a photocatalytic species, that is able to absorb light and transfer its energy to the reagents, without being consumed in the reaction itself.[89] This section will describe a few examples of photocatalytic systems which use POSS to enhance the stability and catalytic properties. Due to the aqueous environment, many photocatalysts used in this application see their photoactivity reduced due to aggregation or photobleaching. POSS structures have been shown to minimize these effects. For example, in an attempt to obtain heterogeneous water-splitting photocatalysts, Prabu et al. combined a cationic monoamino POSS cage with a series of anionic electron acceptor polyoxometalates ([PW_{12}O_{40}], [PMo_{12}O_{40}] and [PMo_{10}V_{2}O_{40}]) through electrostatic interactions.[90] The incorporation of the hydrophobic POSS created water-stable heterogeneous photocatalysts, which also benefitted from enhanced thermal, chemical, and mechanical properties. Moreover, the generation of H_{2} (from the splitting of water) was promoted due to a red shift in the absorption of the photocatalyst and an enhanced charge carrier separation, which arose due to the immobilization of the polyoxometalate anion. Unfortunately, the photocatalytic activity of the polyoxometallate photocatalysts in the absence of POSS was not reported, so it is difficult to conclusively determine the contribution of POSS in this study.

In another study, Monticelli and coworkers reported a POSS-based photocatalyst, with a titanium atom replacing one of the Si atoms in the core POSS molecule.[16] This structure enabled the photocatalytic titania to be grafted to poly(styrene-co-maleic anhydride) nanofibers through the use of POSS as a bridging and complexing agent, which allowed for a heterogeneous catalyst to be obtained. The photocatalytic behavior was demonstrated through the degradation of sulfonhodamine B under UV irradiation. This is one of the few examples of a photocatalytic metal containing POSS, but this shows great potential for the trapping of other photoactive metals directly onto the POSS cage, which remains to be investigated.

Figure 13. A POSS-based energy transfer system incorporating a cationic conjugated oligoelectrolyte donor and porphyrin acceptor for use in photodynamic antimicrobial chemotherapy. a) Normalized absorption and PL spectra of the pure OPVE donor (solid line) and porphyrin acceptor (dashed line) molecules. b) Normalized absorption and PL spectra of the porphyrin–POSS–OPVE system, showing significant contribution from the abundant OPVE fragments. c) Rate of singlet-oxygen generation from the porphyrin–POSS–OPVE system, porphyrin, OPVE, and water (blank) by measuring the absorbance changes of 9,10-anthracenediy-bis(methylene)dimalonic acid at 378 nm. The graph shows a much higher singlet-oxygen generation rate for the porphyrin–POSS–OPVE system. d) Confocal laser scanning microscopy images of E. coli incubated with porphyrin–POSS–OPVE (Em: 500–550 nm), showing the presence of the photoactive compound in the bacterial membrane. Reproduced with permission.[88] Copyright 2018, American Chemical Society.
3. Device Applications of POSS

There has been significant, though not extensive, research into the use of POSS in optoelectronic devices. In the field of PV, POSS has been mainly used as a surface passivator, improving the thermal stability and morphology of dye-sensitized solar cell (DSSC) thin films,[31] passivating perovskite films,[91] and reducing surface defect densities in quantum dot (QD) solar cells.[86] Significant opportunities for the development of POSS incorporation exist within both PV and light-emitting diodes (LEDs). While POSS has been used in the fabrication of highly emissive, stable materials with applications in LEDs and organic LEDs (OLEDs), incorporation into devices remains an area to be further explored. The following sections outline the use of POSS in optoelectronic devices, first describing the inclusion of POSS in emerging PV technologies—organic, dye-sensitized, perovskite, and QD solar cells—and applications in the field of LEDs are then described.

3.1. Solar Cells

3.1.1. Organic Solar Cells

While power conversion efficiencies (PCEs) of polymer-based organic photovoltaics (OPV) remain low (<20%) compared with alternative PV technologies,[92] OPV still has the potential to provide low weight, flexibility, and easy-to-fabricate solar cells.[93] In OPV, the PCE is greatly influenced by the efficiency of charge carrier separation at the interface between a p-type donor (e.g., poly[3-hexylthiophene-2,5-diyl] (P3HT)) and n-type acceptor (e.g., phenyl-C_{61}-butyric acid methyl ester [PCBM]), which in turn is determined by the separation of donor and acceptor domains. The size of these domains can be tuned by the careful control of deposition, crystallization, and subsequent morphology of the donor and acceptor components.[31,93] POSS has been used to enhance the quality of these donor and acceptor domains by leading to greater phase separation,[31] enhancing charge transfer through improved crystallization,[94] and improving film morphology.[31]

Wu et al. showed that blending POSS into the organic photosactive layer in an OPV device improved the morphology of air-processed films of P3HT and PCBM, as well as prevented agglomeration of the two organic materials.[31] The study found that the use of Ph-POSS and SH-POSS had opposing effects on P3HT:PCBM OPV cells due to differing interactions. Through Raman spectroscopy and atomic force microscopy, it was seen that SH-POSS interacted strongly with P3HT domains, whereas Ph-POSS interacted with the PCBM domains, likely due to strong π–π interactions. The blending of Ph-POSS in a P3HT:PCBM layer showed enhanced absorption and film morphology when compared with unmodified devices. In contrast, SH-POSS-modified cells demonstrated poorer performance due to an irregularity in the morphology of the films. The study highlights the importance of the choice of POSS used in specific applications. More recently, Zhu et al. covalently grafted monofunctional Ph-POSS to P3HT, instead of simply mixing POSS with the donor and acceptor components.[94] The POSS monofunctionalized with P3HT crystallized into a 2D lamellar structure, forming layers with a thickness of 26.7 nm, equivalent to two layers of POSS:P3HT. This structure contributed to high charge carrier mobility when compared with reference devices, which translated to improved short-circuit current densities (J_{SC}), fill factors (FF), and a 40% improved PCE.

3.1.2. Dye-Sensitized Solar Cells

Similar to OPV, DSSCs have struggled to achieve efficiencies far above 10%,[92] although they also show potential for applications in flexible thin-film devices. DSSCs have the benefits of exhibiting good low-light performance (useful in shaded or diffuse light conditions) and are seen as environmentally friendly with a low energy manufacturing process.[95,96] A key component in DSSCs is the liquid or solid electrolyte, the conductivity of which is critical to device performance. POSS has been blended with imidazolium iodides—additives used in DSSC electrolytes as ionic conductors—to decrease the crystallinity of the electrolyte layer in solid-state DSSCs, a typical barrier to high efficiencies.[97] Zhang and Wang covalently attached propyl- and allyl-substituted imidazolium iodides to POSS,[97] forming a difunctional POSS-based solid-state electrolyte additive. These materials improved the contact between the solid electrolyte and TiO_{2} layers through the reduction of the electrolyte crystallinity, thereby improving charge transfer and resulting in an improvement in device efficiencies.

POSS has also been used to lower the glass transition temperature of imidazolium iodide electrolytes for use in solid-state DSSCs. Lv et al. demonstrated a transition temperature of −8.8 °C (264 K) for POSS-based imidazolium iodide, resulting in solid-state DSSCs retaining 93% of their efficiency at −4 °C when compared with performance at room temperature.[98] Addition of POSS to the solid-state electrolyte also resulted in the recording of a stable PCE over 1000 h of continuous illumination.[97]

3.1.3. Perovskite Solar Cells

Since first being included in PV devices in 2009, hybrid–inorganic perovskite solar cell research has exploded, resulting in efficiencies surpassing thin-film PV—such as copper indium gallium selenide or CIGS—and rivaling crystalline silicon cells.[92] The term perovskite typically refers to a material with an ABX_{3} structure and the archetypal PV perovskite, methylammonium lead iodide (MAPbI_{3}), has been extensively studied.[99] However, perovskite devices are notoriously unstable to oxygen, moisture, and UV light. These instabilities are typically combated through a combination of site substitution—where ions at any one of the A, B, or X sites of the perovskite are altered—and optimizing device design.[100,101] Crucially, the incorporation of POSS has been shown to increase perovskite PV stability even without complex site substitution or advanced device optimization.[91]

POSS has been used as a hydrophobic coating and passivating layer for perovskite PV.[91,102,103] Zhang et al. spin coated layers of POSS-NH_{2} and POSS-SH onto MAPbI_{3} and FA_{0.85}MA_{0.15}Pb_{1.85}I_{3.05} (BF_{3})_{0.15} perovskite films.[91] Figure 14 shows the X-ray diffraction patterns of reference and POSS-modified films, where the presence of POSS appears to suppress
the formation of the PbI₂ degradation product. Through additional contact angle measurements, it was proposed that the presence of POSS enhanced the moisture resistance of the perovskite films, a known cause of degradation. The improved stability imparted by the passivating POSS components was reflected in improved PV performance, where modification with POSS-NH₂ resulted in the greatest efficiency gains and a retention of 89% of the initial PCE after 90 days. The absorption energies of POSS onto the perovskite surface were also investigated by DFT. POSS monofunctionalized with a phosphine (PH₂) and hydroxyl (OH) group was also considered, alongside that of POSS-NH₂ and POSS-SH. The strongest absorption energy (86 kJ mol⁻¹) was shown by POSS-NH₂, in line with the experimental results. The passivating effect of POSS-NH₂ on MAPbI₃ devices has also been shown to improve charge carrier lifetimes and reduce charge trap densities, resulting in greater PCEs.⁶⁸,⁷¹

3.1.4. QD Solar Cells

QD solar cells show improved open circuit voltage and stability when compared with perovskite thin-film devices.⁷⁴ However, PCEs still lag behind conventional PV, with champion devices achieving less than 15% efficiency.⁷⁵ A key area of development to improve these cells is to optimize the QD solar-absorbing material, which typically displays lower charge carrier diffusion rates and high recombination, often attributed to defects on the QD surfaces.⁸³,¹⁰⁶

One or a combination of the QDs CdS, CdSe, CdSeTe, and ZnS are commonly deposited as the photoactive layer within QD solar cells.⁸³ Blending QDs separately with OA-POSS and octa-mercaptopropyl POSS (OM-POSS) has been shown to inhibit the release of Cd²⁺ from the CdTe QDs and decrease ACQ effects, both of which cause efficiency losses in QD solar cells. Despite the potential benefits of POSS in QD solar cells, their use has not been extensively investigated. Zhao et al. coated CdTe QDs in OA-POSS, resulting in a decrease in surface defect density in CdTe QD solar cells and a subsequent 40% increase in PCE when compared with reference devices.⁸⁸ A reduction in surface trap states on the CdTe QDs was suggested by an increase in the PL intensity post-POSS modification. The reduction in surface trap states was also attributed to the observed improvement in the incident photon conversion efficiency, resulting in reduced recombination within the QDs and at the TiO₂/QD/electrolyte interfaces.

In addition to being a surface passivator, POSS has been used to alter the photophysical properties of QDs themselves. Wang

![Figure 14](https://www.advancedsciencenews.com/figs/1000196/fig14.png)

**Figure 14.** POSS forms an effective hydrophobic and passivating coating for moisture-sensitive perovskite films. X-ray diffraction patterns of aging MAPbI₃ films exposed to a relative humidity of 90% are shown. a) Reference MAPbI₃ device, b) POSS-NH₂-modified and c) POSS-SH-modified devices. d) The ratios of the (110) perovskite and (001) PbI₂ (degradation product) peaks show that the inclusion of the POSS layer reduces degradation. Reproduced with permission.⁹¹ Copyright 2019, American Chemical Society.
et al. capped CdSe QDs with SH-POSS to act as a steric stabilizer, enabling the synthesis of QDs with different sizes and therefore different colors (Figure 15). The POSS-capped CdTe QDs showed superior PLQY and PL lifetimes when compared with standard capping ligands due to improved electron transport to the CdTe QD surface. This could have important implications for CdTe QD solar cells, enabling more efficient charge transfer between interfaces, but could also be exploited in LEDs.

3.2. Light-Emitting Devices

A wide variety of red-, yellow-, green-, and blue-emitting POSS compounds have been considered as promising candidates for use in inorganic LEDs, OLEDs, and white LEDs (WLEDs), though efficiencies remain low, and there is scope to optimize device design to take advantage of the high PLQYs and stability shown by POSS-modified luminescent materials.

POSS-based materials for OLED applications have been previously reviewed. Similar to the other photonic applications described in this Review, POSS has been predominantly used as a spacer molecule in materials for OLEDs to prevent the ACQ of organic molecules. However, recently, focus has shifted to the use of POSS with inorganic nanocrystals, which have shown tremendous potential as highly emissive, color pure materials for solid-state LEDs. Similar to their thin-film counterparts used in PV, perovskite nanocrystals (PNCs) show poor stability in the presence of water, though all-inorganic PNCs (CsPbX₃, where X is typically I or Br) show increased moisture resistance; however, this is still not sufficient for use in long-lasting LEDs. There have been attempts to increase PNC stability through organic ligand exchange, although coating the nanocrystals with POSS potentially presents a facile method to achieve the same goal. It has been shown that inorganic PNCs (CsPbBr₃, CsPbI₃, CsPb(I/Br)ₓ) coated with SH-POSS demonstrated increased water resistance, with strong green emission from CsPbBr₃ observed even after ten weeks of storage in water. These red (CsPb(I/Br)ₓ)- and green (CsPbBr₃)-emissive POSS-coated powders were deposited onto a blue LED to generate a WLED with a luminance of 14.1 lm W⁻¹. Subsequent work demonstrated the addition of SH-POSS to CsPbBr₃ nanocrystals in a green LED to act as a hole-blocking layer, which resulted in a 17-fold increase in the luminance of POSS-containing LEDs when compared with reference devices.

Improvements to PNC stability have also been achieved through the synthesis of methacrylate-capped CsPbX₃ and methacrylate-functionalized POSS (MA-POSS) copolymers. The resulting nanocomposites demonstrated excellent stability in water and good processability, capable of forming luminescent inks (Figure 16) when dissolved in toluene, which could then be painted as a downshifting layer on a WLED. When deposited as films, the PNC–POSS–polymer nanocomposite showed only a 5% decrease in PLQY when immersed in water for 60 days. The

Figure 15. POSS-capped CdTe QDs show superior PL properties. a) Absorption, b) PL, and c) PL decay curves (λex = 405 nm). d) Photograph showing the emission of POSS–CdSe QDs as a function of particle size under UV light. Adapted with permission. Copyright 2013, American Chemical Society.
exceptional water resistance was attributed to migration of the hydrophobic POSS to the film surface.\textsuperscript{[120]}

Moving away from PNCs, polyfunctional POSS-based polymers, referred to as fluorescent HPPs, have been synthesized with potential applications in light-emitting devices.\textsuperscript{[112,66]} Wang et al. demonstrated the synthesis of a series of two HPPs synthesized via the Heck reaction of octavinylsilsesquioxane with 2,2’,7,7’-tetrabromo-9,9’-spirobifluorene and 1,3,6,8-tetrabromopyrene.\textsuperscript{[66]} Controlling the reaction conditions—such as altering the catalyst used in the Heck reaction—resulted in tunable PL in both solid state and solution.

Sun et al. also synthesized HPPs via the Heck reaction, coupling the lumophores pyrene and biphenyl in various molar ratios, resulting in emissive powders and suspensions spanning the visible spectrum (Figure 17). The optical bandgap could be tuned from 2.46 eV (for 100% biphenyl) to 1.91 eV (for 100% pyrene). However, the PLQY varied from 22.42% down to 2.46% for 100% biphenyl and pyrene, respectively. HPPs were also cast as a series of polysiloxane-based fluorescent composites which maintained the strong fluorescence of the original powders and exhibited good UV resistance. Multicolored-emitting UV LEDs were then fabricated as a proof of concept.\textsuperscript{[32]}

POSS-coated carbon dots (CDs) have also been investigated for use in WLEDs. CDs were dispersed in octa(tetramethylammonium) POSS (TMA-POSS), resulting in water-soluble solid-state composites with deep blue emission. As with other studies on POSS in CDs,\textsuperscript{[51,53,54]} TMA-POSS acted as a surface passivator and spacer, preventing solid-state PL quenching typically seen in CDs. When this blue-emitting POSS-based CD system was combined with green- and red-emitting CdTe QDs embedded in a NaCl matrix, the resultant solid-state WLED exhibited a PLQY of 34%.\textsuperscript{[52]}

The work outlined in this section demonstrates the potential for the use of POSS-modified emissive materials in LEDs;\textsuperscript{[10,114,115,121]} however, incorporation into devices is often used as a proof of concept as opposed to being the focus of work. Therefore, an opportunity exists to build on the extensive literature surrounding highly emissive POSS-modified composites and optimize LED device design as well as investigate the effect of POSS on charge transfer mechanisms across device interfaces.

4. Outlook and Perspectives

Over the past two decades, POSS has proved increasingly popular due to its desirable properties of low toxicity, good biocompatibility, and stability. The rigid cage-like structure of the POSS inorganic core remains when any one of the arms on its eight vertices are functionalized. Functionalization of the molecule is well established and a wide variety of functionalized POSS samples are available to purchase. Combination with POSS—either through coating, blending, or covalent bonding—does not have a significant effect on the intrinsic photophysical properties of attached photoactive materials, thus making POSS an attractive additive for use in light-emitting systems.

In this Review, the use of POSS in a wide variety of light-emitting systems has been summarized. Applications of POSS-containing emissive materials in solution and solid-state forms in the fields of ion sensing, bioimaging, and PDT were reviewed. The use of POSS in photocatalysis and in optoelectronic devices was also explored. The key benefits of the use of POSS in these systems are as follows. 1) The rigid cage-like structure acts as a spacer molecule, preventing aggregation of both organic lumophores and inorganic nanocrystals. 2) POSS can act as a template to control lumophore placement, for example, controlling the special separation of donor and acceptor molecules in FRET systems. 3) The porosity of composites can be increased, which in turn enhances ion diffusion rates for sensing applications. 4) POSS has also been shown to be an effective passivating agent for nanocrystals and thin films, reducing surface trap states which can quench PL.

There are a number of areas of potential future development of light-emitting POSS systems. For example, POSS-based...
porphyrin and anthracene systems have been investigated for applications in PDT and ion sensing but have not been extensively investigated for upconversion by triplet–triplet annihilation (TTA), despite these being common sensitizer–emitter pairs.\textsuperscript{122–124} TTA requires careful placement of sensitizer–emitter pairs for which the templating potential of POSS could prove useful. There is also opportunity within the field of optoelectronic devices, especially for LEDs, where a number of promising POSS-containing light-emitting materials have been identified, although devices have not been optimized. Ultimately, POSS-containing light-emitting materials have shown significant potential across many fields and improvement of these systems would benefit from the consolidation of knowledge across disciplines.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

bioimaging, light-emitting diodes, optical nanostructures, photoluminescence, photonic devices, photovoltaics, polyhedral oligomeric silsesquioxane

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**Figure 17.** Color-tunable POSS-based HPPs are prepared by varying the molar ratio of the emissive appended organic lumophores. a) PL spectra of HPP, where the numbers 1–9 represent the molar ratio of biphenyl:pyrene increasing from 100% biphenyl (1) to 100% pyrene (9). b) Positions of HPP1-9 on CIE chromaticity diagram, which represents the color of the observed emission. Photographs of c) suspensions in ethanol and d) solid-state samples of HHP1-9 under UV light. e) HPP1-9 cast as polysiloxane-based fluorescent composites under UV light. f) Structure of HPPs, biphenyl (BP), and pyrene (Py). Adapted with permission.\textsuperscript{[32]} Copyright 2018, American Chemical Society.
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