# Formation, Characterization, and Thermal Degradation Behavior of a Novel Tricomponent Aggregate of $\beta$-Cyclodextrin, Ferrocene, and Polypropylene Glycol

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A tricomponent aggregate PPG−Fc−$\beta$-CD formed by polypropylene glycol (PPG), ferrocene (Fc), and $\beta$-cyclodextrin ($\beta$-CD) was obtained and characterized by a series of physical methods, such as $^1$H nuclear magnetic resonance, flame atomic absorption spectrometry, high performance liquid chromatography, UV−vis absorption spectroscopy, thermogravimetry, and gas chromatography coupled to time-of-flight mass spectrometry. First, the tricomponent aggregate exhibited a component ratio of 1:28:32 (PPG/Fc/$\beta$-CD) in the solid state, and showed a completely different order in thermal stability when compared with $\beta$-CD: under a nitrogen atmosphere, $\beta$-CD > PPG−Fc−$\beta$-CD, and in a vacuum, PPG−Fc−$\beta$-CD > $\beta$-CD. Second, the appearance of two peculiar points *p* and *q* at the end of TG curve of the aggregate gave a strong impression that the degradation rate further increased after the sharp decomposition of the aggregate reached point *p* and the amount present in the residual fraction at point *q* about 780.0 K was lower than 1%, both of which were rather different from those reported previously. This finding implied that the molecular assembly resulting from the binding interaction among Fc, PPG, and $\beta$-CD induced more efficiently the degradation of each of them. Third, an interesting phenomenon was found that the order of thermal release of the three assembled components in PPG−Fc−$\beta$-CD was Fc > $\beta$-CD > PPG. Results of this study provide some insight into an initial attempt to construct a supramolecule among a polymer, a coordination compound, and an organic compound.

## Introduction

Cyclodextrins (CDs) are composed of several glucose units linked by α-1,4-linkages, which are arranged in the shape of a hollow truncated cone by leaving the hydroxyl groups outside.[1–3] The presence of a hydrophobic cavity makes them possible to form supramolecular complexes with a variety of guests, such as inorganic ions, organic molecules, and so on,[4–7] and their derivatives also attract many researchers' interests.[8–10] $\beta$-CD (Figure 1), as the most common one which possesses seven glucose units, is widely studied.[11–13]

Ferrocene (Fc, Figure 1) as well as its derivatives, as important organometallic compounds, is commonly applied in material science, catalysis, and synthetic organic chemistry.[14–16] Fc−$\beta$-CD, as the first example of second sphere coordination complexes of CDs with organometallic compounds, was reported in 1984.[17] Since then, there have been many reports on the formation and characterization on CD complexes of Fc analogues.[17–20] A recent study delineates our efforts to elucidate the correlation between the destruction of a second sphere complex through the release of its members and the separate destruction of its members based on the relationship between heating temperatures and fragment compositions of the complex.[21]

Polypropylene glycol (PPG, Figure 1) is an oily liquid and widely used in polymer synthesis. In the 1990s, the polypseudorotaxanes formed by CDs and polymers such as PPG were
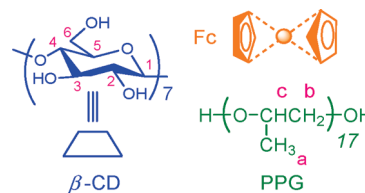


**Figure 1.** Structural features of $\beta$-CD, Fc, and PPG.

reported.[22] Recently, supramolecular structures of polyrotaxanes consisting of cyclic CD molecules, which are threaded on a polymer chain like beads on a string, have been receiving more and more attention,[23–26] since they can be applied in biomaterials such as controlled drug release and delivery systems, biosensors, and biomedical application.[27–29] Polyrotaxanes or polypseudorotaxanes are one of the most important aspects in the fields of polymer science. To progress the fields, we evaluated the effect of different preparation conditions on the stoichiometries and properties of the polypseudorotaxane PPG−$\beta$-CD in a recent work.[30]

In view of the fact that the previous works published on these topics, both for second sphere coordination complexes of CDs and for polyrotaxanes or polypseudorotaxanes of CDs,[1,31–34] were involved in the simple combined effects of the two constituents alone in binary systems, evidence and our successful results about the two binary systems, i.e., Fc−$\beta$-CD and PPG−$\beta$-CD,[30,35] urge us to turn our attention toward possibilities to get a novel tricomponent aggregate PPG−Fc−$\beta$-CD with different properties from several binary complexes. Certain problems worth being studied become apparent in discussion of the ternary system. (1) Is there an interaction between Fc and PPG? If yes,

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Novel Tricomponent Aggregate of β-CD, Fc, and PPG

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can the intermolecular interaction lead to the formation of a solid complex between them? (2) There is doubt on whether the precipitated product obtained from the ternary system really represents a desired tricomponent aggregate, instead of a simple mixture of these complexes. (3) What are the chemical composition and the spectral characteristics of the aggregate? The present work is the first attempt to systematically investigate these issues.

Initially, we carried out a group of experiments revealing that the weak interaction between PPG and Fc cannot cause the formation of an inclusion complex. Next, although PPG as well as Fc can form an inclusion complex with β-CD, our results indicate that the precipitated product obtained from the ternary system of β-CD, PPG, and Fc is a tricomponent aggregate with a defined chemical composition, rather than a simple mixture of the two binary complexes, Fc−β-CD and PPG−β-CD. The spectral differences between the aggregate and the binary complexes were carefully compared to demonstrate that the aggregate has its own spectral characteristics. We consider that this study provides a novel and interesting example to reveal the formation of a tricomponent aggregate among CDs, polymers, and organometallic compounds. It is helpful to understand the linkage among coordination chemistry, host−guest chemistry, and polymer science.

**Experimental Section**

**Materials.** Fc was purchased from Shanghai Chemical Reagent Company and used without further purification. PPG ($M_n$ 1000, $M_w/M_n = 1.12$) was kindly donated by Ms. X. W. Wang. β-CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized water. DMSO-$d_6$ used as a solvent in $^1$H nuclear magnetic resonance ($^1$H NMR) measurements was obtained from Aldrich Chemical Co. All other reagents are of analytical-reagent grade, unless stated otherwise.

**Formation of PPG−Fc−β-CD.** The tricomponent aggregate was prepared according to the method as follows. PPG of 204 mg (0.2 mmol) and Fc of 187 mg (1 mmol) were added to a β-CD aqueous solution (130 mL, 1 mmol) in a beaker at room temperature. The mixed solution was stirred for 1 h at 333.2 K and then for 6 h at room temperature. During stirring, the reaction system was at first homogeneous and then became an emulsion with a light yellow color. When stirring stopped, an amount of precipitate was obtained after the solution was standing for a few minutes. The precipitate was filtered off, washed with a little ethanol and deionized water three times, and then dried under a vacuum at 333.2 K. The dried yellow powder was weighed (0.799 g), and the percentage yield (57.2%) was calculated on the basis of the concentration of β-CD. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm) of PPG−Fc−β-CD δ 5.72−5.62 (m, 14H, O-2,3 H of β-CD), 4.82−4.78 (s, 7H, C-1 H of β-CD), 4.44−4.38 (m, 7H, O-6 H of β-CD), 4.16−4.11 (s, 10H, H of Fc), 3.71−3.22 (m, 42H, C-2, C-3, C-4, C-5, C-6 H of β-CD), 1.03−0.98 (d, 51H, H of terminal methyl groups of PPG). The sample preparation was repeated once, and the two solid products so obtained had the same stoichiometric ratio of PPG, Fc, and β-CD according to the results of $^1$H NMR.

**Instruments and Methods.** Elemental analysis was carried out on an Elementar Vario EL III elemental analyzer. Iron content in the aggregate was determined by flame atomic absorption spectrometry (FAAS) using the atomic absorption spectrophotometer AAnalyst 800 (Perkin-Elmer, USA) after the aggregate was acidified with concentrated nitric acid.

**TABLE 1: Appointed Heating Program for Samples**

| step | temperature range (K) | heating rate (K·min$^{-1}$) | retained time (min) |
|------|----------------------|------------------------------|----------------------|
| 1 | 303.2 | 0 | 3 |
| 2 | 473.2 | 80.0 | 5 |
| 3 | 673.2 | 10.0 | 3 |
| 4 | 873.2 | 80.0 | 10 |

UV−vis absorption spectra were measured on a TU-1901 spectrophotometer (Puxi Ltd. of Beijing, China) over the wavelength range between 190 and 600 nm, using quartz cells with a 1 cm optical path at room temperature, to confirm the content of Fc in the aggregate. The solid samples of free Fc and the aggregate were dissolved in the mixture solvent of ethanol and water (volume ratio, 1:1), with concentrations of $10^{-5}$ and $10^{-6}$ mol·dm$^{-3}$, respectively.

Fourier transform infrared (FTIR) spectroscopy was recorded on a Bruker Equinox 55 spectrometer in KBr pellets in the range 4000−400 cm$^{-1}$.

$^1$H nuclear magnetic resonance experiments were carried out on a Bruker AV-300 NMR spectrometer at 300 MHz at room temperature. Chemical shifts (δ) were given in ppm relative to TMS using the residual solvent signals as an internal reference at 2.500 ppm for DMSO-$d_6$.

High performance liquid chromatography (HPLC) was performed using an Agilent 1100 liquid chromatography system with a column of Agilent ODS C18 250 × 4.6 mm liquid chromatography at a flow rate of 1.0 mL·min$^{-1}$. In all cases, the mobile phase consisted of a mixture of methanol and H$_2$O with the volume ratio of methanol to H$_2$O (85:15). A sample volume of 10 μL was achieved each time by an automated sample-injection system and detected by an UV−visible spectrophotometer with 268, 321, 332, 440, and 451 nm.

Powder X-ray diffraction (PXRD) patterns were acquired on a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu Kα radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range 5° ≤ 2θ ≤ 40°.

Thermogravimetry (TG) measurements were performed on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10.0 K·min$^{-1}$ under a nitrogen atmosphere.

GC-TOF-MS experiments with programmed temperature operations were done on a Micromass GCT-MS spectrometer, using a direct insertion probe for solid samples. The heating program with an increasing temperature was listed in Table 1.

**Results and Discussion**

**Formation and Characterization of PPG−Fc−β-CD. 1. $^1$H NMR and HPLC Analysis.** The $^1$H NMR spectra of free PPG, β-CD, and PPG−Fc−β-CD are shown in Figure 2. From Figure 2C, the values of δ at 3.619 and 3.582 ppm are designated as the signals of H-3 and H-5 protons of β-CD,
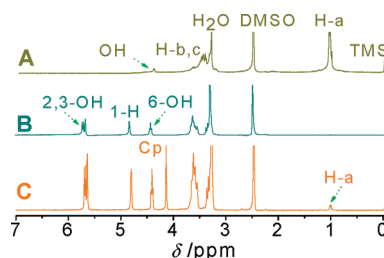


**Figure 2.** 300 MHz $^1$H NMR spectra of free PPG (A), free β-CD (B), and PPG−Fc−β-CD (C) in DMSO-$d_6$.

**TABLE 2: FTIR Spectra Data of Free PPG, β-CD, and PPG−Fc−β-CD**

| IR (cm$^{-1}$) | PPG | β-CD | PPG−Fc−β-CD |
|---|---|---|---|
| $v_{O-H}$ | 3471 | 3397 | 3386 |
| $\delta_{O-H}$ | 1638 | 1638 | 1638 |
| $v_{asC-O}$ | 1107 | 1157, 1079, 1028 | 1156, 1081, 1031 |
| $v_{sC-O-C}$ | 929 | 946 | 945 |

respectively. The $\delta$ value at 4.173 ppm is caused by the protons of cyclopentadienyl (Cp) rings in Fc.[35] Obviously, the relatively small $\delta$ at 1.030 ppm in the figure is due to the proton signal of the side-chain methyl groups in PPG. These results clearly indicate that PPG, Fc, and β-CD are all present at the same time in such a tricomponent aggregate.

The component ratio of PPG, Fc, and β-CD in the tricomponent aggregate is determined to be 1:28:32 on the basis of the results of ^{1}H NMR, FAAS, and elemental analysis. Anal. Calcd for (PPG)·28(Fc)·32(β-CD·5H$_2$O)·12H$_2$O: C, 44.05; H, 6.50; Fe, 3.44. Found: C, 43.84; H, 6.53; Fe, 3.45. The molar number of Fc in 1 mol of the aggregate is in agreement with the calculation result (28.46) according to absorbance at the maxium absorption wavelength ($\lambda_{max}$, 200−202 nm) of UV−vis spectra.

The changes in $\delta$ values of proton signals (CH, CH$_2$, and CH$_3$ of PPG, C$_5$H$_5$ of Fc especially H-3 and H-5 of β-CD) between the free state and the bound state are up to 0.040 ppm, meaning that there is a complexation interaction among the cavity of β-CD, the Cp rings, and the PPG chain.

Two inclusion complexes, Fc−β-CD and PPG−β-CD, were prepared according to reported methods.[11,30] HPLC is a widely used method for qualitative and quantitative analyses with high efficiency and sensitivity.[36,37] The result of HPLC measurements of β-CD, Fc−β-CD, PPG−β-CD, and PPG−Fc−β-CD under the same conditions indicates that β-CD and PPG−β-CD have hardly any absorption at 268, 321, 332, 440, and 451 nm but Fc−β-CD and PPG−Fc−β-CD exhibit a strong absorption peak at 6.945 and 6.890 min, respectively, at 268 nm. Although there is a small time difference between the two peaks, the maximum absorbances of PPG−Fc−β-CD and Fc−β-CD are 0.109 and 0.066, indicating a large difference in intensity. Clearly, the molar absorption coefficient ratio ($\varepsilon_1/\varepsilon_2$) of PPG−Fc−β-CD to Fc−β-CD can be determined by the equation $(A_1 \times C_2)/(A_2 \times C_1)$, in which $A_1$ and $C_1$ are the absorbance and concentration of PPG−Fc−β-CD and $A_2$ and $C_2$ are the absorbance and concentration of Fc−β-CD. When the values of $C_1$ and $C_2$ are $3.244 \times 10^{-5}$ and $6.662 \times 10^{-4}$ mol·dm$^{-3}$, the value of $\varepsilon_1/\varepsilon_2$ is calculated to be 33.92, which is not in agreement with the stoichiometric ratio of Fc (about 28) in PPG−Fc−β-CD and Fc−β-CD. This reflects that the chemical surroundings of Fc in the two complexes are largely different from each other. That is to say, the prepared product is a new tricomponent aggregate, instead of a simple mixture of several binary complexes. A series of measurements such as FTIR, PXRD, TG, and GC-TOF-MS were performed to demonstrate this point.

**2. FTIR Analysis.** The FTIR spectra data of free PPG, β-CD, and the tricomponent aggregate are summarized in Table 2. For free PPG, the absorption bands at 3471, 2971, 2870, and 1375 cm$^{-1}$ are attributed to the $v_{OH}$ vibration band of the chain-end hydroxyl groups, the stretching vibration of CH$_2$ and CH$_3$, and the deformation vibration of C−H in PPG, respectively.[30] Free Fc exhibits the main absorption bands at 1411, 1107, 1002, and 820 cm$^{-1}$. Among them, 1411 and 1107 cm$^{-1}$ are assigned to $v_{C=C}$ vibrations of the multiple ring structures, while 1002 and 820 cm$^{-1}$ are ascribed to $v_{C-C}$ vibrations.[35] The absorption bands
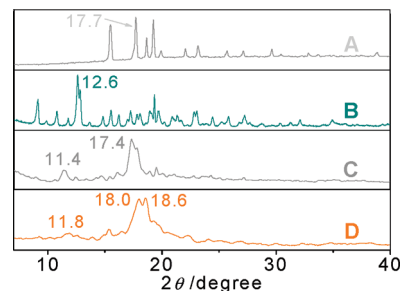


**Figure 3.** PXRD patterns of free Fc (A), free β-CD (B), the physical mixture of Fc−β-CD and PPG−β-CD (C), and PPG−Fc−β-CD (D).

of free β-CD at 3397 and 1028 cm$^{-1}$ are attributed to $v_{OH}$ and $v_{C-O}$, respectively.[30]

The result in Table 2 indicates that, although the number or intensity of peaks in the tricomponent aggregate is similar to that of free β-CD, slight shifts are observed. The $v_{OH}$ band exhibits a clear red shift from 3397 cm$^{-1}$ in free β-CD to 3386 cm$^{-1}$ in the aggregate. This means that there is a decrease of O−H vibration intensity upon inclusion due to an increase of the hydrogen bonding interaction between β-CD molecules. A similar phenomenon also appears in the binary complexes: PPG−β-CD[30] and Fc−β-CD.[35] However, in comparison with the two binary complexes, the tricomponent aggregate has a relatively small red shift for the $v_{OH}$ band, implying such a hydrogen bonding interaction in the binary inclusion systems is stronger than in the ternary system. In addition, the $v_{OH}$ band of free PPG occurs in 3471 cm$^{-1}$, but it has a significant red shift after aggregation. This is associated with the weak hydrogen bonding interaction between PPG molecules because of the limitation in the number of O−H bonds available.

These results indicate that there exists an intermolecular interaction among β-CD, Fc, and PPG, and the interaction is different from those formed in the binary systems. As a result, an important question needs to be raised here. Could the intensity change of the O−H bonds be ascribed to a change in molecular stacking behavior of these components?

**3. PXRD Analysis.** The group of PXRD patterns of free Fc, β-CD, the physical mixture of Fc−β-CD and PPG−β-CD (23:1, molar ratio), and PPG−Fc−β-CD are illustrated in Figure 3.

Initially, there are many peaks in the PXRD spectra of both free Fc and free β-CD, and they are rather sharp and distinct. However, the spectrum of PPG−Fc−β-CD (Figure 3D) displays very few peaks, and most of these peaks have an asymmetric profile. Further, many peaks belonging to β-CD and Fc disappear in the pattern of PPG−Fc−β-CD, including most of the strongest signals. Also, a new strong double peak is present in the range 18.0−18.6°, but it does not occur in PPG−β-CD[30] and Fc−β-CD.[35] These spectral differences indicate that the stacking behavior of β-CD molecules has been largely changed due to the effect of the presence of both PPG and Fc.

Next, the first ($I_1$), second ($I_2$), and third ($I_3$) strongest peaks of free β-CD are 12.6, 19.3, and 9.1°; these peaks as well as other signals in Figure 3B suggest that the β-CD molecules adopt a typical cage-type arrangement based on a comparison between the PXRD data and X-ray structure of β-CD.[38,39] Nevertheless, the diffraction pattern of PPG−Fc−β-CD contains both the characteristic peaks of a cage-type arrangement, such as 9.1 and 19.3°, and those of a channel-type arrangement, such as 11.8, 15.3, and 18.0°.[40,41] The result shows that the molecular stacking form of β-CD in PPG−Fc−β-CD demands a specific combination of both of the arrangements, and the effect of the
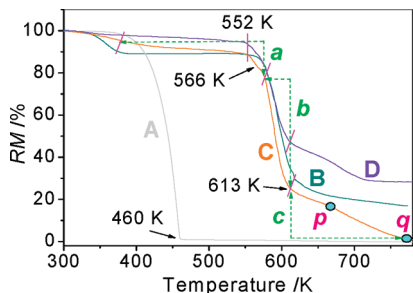
**Figure 4.** TG curves of free Fc (A), free β-CD (B), PPG−Fc−β-CD (C), and the physical mixture of Fc−β-CD and PPG−β-CD (D) at a heating rate of 10.0 K·min⁻¹.



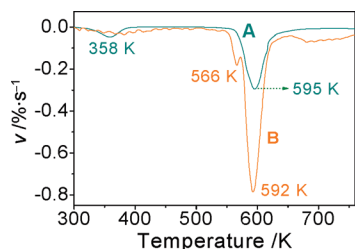**Figure 5.** The fractional mass loss per second ($v$, %·s⁻¹) as a function of temperature for free β-CD (A) and PPG−Fc−β-CD (B).

channel-type arrangement is dominant owing to the higher intensity of the characteristic peaks in the case of this arrangement. This observation clearly proves that the tricomponent aggregate is a new complex because either of the two binary complexes presents a channel-type arrangement.[30,35]

Furthermore, the half-width of the diffraction peaks in PPG−Fc−β-CD is much bigger than that of the corresponding peaks in the two solid complexes Fc−β-CD and PPG−β-CD,[30,35] as well as in free Fc and β-CD. This is likely to come from the lower regularity of the molecular packing in the tricomponent aggregate. Figure 3C shows the PXRD curve of the physical mixture of Fc−β-CD and PPG−β-CD. Actually, the PXRD curve of the mixture of the two binary complexes, whether in shape or configuration, is apparently different from that of the tricomponent aggregate. This result makes us confident that such an aggregate is not a simple mixture of Fc−β-CD and PPG−β-CD but a new ternary complex.

**Interesting Phenomena in TG and DTG Curves. *1. TG Analysis.*** The TG and differential thermogravimetry (DTG) profiles provide information about the thermal stability of PPG−Fc−β-CD. These curves are shown in Figures 4 and 5. The TG curve of the aggregate in Figure 4 can be roughly divided into three stages,[35] a mass loss of water of 6.92%, approximately in accordance with the mass fraction of water (6.79%) in the aggregate, a mass loss of Fc of 11.36%, in good agreement with the result (11.41%) of elemental analysis, and a large mass loss due to the simultaneous decomposition of β-CD and PPG at this stage.

First, there is a large difference between the TG profiles of PPG−Fc−β-CD and the physical mixture of Fc−β-CD and PPG−β-CD (see Figure 4C and D). First of all, the mass loss of PPG−Fc−β-CD is always heavier than that of the mixture at the same temperatures. For instance, at 552.2 K, the mass loss of PPG−Fc−β-CD is 11.8% but 6.4% for the mixture. Besides, at the fastest mass loss stage (552.2−613.2 K, see Figure 4C and D), the mass loss of 64.2% in PPG−Fc−β-CD is 1.36 times that of 46.6% in the mixture. Also, the final residual mass (RM, %) of the mixture at 780.2 K is 28.7%, but that of PPG−Fc−β-CD is less than 1% at the same temperature. These

spectral differences reveal that the thermal stability of PPG−Fc−β-CD is even worse than that of the mixture, which is just indicative that the structure of PPG−Fc−β-CD is a complete new construction. If it is a mixture of Fc−β-CD and PPG−β-CD, its thermal stability is at least better than that of free β-CD, since each of the two binary complexes has a higher stability than free β-CD.[35]

Second, the shape of the TG curve of PPG−Fc−β-CD (Figure 4C) is somewhat similar to that of Fc−β-CD.[35] For example, both of them present three mass loss stages (*a−c*) after the release of water molecules. And the two curves have fewer water molecules released before 384.2 K, when compared with the curve of free β-CD (Figure 4B) under the same drying conditions, as a result of the existence of intermolecular complexation that weakens the hydration of β-CD.

However, there are observable differences between the two complexes. For instance, the temperature ranges corresponding to the three stages are different from each other. For PPG−Fc−β-CD, the three stages occur from 387.2 to 572.2 K (stage *a*), 572.2 to 610.2 K (stage *b*), and 610.2 to 778.2 K (stage *c*), each of which is always below the temperature range of Fc−β-CD.[35] Moreover, the mass loss at any same heating stage is always heavier in PPG−Fc−β-CD than in Fc−β-CD under the same heating conditions.[35] Stage *a* displays the release of Fc, and the protected effect by the β-CD cavity is apparent compared to curve A of free Fc. In addition, the critical sublimation temperature of Fc in stage *a* increases from below 460.2 K in free Fc to about 566.2 K. That is to say, the stability of Fc against heating stress is strengthened after inclusion.

Third, during the process of carbonization and cineration, the mass loss of free β-CD becomes considerably more difficult so that there is a higher ultimate residual disposition (17.4%) at 780.2 K. However, several special phenomena occur in stage *c* of the tricomponent aggregate. (1) The thermal degradation rate still remains comparatively large. (2) There is an obvious inflection (*p*) in the curve for this stage, after which the degradation rate further increases. (3) Surprisingly, the amount present in the residual fraction at point *q* (780.2 K) is lower than 1%, which is different from the residual fraction in the cases of Fc−β-CD (6.5%), PPG−β-CD (17.6%), and the mixture (28.7%).[35] It means that Fc−β-CD has not completely decomposed, and the decomposition degree of PPG−β-CD at a higher temperature is rather similar to that of free β-CD. However, PPG−Fc−β-CD has almost completely decomposed into gaseous species. This is a rare phenomenon which we have never seen in TG spectra of CD complexes. It may be applied for the thermal degradation of carbohydrates, such as to process waste from the agroindustry and household waste. This phenomenon can only occur in the case of the tricomponent aggregate, since the residual fraction of the physical mixture of Fc−β-CD and PPG−β-CD at 780.2 K is higher than 28%, implying that the molecular arrangement resulting from the binding interaction among Fc, PPG, and β-CD induces more efficiently the degradation of each of them. This phenomenon is worth noting and studying not only because of its scientific value but also because of its implications for practical application.

***2. DTG Analysis.*** Figure 5 depicts the DTG curves of PPG−Fc−β-CD and free β-CD. The curve of the latter is quite different from that of the former, since it shows a moderate peak at 595.2 K but the former presents a very strong peak at 592.2 K and a weak shoulder peak at 566.2 K (0.182%·s⁻¹). A much higher decomposition rate and a lower maximum decomposition temperature reveal that the thermal stability of the

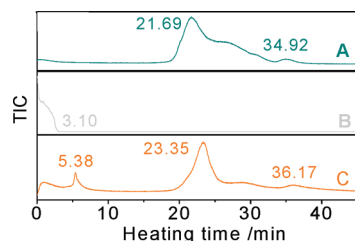**Figure 6.** TIC curves of free $\beta$-CD (A), free Fc (B), and PPG−Fc−$\beta$-CD (C) under the same heating conditions.



**Figure 7.** Mass spectrum of PPG−Fc−$\beta$-CD at 23.35 min.



**Figure 8.** Proposed formation model of $C_6H_6O_3^+$ ion ($m/z$ 126.032) from $\beta$-CD at 23.35 min.



**Figure 9.** Mass spectra of PPG−Fc−$\beta$-CD at 20.54 (A), 22.72 (B), 27.64 (C), and 31.42 min (D).

complexed $\beta$-CD in PPG−Fc−$\beta$-CD is lower than that of free $\beta$-CD under a nitrogen atmosphere.

Similar to PPG−Fc−$\beta$-CD, Fc−$\beta$-CD also shows a small peak due to the release of Fc at 558.7 K (0.090%·s$^{-1}$).[35] Corresponding to the peak at 566.2 K in PPG−Fc−$\beta$-CD, a temperature difference of 7.5 K between them indicates that the release of Fc in the tricomponent aggregate is later than in the binary complex.

Furthermore, the maximum decomposition rate of PPG−Fc−$\beta$-CD (0.786%·s$^{-1}$ at 592.2 K) is much higher than those of Fc−$\beta$-CD (0.297%·s$^{-1}$ at 587.2 K) and PPG−$\beta$-CD (0.235%·s$^{-1}$ at 596.2 K).[30,35] These data indicate the thermal stability of PPG−Fc−$\beta$-CD at higher temperatures is weakened relative to the two binary complexes under a nitrogen atmosphere. The result is associated with the fact that two kinds of packing modes exist in the tricomponent aggregate, but each of the two binary complexes exhibits the stacking behavior of a channel form based on PXRD analyses. In order to further evaluate spectral differences between the aggregate and free components, as well as between the aggregate and the two binary complexes, GC-TOF-MS analysis is performed to investigate the relationship between fragment compositions and heating temperatures of samples.

**Thermal Release Order of Three Assembled Components in the Aggregate. *1. Total Ion Current (TIC) Analysis.*** Figure 6 shows the plots of TIC versus heating time of free $\beta$-CD, free Fc, and PPG−Fc−$\beta$-CD under the same heating conditions. Apparently, the TIC curve of the tricomponent aggregate is distinct from those of free components at the same heating program.

First, there is a weak peak at 5.38 min (kept 0.255 min at 473.2 K) in PPG−Fc−$\beta$-CD, attributed to the first thermal release of some complexed Fc molecules. However, it appears at 5.15 min (kept 0.025 min at 473.2 K) in Fc−$\beta$-CD.[35] As shown in Figure 6B, the complete sublimation of free Fc appears before 3.10 min. The observation suggests that from Fc to Fc−$\beta$-CD to PPG−Fc−$\beta$-CD, the sublimation of Fc becomes more and more difficult.

Second, the strongest peak in PPG−Fc−$\beta$-CD occurs around 23.35 min but at 21.85 min in Fc−$\beta$-CD.[35] The delay of the maximum release time implies that the substantial destruction for PPG−Fc−$\beta$-CD is more difficult than that for Fc−$\beta$-CD under GC-TOF-MS conditions. The difference (about 15 K) in the maximum release temperatures of them shows PPG−Fc−$\beta$-CD has a higher thermal stability than Fc−$\beta$-CD, which is not in accordance with the results of TG and DTG under a nitrogen atmosphere. This reveals different measurement conditions can induce different orders of thermal stability between the binary complex and the tricomponent aggregate.

The mass spectrum of PPG−Fc−$\beta$-CD at 23.35 min, corresponding to the strongest peak in the TIC curve is displayed in Figure 7. This figure shows the relation between the relative 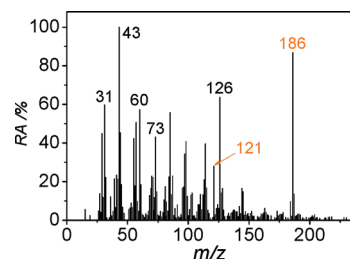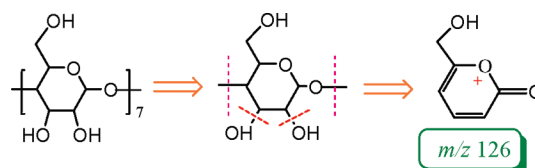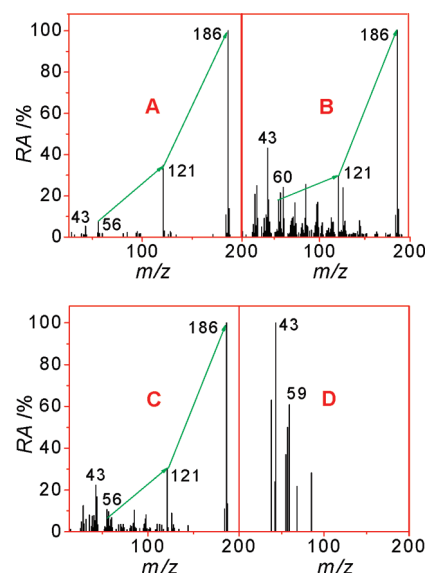abundance (RA, %) of released fragments and their molecular mass. Clearly, the main process of thermal release is driven by the decomposition of the complexed $\beta$-CD, since several very strong signals such as $m/z$ 43.019 ($C_2H_3O^+$, RA, 100.00%), 60.021 ($C_2H_4O_2^+$, 57.27%), 73.030 ($C_3H_5O_2^+$, 43.13%), and 126.032 ($C_6H_6O_3^+$, 63.62%) come from the cleavage of $\beta$-CD.

A proposed formation model and probable structure of $C_6H_6O_3^+$ ion are listed in Figure 8. Furthermore, the occurrence of two observable peaks at $m/z$ 120.974 ($C_5H_5Fe^+$, RA, 27.98%) and 186.013 (Fc$^+$, 86.82%) due to Fc demonstrates that the contribution from the thermal release of the complexed Fc to the main decomposition process of the aggregate is important all the time.

***2. Mass Spectra Analysis at Different Times.*** Figure 9 illustrates the mass spectra of PPG−Fc−$\beta$-CD at several different heating times. By comparison, we find that there is a great difference between the thermal degradation behaviors of Fc−$\beta$-CD and PPG−Fc−$\beta$-CD at the same temperature under the same heating program.

As shown in Figure 9, the fragment signals at $m/z$ 186, 121, and 56 are attributed to the decomposition of the complexed Fc (Fc$^+$, 186.013; $C_5H_5Fe^+$, 120.974; Fe$^+$, 56.936). The RA values of the fragments in particular Fc$^+$ ion are considerably large even at higher temperatures such as 599.2 K (22.72 min)

**TABLE 3: RA Values of Three Typical Fragments from Fc in Fc−β-CD and PPG−Fc−β-CD at Different Heating Times**

| t (min) | complexes | 55.936 | 120.974 RA (%) | 186.013 | ratio of RA |
|---|---|---|---|---|---|
| 20.54 | Fc−β-CD | 4.57 | 36.03 | 100.00 | 1.0:7.9:21.9 |
| | PPG−Fc−β-CD | 7.67 | 34.77 | 100.00 | 1.0:4.5:13.0 |
| 22.72 | Fc−β-CD | 16.77 | 36.82 | 100.00 | 1.0:2.2:6.0 |
| | PPG−Fc−β-CD | 7.21 | 29.63 | 100.00 | 1.0:4.1:13.9 |
| 27.64 | Fc−β-CD | 21.47 | 23.31 | 62.14 | 1.0:1.1:2.9 |
| | PPG−Fc−β-CD | 6.28 | 30.53 | 100.00 | 1.0:4.9:15.9 |
| 31.42 | Fc−β-CD | 22.39 | 5.92 | 16.34 | 1.0:0.3:0.7 |
| | PPG−Fc−β-CD | | | | |

**TABLE 4: RA Values of Three Typical Fragments from PPG in PPG−Fc−β-CD at Different Heating Times**

| heating times (min) | 59.050 | 117.092 RA (%) | 175.134 |
|---|---|---|---|
| 20.54 | | | |
| 22.27 | 2.12 | 1.19 | 1.01 |
| 27.79 | 5.72 | 1.23 | |
| 31.42 | 60.82 | | |

and 648.2 K (27.64 min). However, these characteristic fragments in Fc−β-CD are observed earlier at a lower temperature such as 561.7 K (18.99 min).[35] The fact that the initial release temperature of Fc in PPG−Fc−β-CD is later than that in Fc−β-CD implies Fc is bound more tightly by β-CD in the presence of PPG.

The RA values, as well as the ratio values of RA, of the three fragments at different heating times (t/min) between Fc−β-CD and PPG−Fc−β-CD are listed in Table 3.

Table 3 indicates the RA values of these fragments decrease in the order Fc⁺ > C₅H₅Fe⁺ > Fe⁺ before 31.42 min, and the ratio values of RA at any same heating time for Fc−β-CD and PPG−Fc−β-CD are different from each other. At 31.42 min, all of the fragments are still detected in Fc−β-CD, but the order changes as follows: Fe⁺ > Fc⁺ > C₅H₅Fe⁺. Interestingly, the fragment signals from Fc disappear at 31.42 min (673.2 K) in PPG−Fc−β-CD. These observations show that the second thermal release of Fc is completed in a shorter period of time in PPG−Fc−β-CD than in Fc−β-CD.

These small fragments $C_2H_3O^+$ (43.019), $C_2H_4O_2^+$ (60.021), and $C_3H_5O_2^+$ (73.030) in Figure 9 come from the complexed β-CD.[42] In Figure 9A, only one very small peak at m/z 43.019 (RA, 5.0%) is observable, indicating that the complexed β-CD decomposes very little at least at 20.54 min. With the increase of temperature, the complexed β-CD begins to degrade substantially. Figure 9B and C reveals the fragment distributions before and after the sharp decomposition (23.35 min at the TIC curve) of the tricomponent aggregate. Clearly, the decomposition behavior of the aggregate in the two figures is mainly reflected by the thermal release of Fc in the complex, since the molecular ion peak at m/z 186.013 is the strongest peak. At 31.42 min, the fragment $C_3H_7O^+$ at m/z 59.050 from PPG in the aggregate displays a considerable signal (RA, 60.82%).

However, as shown in Table 4, the fragment at m/z 59.050 as well as other fragments such as $C_6H_{13}O_2^+$ (m/z 117.092) and $C_9H_{19}O_3^+$ (m/z 175.134) from PPG exhibits very low signal intensity before 31.42 min or even does not occur at all at 20.54 min or earlier. This result is completely different from those of both free PPG and PPG−β-CD,[35] because the decomposition processes of the two samples provide a series of observable signals from PPG before 20.54 min. This finding suggests that the thermal degradation of PPG is significantly delayed owing to the formation of the tricomponent aggregate.
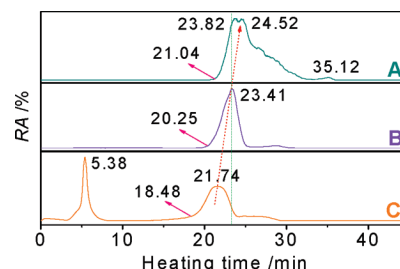


**Figure 10.** TTC curves of the fragments of m/z 59.050 (A), 60.021 (B), and 186.013 (C) from PPG−Fc−β-CD.

***3. Analysis on the Time-Trace Curves (TTC) of Several Typical Fragments.*** According to data derived from the mass spectra above, the TTC curves of three typical fragments Fc⁺ (m/z 186.013), $C_2H_4O_2^+$ (m/z 60.021), and $C_3H_7O^+$ (m/z 59.050) due to the decomposition of Fc, β-CD, and PPG, respectively, are shown in Figure 10.

First, the TTC curve of the fragment at m/z 186.013 indicates two main release processes of Fc⁺ at 5.38 and 21.74 min in PPG−Fc−β-CD, corresponding to around 480.2 and 589.2 K, respectively, which differ from the release behavior of Fc⁺ in Fc−β-CD with the two peaks at 5.22 and 20.27 min.[30] Besides, the initial time for the second release process is later in PPG−Fc−β-CD (18.48 min) than in Fc−β-CD (16.94 min). The results demonstrate that the complexed Fc is more stable in PPG−Fc−β-CD than in Fc−β-CD under GC-TOF-MS conditions.

Second, the appearance of the fragment $C_2H_4O_2^+$ (m/z 60.021) means the rupture of both C−C and C−O bonds in α-1,4-D-glucopyranosyl units of β-CD. As shown in Figure 10B, the TTC curve of the fragment only shows a sharp peak at 23.41 min, and it ranges from 20.25 to 25.05 min. In Fc−β-CD, the peak appears at 21.67 min, over a very broad range from 18.53 to 32.72 min.[30] These results imply the decomposition of β-CD in the tricomponent aggregate experiences a process of rapid mass loss.

Third, the rapid massive gasification of the fragment ($C_3H_7O^+$, m/z 59.050), as the smallest repeat unit of PPG, reflects the efficient cleavage for the PPG chain. As seen in Figure 10A, the initial point of the strong double peak (at 23.82 and 24.52 min) is at 21.04 min, which is later than those of Fc and β-CD. And the signal appears in a long time range from around 21 to 32 min. Furthermore, a small number of fragments are still detected up to 35.12 min (about 833.2 K). Therefore, we conclude that PPG degrades at the end of the period of decomposition of the tricomponent aggregate. That is to say, the order of decomposition of the three assembled components in PPG−Fc−β-CD is Fc > β-CD > PPG.

**Conclusions**

A novel tricomponent aggregate PPG−Fc−β-CD was obtained and characterized by a series of measurements such as ¹H NMR, FAAS, HPLC, UV−vis, FTIR, PXRD, TG, DTG, and GC-TOF-MS. This tricomponent aggregate exhibited a special accelerated decomposition point at high temperature stage and a rare phenomenon of an extremely low ultimate residual mass (less than 1%) in its TG curve. The thermal stability of β-CD and PPG−Fc−β-CD indicated the opposite order in a vacuum and under a nitrogen atmosphere. Furthermore, our results provided significant insight into the thermodynamic properties of the tricomponent aggregate, which were significantly different from those of corresponding binary

complexes. Also, the almost complete thermal degradation of the tricomponent aggregate consisting of a carbohydrate, a coordination compound, and a polymer at a lower temperature appeared promising for applications in waste disposal. The present work not only offered the possibility to extend the field of research on molecular assembly for multicomponent systems but also provided a very helpful way to raise a wide range of interests both in basic and in industrial research. Also, the arrangement of the different components in a multicomponent aggregate is worth further examination.

**Supporting Information Available:** Data of UV−vis absorption, FTIR spectra, and TG and DTG curves of the complex PPG−Fc−$\beta$-CD; $^1$H NMR spectra, FTIR spectra, TG and DTG curves, and PXRD and 2D NMR spectra of the binary complexes PPG−($\beta$-CD)$_5$ and Fc−$\beta$-CD. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Wenz, G.; Han, B. H.; Muller, A. *Chem. Rev.* **2006**, *106*, 782–817.

(2) Song, L. X.; Bai, L. *J. Phys. Chem. B* **2009**, *113*, 11724–11731.

(3) Kikuzawa, A.; Kida, T.; Akashi, M. *Macromolecules* **2008**, *41*, 3393–3395.

(4) Song, L. X.; Wang, H. M.; Guo, X. Q.; Bai, L. *J. Org. Chem.* **2008**, *73*, 8305–8316.

(5) Song, L. X.; Bai, L. *J. Phys. Chem. B* **2009**, *113*, 9035–9040.

(6) Ikeda, T.; Watabe, N.; Ooya, T.; Yui, N. *Macromol. Chem. Phys.* **2001**, *202*, 1338–1344.

(7) Song, L. X.; Bai, L.; Xu, X. M.; He, J.; Pan, S. Z. *Coord. Chem. Rev.* **2009**, *253*, 1276–1284.

(8) Perl, A.; Kumprecht, L.; Kraus, T.; Armspach, D.; Matt, D.; Reinhoudt, D. N.; Huskens, J. *Langmuir* **2009**, *25*, 1534–1539.

(9) Kraus, T.; Budesinsky, M.; Cisarova, I.; Zavada, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1715–1717.

(10) Tilloy, S.; Crowyn, G.; Monflier, E.; Leeuwen, P. W. N. M. Van; Reek, J. N. H. *New J. Chem.* **2006**, *30*, 377–383.

(11) Canipelle, M.; Caron, L.; Christine, C.; Tilloy, S.; Monflier, E. *Carbohydr. Res.* **2002**, *337*, 281–287.

(12) Kikuzawa, A.; Kida, T.; Akashi, M. *Org. Lett.* **2007**, *9*, 3909–3912.

(13) Song, L. X.; Dang, Z. *J. Phys. Chem. B* **2009**, *113*, 4998–5000.

(14) Muratsugu, S.; Kume, S.; Nishihara, H. *J. Am. Chem. Soc.* **2008**, *130*, 7204–7205.

(15) Ruhland, T.; Svejgaard, L.; Rasmussen, L. K.; Andersen, K. *J. Comb. Chem.* **1994**, *6*, 934–941.

(16) Harada, A.; Takahashi, S. *J. Inclusion Phenom.* **1984**, *2*, 791–798.

(17) Petrovski, Z.; Norton de Matos, M. R. P.; Braga, S. S.; Pereira, C. C. L.; Matos, M. L.; Goncalves, I. S.; Pillinger, M.; Alves, P. M.; Romao, C. C. *J. Organomet. Chem.* **2008**, *693*, 675–684.

(18) Mitkina, T. V.; Zakharchuk, N. F.; Naumov, D. Y.; Gerasko, O. A.; Fenske, D.; Fedin, V. P. *Inorg. Chem.* **2008**, *47*, 6748–6755.

(19) Mitkina, T. V.; Sokolov, M. N.; Naumov, D. Y.; Kuratieva, N. V.; Gerasko, O. A.; Fedin, V. P. *Inorg. Chem.* **2006**, *45*, 6950–6955.

(20) Hapiot, F.; Tilloy, S.; Monflier, E. *Chem. Rev.* **2006**, *106*, 767–781.

(21) Song, L. X.; Xu, P.; Dang, Z. *J. Organomet. Chem.* **2010**, *695*, 177–182.

(22) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821–2823.

(23) Liu, K. L.; Goh, S. H.; Li, J. *Macromolecules* **2008**, *41*, 6027–6034.

(24) Yang, C.; Wang, X.; Li, H. Z.; Ding, J. L.; Wang, D. Y.; Li, J. *Polymer* **2009**, *50*, 1378–1388.

(25) Yang, C.; Yang, J. S.; Ni, X. P.; Li, J. *Macromolecules* **2009**, *42*, 3856–3859.

(26) Ikeda, T.; Higuchi, M.; Kurth, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 9158–9159.

(27) Yui, N. *Macromol. Symp.* **2009**, *279*, 158–162.

(28) Yui, N.; Katoono, R.; Yamashita, A. *Inclusion Polymers: Functional Cyclodextrin Polyrotaxanes for Drug Delivery*; Springer: Berlin, Heidelberg, 2009.

(29) Meng, F. H.; Hennink, W. E.; Zhong, Z. Y. *Biomaterials* **2009**, *30*, 2180–2198.

(30) Guo, X. Q.; Song, L. X.; Dang, Z.; Du, F. Y. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1209–1213.

(31) Araki, J.; Zhao, C. M.; Ito, K. *Macromolecules* **2005**, *38*, 7524–7527.

(32) Harada, A.; Okada, M.; Kawaguchi, Y.; Kamachi, M. *Polym. Adv. Technol.* **1999**, *10*, 3–12.

(33) Cacialli, F.; Wilson, J. S.; Michels, J. J.; Daniel, C.; Silva, C.; Friend, R. H.; Severin, N.; Samorì, P.; Rabe, J. P.; O'Connell, M. J.; Taylor, P. N.; Anderson, H. L. *Nat. Mater.* **2002**, *1*, 160–164.

(34) Yang, C.; Yang, J. S.; Ni, X. P.; Li, J. *Macromolecules* **2009**, *42*, 3856–3859.

(35) See the Supporting Information.

(36) Qi, M. H.; Zhou, H. Y.; Ma, X. F.; Zhang, B. *J. Comb. Chem.* **2008**, *10*, 162–165.

(37) Porcheddu, A.; Giacomelli, G.; De Luca, L.; Ruda, A. M. *J. Comb. Chem.* **2004**, *6*, 105–111.

(38) Harata, K. *Chem. Rev.* **1998**, *98*, 1803–1827.

(39) Saenger, W.; Jacob, J.; Gessler, K.; Steiner, T.; Hoffmann, D.; Sanbe, H.; Koizumi, K.; Smith, S. M.; Takaha, T. *Chem. Rev.* **1998**, *98*, 1787–1802.

(40) Rusa, C. C.; Luca, C.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 1318–1322.

(41) Braga, S. S.; Ribeiro-Claro, P.; Pillinger, M.; Goncalves, I. S.; Fernandes, A. C.; Pereira, F.; Romao, C. C.; Correia, P. B.; Teixeira-Dias, J. J. C. *J. Inclusion Phenom. Macrocyclic Chem.* **2003**, *47*, 47–52.

(42) Xu, P.; Song, L. X.; Wang, H. M. *Thermochim. Acta* **2008**, *469*, 36–42.

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