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Research Article

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Synthesis and Characterization of hybrid Organic–inorganic near infrared Absorption OV-POSS-Squaraine-amine and improve the Properties

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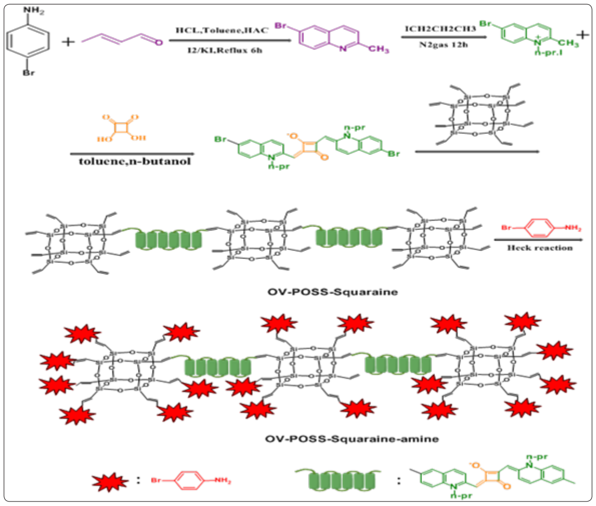
Abstract
Recently Squaraine dye have been receiving the interest of researchers due to its improved solution process ability, scalable synthesis, tunable chemical and physical properties via molecular design and of course its low cost. However, problems of compatibility and wet-ability have limited broad application of Squaraine dye. In this study, we used octavinyl-polyhedral oligomeric silsesquioxane OV-POSS to prevent all these problems and to enhance the dye properties. This is the first time to designe a novel near-IR absorption multifunctional materials over a wide PH (2-9) with excellent properties of compatibility. A novel system of organic-inorganic hybrids optical material near-IR was prepared by OV-POSS with 6-Bromoquanaldine and Squaric acid to get system1 of (OV-POSS-Squaraine) then reacted with 4-bromaniline to get our last system OV-POSS-Squaraine-amine. Our structure, composition, properties were characterized and evaluated by ^{1}HNMR spectrum, contact angle and FE-SEM. we believe that the novelty would open new path for more synthesis and applications.

Keywords: OV-POSS-Squaraine-amine, Near-IR absorption, Compatibility, Synthesis and Characterization

Introduction
Octavinyl-polyhedral-oligomeric-silsesquioxane OV-POSS are small silica nanoparticles with nanoscale cage-shaped structure, consisting of an inorganic Si–O framework and organic ligands bonded to the corner silicon atoms. Due to high thermal stability, low density and well-defined functionalities, OV-POSS have been used as the building blocks to prepare organic–inorganic multi-functional material [1-6]. OV-POSS are defined nanostructures, have high compatibility with materials, and the commercial availability of various useful precursors. Additionally, OV-POSS derivatives impart excellent thermal and mechanical properties to material, and has witnessed significant advances in biomedical applications, such as bio imaging, tissue engineering, bio-detection, antimicrobial treatment and drug delivery [4,7-20]. Also OV-POSS connected with Squaraine dye which has been wide-band absorption from 400 nm to 900 nm however, easy molecular design, strong absorption properties and near-IR regions these types of materials are suffering from poor compatibility and aggregation [21]. OV-POSS cages can be interred into the main chains of the material to produced organic–inorganic hybrids which display new development properties. Recently, there have been a few reports on the synthesis of polyimide class of organic–inorganic hybrids; of high-performance materials, with the wide-spread application in microelectronics, aerospace industry and other fields [22-25]. Considerable interest has been shown to improve the properties of polyimide by the use of OV-POSS [25-33]. Most of these previous studies deal with the preparation of the OV-POSS-containing polyimide. In 2003, Wright and Feheret al reported the synthesis of OV-POSS framework bearing two aniline groups [34]. This well-defined OV-POSS diamine was then used as one of the copolymerization monomers for polyimides [35]. It is worth noting that the OV-POSS-polyimides possessed good thermal stability, low water absorption and, alkali resistance as well as a low dielectric constant.

In this study, macrostructure multi-functional of hybrid OV-POSS-Squaraine connecting with 4-bromoaniline (OV-POSS-Squaraine-amine) by Heck reaction was fabricated successfully, as shown in Scheme 1. Our system aims to hence the properties which traditional material suffering of it and open new gate for synthesis a novel hybrid and improved the system for more application.



Scheme1: Synthetic Routes of OV-POSS-Squaraine and OV-POSS-Squaraine-amine

Experimental

Synthesis of Squaraine Dye

Squaraine was prepared in 50 mL reaction tube a mixture of *N*-propyl 6-bromoquinaldinium salt 784 mg, was added, followed by addition squaric acid 114 mg, and quinoline 1 mL then was refluxed in a mixture of n-butanol and toluene in the ratio of 1:1 (v/v, 10 mL) with azeotropicremoval of water for 24 h. The solvent was removed by distillation under reduced pressure to obtain a residue which was purified by column chromatography on silica gel (eluent: methanol/chloroform) = 1:9.

Synthesis of OV-POSS-Squaraine

OV-POSS-Squaraine was prepared in 50mL sealed three necked bottle the reactions were carried out under a nitrogen atmosphere, using a vacuum line system. Added a mixture of Squaraine 121mg, followed by addition OVPOSS 127 mg and palladium acetate 16 mg and K_2CO_3 83 mg the bottle was evacuated under vacuum and then flushed with dry nitrogen three times. Then N--methyl pyrrolidone was added, the reaction mixture was refluxed at 120°C under nitrogen for 12 h and then cooled to room temperature. The mixture was diluted with 50 mL of water and faltered. The precipitate was washed with toluene first, and then redissolved in DMSO. The DMSO solution was added drop wise into 100 mL H_2O the purification procedure was repeated three times [21].

Preparation of hybrid OV-POSS-Squaraine-amine

It was synthesized by Heck reaction. 800mg of OV-POSS-Squaraine was added in 50 ml tube with 50 mg 4-bromoaniline, 0.022g palladium acetate and 10 mg triphenlphosphine under nitrogen.10 ml dimethyl formamide and 3ml triethyl amine were added and reacted at room temperature for 12 h, then continued at 100°C for 48 h. The solution was rotary evaporated. It dissolved in small amount of THF and precipitated in 200 mL hexane this purification procedure was repeated three times [35].

Results and discussion

Morphology FE-SEM characterization of the system

The FE-SEM images in Figure1-a show the morphology of Squaraine as a needle and spherical shape. Images in Figure1-b show cubic shapes of OV-POSS, Figure1-c shows the morphology of OV-POSS-Squaraine. The homogenous morphology formed between the OV-POSS and Squaraine indicates that OV-POSS particles are locate between Squaraine so that movement between the particles became easy which confirms compatibility enhancement of our system. The image in Figure1-d is morphology of OV-POSS-Squaraine-amine. The flat and smooth film indicates its homogenousity and super morphology.

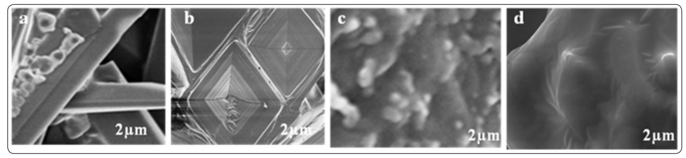


Figure 1: FE-SEM images of (a) the molecular structure of Squaraine (b) the inset of and OV-POSS (c) OV-POSS-Squaraine (d) OV-POSS-Squaraine-amine

The contact angle characterization of the system

The Squaraine dye shows a contact angle of 95°C, Figure2-a, while the OV-POSS have a hydrophobic surface behavior with contact angle of 120°C, Figure2-b, OV-POSS-Squaraine is even more hydrophobic where a contact angle of 127°C was observed as shown in Figure2-c, and the contact angle of OV-POSS-Squaraine-amine was 133°C as shown in Figure2-d. The increase of hydrophobicity can be explained by the chemical bonding between dye and OVPOSS, where the reaction between the two groups (on the dye surface and OV-POSS) leads to significant increase in hydrophobicity.

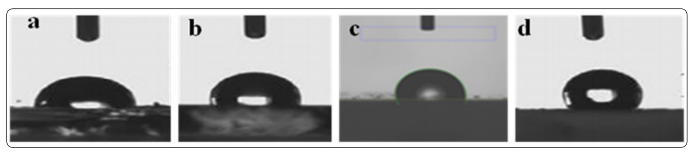


Figure 2: The contact angle of (a) Squaraine (b) OV-POSS (c) OV-POSS-Squaraine(d) OV-POSS-Squaraine-amine.

^{1}H-NMR characterization

The ^{1}H-NMR of OV-POSS-Squaraine is given in Figure.3. all the characteristic signals of at δ≈ 7.5–9.3 ppm associate to the quinolone, sharp signal peaks in the range of 4.7 ppm corresponding to the olefintc proton, whereas the aromatic protons locate in the range from 4.7 to 5.3 ppm and the N-pr protons locates at 3.1-3.7 ppm. This indicates that the heck reaction was occurred successfully. The ^{1}H-NMR spectra of OV-POSS-Squaraine-amine showed that the amine protons NH_2 at 3.2 ppm (a) and the proton of aniline ring at 6.3-7.2 ppm. These results confirmed that the successful incorporation of our system.

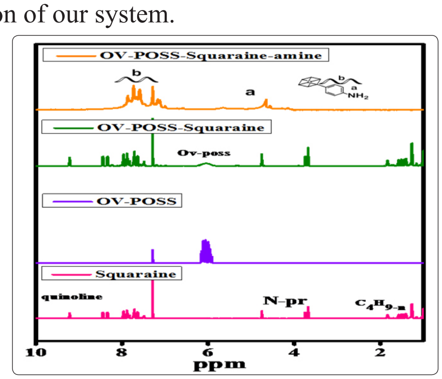


Figure 3: NMR spectra Squaraine, OV-POSS, OV-POSS-Squaraine and OV-POSS-Squaraine-amine

PH of OV-POSS-Squaraine-amine

In addition, the effect of pH (2.0~9.0) on the fluorescence property of OV-POSS-Squaraine-amine was investigated as shown in the Figure 4. It was found that the fluorescent intensity has kept almost the same in the PH 2.0~9.0, which indicates that our system is in a large span of pH.

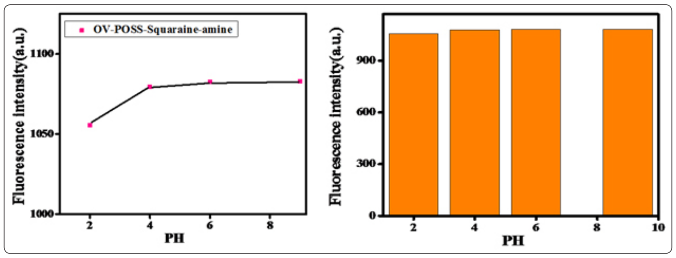


Figure 4: The effect of pH OV-POSS-Squaraine-amine

Aggregation Effect Characterization

In this regard, the absorption spectrum of Squaraine without OV-POSS and OV-POSS-Squaraine is shown in Figure 5-a and Figure 5-b, respectively. DMSO and DMSO–water solvents with a volume ratio at 1:1 and 1:9 are recorded. The Squaraine without OV-POSS shows a big aggregation in the mixed solvent. This result means that the optical properties of Squaraine without OV-POSS are not stable in a poor solvent, even in a mixed solution containing a small fraction of poor solution. The OV-POSS-Squaraine there was no more change n the absorbance which indicates that with the OV-POSS there is no aggregation.

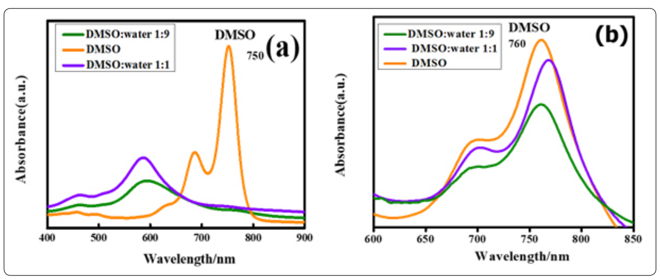


Figure 5: (a) The absorption spectra in DMSO and DMSO–water of Squaraine and (b) OV-POSS-Squaraine

Conclusion

We have highlighted recent progress towards the development of near-IR absorption system OV-POSS-Squaraine-amine designed and prepared successfully. It solved the problems of aggregation effect, biocompatibility and wet-ability that traditional materials were suffering of it upon applying in chemo and biological imaging. Our work has opened new road for the novelty of new synthesis.

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