Dendritic molecular brushes: synthesis via sequential RAFT polymerization and cage effect for fluorophores†

Sipei Li and Chao Gao*

Multifunctional dendritic molecular brushes (DMBs) with pendent poly(glycidyl methacrylate) (PGMA) chains were synthesized via a sequential reversible addition–fragmentation chain transfer (RAFT) polymerization approach. By controlling the kinetics of the polymerization, DMBs with a high number-averaged molecular weight ($M_n$) of $\sim 1.4 \times 10^6$ g mol$^{-1}$ and narrow polydispersity index (PDI) of 1.50 were obtained. DMBs were reacted with sodium azide, giving rise to giant macromolecules with a high density of hydroxyl and azide bifunctional groups. Pyrene moieties (with a conventional chromophore) were efficiently attached to the DMBs by esterification, affording solution-emissive blue-light DMBs. Ultrahigh excimer emission at 475 nm was achieved for these fluorescent DMBs at a very low concentration of pyrene ($\sim 10^{-7}$ mol L$^{-1}$). Alternatively, tetraphenylethylene (TPE, with an aggregation-induced emission (AIE) chromophore) units were attached to DBMs with a conversion of 100% by copper-catalyzed alkyne–azide click chemistry. The solid-state-emissive blue-light TPE-functionalized DMBs exhibited typical AIE (rather than aggregation-enhanced emission, AEE) effect which was rarely observed for dendritic scaffolds and its quantum yield at aggregated state is two times higher than that of fluorophore monomer. Such topology-induced unusual emission phenomena were attributed to the cage effect of DMBs.

Introduction

With the developments of well controlled polymerization techniques and precise conjugation chemistry, chemists have made great efforts to shape macromolecules into different architectures, including circles, stars, tadpoles, brushes and so on. Among them, the molecular brush is a major category consisting of 1D brush, 2D brush and 3D brush (Fig. 1a–c). In spite of the well developed dendritic polymers, dendritic molecular brushes (DMBs), a kind of 4D brushes with side-chains grown along a segmented dendritic polymer scaffold, were rarely reported, which is likely to be due to the lack of multifunctional sparsely branched backbones. To solve this dilemma, our group recently explored DMBs with short hydrophobic, hydrophilic or amphiphilic side-chains through a “grafting to” approach based on multifunctional segmented hyperbranched polymer (SHP) scaffolds. Compared with the SHPs and those conventional hyperbranched polymers (CHPs), DMBs possess higher density of full-scaffold functionality, just like trees with thick leaves along the whole branches (Fig. 1). However, the unique topology-induced properties of DMBs have not been disclosed yet.

On the other hand, in the area of photochemistry, two kinds of chromophores are becoming the focus, i.e. pyrene and tetraphenylethylene (TPE). The potential of pyrene to readily form excimers makes it attractive for applications in solution-based fluorescent sensors, and the unique aggregation-induced emission (AIE) attribute of TPE makes it very promising for application in solid-state devices. To date, most of the pyrene-based polymers exhibited no or negligible excimer emission in highly diluted solutions, and most of the dendritic polymers with AIE moieties only exhibited the aggregation-enhanced emission (AEE) phenomenon, rather than the typical AIE effect as shown in the linear polymer analogues. Hence, to facilely fabricate pyrene-based polymer materials with high excimer emission and to realize AIE performance in dendritic polymer systems are still challenges.

To answer the aforementioned questions, here we synthesized DMBs based on multifunctional SHP backbones via a “grafting from” approach that allows convenient control over the length of side chains. The facile availability of the complex DMBs paves the way for further functionalization and exploiting their properties. Subsequent post-modification of DMBs with pyrene and TPE moieties gave birth to compact dendritic macromolecules showing ultrahigh excimer-emission at extremely low concentrations and classic AIE effect, respectively, due to the significant cage effect of DMBs. The high...

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solubility, ease of solution processing, and unique cage effect of DMBs would foster the advancements in design and fabrication of novel organic electronic devices. As a prototype, we made a complex solid pattern that emits strong blue light using the TPE-attached DMBs as printable ink.

**Experimental section**

**Materials**

Mono-ethynyl TPE (METPE), (s)-1-docyl-(s)-z,z'-dimethyl-z'-acidic acid) trithiocarbonate (DDMAT) and 2-((2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl acrylate (ACDT) were synthesized according to previous literature. Glycidyl methacrylate (GMA, 97%), sodium azide (99.5%), propargyl alcohol (99%), CuBr (98%) and 2,2'-azobisobutyronitrile (AIBN) were purchased from Sigma-Aldrich Corporation. 4-Dimethylaminopyridine (DMAP, 99%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 98.5%), and 1-pyronebutyric acid were purchased from Aladdin Chemical Co. China. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, 98%), propargyl bromide and N,N-dimethylpropargylamine were purchased from Alfa Aesar Corporation. Chloroform-d (99.8 atom %D, stabilized with silver foil), dimethyl sulfoxide-d6 (99.9 atom %D) were purchased from J&K chemical. Dimethylformamide (DMF), 1,4-dioxane, chloroform, dichloromethane, ammonium chloride and other organic solvents were purchased from Sino-pharm Chemical Reagent Co. Ltd. GMA was passed through a column of basic alumina before use and other materials were used as received.

**Instrumentation**

Gel permeation chromatography (GPC) was carried out on a Perkin Elmer HP 1100, using DMF/LiBr (0.02 mol L⁻¹) as the
eluent at a flow rate of 1 mL min\(^{-1}\), RI-WAT 150 Cvt + as the detector and linear poly(methyl methacrylate) as the calibration standard at 60 °C for detection of apparent molecular weights. Light scattering data were recorded through gel permeation chromatography with multiple angle laser scattering detector (GPC-MALLS) system using LiBr/DMF (0.05 mol L\(^{-1}\)) as eluent at a flow rate of 1 mL min\(^{-1}\) and linear poly(methyl methacrylate) as the calibration standard at 60 °C for characterization of absolute molecular weights. The detection system consisted of a dn/dc RI detector (Dawn DSP Laser Photometer, Wyatt Technology) and multiangle laser light scattering detector (OPILAB DSP Interferometric Refractometer, Wyatt Technology). \(^1\)H NMR (400 MHz) spectroscopy measurements were carried out on a Varian Mercury plus 400 NMR spectrometer using CDCl\(_3\) or DMSO-d\(_6\) as solvent. Fourier transform infrared (FTIR) spectra were recorded on a Varian Cary 300 Bio UV-visible spectrophotometer. Fluorescence spectra were measured with a RF-5301PC fluorophotometer (Shimadzu Corp.). Atomic force microscopy (AFM) was performed under tapping mode on a NanoScope IIIa SPM from Digital Instruments Inc. The AFM samples were obtained via a dip-coating method on a freshly peeled mica wafer. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope at 200 kV. Dynamic light scattering (DLS) was measured on a Brookhaven 90 Plus particle size analyzer. The samples for dynamics studies were obtained under nitrogen gas purge and subjected to characterization directly without any purification.

**Synthesis of alkynyl chain transfer agent (alk-CTA)**

1 g DDMAT (1 equiv.), 0.5 mL propargyl alcohol (3.26 equiv.), 0.783 g EDCI (1.5 equiv.) and 0.5 g DMAP (1.5 equiv.) were dissolved in 10 mL dichloromethane in a 25 mL round bottom flask deoxygenated with nitrogen purge. The solution was stirred at room temperature for 24 h and then subsequently washed with 1.2 M HCl and deionized water. After dried with anhydrous magnesium sulfate and filtered, the solution was evaporated using a vacuum evaporator and kept in a vacuum oven at room temperature for 24 h. Viscous yellow product was obtained and subjected to \(^1\)H NMR analysis. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 4.70 (s, CH\(_2\)C\(_{10}\)H\(_{10}\)), 3.28 (t, C\(_{11}\)H\(_{23}\)CH\(_2\)SC(=S)SC(CH\(_3\))\(_2\)), 2.48 (t, CH\(_3\)C\(_{10}\)H\(_{10}\)), 1.72 (s, C\(_{11}\)H\(_{23}\)CH\(_2\)SC(=S)SC(CH\(_3\))\(_2\)), 1.26 (m, CH\(_3\)C\(_{10}\)H\(_{10}\)SC(=S)SC(CH\(_3\))\(_2\)), 0.89 (t, CH\(_3\)C\(_{10}\)H\(_{10}\)CH\(_2\)SC(=S)SC(CH\(_3\))\(_2\)).

**Synthesis of segmented hyperbranched poly(chain transfer agent) (SHP-CTA)**

Segmented hyperbranched poly(glycidyl methacrylate) (SHP-1) was synthesized via reversible addition–fragmentation chain transfer self-condensing vinyl polymerization (RAFT-SCVP) of GMA and ACDT in a feed ratio of 30:1. The composition of the two components in the obtained SHP-1 was close to the feed ratio and each segment contains about 30 GMA units. Subsequently, SHP-1 was reacted with NaN\(_3\) in DMF at 50 °C for 24 h, yielding SHP backbone (SHP-2) with both hydroxy and azido groups at each repeating unit.\(^1\) SHP-CTA was synthesized by reacting SHP-2 with alk-CTA. Typically, 530 mg SHP-2 (1 equiv.), 2.31 g alk-CTA (2 equiv.), and 0.55 mL PMDETA (1 equiv.) were charged into a 10 mL Schlenk flask with a mixture of 9 mL DMF and 9 mL chloroform. After deoxygenation, 383 mg CuBr (1 equiv.) were instantly added to the solution under nitrogen purge. The solution was kept at room temperature for 24 h and then poured into 200 mL methanol for purification. The dried product of SHP-CTA was characterized by FTIR and \(^1\)H NMR analyses. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.90 (methine proton on the triazole ring), 5.20 (triphenyl-CH\(_2\)OSOCC(CH\(_3\))\(_2\)SC(=S)SC(CH\(_3\))\(_{10}\)CH\(_3\)), 4.80–3.91 (C(==O)CH\(_2\)CH(CH\(_2\))CH\(_3\)-triazole, 3.26 (triphenyl-CH\(_2\)OSOCC(CH\(_3\))\(_2\)SC(=S)SC(CH\(_3\))\(_{10}\)CH\(_3\)), 1.76 (triphenyl-CH\(_2\)OSOCC(CH\(_3\))\(_2\)SC(=S)SC(CH\(_3\))\(_{10}\)CH\(_3\)), 1.27 (triphenyl-CH\(_2\)OSOCC(CH\(_3\))\(_2\)SC(=S)SC(CH\(_3\))\(_{10}\)CH\(_3\)), 0.89 (triphenyl-CH\(_2\)OSOCC(CH\(_3\))\(_2\)SC(=S)SC(CH\(_3\))\(_{10}\)CH\(_3\)). For \(^1\)H NMR information for SHP-1 and SHP-2, see ref. 12.

**Synthesis of DMB with poly(glycidyl methacrylate) side-chains (DMB-1)**

In a typical procedure, 25 mg SHP-CTA (1 equiv.), 2.977 g GMA (500 equiv.) and 1.375 mg AIBN were charged into a 10 mL round bottom flask with 4.2 mL dioxane. After the solution was bubbled with nitrogen gas in an ice bath for deoxygenation, the flask was put into a 75 °C thermostatic oil bath. After 1.25 h, the solution was quenched by liquid nitrogen. After thawing, the diluted solution was then precipitated into 10-fold excess of methanol. The precipitates were collected and dried in vacuo at room temperature for 1 h. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 4.30 (COOC\(_2\)H\(_2\)CH\(_2\)OCO), 3.73 (COOC\(_2\)H\(_2\)CH\(_2\)O), 3.20 (COOC\(_2\)H\(_2\)CH\(_3\))\(_{10}\)CH\(_3\)), 2.80 and 2.66 (CH\(_2\)-O-in epoxide ring), 2.2–1.4 (side chain proton), 1.24 (SC\(_{10}\)H\(_{10}\)CH\(_3\)), 0.98 (methyl protons on side chain backbone), 0.8 (SC\(_{10}\)H\(_{10}\)CH\(_3\)).

**Synthesis of DMB with poly(2-hydroxy-3-azidopropyl methacrylate) side-chains (DMB-2)**

In a typical procedure, 264 mg DMB-1 (1 equiv.), 121 mg sodium azide (3 equiv.) and 100 mg ammonium chloride (3 equiv.) were dissolved in 12 mL dry DMF in a 25 mL round bottom flask equipped with a stirring bar. After deoxygenation, the flask was immersed in a 50 °C oil bath and stirred for 24 h. The solution was then precipitated into 10-fold excess of deionized water. The precipitates were then desiccated via a vacuum freeze-drier. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): 5.44 (hydroxyl proton), 3.87 (COOC\(_2\)H\(_2\)CH(OH)CH\(_3\)), 3.35 (COOC\(_2\)H\(_2\)CH\(_3\))\(_{10}\)CH\(_3\)), 2.20–1.40 (side chain proton), 1.23 (SC\(_{10}\)H\(_{10}\)CH\(_3\)), 0.92 (methyl protons on side chain backbone), 0.76 (SC\(_{10}\)H\(_{10}\)CH\(_3\)).

**Synthesis of pyrene-functionalized DMB (DMB-Py)**

In a typical procedure, 50 mg DMB-2 (1 equiv.), 225 mg 1-pyr- enbutyric acid (3 equiv.), 140 mg EDCI (3 equiv.) and 105 mg DMAP (3 equiv.) were dissolved in 1.5 mL dry DMF in a 10 mL round bottom flask sealed with a rubber septum. After purging with nitrogen in an ice bath for 15 min, the solution was
immersed in a 60 °C thermostatic oil bath and stirred for 24 h. The solution was poured into 10-fold excess of deionized water. The precipitates were dried in a vacuum freeze-drier and redissolved in 1.5 mL chloroform. The solution was precipitated into 30 mL ethyl acetate and dried. The excitation and emission slit widths for PL spectrum were both 5 nm. 1H NMR (400 MHz, CDCl3): 8.08–7.45 (aromatic protons of pyrene ring), 5.04 (CHCH2N3), 4.31–3.66 (COOCH2CH2OCO, COOCH2CHCH2N3), 3.36–2.79 (pyrene-CH2CH2CH2COOH, COOCH2CHCH2N3, SCH2(CH2)3CH3), 2.26 (pyrene-CH2CH2CH2COOCH), 1.93 (pyrène-CH2CH2CH2COOCH), 1.27 (S=CSCH2(CH2)10CH3), 1.04 (methyl protons on side chain backbone), 0.87 (S=CSCH2(CH2)10CH3).

Synthesis of TPE-functionalized DMB (DMB-TPE)

In a typical procedure, 52.6 mg DMB-2 (1 equiv.), 97 mg METPE (2 equiv.) and 30 μL PMDETA (0.5 equiv.) were dissolved in 0.5 mL DMP in a 10 mL Schlenk flask and purged with nitrogen gas for 15 min. Afterwards, 11.5 mg CuBr was added under nitrogen protection. The reaction was kept at room temperature and stirred for 36 h. The solution was then precipitated in 14 mL diethyl ether. The precipitates were then redissolved in 6 mL chloroform and passed through a column of basic alumina to remove residual copper. The excitation and emission slit widths for PL spectrum were both 5 nm. 1H NMR (400 MHz, DMSO-d6): 8.08 (proton on triazole ring), 6.92 (aromatic protons on TPE ring), 5.52 (hydroxyl proton), 4.70 (C(=O)CH2CH(OH)-CH2-triazole), 2.21–2.61 (side chain proton). 41–0.86 (S=CSCH2(CH2)10CH3, S=CSCH2(CH2)10CH3, methyl protons on side chain backbone).

Results and discussion

Synthesis of DMBs via “grafting from” approach

Three methodologies called “grafting to”, “grafting through” and “grafting from” have been developed to synthesize polymer brushes.7 The “grafting to” strategy has been employed to synthesize DMBs in our previous work,3,12 which allows the convenient immobilization of short side chains onto the SHP backbone but is of limited use for growing long multifunctional pendant chains. Accordingly, we designed an alternative route to synthesize DMBs with long multifunctional chains via “grafting from” approach (Scheme 1). Firstly, the SHP-1 was prepared by RAFT-SCVP of GMA and ACDT with a feed ratio of 30:1. Subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit. A subsequent ring-opening of epoxide groups of SHP-1 in the presence of NaN3 gave SHP-2 with both hydroxy and azido groups at each repeating unit.

Based on the sparsely branched dendritic macro-CTA (SHP-CTA), we prepared series of DMBs with different lengths of side arms through RAFT polymerization of GMA by adjusting the reaction conditions such as the feed ratio of GMA to CTA, the concentration of GMA, and polymerization time (Table 2).
Table 1 Molecular parameters and sizes of synthesized dendritic polymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>$M_n^a$ (g mol$^{-1}$)</th>
<th>$M_w^a$ (g mol$^{-1}$)</th>
<th>$M_z^a$ (g mol$^{-1}$)</th>
<th>PDI$^a$</th>
<th>$M_n^b$ (g mol$^{-1}$)</th>
<th>Size$^c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHP-1</td>
<td>52 400</td>
<td>52 300</td>
<td>74 000</td>
<td>1.234</td>
<td>18 400</td>
<td>135.0</td>
</tr>
<tr>
<td>SHP-2</td>
<td>64 900</td>
<td>119 200</td>
<td>262 900</td>
<td>1.835</td>
<td>26 700</td>
<td>155.4</td>
</tr>
<tr>
<td>DMB-1</td>
<td>346 000</td>
<td>521 200</td>
<td>988 400</td>
<td>1.507</td>
<td>113 000</td>
<td>164.4</td>
</tr>
<tr>
<td>DMB-Py</td>
<td>964 900</td>
<td>1 264 000</td>
<td>2 595 000</td>
<td>1.310</td>
<td>192 700</td>
<td>182.2</td>
</tr>
<tr>
<td>DMB-TPE</td>
<td>1 164 000</td>
<td>2 148 000</td>
<td>4 167 000</td>
<td>1.845</td>
<td>223 400</td>
<td>176.7</td>
</tr>
</tbody>
</table>

$^a$ Absolute number-averaged molecular weight ($M_n$), weight-averaged molecular weight ($M_w$), $z$-averaged molecular weight ($M_z$) and polydispersity index (PDI) determined by GPC-MALLS. $^b$ Apparent number-averaged molecular weight ($M_n$) determined by conventional GPC. $^c$ Determined by DLS at concentration of $1 \times 10^{-3}$ mg mL$^{-1}$ at 25 °C.

Fig. 2 (a) $^1$H NMR spectrum of SHP-CTA in CDCl$_3$. (b) FTIR spectra of SHP-CTA and SHP-2.

Codes 1–4 show that higher monomer and CTA concentration give rise to quicker polymerization but poorer polydispersity. Codes 5 and 6 show that higher monomer/CTA ratio guarantees better control over the polydispersity. The conditions with feed ratio of 500 : 1 and GMA concentration of 0.5 M were selected for further kinetics study. The results are shown in Table 3 and Fig. 3. The curve of “ln([M$_0$]/[M$_t$]) vs. time” showed ideal linearity at the early stage of the polymerization, revealing the “living/controlled” nature of RAFT polymerization during this stage (the first two hours) (Fig. 3a). The increasing trend of the absolute $M_n$ detected by GPC-MALLS was much sharper than that of the apparent $M_n$ detected by conventional GPC technique (Fig. 3b). Given that conventional GPC technique is based on detecting molecular volume, the difference between the apparent $M_n$ and the absolute $M_n$ means that although the DMB’s molecular weight increased dramatically, its molecular size did not increase obviously. During the later period of polymerization, a shoulder peak gradually appeared (Fig. 3c), suggesting the happening of intermolecular coupling caused by the limited motion of the high density free radicals in the hyperbranched macro-CTA systems (after the first two hours). This is also confirmed by the ln([M$_0$]/[M$_t$]) vs. time curve that it gradually deviated from the fitted linear curve (Fig. 3a). Therefore, the key to obtaining high molecular weight DMBs with narrow polydispersity is to decrease the monomer concentration, increase the monomer/CTA ratio and to stop the polymerization at low conversion. This is because lower monomer concentration leads to lower free-radical concentrations and higher monomer/CTA ratio makes the high-density free radicals around the DMB backbones surrounded by more uninitiated monomer, reducing the inter-radical contact rate. According to the aforementioned kinetics analyses, the DMB sample with both high $M_n$ (~350 000 g mol$^{-1}$), relatively low PDI (~1.3) and about 33 repeating units on the side chain (Code 5, Table 3) was chosen for subsequent functionalization.

DLS measurements also proved that the sizes of SHP-1 and DMB-1 were close (135.0 nm and 164.4 nm, respectively) (Table 1). The relatively large hydrodynamic radius of SHP-1 indicates the sparsely branched structure of SHP-1 which accounts for its high functionality. The similar molecular size of the DMBs to their

Table 2 Selected conditions and results for RAFT polymerization of DMB-1

<table>
<thead>
<tr>
<th>Code</th>
<th>Feed ratio</th>
<th>Time</th>
<th>[GMA] (mol L$^{-1}$)</th>
<th>$M_n^a$ (g mol$^{-1}$)</th>
<th>$M_w^a$ (g mol$^{-1}$)</th>
<th>$M_z^a$ (g mol$^{-1}$)</th>
<th>PDI$^a$</th>
<th>Conversion</th>
<th>$M_n^b$ (g mol$^{-1}$)</th>
</tr>
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<tr>
<td>1</td>
<td>500 : 1</td>
<td>40 min</td>
<td>1</td>
<td>133 700</td>
<td>170 900</td>
<td>301 100</td>
<td>1.279</td>
<td>—</td>
<td>36 000</td>
</tr>
<tr>
<td>2</td>
<td>500 : 1</td>
<td>90 min</td>
<td>1</td>
<td>382 300</td>
<td>651 600</td>
<td>1 461 000</td>
<td>1.704</td>
<td>10.7%</td>
<td>141 200</td>
</tr>
<tr>
<td>3</td>
<td>500 : 1</td>
<td>40 min</td>
<td>2</td>
<td>245 000</td>
<td>372 700</td>
<td>662 000</td>
<td>1.521</td>
<td>2.9%</td>
<td>83 460</td>
</tr>
<tr>
<td>4</td>
<td>500 : 1</td>
<td>70 min</td>
<td>2</td>
<td>394 200</td>
<td>813 900</td>
<td>2 377 000</td>
<td>2.065</td>
<td>13.0%</td>
<td>126 600</td>
</tr>
<tr>
<td>5</td>
<td>2000 : 1</td>
<td>3 h</td>
<td>0.5</td>
<td>934 200</td>
<td>1 240 000</td>
<td>4 189 200</td>
<td>1.328</td>
<td>7.4%</td>
<td>264 200</td>
</tr>
<tr>
<td>6</td>
<td>2000 : 1</td>
<td>6 h</td>
<td>0.5</td>
<td>1 457 000</td>
<td>2 194 000</td>
<td>4 140 000</td>
<td>1.506</td>
<td>41.2%</td>
<td>381 000</td>
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$^a$ Absolute number-averaged molecular weight ($M_n$), weight-averaged molecular weight ($M_w$), $z$-averaged molecular weight ($M_z$) and polydispersity index (PDI) determined by GPC-MALLS. $^b$ Apparent number-averaged molecular weight ($M_n$) determined by conventional GPC.
SHP precursors indicates that they have a much more compact structure than the precursor. TEM observations showed that the dry-state size of DMB-1 was \( \frac{100}{24} \text{nm} \) (Fig. 4a) which was also confirmed by the AFM data (Fig. 4b and c). Moreover, the molecular height is about \( 3 \text{nm} \) similar to the data of the linear counterpart of DMBs - the cylindrical molecular brushes (1.8 - 4.2 nm in height), indicating the mono-layer dispersion of the macromolecules.

Notably, given the highly compact structural nature of DMB-1, a small amount of physical coupling and self-assembly might take place even at extremely low sampling concentrations. It is smaller than the DMB size in the solution-state, indicating that the DMB backbone is relatively soft and scaffold shrinkage takes place in the dry state. AFM measurements revealed that dry-state DMB-1 had a lateral size of \( \sim 100 \text{nm} \) and a height of \( \sim 3 \text{nm} \) (Fig. 4b-d), confirming the shrinkage of soft DMB backbone.

The following azidation on oxirane units of DMB-1 yielded DMB-2, which is the first case of polymer brushes with hetero-bifunctional side-chains. The structure of DMB-2 was characterized by \(^1\text{H NMR}\) and FTIR analyses. The peaks at 4.3 and 3.8 ppm representing the methene protons near the oxirane ring and the peaks at 3.2, 2.8 and 2.6 ppm assigned to the protons on the oxirane ring were not detected any more in the \(^1\text{H NMR}\) spectrum of DMB-2 (Fig. 5a), demonstrating a very high conversion (\( \sim 100\% \)) for the ring-opening reaction despite the extremely high compactness of DMBs. A new peak was found at 5.4 ppm belonging to the hydroxy groups of DMB-2. The strong absorption peak at \( 2100 \text{ cm}^{-1} \) in the FTIR spectrum of DMB-2 declared the presence of azido groups. This hetero-bifunctional DMB promises the controlled immobilization of different types of fluorophores.

### Table 3 Kinetics information for RAFT polymerization of DMB-1 at feed ratio of 500 : 1

<table>
<thead>
<tr>
<th>Code</th>
<th>Time</th>
<th>Conversion</th>
<th>( M_n^a ) (g mol(^{-1}))</th>
<th>( M_w^a ) (g mol(^{-1}))</th>
<th>( M_z^a ) (g mol(^{-1}))</th>
<th>PDI (^a)</th>
<th>( M_n^b ) (g mol(^{-1}))</th>
<th>( m^c )</th>
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<tr>
<td>1</td>
<td>10 min</td>
<td>—</td>
<td>115 900</td>
<td>207 800</td>
<td>477 900</td>
<td>1.793</td>
<td>27 000</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>20 min</td>
<td>—</td>
<td>188 100</td>
<td>233 100</td>
<td>325 800</td>
<td>1.239</td>
<td>43 000</td>
<td>—</td>
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<tr>
<td>3</td>
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<td>345 800</td>
<td>592 000</td>
<td>1.415</td>
<td>79 900</td>
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<td>4</td>
<td>45 min</td>
<td>3.8%</td>
<td>317 300</td>
<td>450 400</td>
<td>779 700</td>
<td>1.419</td>
<td>126 200</td>
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<td>1 h</td>
<td>6.5%</td>
<td>346 000</td>
<td>521 200</td>
<td>988 400</td>
<td>1.507</td>
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<td>3 h</td>
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<td>10 660 000</td>
<td>3.115</td>
<td>173 600</td>
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</tbody>
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\(^a\) Absolute number-averaged molecular weight \((M_n)\), weight-averaged molecular weight \((M_w)\), z-averaged molecular weight \((M_z)\) and polydispersity index \((PDI)\) determined by GPC-MALLS. \(^b\) Apparent number-averaged molecular weight \((M_n)\) determined by conventional GPC. \(^c\) Number of GMA repeating unit on each of the graft side-chain.

![Fig. 3](https://example.com/fig3.png)  
(a) Dependence of \( \ln([M_0]/[M_t]) \) on time. (b) Dependence of \( M_n \) on GMA conversion. (c) GPC peak evolution of DMB-1 during RAFT polymerization of GMA. Dotted lines are linear fitting curves.
Cage effect: excimer-enhanced DMB-Py

With the characters of easy excimer formation and structural sensitivity, pyrene was widely used in material science and analysis chemistry. In particular, the switch between excimer emission and monomer emission makes them hot in the area of ratiometric fluorescent sensors. However, the materials with a high $I_E/I_M$ ratio (excimer emission intensity/monomer emission intensity) at a low concentration were rarely developed, which greatly limits the application of pyrenyl compounds in high-resolution sensors. The crux of this challenge is to improve the intermolecular contact rate of excited pyrene moieties and the ground-state pyrene moieties. Based on this principle, DMB-Py with a highly compact structure was designed and synthesized by esterification between DMB-2 and 1-pyrenebutyric acid (Scheme 1). In the corresponding $^1$H NMR spectrum (Fig. 5a), the overlapped peak around 8.0 ppm represents the aromatic signal of the attached 1-butyricpyrene acid, and the integration ratio of peak at 5.1 ppm to peak at 3.2 ppm equals 1 : 4, which indicates the complete conversion of hydroxy groups and that about 33 pyrene units were attached onto each of the side chains. The remaining azido groups showed a strong absorption peak at $\sim 2100 \text{ cm}^{-1}$ in the FTIR spectrum of DMB-Py (Fig. 5b). DMB-Py showed a molecular size of 182.2 nm in solution-state (DLS data, Table 1) and $\sim 150$ nm at dry-state (TEM result, Fig. S1†), which are close to the corresponding values of its precursor of DMB-1. Such a cage-like compact structure filled with pyrene moieties makes their higher contact rate possible. We then measured the fluorescent spectra of DMB-Py at various concentrations (Fig. 6a). Very strong excimer emission at 475 nm and ultrahigh $I_E/I_M$ value were found at extremely low concentrations ($\sim 10^{-7}$ M). Such concentrations are compared with our recently reported pyrene-based SHPs with very strong excimer emission. Significantly, both the excimer emission and $I_E/I_M$ are higher than those of the highly emissive pyrene-based SHPs at the comparable pyrene concentrations (Fig. 6b). For instance, the $I_E/I_M$ value of

Fig. 4 (a) Representative TEM image of DMB-1. The scale bar corresponds to 1 µm (large picture) and 200 nm (inset picture) respectively. Sample concentration: $1 \times 10^{-3}$ mg mL$^{-1}$. (b) AFM image of DMB-1. The scale bar corresponds to 500 nm. Samples concentration: $1 \times 10^{-5}$ mg mL$^{-1}$. (c) Section analysis of diameter of typical particle in (b) ($\sim 98$ nm). (d) Section analysis of height of typical particle in (b) ($\sim 3$ nm).

Fig. 5 $^1$H NMR spectra (a) and FTIR spectra (b) of DMB-1, DMB-2, DMB-Py and DMB-TPE.
DMB-Py reached 7.76 at pyrene concentration of 0.181 μM, ~32% higher than that of pyrene-based SHP at a roughly two-fold higher concentration of 0.349 μM. Moreover, compared with other compact macromolecular pyrene-conjugated structures, like dendrimers (I_{f} / I_{M} value of 2.19 at pyrene concentration of 1.5 × 10^{-6} M) and hollow polymer capsules (I_{f} / I_{M} value of 1.29 at polymer concentration of 1 mg mL^{-1}), DMB-Py also showed higher I_{f} / I_{M} at much lower concentration. These facts prove that the highly compact structure of DMB has a strong amplifying influence on the emission of conventional chromophores such as pyrene, which is coined as the “cage effect” in this article. In addition, the remaining clickable azido sites along the scaffold promises broader applications of DMB-Py. In a preliminary attempt, the azido sites were completely converted into tertiary amine sites and then cationic alkyne sites via a sequential click chemistry approach (Scheme S1 and Fig. S2–S4).

Cage effect: AIE-featured DMB-TPE

The serious problem of fluorescence quenching in aggregation-state, against which scientists have been fighting for decades, limits the application of conventional chromophores in solid-state fluorescence. Alternatively, Tang and co-workers recently discovered the novel effect of aggregation-induced emission (AIE) for some conjugated molecules, which essentially furthers the advancement of organic electronic devices. As has been reported, when the AIE moieties were introduced into dendritic systems, they usually exhibited aggregation-enhanced emission (AEE) rather than the typical AIE effect mainly because the rigidity of dendritic scaffolds caused the restriction in rotation (RIR) effect of the AIE units in solution-state. Most recently, Tang and Qin et al. reported a kind of spring-like hyperbranched TPE macromolecule which exhibited typical AIE features. This inspired us to attach a TPE moiety to our shrinkable DMBs. Through simple click coupling between METPE and DMB-2, we synthesized DMB-TPE (Scheme 1).

Fig. 5a shows the 1H NMR spectrum of DMB-TPE, and the overlapped peaks around 7.2 ppm represent the attached TPE moieties. No absorption peak was detected at ~2100 cm^{-1} in the FTIR spectrum of DMB-TPE, indicating the 100% conversion of the click chemistry reaction (Fig. 5b) and that about 33 TPE units were attached onto each of the side chains. Fig. 7 shows the PL spectra and quantum yields (QYs) of DMB-TPE upon gradual addition of water to the THF solution of DMB-TPE. The PL intensity at 475 nm only slightly increased to 72 when the water faction (f_w) arose to 60 vol%, and then dramatically increased to 185 at f_w of 70 vol%, and jumped to 975 at f_w of 90 vol% (Fig. 7a), which is apparently a typical AIE phenomenon. The corresponding QYs displayed the same regular pattern as a function of f_w (Fig. 7b). When f_w is below 70 vol%, the curve is almost parallel to the abscissa, while as f_w increased to 90 vol%, the QY rapidly increased from 3.69% to 36.6%, confirming the AIE effect of DMB-TPE. The photograph of DMB-TPE with different f_ws excited at 365 nm (Fig. 7b, inset), it is obvious that visible blue light appeared at f_w of 70 vol% and the light quickly became stronger at f_w of 80 and 90 vol%. This typical AIE effect is attributed to the unique structure of DMB, just like a “spring-like cage” that can more tightly hold loads when shrunken but won’t hamper the rotation of the TPE group in the solution state. This cage effect makes the rotation of TPE moieties more confined in the shrinking DMBs upon addition of water, resulting in a sharp transition of PL intensity at the critical shrinking point (f_w ~ 70 vol% in our case), realizing the AIE effect in this high molecular weight dendritic systems. Moreover, compared with the AIE-effect-featured METPE monomer, the QY of the DMB-TPE is about two times higher (Fig. 7b), indicating that this shrunken cage also exerted an amplifying effect for the AIE fluorophore at aggregation state. This solid-state fluorescent dendritic material guarantees wide applications in functional ink and coating. As a prototype for application, we made a complex pattern (Zhejiang University school badge) by Chinese-brush painting with the ink of DMB-TPE, which emits strong blue light under UV radiation (Fig. 8).
Conclusions

In this work, we presented a sequential RAFT polymerization “grafting from” approach to synthesize multifunctional long-chain dendritic molecular brushes (DMBs). The sparsely branched segmented hyperbranched backbone was firstly synthesized via a SCVP-RAFT approach, which allows the complete immobilization of CTA on the whole scaffold. Subsequent RAFT polymerization on the macro-CTA precursor gave birth to the clickable DMBs with a high molecular weight of /C241.4/C2106 g mol/C01 and low PDI of 1.50. Further azidation on the epoxy ring yielded DMBs with azide/hydroxy hetero-bifunctionality. When conjugated with conventional fluorophores (pyrene) and AIE chromophores (tetraphenylethylene, TPE) respectively, the compact and flexible scaffold of the DMBs showed unique “cage effect” for both fluorophores. The compactness makes pyrene-based DMBs have high intramolecular contact rate and thus exhibit unprecedented strong excimer emission at highly diluted concentration. The flexibility makes TPE-based DMBs have a spring-like scaffold and therefore exhibit typical AIE effect which is precious and rarely found in dendritic systems. Such DMBs were used as printable ink to make a complex pattern that can emit strong blue light at solid state when excited under UV-irradiation. These blue-light fluorescent macromolecules with special structures probably have promising applications in high-resolution solution sensors and solid-state organic electronic devices. This is the first report regarding the strong influence of dendritic brush architecture on the optical behavior of different kinds of chromophores, breaking new ground for design, synthesis, and applications of multifunctional dendritic molecular brushes.

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Notes and references


