# Supporting Information

## Morphology Control and Property Design of Boronate Dynamic Nanostructures

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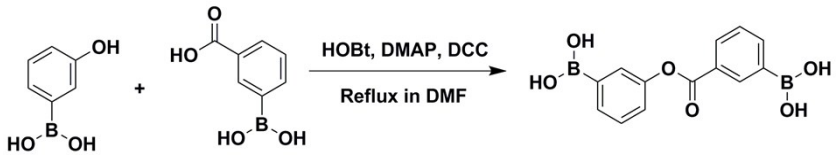
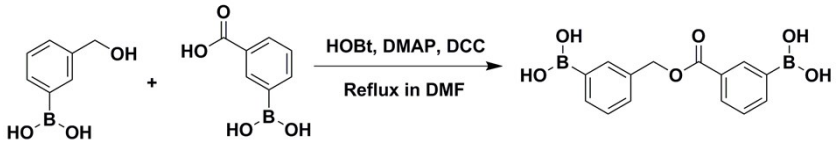
# 1. Synthetic Procedures

## 1.1 Synthesis of Ester-Linked Diboronic Acid Monomers PBA-$E_n$ (n = 1, 2, 5 and 6)

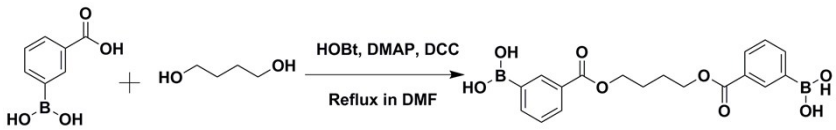



**Scheme S1.** Synthetic route of PBA-$E_1$




**Scheme S2.** Synthetic route of PBA-$E_2$


**Scheme S3.** Synthetic route of PBA-$E_5$



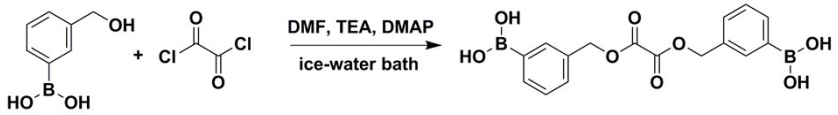

**Scheme S4.** Synthetic route of PBA-$E_6$

The synthetic routes of PBA-$E_n$, n = 1, 2, 5 and 6 are shown in **Scheme S1~S4**, referred to Mothana's work.[1] Taking PBA-$E_1$ as example, (3-carboxyl phenyl)boronic acid (4 mmol, 664 mg), (3-hydroxyl phenyl)boronic acid (1 mmol, 138 mg), HOBt (4 mmol, 541 mg) and DMAP (4 mmol, 489 mg) were dissolved in *N*,*N*-dimethylformamide (DMF, 5 mL) and stirred for 0.5 h at room temperature. And then, DCC (4 mmol, 825 mg) was added and the mixture was stirred at 80 °C for 5 h. After that, the mixture was removed to room temperature and stirred overnight. The precipitate was removed by filtration and the filtrate was drop in cold distilled water (50 mL). The off-white powders would be precipitated from the solution and collected by filtration. To further increase the purity, the crude products were dissolved in methanol and precipitated from cold water for twice. PBA-$E_2$, PBA-$E_5$ and PBA-$E_6$ were prepared as the same way except that (3-hydroxyl phenyl)boronic acid (1 mmol) was replaced by (3-

hydroxymethyl phenyl)boronic acid (1 mmol, 152 mg), glycol (0.5 mmol, 31 mg) and butanediol (0.5 mmol, 45 mg), respectively.

$^1$H-NMR spectra of PBA-$E_n$ (n = 1, 2, 5 and 6) are given in **Fig. S1**, **S2**, **S5** and **S6,** respectively.

### 1.2 Synthesis of Ester-Linked Diboronic Acid Monomer PBA-$E_3$

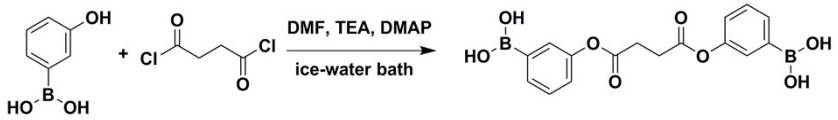



**Scheme S5.** Synthetic route of PBA-$E_3$

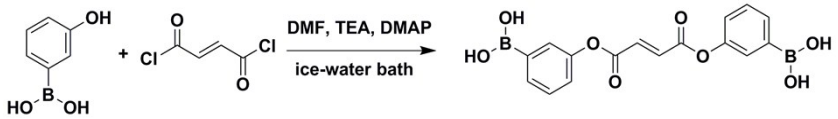
As shown in **Scheme S5**, (3-hydroxymethyl phenyl)boronic acid (6 mmol, 912 mg), triethylamine (TEA, 6 mmol, 832 μL) and DMAP (0.04 mmol, 5 mg) was dissolved in DMF (5 mL) and cooled with an ice-water bath. Ethanedioyl chloride (2 mmol, 254 mg) was dissolved in tetrahydrofuran (THF, 3 mL) and dropped in the above solution for 20 min. After stirred overnight at room temperature, the resulting mixture was dropped into water and left undisturbed under 4 °C for 6 hours. The crude products would be collected by filtration and purified as same as PBA-$E_1$.

$^1$H-NMR spectrum of PBA-$E_3$ is given in **Fig. S3.**

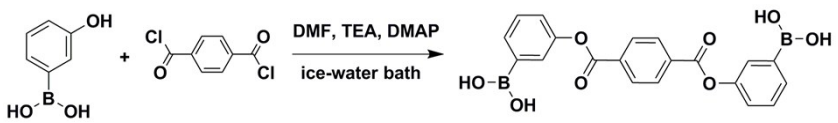
### 1.3 Synthesis of Ester-Linked Diboronic Acid Monomers PBA-$E_n$ (n = 4, 7 and 8)




**Scheme S6.** Synthetic route of PBA-$E_4$




**Scheme S7.** Synthetic route of PBA-$E_7$

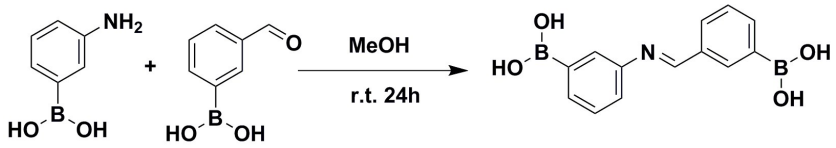



**Scheme S8.** Synthetic route of PBA-$E_8$

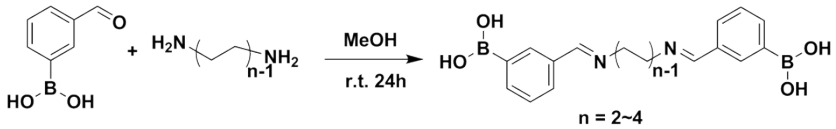
The synthetic routes of PBA-$E_n$ (n=4, 7 and 8) are given in **Scheme S6~S8,** respectively. Briefly, (3-hydroxyl phenyl)boronic acid (6 mmol, 828 mg), TEA (6 mmol, 832 μL) and DMAP (0.04 mmol, 5 mg) was dissolved in DMF. And butanedioyl chloride (2 mmol), trans-2-butenedioyl dichloride (2 mmol) or 1,4-benzenedicarbonyl chloride (2 mmol) was added with THF into the above solution cooling with an ice-water bath. And then, the mixture was stirred overnight. Separation and purification steps were as same as those of PBA-$E_3$.

$^1$H-NMR spectra of PBA-$E_n$ (n = 4, 7 and 8) are given in **Fig. S4, S7,** and **S8**, respectively.

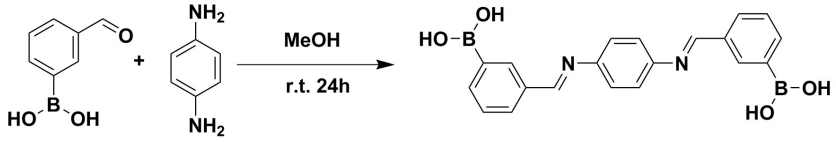
### 1.4 Synthesis of Imide-Linked Diboronic Acid Monomers PBA-$I_n$ (n = 1~6)



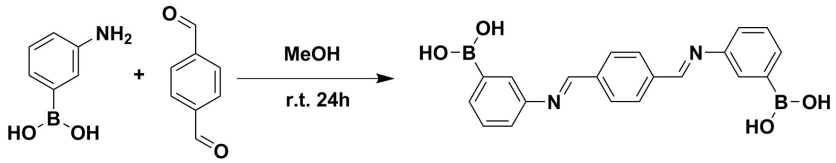

**Scheme S9.** Synthetic route of PBA-$I_1$




**Scheme S10.** Synthetic route of PBA-$I_n$ (n=2~4)




**Scheme S11.** Synthetic route of PBA-$I_5$



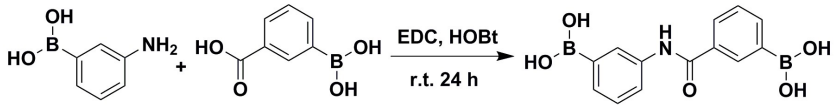

**Scheme S12.** Synthetic route of PBA-$I_6$

The synthetic routes of PBA-$I_n$ (n = 1~6) are shown in **Scheme S9~S12**, which are according to Thayumanavan's work.[2] For PBA-$I_1$, (3-formyl phenyl)boronic acid (8 mmol, 1.20 g) was dissolved in methanol (3 mL), and (3-amino phenyl)boronic acid (8 mmol, 1.10 g) was dissolved in another 3 mL

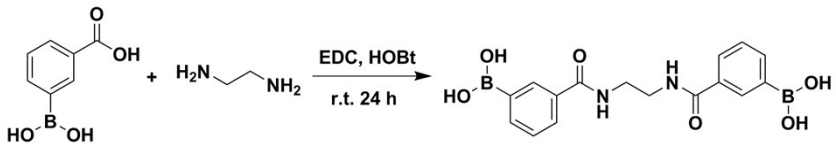
methanol. And then, the two solutions were mixed and stirred for 24 h at room temperature. The products could be collected by centrifugation and washed with cool methanol. PBA-$I_n$ (n = 2~5) were prepared as the same way but (3-amino phenyl)boronic acid was replaced by alkane diamine or 1,4-phenylenediamine (4 mmol). PBA-$I_6$ was synthesized by the reaction between (3-amino phenyl)boronic acid and 1,4-phthalaldehyde with the same method.

$^1$H-NMR spectra of PBA-$I_n$ (n = 1~6) are given in **Fig. S9~S14**, respectively.

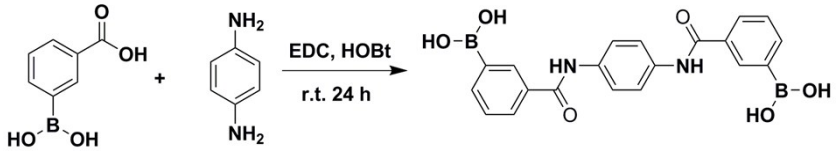
### 1.5 Synthesis of Amide-Linked Diboronic Acid Monomers PBA-$A_n$ (n = 1, 10 and 13)




**Scheme S13.** Synthetic route of PBA-$A_1$




**Scheme S14.** Synthetic route of PBA-$A_{10}$

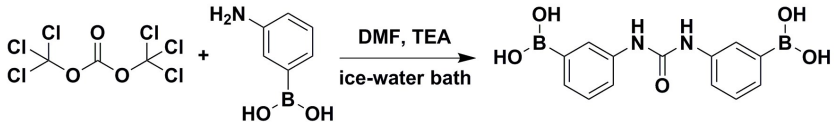



**Scheme S15.** Synthetic route of PBA-$A_{13}$

The synthetic routes of PBA-$A_n$ (n = 1, 10 and 13) are shown in **Scheme S13~S15**. Normally, 3-carboxyphenylboronic acid (10 mmol, 1.57 g), EDC (12 mmol, 2.30 g) and HOBt (8 mmol, 1.08 g) were dissolved in DMF (16 mL) and activated in room temperature for 0.5 h. And then, (3-amino phenyl)boronic acid (8 mmol), alkane diamine (4 mmol) or 1,4-phenylenediamine (4 mmol) was dissolved in DMF (4 mL). The two solutions were mixed and stirred at room temperature. After 24 h, the mixtures were dropped in distilled water (140 mL) and crude products could be collected by filtration. Through dissolved in DMF and precipitated from water for twice, white products were prepared after drying in vacuum.

$^1$H-NMR spectra of PBA-$A_n$ (n = 1, 10 and 13) are given in **Fig. S15, S24** and **S27**, respectively.

### 1.6 Synthesis of Amide-Linked Diboronic Acid Monomer PBA-$A_2$

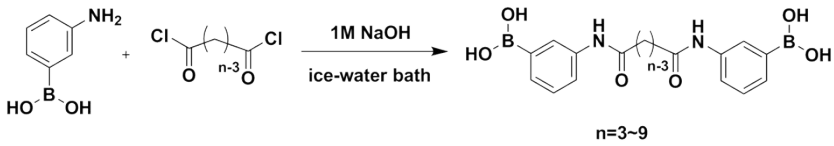



**Scheme S16.** Synthetic route of PBA-$A_2$

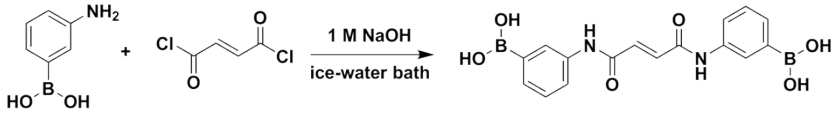
PBA-$A_2$ was synthesized as **Scheme S16** showing. 3-aminophenylboronic acid (9 mmol, 1.23 g) was dissolved in DMF (10 mL) with TEA (2.5 mL) and cooled with ice-water bath. Then, triphosgene (1.5 mmol, 0.45 g) was dissolved in THF (5 mL) and added dropwise into the above mixture. The ice-water bath was removed after 1 h and the mixture was stirred overnight at room temperature. The crude products could be collected after dropping the mixture into 0.1 M HCl (100 mL) and filtration. Through dissolved in DMF and precipitated from 0.1 M HCl for twice, bright brown crystals were ready after filtration and vacuum drying.

$^1$H-NMR spectrum of PBA-$A_2$ is shown in **Fig. S16**.

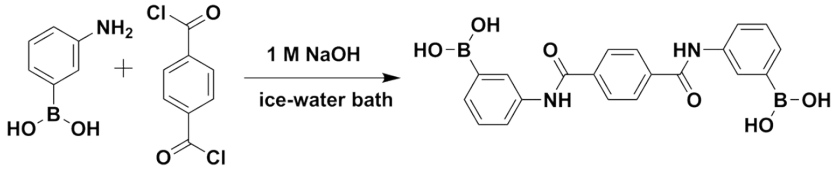
### 1.7 Synthesis of Amide-Linked Diboronic Acid Monomers PBA-$A_n$ (n = 3~9, 11 and 12)




**Scheme S17.** Synthetic route of PBA-$A_n$ (n = 3~9)




**Scheme S18.** Synthetic route of PBA-$A_{11}$




**Scheme S19.** Synthetic route of PBA-$A_{12}$

The synthetic routes of PBA-$A_n$ (n = 3~9, 11 and 12) are given in **Scheme S17~S19**, which refers to our previous work.[3] Briefly, 3-aminophenylboronic acid (9 mmol, 1.23 g) was dissolved in NaOH

aqueous solution (1 M, 12 mL) and cooled down with an ice-water bath. alkane dioyl chloride, trans-2-butenedioyl dichloride or 1,4-benzenedicarbonyl chloride (3 mmol) was added by drop with THF (3 mL). After stirred overnight, the crude products could be collected by filtration. Light brown or off-white products were prepared after recrystallization from water.

$^1$H-NMR spectra of PBA-$A_n$ (n = 3~9, 11 and 12) are given in **Fig. S17~S23, S25** and **S26**, respectively.

## 2. [1]H-NMR Spectra of Duplex Boronic Acid-Contained Molecules

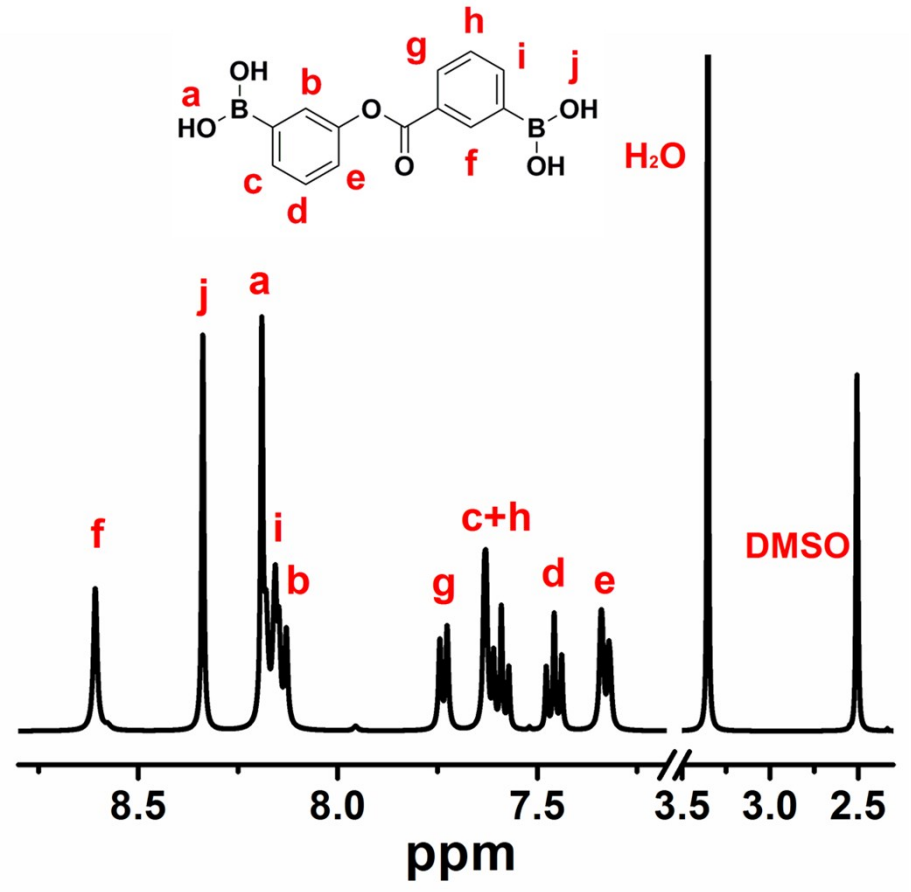



**Fig. S1.** [1]H-NMR spectrum of PBA-$E_1$.

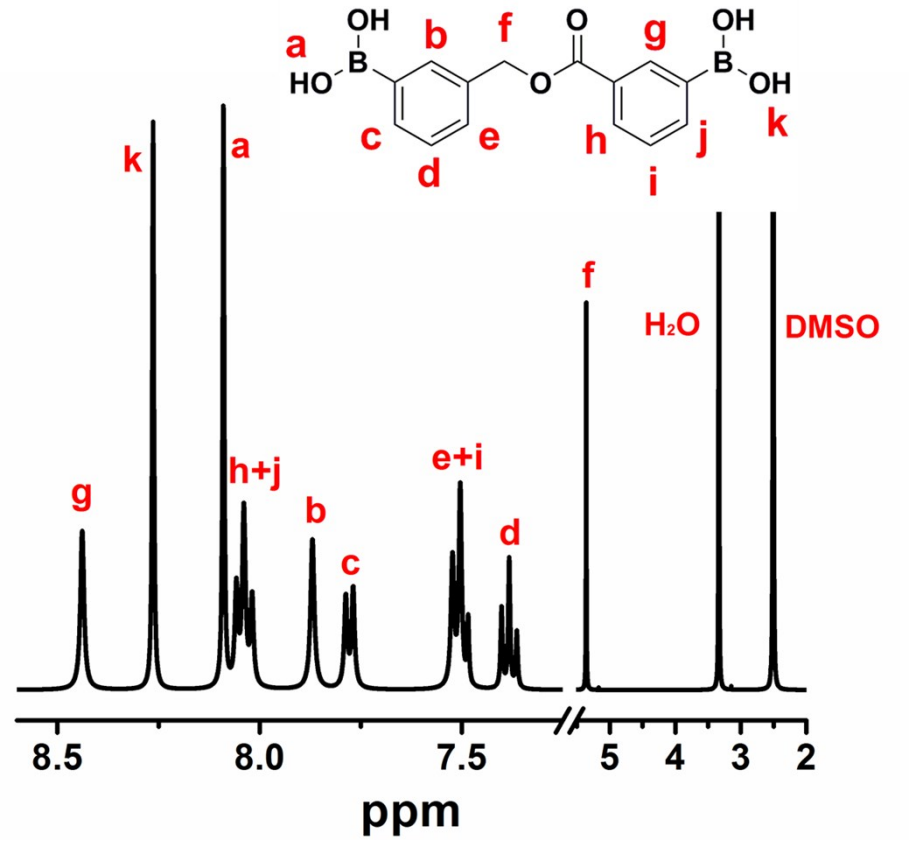



**Fig. S2.** $^{1}$H-NMR spectrum of PBA-$E_2$.

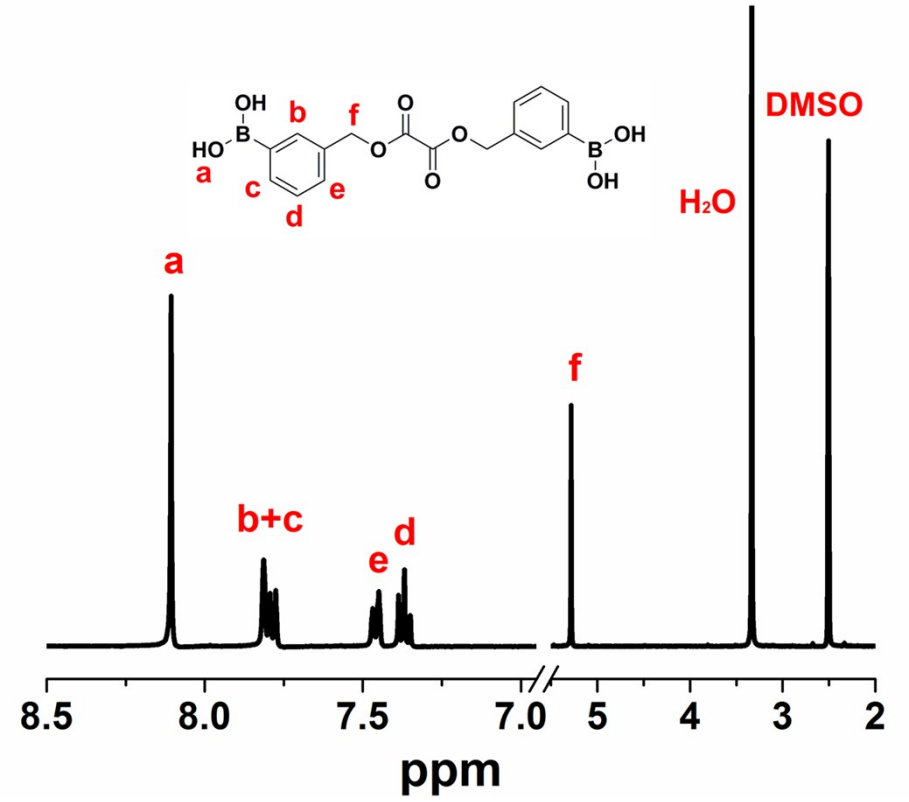



**Fig. S3.** $^{1}$H-NMR spectrum of PBA-$E_3$.

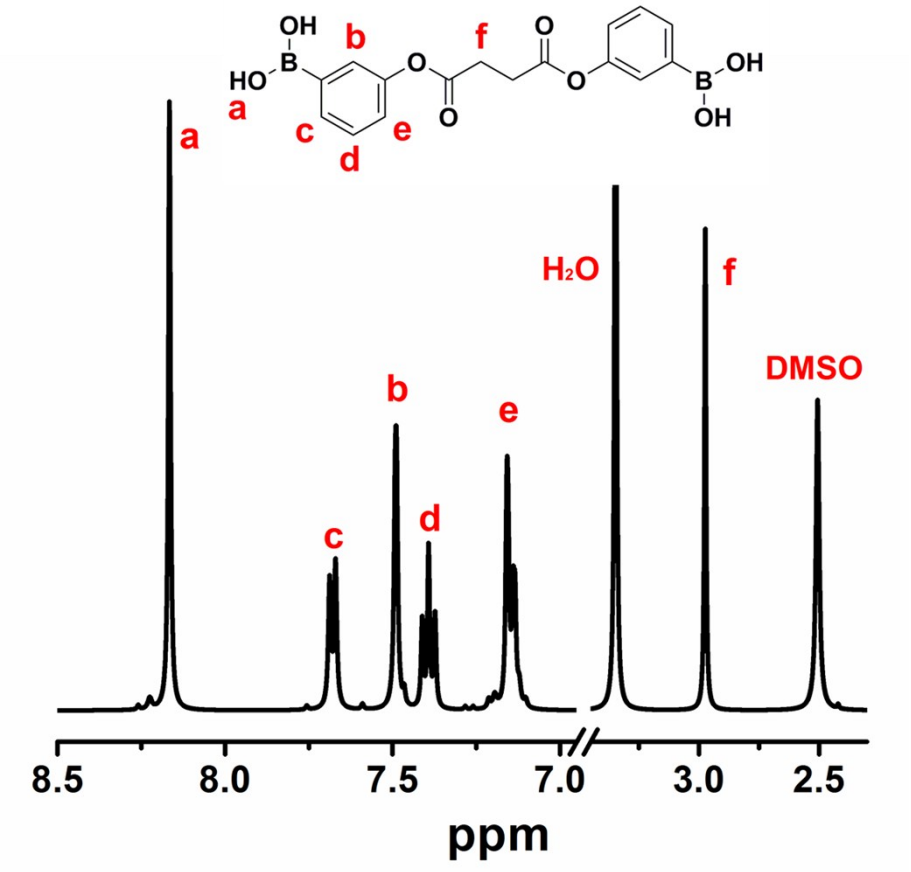



**Fig. S4.** $^{1}$H-NMR spectrum of PBA-$E_4$.

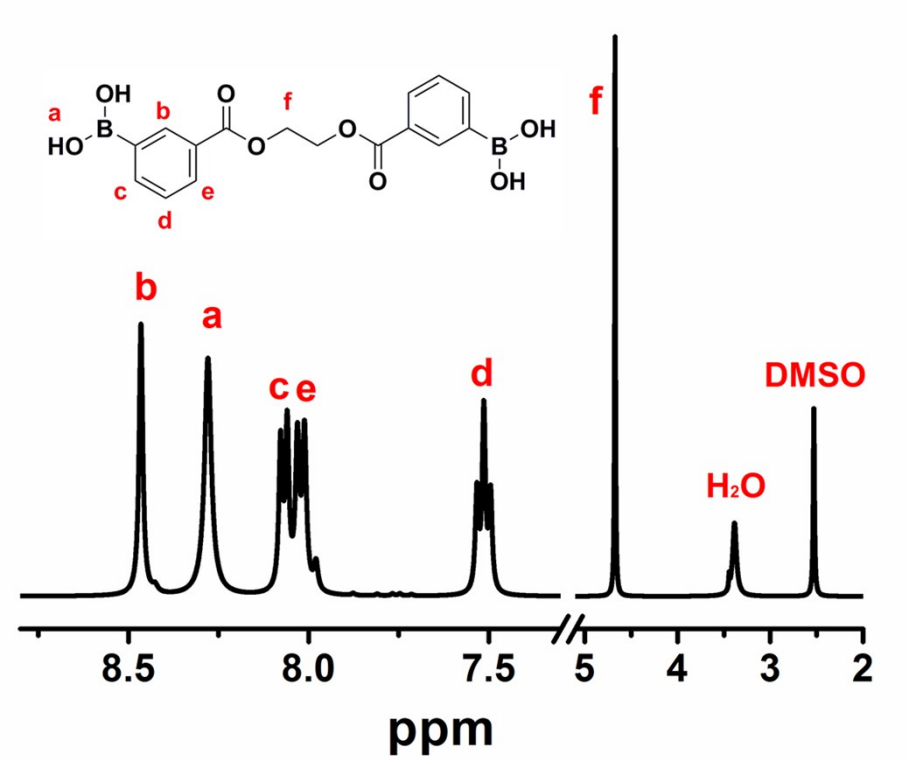



**Fig. S5.** $^{1}$H-NMR spectrum of PBA-$E_5$.

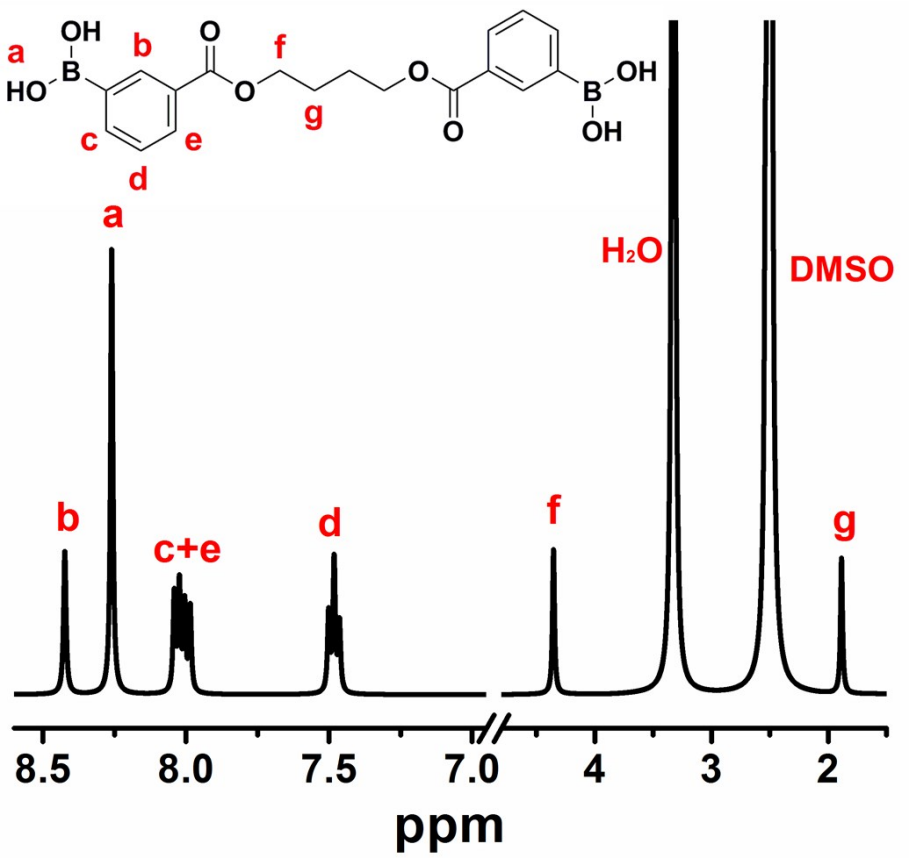



**Fig. S6.** $^{1}$H-NMR spectrum of PBA-$E_6$.

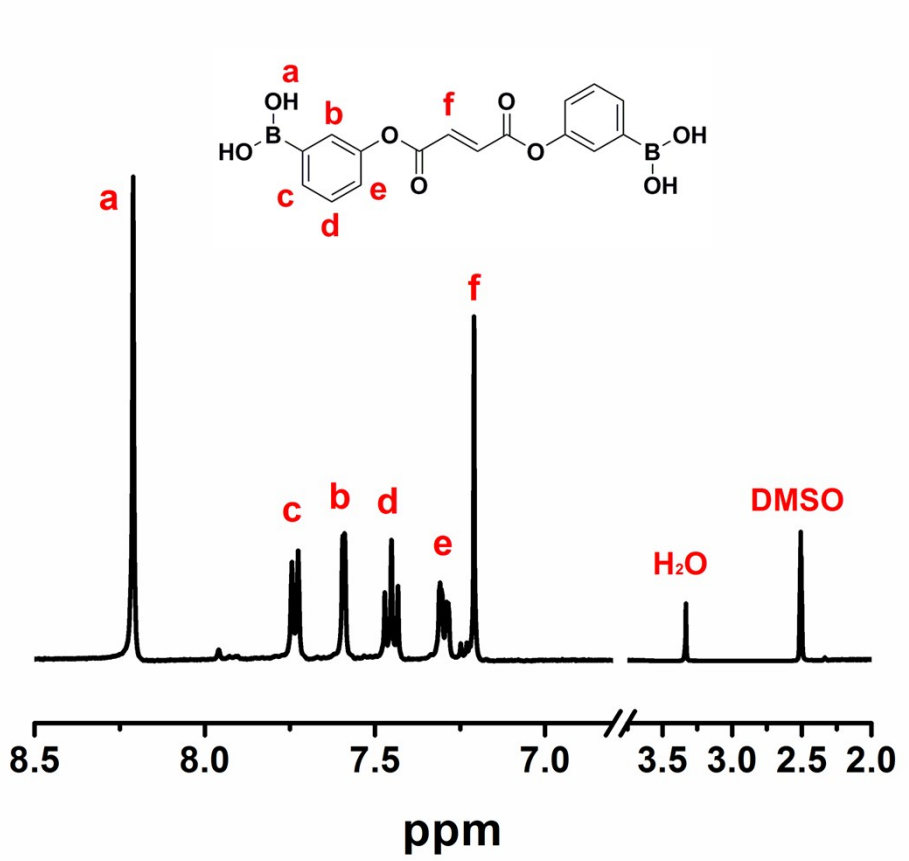



**Fig. S7.** $^{1}$H-NMR spectrum of PBA-$E_7$.

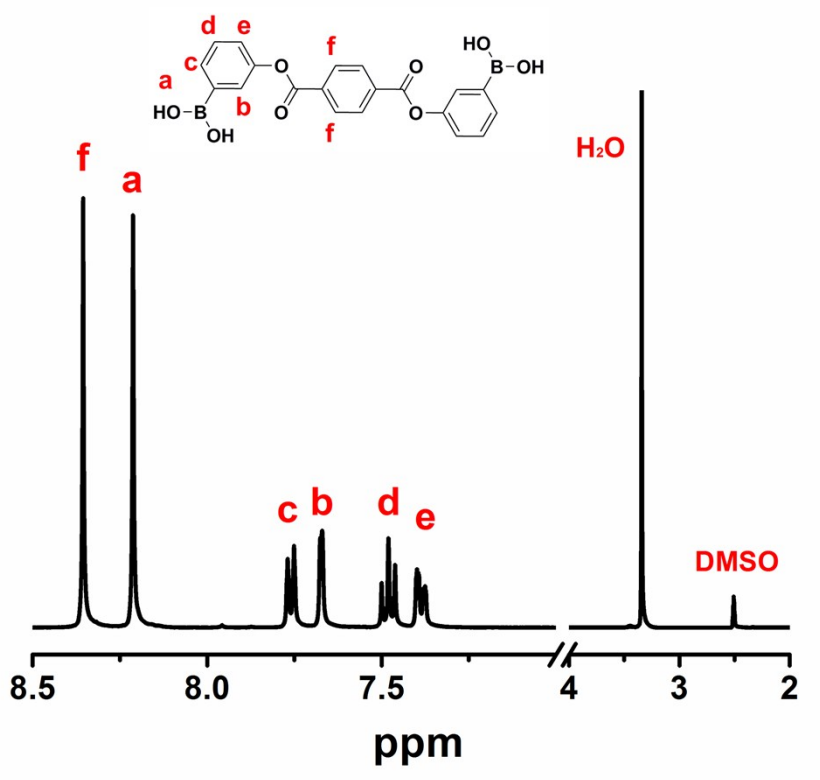



**Fig. S8.** $^{1}$H-NMR spectrum of PBA-$E_8$.

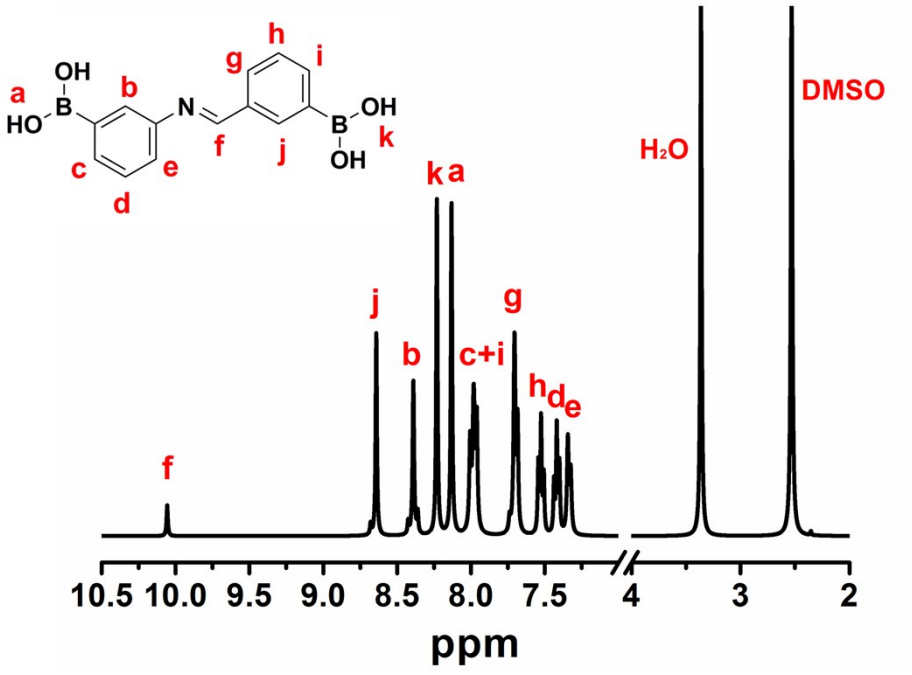



**Fig. S9.** $^{1}$H-NMR spectrum of PBA-$I_1$.

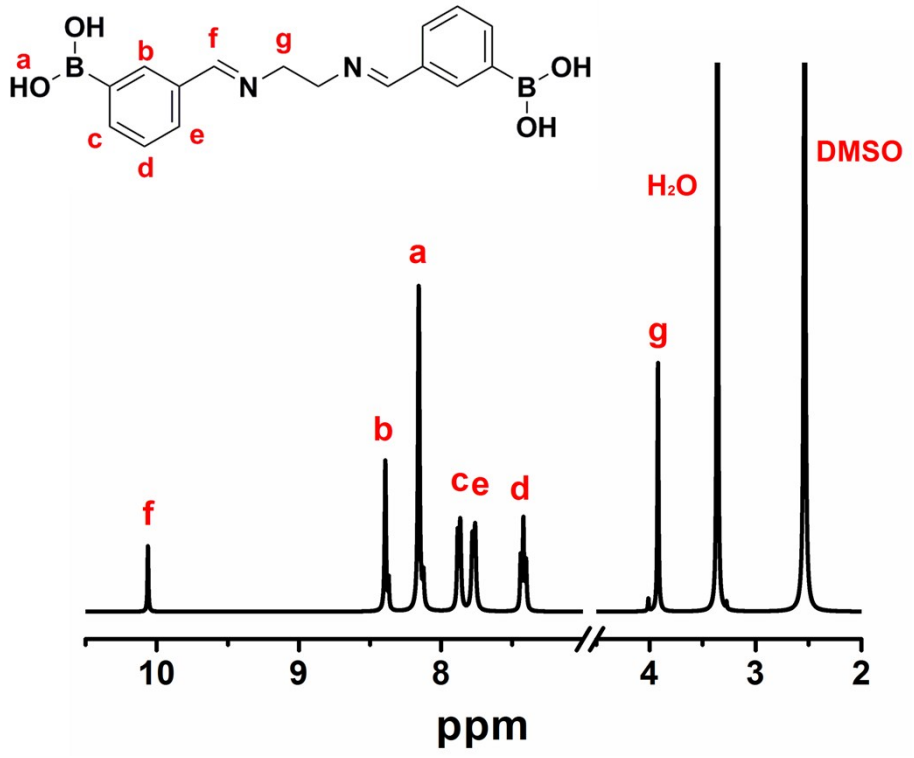



**Fig. S10.** $^{1}$H-NMR spectrum of PBA-$I_2$.

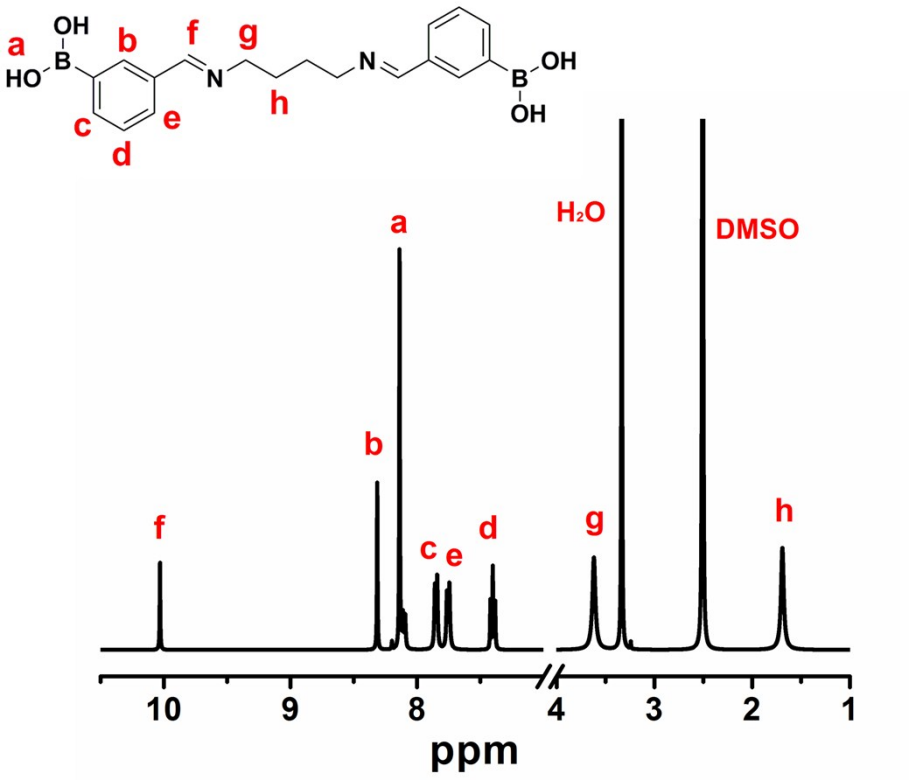



**Fig. S11.** $^{1}$H-NMR spectrum of PBA-$I_3$.

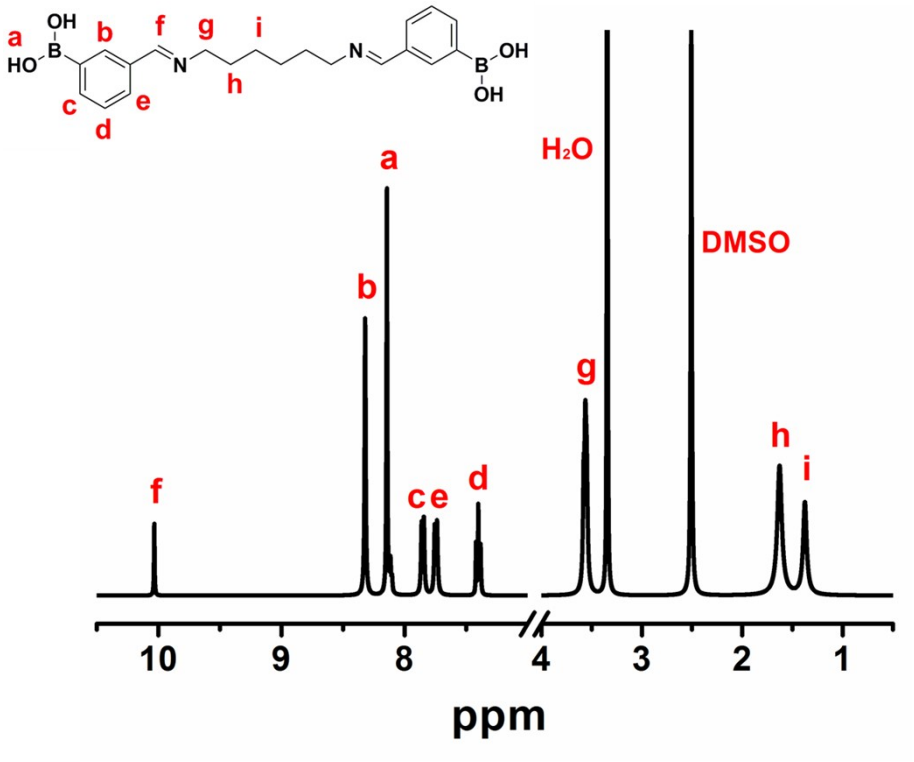



**Fig. S12.** $^{1}$H-NMR spectrum of PBA-$I_4$.

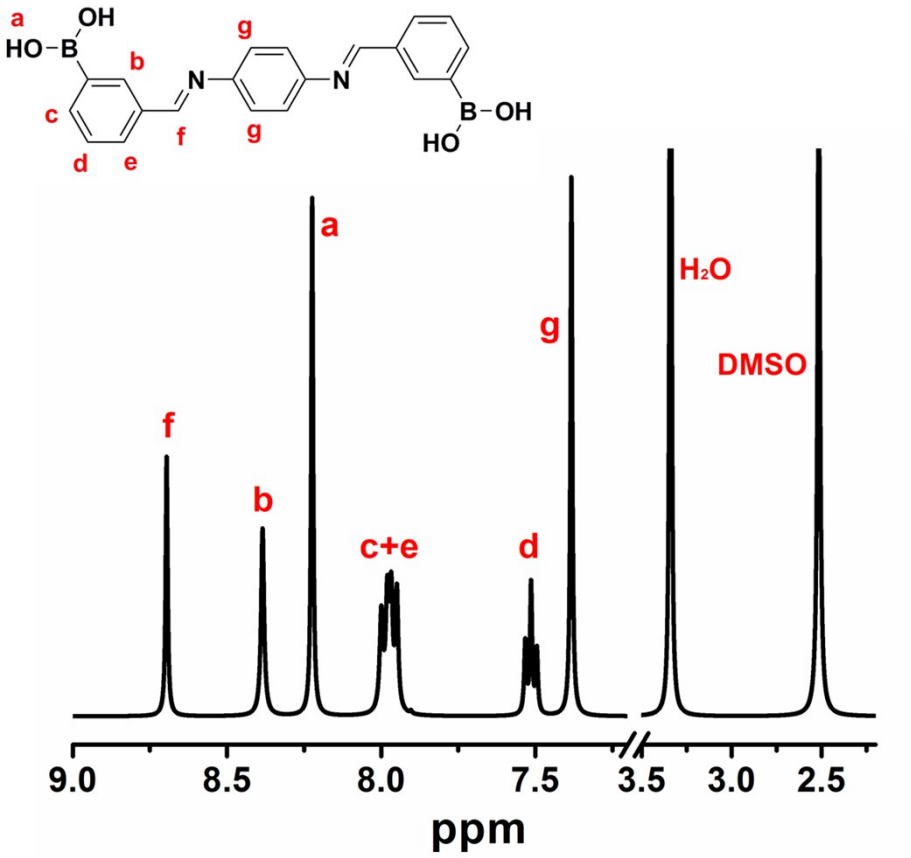



**Fig. S13.** $^{1}$H-NMR spectrum of PBA-$I_5$.

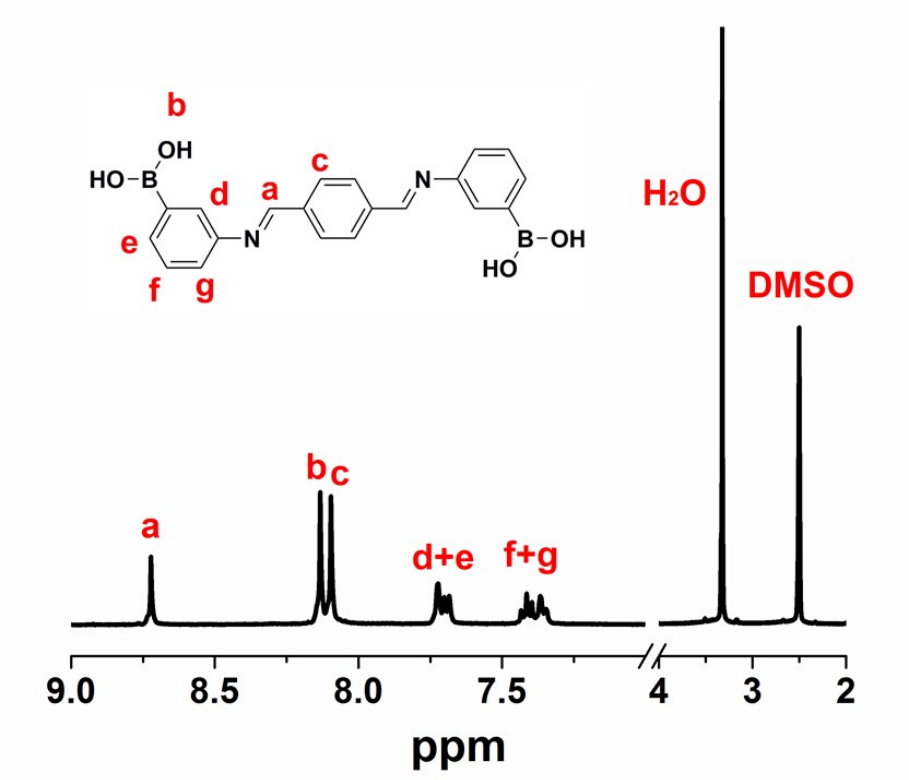



**Fig. S14.** $^{1}$H-NMR spectrum of PBA-$I_6$.

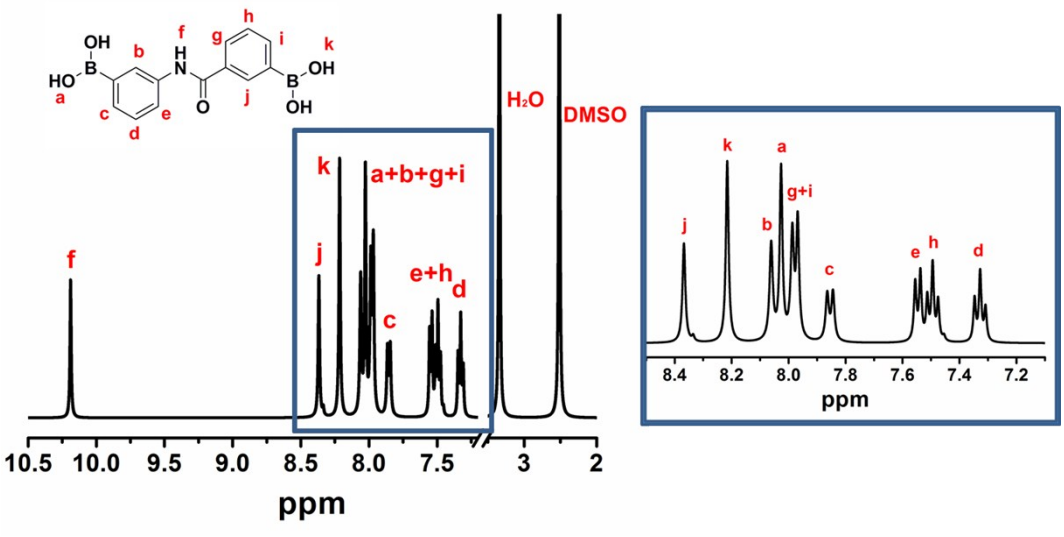



**Fig. S15.** $^{1}$H-NMR spectrum of PBA-$A_1$.

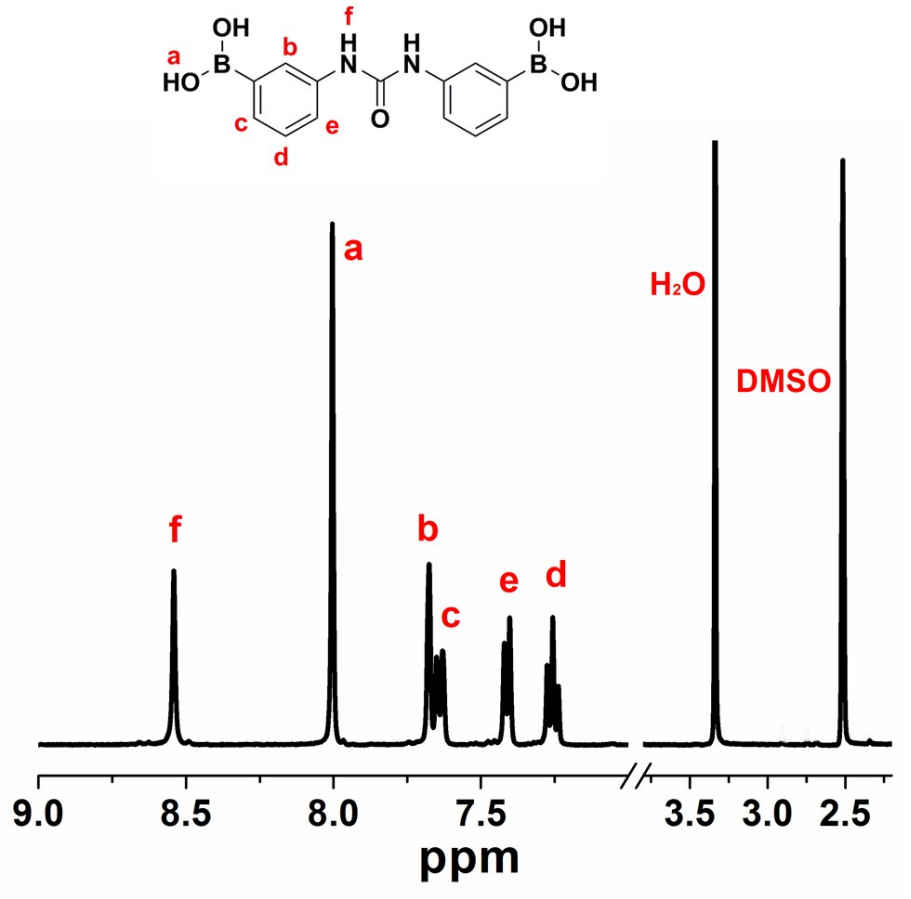



**Fig. S16.** $^{1}$H-NMR spectrum of PBA-$A_2$.

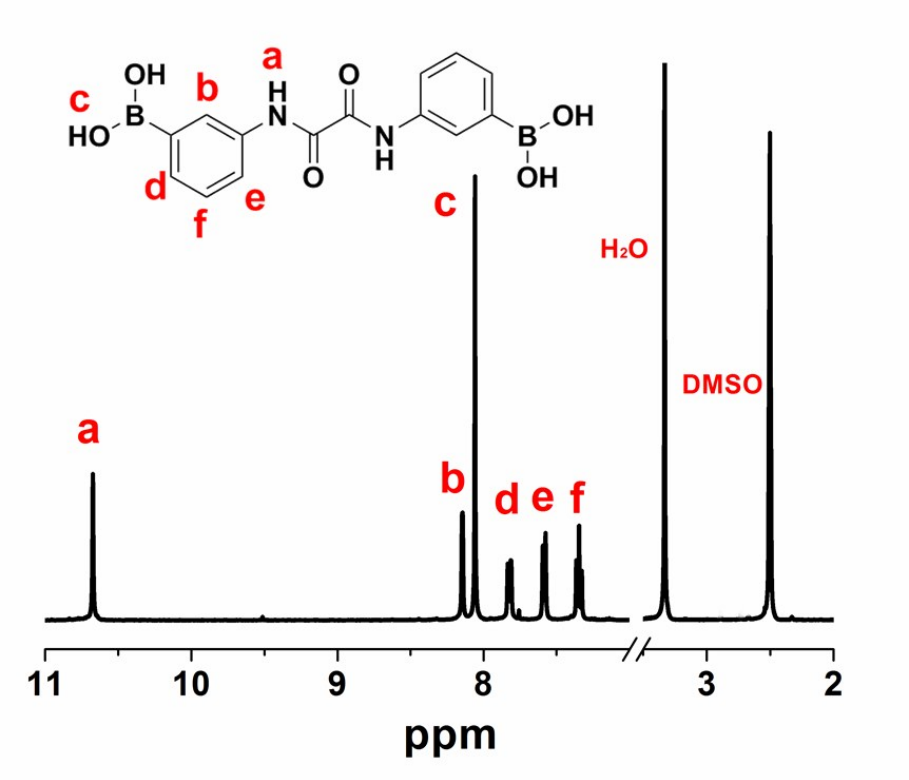



**Fig. S17.** $^{1}$H-NMR spectrum of PBA-$A_3$.

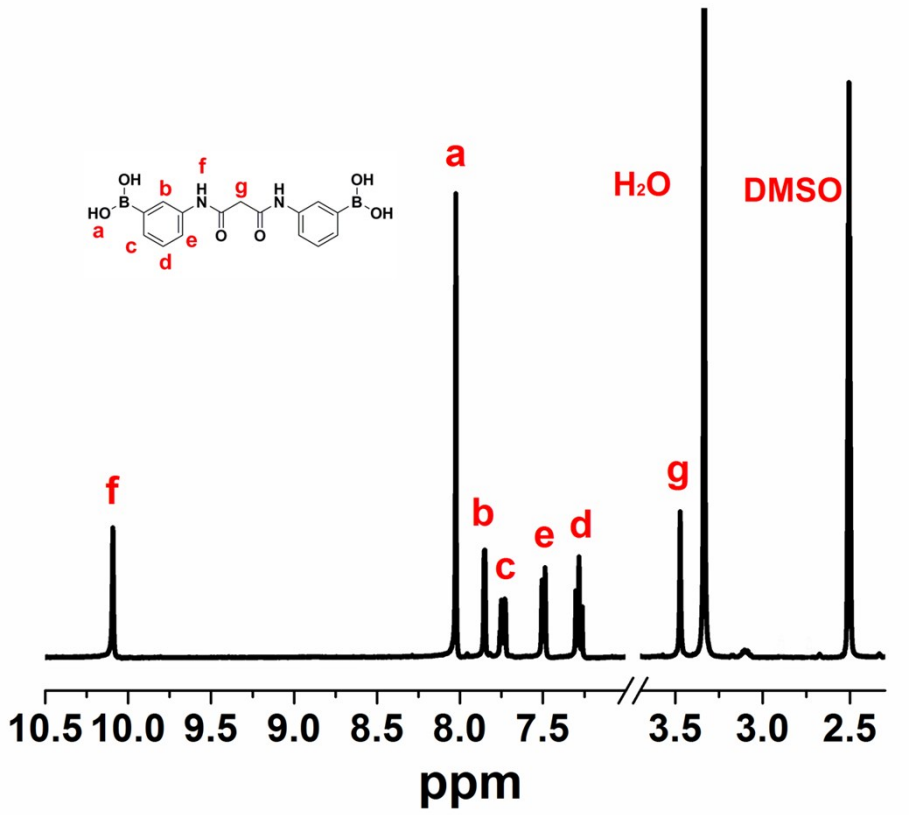



**Fig. S18.** $^{1}$H-NMR spectrum of PBA-$A_4$.

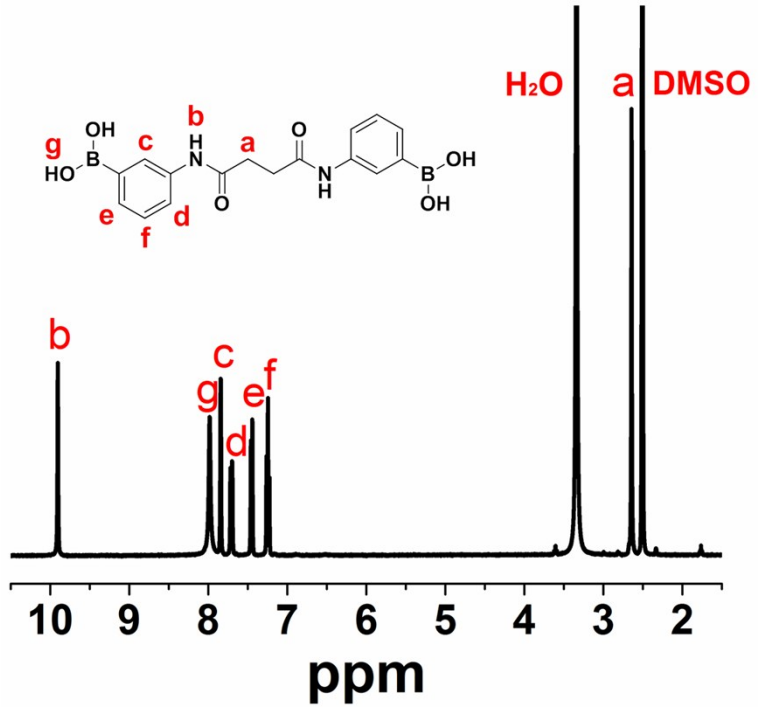



**Fig. S19.** $^{1}$H-NMR spectrum of PBA-$A_5$.

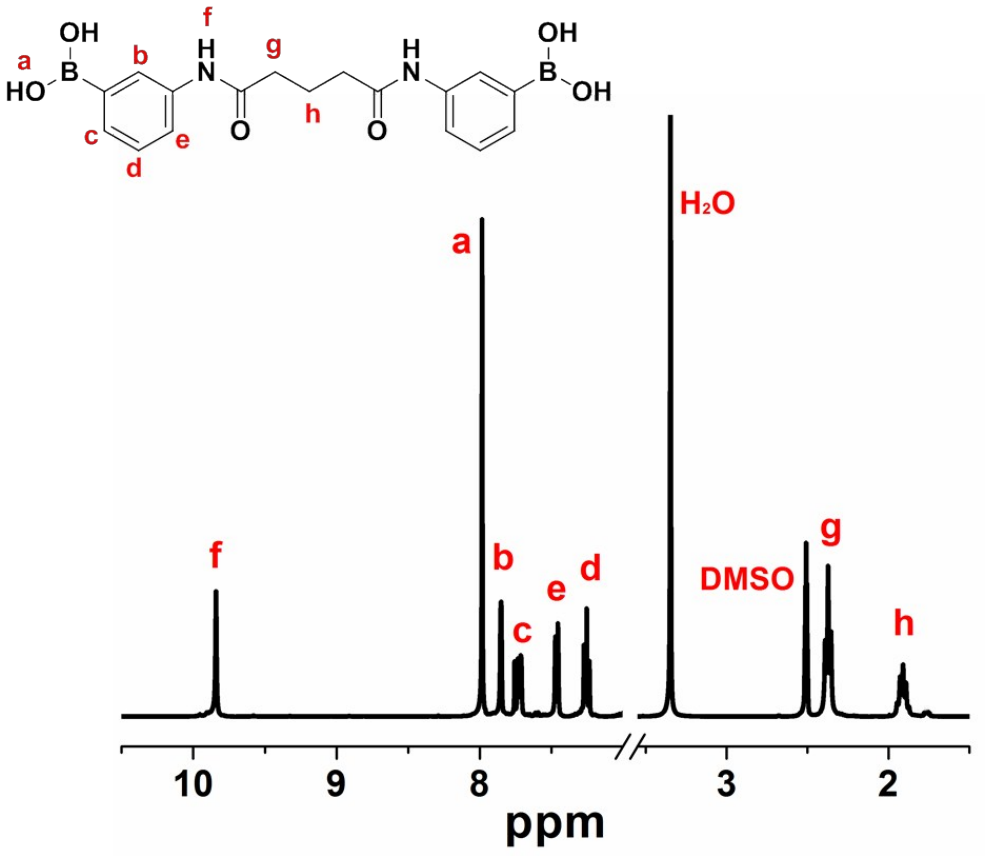



**Fig. S20.** $^{1}$H-NMR spectrum of PBA-$A_6$.

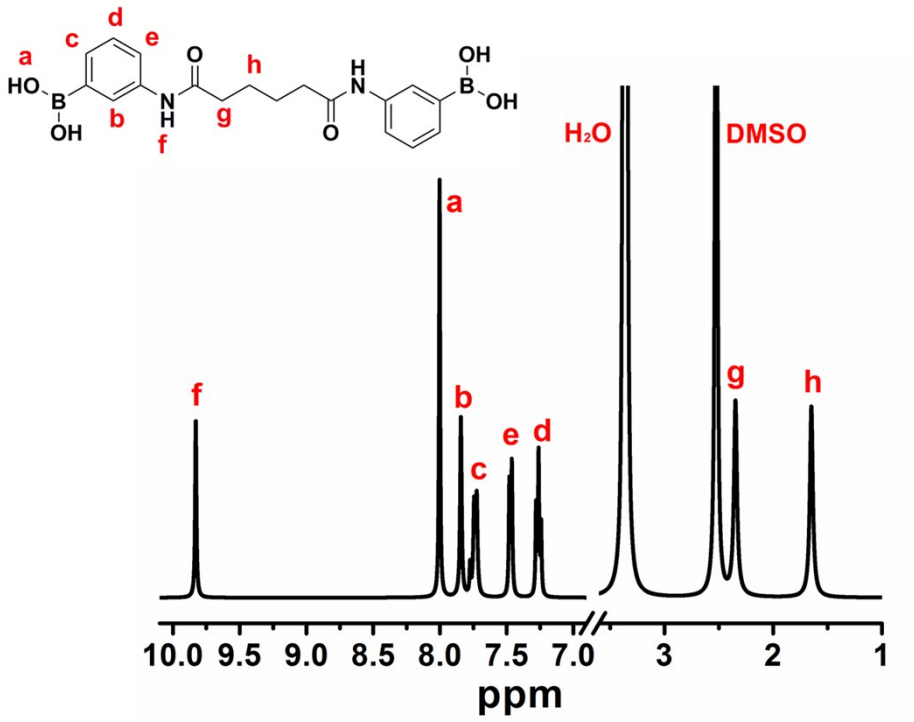



**Fig. S21.** $^{1}$H-NMR spectrum of PBA-$A_7$.

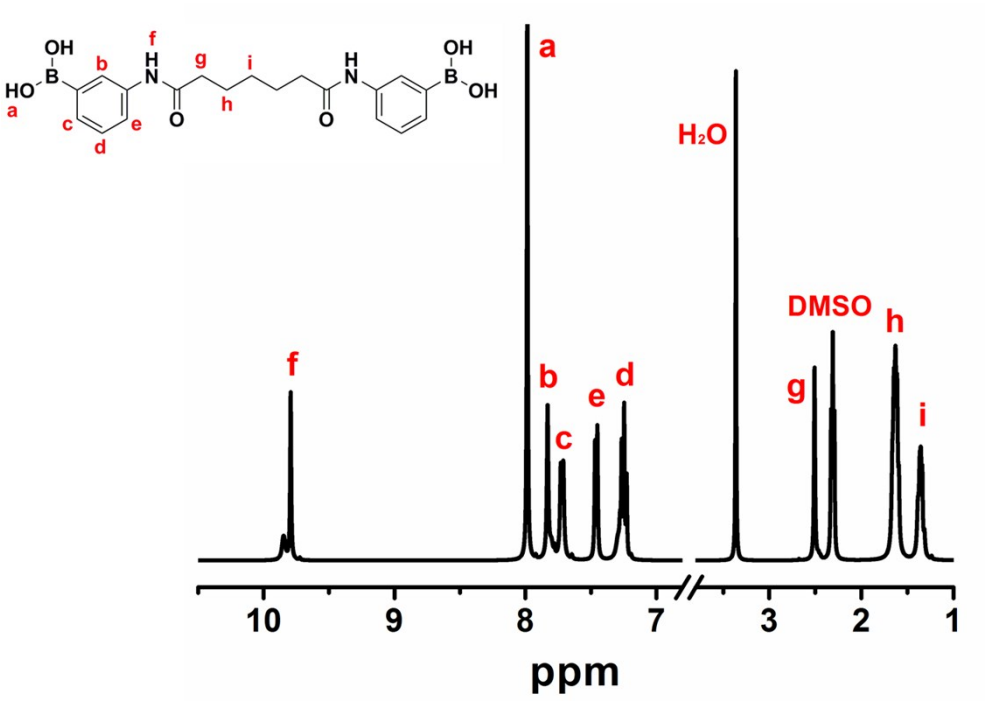



**Fig. S22.** $^{1}$H-NMR spectrum of PBA-$A_8$.

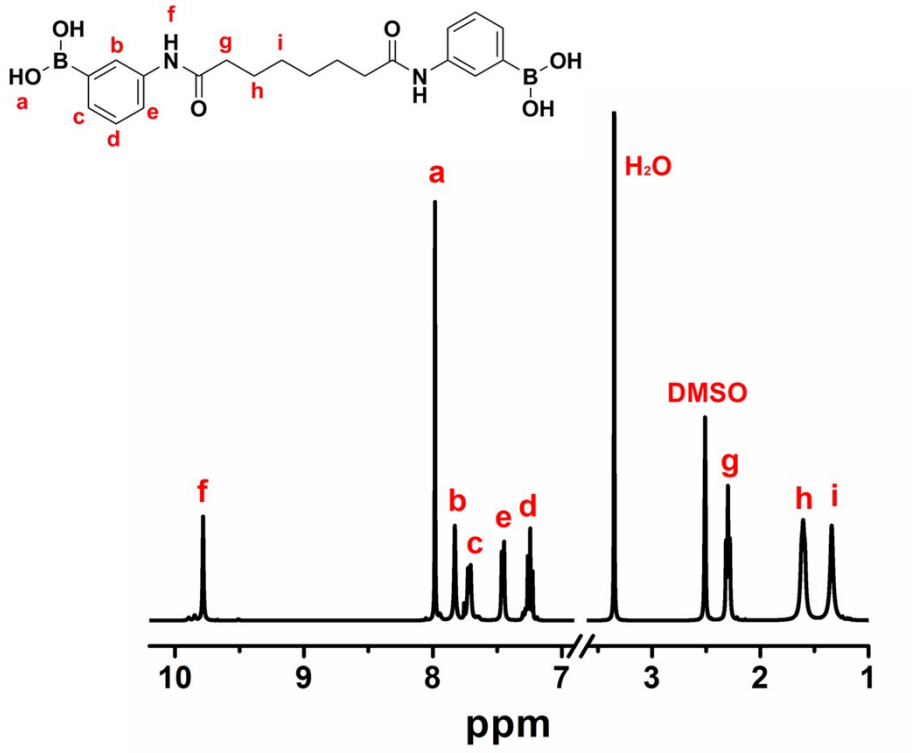



**Fig. S23.** $^{1}$H-NMR spectrum of PBA-$A_9$.

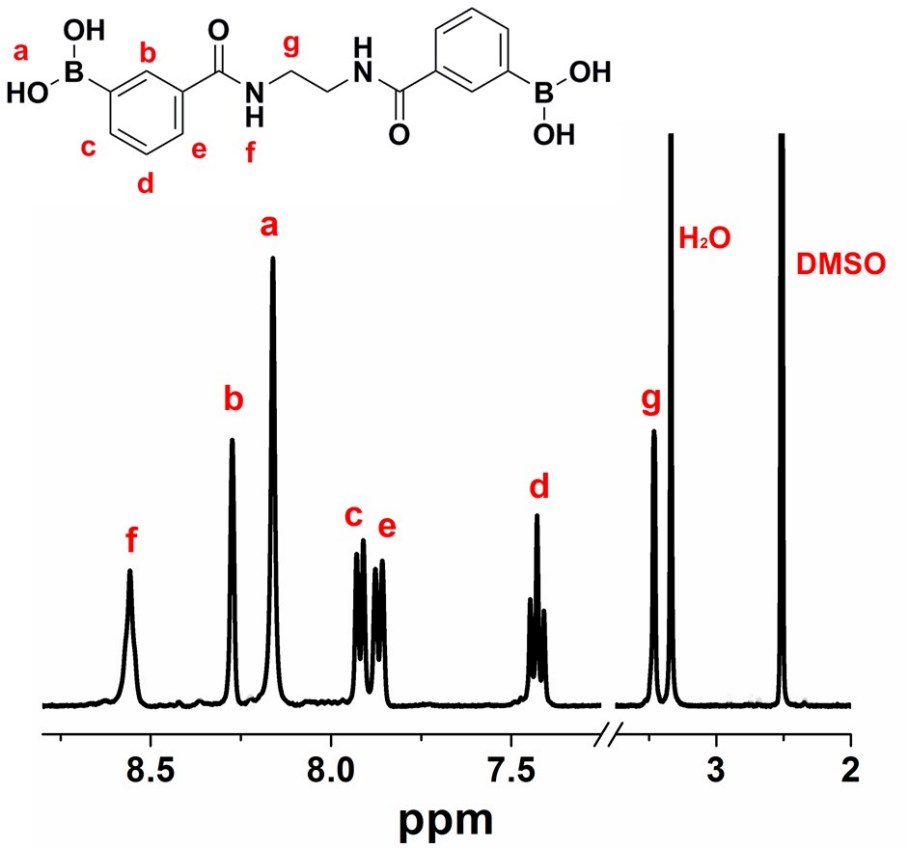



**Fig. S24.** $^{1}$H-NMR spectrum of PBA-$A_{10}$.

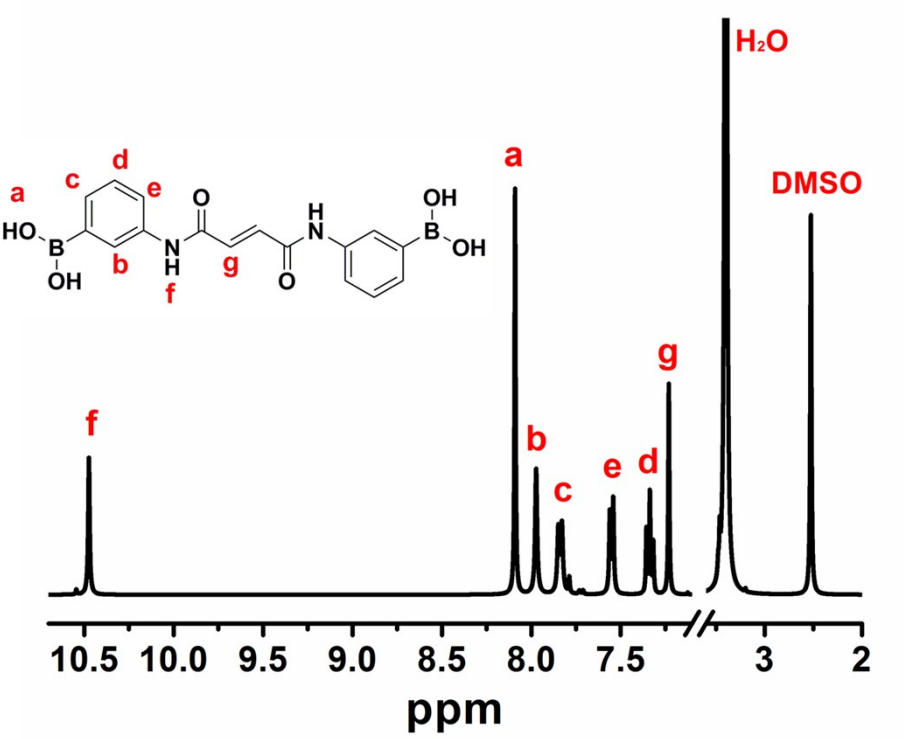



**Fig. S25.** $^{1}$H-NMR spectrum of PBA-$A_{11}$.

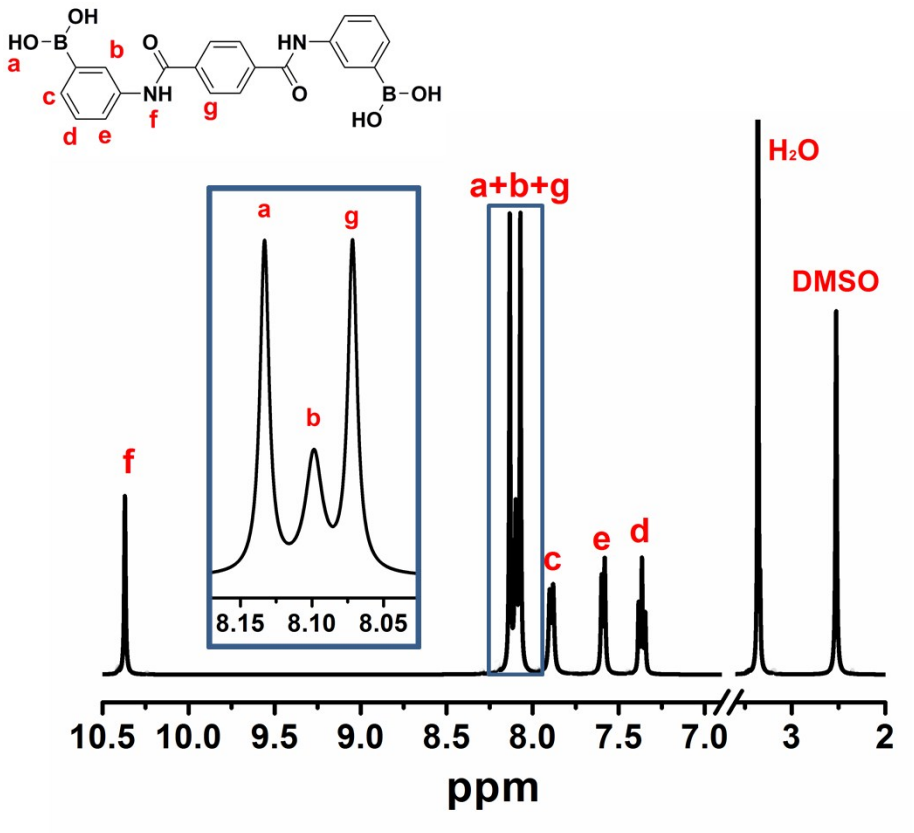



**Fig. S26.** $^{1}$H-NMR spectrum of PBA-$A_{12}$.

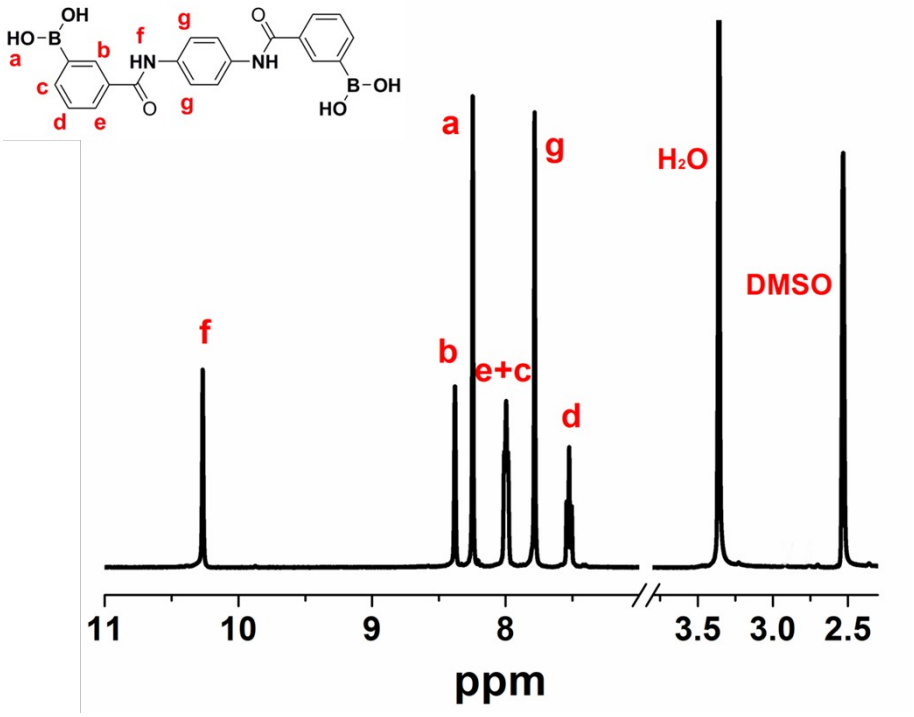



**Fig. S27.** $^{1}$H-NMR spectrum of PBA-$A_{13}$.

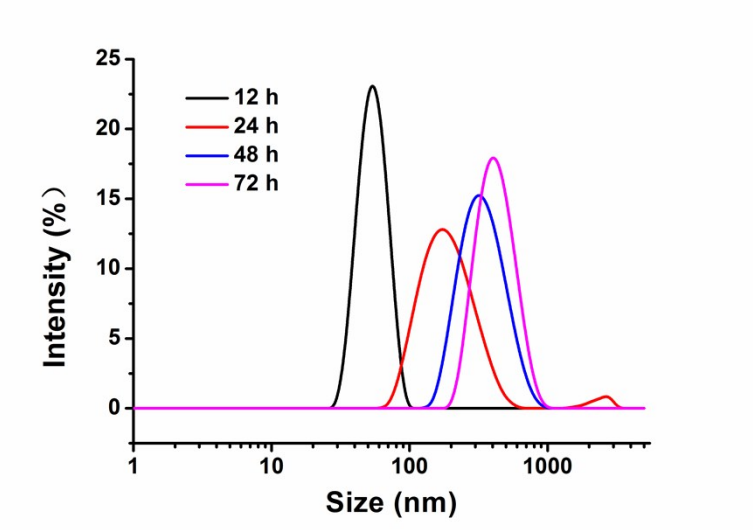



**Fig. S28.** Particle size changes of BDNs-$E_1$ with time.

## 3. Reference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