Supplementary Information

Effect of branching architecture on the optical properties of polyazomethines

Hongping Deng,[a] Bangshang Zhu,*[a] Liang Song,[b] Chunlai Tu,[b] Feng Qiu,[b] Yunfeng Shi,[b] Dali Wang,[b] Lijuan Zhu[b] and Xinyuan Zhu[ab]

[a] *Instrumental Analysis Center, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R.*

China.

[b] *School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai*

Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China.
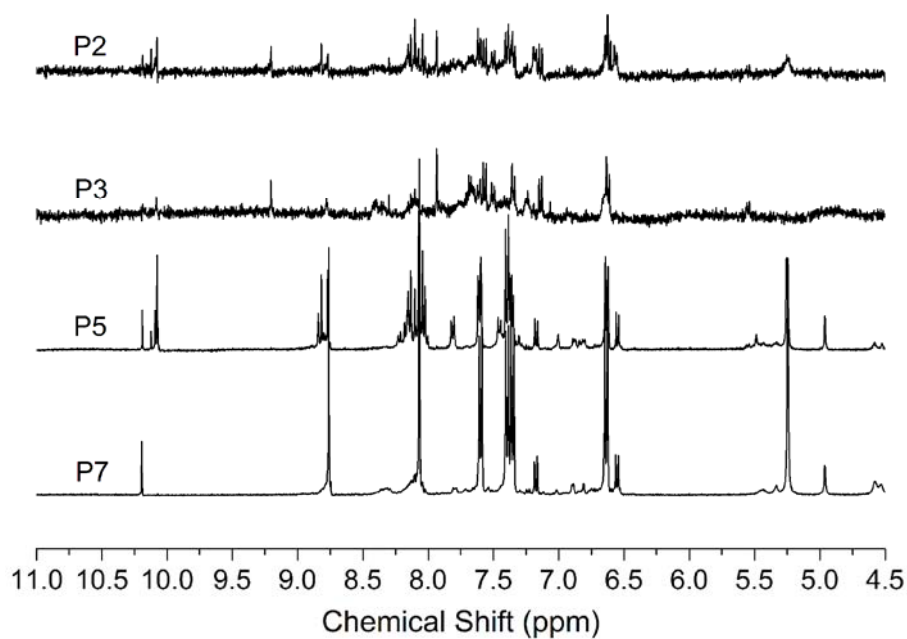
S1. Nuclear magnetic resonance (NMR)

Fig. S1 ^{1}H NMR spectra of P2, P3, P5 and P7 (400 MHz, in DMSO-d_6, 298 K).

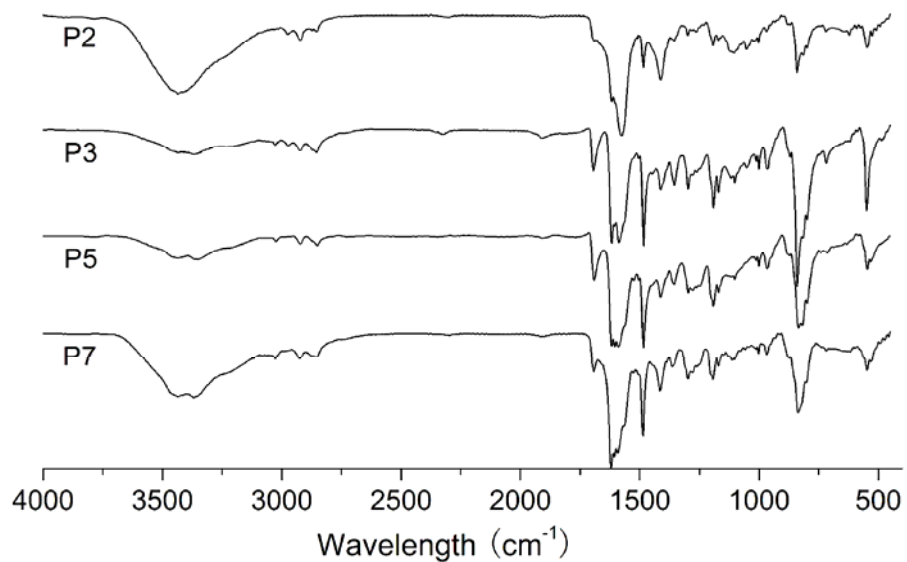## S2. Fourier transform infrared spectroscopy (FT-IR)

Fig. S2 The FT-IR spectra of P2, P3, P5 and P7.

Figures S1 and S2 present the ^{1}H NMR and FT-IR spectra of other samples, P2, P3, P5 and P7, respectively. The results are listed below:

P2: an orange powder, yield=58%; IR (KBr): 3436 (NH_2), 2974, 2922, 2854 (CH), 1891 (C=O), 1619 (CH=N), 1575, 1485, 1412 (phenyl), 1299 (Ph-N), 1196 (Ph-N=), 969, 841 (CH), 548 (Ph) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ=10.0-10.1 (m, CH=O), 8.8-9.2 (m, CH=N), 6.6-8.6 (m, phenyl), 4.1-5.3 (m, NH_2).

P3: an orange powder, yield=51%; IR (KBr): 3435, 3369 (NH_2), 3028, 2973, 2923, 2872 (CH), 1908 (C=O), 1694, 1617 (CH=N), 1588, 1484, 1413 (phenyl), 1298 (Ph-N), 1191 (Ph-N=), 965, 840 (CH), 550 (Ph) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ=10.1-10.2 (m, CH=O), 8.8-9.2 (m, CH=N), 6.7-8.3 (m, phenyl), 4.1-5.5 (m, NH_2).

P5: an red powder, yield=49%; IR (KBr): 3436, 3352 (NH_2), 3025, 2922, 2851 (CH), 1907 (C=O), 1692, 1618 (CH=N), 1590, 1484, 1413 (phenyl), 1297 (Ph-N), 1192 (Ph-N=), 966, 834 (CH), 547 (Ph) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ=10.1-10.2 (m, CH=O), 8.8-8.9 (m, CH=N), 6.5-8.2 (m, phenyl), 4.1-5.5 (m, NH_2).

P7: an red powder, yield=62%; IR (KBr): 3436, 3369 (NH_2), 3027, 2926, 2854 (CH), 1901 (C=O), 1692, 1620 (CH=N), 1592, 1486, 1415 (phenyl), 1298 (Ph-N), 1193 (Ph-N=), 968, 836 (CH), 548 (Ph) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ=10.1-10.2 (m, CH=O), 8.7-8.8 (m, CH=N), 6.5-8.4 (m, phenyl), 4.1-5.4 (m, NH_2).

Figure S3 shows the structure units of all PAs including linear, branched and terminal units, respectively, which is useful for the calculation of DB. The method for the calculation of PAs' DB is the same as previously reported work.[13a] Figure S4 gives the stoichiometry calculation of P8 as an example.
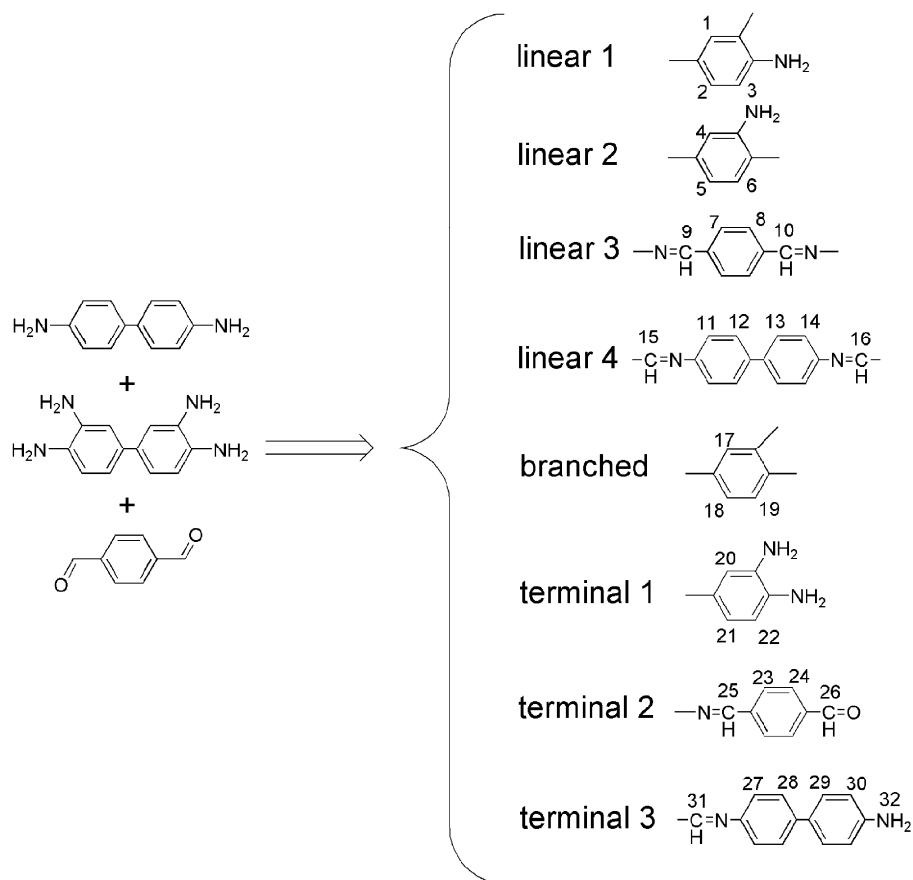

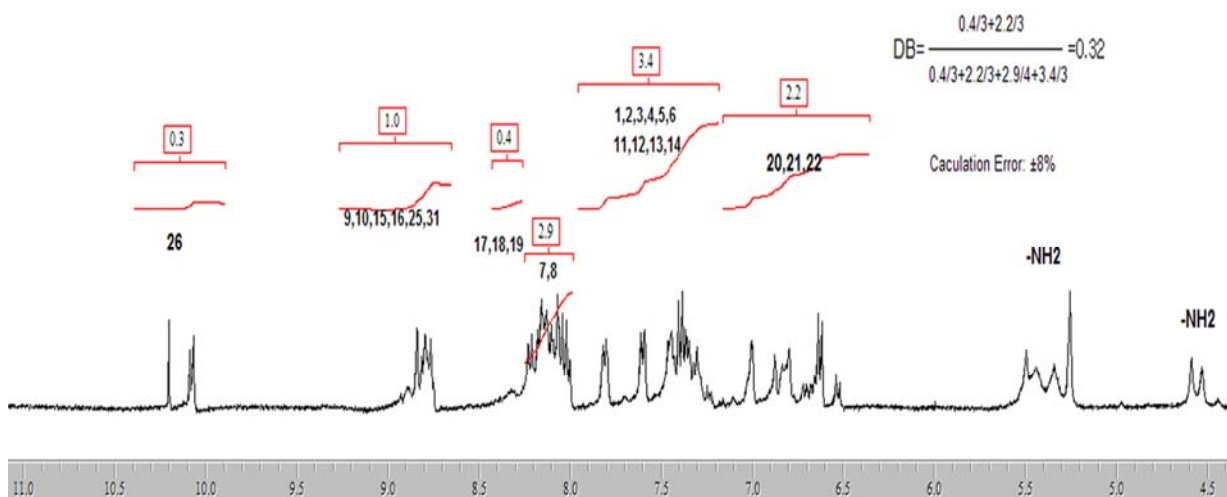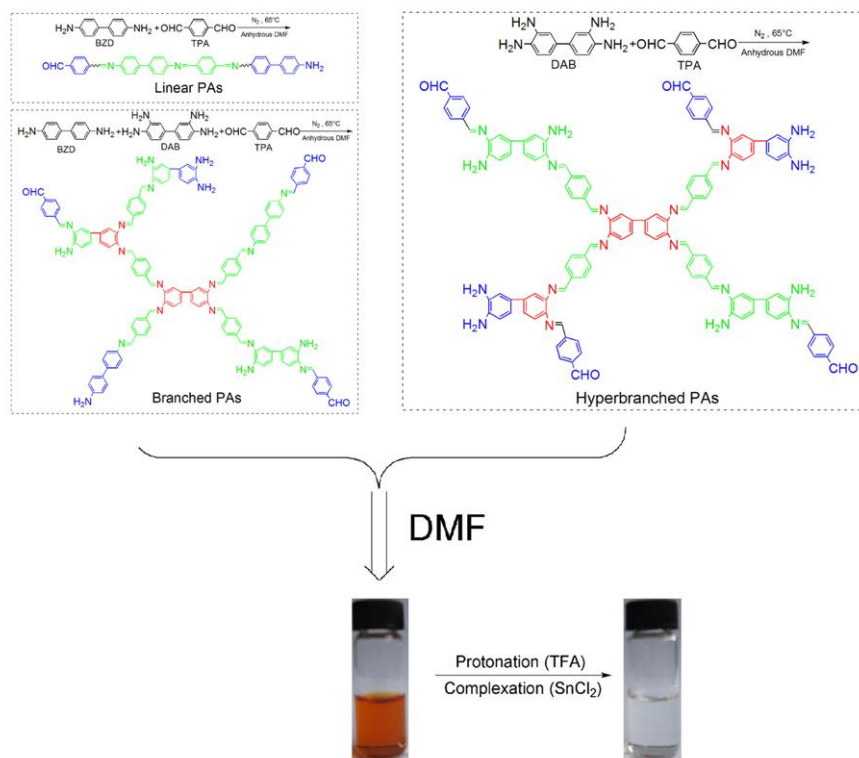**Fig. S3** Structure units of linear and branched PAs.

Fig. S4 Stoichiometry calculation of P8.

Scheme S1 gives the synthetic route of PAs with different DBs. After dissolving in DMF, the solution shows red or brown. With the addition of TFA or SnCl$_2$, the color changes due to the protonation or complexation with stannum ions.

Scheme S1. Picture shows the color change after the complexation of polyazomethine with SnCl$_2$ and/or protonation with TFA.

Figure S5 presents the ^{1}H NMR spectra of sample P9 after adding different doses of TFA. When adding a small amount of TFA (a), all signals at about 6.5-9.0 ppm are detected and the ^{1}H NMR spectrum is almost unchanged with time. On the other hand, when a large amount of TFA is added (b), the ^{1}H NMR spectrum changes greatly and many signals disappear. The ^{1}H NMR observations confirm that no degradation of the polymer happens in our experiment condition.
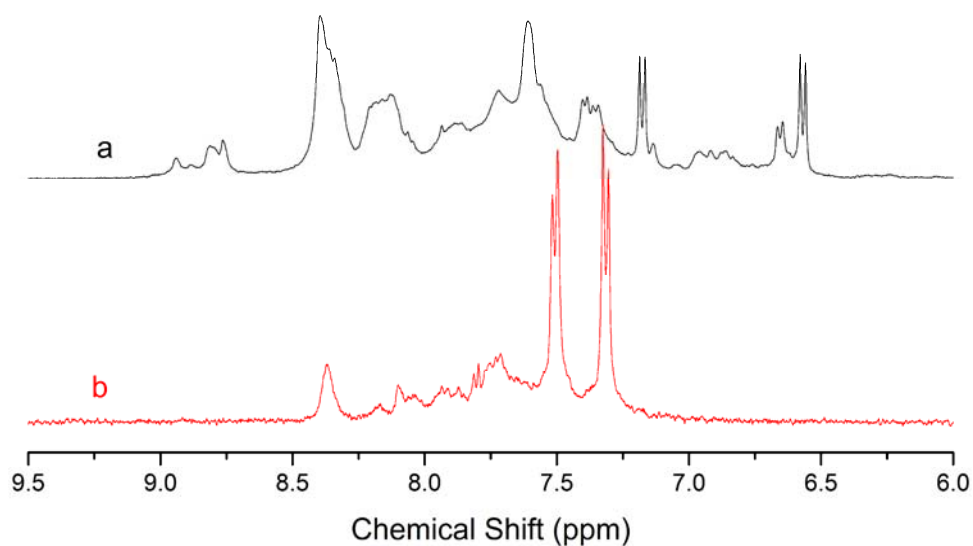

Fig. S5 ^{1}H NMR spectra of P9 after adding different doses of TFA: (a) 1 uL; (b) 50 uL.