Journal of Materials Chemistry

www.rsc.org/materials

Volume 21 | Number 12 | 28 March 2011 | Pages 3973-4704



ISSN 0959-9428

RSCPublishing

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Anjun Qin and Ben Zhong Tang *et al.* Hyperbranched polytriazoles with high molecular compressibility: aggregation-induced emission and superamplified explosive detection

Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2011, 21, 4056

www.rsc.org/materials



Hyperbranched polytriazoles with high molecular compressibility: aggregation-induced emission and superamplified explosive detection[†]

Jian Wang,^a Ju Mei,^a Wangzhang Yuan,^b Ping Lu,^c Anjun Qin,^{*a} Jingzhi Sun,^a Yuguang Ma^c and Ben Zhong Tang^{*ab}

Received 26th November 2010, Accepted 18th January 2011 DOI: 10.1039/c0jm04100a

Hyperbranched polytriazoles with spring-like architectures exhibit the feature of aggregation-induced emission (AIE) due to the high compressibility of polymer spheres from solution to aggregate. Thanks to their AIE effect, the polymer nanoaggregates can detect explosives with superamplification effect.

Development of efficient solid-state luminescent materials is of great importance for practical application in diverse areas, such as organic light-emitting diodes, organic solid-state lasers, and organic fluorescent sensors *etc.*¹ The thorny problem encountered is that the emission of traditional fluorophores is strong in solution but weakened or nonemissive in condensed phases, such as thin films or aggregates, that is, these fluorophores suffer from the aggregation-caused quenching (ACQ).² Various chemical, physical, and engineering approaches have been taken to prevent fluorophore aggregation and to alleviate the notorious ACQ effect, but met with limited success.³

Exactly opposite to ACQ effect, we recently discovered a unique phenomenon of aggregation-induced emission (AIE): a series of propeller-shaped molecules such as tetraphenylethene (TPE) and hexaphenylsilole (HPS) as well as their derivatives are nonemissive when molecularly dissolved, but induced to emit efficiently by aggregate formation.⁴ Restriction of intramolecular rotation (RIR) of their multiple phenyl rotors in the aggregates has been proven theoretically and experimentally as the main cause for AIE effect.^{5,6}

Attracted by the exotic prospects, our and other groups have been actively involved in the exploration of new AIE systems.^{5,6} A large number of AIE active low molecular weight luminogens have been developed for diverse applications such as in fluorescent sensors and bioprobes, stimuli-responsive nanomaterials, and active layers in efficient organic light-emitting diodes.³ For practical applications, these luminogens have to be fabricated into solid films using

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expensive equipment and complicated processes, which are not well suited to the manufacture of large-area, flat-panel devices. Whereas high molecular weight polymers can surmount these disadvantages because they can form films readily by simple processing techniques such as spin-coating, static casting and ink printing *etc*.

The AIE features have been developed in polymers with linear structures by incorporating the easy-to-prepare and ready-to-functionalize TPE moieties in our group,⁷ but it remains a challenge in the hyperbranched polymer system. Due to their remarkable features, such as one-pot synthesis, high solubility, low viscosity, threedimensional (3D) structure and multiple end groups *etc*, hyperbranched polymers have drawn growing attention.⁸ We have tried to prepare the hyperbranched polymers with AIE features but polymers obtained mostly feature aggregation-enhance emission (AEE) characteristics, that is, the polymers are emissive in solution.⁹

We first polycyclotrimerized the AIE-active 1,1-diethynylsilole moieties to produce hyperbranched poly(1,1-silole) in 2003.¹⁰ Surprisingly, the obtained polymer is AIE-inactive. The rigid and crowded architectures of the polymer have already restricted the intramolecular rotation of the phenyl rotors of silole even in solution, making the polymer emissive. The size and volume of polymer is, however, scarcely changed in aggregate state due to its rigid structure, and the fluorescence intensity is almost identical to that in solution



Fig. 1 Illustration of the size/volume changes of hyperbranched polymers in solution and aggregate states. The spheres are symbolized as hyperbranched polymers.

^aMoE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: qinaj@zju.edu. cn; tangbenz@ust.hk; Fax: (+852) 2358–1594

^bDepartment of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

^cState Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, China

[†] Electronic supplementary information (ESI) available: Experimental details and characterization data and spectra for the monomers, model compound and polymers. See DOI: 10.1039/c0jm04100a

(Fig. 1a). Altering the ethynyl groups from 1,1- to 2,5-positions in silole moieties, the yielded hyperbranched poly(2,5-silole)s are AEE-active.^{9a} Though the obtained polymers are relatively "softer" and possess larger free volume and lower steric hindrance than the poly(1,1-silole), the polymers are still emissive in solution because the rotation of the phenyl rotors of siloles is still partially restricted. Adding nonsolvents into their molecularly dissolved solutions intensified the emission due to the aggregate formation, demonstrating an AEE phenomenon. The α_{AIE} , which is defined as the ratio of the quantum yields or emission intensities of an AIE luminogen in aggregate and solution states,¹¹ is calculated to be only 3–5.

Introducing a flexible node such as silicon atom into the hyperbranched poly(silylenephenylene)s has enabled the polymers with much free volume and to shrink slightly in the aggregate state, but the obtained polymers still feature AEE characteristics with α_{AIE} of 3.3 (Fig. 1b).^{96,9c} If such hyperbranched polymers are employed as fluorescent chemosensors in solution state, the background fluorescence will decrease the signal to noise ratio, which will lower the sensitivity of the detection. It thus will be nice if the hyperbranched polymer is nonemissive in solution but emits intensely in aggregate state, that is, the polymer is AIE-active.

On the basis of aforementioned efforts, we envisage that if springlike flexible spacers are introduced into hyperbranched architectures, the obtained polymers will have considerably extended conformation in solution but be tightly compressed in aggregate state, which will be promising for possession of the AIE feature according to the RIR mechanism (Fig. 1c).

With this idea in mind, we designed triazides **1a** and **1b** with varying space lengths for the purpose of investigating their effects on the AIE feature when they are integrated into hyperbranched structures by the well-established copper(1)-catalyzed click polymerizations with diyne (Scheme 1).¹² Due to its simple preparation procedure, easy modification, and high α_{AIE} value (61),¹¹ TPE derivative of diyne **2** was designed as the comonomer for the preparation of hyperbranched polytriazoles.³ The triazides **1a** and **1b** and diyne **2** were synthesized according to our previous published procedures (Schemes S1 and S2, ESI†). Cu(PPh₃)₃Br-mediated click polymerizations of **1** and **2** in DMF at 60 °C for 5–7 h, readily furnish 1,4-regioregular hyperbranched polytriazoles *hb*-P**1a** and *hb*-P**1b** with satisfactory molecular weights (M_w up to 12400) in high yields (up to 88.3%) (see Table S1, ESI†).

hb-Pla and *hb*-Plb are soluble in common organic solvents such as THF, dichloromethane, chloroform *etc*, which enable the



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characterization of their structures using "wet" spectroscopic techniques. To facilitate the structure characterization, model compound **11** was also synthesized (Scheme S3, ESI†). By comparing the ¹H NMR spectra of *hb*-P**1a** and its monomers (**1a** and **2**) as well as **11** in DMSO- d_6 (Fig. S1, ESI†), we found that all the peaks of the polymer are unambiguously assigned corresponding to its expected molecular structure. Satisfactory analysis data were also obtained for *hb*-P**1b** (Fig. S2, ESI†). As can be seen from the thermogravimeteric analysis curves shown in Fig. S3 in the ESI†, *hb*-P**1a** and *hb*-P**1b** are thermally stable with 5% of their weights loss at temperatures of 378 and 366 °C, respectively. The detailed synthetic procedures and characterization data for monomers and polymers are given in the ESI†.

The TPE moiety is AIE active. Will such feature be preserved in the TPE-containing hyperbranched polymers with flexible spacers? We thus investigated the photoluminescence (PL) behaviours of *hb*-Pla and *hb*-Plb in solution and aggregate states. Excitingly, the PL spectra of polymers are almost flat lines parallel to the abscissa in THF solution, manifesting that they are virtually nonluminescent when molecularly dissolved in their good solvent. The emission peaked at 490 nm is, however, continuously intensified with gradual addition of water (Fig. 2a, and Fig. S4 in the ESI†). Such PL behaviours are the typical AIE processes, indicative of *hb*-Pla and *hb*-Plb are AIE-active.

The trajectories in the quantum yields ($\Phi_{\rm F}$) of *hb*-P1a and *hb*-P1b in the aqueous mixtures further confirm their AIE characteristics (Fig. 2b). The $\Phi_{\rm F}$ values of *hb*-P1a and *hb*-P1b are both negligible (0.11 and 0.14%, respectively) in pure solvents and remain almost unchanged until ca. 40% of water is added. The highest $\Phi_{\rm F}$ values of *hb*-P1a and *hb*-P1b are recorded at water fractions (f_w) of 90%, which reach 38.31 and 32.25, respectively. The α_{AIE} of *hb*-P1a and *hb*-P1b are thus calculated to be 348.3 and 230.4, which are two orders higher than our aforementioned polymers and even better than the famous AIE luminogens of TPE and HPS (220).5f The encouraged results of hyperbranched polytriazoles prompted us to further investigate their emission in the solid states. The $\Phi_{\rm F}$ values of the spin-coated films of *hb*-P1a and *hb*-P1b are both measured to be 100% by integrating sphere. Of the reported hyperbranched polymers, the highest $\Phi_{\rm F}$ values are for hb-P1a and hb-P1b, indicating their bright prospects for application in polymeric light-emitting diodes.13



(b)

(a)

Fig. 2 FL spectra of (a) *hb*-P1a in THF/water mixtures with different fractions of water. $\lambda_{ex} = 333$ nm. Polymer concentration: 10 µM. (b) Variation in quantum yield ($\Phi_{\rm F}$) of *hb*-P1a and *hb*-P1b with water fraction ($f_{\rm w}$) in THF/water mixture. The $\Phi_{\rm F}$ values were estimated using quinine sulfate in 0.1 N H₂SO₄ ($\Phi_{\rm F} = 54.6\%$) as standard. Inset shows the fluorescent images of *hb*-P1a solution in THF and THF/water mixture ($f_{\rm w} = 90\%$).



The unprecedented AIE feature of *hb*-Pla and *hb*-Plb could be attributed to their innovative spring-like architectures with flexible spacers. When molecularly dissolved in good solvents, the alkyl chains (spring) of the hyperbranched polymers are probably fully stretched, endowing the polymers a bulky sphere with considerable cavities. The large free volumes enable the phenyl rings of the TPE units to rotate freely, making the polymers nonemissive. When large amount of water was added, the solvating power of the aqueous mixtures become worse, causing the flexible and hydrophobic polymer branches agglomerated and the bulky spheres compressed to smaller ones. The reduced cavities within the spheres greatly restricted the intramolecular rotation of phenyl rings, which effectively blocks the non-radiative energy dissipation channels, populates the radiative decay of the excitons and then turns the emission of polymers on. It is also deduced from the α_{AIE} values of *hb*-P1a and *hb*-P1b that the longer the alkyl spacers, the higher the compression ratio. The Brunauer-Emmet-Teller (BET) surface area of 5.8 m²g⁻¹ of hb-Pla are negligibly low compared to other hyperbranched polymers (>1000 m²g⁻¹),¹⁴ suggesting the polymer is tightly compressed with almost no cavities in the solid state (Fig. S5, ESI[†]). Thus, the AIE-active hb-P1a and hb-P1b could be potentially regarded as organic "quantum dots" with low cytotoxity in the solid state.

The flexible alkyl chains (spring) enable *hb*-**P1a** and *hb*-**P1b** to possess good filming abilities and high optical transparency in their film states (Fig. S6, ESI[†]). The light transmittances of *hb*-**P1a** and *hb*-**P1b** reach 99% at wavelengths as short as 437 and 420 nm for their thin films with thickness of 24.1 and 20.0 nm, respectively, making them promising for photonic applications.

The intriguing AIE effect of *hb*-P1a and *hb*-P1b prompted us to explore their potential applications as chemosensors. Although they are free from the noise of fluorescence background in their solution state, the high sensitivity of the polymer aggregates will be more attractive because it can decrease the sensing limitation.^{7b,9b} Detection of explosives is of great importance and receiving extensive interest because of its homeland security and anti-terrorism implications.¹⁵ Picric acid (PA) and 2,4,6-trinitrotoluene (TNT) are employed as model explosives among the nitroaromatic compounds. We prepared the polymer aggregates in THF/water and THF/methanol mixtures with water or methanol fraction ($f_{\rm m}$) of 90% in according to the different solubility of PA and TNT, respectively. Importantly, the emissions in the THF/water and THF/methanol mixtures are both efficient with no peaks shift, suggesting that the solvent imparts little effect on the polymer aggregate emission.

Upon addition of the explosives into the aggregates suspended in the mixture solvents, for example, the emission intensities of *hb*-**P1a** decrease progressively but with no change in spectral profiles (Fig. 3a, and Fig. S7 in the ESI†). When the concentration of PA and TNT are below 0.09 and 1.0 mM, the Stern–Volmer plots of *hb*-**P1a** are linear and give quenching constants of 56484 and 704 M^{-1} , respectively (Fig. 3b). Afterwards, both plots bend upward, indicative of superamplified quenching effect.^{96,16} The unique phenomenon could be attributed to the 3-dimensional topological structures of the aggregates that generate more small cavities, which enable the small explosive molecules to enter through electrostatic interactions and offer more diffusion channels for the excitons to migrate, allowing them to be more quickly annihilated by the explosive quenchers.

From Fig. 3b, we also notice that the quenching of the emission of polymer aggregates is more sensitive to PA than TNT. Although a similar phenomenon was observed previously,¹⁷ to the best of our



Fig. 3 (a) PL spectra of *hb*-P1a in THF/water mixture (1 : 9 v/v) containing different amounts of PA. Concentration of *hb*-P1a: 10 μ M; $\lambda_{ex} =$ 333 nm. (b) Stern–Volmer plots of I_0/I versus [PA] in THF/water with $f_w = 90\%$ and [TNT] in THF/methanol with $f_m = 90\%$. Inset: enlarged plot of I_0/I versus [PA]. [Q] represents the concentration of PA and TNT; I = peak intensity and $I_0 =$ peak intensity at [Q] = 0 mM.

knowledge, there is little literature to account for the intrinsic reason. We tried to account for this phenomenon by investigating the UV spectra of PA and TNT as well as the PL spectrum of *hb*-P1a. The obvious spectral overlap of the absorption of PA and emission of the polymer in the range of 390 to 500 nm reveals that the energy transfer from the excited state of the *hb*-P1a to the ground state of PA will be the main quenching pathway.^{7a,15a} This mechanism, however, cannot be applied to explain the quenching effect of TNT because there is no spectral overlap between the absorption of TNT and the emission of polymer (Fig. 4a).

Further investigating the UV spectra of the mixtures of explosives with *hb*-Pla, we found a tail in the mixture of *hb*-Pla and TNT (Fig. 4b, and Fig. S8 in the ESI[†]) which is probably ascribed to their interaction, which may facilitate the charge transfer between them.^{17a,18} Cyclic voltammetry measurement of *hb*-Pla further substantiates the conclusion (Fig. S9, ESI[†]): the higher energy of lowest unoccupied molecular orbital (LUMO, -3.28 eV) of the polymer facilitates the electron to jump to the lower one of TNT (-3.7 eV).^{15a,19}

The above experimental results indicate that the main quenching mechanism for PA is the energy transfer, whereas, that for TNT is the charge transfer. It is well known that the energy transfer is a long-range process and the charge transfer is a short-range one.²⁰ In the



Fig. 4 (a) Normalized absorption spectra of TNT and PA, as well as the PL spectrum of *hb*-**P1a** in THF/methanol ($f_m = 90\%$) and THF/water ($f_w = 90\%$). (b) Absorption spectra of TNT, *hb*-**P1a** and their mixture in THF/methanol ($f_m = 90\%$). Inset: enlarged UV spectra of TNT, *hb*-**P1a** and their mixture in the range of 380–700 nm. [TNT]: 90 μ M, [*hb*-**P1a**]: 10 μ M.

polymer aggregates, PA can interact with the fluorophores surrounding it, but TNT can only quench the emission of the fluorophores that have interaction with it. Thus, quenching the emission of polymer aggregates is more sensitive to PA than TNT.

In summary, by taking advantage of the innovative spring-like architectures, we have synthesized AIE-active hyperbranched polytriazoles by the well-established Cu(PPh₃)₃Br-mediated triazide-diyne click polymerization. The α_{AIE} values (up to 348.3) of hyperbranched polytriazoles are larger than those of many AIE luminogens, such as TPE and HPS. Thanks to the high compression ratio of the polymers from solution to solid states, the intramolecular rotation of phenyl rings was greatly restricted and efficient light emission in aggregate ($\Phi_{\rm F}$ up to 38.31) and solid state ($\Phi_{\rm F} = 100\%$) was obtained. The polymers are soluble and thermally stable, and possess good filmforming ability. Using the novel AIE effect, the polymers can act as chemosensors for the superamplified detection of explosives in their aggregate states. The main mechanism for the detection of PA is ascribed to the energy transfer, and that for TNT is the charge transfer. The concept of spring-like polymeric structures is of great value in terms of guiding future molecular engineering endeavors in designing hyperbranched polymers with AIE characteristics. The possibility of using these AIE-active hyperbranched polymers for other high-tech applications is currently under exploration in our laboratories.

Acknowledgements

This work is partially supported by the National Natural Science Foundation of China (20634020, 50703033, 20974098), the Ministry of Science and Technology of China (2009CB623605), the University Grants Committee of Hong Kong (AoE/P-03/08), the Research Grants Council of Hong Kong (603509, 601608, 602707, and ITS/ 168/09). A.J.Q. and B.Z.T acknowledge the supports from the Fundamental Research Funds for the Central Universities (2010KYJD005), and the Cao Guangbiao Foundation of Zhejiang University, respectively.

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