Supporting Information

A fluorescent hyperbranched supramolecular polymer based on triple hydrogen bonding interactions

Xin Fu, Qiwei Zhang, Gang Wu, Wei Zhou, Qiao-Chun Wang and Da-Hui Qu*

Experimental section

General: $^1$H NMR and $^{13}$C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The UV-Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell used), respectively. Viscosity measurements were carried out with Ubbelohde microdilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 303 K in dichloromethane. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 303K. AFM images were measured on Solver P47-PRO, NT-MDT. TEM images were recorded on a JEOL JEM-1400 and JEM-2100 apparatus.

Materials: Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures of the unknown compounds were confirmed via $^1$H NMR, $^{13}$C NMR and High Resolution ESI mass spectroscopy.

Synthesis

PBI 1 and PBI 2 has been synthesized according to the procedure described in the literature.1-3

Synthesis of PTDA

6,6',6''-(2,4,6-trimethyl-1,3,5-phenylene)tris-1,3,5-triazine-2,4-diamine 3 has been synthesized according to the previous literature.4, 5

6,6',6''-(2,4,6-trimethyl-1,3,5-phenylene)tris-1,3,5-triazine-2,4-dipivaloyl amide (PTDA)

Compound 3 (0.27 g, 0.6 mmol) was dissolved in 5ml dry pyridine in a Schlenk tube, after stirred at reflux under argon atmosphere for 10 min, pivaloyl chloride (0.87 g, 7.2 mmol) was injected slowly and then stirred for another
3 h. After cooled to room temperature, the reaction mixture was poured into water (50 ml), the resulting suspension was filtered, and the residue was washed with ethanol and hexane to give PTDA (0.31 g, 54 %) as a white solid. $^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ 8.65 (s, 6H), 1.96 (s, 9H), 1.32 (s, 54H). $^{13}$C-NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ 177.81, 176.55, 164.44, 135.94, 133.45, 40.68, 27.10, 17.87. HRMS (ESI) m/z: [M+Na]$^+$ calcd for C$_{48}$H$_{69}$N$_{15}$NaO$_6$ 974.5453, found 974.5483.

**Supplementary Figures**

**Fig. S1** Partial $^1$H NMR spectra of SO (CDCl$_3$, 400 MHz, 298 K) at various concentrations of PBI 2: (a) 0.2, (b) 0.5, (c) 1.0, (d) 2.0, (e) 5.0 and (f) 10.0 mM.

**Fig. S2** Partial $^1$H NMR spectra of HSP (CDCl$_3$, 400 MHz, 298 K) at various concentrations of PBI 1: (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, (e) 2.0, (f) 5.0 and (g) 10.0 mM. ▼ stands for imide N-H of PBI 1, while ■ stands for imide N-H of PTDA.
**Fig. S3** UV-vis absorption spectra of a) PBI 1·PTDA (3 : 2 in molar ratio) and b) PBI 1, in dichloromethane at different concentrations.

**Fig. S4** Molar extinction coefficient compare of PBI 1·PTDA complexes and pure PBI 1 at 579nm.
Fig. S5 Fluorescence spectra of PBI 1 (5 × 10⁻⁵ M, black) and supramolecular copolymers HSP formed by the 3:2 complexation of PBI 1 · PTDA ([PBI 1] = 5 × 10⁻⁵ M, red).

Reference

$^1$H NMR spectrum of PTDA

$^{13}$C NMR spectrum of PTDA
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotopes peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
216 formulas evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0.48  H: 0.70  N: 0.16  O: 0.6  Na: 0.1

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>FMM</th>
<th>DEB</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>974.543</td>
<td>974.543</td>
<td>5.0</td>
<td>3.1</td>
<td>15.5</td>
<td>21.4</td>
<td>0.0</td>
<td>C48 H68 N15 O6 Na</td>
</tr>
</tbody>
</table>

ESI-Mass spectrum of PTDA