A covalently bonded AlQ_3/SiO_2 hybrid material with blue light emission by a conventional sol–gel approach†

Hongyu Zeng, Weimin Huang and Jianlin Shi*

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We report the design and synthesis of a covalently bonded AlQ_3/SiO_2 hybrid material with strong blue light emission by a sol–gel approach, which make AlQ_3 solution-processable and chemically stable.

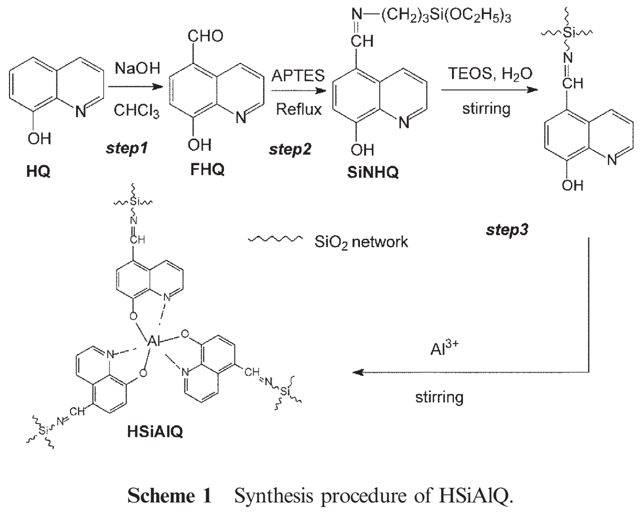
Tris(8-hydroxyquinoline)aluminium (AlQ_3) is one of the most common light emission and electron transport materials in OLEDs for next generation panel displays.[1–3] Its luminescence can be blue- or red-shifted through substitution on the 8-hydroxyquinoline (HQ) ligand or the introduction of optically inactive spacer molecules into the crystalline network of AlQ_3.[4,5] Though much work has been done on the optical properties of AlQ_3, it has to be vacuum sublimed and deposited[5,6] in device fabrication due to its low solubility in solvents. This drawback limits its practical applications and the problem remains unsolved to date. Another drawback with the material is its instability in the presence of water or oxygen. Currently the large scale applications of the materials require a low cost and simple processing route, such as solution-processing based ink-print techniques, for the fabrication of OLEDs. One solution to this problem is to disperse AlQ_3 in some solution-processable matrix. Herein we report the first example of an organic–inorganic hybrid material with AlQ_3 molecules covalently linked to the silica matrix by a conventional sol–gel approach.

Organic–inorganic hybrid materials have received great interest nowadays.[7–9] The hybrid system combines the chemical and thermal stability, the mechanical strength and the process flexibility of the inorganic matrix, together with the functional characteristics of active organic molecules. The sol–gel method, due to its low processing temperature, which is required to retain the activity of the organic moieties, has been proven to be a suitable approach for the preparation of hybrid materials.[7] Some hybrid materials with rare earth ion complexes and dye molecules have been reported.[10–13] However, reports on AlQ_3 organic–inorganic hybrid materials are not found as AlQ_3 has been reported to be unstable in the presence of water and oxygen,[14,15] while water exists throughout the common sol–gel process.

Physical mixing of hybrid materials is easy to achieve, but in such a mixture organic and inorganic moieties are linked together by weak interactions (such as hydrogen bonds and van der Waals forces), which may cause phase separation, inhomogeneous dispersion, and leaching and optical quenching of the dopants. To overcome these shortages, we designed and synthesized an organic–inorganic hybrid material with AlQ_3 molecules covalently linked to the silica matrix by C–Si bonding through a conventional sol–gel approach, making the AlQ_3 system highly solution processable while maintaining its excellent luminescent characteristics. Comparing to some AlQ_3 containing polymer materials,[16,17] this sol–gel route for covalently-bonded organic–inorganic hybrid materials is of convenience, low cost, and may be adaptable to many inorganic material hosts.

To make such a covalent bonding of AlQ_3 to the inorganic silica matrix, a new compound (denoted as SiNHQ) is synthesized as a dual-functional ligand, which not only acts as a bridge to link the organic and inorganic moieties, but also affects the luminescent properties of AlQ_3. The synthesis mainly contains three steps: 1st, synthesis of a derivative (5-formyl-8-hydroxyquinoline, denoted as FHQ‡)[18] from HQ with a certain active functional group; 2nd, formation of a silylated HQ derivative ligand by grafting (3-aminopropyl)triethoxysilane (APTES) onto FHQ; 3rd, processing of the hybrid material by a conventional sol–gel process. This synthesis procedure is illustrated in Scheme 1. A physically mixed AlQ_3–SiO_2 material sample (PMAlQ) was prepared by the direct mixing of HQ and Al^{3+} with TEOS and water in DMF, and then following the same sol–gel procedure with HSiAlQ.

The IR spectra for FHQ, SiNHQ, and HSiAlQ samples are shown in ESI† (Fig. S3). The silylation of the FHQ ligand is supported by the following three bands: the sharp band at 1641 cm^{-1} of C=N bond, with a red-shift from the C=O absorption in FHQ (1662 cm^{-1}); a group of bands at 2888–2971 cm^{-1} of C–H vibration stretching on O–R groups, and the



Scheme 1 Synthesis procedure of HSiAlQ.

State Key Laboratory of High-Performance Ceramics and Superfine Microstructures. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China. E-mail: jlshi@sunm.shcnc.ac.cn; Fax: +86-21-5241-3122

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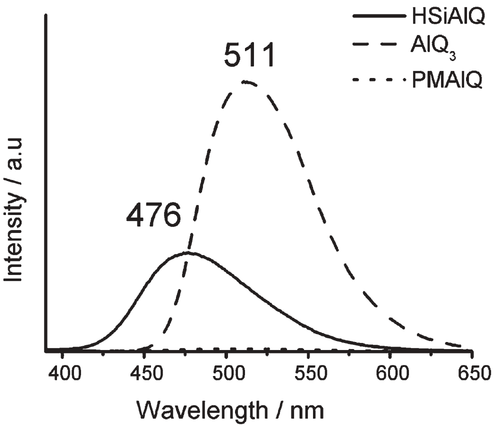

Fig. 1 Photoluminescent spectra of HSiAlQ, PMAlQ and AlQ_3 in the solid state.

Table 1 Photoluminescent data of the samples

Sample	Excitation λ_{max}/nm	Solution[a] emission λ_{max}/nm	Solid state emission λ_{max}/nm
SiNHQ	380	475	—
AlQ_3	385	510	511
PMAlQ	385	—	480–520
HSiAlQ	368	470	476

[a] 10^{-4} M DMF solution.

Si–O–C stretching band of alkoxy silane located at 1090 cm^{-1}. While these three band cannot be seen in the FHQ spectrum, suggesting that APTES has been grafted onto FHQ. Good agreement between the calculated molecular weight of SiNHQ (376.5) and the detected value (*m*/*z*: 376.1) by mass spectroscopy also confirms the formation of this intermediate product. The C–H vibration stretching in O–R groups disappeared from the HSiAlQ spectrum, together with the emergence of a broad Si–O–Si absorption band around 1010–1180 cm^{-1}, suggesting the full hydrolysis/condensation reactions between SiNHQ and TEOS.

From the UV-Vis absorption spectra, we can find a slight red-shift from 327 nm and 410 nm for FHQ to 331 nm and 415 nm for SiNHQ, respectively, owing to the silylation of the ligand and the substitution of C=O with C=N bond, and the absorption peak at 375 nm in the spectrum of HSiAlQ may be attributed to the π–π* transition of the metal complex, indicating the complexation of the ligands to Al^{3+}.

Fig. 1 shows the photoluminescent spectra of HSiAlQ, PMAlQ and AlQ_3 respectively, and the related data are summarized in Table 1.The solid state HSiAlQ shows a blue emission at 476 nm, an apparent blue-shift by 35 nm from the AlQ_3 PL spectrum (511 nm), confirming the formation of the metal complex. On the other hand, PMAlQ shows very weak light emission in the range from 480 nm to 520 nm.

It is known that the luminescence of the AlQ_3 complex molecules originates from the π–π* transitions on the quinolate ligands. The filled π orbitals (HOMOs) are located on the phenoxide side of the HQ ligands, and an electron-withdrawing substitution at C-5 on the HQ ligand will cause a blue-shift.[5] So this blue-shift may be partly due to the C=N bond formation as well as the silane grafting, which enhance the π conjugation, lower the energy level of the π orbital, and thus increase the π–π* transition band gap of the HQ ligands. Furthermore, according to a previous report,[4] the Si–O–Si network linked to $Al(SiNHQ)_3$ in the hybrid system may act as optically inactive spacer molecules, reducing the packing density of AlQ_3 and the direct intermolecular interactions between the chromophore molecules, also causing a blue-shift of the emission. Therefore, it is the silylation of the ligand and the covalent bonding between the silica matrix and the organic complex that affect the luminescent properties of AlQ_3.

Also we can see a great intensity difference in the PL spectra between HSiAlQ and PMAlQ. PMAlQ's emission is negligible, while HSiAlQ does show a strong blue emission though there is only one fiftieth of HQ in the hybrid, and the PL intensity shows no apparent change after being exposed in air for four weeks. The most probable reason for the luminescent failure of PMAlQ is the degradation of AlQ_3 in the presence of water.[14,19] The only difference between PMAlQ and HSiAlQ is that there is a large polar alkoxy silane end in the HSiAlQ system, so it can be confirmed that it is the ligand's chemical nature that makes HSiAlQ stable in the presence of water. Furthermore, in HSiAlQ, the complex is well dispersed due to the covalent bonding between the matrix and the organic moiety, thus avoiding the leaching and quenching effects in the system which may occur in PMAlQ. We can expect the chemically stable HSiAlQ will greatly expand the application of AlQ_3 related materials.

In conclusion, we have designed and synthesized the first example of organic–inorganic hybrid materials with AlQ_3 covalently bonded to a silica matrix through a conventional sol–gel approach, making it a solution-processable material, and determined its blue luminescent property together with its chemical stability against water and oxygen.

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