Competitive Supramolecular Encapsulation of Amphiphilic Hyperbranched Polymers Made from A_2 and BB'_2 Type Monomers. 1. Polyaddition of 1-(2-aminoethyl)piperazine to Divinyl Sulfone

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Abstract: The competitive host-guest encapsulations of palmityl chloride-modified amphiphilic hyperbranched poly(amido-amine) (HPAMAM-PC) and poly(sulfone-amine) (HPSA-PC) to selected pairs of dyes are reported. Water-soluble and chloroform-insoluble dyes, such as methyl orange (MO), methyl blue (MB), rose bengal (RB), fluorescein sodium (FSS), eosin Y (EY) and phloxine B (PB), can be transferred from aqueous phase into chloroform phase by the HPAMAM-PC and HPSA-PC. UV/Vis spectra were used to determine the loading capabilities (C_{load}s) of different dyes in the case of single-dye encapsulations (Exp I). Four pairs of dyes: (1) MO and RB, (2) MO and PB, (3) MO and EY, (4) MO and FSS, were chosen to perform comparative experiments to investigate the influence of competitive interactions on the C_{load}s of dye pairs. As a result, in the cases of one-step double-dye encapsulations (Exp II) and gradual double-dye encapsulations (Exp III), we found three kinds of competitive relationships: (1) The C_{load} of MO decreased significantly in the presence of either RB or PB, compared with the C_{load} in the single-dye encapsulation, while the existence of MO did not affect the encapsulations to RB and PB greatly, (2) the C_{load}s of both dyes decreased if they were encapsulated simultaneously by HPAMAM-PC or HPSA-PC (MO & EY), (3) FSS can hardly be encapsulated by the hyperbranched polymers with the existence of MO in the aqueous solution. ^{1}H NMR, FTIR and thermogravimetric analysis (TGA) were used to confirm the resulting competitive encapsulations. Relatively selective constant to MO ($R_{dye/MO}$) was defined to measure the competitive ability of each dye to MO quantitatively. The competitive abilities of RB, PB were larger than that of MO, while EY almost equal to MO and FSS lower than MO. The size of the dye molecules, electrostatic acid-base interactions between the dye molecules and the polymers, the interaction between different dyes were considered to be the main causes of the results.

Keywords: amphiphilic, competition, host-guest encapsulation, hyperbranched polymer.

INTRODUCTION

In 1982, Maciejewski [1] first proposed that the egg-shell like molecules could trap guest molecules and since then, the supramolecular host-guest chemistry based on the host of dendritic polymers have grown very fast [2-12]. Most research efforts paid their attention to the systems that dendrimers worked as the hosts [13-24], for instance, their encapsulation of metal nanoparticles [25-27], their working as the catalysts [28-30], their application in delivering hydrophobic compounds and transferring water-soluble dyes from aqueous solution to organic solvent [13, 14, 21, 31-37].

However, the synthesis of dendrimers is time consuming, which currently limits their practical use in a large scale. For that reason, hyperbranched polymers are a potential alternative to dendrimers, which can be prepared readily by one-step polymerization [38, 39] without the heavy and tedious protection, deprotection and purification steps. Hyperbranched polymers, which are imperfectly branched, also have some unique physical and chemical properties, such as high solubility, low viscosity, free/rare of chain entangle-

ment, and abundant functional groups, and thus they promise a wide range of applications in supramolecular science [40, 41]. Hyperbranched polyglycidol has been used to prepare amphiphilic "molecular nanocapsules" for encapsulating polar guests from water [35, 42, 43]. Haag *et al.* [37] have synthesized pH-responsive hyperbranched polymers (modified polyglycerol and polyethyleneimine). Both polymers can encapsulate some anionic dyes, such as congo red, and the trapped guests could be released from the host by adjusting the pH. Recently, they also did some further dye-loading research on core-shell amphiphilic hyperbranched polyethyleneimine [44, 45]. Gao *et al.* reported that aliphatic chain-modified hyperbranched poly(sulfone-amine) (HPSA) and poly(amido-amine) (HPAMAM) could trap water-soluble dyes into chloroform phase efficiently [46-49]. Besides this kind of molecule-level encapsulation, Edirisinghe *et al.* [50-53] also reported some new methods to prepare different kinds of encapsulated microspheres.

We named such one kind of guest (dye)-host interaction "single-guest (dye)" supramolecular encapsulation. Nevertheless, if there is more than one kind of dyes in the aqueous solution mixed with the organic (e.g., chloroform) solution of an amphiphilic hyperbranched polymer, the situation will be much more complex. The interaction between different

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dyes and the interaction between dye and host should both be taken into consideration. Four consequences can be conceivable: (1) synergistic encapsulation, as Gao *et al.* have reported [48], which means that the loading capability (C_{load}) of one dye increases significantly as compared with that of single-dye encapsulation with the assistant of another one, (2) selective (or competitive) encapsulation [11, 22, 36, 37], which means that the host prefers one dye to the others, (3) random encapsulation, which means that the dyes are encapsulated in a statistical way and the C_{load} of each dye decreases as compared with that of single-dye encapsulation, and (4) negative (or minus) encapsulation, which means that one dye cannot be encapsulated efficiently and its existence is the obstacle of the encapsulation of the host to the other dyes. Herein, we focus on the second kind of encapsulation—competitive encapsulation with the incidental reports on the third and the fourth.

The competitive encapsulation may have potential application in molecules separation for the encapsulated molecules can be removed from the mixture with the giant host polymers, while the other molecules leave behind because they cannot enter the cavity of the host polymers due to the low competitive ability compared to the encapsulated molecules. In this paper, we chose two kinds of amphiphilic hy-

perbranched polymer—palmityl chloride-modified poly (amido-amine) (HPAMAM-PC) and poly(sulfone-amine) (HPSA-PC) as the host polymers and four dye-pairs— methyl orange (MO) & rose bengal (RB), MO & phloxine B (PB), MO & fluorescein sodium (FSS), and MO & eosin Y (EY) performed as the gusts. The encapsulation phenomena between different hosts and guests were discussed properly in the following paragraph. At the end of this article, we proposed a model to explain the different host-guest encapsulations.

EXPERIMENTAL SECTION

Materials

HPAMAM-PC (M_n = 10 780, PDI = 2.39, ca. 61% amino groups were end-capped.) and HPSA-PC (M_n = 11 150, PDI = 1.67, ca. 65% amino groups were end-capped) were synthesized according to the article published before [48]. HPAMAM was synthesized by polycondensation of methyl acrylate (MA) and diethylenetriamine (DETA) (molar ratio 1.2:1) [47] and HPSA was synthesized by polyaddition of divinyl sulfone and 1-(2-aminoethyl)piperazine (1/1 mole ratio) according to the "couple-monomer" methodology [39, 49]. MO was purchased from Tianjin No.3 Chemical Rea-

R = -(CH₂)₁₄CH₃
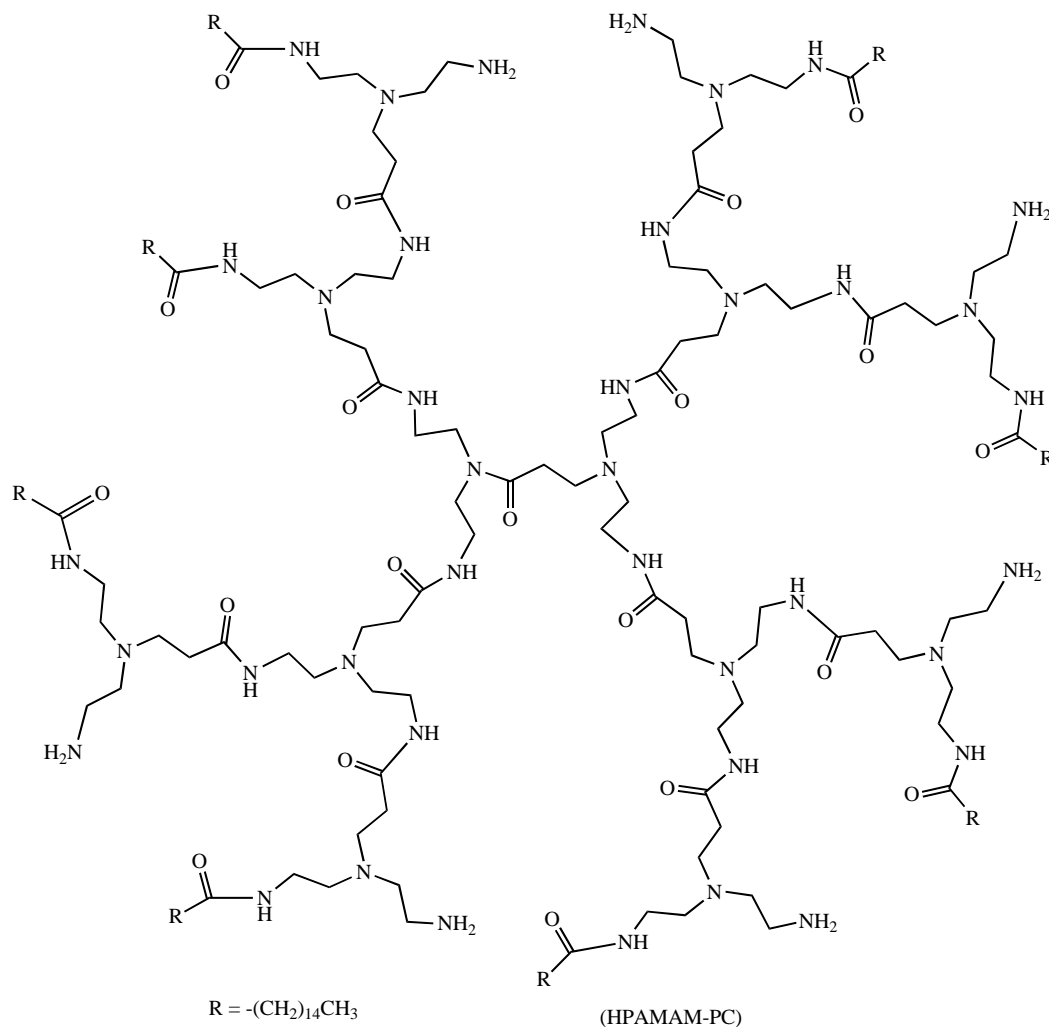
(HPAMAM-PC)

Scheme 1. Chemical structure of HPAMAM-PC.

gent Factory. RB and FSS were purchased from Shanghai No.3 Chemical Reagent Factory and chloroform was from Sinopharm Chemical Reagent Co., Ltd. EY and PB were purchased from Acros. All reagents were used as received. The deionized water was further purified by distillation prior to use.

Instrument

UV/Vis spectra were recorded on a Perkin Elmer Lambda 20/2.0 UV/Vis spectrometer. ^{1}H NMR measurements were carried out on a Varian Mercuryplus 400 NMR spectrometer using CDCl$_3$ as solvent. Thermogravimetric analysis (TGA) was performed under nitrogen on a Perkin-Elmer Pyris-7 thermal analyzer and the heating rate of all the samples was 20°C/min.

Single-Dye Encapsulation (Exp I)

The typically experimental procedures were reported previously [48]. In a typical Exp I (dye A (or B)), 6 mL aqueous solution containing 1.0×10^{-3} M dye A (or B) was mixed with an equal volume of 0.05 g/L HPAMAM-PC chloroform solution. Then the mixture was shaken to make sure that the two phases were mixed adequately. After the two phases were separated completely, the UV/Vis spectrometer was used to measure the UV/Vis spectra of the chloroform solution. In all of the experiments, the dye in the aqueous solution was greatly excess to achieve a saturated encapsulation.

One-Step Double-Dye Encapsulation (Exp II)

In a typical Exp II (A & B), 6 mL aqueous solution containing 1.0×10^{-3} M dye A and 1.0×10^{-3} M dye B was mixed

with an equal volume of 0.05 g/L HPAMAM-PC chloroform solution. The same protocol as Exp I was used to obtain UV/Vis spectrum of the chloroform solution.

Gradual Double-Dye Encapsulation (Exp III)

In a typical Exp III [first A (or B) then B (or A)], after dye A (or B) was encapsulated in the polymer chloroform solution in Exp I (dye A (or B), the aqueous solution of the other dye B (or A, 4×10^{-3} M) was added to the mixture gradually with given volumes. The same protocol as Exp I was used to record UV/Vis spectrum after every addition.

RESULTS AND DISCUSSION

Three kinds of experiments (Exp I, Exp II, Exp III) were designed to investigate the influence of interaction among different systems on the C_{load}s of HPAMAM-PC and HPSA-PC to selected pair dyes. Comparing with the synergetic encapsulation of the two kinds of amphiphilic hyperbranched polymers to MO & methyl blue (MB), the experimental phenomena were totally different if MO & RB, MO & PB, MO & EY, and MO & FSS were chosen as the dye-pairs. The structures of the host polymers and the guest dyes were shown in Scheme **1**, Scheme **2**, and Scheme **3**, respectively.

We assumed the same absorption coefficients of the dyes in both the aqueous solution and amphiphilic hyperbranched polymers chloroform solution [35], so the absorption coefficients could be gained from calibration curves of the dyes in aqueous solution, and thus the obtained absorption coefficients were used to calculate the C_{load}s of dyes in each experiment. In Table **1**, the C_{load}s of each dye in Exp I and Exp II were listed.
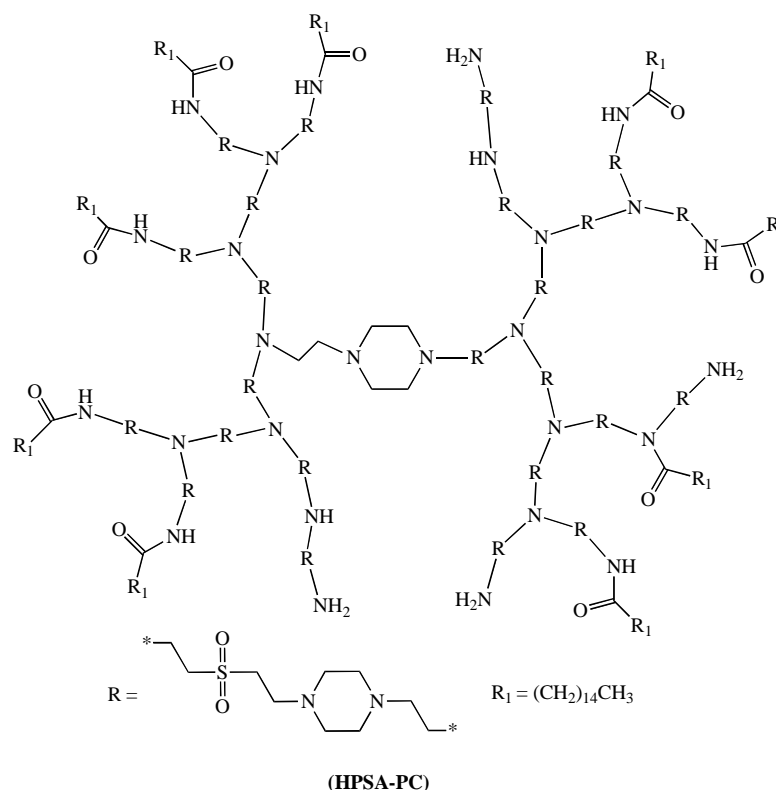
(HPSA-PC)

Scheme 2. Chemical structure of HPSA-PC.
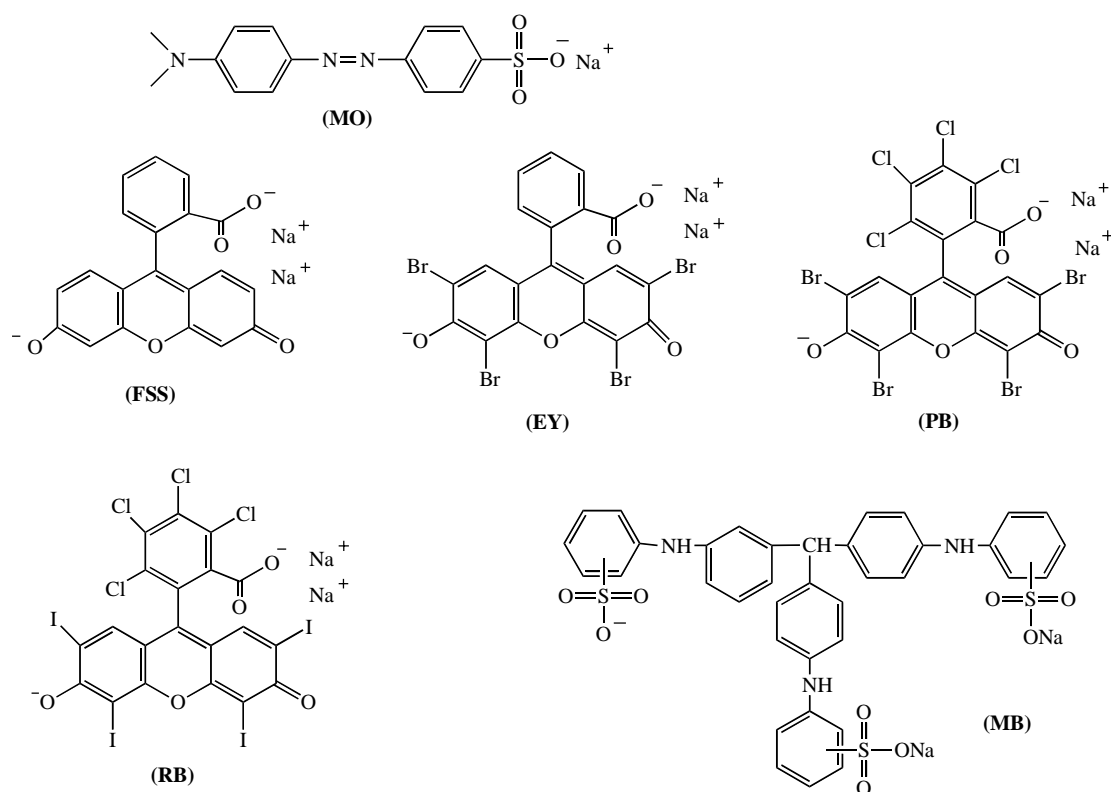
Scheme 3. Chemical structures of the guest dyes: MO, RB, PB, FSS, EY and MB.

Table 1. Selected Results for the Encapsulations of Amphiphilic Hyperbranched Polymers to Dyes

Guest	Exp[a]	A[b]		C_{load} (d.m./M.) [c]	
		HPAMAM-PC	HPSA-PC	HPAMAM-PC	HPSA-PC
MO	Exp I(MO)	0.536	1.645	5.26	16.70
	Exp II(MO & RB)	—[d]	—[d]	—[d]	—[d]
	Exp II(MO & PB)	—[d]	—[d]	—[d]	—[d]
	Exp II(MO & EY)	0.282	0.227	2.77	2.31
	Exp II(MO & FSS)	0.367	0.135	3.60	1.37
	Exp II(MO & MB)	0.924	1.695	9.08	17.21
RB	Exp I(RB)	0.732	0.724	3.09	3.16
	Exp II(MO & RB)	0.773	0.718	3.26	3.14
PB	Exp I(PB)	1.221	0.918	3.18	2.47
	Exp II(MO & PB)	1.207	0.933	3.14	2.51
EY	Exp I(EY)	0.691	0.403	1.81	1.09
	Exp II(MO & EY)	0.259	0.353	0.68	0.96
FSS	Exp I(FSS)	0.110	0.014	0.73	0.10
	Exp II(MO & FSS)	—[e]	—[e]	—[e]	—[e]
MB	Exp I(MB)	0.164	0.009	0.90	0.05
	Exp II(MO & MB)	0.0812	0.359	0.45	2.04

[a]Exp I for single-dye encapsulation and Exp II for one-step double-dye encapsulation. [b]UV/Vis absorptions of the dyes encapsulated by the host polymers. [c]Molecular numbers of dye encapsulated by per host macromolecule. [d]No obvious absorption of MO was observed in the UV/Vis spectrum. [e]No obvious absorption of FSS was observed in the UV/Vis spectrum.

DYE ENCAPSULATIONS OF HPAMAM-PC

MO & RB as the Guest-Pair

According to the UV/Vis spectra of sample in Exp II (MO & RB) (see Fig. **1**), almost no absorption of MO was observed in the organic phase, but 3.26 RB molecules were trapped per HPAMAM-PC molecule in Exp II (MO & RB), to be compared with 5.26 MO and 3.09 RB molecules in Exp I (MO) and Exp I (RB), respectively. The amounts of MO molecules decreased significantly with the existence of RB in the organic phase. The phenomenon resulted in the conclusion that the competitive ability of RB was much stronger than that of MO, so HPAMAM-PC selectively extracted RB from the aqueous solution containing both MO and RB.
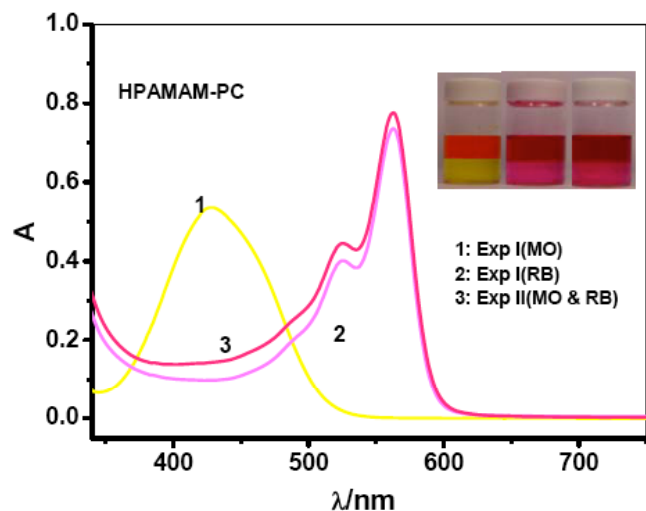
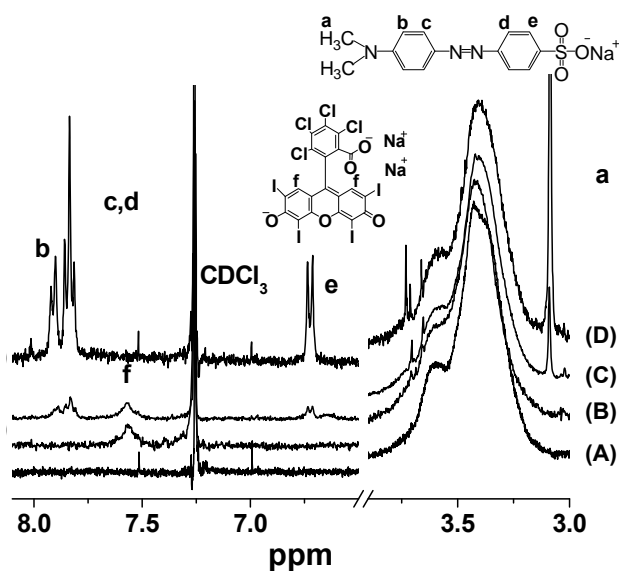**Fig. (1).** UV/Vis spectra of dyes encapsulated in HPAMAM-PC in Exp I (MO), Exp I (RB) and Exp II (MO & RB).

Fig. (2). ^{1}H NMR spectra of pure HPAMAM-PC (**A**), HPAMAM-PC loading RB in Exp I(RB) (**B**), HPAMAM-PC loading MO and RB in Exp II(MO & RB) (**C**), and HPAMAM-PC loading MO in Exp I(MO) (**D**).

The conclusion was further confirmed by ^{1}H NMR spectra (Fig. **2**). The solid dye-encapsulated HPAMAM-PC was

obtained by evaporating the chloroform solvent of the separated organic phase under vacuum. The relative integral area of the MO peak at ca. 3.07 ppm (-N(CH$_3$)$_2$, signal a) in the ^{1}H NMR spectrum of the sample getting from Exp II (MO & RB) (spectrum C of Fig. **2**) was much less than that from Exp I (MO) (spectrum D of Fig. **2**) using the peak of HPAMAM-PC (around 3.5 ppm) as the reference and the quantity of MO was so small that even the UV/Vis spectrometer could hardly detect the existence of MO. Similarly, Vincenzo Balzani *et al.* found that their dendrimers could selectively extract RB from a water solution containing an excess of both RB and EY [54].

In order to understand more details on the selective encapsulation described above, we conducted gradual double-dye encapsulations (Exp III).

In Exp III (first MO then RB), 4.0×10^{-3} M RB aqueous solution was added to the mixture of HPAMAM-PC chloroform and MO aqueous solutions in Exp I (MO) gradually with given volumes (the concentration of added RB solution was much higher than that of MO in order not to change the concentration of MO too much). The color of the bottom layer turned from yellow to red (Fig. **3a**). The absorption peak of MO decreased and finally almost disappeared, while that of RB increased gradually with the increasing volume of RB aqueous solution. The maximum absorption value of RB waved around 0.8, which was close to the value gotten in Exp II (MO & RB) (0.773) and Exp I (RB) (0.732) after the added volume of RB aqueous solution reached 0.2 mL. When the experiment was performed inversely, that was Exp III (first RB then MO), adding MO aqueous solution to the mixture of HPAMAM-PC chloroform and RB aqueous solutions in Exp I (RB) gradually with the given volumes. The absorption peak of MO was almost not observed from the UV/Vis spectra and that of RB changed little during the whole adding procedure, vibrating around 0.74 (Fig. **3b**).

The one-step double dye and gradual double dye encapsulations both indicated that, normally, RB molecules could be trapped into the polymer chloroform solution while MO molecules were driven out and MO could hardly take the place of RB that had been encapsulated by the host polymer. Obviously, HPAMAM-PC was inclined to selectively encapsulate RB when both MO and RB existed in the aqueous solution.

In order to confirm the result gotten from the UV/Vis spectrum, other instrument was also used to testify the conclusion in different ways.

TGA Result for the Selected Pair of Dyes (MO & RB)

TGA was used to confirm the locations and calculate the approximate quantities of the dyes in the Exp I, Exp II and Exp III (Fig. **4**).

The decomposition temperatures (T_d) of the HPAMAM-PC loading small dye molecules should be lower than that of pure HPAMAM-PC because of the weakened interaction between polymer arms due to the intrusion of dye molecules [48]. Actually, the temperatures of 5% and 10% weight losses ($T_{d,5\%}$ and $T_{d,10\%}$) of MO-encapsulated HPAMAM-PC were ca. 256.8°C and 288.8°C, respectively, and the $T_{d,5\%}$ and $T_{d,10\%}$ of the one-step double-dye (MO & RB) encapsulated HPAMAM1-PC were ca. 208.3°C and 250.4 °C. Both
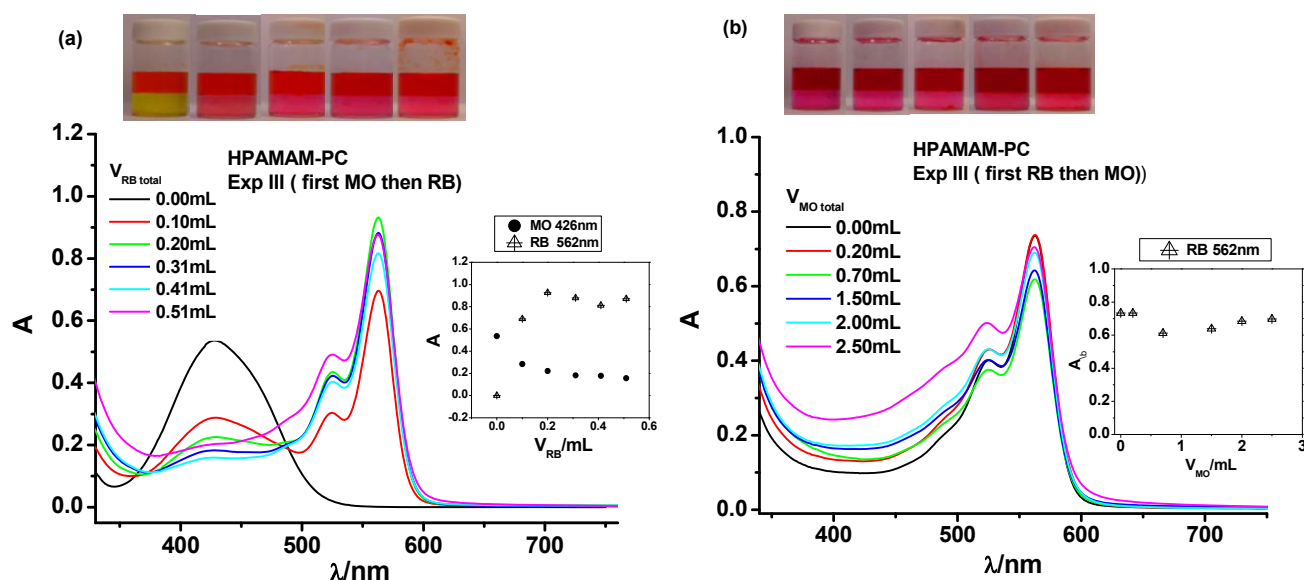
Fig. (3). UV/Vis spectra of MO and RB encapsulated in HPAMAM-PC in Exp III (first MO then RB) (**a**) and in Exp III (first RB then MO) (**b**), and the corresponding photographs of gradual double-dye encapsulations.
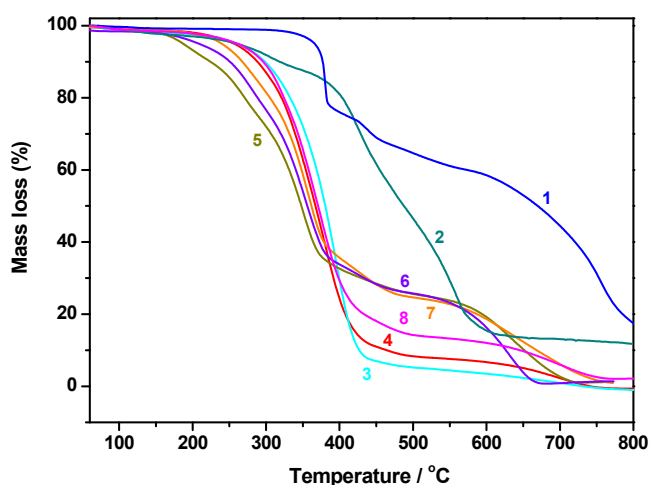

Fig. (4). TGA weight loss curves of pure MO (**1**), pure RB (**2**), pure HPAMAM-PC (**3**), the MO-encapsulated HPAMAM-PC (**4**), the RB-encapsulated HPAMAM-PC (**5**), the one-step double-dye encapsulated HPAMAM-PC (MO & RB) (**6**), gradual double-dye encapsulated HPAMAM-PC (first MO then RB) (**7**), the mixture of MO and HPAMAM-PC (0.2:1 by mass) (**8**).

T_ds of the two samples were obviously lower than those of neat HPAMAM-PC ($T_{d,5\%}$ and $T_{d,10\%}$ were ca. 260.4°C and 298.4°C, respectively). By comparison, the $T_{d,5\%}$ and $T_{d,10\%}$ of the MO-mixed HPAMAM-PC were ca. 260.8°C and 296.2°C, respectively, which were almost the same as those of pure HPAMAM-PC, also higher than that of dye-encapsulated HPAMAM-PC. All the data indicated that the dye molecules were located in the cavities of the macro-molecules, rather than inter-molecules.

The total weight losses of the pure MO and pure HPAMAM-PC below 500 °C were ca. 34.961% and ca. 94.758% respectively, while that of the MO-encapsulated HPAMAM-PC was ca. 91.661%, just between the former two calculated results, which qualitatively confirmed the

existence of the MO molecules in the cavities of the host polymer. The weight loss values of RB-encapsulated HPAMAM-PC, the one-step double-dye encapsulated HPAMAM-PC, and the gradual double-dye encapsulated HPAMAM-PC (first MO then RB) below 500°C were ca. 74.382%, 74.252%, and 75.351%, respectively. The results that the three curves even overlapped with each other in the temperature region from 450°C to 550°C again testified the conclusion that almost few or even no MO molecules were extracted from aqueous solution to the chloroform phase by the HPAMAM-PC in the competitive encapsulations, namely, the host preferring RB to MO obviously.

The results derived from TGA curves and UV/Vis spectra were compatible with each other, further demonstrating that (1) the dye molecules were encapsulated by the HPAMAM-PC forming host-guest supramolecular structure, instead of their mechanical mixture, and (2) competitive (or selective) encapsulation did exist between MO and RB in the double dye encapsulations.

MO & PB (or EY, FSS) as the Guest-Pair

As shown in Scheme **3**, PB, RB, and EY are the halogen derivatives of FSS, and they have similar molecular structures. So the other three dyes, PB, EY, and FSS, were also selected to investigate their competitive ability with MO in the double-dye encapsulations.

When PB was chosen as dye B, we could find similar competitive relationship between the two dyes. If the two dyes existed at the same time in Exp II (MO & PB) (Fig. **5**), almost no MO was encapsulated by HPAMAM-PC, while the encapsulation quantity of PB (C_{load} = 3.14) almost reached its maximum C_{load} (3.18) obtained in Exp I (PB) (Table **1**).

In Exp III (first MO then PB) (Fig. **6a**), the absorption peak of PB in chloroform phase increased from zero to 0.99 with the addition of PB aqueous solution, while that of MO almost decreased to zero. In the inverse Exp III (first PB then MO) (Fig. **6b**), MO could be hardly extracted to the chloro-
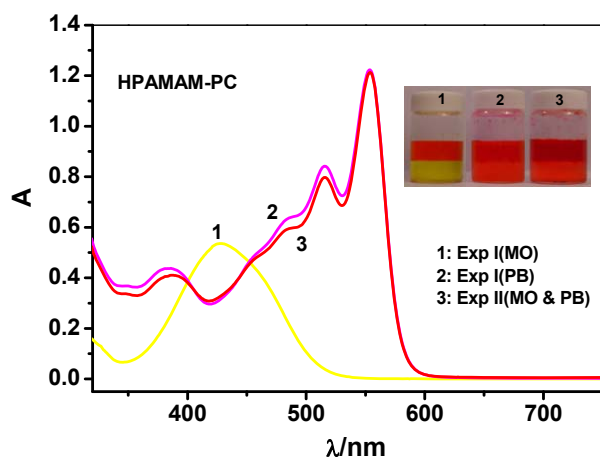
Fig. (5). UV/Vis spectra of dyes encapsulated in HPAMAM-PC in Exp I (MO), Exp I (PB) and Exp II (MO & PB).

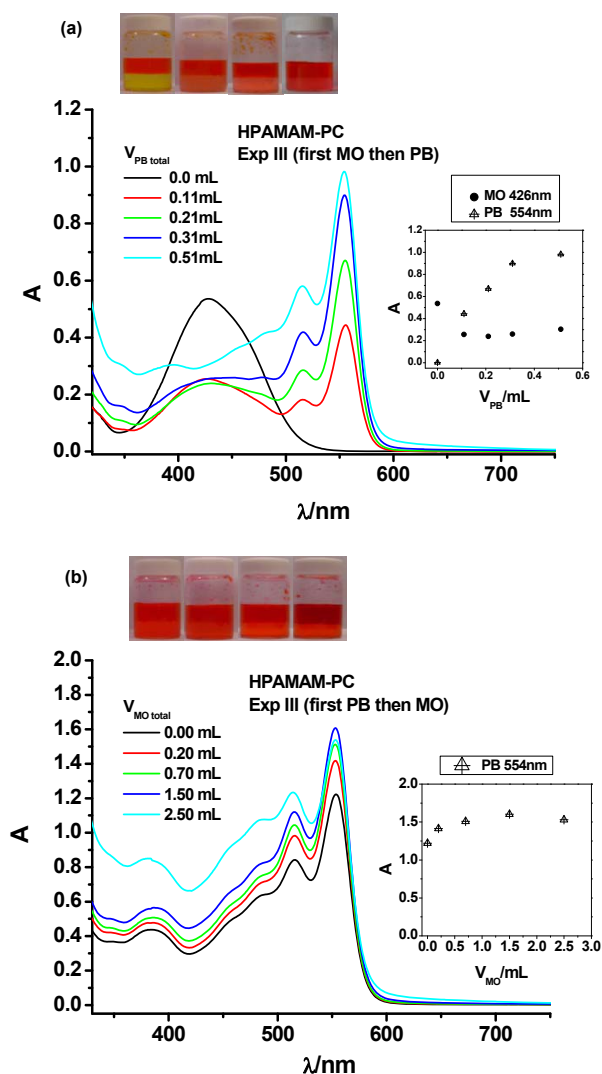form phase from its aqueous solution with the existence of PB in the organic phase already.

Fig. (6). UV/Vis spectra of MO and PB encapsulated in HPAMAM-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then PB); (**b**) in Exp III (first PB then MO).

When EY was chosen as dye B, the numbers of MO and EY molecules hosted in HPAMAM-PC in Exp II (MO & EY) (Fig. **7**) decreased to about 2.77 and 0.68, to be compared with 5.26 in Exp I (MO) and 1.81 in Exp I (EY), respectively (Table **1**). The C_{load}s of both dyes decreased in Exp II (MO & EY). In Exp III (first MO then EY) (Fig. **8a**), with the addition of EY aqueous solution, the UV/Vis absorption of EY increased while that of MO decreased (but the added EY could not completely take the place of the trapped MO molecules) and vice versa in Exp III (first EY then MO) (Fig. **8b**). The selectivity of HPAMAM-PC between MO and EY was not obvious and the host HPAMAM-PC tended to encapsulate the two kinds of dyes freely.
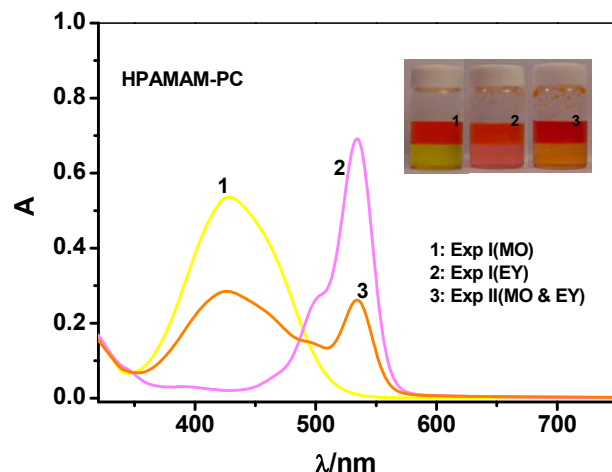

Fig. (7). UV/Vis spectra of dyes encapsulated in HPAMAM-PC in Exp I (MO), Exp I (EY) and Exp II (MO & EY).

Strangely, in Exp II (MO & FSS) (Fig. **9**), almost no absorption of FSS was observed in the UV/Vis spectrum and the absorption of MO (0.367) was lower than that in Exp I (MO) (0.536) (Table **1**). In Exp III (first MO then FSS) (Fig. **10a**), with the addition of the FSS aqueous solution stepwisely, the absorption peak value of MO decreased and finally vibrated around 0.35 without the obvious absorption of FSS. The phenomenon meant that the MO molecules could be drawn away from the chloroform solution by FSS, but with the existence of MO, FSS could not be extracted to the organic phase. Inversely, as to Exp III (first FSS then MO) (Fig. **10b**), the added MO aqueous solution resulted in the disappearance of FSS in chloroform phase. There was also strong selectivity of HPAMAM-PC between MO and FSS, which indicated HPAMAM-PC preferred MO to FSS if the two kinds of dyes were both in the aqueous solution.

Above experiments showed that HPAMAM-PC selectively trapped RB (or PB) in Exp II (MO & RB (or PB)) and changed to select MO in Exp II (MO & FSS), while the selectivity between MO and EY was not obvious and both of them could be trapped in Exp II (MO & EY).

DYE ENCAPSULATION OF HPSA-PC

Are such competitive behaviors just the particular phenomena of HPAMAM-PC or general to some other similar amphiphilic hyperbranched polymers? Another amphiphilic hyperbranched poly(sulfone-amine) (HPSA-PC) (Scheme **2**) was also used as a host to perform the same experiments
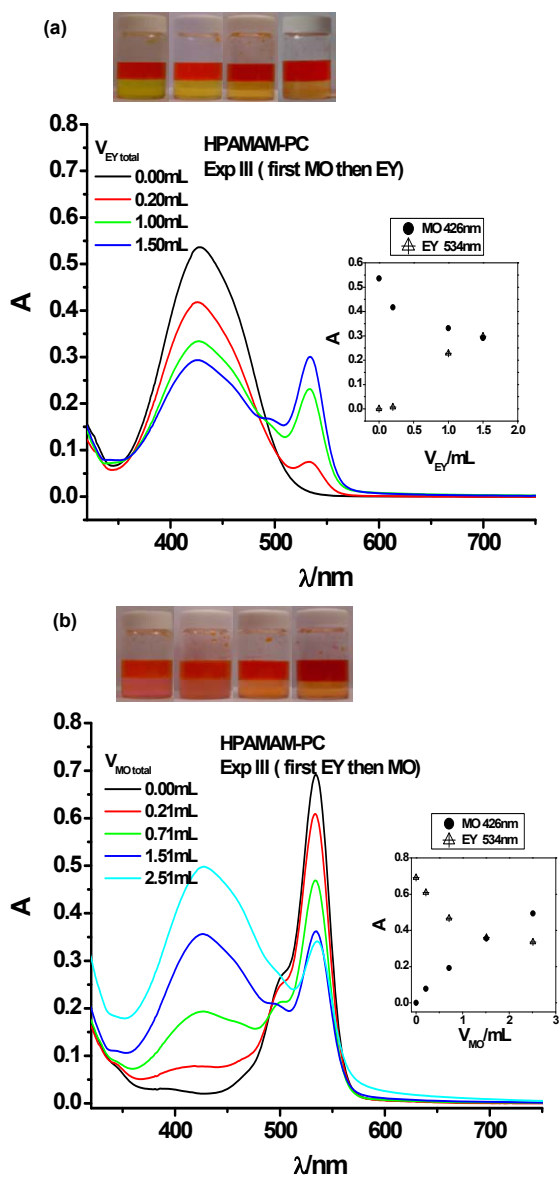
Fig. (8). UV/Vis spectra of MO and EY encapsulated in HPAMAM-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then EY); (**b**) in Exp III (first EY then MO).
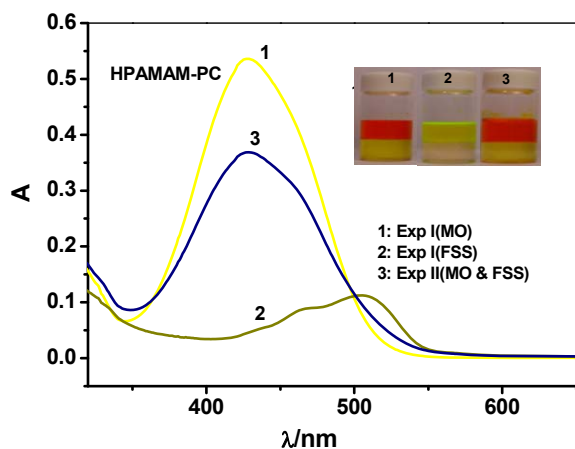

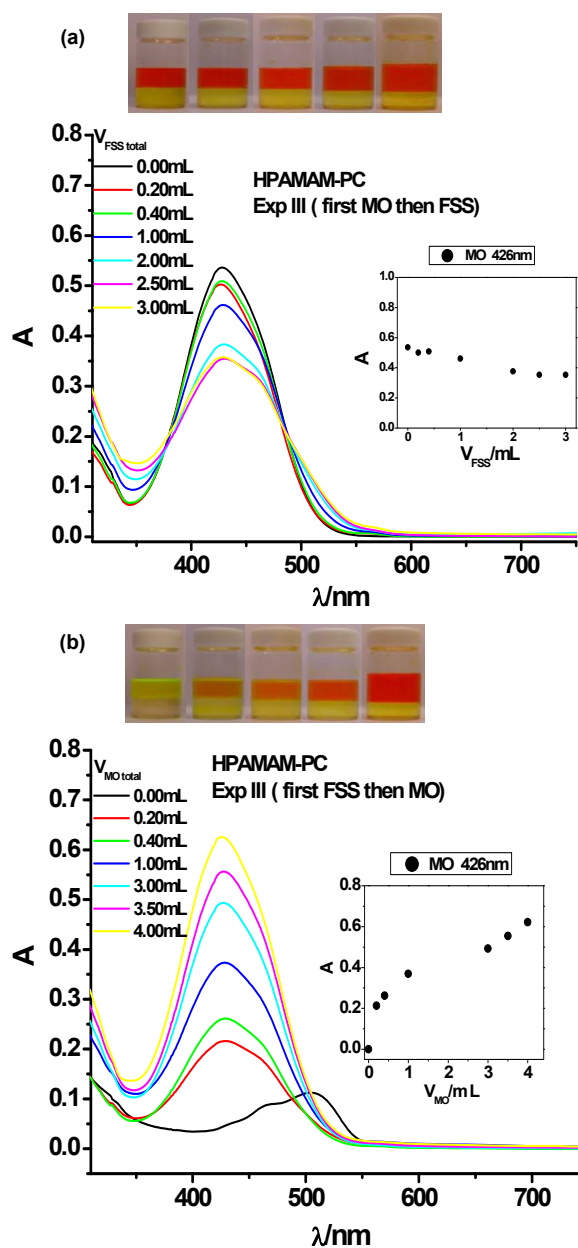**Fig. (9).** UV/Vis spectra of dyes encapsulated in HPAMAM-PC in Exp I (MO), Exp I (FSS) and Exp II (MO & FSS).

Fig. (10). UV/Vis spectra of MO and FSS encapsulated in HPAMAM-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then FSS); (**b**) in Exp III (first FSS then MO).

accordingly. Gladly, we obtained the similar results, as shown in Table **1**.

MO & RB as the Guest-Pair

As to the UV/Vis spectra of Exp II (MO & RB) for HPSA-PC, we could not find the MO absorption peak at 426 nm, while that of RB at 562 nm just reduced a little from 0.724 in Exp I (RB) to 0.718 (Fig. **11**). This meant that the relationship between MO and RB was competition, which was similar to the results gotten from the experiments in which HPAMAM-PC performed as the host, and thus MO could hardly be encapsulated by HPSA-PC with the existence of RB.
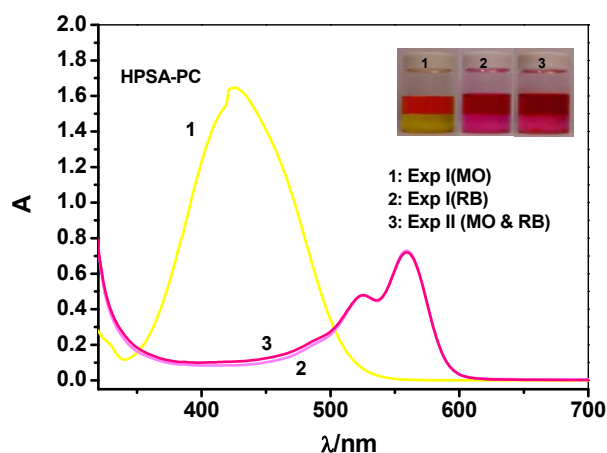
Fig. (11). UV/Vis spectra of dyes encapsulated in HPSA-PC in Exp I (MO), Exp I (RB) and Exp II (MO & RB).

In Exp III (first MO then RB), with the addition of RB aqueous solution to the saturated encapsulation mixture of MO in Exp I (MO) with given volumes, the color of the organic phase turned from orange to red (Fig. **12a**), indicating the entrance of RB into the organic phase. UV/Vis spectrum also showed the decrease of MO absorption from 1.64 to zero, while the absorption value of RB increased firstly to 1.76 and then decreased to 0.94, which was a little larger than that in the single-dye encapsulation of HPSA-PC to RB (0.724). Inversely, the addition of MO could not change the color of the organic phase, which kept red during the whole Exp III (first RB then MO) (Fig. **12b**). We could not detect the absorption of MO by UV/Vis spectrometer with adding the MO aqueous solution, while that of RB kept decreasing from 0.72 to about 0.22, implying that the existence of MO in the aqueous solution might block the transfer of RB to the chloroform solution.

From the above results, we could make a conclusion that there did exist the competitive relationship between MO and RB in the situation of both HPAMAM-PC and HPSA-PC working as the hosts. The encapsulations of the two amphiphilic hyperbranched polymers to MO were greatly affected by the existence of RB and nearly decreased to zero in Exp II (MO & RB), while the absorption values of RB did not change too much compared with that in Exp I (RB).

MO & PB (or EY, FSS) as the Guest-Pair

The relationships between MO and the other three dyes could obviously be traced from the UV/Vis spectra, which were quite similar to those corresponding cases of HPAMAM-PC.

If MO and PB were chosen as the dye pair, the UV/Vis spectra of the samples from Exp II (MO & PB) and Exp I (PB) almost overlapped with each other and the absorption peak of PB was about 0.93 while without obvious existence of MO in Exp II (MO & PB) (Fig. **13**). During the gradual double-dye encapsulation (Exp III (first MO then PB)), with the addition of PB solution, the color of the chloroform solution changed from orange to red, suggesting the entrance of PB molecules into the organic phase. The UV/Vis spectra also lead to the same conclusion that the MO absorption peak at 426 nm disappeared finally due to the increased
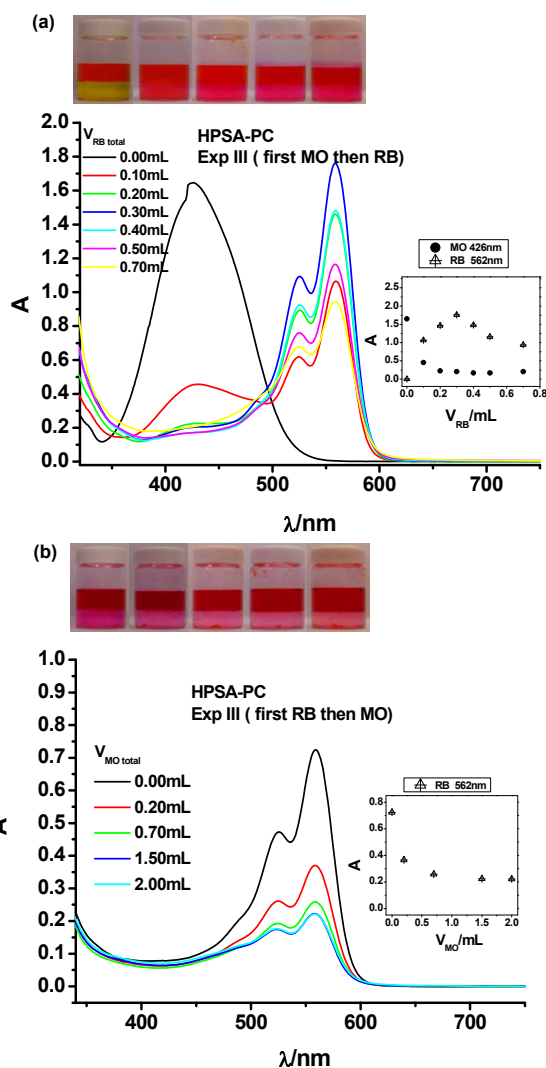

Fig. (12). UV/Vis spectra of MO and RB encapsulated in HPSA-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then RB); (**b**) in Exp III (first RB then MO).
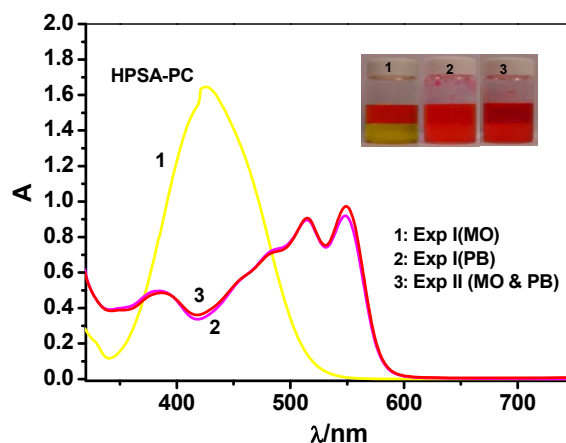

Fig. (13). UV/Vis spectra of dyes encapsulated in HPSA-PC in Exp I (MO), Exp I (PB) and Exp II (MO & PB).

amount of RB, as shown in Fig. (**14a**) (the absorption peak at 554 nm reached 0.94 eventually). When the experiment was

performed inversely, the color of chloroform kept red and the absorption of MO could not be observed during the whole adding process of MO solution, while the absorption value of PB just waved between 0.92 and 1.29 (Fig. **14b**). The experiments demonstrated that the competitive ability of MO was much lower than that of PB in the double-dye encapsulations with the host of HPSA-PC.
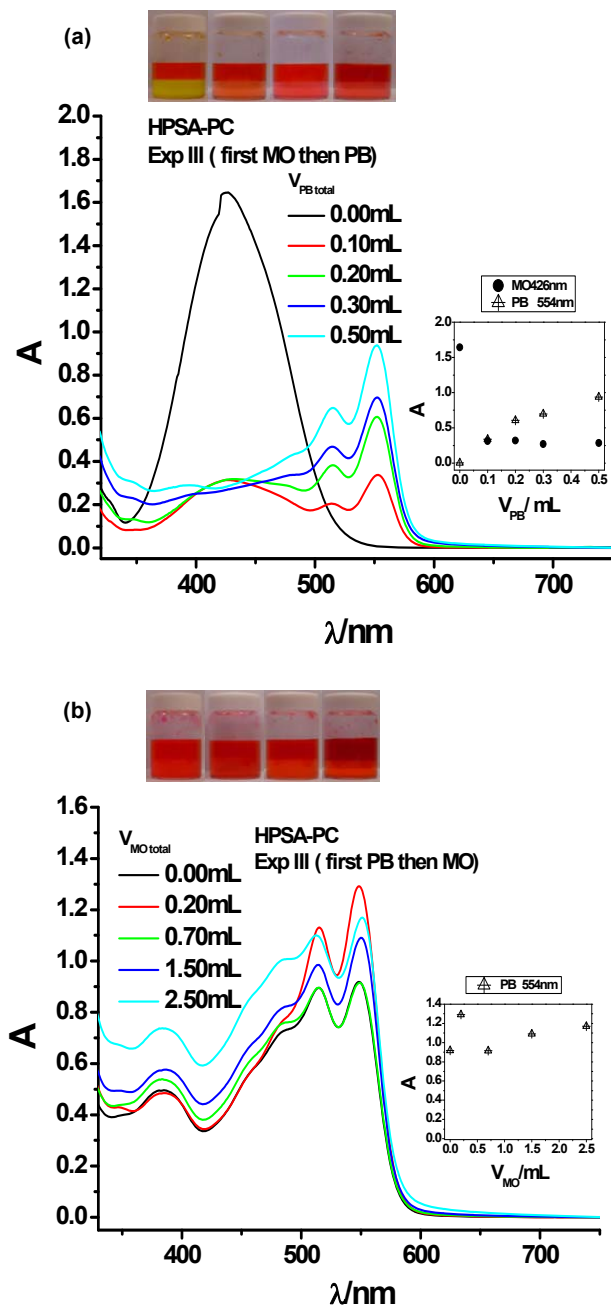

Fig. (14). UV/Vis spectra of MO and PB encapsulated in HPSA-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then PB); (**b**) in Exp III (first PB then MO).

In Exp II (MO & EY) for HPSA-PC, the absorptions of the two dyes both appeared in the UV/Vis spectrum (Fig. **15**), but the peak values were lower than that in the single dye encapsulations, decreasing from 1.645 to 0.227 for MO, from 0.403 to 0.353 for EY, respectively. As to the gradual
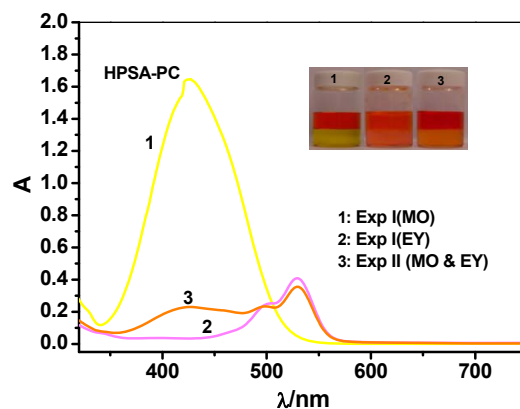

Fig. (15). UV/Vis spectra of dyes encapsulated in HPSA-PC in Exp I (MO), Exp I (EY) and Exp II (MO & EY).
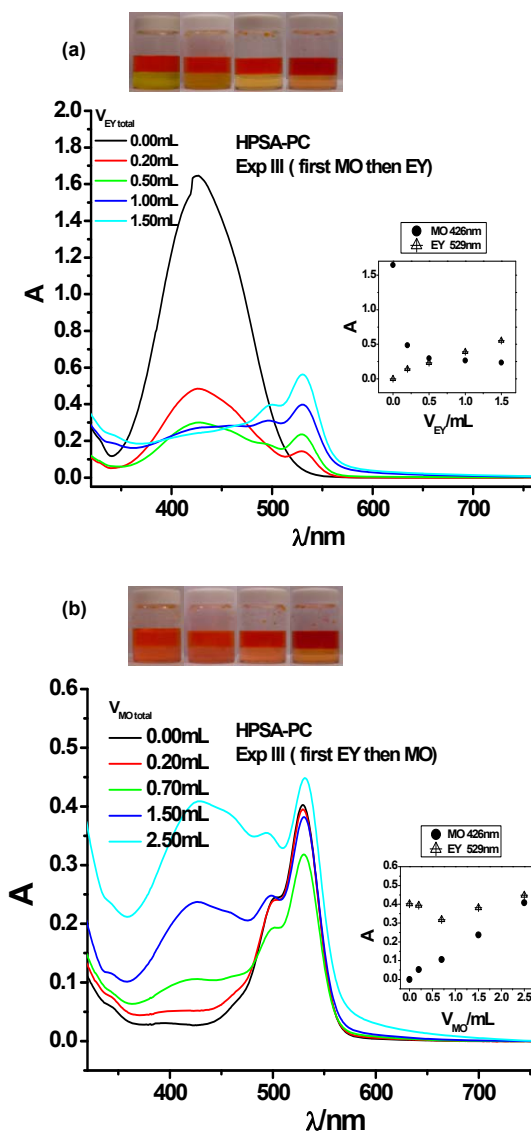

Fig. (16). UV/Vis spectra of MO and EY encapsulated in HPSA-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then EY); (**b**) in Exp III (first EY then MO).

double-dye encapsulation (Fig. **16**), no matter which dye was chosen as the added one, the addition of one dye caused the

release of the other encapsulated dye molecules, but could not substitute for the whole. The conclusion was that the relationship between MO and EY was competition, not the same as that between MO and RB (or PB). The competition ability of MO was almost equivalent to that of EY and the two guests could both be trapped by the hyperbranched polymers with the cost of the decrease of encapsulated amounts of both dyes.

In the situation of MO and FSS chosen as the dye pair, both dyes could hardly be encapsulated by HPSA-PC. As for Exp II (MO & FSS) (Fig. **17**), the absorption value of MO at 426 nm decreased significantly from 1.645 (the saturated value of single dye encapsulation of MO) to 0.135, even worse, no detectable FSS molecules were trapped by HPSA-PC according to the UV/Vis spectra. With the addition of FSS aqueous solution to the saturated MO chloroform solution (Fig. **18a**), the absorption value of MO dramatically fell to 0.11, without the appearance of FSS in the spectra during the whole adding process, indicating that FSS could pull the MO molecules out of from the chloroform solution and the existing MO avoided the entrance of FSS to the organic phase. During the inverse addition process (adding MO solution to the saturated FSS chloroform solution) (Fig. **18b**), the amount of FSS reduced gradually to zero, while the absorption value of MO ascended to 0.194, still much smaller than that in the single dye encapsulation (1.645). There still existed competition between MO and FSS, but the competitive ability of MO was higher than that of FSS, quite different from the former three dye pairs. This situation is the so-called negative (or minus) encapsulation.
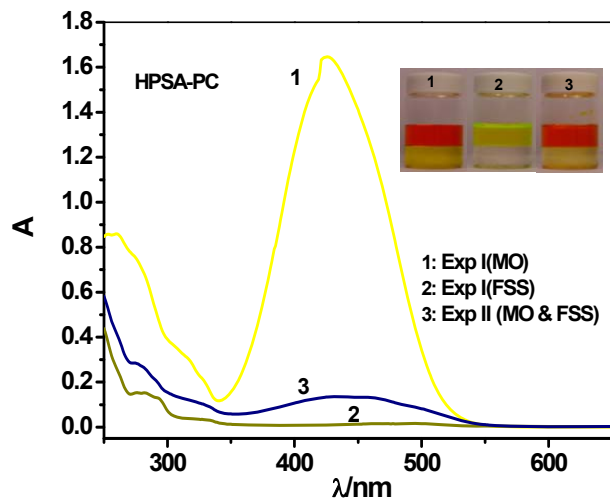

Fig. (17). UV/Vis spectra of dyes encapsulated in HPSA-PC in Exp I (MO), Exp I (FSS) and Exp II (MO & FSS).

CONTROL EXPERIMENTS

Is the absorption change of MO caused by the disturbance of the other dye? Control experiments were performed to investigate the influence between the dyes pairs (MO & RB) by measuring the UV/Vis spectra of the aqueous solutions (Fig. **19**), containing (a) 5.0×10^{-5} M MO, (b) 5.0×10^{-5} M MO and 1.0×10^{-5} RB, respectively.

It was found that the absorption of MO at 464 nm did not decrease but increased from 1.1036 to 1.1566 and the UV/Vis absorbance of MO showed a red shift from 464 nm
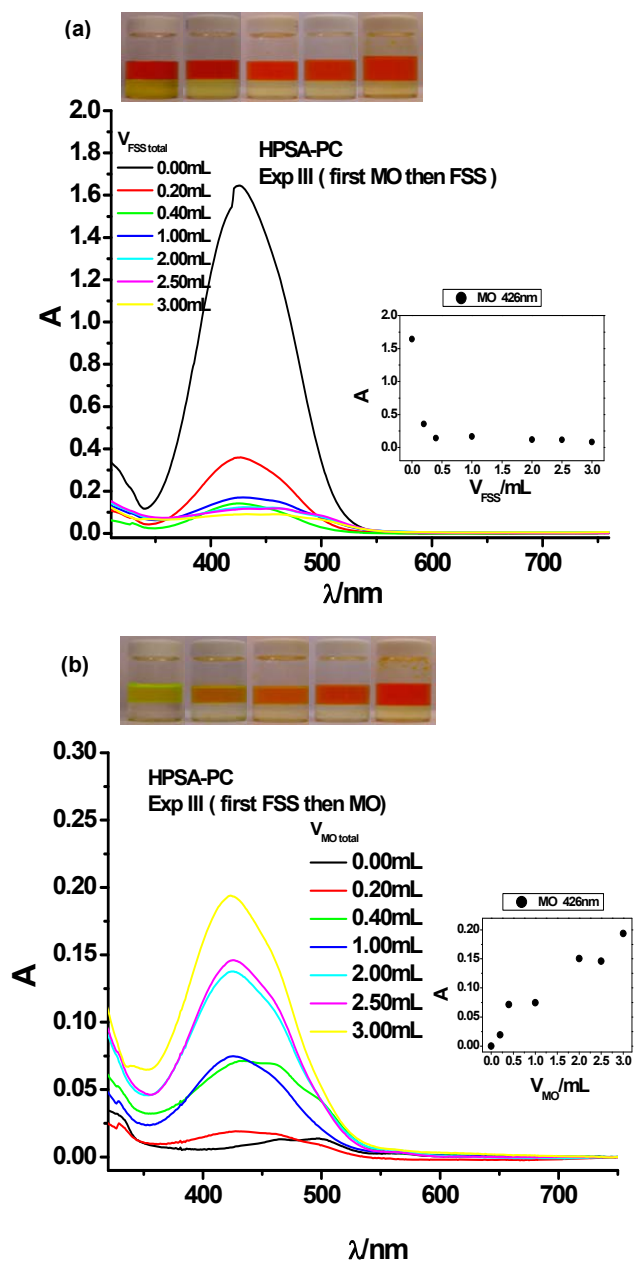

Fig. (18). UV/Vis spectra of MO and FSS encapsulated in HPSA-PC and their corresponding photographs of gradual double-dye encapsulations: (**a**) in Exp III (first MO then FSS); (**b**) in Exp III (first FSS then MO).

to 467 nm with the existence of RB. The little red shift and increment of A_{max} can be explained by the partial overlap of the absorption of MO at 464 nm and that of RB at 542 nm. The control experiments indicated that the existence of RB cannot make the absorption of MO decrease in the UV/Vis spectra and the absorbance interference between the pair dyes is negligible.

RELATIVE SELECTIVITY CONSTANTS TO MO ($R_{dye/MO}$)

In order to measure the competitive abilities of different dyes to MO quantitatively, relative selectivity constant to MO ($R_{dye/MO}$) is introduced and defined as,
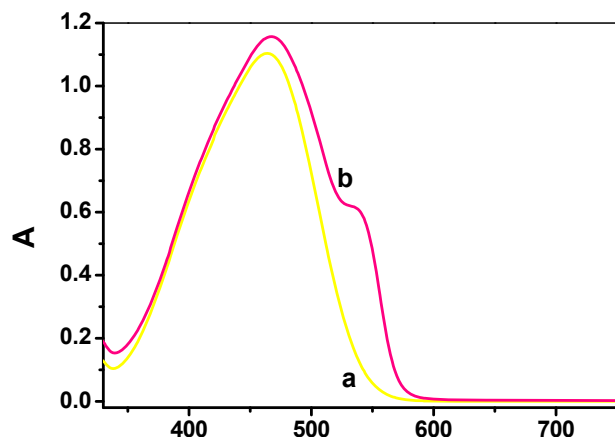
Fig. (19). UV/Vis spectra of MO and RB in the control experiments: (**a**) aqueous solution containing 5.0×10^{-5} M MO, (**b**) aqueous solution containing 5.0×10^{-5} M MO and 1.0×10^{-5} M RB.

$$R_{\text{dye/MO}} = \frac{C_{\text{load II (dye)}} / C_{\text{load I (dye)}}}{C_{\text{load II (MO)}} / C_{\text{load I (MO)}}} \qquad (1)$$

Where $C_{\text{loadI(dye)}}$ is the C_{load} of dye in Exp I (dye) and $C_{\text{loadII(dye)}}$ is that in Exp II (MO & dye). The calculated results of $R_{\text{dye/MO}}$ are listed in Table **2**. We assume that, (1) if the value of $R_{\text{dye/MO}}$ is in the range of 0.1~10, the polymer host tends to encapsulate the guests statistically, (2) if $R_{\text{dye/MO}} > 10.0$, the host can load the guest dye (except MO) selectively, and the higher the $R_{\text{dye/MO}}$, the better the selectivity, and (3) if $R_{\text{dye/MO}} < 0.1$, the host can load MO selectively, and the lower the $R_{\text{dye/MO}}$, the greater the selectivity for MO.

The value of $R_{\text{MB/MO}}$ for HPSA-PC was 39.61, much larger than 10.0, which indicated that the HPSA-PC was more likely to select MB in the double-dye encapsulations. At the same time, the absolute C_{load} of MB in the presence of MO was considerably higher than that in the single-dye encapsulation. Hence, we defined this phenomenon as synergistic encapsulation as reported in our previous work [48].

The value of $R_{\text{RB/MO}}$ for HPAMAM-PC was far more larger than 10.0, which was infinity, for the C_{load}s of MO in Exp II(MO & RB) was zero, and thus the denominator became zero. But the relationship between these two dyes was not synergistic, because the C_{load}s of RB in Exp I(RB) and Exp II(MO & RB) were almost the same (3.09 and 3.26, respectively), in other words, the existence of RB only avoided the encapsulation of the hyperbranched polymers to MO. The relationship between RB and MO was thus defined as selective encapsulation according to the experiment results.

The selectivity constants of EY to MO were in the range of 0.1~10 (0. 71 for HPAMAM-PC and 6.37 for HPSA-PC, respectively), so the competition abilities of the two dyes should be comparable and the C_{load}s of both dyes would reduce if they were mixed in the same aqueous solution in Exp II (MO & EY). For example, as to MO encapsulated by HPAMAM-PC, the C_{load} reduced from 5.26 in Exp I (MO) to 2.77 in Exp II (MO & EY); as to EY encapsulated by HPAMAM-PC, the C_{load} reduced from 1.81 in Exp I (EY) to 0.68 in Exp II (MO & EY).

As to the situation of FSS and MO, the competitive abilities were totally reversed. The value of the selectivity constants of FSS was zero, much smaller than 0.1, which consisted with the experimental results that the existence of MO in aqueous solution had strong negative effect on the encapsulation of hosts to FSS—that is to say, the competitive ability of FSS was much weaker than that of MO and the hosts were more likely to chose MO if both the dyes existed in the aqueous solution.

SUPPOSED MECHANISM

Basing on the results illustrated above and other comparative experiments, we present a modified polytopic receptor-substrate or host-guest model to explain the competitive and other multi-guest encapsulation phenomena, as shown in Fig. (**20**). The multi-tooth cavity H represents a host or a host section, G_1 and G_2 figure as two kinds of guests, respectively. The loading capacities of G_1 and G_2 (C_{load}s) are denoted as C_1 and C_2 corresponding to single-guest encapsulation, and as C_{12} and C_{21} in double-guest encapsulation, respectively. If only one kind of guests can be caught tightly by the teeth or cavities of H in the presence of other one, that is to say, $C_{12} \approx C_1$ and $C_{21} \to 0$ or $C_{21} \approx C_2$ and $C_{12} \to 0$, a H-G_1 or H-G_2 type supramolecular complex would be formed, which is the so called competitive or selective encapsulation and indicates the existence of one guest strongly blocked the entrance of the other guest to the cavities of H. The interaction between H and G_1/G_2 ($F_{\text{H,G1}}$/$F_{\text{H,G2}}$) is stronger than that among H, G_1, G_2 ($F_{\text{H,G1,G2}}$), and thus H is more likely to catch G_1 or G_2 only. If both guests can be caught by H but $C_{12} < C_1$ and $C_{21} < C_2$, a H-G_1-G_2 type supramolecular complex would be generated, which is the random encapsulation and the interaction between H and G_1 are quite close to that between H and G_2. If one or both guests can be caught by H and $C_{12} > C_1$ or $C_{21} > C_2$, a H-nG_1-nG_2 (herein, n represents several G_1 or G_2) type supramolecules would be produced, which is the synergetic encapsulation, meaning that the loading capacity of one guest could increase with the assistance of the other guest. Under this kind of situation, the binding force among H, G_1, G_2 is much stronger than that between H and G_1 (or G_2). If one or both guests cannot be loaded by H ($C_{12} < C_1$ and $C_{21} \to 0$ or $C_{21} < C_2$ and $C_{12} \to 0$), a H-G_1 or H-G_2 type, even no supramolecular complex

Table 2.   Relative Selectivity Constants of Dyes Encapsulated by the Two Polymers

Dye	RB	PB	EY	FSS	MB
$R_{\text{dye/MO}}I^{a}$	∞	∞	0.71	0	0.29
$R_{\text{dye/MO}}II^{b}$	∞	∞	6.37	0	39.61

[a]Relative selectivity constants of dyes encapsulated by HPAMAM-PC. [b]Relative selectivity constants of dyes encapsulated by HPSA-PC.
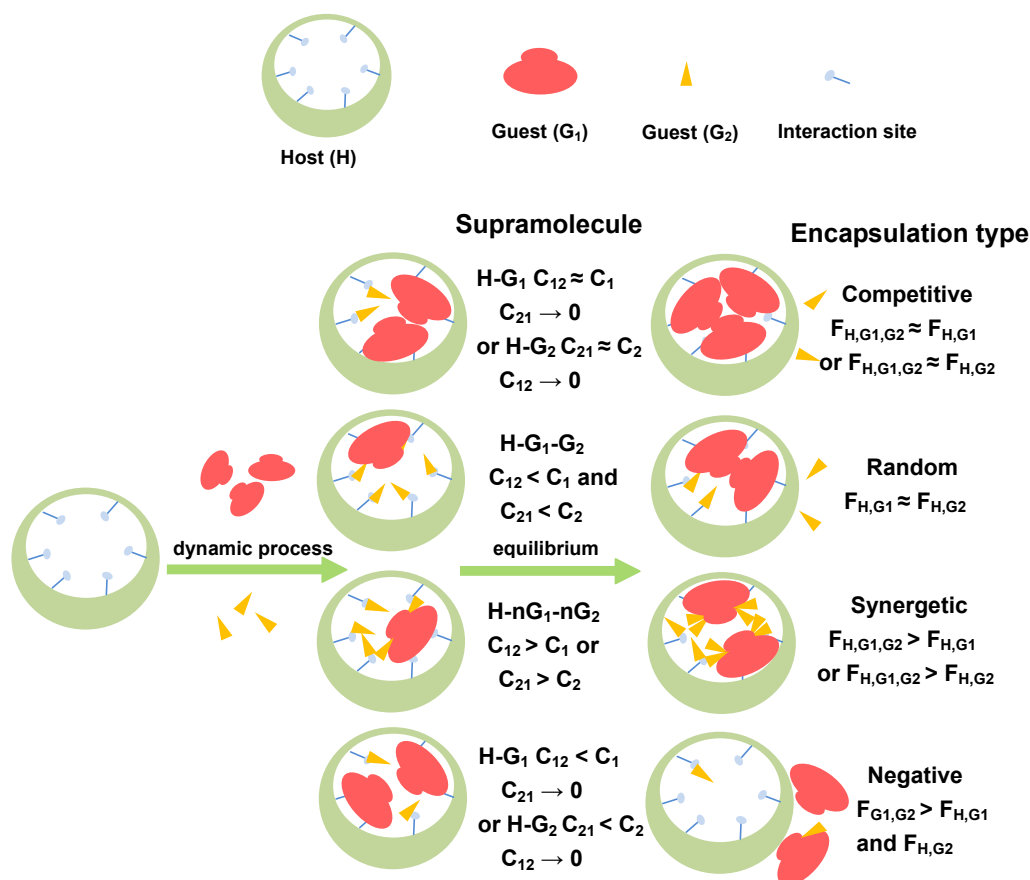
Fig. (20). "Host-guest" model for double-guest supramolecular encapsulations.

would be found, which is the negative (or minus) cooperation encapsulation. The binding force between H and G_1 (G_2) is weaker than that between the two guests ($F_{G1,G2} > F_{H,G1}$ and $F_{H,G2}$).

The interactions, which result in the different encapsulation types, also the coordination or recognition factors among the host and guests not only include the spatial matching but also include the similar or complementary structure and properties, and non-covalent interactions among them such as electrostatic force, hydrogen bonds and van der Waals forces.

Such a simple "host-guest" model of multi-guest encapsulation can explain many different host-guest systems. For example, the double-dye encapsulations could be explained by the compatible functions of the sizes of dye molecules, the structures of dyes, the electrostatic acid-base interactions among the dyes and the polymer, the polymer structure, the sizes of cavities in the polymer, and the interactions between different dyes.

Hydrogen bonding interactions and electrostatic acid-base interactions are thought to affect the amount of encapsulated dyes. The structures of the dyes (Scheme **3**) indicate that there are sulphonyl groups in MO and carboxyl groups in the other four dyes, respectively. It is known that sulfonic acid, a strong acid, is easier to form acid-base complex with compound containing amino groups than carboxylic acid, a weak acid. The interaction between the sulphonyl and amino of HPAMAM-PC is stronger than that between the carboxyl

and amino, so the interaction between MO and HPAMAM-PC is stronger than that between FSS and HPAMAM-PC. Michael Pittelkow *et al.* also found from competition experiments that sulfonic acid guest had a stronger affinity for the dendrimer host than the carboxylic acid guest [22]. The conclusion can be used to explain the phenomena that the existence of MO forbids the encapsulations of the hosts to FSS, which are observed in our experiments of double-dye encapsulations. For the decreased amount of encapsulated MO in the double-dye encapsulations, one possible reason is that the existence of carboxyl groups of FSS in the aqueous solution may reduce the efficient amino groups that can form acid-base complex with the sulphonyl groups of MO, and another possible one is that the strong interaction between MO and hydrated FSS increases the instability of the MO-host complex.

Any one of RB, PB or EY molecules contains the same number of carboxyl group as one FSS molecule, but the encapsulation results are so different-the HPAMAM-PC selectively encapsulated MO in Exp II (MO & FSS), while it encapsulated not MO but RB (PB) in Exp II (MO & RB (PB)). The side groups on the molecular framework, which are the only difference between the four oxanthrone-dyes, are considered to cause the different results of encapsulations to MO with the existence of any one of the four oxanthrone-dyes. As shown in Scheme **3**, there are four iodine atoms and four chlorine atoms in RB, four bromine atoms and chlorine atoms in PB, four bromine atoms in EY, and no side groups in FSS. Thus, the molecular size can be arranged according to

the order of RB>PB>EY>FSS. The host-guest encapsulation process is considered as a dynamic equilibrating process. The interactions between dyes and polymer, the structures of dyes, and the sizes of dyes may affect the equilibrating process. In our experiments, it might be faster and easier for MO to go into or out of the polymer than RB molecules since the size of MO molecule is smaller, and the rod-like structure of MO does not fit the cavities of the host polymer so well as the oblate structure of RB. Therefore, the polymer host preferred to load RB to MO in the Exp II (MO & RB). H. Frey *et al.* also considered that more RB (C_{load} = 1.4) could be encapsulated by their amphiphilic hyperbranched polyglycerols than Congo red (C_{load} = 0.7) was related to the more compact structure of RB in comparison to the extended rod-like structure of Congo red [35].

For MO & RB and MO & PB, the factor of the matching size of the dye molecules and the cavities of the polymer is preponderant, for MO & FSS, the electrostatic acid-base interactions predominate, and for MO & EY, the influence from the size and the electrostatic acid-base interactions is almost equivalent. The order of relative competitive abilities to MO is

PB, RB > EY > FSS

As to the synergetic encapsulation, another factor, the complementary structure of the dye pair, should be considered. The size of MB is much larger than that of MO, so the rod-like MO molecule and triangular pyramid-like MB molecule may form relatively stable complex-like species in the cavities of the polymer host. The complex may fit the cavities much better than each dye and cannot leave the host easily once encapsulated, so the amount of encapsulated MO molecules increases with the help of MB. This hypothesis could also explain the phenomenon, as we have reported, that the existence of MB can promote the C_{load} of MO in the double dye encapsulation experiments.

CONCLUSIONS

In summary, there was either competitive or synergic interaction between different dyes, and the interaction will lead to four different results: (1) C_{load} of MO decreased significantly in the presence of the other one (MO & RB, MO & PB), (2) C_{load}s of both dyes decreased (MO & EY), (3) C_{load}s of MO decreased and that of the other dye almost decreased to zero (MO & FSS), and (4) C_{load} increased for one or both of the pair dyes (MO & MB).

Both Exp II and Exp III indicated the existence of competition relationship between MO and anyone of the other three dyes. For instance, if MO & RB was selected as the dye-pair, both kinds of amphiphilic hyperbranched polymers (HPAMAM-PC and HPSA-PC) nearly only caught RB and MO could hardly be trapped once RB had been encapsulated, even substituted by the addition of RB. The results were confirmed by the combination of UV/Vis, ^{1}H NMR, IR and, TGA measurements and control experiments.

We also introduced the relative selectivity constants to measure the competition abilities of different dyes to MO quantitatively. The "host-guest" hypothesis could, in a way, explain the four types of encapsulation that took place in our experiments by analyzing the interaction, such as the electrostatic acid-base interactions and the sizes of the dye molecules, among the amphiphilic hyperbranched polymers (host) and different paired dyes (guest). We believe that this model will has further application in the field of supramolecular host-guest chemistry of dendritic and other complex polymeric systems.

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