New bead type and high symmetrical diallyl-POSS based emissive conjugated polyfluorene

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A new bead type and diallyl-POSS based polyfluorene (P2) with high symmetrical structure was synthesized via Heck coupling reaction between oligomeric alkylnyl fluorene (P1) and diallyl polyhedral oligomeric silsesquioxanes (diallyl-POSS). The molecular weight and the conjugated length of P1 and P2 were well controlled to acquire good solubility and excellent optical property. The bead-type POSS based polymer was characterized by gel permeation chromatography (GPC), FT-IR, 1H NMR and photoluminescence (PL) spectra. High Resolution Transmission Electron Microscopy (HRTEM) micrographs showed that diallyl-POSS were uniformly nano-dispersed in the polymer matrix. Compared with P1, the POSS based polyfluorene P2 exhibited not only a higher thermal stability, but also an improved photophysical property in solution and solid states. The incorporation of diallyl-POSS resulted effectively in inhibiting the strong stacking/dipole–dipole interaction between fluorescent groups in the polyfluorene. The experimental results indicate that the bi-functional POSS based light-emitting polymers with high symmetrical structure can have great potential in optical materials and devices, such as OPV or PLED, etc.

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and a diallyl-POSS-based hybrid polymer with bead type structure was then prepared (Scheme 1). Meanwhile, the conjugation length of oligomeric alkynylfluorene structure between the adjacent diallyl-POSS, which was nailing on the main chain of polymer via Heck cross-coupling reactions, was well controlled in order to acquire excellent luminescent properties and solubility. The incorporation of “huge” inorganic POSS nanoparticles to form bead type and high symmetrical diallyl-POSS based polymer molecular chain was expected to improve not only the thermal property of light-emitting polymer, but also the optical properties including a higher fluorescent quantum yield, enhanced photo-stability and much improved two-photon fluorescence (TPF) property. It is expected that bifunctional-POSS based polymer will have great impact on applications in optical materials and devices, such as OPV or PLED, etc.

2. Experimental section

2.1. Materials

1-Bromodecane (98%), 2,7-dibromofluorene (98%), tetrabutyl ammonium bromide (8%) and carbozole (98%), bis(triarylphosphine) palladium(II) chloride (98%) purchased from Nanjing Carbon Resagent Co.,Ltd. Cuprous iodide (95%), 2-methylbut-3-yn-2-ol (98%), 1,10-dibromodecane (98%), sodium hydroxide and anhydrous potassium carbonate (98%) were used as received from Adams. Allyl(dichloromethyl)amine (95%) was obtained from TCI (Shanghai) Chemical Industry Development Co., Ltd. Tetrasilanolphenyl POSS was purchased from Hybrid Plastics. All organic solvents were purchased from commercial sources and were carefully dried and distilled prior to use.

2.2. The synthesis of monomers and polymers

2.2.1. 2,7-dibromo-9,9-didecylfluorene (1)

1-Bromodecane (4.42 g, 20.0 mmol) was added by syringe to a mixture of 2,7-dibromofluorene (2.59 g, 8 mmol), tetrabutyl ammonium bromide (0.02 g, 0.064 mmol) and 2.50 mL of triethylamine at 95 °C for 6 h. After cooling to room temperature, insoluble substance was filtered off. Then the solvent was removed under reduced pressure and the precipitate was purified by column chromatography on silica gel to afford 9,9-didecyl-2,7-diethynyl fluorene as white crystals (0.46 g, Yield 71%).

2.2.2. 4,4′-(9,9-didecyl-9H-fluorene-2,7-diyli)bis(2-methylbut-3-yn-2-ol) (2)

Under argon atmosphere, 2,7-dibromo-9,9-didecylfluorene (1.21 g, 2 mmol), 2-methylbut-3-yn-2-ol (1.6 mL, 16 mmol), bis(triarylphosphine) palladium(II) chloride (24 mg, 0.08 mmol) and cuprous iodide (8 mg, 0.04 mmol) were dissolved in 20 mL of tetrahydrofuran. The mixture was refluxed at 70 °C for 24 h. After cooling to room temperature, the insoluble substance was filtered off. Then the solvent was removed under reduced pressure. The mixture was extracted three times with dichloromethane. The organic phase was puriﬁed by column chromatography on silica gel with ethyl acetate/petroleum ether (1:8 v/v) to afford 4,4′-(9,9-didecyl-9H-fluorene-2,7-diyli)bis(2-methylbut-3-yn-2-ol) as a yellow powder (0.87 g, Yield 71%).

2.2.3. 9,9-didecyl-2,7-diethynylfluorene (3)

Under argon atmosphere, 4,4′-(9,9-didecyl-9H-fluorene-2,7-diyli)bis(2-methylbut-3-yn-2-ol) (0.61 g, 1 mmol) and sodium hydroxide (0.60 g, 10 mmol) in 40 mL of 1,4-dioxane were refluxed at 80 °C for 6 h. After cooling to room temperature, water and dichloromethane were added to the mixture, and the organic phase was puriﬁed by column chromatography on silica gel with petroleum to get 9,9-didecyl-2,7-diethynylfluorene as white crystals (0.46 g, Yield 92%).

2.2.4. 9-(10-bromodecyl)-9H-carbazole (4)

Under argon atmosphere, carbozole (1.67 g, 0.01 mol), anhydrous potassium carbonate (2.77 g, 0.02 mol), and 1,10-dibromodecane (6.00 g, 0.02 mol) in 40 mL of anhydrous acetonitrile were refluxed at 95 °C for 36 h. After cooling to room temperature, insoluble substance was ﬁltered, and the solvent was removed under reduced pressure. The crude product was puriﬁed by column chromatography on silica gel with petroleum to get 9-(10-bromodecyl)-9H-carbazole as white crystals (1.66 g, Yield 43%).

2.2.5. 9-(2,7-dibromo-9H-fluorene-9,9-diyli)bis(decane-10,1-diyli)bis(9H-carbazole) (5)

9-(10-bromodecyl)-9H-carbazole (1.55 g, 4 mmol) was added by syringe to a mixture of 2,7-dibromofluorene (0.32 g, 1 mmol), tetrabutyl ammonium bromide (3 mg, 0.008 mmol) and 0.313 mL of 50% aqueous sodium hydroxide dissolved in dimethyl sulfoxide (10.0 mL). After stirring at 40 °C for 6 h, the mixture was poured into water and extracted three times with dichloromethane. The solvent was removed under reduced pressure. The precipitate was puriﬁed by column chromatography on silica gel ethyl acetate/petroleum ether (1:20 v/v) to afford 9-(2,7-dibromo-9H-fluorene-9,9-diyli)bis(decane-10,1-diyli)bis(9H-carbazole) as white crystals (0.36 g, Yield 38%).

2.2.6. 3,13-di((3-propenyl)-5,5-dimethyl-1,5,7,9,11,15,17,19-octaphenylhexacyclo[15.3.1(1,13).1(3,11)0.1(5,17)0.1(9,15)]decasiloxane (6)

6 was synthesized according to the pathway shown in Scheme 2; Under dry argon atmosphere, allyl(dichloromethyl)methylsilane (3.102 g, 1.46 mL, 10 mmol) was added dropwise to a mixed solution
of 40 mL of anhydrous tetrahydrofuran, tetrasilanolphenyl POSS (5.350 g, 5 mmol), and triethylamine (0.81 mL, 5 mmol) at room temperature. After 30 min, the insoluble solid was filtered off and the solvent and other volatile compounds were removed under reduced pressure. The crude product was washed with 50 mL of methanol, 5 mL of ether and 2 mL of hydrochloric acid (1 mol/L) to afford cis- and trans-6 as a white powder (3.89 g, Yield 63%). cis- and trans-6 (in the presence of isomeric mixture of 1:1 ratio): 1H NMR (500 MHz, CDCl3, δ): 7.53–7.19 (m, 40H, Ar–H), 5.76 (m, 2H, CH=CH2), 4.88–4.76 (m, 4H, CH=CH2). 1.77 (d, 4H, J = 7.8 Hz, CH2), 0.30 (s, 6H, CH3) indicated isomeric mixture. 29Si NMR (500 MHz, CDCl3, δ): -21.96, -78.58, -79.49 (trans-6; relative intensity ratio 1:2:2); -21.96, -78.58, -79.45, -79.53 (cis-6; relative intensity ratio 1:2:1:1). FT-IR (cm⁻¹, KBr): 1639, 1591 (w; Ar), 1097 (s; Si–O–Si). Anal. Calcd. For C56H56O14Si10 (10 mg, 5 mol%), triphenylphosphine) palladium(0) (23 mg, 2 mol %), copper iodide (10 mg, 5 mol %), 2,2'-bipyridyl-1,10-phenanthroline as a catalyst, anhydrous potassium carbonate as an acid cating agent, and waters 1515 HPLC pump. Tetrahydrofuran was used as a carrier solvent at a flow rate of 1.0 mL/min at 25 °C. A calibration curve was made to determine Mw and Mn/Mw values with polystyrene standards, Mw = 900.1 × 10⁶ g/mol, D < 1.1. Simultaneous TG-DTA Netzsch STA 449F3 was used to investigate the thermal stability.

2.2.7. Synthesis of oligomeric alkenyl fluorene (P1)

9,9′-(2,7-dibromo-9H-fluorene-9,9′-diyl)bis(9H-carbazole) (701 mg, 0.75 mmol), 9,9-dicyclopentadienylfluorene (247 mg, 0.5 mmol), triakis(triphenylphosphine) palladium(0) (23 mg, 2 mol %), copper iodide (10 mg, 5 mol %), N,N-diisopropylamine (5 mL), and toluene (10 mL) were added into a Schlenk flask in a nitrogen-filled glove box. After stirring at 60 °C for 12 h, the dibromo monomer (5 mol %) and diallyl-POSS (23 mg, 0.3 mmol), palladium acetate (4 mg, 0.05 mmol), DMG (31 mg, 0.3 mmol), palladium acetate (4 mg, 0.015 mmol), anhydrous potassium carbonate (21 mg, 0.015 mmol) and N-methyl pyrrolidone (5 mL) were added into a Schlenk flask in a nitrogen-filled glove box and stirred at 120 °C for 20 h. After cooling to room temperature, solvent was removed by vacuum distillation. The polymer was then precipitated into water and filtered, washed in a Soxhlet extractor with acetone/dichloromethane (6:1 v/v). The crude product was purified by column chromatography on silica gel tetrahydrofuran. In this way, the much high molecular weight product could be removed to improve the solubility of P2. The yield was 35% as a dark green solid. Mw = 3.93 × 10⁶ Da, Mn = 1.45 × 10⁶ Da, PDI = 2.71, (GPC, polystyrene); 1H NMR (500 MHz, CDCl3, δ): 8.09 (br, Ar–H), 7.67–7.36 (br, Ar–H), 7.20 (br, Ar–H), 5.45 (br, CH–CH), 4.26 (br, N–CH2), 1.97–0.60 (br, (CH2)0 and (CH2)0CH3). 29Si NMR (79.49 MHz, solid, δ): -18.12, -65.22, -79.10. FT-IR (cm⁻¹, KBr): 2923, 2852 (CH), 1681, 1663, 1581 (Ar), 1118 (Si–O–Si).

2.3. Preparation fluorescent composite film

8.89 g (0.04 mol) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), 20 g (0.02 mol) of polycaprolactone diol (PCL Mw = 1000) and 50 ml of dibutyltin dilaurate were added to a three-necked bottle with mechanical agitation, and reacted 6 h at 80 °C. 1.80 g (0.02 mol) of 1,4-butylen glycol (BDG) and 30 ml of THF were added after cooling to room temperature. The mixture was used as matrix solution. 6 mg/ml THF solutions of P1 and P2 were prepared respectively, and different volumes of P1 and P2 THF solution, according to different mass fractions of P1 and P2 in fluorescence composite films, were added to 2 ml of the former matrix solution with magnetic stirring. The mixture was then added to the teflon plate. The solvent was evaporated 24 h at room temperature, and then was placed into an oven at 60 °C for 2 days. Finally, the residue solvent was evaporated under vacuum at 30 °C for 10 h.

2.4. Measurements and techniques

2.4.1. Molecular structure characterizations

Infrared spectra were obtained with a Bruker VECTOR 22 Fourier-transform infrared (FT-IR) spectrometer. The 1H NMR, 13C HNMR and 29Si NMR spectra were recorded in chloroform-d using tetramethylsilane as internal standard on a Bruker 500 (500 MHz). The solid 29Si NMR spectrum of P2 was obtained with Bruker AVANCE III (400 MHz).

Elemental Analysis data were obtained using a CHN–O–Rapid elemental analyzer (Foss. Heraeus, Germany). Matrix-assisted ultraviolet laser desorption/ionization time of flight mass spectropscopy (MALDI-TOF/TOF) of diallyl-POSS monomer was performed using a Bruker Daltonics Autoflex TOF/TOF in linear and reflection modes. Gentisic acid (2,5-dihydroxybenzoic acid, DHB) was used as the matrix with tetrahydrofuran as the solvent. Sodium was used as the cationizing agent.

Molecular weight of polymers was measured on gel permeation chromatography (GPC) apparatus equipped with UV–vis detection and Waters 1515 HPLC pump. Tetrahydrofuran was used as a carrier solvent at a flow rate of 1.0 mL/min at 25 °C. A calibration curve was made to determine Mw and Mn/Mw values with polystyrene standards, Mw = 900.1 × 10⁶ g/mol, D < 1.1. Simultaneous TG-DTA Netzsch STA 449F3 was used to investigate the thermal stability.

Scheme 2. Synthesis of 3,3-di-3-propenyl-1,3-dimethyly-1,5,7,9,11,13,17,19-octaphenylhexacyclo [15.3.11.3](1,3,11,13,17,19-2), (15.3.11.3)decasiloxane.
of the polymers in nitrogen atmosphere from ambient temperature to 700 °C at a heating rate of 10 °C min⁻¹.

2.4.2. Morphological characterizations

Morphological observations were done by High Resolution Transmission Electron Microscopy (HRTEM). The polymers were embedded by epoxy resin, and ultrathin sections were made by using LeicaULTRACUT UC6 with approximate thickness about 70 nm. The ultrathin sections were then collected onto copper grids. The copper grids were imaged using a JEM-2100 transmission electron microscope at 200 kV.

Surface topography was characterized by atomic force microscopy (AFM) in tapping mode using silicon tips with Olympus OMCL-AC160TS and controller from Veeco Corporation. The sample was spin-coated on silicon wafer surface by THF solutions of P2 films (0.2 wt%) and cured in a vacuum oven at 334 K for 12 h.

2.4.3. Optical performance characterizations

Ultraviolet-visible (UV-vis) absorption of the obtained polymers solution was carried on a UV-1800 (PC) UV-vis spectrophotometer (Mapada, China). The solution fluorescence spectrums of the compound were measured with a FluoroMax-4 spectrofluorometer (HORIBA Scientific, Japan). The solid thin films of polymers were prepared by spinning coating 10 mg/ml polymer solution on the quartz glass plate with a spin rate of 2000 rpm. The solid thin film of polymers and the fluorescent composite films fluorescence spectrums were recorded on a FP-6600 (Jasco Inc.) spectrophotometer using a quartz cell with an optical path length of 1 mm. The photoluminescence QYs were determined on the spectrophotometer with an integrating sphere (ISF-513). TPF spectra of P1 and P2 in dilute solution and TPF imaging of composite films were performed using Leica TCS SP5 laser scanning confocal microscope with a Ti:sapphire laser (Mira Optima 900F, Coherent) as the excitation source. The laser is tuned at 780 nm with 0.5 mW power.

![Scheme 3. Synthesis of diallyl-POSS bridged linear polymer.](image-url)
after the objective and provides ca. 100-fs pulses at a repetition rate of 76 MHz. The details of the two-photon technique experimental setup are described elsewhere [19].

3. Results and discussion

3.1. Synthesis and characterization

An appropriate conjugation length and molecular weight are crucial factors to influence the property of solubility and emission for the light-emitting polymer. In this work, the molecular weight and the conjugated length of P1 were controlled by adding excess amount of monomers 5 step by step in the synthesis procedure, followed by washing repeatedly with acetone to remove small molecules in the purification procedure and using column chromatography to take away high molecular weight polymers to prevent insoluble substance generating in the next step reaction (see Experimental Section). P1 was first synthesized through the Sonogashira coupling reaction based on dibromo monomer 5 and double alkynyl monomer 3 with a molar ratio of 1:7:1. At beginning of the reaction, dibromo monomer and alkynyl monomer were added according to 1.5 eq. to 1 eq. After 12 h, another 0.2 eq. of dibromo monomer was added into the mixture to ensure P1 was bromo-terminated polymer (Scheme 3) according to the reported end-capped control method [20]. The linear polymer (P2) was then prepared from (P1) and diallyl-POSS (molar ratio 1:1) through classic Heck coupling reaction. The conjugated length of P2 was entirely depended on oligomeric alkynyl fluorene moiety from P1, and the molecular weight of P2 was also controlled by column chromatography (see Experimental section 2.2.8).

The molecular weight and distribution of polymers were investigated by GPC. Fig. 1 shows the retention time versus UV absorbance curves of P1 and P2. The molecular weight of P1 is \( M_w = 8.79 \times 10^3 \, \text{Da} \) and \( M_n = 4.61 \times 10^3 \, \text{Da} \), while P2 is \( M_w = 3.93 \times 10^4 \, \text{Da} \) and \( M_n = 1.45 \times 10^4 \, \text{Da} \). The GPC data indicated the linear polycondensation reaction between P1 and diallyl-POSS has happened.

The polycondensation reaction and the structures of P1, P2 and diallyl-POSS were confirmed by the \(^1\)H NMR (Fig. 2), solid\(^29\)Si NMR, MALDI-TOF-MS and FT-IR spectra (see Supplementary material). The proton peaks of P1 at aromatic ring area are amplified and shown at \( \delta = 8.09 \) and 7.67–7.36 ppm, respectively. While the broadening phenomenon of proton peak for P2 could be observed at aromatic ring area, which are corresponded to the larger molecular weight of P2. The characteristic peak of P1 at aromatic ring area of P1 and P2 could be observed at aromatic ring area, which are corresponded to the larger molecular weight of P2. On the one hand, the characteristic peaks at \( \delta = 5.76 \) and 4.88–4.76 ppm are corresponded to olefin proton of diallyl-POSS. For P2, the characteristic peak of olefin proton of diallyl-POSS moiety turns into a doublet and broad peak at 5.45 ppm with the integral area ratio of 1:1, which also confirms that P2 has been synthesized and the Heck coupling reaction was successful. In the \(^29\)Si NMR

![Fig. 1. GPC profiles of P1 and P2.](image1)

![Fig. 2. The \(^1\)H NMR spectra of P1, P2 and diallyl-POSS.](image2)
spectrum of $P_2$ (see Supplementary material), $P_2$ displayed three broad characteristic signals at $\delta = -18.12$, $-65.22$, and $-79.10$ ppm, respectively. The signal at $-18.12$ ppm is assignable to the silicon nucleus of Si(CH$_2$CH=CH)CH$_3$ bond, and the signal at $-65.22$ ppm and $-79.10$ ppm belong to the other two kinds of the silicon nucleus of Si–O–Si cage. Furthermore, the FT-IR spectrum of $P_2$ shows an intense characteristic Si–O–Si stretching vibration at 1118 cm$^{-1}$ for diallyl-POSS (see Supplementary material). The characteristic signals at 3055, 2923, 2852, 1681, 1663, and 1581 cm$^{-1}$ respectively are corresponded to the oligomeric alkynyl fluorene moiety.

3.2. Thermal stability

The thermal stability of the polymers was measured via the thermogravimetric analysis (TGA) to study the influence of the introduction of diallyl-POSS. From TGA curves of $P_1$ and $P_2$ under nitrogen (Fig. 3), it was observed that the thermal decomposition temperature ($T_d$, 5% weight loss temperature) were 321 °C ($P_1$) and 382 °C ($P_2$), respectively. In other words, the $T_d$ value of $P_2$ was 61 °C higher than that of $P_1$. It indicates that the incorporation of diallyl-POSS can effectively enhance the thermal stability of the luminescent material due to the presence of inorganic Si–O cage shielding effect, which limits the heat transfer and protects the organic part of polymer from the heat effect of attack [21].

3.3. The morphologies of $P_1$ and $P_2$ films

HRTEM was used to analyze the microstructure of $P_2$ and $P_1$. The diallyl-POSS connected to polyfluorene could be seen from the ultrathin sections of polymer embedded in epoxy resin. There are only a small quantity of 5–10 nm nanoparticles in $P_2$ sample [Fig. 4(a)], corresponding to diallyl-POSS aggregates. The same phenomenon can be seen in our previous work [22]. While a certain amount of smaller nanoparticles with the size of 2–3 nm are shown in the polymer matrix [Fig. 4(b) and (c)], which are uniformly nanodispersed. It reveals that aggregation of the inorganic POSS could be reduced, in that diallyl-POSS is fixed on the main chain of polyfluorene via chemical bond and the bead-type POSS-based polymer has the symmetric structure. It could also benefit for attenuate the strong dipole–dipole and π–π stacking interactions between chromophores, which would acquire better properties for emissive conjunction polymers. This result has been further confirmed with AFM images (Fig. S1), in which the aggregation of diallyl-POSS multi-molecules are absent on the micron scale.

3.4. Optical properties

3.4.1. One-photon fluorescent emission and enhancement fluorescent quantum yield (QY)

To study the impact of the incorporation of diallyl-POSS on the fluorescence emission of the fluorescent polymers, the one-photon fluorescence spectra of $P_1$ and $P_2$ both in solution and solid thin film state were acquired. The solid thin films of $P_1$ and $P_2$ were prepared by spin coating method on the quartz plate, and then, the PL spectra of $P_1$ and $P_2$ in thin solid film were measured (Fig. 5).
The maximum emission peaks of P1 and P2 at 428 nm are similar in THF solutions, located at blue emission region. While in solid state, the aggregation effect leads to red shift (in web version) of the main peaks to 538 nm (P1) and 475 nm (P2), respectively. Compared with P1, P2 shows a larger blue-shift, which is attributed to the reduction of the molecular-stacking-led aggregations by the incorporation of large and rigid Si–O–Si cage [12b].

Simultaneously, the QY of P2 in dilute solution was calculated as 77.6% via reference method [23], which is higher than P1 of 71.3% (Table S1). The QYs of P1 and P2 in solid state were also measured by a calibrated integrating sphere (ISF-513). The QY rises from P1 of 3.1% to P2 of 5.7%. The experimental results suggest that the oligomeric alkynyl fluorene moiety, when was nailed on the both ends of diallyl-POSS with highly symmetrical structure, can prevent the chromophoric groups close to each other, resulting the decreased emission quenching and the increased fluorescence quantum efficiency.

### 3.4.2. Two-photon fluorescence enhancement

To explore the two-photon fluorescence (TPF) enhancement effect of the incorporation of diallyl-POSS with symmetrical structure, the THF solutions of P1 and P2 with the same concentration (8.0 × 10⁻⁶ mol/L) of fluorescent groups (carbazole-fluorenyl and alkynyl-fluorenyl copolymer unit) were prepared, and the two-photon fluorescence spectra are shown in Fig. 6. Compared with P1, P2 afforded the greater TPF enhancement. At the same time, taking emission peak at 428 nm as reference, the relative intensity of emission peak at 454 nm of P2 was obviously weaker than that of P1. It reveals that, for P2, less excimers are formed in the solution and the aggregation effect attenuates. The remarkable TPF enhancement could also be attributed to the abatement of aggregation effect between fluorescent groups when diallyl-POSS is coupled into polymer molecular chain.

### 3.4.3. Photo-fading experiment

Photo-stability is another crucial property for luminescent material, so photo-fading experiment of P1 and P2 (Fig. 7) is performed to probe the influence of incorporation of diallyl-POSS into the main chain of the light-emitting polymer. The THF dilute...
solutions of the polymers in 50 ml volumetric flasks were placed 25 cm from a 1000 W iodine–tungsten lamp. A cold trap (10 L solution of 50 g/L NaNO₂ and 20 cm in length) was setup between the sample and the lamp. The absorption spectra were recorded every 6 h until 24 h.

From the inserted figure, the attenuation degree of the maximum absorption peak value of P1 was obviously greater than that of P2 over time. Under low concentration, photo-degradation reaction equation can be simplified as ln (A₀/Aₜ) = kt [24], in which “A₀” represents the initial absorption of λmax , “Aₜ” means the absorption of λmax during irradiation, and “k” is the photo-degradation reaction rate constant. Accordingly, “k” value could be acquired from the equation, and the fitting curves of “ln (A₀/Aₜ)–Time” are given in Fig. 7. The slope of straight line after fitting is the photo-degradation reaction rate constant, and the “k” values of P1 and P2 are k₁ = 4.8 × 10⁻⁴ mol/min and k₂ = 1.1 × 10⁻⁴ mol/min, respectively (Table S3). Obviously, an enhanced photo-stability effect is obtained via the addition of diallyl-POSS into organic light-emitting material. Although the specific photo-stability enhancement mechanism is still unclear, it could be owing to the inorganic POSS nanoparticles, which is unfavorable towards photo-oxidation and stable against oxidation [25].

3.4.4. Decoupling effect of the hybrids under the state of aggregation

Absorption spectra and fluorescence emission spectra of polymers in good/poor mixed solutions were tested to explore the effect of aggregation for optical polymers according to the method reported in the literature [26]. In this regard, the polymers can form aggregations and excimers in THF/water solvents by adding different proportions of water. The absorption spectra and fluorescence emission spectra of P1 and P2 in THF and in mixed THF/water solvents were recorded.

As shown in Fig. 8(a) and (b), both P1 and P2 molecular chains can be well-dispersed in the dilute THF solution due to the weak intermolecular interaction. Nevertheless, the absorbances at λmax of P1 and P2 are obviously enhanced and undergo red shift (in web version) with the increase of water content (3:7 v/v and 1:9 v/v THF–water), which indicates that the two polymers have formed J-type aggregations [27].

On the other hand, the conspicuous emission quenching of P1 by adding different proportions of water in THF were observed. The excimer peak at 482 nm in the P1 emission spectra appeared clearly in a 1:9 (v/v) THF–water mixed solvent [Fig. 8(c)]. The fluorescence emission intensity of P2 in 3:7 (v/v) and 1:9 (v/v) THF–water is much greater than that of P1, and the emission spectra of P2 still has no excimer peak in a 1:9 (v/v) THF–water mixed solvent [Fig. 8(d)]. These results indicate that the optical property of P2 is stable in THF/water solvents owing to the incorporation of diallyl-POSS, while that of P1 is not.

Simultaneously, the QY values of P2 are 23.8% and 12.3% in 3:7 (v/v) and 1:9 (v/v) THF–water mixed solvent respectively, which are much higher than those of P1 (10.6% and 4.9%, Table S1). It suggests that the strong dipole–dipole and π–π stacking interactions between organic optical chromophoric groups can lead to forming J-type aggregations, which would affect luminescent properties and application of light-emitting polymers. Therefore, the incorporation of “huge” and “rigid” diallyl-POSS into optical materials via chemical bonds to form bead-type condensation polymer can effectivity improve the optical performances under the state of aggregation.

3.5. Fluorescent composite film

The fluorescence composite films of P1 and P2 were prepared, and the purpose of which was to lay the foundation for the application of difunctional-POSS based polymer in developing new photoelectric material. In this paper, fluorescence composite films were fabricated using the 3-isocyanatomethyl-3,5,5-trimethyl-cloxyethyl isocyanate (IPDI) and poly-caprolactone diol (PCL Mw 1000) as matrix, and doped with different proportions of light-emitting polymer molecules (Fig. 9). The influence of doped mass fraction of P1 and P2 on PL spectra of the fluorescent composite films was investigated to elucidate the effect of incorporation of diallyl-POSS into luminescent material (Fig. 10). Meanwhile, the QYs of fluorescent composite film with different doped mass

Fig. 8. Partial absorption spectra of a) P1, b) P2 and photoluminescence spectra of c) P1, d) P2 in THF, THF–water (3:7, v/v), and THF–water (1:9, v/v).
fractions of \( P_1 \) and \( P_2 \) were measured, and photoluminescence spectra were also obtained (Table S4). There was no obvious change for PL spectra when the mass fractions of \( P_1 \) and \( P_2 \) were \( 1 \times 10^{-6} \) and \( 5 \times 10^{-5} \). The maximum emission peaks of \( P_1 \) and \( P_2 \) were both located at 427 nm, which are similar to \( P_1 \) and \( P_2 \) in dilute solution. This phenomenon shows that the aggregation of fluorescent groups does not appear when the fluorescent composite films doped with low mass fraction of \( P_1 \) and \( P_2 \).

Compared with fluorescent composite films of \( P_2 \), the emission spectra of \( P_1 \) fluorescent composite films showed larger red shift and more excimer peaks in longer wavelength with the increase of the mass fraction of \( P_1 \). It reveals that a more serious aggregation effect of fluorescent groups has occurred in the fluorescent composite films of \( P_1 \). Furthermore, the intensity of excimer emission peak at 535 nm increased dramatically when composite film doped with higher mass fraction of \( P_1 \) (\( 1 \times 10^{-3} \) and \( 5 \times 10^{-3} \)), while the composite film of \( P_2 \) merely showed a weak shoulder peak at 535 nm under the same conditions. This is a powerful evidence to demonstrate that the strong dipole–dipole and \( \pi-\pi \) stacking interactions between organic chromophoric groups are suppressed owing to the introduction of diallyl-POSS.

Meanwhile, the maximum QY of \( P_1 \) fluorescent composite film was 18.8% as doped with \( 5 \times 10^{-5} \) mass fractions of \( P_1 \), while that of \( P_2 \) was 20.5% as doped with \( 1 \times 10^{-4} \) mass fractions of \( P_2 \). Namely, the maximum QY of the fluorescent composite film of \( P_2 \) appears at higher doped mass fraction (\( 1 \times 10^{-4} \)) than that of \( P_1 \) fluorescent composite film (\( 5 \times 10^{-5} \)), which insinuates that the incorporation of “huge” and “rigid” diallyl-POSS could prevent excessive aggregation in solid state. The diallyl-POSS bridged polyfluorene hybrid material with symmetrical structure has higher QY.

No microphase separation was observed when QYs of fluorescent composite films of \( P_1 \) and \( P_2 \) reached the maximum (Fig. 9 and Fig. S2), and the fluorescent composite films of \( P_1 \) and \( P_2 \) showed excellent TPF property and could be applied in real-time 3D high-resolution TPF imaging (Fig. S3).

**Fig. 9.** a) Schematic illustration of preparation of fluorescent composite films (taking \( P_2 \) for example); b) The fluorescent composite film doped with \( 5 \times 10^{-5} \) mass fraction of \( P_1 \) and \( 1 \times 10^{-4} \) mass fraction of \( P_2 \) under sunlight and 365 nm UV-light.

**Fig. 10.** The PL spectra of fluorescent composite films with different mass fractions of a) \( P_1 \) and b) \( P_2 \).
4. Conclusion

In a summary, a bead and diallyl-POSS based polyfluorene (TaD2 type) with high symmetrical structure (P2) was synthesized via Heck coupling reaction. The molecular weight of P1 and P2 was well controlled to provide the polymers with good solubility and process ability. The HRTEM micrographs showed that diallyl-POSS was uniformly nano-dispersed in the polymer matrix. And the thermal decomposition temperature (T_d, 5% loss) increased from 321 °C for P1 to 382 °C for P2.

Simultaneously, the well controlled conjugated length gave P1 and P2 with high QYs, and cooperating “rigid,” “symmetrical” and “huge” diallyl-POSS could further enhance quantum efficiency in solution and solid state. The rate constants of photo-degradation reaction under a 1000 W iodine–tungsten lamp were \( k_{\text{P1}} = 4.8 \times 10^{-4} \text{ mol/min} \) and \( k_{\text{P2}} = 1.1 \times 10^{-4} \text{ mol/min} \), respectively, which confirmed the significantly enhanced photo-stability by adding unfavorable photo-oxidation diallyl-POSS to emissive conjugated polymer. Moreover, a better TPF property was found for P2, which could also be attributed to the incorporation of diallyl-POSS, and the strong dipole–dipole and π–π stacking interactions between organic optical chromophoric groups could be inhibited. Finally, fluorescent composite films were prepared, and the maximum QY of P2 reached to 20.5%. These results suggest that bi-functional POSS based polymer may be considered a class of compounds/materials with anticipated novel properties of value in developing new components for electronic and photonic applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.07.017.

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