Supporting Information

Supramolecular Copolymerization Through Self-Correction of Non-polymerizable Transient Intermediates

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1. Experimental Materials and methods

Materials. All reagents were commercially available from Energy, and were used without further purification. Cucurbit[7]uril (CB[7]) and Cucurbit[8]uril (CB[8]) were synthesized according to the published procedure.¹ Monomer NPN (Naph-Phen-Naph), ethyl-NPN, and model compounds (Naph and Phen) were synthesized according to the previous report.²

Nuclear Magnetic Resonance Spectroscopy (NMR). ¹H NMR, ¹³C NMR, ¹H-¹³C HSQC, ¹H-¹³C HMBC, ¹H-¹³C HSQC-NOESY, NOESY, and DOSY spectra were acquired in D₂O and recorded on a Bruker Avance III 500 MHz spectrometer with PABBO probe, a Bruker Avance III 600 MHz spectrometer with BBFO Cryoprobe, a Bruker Avance III 850 MHz spectrometer with TCI Cryoprobe at 298 K. ¹H-¹³C HSQC experiments were carried out using a pulse sequence 'hsqcedetgpsisp2.3', ¹H-¹³C HSQC-NOESY experiments were carried out using a pulse sequence 'hmbcetgpl3nd', ¹H-¹³C HSQC-NOESY experiments were carried out using a pulse sequence 'hsqcetgpnosp' with a 1s relaxation delay and a 0.3 s mixing time, and NOESY experiments were carried out using the pulse sequence 'noesyphpp' with a 2 s relaxation delay and a 0.5 s mixing time on an 850 MHz NMR instrument. DOSY experiments were carried out using a pulse sequence service out using a pulse sequence 'stebpgp1s' with a 0.08 s diffusion time and a 5000 µs length of the gradient pulse on a 500 MHz NMR instrument. Note that the conventional DOSY as well as ¹H NMR monitoring experiments were carried out immediately loaded after the vortex mixing.

Microfluidic-NMR (\muF-NMR). The microfluidic-NMR experiments were carried out using a Varian NMR system (USA) operating at a proton Larmor frequency of 500 MHz. The original probe was replaced with our custom-built transmission line NMR probe head. The radio-frequency magnetic field transmitted by the double-stripline is concentrated in the rectangular sample chamber to ensure enough sensitivity. PMMA chips were used, which consist of a mixing channel, a 2 μ L buffering section, and a 2

 μ L NMR sampling section. The volume from the front end of buffering section to the center of the sampling chamber was about 3 μ L, thereby the reaction time at the detecting region equals 3 μ L divided by the total volumetric flow rate. For example, to obtain the NMR spectrum of the polymerization system at 1.5 s, the initial flow rate was set as 60 μ L/min for both reactants. Then the flow rate varied from 60 μ L/min to 0.25 μ L/min in our study, corresponding to the time points from 1.5 s to 360 s. It should be noted that the relaxation delay was set to 4 s to ensure the full relaxation of the system before the next measurement, therefore the quantitative feature of μ F-NMR did not affect by the flow rate changes, despite the signal to noise ratio (S/N) as well as linewidth may increase as the flow rate increase.^{3, 4} More detailed information about the μ F-NMR setup as parameters setting can be found in previous papers.⁵⁻⁷



Scheme S1. Schematic representation of μ F-NMR.

2. Results and discussion



Table S1. Association constants between mentioned hosts and guests²

7.3 7.1 6.9 6.7 5.9 5.7 5.5 5.3 4.3 4.2 4.1 4.0 4.0 3.5 3.3 3.1 2.9 2.7 Figure S1. ¹H NMR spectra of a) NPN • CB[7]₃, b) depolymerization sample at about c) 3min and d) 1 h. Several peaks of the depolymerization sample and polymerization sample have chemical shifts similar to the ones of NPN•CB[7]₃, suggesting similar structural fragments.

In the following NMR studies (Figure S2-S15), the peak assignment of ¹H NMR spectra of NPN•CB[7]₃ and depolymerization sample were carried out under the assistance of 2D NMR spectra. Finally, the peak assignment of transient ¹H NMR spectrum of polymerization sample were carried out referring to the spectra of NPN•CB[7]₃ and depolymerization sample.



Figure S2. The ¹H-¹³C HSQC spectrum of NPN•CB[7]₃. The protons α and β of CB[7] bond to the same carbon atom C1, therefore they are correlated with a same carbon peak. Besides, both the protons α and β of CB[7] are methylene protons and the protons γ of CB[7] are methine protons, therefore they were readily distinguished by the phase-sensitive HSQC experiment. Note: for all the HSQC spectra in this study, CH and CH₃ signals were marked with blue color, and CH₂ signals were marked with green color, unless otherwise stated.



Figure S3. Superimposed spectra of HSQC (blue & green) and HMBC (red) of NPN• CB[7]₃. Since the HMBC experiment gives correlations between long-range coupled ¹H and ¹³C, all the signals of NPN in HSQC spectrum were then assigned under the assistance of HMBC spectrum. Only half of the NPN structure was shown for clarity.



Figure S4. The assignment of ¹H NMR peaks of NPN•CB[7]₃ according to the analyses in figures S2 & S3. Only half of the NPN structure was shown for clarity.



Figure S5. The HSQC spectrum of depolymerization sample. The protons of CB[7] together with CB[8] were assigned as shown in the spectrum. The protons α and β of CB[7] bond to the carbon atom C1, therefore they are correlated with a same carbon peak. Then the signal of C2 was readily distinguished from the signal of C1. The assignment of signals of CB[8] followed the same rules.



Figure S6. a) Superimposed HSQC spectra of depolymerization sample (blue and green) and NPN•CB[7]₃ (CH and CH₃ signals in red and CH₂ signals in pink). The protons of CB[7] complexed with the naphthalene and *p*-phenylene groups, the protons of CB[8] and methylene of NPN in the depolymerization sample were assigned according to the assignment results of NPN • CB[7]₃ in Figure S2&S4. b) NOESY spectrum of depolymerization sample. The correlation signals further confirmed the proton assignment of CB[7] that complexed with the naphthalene group.



Figure S7. The HSQC spectrum of depolymerization sample (blue) superimposed on the spectrum of NPN•CB[7]₃ (red). The protons of naphthalene, *p*-phenylene, and methyl of NPN in the depolymerization sample were assigned according to the assignment results of NPN•CB[7]₃ in Figures S3&S4.



Figure S8. The HSQC-NOESY spectrum of depolymerization sample. The protons of *p*-phenylene, and methyl adjacent to *p*-phenylene of NPN, were assigned as shown in the spectrum. The results further confirmed the assignment results in Figure S7.



Figure S9. The assignment of ¹H NMR peaks of depolymerization sample. The integration results further confirmed the above assignment results in Figure S5-S8.



Figure S10. DOSY spectrum of depolymerization sample. Three states of *p*-phenylene can be distinguished from three different diffusion coefficients in the spectrum.



Figure S11. The NOESY spectrum of depolymerization sample. The cross peak between two doublets means the protons are close to each other, indicating that this state of *p*-phenylene of NPN is in an asymmetric chemical environment.



Figure S12. Three states of *p*-phenylene of NPN were proposed based on the results of figures S10&S11, and the protons were assigned as shown in the spectrum. The integration results suggested the ratio of P1, P2, and P3 was about 1:2:1. The reason may be the same binding free energies for the two naphthalene end groups,⁸ which was further confirmed in Figure S13.



Figure S13. a) The DOSY spectrum and b) the ¹H NMR spectrum of NPN+2CB[7]. The results displayed a discrete binomial distribution of the three species NPN•CB[7], NPN•CB[7]₂, and NPN•CB[7]₃ in a ratio of about 1:2:1. The results further confirmed that the binding free energies for the two naphthalene end groups are the same, and the complexation between CB[7] and naphthalene is independent of the state of *p*-phenylene.



Figure S14. The HSQC spectrum of polymerization sample at equilibrium. The protons of CB[7] and CB[8] were assigned according to the assignment results of the depolymerization sample in Figure S6.



Figure S15. The HSQC spectrum of supramolecular polymers (blue) superimposed on the spectrum of depolymerization sample (CH and CH₃ peaks in red). The protons of naphthalene and *p*-phenylene of NPN, the protons of methyl adjacent to naphthalene and *p*-phenylene are assigned according to the assignment results of the depolymerization sample in Figure S7-S9.

2.4 The identification of intermediates during supramolecular polymerization

Multiple dynamic peaks of the polymerization sample have similar chemical shifts to the ones of the depolymerization sample (Figure S1), suggesting similar structure fragments. In this section, we confirmed that the peak at 5.35 ppm represents the N7 structure in all intermediates, and the peak at 3.20 ppm represents the N7P7 structure. Besides, two new peaks at 2.79 ppm and 2.82 ppm were observed during polymerization. The former was observed by convention NMR while the latter was only observed by μ F-NMR. The peak at 2.79 ppm represents the structure of N₂8P8, and the peak at 2.82 ppm represents the structure of N7P8.



Figure S16. ¹H NMR spectra of a) CB[7], b) NPN+CB[8], polymerization sample at about c) 3min and d) 35 min, e) NPN•CB[7]. Multiple dynamic peaks in ¹H NMR spectra were observed during the polymerization. Most of the peaks from the two raw materials for polymerization, NPN+CB[8] and CB[7], were not observed in spectrum c, suggesting that the raw materials immediately converted to various intermediates.



Figure S17. Time-dependent ¹H NMR spectra of polymerization process within ~35 min monitored by conventional NMR technique. The spectra were acquired at 200 s interval. The dynamic peaks were identified according to the following NMR studies (Figure S18-S32).



Figure S18. a) Superimposed HSQC spectra of polymerization sample (blue) recorded immediately after mixing NPN+CB[8] with CB[7] solutions, and depolymerization sample (red). The proton γ of CB[7] combined with the naphthalene group was assigned according to the assignment results of the depolymerization sample in Figure S6 as shown in the spectra. b) The NOESY spectrum of polymerization sample recorded immediately after mixing. The protons α and β of CB[7] that combined with the naphthalene group were assigned as shown in the spectrum.



Figure S19. Partial ¹H NMR spectra of a) model compound Naph⁺, b) Naph⁺•CB[7], c) Naph⁺+CB[8], d) Naph⁺₂•CB[8], e) model compound Phen²⁺, f) Phen²⁺•CB[7], and g) Phen²⁺•CB[8]. The methyl protons of Phen²⁺ experienced a significantly upfield shift after complexing with CB[8].



Figure S20. Partial ¹H NMR spectra of a) model compound Naph²⁺, b) Naph²⁺•CB[7], c) Naph²⁺⁺CB[8], d) Naph²⁺₂•CB[8], e) model compound Phen⁴⁺, f) Phen⁴⁺•CB[7], and g) Phen⁴⁺ • CB[8]. The methyl protons of Phen⁴⁺ adjacent to *p*-phenylene experienced a significantly upfield shift after complexing with CB[8], while the methyl protons adjacent to naphthalene experienced a downfield shift after complexing with CB[8]. Besides, all the methyl protons of Naph²⁺ experienced downfield shifts after complexing with CB[8] in a 2:1 mode.



Figure S21. NMR titration experiments. Specifically, 15 mM of NPN was titrated into 2 mM of NPN+CB[8]. Based on the binding constants of CB[8] with naphthalene (K₁ = $2.6 \times 10^5 \text{ M}^{-1}$, K₂ = $2.3 \times 10^5 \text{ M}^{-1}$) and with *p*-phenylene (K₁ = $4.1 \times 10^7 \text{ M}^{-1}$), it could be calculated that only the structures that CB[8] complexed with two naphthalene (abbreviated as N₂8P) and free monomer (abbreviated as NP) exist when excess NPN added. As the increase of CB[8], partial CB[8] were complexed with *p*-phenylene, resulting in the formation of N₂8P8 and NP8 as shown in the figure. Combining the NMR results in Figure S19&20, the methyl protons were assigned as shown in the spectrum.



Figure S22. Partial ¹H NMR spectra of a) polymerization sample at about 3min after mixing, b) NPN+2CB[7], c) NPN+CB[8]. Peaks with similar chemical shifts suggest similar chemical structures.



Figure S23. Superimposed HSQC spectra of polymerization sample (blue) recorded immediately after mixing, NPN+2CB[7] (red), and NPN+CB[8] (purple). The peak at 3.20 ppm represents the protons 5 from N7P7 (abbreviated as 5(N7P7)), and the peak at 2.79 ppm represents the protons 2 from P8. Since either CB[8] or CB[7] complexed with the naphthalene group can induce downfield NMR shifts of the methyl protons adjacent to *p*-phenylene (Figure S20), the peak at 2.79 ppm may represent the structures of N₂8P8 or N7P8 as shown in the figure.



Figure S24. NMR titration experiments of polymerization. Specifically, 4 mM of CB[7] was titrated into 4 mM of NPN+CB[8]. The peak at 2.80 ppm has a similar chemical shift to the dynamic peak of 2.79 ppm of the polymerization mixture.



Figure S25. Superimposed HSQC spectra of polymerization sample (blue) recorded immediately after mixing, NPN+CB[8]+0.5CB[7] mixture (red), and the partial ¹H NMR spectra of NPN+CB[8]+0.5CB[7] (green). Since the strongest binding affinity between CB[7] and *p*-phenylene (K = 7.4E9 M⁻¹), it is highly unlikely that CB[7] can still combine with the naphthalene group when the monomer NPN is excess. Therefore, the peak at 2.80 ppm of NPN+CB[8]+0.5CB[7] does not represent the structure of N7P8. It is reasonable to deduce that the peak at 2.79 ppm represents the structure of N₂8P8 rather than N7P8.



Figure S26. NOESY spectra of polymerization sample recorded immediately after mixing NPN+CB[8] with CB[7] solutions. The protons of N_28P8 were assigned as shown in the spectra.



Figure S27. Time-dependent ¹H NMR spectra of polymerization process monitored by μ F-NMR technique. Specifically, 4 mM of CB[7] and 4 mM of NPN+CB[8] were pumped into the microfluidic chip simultaneously in a same volumetric flow rate.



Figure S28. Integration of the ¹H NMR spectrum of the complexation between CB[7] and NPN at 1.5 s. The spectrum was monitored by μ F-NMR. All the μ F-NMR spectra were integrated in this way, and the average concentration at each time point was obtained from three parallel μ F-NMR experiments.



Figure S29. A transient peak at 2.82 ppm was observed from the onset to 15 s during polymerization. Because the complexation of CB[7] with the naphthalene group can induce the downfield shift of the methyl protons adjacent to p-phenylene (Figure S20), the peak at 2.82 ppm probably comes from the structure of N7P8 as shown in the figure.



Figure S30. Partial ¹H NMR spectra of free NPN, NPN+2CB[7], and polymerization titration experiments. Protons of naphthalene and *p*-phenylene which are free or complexed were assigned as shown in the spectra.



Figure S31. Partial time-dependent ¹H NMR spectra of polymerization monitored by μ F-NMR. Free naphthalene or *p*-phenylene groups were determined based on the results of Figure S30. It indicates the existence of metastable intermediates bearing free naphthalene or *p*-phenylene group during polymerization on the time scale of seconds.



to the results of Figures S1 to S31.

2.5 Complexation between NPN and CB[7]



Figure S33. Time-dependent ¹H NMR spectra of complexation process between CB[7] and NPN monitored by μ F-NMR. Specifically, 4 mM of CB[7] and 4 mM of NPN were pumped into the microfluidic chip in a same volumetric flow rate.



Figure S34. Partial time-dependent ¹H NMR spectra of complexation process between CB[7] and NPN monitored by μ F-NMR. Free monomer, NPN•CB[7], NPN•CB[7]₂, and NPN•CB[7]₃ were observed during the process. All of them finally converted into the equilibrium product NPN•CB[7].



Figure S35. a) Proposed complexation pathways between CB[7] and NPN; b) Timedependent concentrations of free NPN, NPN•CB[7], NPN•CB[7]₂, and NPN•CB[7]₃.



Figure S36. Pathways and kinetic study of the complexation between NPN and CB[7]. Considering the symmetry of the molecular structure, the schematic shows only half of the NPN structure for clarity. a) Formation pathways of NP7. The red arrow lines represent the rate-determining step. b) Time-dependent concentrations of reactant NP, intermediate N7P7, and product NP7, and the simulated kinetic traces with $R^2 = 0.985$, 0.986, and 0.985, respectively. Initial concentrations: $[NPN]_0 = 2 \text{ mM}$, $[CB[7]]_0 = 2 \text{ mM}$.

2.6 The starting species of supramolecular polymerization



Figure S37. Partial ¹H NMR spectrum of NPN+CB[8] at 4 mM. The integration results indicated that about 25% of CB[8] (calculated by 3.27/12) are complexed with the *p*-phenylene group. For the detailed assignment sees Figure S21.



Figure S38. DOSY spectrum of NPN+CB[8] at 4 mM. A uniform structure of oligomers composed of NPN and CB[8] was proposed according to the DOSY result, and the conclusion that the ratio of CB[8] complexed with naphthalene to *p*-phenylene is about 3:1 obtained from Figure S37.

2.7 The change of averaged molecular weight during supramolecular polymerization



Figure S39. a) The mathematical relationship between molecular weight (M) of polymer and diffusion coefficient (D) was established according to the literature⁹ as well as the three model structures with defined M and D. b) Plots of the diffusion coefficient of proton γ of CB[7] which complexed with *p*-phenylene within the polymer (γ (polymer, P7)). Note that three parallel DOSY monitoring experiments were carried out and the samples were immediately loaded after the vortex mixing. To further reduce the error in the timing, the time points of the three parallel experiments were averaged.

2.8 The dissociation rate constants of CB[7] from naphthalene for N7P7 and N7P structures

The N7P7 was constructed by mixing CB[7] with NPN, and the N7P was constructed by mixing CB[7] with ethyl-NPN. The structure of N7P7 and N7P were confirmed by the NMR titration experiments.



Figure S40. a) ¹H NMR (D₂O, 298 K) titration spectra of NPN and CB[7]. b) ¹H NMR (D₂O, 298 K) titration spectra of ethyl-NPN and CB[7]. Note: calculated volume of NPN/ ethyl-NPN (5 mM) was added to the 500 μ L of CB[7] (1 mM).

The above results showed that CB[7] could thread to the *p*-phenylene group of NPN,

but could not thread to the p-phenylene group of ethyl-NPN. Therefore, N7P7 and N7P with or without *p*-phenylene complexed by CB[7] were constructed respectively after adding excess CB[7].



Figure S41. a) 1D EXSY (D₂O, 318 K) experiment of NPN with 5 equivalents of CB[7].

b) 1D EXSY (D₂O, 318 K) experiment of ethyl-NPN with 4 equivalents of CB[7]. Note: the concentration of unbound CB[7] plotted versus mixing time was fitted by the first order approaching equilibrium to obtain the rate constant.¹⁰ [NPN]₀ = [ethyl-NPN]₀ = 1 mM. Since the exchange rates are too slow for the 1D EXSY experiment at 298 K, the temperature was increased to 318 K. The significant displacements of chemical shifts compared with the spectra in Figure S40 resulted from the increase of temperature.

The above results showed that the two dissociation rate constants of CB[7] from naphthalene to solution are 0.463 s⁻¹ and 0.432 s⁻¹ either with or without *p*-phenylene complexed by CB[7]. These two rate constants only have difference less than 7 percent. Therefore, it is reasonable to assume that the rate constant for the association or dissociation of CB7 or CB[8] with naphthalene was independent of the status of *p*-phenylene.

2.9 Kinetic models

Considering the fact that the association/dissociation rate constants of CB[7] with naphthalene are independent of the status of p-phenylene (Figure S40&41), the rate constants were set to be the same in the following models, no matter the p-phenylene complexes with CB[7] or not. This principle also applies to the case of CB[8] with naphthalene.

2.9.1 Kinetic model for the complexation between NPN and CB[7]

The process is given by:

NP+CB7
$$\xrightarrow{k_{7,1}}$$
 N7P $\xrightarrow{k_{ex}}$ 2NP7
NP7+CB7 $\xrightarrow{k_{7,1}}$ N7P7

In the process, the dissociation of CB[7] from naphthalene is the rate-determining step. and the corresponding rate equations are given by:

$$\frac{\partial [N7P7]}{\partial t} = k_{7,1}[NP7][CB7] - k_{7,-1}[N7P7]$$
$$\frac{\partial [NP]}{\partial t} = -k_{7,1}[NP](0.5[NP] - [N7P7])$$

with

$$[N7P7] + [NP7] + [NP] = [N]_0 = 2c_0$$
$$[CB7] + 1.5[N7P7] + 0.5[NP7] = [CB7]_0 = c_0$$

The Equation can be simplified as:

$$[N7P7] = A \cdot (1 - e^{-k_{7,-1} \cdot t})$$
$$\frac{2\partial [NP]}{[NP]([NP] - 2[N7P7])} = -k_{7,-1}\partial t$$
$$\left[\frac{1}{[NP] - 2[N7P7]} - \frac{1}{[NP]}\right]\partial [NP] = -k_{7,-1}[N7P7]\partial t$$

The exact solutions of this equation were solved in Mathematica. The code is given by:

$$DSolve[{y'[t]==k2 y[t] (y[t]-c1 Exp[-k1 t]),y[t],t]}$$

The approximate solutions are shown as follows:

$$[NP] = A \cdot exp(B \cdot exp(C \cdot t)) + A \cdot exp(-C \cdot t) + D$$
$$[NP7] = A \cdot exp(B \cdot exp(C \cdot t)) + D$$

In these equations, A represents the maximum concentrations of the species, B

represents a complex integral formula including $k_{7,1}$, $k_{7,-1}$, k_{ex} , and C_0 , C represents $k_{7,-1}$, and D represents a correction term of concentration.

2.9.2 Kinetic model for the stage I of supramolecular polymerization

The process is given by:

$$N_{2}8P \xrightarrow{k_{8,-2}} N8P+NP$$

$$N8P \xrightarrow{k_{ex}} 2NP8$$

$$NP+CB7 \xrightarrow{k_{7,1}} N7P \xrightarrow{k_{ex}} 2NP7$$

$$NP7+CB7 \xrightarrow{k_{7,1}} N7P7$$

$$NP8+CB7 \xrightarrow{k_{7,1}} N7P8$$

Stage I of the polymerization can be summarized into three processes: 1) the dissociation of CB[7] or CB[8] from naphthalene, 2) the threading of CB[7] or CB[8] from naphthalene to *p*-phenylene, and 3) the association of naphthalene with CB[7]. The processes are similar to the ones between NPN and CB[7], and the concentration of N7 is described as follows:

$$[N7] = A \cdot exp(B \cdot exp(C \cdot t)) + D$$

In the equation, *A* represents the maximum concentration of N7, *B* represents a complex integral formula including $k_{8,-2}$, $k_{7,1}$, $k_{7,-1}$, k_{ex} , and C₀, and C represents the sum of $k_{7,-1}$ and $k_{8,-2}$, D represents the initial concentration of N7.

2.9.3 Kinetic model for the error-correction pathways in stage II of supramolecular polymerization

For the error correction of N7, two parallel pathways are involved: 1) the disassociation of N7, and then the association of released CB[7] to free *p*-phenylene from the disassociation of N₂8; 2) the disassociation of N₂8, and then the fast sequential threading from naphthalene to *p*-phenylene. The former pathway follows second-order kinetics, and the latter one follows first-order kinetics, the corresponding rate equations are given by:

$$\frac{\partial [N7]_1}{\partial t} = k_{8,-2} \cdot [N7] \cdot k_{7,-1} \cdot [N7]$$
$$\frac{\partial [N7]_2}{\partial t} = k_{8,-2} \cdot [N7]$$

the N7₁, N7₂, and N7 can be solved as:

$$[N7]_{1} = \frac{1}{k_{7,-1} \cdot k_{8,-2} \cdot c' \cdot t + \frac{1}{c'}}$$
$$[N7]_{2} = (c_{0} - c') \cdot e^{-k_{8,-2} \cdot t}$$
$$[N7]_{1} + [N7]_{2} = (c_{0} - c') \cdot e^{-k_{8,-2} \cdot t} + \frac{1}{k_{7,-1} \cdot k_{8,-2} \cdot c' \cdot t + \frac{1}{c'}}$$

In the equations, $[N7]_1$ and $[N7]_2$ represent the concentration of N7 following the pathway 1 and 2 respectively, c_0 represents the maximum concentration of N7, c' represents the total concentration of $N7_1$, $k_{8,-2}$ represents the rate constant of one naphthalene dissociated from CB[8], $k_{7,-1}$ represents the rate constant of naphthalene dissociated from CB[7].

2.9.4 Kinetic model for the supramolecular depolymerization

The depolymerization mainly includes two processes which are the dissociation of one naphthalene from CB[8], and then the association of naphthalene with CB[7]. The corresponding rate equations are given by:

$$\frac{\partial [NP7]}{\partial t} = k_{8,-2} \cdot [N_2 8P7]$$

with

$$[N7P7] = K_7 \cdot [CB7] \cdot [NP7]$$
$$[N_28P7] + [NP7] + [N7P7] \approx [N_28P7] + [N7P7] = c_0$$
$$[CB7] + [N7P7] = c_0$$

the N7P7 can be solved as:

$$[N7P7] = c_0 \cdot e^{k_{8,-2} \cdot t} \cdot (c_1 - c_0 \cdot e^{k_{8,-2} \cdot t})$$

In this equation, c_0 represents final concentration of N7P7, c_1 represents the total concentration of additional added CB7, $k_{8,-2}$ represents the rate constant of the dissociation of one naphthalene from CB[8] ternary complex.

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