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1 Introduction

The self-assembly of hyperbranched polymers (HBPs) has received a great deal of attention because of its fundamental importance in fabricating novel ordered supramolecular structures¹ and fascinating applications.^{2,3} HBPs containing various functional terminal groups, such as carboxyl, hydroxyl, vinyl, and amino groups, provide unique properties for the encapsulation of small molecules or inorganic nanoparticles to form self-assembled structures.^{4,5} Self-assembled HBPs materials have been extensively used in the field of biomaterials.⁶⁻¹⁰ Amphiphilic HBPs which have been reported so far^{9,11,12} represent only a minority of the HBPs that can be readily self-assembled into micelles, fibers, tubes, vesicles, films and large compound vesicles (LCVs). This is done under

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spectra, DLS curve, TGA curve and optical microscope images. See DOI: 10.1039/ c3ra42057d

2D Self-assembly of an amido-ended hyperbranched polyester induced by platinum ion coordination effect[†]

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Compared with amphiphilic hyperbranched polymers (HBPs), the self-assembly of hydrophilic HBPs remains a challenging area. In this article, we report the self-assembly of an amido-ended, hydrophilic hyperbranched polyester (HTDA-2), by taking advantage of the induction effect of the platinum ion. Self-assembled HTDA-2-Pt polymers are composed of ordered 2D tree-like structures with a diameter of about 500 μ m and a trunk-width of approx. 1–2 μ m, as shown by transmission/reflection polarizing optical microscopy (TRPOM), scanning electron microscopy (SEM) and dynamic light scattering (DLS). Factors such as temperature, time, solvent, concentration and humidity which influence the morphology of the self-assemblies were investigated using XPS, XRD, SEM, and FT-IR techniques. It is proposed that the coordination between the platinum and oxygen atoms in the amido groups together with hydrogen bonding may induce individual aggregation of core chains and peripheral chains, resulting in micro-phase separation and formation of micelles. These micelles then aggregate and self-assemble into perfect tree-like structures on the surface of a glass substrate in a limited region. The dimension (D_f) of about 1.59 for the fractal tree-like morphology suggests perfect fractal behavior of the self-assemblies as revealed by XRD analysis.

a restrictive ratio of the hydrophilic and hydrophobic segments through interfacial/surface self-assembly or using selective solvent self-assembly,^{7,12} resulting in the formation of honeycomb morphologies^{13,14} and mesoscopic pattern morphologies.¹⁵ Although the preparation of amphiphilic HBPs involves complex and tedious synthetic processes, such as grafting modification and copolymerization by the RAFT process,^{7,9} self-assembly of amphiphilic HBPs has been highly successful, and their applications as drug delivery and reaction vessels for charge storage⁹ have been well developed.

The ability of most amphiphilic HBPs to self-assemble is attributable to the individual aggregation of two blocks or the micro-phase separation resulting from the different solubilities of amphiphilic segments in selected solvents.⁷ The interactions between the aggregates play an important role in controlling the size and stability of self-assemblies. On the contrary, non-amphiphilic HBPs, including hydrophilic and hydrophobic HBPs, as a majority of HBPs, are still difficult to assemble into ordered supramolecular structures because the relative property variation between "core" chains and end groups chains is not strong enough to induce micro-phase separation. Therefore, the self-assembly of hydrophilic HBPs is still a challenging work up to now.

A poly(amidoamine) (PAMAM) dendrimer containing amino-ended groups has shown potential in being able to electrostatically self-assemble with a virus.¹⁶ Moreover,

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PAMAM dendrimer aggregates with fractal features have a crucial impact on the intrinsic emission properties.¹⁷ Therefore, it is significant to develop new assembly processes for amino-ended HBPs to obtain advanced biohybrid materials.¹⁶ Our recent paper¹⁸ reported the self-assembly of a non-amphiphilic carboxyl-ended hyperbranched polyester by platinum induction, and ordered 1D microrod self-assemblies with a length of 10–20 μ m and a width of 1 μ m were obtained. It was revealed that the coordination induction of platinum ions played a key role in driving micro-phase separation between core chains and peripheral segments of the carboxyl-ended hyperbranched polyester/platinum complex. The coordination induction of the platinum ion can be used as a new tool to realize the self-assembly of non-amiphphilic HBPs.

In this article, we reveal that another non-amphiphilic or hydrophilic HBP containing amido-ended groups (HTDA-2) can be self-assembled into ordered micrometer 2D tree-like supramolecular structures by use of the platinum ions' coordination induction. In comparison to a method for selfassembling a polymer complex containing a metal with a certain chemical structure,^{19,20} the approach in this work is rather simple and easily available. The 2D self-assembly of HTDA-2-Pt shows fractal properties and crystal behavior, which is generally difficult to obtain from amiphiphilic HBPs due to their soft-loose amorphous morphology. This discovery may help new applications of hydrophilic selfassemblies as multi-functional semiconductors materials^{19,21-23} due to the existence of metal ions, as well as being optical, magnetic and bioactive materials²⁴ owing to their fractal and crystal properties.¹⁶

2 Experimental

2.1 Materials

Analytical materials, including trimellitic anhydride (TMA), xylene, diethylene glycol (DEG), tetrabutyl titanate (TBT), urea, triethylamine, isopropanol, chloroplatinic acid, pyridine, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), ether, ethyl acetate and NaHCO₃ were purchased from Sinopharm Chemical Reagent Corporation and used without further purification unless noted otherwise.

2.2 Preparation of HTDA-2

The synthesis of an amido-ended hyperbranched polyester (HTDA-2) is shown in Fig. 1. First, an AB2 monomer was prepared from the reaction between trimellitic anhydride (TMA, 0.09 mol) and diethylene glycol (DEG, 0.09 mol) using 100 mL xylene as solvent at 393 K for 3 h in a four-necked reaction flask equipped with stirrer, cooler, nitrogen inlet and water-trap (Dean-Stark), followed by addition of 0.01 mol "core" TMA and TBT (0.2 g). The reaction temperature was raised to 413 K and the reaction continued for 6 h. The solvent was then removed under a pressure of 3-5 mmHg at 413 K for 30 min. A yellowish transparent solid was obtained, which was proved to be a carboxyl-ended hyperbranched polyester (HTD-2) containing 12 molar carboxyl groups with number average molecular weight (M_n) of about 4260 g mol⁻¹ and polymerization distribution index (PDI) of about 2.2325,26 from gel permeation chromatography (GPC), and its degree of branching (DB) was about 0.71.

HTD-2 (3.5 g), urea (2.5 g), triethylamine (20 g) and deionized water (20 mL) were added to a flask for reaction at 368 K for about 6 h using a mechanical stirrer. The solution was put into a separating funnel for delaminating, and the solvent in the up-layer yellow solution was removed under a pressure of 3–5 mmHg at 363 K for 30 min to give a powdered



Fig. 1 Synthesis of HTDA-2 and HTDA-2-Pt.

solid, which was proved to be the amido-ended hyperbranched polyester (HTDA-2). FT-IR and ¹H-NMR spectra of HTDA-2 and HTD-2 are shown in Fig. S1 and Fig. S2, ESI[†] respectively. For comparison, absorption peaks of $-NH_2$ in HTDA-2 are observed at 3460 cm⁻¹ and 3260 cm⁻¹, and a sharp absorption peak of -C-N appears at 1370 cm⁻¹. These characteristic peaks confirm the formation of amido-ended groups, supporting the appearance of a blunt peak about $-CONH_2$ at δ 6.4–6.7 ppm in Fig. S2, ESI.[†]

2.3 Preparation of HTDA-2-Pt

The synthesis of an amido-ended hyperbranched polyester/ platinum complex (HTDA-2-Pt) is shown in Fig. 1. Chloroplatinic acid (0.4 g), isopropanol (12 g) and THF (6 g) were added to a four-neck flask fitted with a mechanical stirrer, a condenser, a thermometer and a nitrogen inlet. Stirring continued for 1 h at room temperature. Then HTDA-2 (2 g) and NaHCO₃ (0.7 g) were added into the flask. The reaction took place under ultra-sonication (700 W) for 10 min. The mixture was heated to approximately 315 K and stirred for 2 h under nitrogen protection. The solvent was then removed under a 3-5 mmHg vacuum at 338 K. The remaining solid was washed twice with 5 mL of deionized water in a Buchner funnel, resulting in a yellowish fluffy solid amido-ended hyperbranched polyester/platinum complex (named HTDA-2-Pt). The content of elemental platinum in HTDA-2-Pt is about 7.78 wt%, taken from its TGA curve in Fig. S3, ESI† and close to its theoretical content of 7.00 wt%.

2.4 Preparation of hybrid self-assemblies

In a typical experiment, HTDA-2-Pt (0.1 g) was dispersed in the corresponding solvent (7.9 mL) and followed by ultra-sonication for 20 min. The solution was dropped onto a clean surface of glass substrate and controlled at given conditions to allow for self-assembly. The morphology of the self-assemblies was measured real-time by TRPOM under a designated temperature and relative humidity.

2.5 Characterization

FT-IR measurements were performed on a Bruker Vector 33 spectrometer using sealed cell (KBr 0.5 mm). ¹H NMR measurements was conducted on an AVANCE III-400 (Bruker) nuclear magnetic resonance spectrometer using DMSO-d₆ as the solvent. A low-voltage scanning electron microscope (SEM, XL-30FEG, Philip) and a transmission/ reflection polarizing optical microscope (TRPOM, XPV-203E,

China) equipped with a thermal platform were used to examine the morphology of the self-assemblies. The X-ray diffraction (XRD) patterns were obtained using a Bruker-D8 diffractometer with monochromatized Cu-K α radiation (λ = 1.54 Å) at 40 kV and 40 mA. The surface compositions of the samples were determined using a Vacuum Generator Mutilab 2000 X-ray photoelectron spectrometer (XPS) with the C1s (284.6 eV) peak of the contamination carbon as the internal standard. Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (NETZSCH TG209) at a heating rate of 10 K min⁻¹ and a nitrogen flow of 20 mL min⁻¹. Dynamic light scattering (DLS) measurements of samples with a concentration of 1.0 mg mL⁻¹ were performed on a ZetaSizer Nano ZS90 (Malvern Instrument, Worcs, UK) equipped with 4 mW He-Ne Laser at about 25.0 °C and at a scattering angle of 90° . The apparent *z*-average hydrodynamic diameter $(D_{\rm h})$ and polydispersity index (PDI) were calculated by the dispersion technology software provided by Malvern.

3 Results and discussion

3.1 Self-assembly of HTDA-2-Pt under different conditions

3.1.1 Platinum ion effect. Fig. 2 compares the morphology of HTD-2, HTDA-2 and HTDA-2-Pt self-assemblies. HTD-2 can be self-assembled into uniform star and crew-cut micelles with diameter about 1.0-1.5 μ m as shown in Fig. 2a. This formation of the micelles can be attributed to the secondary aggregation of unimolecular micelles stabilized by intermolecular hydrogen bonding²⁷. A rudimentary tree-like structure is shown by self-assembling HTDA-2 in Fig. 2b, indicating that the HTDA-2 should be easier to self-assemble than HTD-2 due to the much stronger hydrogen bonds in HTDA-2. If HTDA-2-Pt was used to self-assemble under the same conditions as HTDA-2, a perfectly ordered tree-like supramolecular structure was obtained as shown in Fig. 2c. This result demonstrates that the platinum ion plays an important role in promoting the self-assembly of HTDA-2.

3.1.2 Solvent effect. It is well known that a solvent with similar polarity and solubility parameter to partial chains of HTDA-2-Pt helps its dissolution or dispersion according to the theory of similarity and compatibility. Herein, the formation of micelles resulting from the dissolution of partial chains and the aggregation of other chains in HTDA-2-Pt is key to the self-assembly of HTDA-2-Pt. The core segments of HTDA-2-Pt have



Fig. 2 Optical micrographs of self-assemblies at 298 K and 40% relative humidity: (a) HTD-2 (0.10 g)/pyridine (7.90 mL), (b) HTDA-2(0.10 g)/pyridine (7.90 mL), and (c) HTDA-2-Pt (0.10 g)/pyridine (7.90 mL).

relative lower solubility than that of the end groups in pyridine or DMF, one reason is that the core segments are made up of a large number of ester groups with a low solubility parameter, and another reason is that the end groups have chemical structures similar to pyridine or DMF. Consequently, the solubility difference between the end groups and core segments of HTDA-2-Pt may result in micro-separation and the formation of micelles in pyridine or DMF solvent. The selfassemblies obtained have uniformly ordered supramolecular structures when pyridine (Fig. 2c) or DMF (Fig. S4d, ESI[†]) is used as the solvent, but the self-assemblies are irregular and the morphology is vague (Fig. S4a and Fig. S4c, ESI[†]) when using acetone (δ 20.50 (J cm⁻³)^{0.5}, b.p. 329.6 K) or ether (δ 15.40 (J cm⁻³)P^{0.5}, b.p. 307.7 K) as solvents. This interesting result may be attributable to the solubility parameter (δ 18.60 $(J.cmP^{-3})^{0.5}$, b.p. 350.3 K) of ethyl acetate being close to that (δ 19.44 (J cm $^{-3}$)^{0.5}) of the core segments of HTDA-2-Pt, resulting in separation and aggregation of the core segments and end groups in HTDA-2-Pt and the formation of clear selfassemblies (Fig. S4b, ESI[†]). However, the lower boiling points of acetone and ether may result in their easy evaporation, and so HTDA-2-Pt micelles have not enough time for self-assembly on the surface, thus producing vague morphologies.¹⁸

3.1.3 Humidity effect. Another factor, relative humidity, which affects the self-assembled morphology of HTDA-2-Pt also is discussed. As we known, the higher the relative humidity is, the lower the volatilization rate of the solvent is. Micelle particles spreading on surface of glass substrate do not have enough time to self-assemble in low relative humidity because they can not move freely and aggregate without solvent, so the resulting self-assemblies are composed of small branch-like (Fig. S5a, ESI†) and not tree-like. On the contrary, the micelle particles may move easily and but can not root in some regions in high relative humidity, and a vague tree-like morphology of the self-assemblies is formed (Fig. S5c, ESI†). Therefore, in medium relative humidity between 40% (Fig. S5b, ESI†) and 70% (Fig. 2c), it is suitable to obtain uniformly ordered structures.

3.1.4 Temperature effect. The effect of temperature on the stable morphologies of self-assembled HTDA-2-Pt is shown in Fig. S6, ESI.[†] Tree-like self-assemblies are observed on the surface of the glass substrate at medium and low temperatures (Fig. S6a–b, ESI[†]) under a same self-assembly period of one day, however, at high temperatures, the self-assemblies' morphologies are tree-like skeletons containing vague patterns (Fig. S6c, ESI[†]). The self-assembly temperature influences not only the volatilization rate of the pyridine and but also the moving velocity of the micelles. By increasing the self-assembly temperature, many micelles do not have enough time to re-array and aggregate, preferring a stable morphology because of the increase in both the volatility rate of the pyridine and the moving velocity of the micelles, resulting in a vague morphology in Fig. S6c, ESI.[†]

3.1.5 Effect of the loading amount of Pt ions on HTDA-2. The morphologies shown in Fig. S7, ESI[†] result from self-assembly of a HTDA-2-Pt (0.10 g)/pyridine (7.90 mL) solution containing various platinum ion content at 298 K and 40% relative humidity. The HTDA-2-Pt could be self-assembled into

a tree-like structure at a relatively low platinum ion content (3.81 wt%) in Fig. S7a, ESI,[†] compared with only micelle aggregates being obtained at a high platinum content (15.1 wt%) in Fig. S7b, ESI,† indicating that an appropriate loading amount of platinum ions on HTDA-2 is necessary for the formation of ordered self-assemblies. When the loading amount of platinum ions on HTDA-2 is 7.78wt% (see Section 2.3) in fact, the molar ratio of the amido groups to platinum is just about 10:1 in HTDA-2-Pt in Fig. 2c, close to the 6-coordination number of Pt4+, resulting in coordination between the platinum atom and most of the amido groups. When the platinum content in the complex was increased, excess platinum dispersed in the matrix of the complex (in addition to the formation of the complex with a 6-coordination number). This made the formation of regular micelles very difficult, so only disordered micelle aggregates could be obtained (Fig. S7b, ESI[†]). In contrast, a HTDA-2-Pt solution with lower platinum ion content may contain non-coordinated HTDA-2, resulting in the tree-like self-assemblies with some vague aggregates (Fig. S7a, ESI[†]).

3.1.6 HTDA-2-Pt concentration effect. The morphologies of the hybrid self-assemblies using various HTDA-2-Pt concentrations are all shown in Fig. S8, ESI.[†] With the increase of the HTDA-2-Pt concentration in the HTDA-2-Pt/pyridine solution, the density of self-assemblies on the surface increases notably in Fig. S8, ESI.[†] Many micelles can not self-assemble into an ordered tree-like structure at low HTDA-2-Pt concentration, which is attributed to an absence of enough opportunities for the micelles' aggregation on the surface (Fig. S8a, ESI[†]). Using an HTDA-2-Pt/pyridine solution with a high concentration of HTDA-2-Pt for self-assembly, worm-like self-assemblies (Fig. S8d, ESI[†]) were obtained on the surface because there is not enough space for rearrangment and aggregation of a large number of micelles. Therefore, HTDA-2-Pt can self-assemble into uniformly ordered structures with fractal properties at a medium concentration in solution (Fig. S8b-c, ESI[†]).

3.2 Mechanism of self-assembly

The influence of the different factors described above on the resulting self-assembled morphologies of HTDA-2-Pt suggest that platinum ions play an important role in inducing selfassembly. The platinum atom in chloroplatinic acid can usually coordinate with the oxygen and nitrogen atoms from the ether (-C-O-C-), ester (-COO-) and amino (-NH₂) groups in HTDA-2. The FT-IR spectra of HTDA-2, HTDA-2-Pt and selfassembled HTDA-2-Pt are shown in Fig. S1, ESI.[†] Absorption peaks of ester (-COO-) groups is observed at 1730 cm⁻¹, and the peaks at 1622 cm^{-1} and 1575 cm^{-1} which may be attributed to the stretching vibration of amide groups (-CON-) bonds in HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-Pt,²⁸ respectively. In comparison with the difference before and after coordination of platinum, the peak area at 1575 $\rm cm^{-1}$ becomes bigger after adding the platinum to HTDA-2, and all of the absorption peaks about $-NH_2$ (3460 cm⁻¹, 3260 cm⁻¹) and -C-N (1370 cm⁻¹) remain invariably in HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-Pt, confirming the appearance of an interaction between the platinum and oxygen in the amide groups.



Fig. 3 XPS spectra of C1s, O1s, N1s and Pt4f electrons in HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-Pt.

The XPS spectra of HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-Pt are shown in Fig. S9, ESI.[†] Peaks of binding energy (BE) at about 285 eV and 532 eV are attributed to C1s and O1s electrons, respectively, and the peaks at around 75.9 eV and 73.1 eV are attributed to their $Pt4f_{5/2}$ and $Pt4f_{7/2}$ electrons. From the XPS spectra (Fig. 3) of the narrow scan in ranges of 526-540 eV, 278-295 eV, 70-80 eV and 388-407 eV, the BEs at 531.3 eV, 531.6 eV and 533.2 eV in the XPS spectrum of HTDA-2 are attributed to the O1s electrons in -C-O-C-, -CO- and -CONH₂, respectively. After HTDA-2 reacts with chloroplatinic acid, some distinct changes are shown in Fig. 3a, including an increase (from 533.2 eV to 533.5 eV) in BE about O1s electron in -CONH₂, an increase from 288.1 eV to 288.5 eV in BE about C1s electron, and unchanged BE data about N1s (399.8 eV) and about O1s electrons in -C-O-C- and -CO- in HTDA-2 and HTDA-2-Pt (Fig. 3b). This indicates that coordination occurs between platinum and oxygen atom in amide groups (-CON-) of HTDA-2.29 Comparing the XPS spectra (Fig. 3b) of selfassembled HTDA-2-Pt and HTDA-2-Pt, the decrease from 73.1 eV to 72.6 eV in BE about Pt4f7/2 electrons, increase from 398.6 eV to 399.3 eV in BE about N1s electrons of pyridine and invariability of the BE (399.8 eV) about N1s electrons in amido groups,³⁰ suggest that platinum ions in self-assembled HTDA-2-Pt have an interaction with the nitrogen element in pyridine and not in amido groups.

Hyperbranched polymers or star polymers without metal ions usually can be self-assembled into honeycomb supramolecular structures, and their mechanism was supposed to be a solvent evaporation, water condensation, and core-shellmicelles aggregation uniformly process.^{13–15,31} The self-assembly mechanism of 1D micro-rod-like self-assemblies was discussed.¹⁸ Hitherto, the perfectly ordered 2D tree-like supramolecular structures obtained from the amido-ended hyperbranched polyester containing platinum ions has rarely been reported, but the solvent-evaporation water-concentration process involved should be similar to those of our previous papers.^{18,32} The effect of self-assembly time on the resulting morphology of HTDA-2-Pt (Fig. 4) suggests that the ordered tree-like structures should grow gradually and form stable tree-like self-assemblies with a diameter of about 500 μ m (Fig. 4f) and a trunk width of about 1–2 μ m (Fig. 5a) with an increase in self-assembly time. Moreover, an important discovery is that the tree-like morphology is extremely similar to the "hyperbranched structure" of conjugated polymers' selfassembly³³ and dendrimers growth patterns,³⁴ so self-assembly of HTDA-2-Pt may be explained by diffusion-limited aggregation (DLA) theory.35

According to the chemical properties of HTDA-2-Pt and the self-assembly process, we propose a possible self-assembly mechanism by the following schematic representation (Fig. 6): (1) The solubility parameter of the core chains of the HTDA-2-Pt is calculated to be 19.44 $(J \text{ cm}^{-3})^{0.5}$ without considering the coordinate bonds and the amido-ended groups (-CONH₂). The solubility parameter of pyridine is about 21.90 (J cm^{-3})^{0.5} and close to that of the coordinate bonds and the amido-ended (-CONH₂) groups with high polarity. So the HTDA-2-Pt may be regarded as an amphiphilic polymer in pyridine. When it is dispersed in pyridine, the peripheral chains would swell and dissolve gradually and but the core chains may shrink and deform. Then the two blocks aggregate to form micelles with an apparent z-average hydrodynamic diameter (D_h) of about 1718 nm and a PDI of about 0.341 in Fig. S10, ESI.[†] (2) The HTDA-2-Pt solution is dropped and spread on the substrate homogeneously (Fig. 6a) to form spherical bubbles because of surface tension. As the solvent evaporates, the surrounding temperature of the bubbles decreases and the flowing moist water vapor forms water droplets (Fig. 6a) on the surface of the bubbles.³¹ Because the evaporation rate of pyridine is quicker than that of water concentration, the bubbles shrink all the time (Fig. 6b). (3) The evaporation of pyridine also forces the bubbles to move together and aggregate through hydrogen bonding and coordination of HTDA-2-Pt, resulting in the formation of a primitive self-assembly in Fig. 6b and Fig. 4b. With the further evaporation of solvent, some single bubbles move at random and aggregate while they meet the primitive self-assembly in a limited region. The moving process of the single bubbles is similar to that of particles in the diffusionlimited aggregation (DLA) model;³⁵ therefore, the aggregation process of the single bubbles can be explained by DLA theory. DLA theory³⁵ is an idealization of the process by which matter irreversibly combines to form dust, soot, dendrites, and other



Fig. 4 Optical micrographs of a HTDA-2-Pt/pyridine solution after self-assembly for different times at 303 K and 50% relative humidity: (a) 5 min, (b) 13 min, (c) 90 min, (d) 160 min, (e) 300 min, (f) local magnification image of Fig. 4e.

random objects in the case where the rate-limiting step is diffusion of matter to the aggregate. The model was mainly used to research aggregation of inorganic nanoparticles,³⁶⁻³⁸ assembly and fractal of block polymers,39,40 fractal behavior of dendrimers.¹⁷ A seed particle, as a single bubble in the selfassembly system, is situated at the origin of a local region, and then a second particle (or bubble) is near the original region. The second particle (or bubble) moves randomly with evaporation of the solvent until it meets a site adjacent to the seed. (4) Then the moving particle becomes a part of the primitive self-assembly. Another particle is now introduced at a random distance point, and it moves randomly until it joins the self-assembly in Fig. 6c, and gradually forms "hyperbranched structure" self-assembly, which can be demonstrated by an appearance of some nanometer claw-like aggregates of micelles on sides of the trunks in Fig. 5a. If a particle touches the boundaries of the surface during its random move, it is removed and another introduced. The exposed ends of the self-assembly tend to grow more rapidly than other perimeter sites because perimeter sites near the center are "shadowed". Finally, a tree-like self-assembly with excellent supramolecular structure forms in Fig. 6d.

Fig. 5 SEM micrographs of self-assembled HTDA-2-Pt in Fig. 4f.

3.3 Crystal and fractal properties of self-assemblies

The self-assemblies from amphiphilic HBPs reported previously are amorphous,^{5,9,41,42} except for the addition of crystalline polyethylene glycol (PEG)⁴³ and polyhedral oligomeric silsesquioxane (POSS)⁴⁴ segments. Recently, we obtained a crystal structure by self-assembling a carboxylended hyperbranched polyester/platinum complex¹⁸ and a HTD-2-Cu complex.³² The self-assembled micrometer tree-like structure may have crystal properties from the above ordered self-assemblies' morphology, especially the smooth micro-



Fig. 6 Schematic mechanism description for the hybrid self-assembly of HTDA-2-Pt.



Fig. 7 XRD spectra of HTD-2, HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-

structure in Fig. 5b. Therfore we investigated the XRD spectra (Fig. 7) of HTDA-2, HTDA-2-Pt and self-assembled HTDA-2-Pt.

In comparison with the XRD spectrum of amorphous HTD-2 which has a wide and blunt peak at 2θ degrees between 18° and 30°, some strong crystalline peaks (marked with a rectangle) at 2θ degrees between 9° and 30° are observed for HTDA-2 (Fig. 7), which may be attributed to the crystal structures of amido groups⁴⁵ and phenyl⁴⁶ and ethylene oxide⁴⁷ chains. The resultant HTDA-2-Pt complex from HTDA-2 and chloroplatinic acid shows some additional crystalline peaks larger than 30°. As shown in the XPS spectrum (Fig. S9, ESI[†]), some chorine atoms remain in the HTDA-2-Pt complex because the Cl-Pt bonds can not be completely converted into a platinum coordination bond; this results in the additional crystalline peaks (marked with black circle). The peaks at 2θ degrees between 9° and 30° for selfassembled HTDA-2-Pt are stronger than those in HTDA-2-Pt, indicating a higher degree of crystal order.



Fig. 8 Relationship between logN(r) and log(r) in morphology of ordered treelike self-assemblies.

As seen from Fig. 4, the tree-like self-assemblies with selfsimilarity should have fractal properties. The dimension of the fractal micrographs is between 1D and 2D in many clusters and aggregates from DLA, commonly between 1.46 and 1.71, and a higher fractal dimension has a higher order structure.⁴⁸ According to the DLA model and the following equation:⁴⁹

$$D_{\rm f} = \lim_{r \to 0} \frac{\log N(r)}{\log(r)}$$

where *r* is the length unit, N(r) is the size of the geometric object measured with the unit *r*. A relationship between logN(r) and log(r) in the morphology of self-assembled HTDA-2-Pt (Fig. 4e) is shown in Fig. 8, and its $D_{\rm f}$ is about 1.59 that demonstrates perfect and uniform supramolecular structure of the self-assemblies.

4 Conclusions

A new method was used to prepare micrometer scale 2D ordered tree-like supramolecular structures by hybrid selfassembly of an amido-ended hyperbranched polyester/platinum complex on the surface of a glass substrate. The morphology of self-assemblies is influenced significantly by temperature, time, solvent, concentration and relative humidity. A hybrid self-assembly mechanism was also analyzed by XPS, FT-IR, TRPOM, DLS and SEM, indicating that the formation of ordered tree-like self-assemblies with hyperbranched structure could be attributed to the synergy of the platinum coordination induction and micro-phase separation between core segments and end group of HBPs resulting from the solubility parameters of the solution, supporting DLA theory. The new hybrid self-assembly method and mechanism, as well as crystal behavior and fractal property of selfassemblies may play important role in developing the selfassembly and applications of hyperbranched polymers in the field of biomaterials.

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References

- 1 T. Aida, E. Meijer and S. Stupp, Science, 2012, 335, 813-817.
- 2 D. Konkolewicz, M. J. Monteiro and S. b. Perrier, Macromolecules, 2011, 44, 7067-7087.
- 3 D. Yan, C. Gao and H. Frey, *Hyperbranched Polymers:* Synthesis, Properties, and Applications, Wiley, 2011.
- 4 B. I. Voit and A. Lederer, Chem. Rev., 2009, 109, 5924-5973.
- 5 Y. Zhou and D. Yan, Chem. Commun., 2009, 10, 1172-1188.
- 6 C. Chen, G. Liu, X. Liu, S. Pang, C. Zhu, L. Lv and J. Ji, *Polym. Chem.*, 2011, 2, 1389–1397.

- 7 S. Chen, S. X. Cheng and R. X. Zhuo, *Macromol. Biosci.*, 2011, **11**, 576–589.
- 8 R. Wang, X. Jiang, B. Yu and J. Yin, *Soft Matter*, 2011, 7, 8619–8627.
- 9 S. Peleshanko and V. V. Tsukruk, J. Polym. Sci., Part B: Polym. Phys., 2012, 50, 83–100.
- 10 W. Tao, Y. Liu, B. Jiang, S. Yu, W. Huang, Y. Zhou and D. Yan, J. Am. Chem. Soc., 2012, 134, 762–764.
- V. Percec, D. A. Wilson, P. Leowanawat, C. J. Wilson, A. D. Hughes, M. S. Kaucher, D. A. Hammer, D. H. Levine, A. J. Kim and F. S. Bates, *Science*, 2010, **328**, 1009–1014.
- 12 Y. Zhou, W. Huang, J. Liu, X. Zhu and D. Yan, *Adv. Mater.*, 2010, 22, 4567–4590.
- 13 G. Widawski, M. Rawiso and B. François, *Nature*, 1994, 369, 387–389.
- 14 C. Liu, C. Gao and D. Yan, Angew. Chem., Int. Ed., 2007, 46, 4128-4131.
- 15 N. Maruyama, T. Koito, J. Nishida, T. Sawadaishi, X. Cieren, K. Ijiro, O. Karthaus and M. Shimomura, *Thin Solid Films*, 1998, 327, 854–856.
- 16 M. A. Kostiainen, P. Hiekkataipale, J. A. de la Torre, R. J. M. Nolte and J. J. L. M. Cornelissen, *J. Mater. Chem.*, 2011, 21, 2112–2117.
- 17 M. J. Jasmine and E. Prasad, *J. Phys. Chem. B*, 2010, **114**, 7735–7742.
- 18 D. Zhang, J. Wang, S. Chen, X. Cheng, T. Li, J. Zhang and A. Zhang, *Langmuir*, 2012, 28, 16772–16781.
- 19 I. Manners, Science, 2001, 294, 1664-1666.
- 20 R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, 327, 313–315.
- 21 S. Park, J. H. Lim, S. W. Chung and C. A. Mirkin, *Science*, 2004, **303**, 348–351.
- 22 W. J. Parak, Science, 2011, 334, 1359-1360.
- 23 R. Mezzenga, J. Ruokolainen, G. H. Fredrickson, E. J. Kramer, D. Moses, A. J. Heeger and O. Ikkala, *Science*, 2003, 299, 1872–1874.
- 24 S. Mann, Nat. Mater., 2009, 8, 781-792.
- 25 D. Zhang and D. Jia, Eur. Polym. J., 2006, 42, 711-714.
- 26 D. Zhang, D. Jia and S. Chen, *Macromol. Chem. Phys.*, 2009, 210, 1159–1166.
- 27 W. Dong, Y. Zhou, D. Yan, H. Li and Y. Liu, *Phys. Chem. Chem. Phys.*, 2007, 9, 1255–1262.
- 28 T. Freeman, S. Evans and A. Ulman, *Thin Solid Films*, 1994, 244, 784–788.

- 29 T. Freeman, S. Evans and A. Ulman, *Langmuir*, 1995, 11, 4411–4417.
- 30 A. E. Hooper, D. Werho, T. Hopson and O. Palmer, Surf. Interface Anal., 2001, 31, 809–814.
- 31 M. Srinivasarao, D. Collings, A. Philips and S. Patel, *Science*, 2001, 292, 79–83.
- 32 D. Zhang, J. Li, S. Chen, T. Li, J. Zhou, X. Cheng and A. Zhang, *Macromol. Chem. Phys.*, 2013, **214**, 370–377.
- 33 H. Gan, Y. Li, H. Liu, S. Wang, C. Li, M. Yuan, X. Liu, C. Wang, L. Jiang and D. Zhu, *Biomacromolecules*, 2007, 8, 1723–1729.
- 34 I. Das, N. Goel, N. R. Agrawal and S. K. Gupta, J. Phys. Chem. B, 2010, 114, 12888–12896.
- 35 T. A. Witten Jr. and L. M. Sander, *Phys. Rev. Lett.*, 1981, 47, 1400.
- 36 Z. Liu and X. Kong, Phys. Chem. Chem. Phys., 2010, 12, 9475-9480.
- 37 K. G. M. Laurier, M. Poets, F. Vermoortele, G. D. Cremer, J. A. Martens, H. Uji-i, D. E. De Vos, J. Hofkens and M. B. J. Roeffaers, *Chem. Commun.*, 2012, 48, 1559–1561.
- 38 V. Polshettiwar, B. Baruwati and R. S. Varma, ACS Nano, 2009, 3, 728–736.
- 39 L. Gao, L. Shi, Y. An, W. Zhang, X. Shen, S. Guo and B. He, *Langmuir*, 2004, 20, 4787–4790.
- 40 M. Schor and P. G. Bolhuis, *Phys. Chem. Chem. Phys.*, 2011, 13, 10457–10467.
- 41 K. Khanna, S. Varshney and A. Kakkar, *Polym. Chem.*, 2010, 1, 1171–1185.
- 42 K. C.F. Leung and K. N. Lau, *Polym. Chem.*, 2010, 1, 988–1000.
- 43 A. Z. Samuel and S. Ramakrishnan, *Macromolecules*, 2012, 45, 2348–2358.
- 44 B. Jiang, W. Tao, X. Lu, Y. Liu, H. Jin, Y. Pang, X. Sun, D. Yan and Y. Zhou, *Macromol. Rapid Commun.*, 2012, 33, 767–772.
- 45 L. Jasinska, M. Villani and J. Wu, *Macromolecules*, 2011, 44, 3458–3466.
- 46 X. Ji, W. Zhang and H. Na, *Macromolecules*, 1997, **30**, 4772–4774.
- 47 J. Maiz, J. Martin and C. Mijangos, *Langmuir*, 2012, 28, 12296–12303.
- 48 T. A. Witten and L. M. Sander, *Phys. Rev. B*, 1983, 27, 5686–5697.
- 49 A. Lomander, W. M. Hwang and S. G. Zhang, *Nano Lett.*, 2005, 5, 1255–1260.