Supplementary Information

Supramolecular assembly of crosslinkable monomers for degradable and fluorescent polymer nanoparticles

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Fig. S1 ¹H NMR spectrum of N-(4-aminophenyl)methacrylamide in DMSO-D₆.

![N-(4-aminophenyl)methacrylamide NMR spectrum](image)
Fig. S2 $^{13}$C NMR spectrum of N-(4-aminophenyl)methacrylamide in DMSO-$d_6$.

Fig. S3 $^1$H NMR spectrum of BM in DMSO-$d_6$. 
Fig. S4 $^{13}$C NMR spectrum of BM in DMSO-D$_6$.

Fig. S5 $^1$H NMR spectrum of CM in DMSO-D$_6$. 
Fig. S6 $^{13}$C NMR spectrum of CM in DMSO-D$_6$.

Fig. S7 $^1$H NMR spectra of FHBe in CDCl$_3$(a) and methanol-D$_4$ (b). These two spectra are almost the same, indicating that FHBe is stable in methanol solution without solvolysis.
Fig. S8 $^{13}$C NMR spectrum of FHBe in CDCl$_3$. 
Fig. S9 $^1$H NMR spectra of BCe in D$_2$O (a, pH=5.5, a little methanol-D$_4$ was added to increase the solubility of BCe) and in methanol-D$_4$ (b). These $^1$H NMR spectra were obtained after BCe was dissolved in the solutions for 4 h.
Fig. S10 $^{13}$C NMR spectra of BCe in D$_2$O (a, pH=5.5, a little methanol-D$_4$ was added to increase the solubility of BCe) and in methanol-D$_4$ (b). These $^{13}$C NMR spectra were obtained after BCe was dissolved in the solutions for 4 h.

Combining the results from both Fig. S9 and S10, it is obvious that the $^1$H NMR and $^{13}$C NMR spectra in D$_2$O solution represent the right structure of BCe. The concurrent emergence of a signal at 9.65 ppm in Fig. S9a and a peak at 194.6 ppm in Fig. S10a is induced by the degradation of imine moiety in BCe, which affords aldehyde group. However, the signals of aldehyde group in both $^1$H NMR and $^{13}$C NMR spectra are relatively low, and thus we consider that BCe is to some extent stable in water solution and degrades gradually with the prolonging of time. About 2.16 mol% of imine moiety has been degraded after 4.0 h (calculated from the NMR spectra in D$_2$O).

Moreover, the $^1$H NMR and $^{13}$C NMR spectra of BCe in methanol-D$_4$ seem to be more complicated, probably due to the formation of direct or methoxylated B-N coordination.
Fig. S11 $^{11}$B NMR spectra of BM and BCe (a) in methanol-D$_4$ and (b) in solid state. (c) Evolution of $^{11}$B NMR spectra of BCe prepared at different temperatures in methanol-D$_4$; a weak peak appeared at 28.0 ppm can be attributed to the un-reacted BM. The peak at around -5 ppm marked with “*” in the solution $^{11}$B NMR spectra is assigned to boronates in NMR tube, which has been confirmed by Fig. S12 in Supplementary information. (d) DSC thermograms of BCe and BM. The association constant ($K_a$) of B-N coordination of BCe in methanol at room temperature can be calculated from the $^{11}$B NMR, the value of which is $\sim 6.51 \times 10^4$ M$^{-1}$. $^a$

A broad peak at 76 °C in the DSC curve of BCe rather than in that of BM, is likely induced by the evaporation of methanol. Obviously, methanol is in a binding state in the solid BCe because its evaporation temperature is much higher than the boiling point (64 °C). This means that a small amount of methanol is still inserted in the solid BCe, which cannot be detected by the solid state $^{11}$B NMR. The sharp peak at 127 °C in the DSC curve of BCe can be assigned to the breaking of B-N dative bond. The bonding energy of B-N coordination is calculated to be about 12.1 kJ/mol, which is almost equal to the energy of intramolecular B-N bonding. A peak at 158 °C in the DSC curve of BM may be induced by the condensation reaction among boronic acid groups that affords boroxine. $^1$

$^a$ $K_a$ was calculated by equation $K_a=\frac{r C_{\text{boron}} g}{C_{\text{nitrogeous}} (1-r) g C_{\text{boron}}}$; $r$ was calculated by $r=\frac{I_{\text{tert}}}{I_{\text{tetr}}+I_{\text{tert}}}$, where $I_{\text{tert}}$ represents the integral area of tetracoordinated boron and $I_{\text{tetr}}$ represents the integral area of tricoordinated in the $^{11}$B NMR spectra; $C_{\text{boron}}$ and $C_{\text{nitrogeous}}$ represent the concentrations of boron molecule and nitrogeous molecule, respectively.
Fig. S12 (1) $^{11}$B NMR spectrum of BCe in methanol-D$_4$ prepared at -10 °C after staying at room temperature for 24 h; (2) $^{11}$B NMR of NMR tube (the tube was filled with methanol-D$_4$).

Fig. S13 $^{11}$B NMR spectrum of FHBe/N-(4-aminophenyl)methacrylamide mixture (molar ratio:1:1) in methanol-D$_4$. 
Fig. S14 Diameters of supramolecular assemblies in methanol prepared by the condensation reaction between BM and CM at (a) -10 and (b) 0 °C, and (c) formed by cooling the temperature of Bc solution from 25 to -10 °C. (d) The diameter evolution of spherical supramolecular assemblies prepared from 40 mM of BM and CM at -10 °C when staying at 60 °C; no peak can be observed after 60 min, indicating the complete dissolve of the nanoparticles.

Fig. S15 TEM images of layered structures: (a) spherical assemblies formed at -10 °C by the condensation reaction between 40 mM of BM and CM in methanol were firstly dissolved at 60 °C, then the solution was cooled back to 0 °C; (b) spherical assemblies formed at -10 °C by the condensation reaction between 40 mM of BM and CM in methanol were firstly dissolved at 60 °C, then the solution was cooled back to -10 °C.
Fig. S16 Electron diffraction pattern of spherical supramolecular assemblies formed at (a) -10 and (b) 0 °C by condensation reaction between 40 mM of BM and CM in methanol, and (c) layered structures prepared by cooling 40 mM of BCe methanol solution from 25 to -10 °C.

Fig. S17 (a) TEM image of P(BCe) NPs prepared from the photo polymerization of spherical assemblies at -10 °C, these assemblies were formed by using 60.0 mM of BM and CM. (b) TEM image of P(BCe-MAPEG) NPs prepared by using BCe assemblies that were obtained from 60.0 mM of BM and CM.
**Fig. S18** FT-IR spectra of BCe, P(BCe) and P(BCe-MAPEG) NPs.

**Fig. S19** DLS results of P(BCe) and P(BCe-MAPEG) NPs in water solution with different pH values after equilibrium (a). Diameter evolutions of P(BCe-MAPEG) NPs in acidic solution (pH=5.5) without (b) and with 0.6 mM of D-glucose (c).
Fig. S20 (a) And (b) are the diameters of the degraded P(BCe) NPs after self-healing in methanol. (c) $^{11}$B NMR spectrum of degraded P(BCe) NPs after staying in methanol-D$_4$ at -10 °C for 12 h.

Fig. S21 Photographs of BM, CM and BCe in methanol: (a) with natural light and (b) with UV irradiation.
Fig. S22 UV/vis spectra of BM, CM and BCe in methanol (a), in water with pH=7.4 (b) and BCe in acidic solutions (c).

Fig. S23 Excitation spectra of BCe in water solution (pH=5.5) with different emission wavelengths. It is obvious that the excitation wavelength exhibits no change with the variation of emission wavelength. The highest excitation intensity is observed at a 480 nm emission wavelength.
Fig. S24 Photographs of samples in water, (a) and (c) in natural light, (b) and (d) with UV irradiation. The solution pH of (a) and (b) is 5.5, while that of (c) and (d) is 6.5. (1) BM, (2) CM, (3) N-(4-aminophenyl)methacrylamide, (4) FHBe, (5) BCe.
Fig. S25 Fluorescence spectra of (a) BCe and (b) DAPI in water (pH=5.5) with different concentrations. (c) And (d) are the corresponding integrated fluorescence intensities of (a) and (b). (e) The corresponding UV/vis spectra of BCe and DAPI with the same concentrations.

Table S1. Parameters derived from Fig. S25 and the calculated $\phi$.  

<table>
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<tr>
<th>Concentration</th>
<th>$I_A$</th>
<th>$I_{fr}$</th>
<th>$A_A$</th>
<th>$A_{fr}$</th>
<th>$\phi$</th>
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<tr>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.5003</td>
</tr>
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</table>

Where $\phi$ is the quantum yield of BCe; $I$ and $I_{fr}$ represent the integrated fluorescence intensities of BCe and DAPI; $A$ and $A_{fr}$ are the UV absorbances of BCe and DAPI at 360 nm.
Fig. S26 Fluorescence lifetime spectrum of BCe in water solution with pH=5.5.

Fig. S27 Emission evolution of BCe (a) and P(BCe) NPs (b) in water with pH=5.5. These two measurements were performed by using decreased excitation light intensity. This was achieved by decreasing the stimulation slit width from 5.0 nm to 1.0 nm, while keeping the emission slit width at 5.0 nm.

Comparing with the emission evolutions tested by using 5.0 nm of stimulation slit width (Fig. 4f and Fig. 5d), the fluorescence intensity shown in Fig. S27 is much lower. The fluorescence attenuations of BCe and P(BCe) NPs in water solution with pH=5.5 calculated from Fig. 4f and Fig 5d are 30.8 % and 19.0 %, respectively, these results are almost the same with that obtained from Fig. S27. The intensity of excitation light unlikely had impact on the decreasing speed and extent of the fluorescence intensity of BCe and the polymerized nanoparticles. Thus, it is reasonable to believe that the decrease of fluorescence of BCe and the polymerized nanoparticles was not caused by photobleaching.
Fig. S28 Photographs of samples in water with natural light, (1) P(BCe) NPs at pH=7.4, (2) P(BCe-MAPEG) NPs at pH=7.4, (3) P(BCe) NPs at pH=5.5 and (4) P(BCe-MAPEG) NPs at pH=5.5.

References: