基于多面体低聚倍半硅氧烷体系的一种独特发光现象

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摘要：实验发现将 2 种 POSS(多面体低聚倍半硅氧烷)单体氨苯基异丁基 POSS 和八异丁基 POSS 置于四氢呋喃搅拌加热后,原来不发光的 POSS 单体表现出较强的发光。为解释这个发光现象,我们对溶剂处理前后的 POSS 材料进行了结构和发光性能表征,通过 ^{1}HNMR、^{29}Si NMR 及红外光谱等方法表征了 POSS 材料在 THF 中加热处理前后的结构,实验结果表明,这两种 POSS 在处理前后结构几乎没有变化,可以保持完整的笼状结构,但处理后的 POSS 分子 ^{1}H NMR 谱中含有少量的溶剂峰。FTIR 结果也表明处理前后的 POSS 结构几乎不变;我们也通过 XPS 表征了处理后的 POSS 中 Si 原子的价态,结果表明其价态未发生变化。结合这两种 POSS 材料处理前后的发光性能以及结构表征结果,我们认为,这种发光现象可能与 POSS 的吸附效应有关,即溶剂分子进入 POSS 笼中,形成 POSS/溶剂加合物,从而改变了原来的 POSS 的电子结构,使得相应的 POSS 材料出现发光现象。

关键词：多面体低聚倍半硅氧烷；发光；吸附效应
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A Unique Luminescence Behavior Based on Polyhedral Oligomeric Silsesquioxane Compounds

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Abstract: In this study, an unusual luminescence behavior from two polyhedral oligomeric silsesquioxane (POSS) monomers, aminopropyl isobutyl POSS (AIPOSS) and octal isobutyl POSS (OIPOSS) was observed after heating and stirring in their tetrahydrofuran (THF) solution. The chemical structures of these POSS samples were characterized before and after the heat treatment in THF by means of ^{1}H and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The valence state of silicon in the POSS sample was determined by X-ray photoelectron spectroscopy (XPS) as well. The characterization results showed that there is no obvious change in their structures, except tiny difference of the ^{1}H NMR spectra. Photoluminescence (PL) properties of the treated/untreated POSS were studied in detail. According to the PL and structure characterization results, it is speculated that this unusual luminescence from the treated POSS is most likely caused by the adsorption effect of the POSS cage, forming the POSS/solvent adducts, which lead to the change of the electronic structure of the POSS, and consequently the luminescence of the treated POSS.

Keywords: polyhedral oligomeric silsesquioxane; luminescence; adsorption effect

0　Introduction

Since polyhedral oligomeric silsesquioxane (POSS) materials were first pioneered by Scott in 1946, the application of POSS in academic and industrial fields has attracted widespread interest because of their well-defined nanostructure[1-5]. Generally, POSS owns a unique cubic cage-shaped nanostructure with the general formula $(R-SiO_{1.5})_8$ [6-7], which contains a polyhedron silicon-oxygen cube skeleton with intermittent siloxane linkages and tunable organic groups at the silicon atoms[8-9], where the R unit is functional organic or aliphatic groups, such as alkyl, aryl or any of their derivatives[10-11]. The average POSS core diameter falls in the range of approximately 0.45~0.53 nm[12]. POSS have distinct chemical properties, such as facile chemical modification[13], good solubility[14], high temperature and oxidation resistance properties [15-17]. When POSS moieties are incorporated into the compounds, the generated nanocomposites can result in novel interesting physical properties such as increases in glass transition temperature[18-19], thermal stability[20-21], mechanical strength[22-23], and oxidation resistance.

Recently, POSS-based luminescent materials have attracted a great deal of attention due to their good solubility in organic solvents[24-25]. Incorporation of POSS moieties into luminescent materials should not only enhance the fluorescence quantum yields of the aggregate state, but also improve the mechanical properties[26-27]. For example, Zhao used 7-allyl-8-hydroxyquinoline (Hq-allyl) as the ancillary ligand to synthesize a new iridium(Ⅲ) coumarin complex, $Ir(L)_2$ (q-allyl), and carbazole moieties covalently attached to the POSS, gained good thermal stability and photoluminescence performance[28]. At present, most of the POSS-based luminescent materials were chromophores or other groups. In addition, a small amount of POSS-containing luminescent materials were lack of common fluorescent units. For instance, Mohamed synthesized the unusual fluorescent POSS-containing polymers lacking any common fluorescent units: a poly (maleimide isobutyl POSS) homopolymer and poly (styrene-alt-maleimide isobutyl POSS) and poly (4-acetoxystyrene-alt-maleimide isobutyl POSS) alternating copolymers[29-30]. However, much less attention has been paid to the luminescence of POSS itself, because there is no conjugated group in their molecule structures.

In this study, we found a unique luminescence phenomenon in the POSS system, that the POSS compounds without any chromophore showed obvious luminescence after heat treatment in their THF solutions. To verify this luminescence behavior, two different POSS monomers, i.e., the AIPOSS with amino groups and the OIPOSS with all inert groups were investigated. In both of the cases the unique luminescence phenomena were found. For further study of the luminescence mechanism, the chemical structures of the POSS compounds were characterized by means of ^{1}H, ^{29}Si NMR spectroscopy, and FTIR spectroscopy. The results showed that the POSS compounds contained nearly intact in structures. The valence state of silicon was also determined by means of XPS, which verified that the Si atom remained the valence state before/after the treatment. We considered several possible origination of the luminescence of the POSS, and deduced that this unusual luminescence is most likely caused by the adsorption effect of the solvent in the POSS cages.

1　Experiments

1.1　Materials

Aminopropyl isobutyl POSS and octal isobutyl POSS were purchased from Hybrid Plastics Company, USA. THF was purchased from Alfa-Aesar. All chemical reagents were used as received without further purification.

1.2　Characterization

^{1}H, ^{29}Si NMR spectra were obtained on an Avance Ⅲ 400 MHz. FTIR spectra were obtained on a Nicolet-6700 spectrometer. The XPS was conducted with PHI 5000 Versa Probe (ULVAC-PHI, Japan). Fluorescence spectra were collected at room temperature on a Hitachi F-4500 fluorescence spectrophotometer.

1.3　Preparation of F-AIPOSS

Aminopropyl isobutyl POSS (0.3 g) was dissolved

in THF　(20 mL), and then heated under reflux at 66 ℃ for 10 h in the nitrogen atmosphere. The solution changes from colorless and transparent into yellow. Then, the solvent was distilled off under reduced pressure, yielding a deep orange oil-like liquid. The resulted sample was denoted as F-AIPOSS. For further FTIR, NMR and XPS characterization, the resulted sample was dried in the vacuum overnight.

1.4　Preparation of F-OIPOSS

The same procedures as above were carried out, yielding a deep orange oil-like liquid. The resulted sample was denoted as F-OIPOSS. For further FTIR, NMR and XPS characterization, the resulted sample was dried in the vacuum overnight.

2　Results and discussion

The chemical structures of AIPOSS and OIPOSS are depicted in Scheme 1. Generally, both AIPOSS and OIPOSS are regarded as non-luminous materials, because there is no conjugated group in their molecule structures. Interestingly, we found that the treated AIPOSS (denoted as F-AIPOSS) showed bright blue fluorescence after stirred and refluxed in THF solution. To study the unusual luminescence phenomenon, another POSS compound OIPOSS with only inert groups was investigated also. The treated OIPOSS (denoted as F-OIPOSS) showed bright blue emission also. Fig.1 shows the photographs of the F-AIPOSS and F-OIPOSS and their untreated counterparts under 365 nm UV illumination. It could be observed that both the F-AIPOSS and F-OIPOSS showed a strong blue fluorescence.

The luminescence properties of the POSS samples in THF solution and in solid state were investigated. Fig.2 presents the PL spectra of F-AIPOSS, AIPOSS, F-OIPOSS, and OIPOSS in THF solution　(1 mmol·L^{-1}). And Fig.3 exhibited the PL spectra of F-AIPOSS and F-OIPOSS in solid state.

The F-AIPOSS and F-OIPOSS featured strong emission peaks at about 430 nm either in THF solutions or solid states. Contrastively, the AIPOSS and OIPOSS THF solutions showed similar
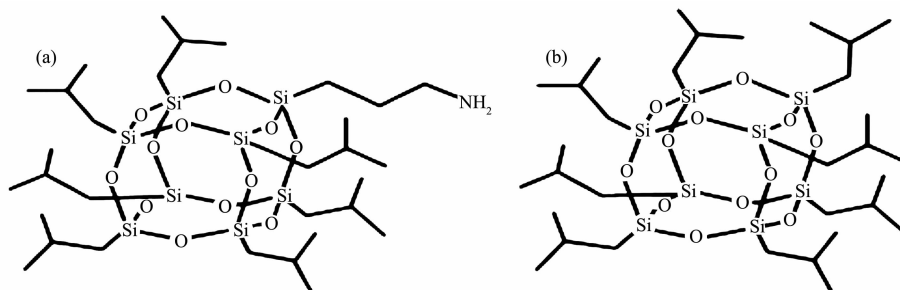
Scheme 1　Chemical structures of: (a) aminopropyl isobutyl POSS (AIPOSS); (b) octal isobutyl POSS (OIPOSS)
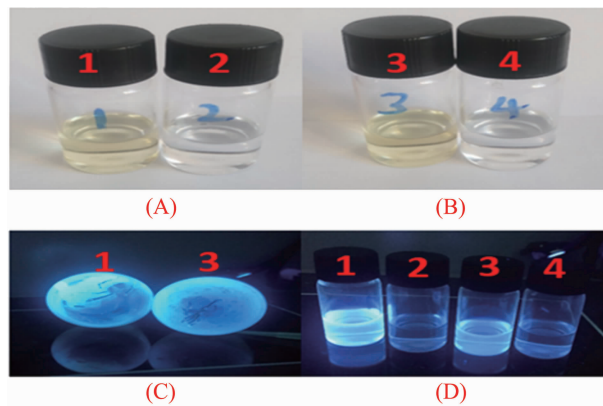

Fig.1　A1: F-AIPOSS/THF solution; A2: AIPOSS/THF solution; B3: F-OIPOSS/THF solution; B4: OIPOSS/THF solution; C1 and C3: Photographs of F-AIPOSS and F-OIPOSS in the solid state under 365 nm UV illumination, respectively; D: Photographs of A1, A2, B3, and B4 under 365 nm UV illumination, respectively
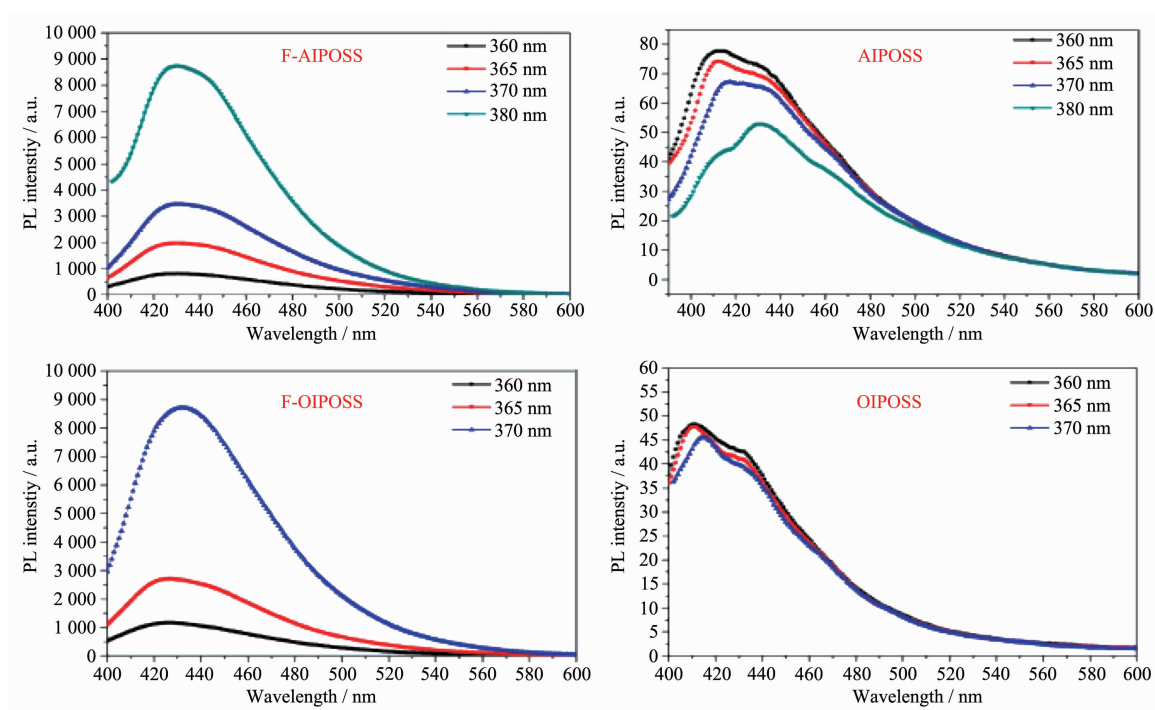
Fig.2　PL spectra of F-AIPOSS, AIPOSS, F-OIPOSS, and OIPOSS solutions in THF (1 mmol·L^{-1})
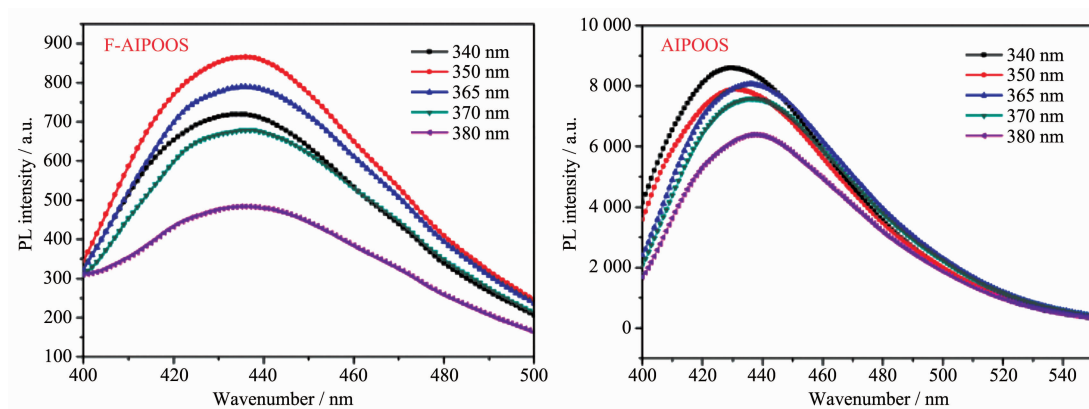under different excitation wavelength

Fig.3　PL spectra of F-AIPOSS and F-OIPOSS under different excitation wavelength in the solid state

luminescence as well, but their emission intensities were rather low, and no luminescence at all could be detected in their solid states. In addition, it was noted that the F-AIPOSS and F-OIPOSS solutions exhibited maximum emission intensity under excitation wavelength of 380 and 370 nm, respectively, which was a little red shift compared with that of the AIPOSS and OIPOSS solutions (360 nm) and the solid F-AIPOSS and F-OIPOSS samples (350 and 340 nm, respectively). The corresponding data were listed in Table 1.

It is interesting that the treatment heating in the

THF solution could result in the luminescence of these POSS compounds. As depicted in Scheme 1,

Table 1　Excitation wavelength for maximum ($\lambda_{Ex, max}$) and minimum ($\lambda_{Ex, min}$) emission intensity of the POSS samples

	$\lambda_{Ex, max}$ / nm	$\lambda_{Ex, min}$ / nm
F-AIPOSS/THF solution	380	360
AIPOSS/THF solution	360	380
F-OIPOSS/THF solution	370	360
OIPOSS/THF solution	360	370
F-AIPOSS in solid state	350	380
F-OIPOSS in solid state	340	380

there is no chromophore in these POSS compounds, and the used solvent has no luminescence also in the visible region. Naturally, it was speculated that the structures of the AIPOSS and OIPOSS changed after heating in the THF solution. So their structures were characterized by means of ^{1}H NMR, ^{29}Si NMR and FTIR, respectively. For the characterization, all the samples were dried in vacuum to insure the purity.

^{1}H NMR spectrum of F-AIPOSS sample in CDCl$_3$ (Fig.S1 in Supporting Information) features a signal at 2.68, 1.85, 1.54, 0.93 for the SiCH$_2$CH$_2$C**H**$_2$NH$_2$ methylene, SiCH$_2$CH(C**H**$_3$)$_2$ methine, SiC**H**$_2$CH$_2$CH$_2$NH$_2$ methylene and SiC**H**$_2$CH(CH$_3$)$_2$ methyl groups, respectively; and a signal at 0.61 for both the SiC**H**$_2$CH$_2$CH$_2$NH$_2$ and SiC**H**$_2$CH(CH$_3$)$_2$ methylene groups. For the AIPOSS (Fig.S2 in Supporting Information), there are signals at 2.72, 1.86, 1.60, 0.96 for the SiCH$_2$CH$_2$C**H**$_2$NH$_2$ methylene, SiCH$_2$C**H**(CH$_3$)$_2$ methine, SiCH$_2$C**H**$_2$CH$_2$NH$_2$ methylene and SiCH$_2$C**H**(CH$_3$)$_2$ methyl groups, respectively; and a signal at 0.66 for both the SiC**H**$_2$CH$_2$CH$_2$NH$_2$ and SiC**H**$_2$CH(CH$_3$)$_2$ methylene groups.

^{1}H NMR spectrum of the F-OIPOSS (Fig.S3 in Supporting Information) features signals at 1.86, 0.96, 0.60 for the SiCH$_2$C**H** (CH$_3$)$_2$ methine, SiCH$_2$CH(C**H**$_3$)$_2$ methyl and SiC**H**$_2$CH(CH$_3$)$_2$ methylene groups, respectively. For the OIPOSS (Fig.S4 in Supporting Infor-

mation), signals arise at 1.86, 0.95, 0.60 for the SiCH$_2$C**H**(CH$_3$)$_2$ methine, SiCH$_2$CH(C**H**$_3$)$_2$ methyl and SiCH$_2$CH(CH$_3$)$_2$ methylene groups, respectively.

According to the ^{1}H NMR results, there is little difference in the POSS samples before/after heating in THF solution, indicating that they keep nearly unchanged chemical structures before/after the treatment. But very tiny difference could be found after amplifying the ^{1}H NMR spectra of the F-AIPOSS/ AIPOSS and F-OIPOSS/OIPOSS, that two signals in the treated POSS (F-AIPOSS and F-OIPOSS) arise at about 1.43 and 1.26, respectively, which might be due to the signals from the residual THF (Fig.S5 in Supporting Information). And if the oil-like F-AIPOSS or F-OIPOSS samples rather than the dried ones were used in the ^{1}HNMR characterization, the THF related signals increased obviously.

To make sure the structures of the POSS samples further, their ^{29}Si NMR spectra were investigated. For the ^{29}Si NMR spectra of F-AIPOSS (Fig.4), two peaks appear, centering at −67.54 (peak a) and −67.82 (peak b), corresponding to their -O**Si**CH$_2$CH$_2$CH$_2$NH$_2$ and -O**Si**CH$_2$CH(CH$_3$)$_2$ units, respectively. For that of AIPOSS, two peaks appear at −67.81 (peak a$_1$) and −67.99 (peak b$_1$), corresponding to their O**Si**CH$_2$CH$_2$CH$_2$NH$_2$ and O**Si**CH$_2$CH(CH$_3$)$_2$ units, respe-ctively. For the F-OIPOSS/OIPOSS cases (Fig.5), only one peak
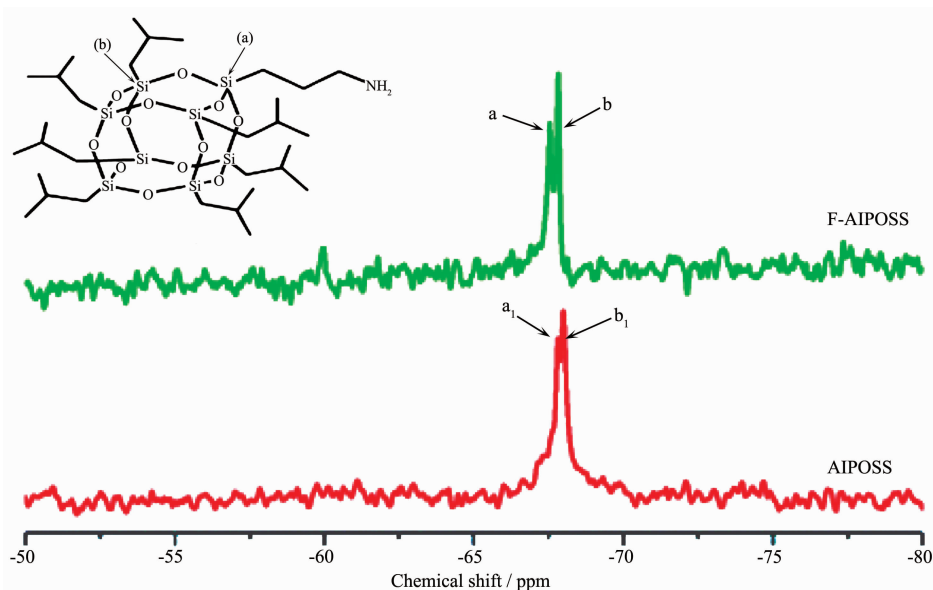

Fig.4 ^{29}Si NMR spectra of F-AIPOSS and AIPOSS in CDCl$_3$

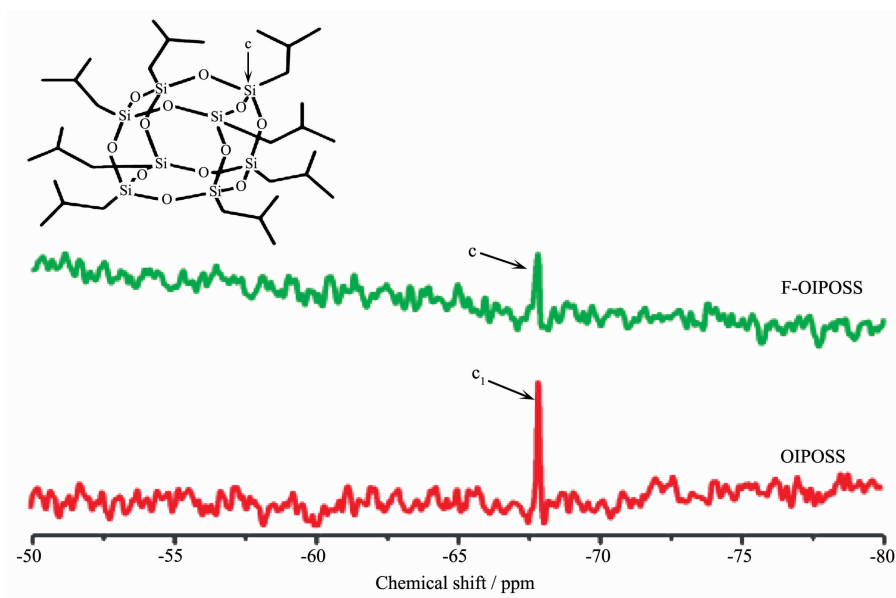Fig.5　^{29}Si NMR spectra of F-OIPOSS and OIPOSS in CDCl$_3$

appears at −67.84 (peak c) or −67.92 (peak c$_1$) for F-OIPOSS and OIPOSS, respectively, attribu-ting to their OSiCH$_2$CH(CH$_3$)$_2$ units.

　　These ^{29}Si NMR spectra results suggest that no cage cleavage occurred in the POSS samples after the heat treatment in THF, proving that the POSS cores of F-AIPOSS and F-OIPOSS remaining intact.

　　Fig.6 displays the FTIR spectra of F-AIPOSS, AIPOSS, F-OIPOSS and OIPOSS at room temperature. Characteristic absorption bands appear at 2 950~2 870 cm^{-1} and 1 110 cm^{-1}, representing the isobutyl C-H stretching and the Si-O-Si stretching in the POSS structure, respectively. This result indicates that no obvious functional groups appear in the treated POSS samples.

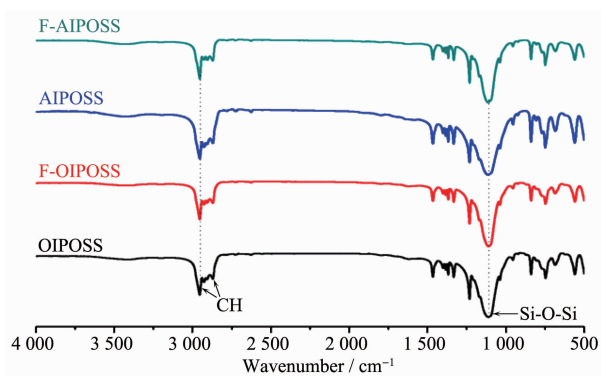　　According the structure characterization results

mentioned above, there is no obvious chemical structure change could be found in the treated POSS compounds. It is obscure what the origination of the luminescence is. Because excellent light-emitting Si nanocrystals could be synthesized from hydrogen silsesquioxane[31], the formation of trace silicon nano-crystals is one of our speculations. But the XPS analysis result of F-AIPOSS did not support this point. As shown in Fig.7, only one peak at 102.0 eV was detected from Si2p region of F-AIPOSS, which is consistent with O-Si-C species, and no signal of Si(0) at 98.9 eV had been detected. Therefore no Si nanocrystal formed in our experiments.

　　Another speculation is the formation of the POSS/ solvent adduct. Considering the cage-shaped
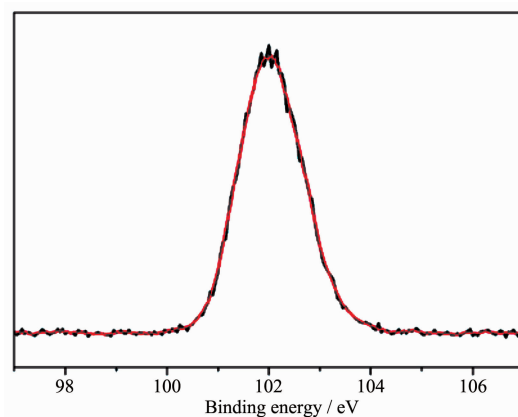

Fig.6　FTIR spectra of F-AIPOSS, AIPOSS, F-OIPOSS and OIPOSS

Fig.7　High resolution XPS spectrum of Si2p region of the F-AIPOSS

nanostructure of the POSS compounds, it is possible that the solvent molecules enter into the cages of the POSS, forming the POSS/solvent adducts, which modulate the electron structures of the POSS, and consequently leads to the luminescence. In our experiments, the resulted F-AIPOSS and F-OIPOSS are oil-like before dried under vacuum, indicating that there is much solvent in the samples. And these samples could not dried entirely from the solvent, tiny THF related ^{1}H NMR signals were still detected in the dried F-AIPOSS and F-OIPOSS samples as mentioned above. We suppose that the formation of the POSS/solvent adduct determines the emission properties of the corresponding samples. After heating in the THF solution, much solvent enters into the POSS cages, and many POSS/solvent adducts form consequently, giving rise to intensive luminescence from the F-AIPOSS and F-OIPOSS THF solutions (Fig.2). When the F-AIPOSS and F-OIPOSS dried further, some of the solvent molecules escape from the cages, which destroys part of the POSS/solvent adducts, resulting in decreased emission intensity of the solid samples (Fig. 3). For the case of untreated AIPOSS and OIPOSS compounds, they have no emission at all in the solid states, because there is no POSS/solvent adduct in the sample. But very weak emission could be detected in their THF solution, it is attributed to a few solvent molecules enter into the POSS cages. Due to the rate of formation of the POSS/solvent adducts is very low at the room temperature, these solutions exhibit weak luminescence only (Fig.2). It is supposed also that the more the POSS/solvent adducts form in the samples, the more the electronic delocalization is resulted to some extent. Therefore, the F-AIPOSS and F-OIPOSS THF solutions exhibited red shift in their $\lambda_{Ex,max}$ compared with their solid counterparts and the AIPOSS and OIPOSS solutions (Table 1). Unfortunately, we have no direct evidences for how the POSS/solvent adducts form. It is still need further investigation for this luminescence behaviour.

3　Conclusions

In summary, an unusual luminescence behavior from the POSS compounds was observed, that the non-luminous POSS compounds showed intensive luminescence after heating and stirring in THF solution. The chemical structures of the corresponding POSS samples were characterized by using ^{1}H NMR, [29]H NMR, XPS, and FTIR spectroscopy. No obvious structure changes could be detected after the POSS compounds heating in the solvent, except the tiny difference of the ^{1}H NMR spectra. It is supposed that this unusual luminescence is most likely ascribed to the formation of the POSS/solvent adducts in the system, which alters the electronic structures of the POSS compounds, and consequently leads to this unusual luminescence behavior.

Supporting information is available at http://www.wjhxxb.cn

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