Host-Guest Supramolecular Chemistry of Dendritic Macromolecules

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Abstract: Dendritic macromolecules are three-dimentional polymers with branch-on-branch topology of which dendrimers and hyperbranched polymers (HPs) are the two most researched subclasses. This paper reviews the recent progress of host-guest supramolecular chemistry in terms of various HPs and dendrimers. Because of the highly branched structure and the presence of internal space and binding sites, dendritic macromolecule can serve as host to encapsulate multiple guests, just like a highly branched “tree” accommodating multiple “bird's nests”. Core-shell structure made by functionalization of dendritic polymer core with shielding shell of opposite polarity is usually needed to obtain a stable host-guest complex. Their encapsulation capacities are dependent on various factors, such as core size or molecular weight, polarity difference between core and shell, interaction strength between core and guests, shell density, and so on. Dendritic polymer-based host-guest encapsulation can be applied in many fields including phase-transfer, noncovalent functionalization, metal nanoparticle growth, and biological imaging.

Keywords: Hyperbranched polymer, dendrimer, dye, nanoparticle, encapsulation, host-guest complex, core-shell structure, unimolecular micelle.

1. INTRODUCTION

Hyperbranched polymers (HPs) and dendrimers are the typical two subclasses of dendritic polymers that are three-dimensional macromolecules with branch-on-branch topology developed in 1980s. Normally, HPs have random branched and irregular structures with degree of branching (DB) of 0.4-0.6 [1-7], while dendrimers are perfect and regularly branched with DB of 1.0 [8]. Nevertheless, they have similar properties such as high solubility and low viscosity, and possess similarly specific topology: the interior branching scaffold, the internal cavities and binding sites, and the end groups in the periphery or the shell. By utilizing these structural features, both of them have been empolyed as dendritic hosts to accommodate various guests, such as dyes, drugs, metal nanocrystals, quantum dots, and so on. Since the pioneer works done by Maciejewski [9], Tomalia [10], Newkome [11], Seebach [12] and Meijer [13] in the 1990s, this field of host-guest chemistry of dendritic hosts has grown into an important area of supramolecular chemistry. In this area, polymer hosts are also denoted as nanocapsule, nanocarrier, dendritic box, template and support material in terms of different usage. The accommodation is generally called encapsulation and sometimes inclusion. The interactions between host and guest involve electrostatic interaction, hydrogen bonding, hydrophobic interaction and in some cases, specific ppinteraction, except covalent bonds. Furthermore, the encapsulation of dendritic polymer host for small functional molecule guests via noncovalent interactions has found a lot of applications, for instance: phase-transfer, a more convenient way to functionalize dendritic polymer and tune the function of nanodevice compared with covalent bonding, detection of structures of dendritic polymers with various guest probes, “smart” control by imposing various external stimulation, enhancement of guest solubility and preven tion of aggregation, size confinement of *in-situ* formed particle, restraint on biological toxicity of guest, sustained release of drugs, etc..

Different from common hosts of organic molecules which generally entrap guests by a one-to-one manner specifically, dendritic polymers could load one or more guests based on their molecular structures nonspecifically (see Fig. **1**). Except organic guests, dendritic polymers can even load inorganic nanoparticles to form organic-inorganic hybrids. In addition, due to their relatively large and multiple cavities, dendritic polymers can also encapsulate different kinds of guests simultaneously.

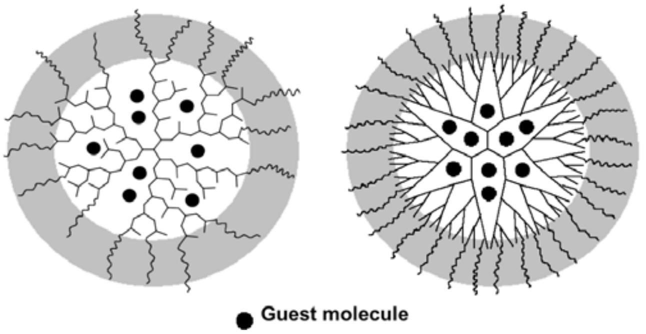

Fig. (1). Cartoon of encapsulation of core-shell amphiphilic hyperbranched polymer (left) or dendrimer (right) to guests [4].

Herein, we mainly focus on the hosts of HPs and dendrimers and their corresponding guests of dyes and nanoparticles. The encapsulation properties, influence factors, and the applications of host-guest complexes are summarized comprehensively.

2. HYPERBRANCHED POLYMER AND DYE

The formation and encapsulation properties of HPs based host-guest complexes have been extensively and deeply investigated. Generally, two types of micelles are involved, micelle (PM) and inverse micelle (IM), in most of cases, as unimolecular inverse micelle (UIM). The former one consists of hydrophobic core and hydrophilic shell and can encapsulate nonpolar guests in polar solvents; the latter one composes of hydrophilic core and hydrophobic

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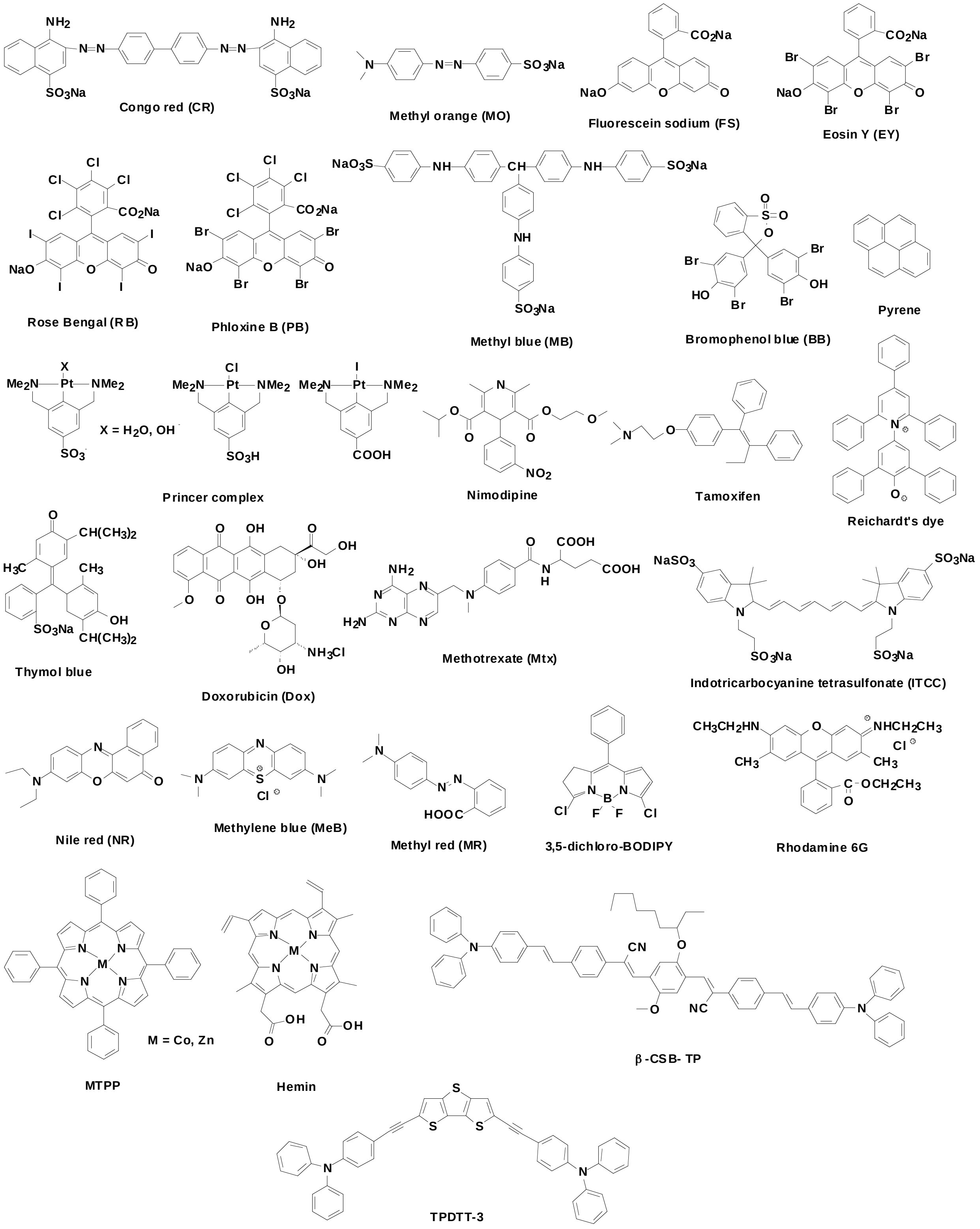


Scheme 1. Chemical structures of the guest dyes and drugs used for hyperbranched polymer hosts.

shell and is able to encapsulate polar guests in nonpolar solvents. They are usually called nanocapsules or nanocarriers. The encapsulation is generally carried out by phase-transfer experiment. The used guest molecules are listed in Scheme **1**. The release of encapsulated guest is often achieved by washing or dilution. Herein, the encapsulation properties are first described in terms of different HP hosts and illustrated in Table **1**, then the influence factors on encapsulation capacity of UIM are summarized in Table **2**, and finally some applications are described.

Table 1. Encapsulation of Hyperbranched Polymers to Dyes

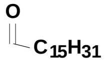
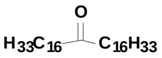
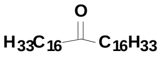
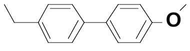
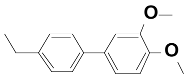
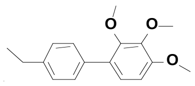
Hyperbranched Polymer Core	M_n of Core	Shell (and DF)	Guest [a]	Solution Property	Release Method	Remark	Ref.
PG	1.8K	C16 (60%) [b]	0.8CR; 1.4RB	UIM	Cleavage by ester hydrolysis	Irreversible encapsulation	[14]
	1.8K	C16 (90%)	0.7CR				
	6.3K	C16 (60%)	2.7CR				
	6.3K	C8 (40%)	1.3CR				
	8K	C16 (60%)	1.3CR				[16]
PG (linear analogue)	8K	C16 (60%)	Not available				
PG	8K	C16 (60%)	3.8-4.1 Princer Complex **3**				[18]
PG-*star*-PHEMA	Total 203K [c]	C16 (30%)	5.2MO; 4.8CR	IM			[19]
	Total 203K	C16 (50%)	4.9MO; 3.6CR				
	Total 203K	C16 (57%)	2.1MO; 0.0CR				
	Total 203K	C2 (59%)	1.0MO; 0.0CR				
PG (70% of hydroxyl groups was modified with quaternaized amine groups)	Total 203K	C16 (30%)	84.6MO; 31.6CR				
PG (30% of hydroxyl groups was modified with PEG550)	Total 203K	Pivaloyl groups (70%)	10 pyrene	PM			
PG	21K	 (25%)	0.15±0.05CR	UIM (below 10^{-3}M)		pH-Sensitive linkages	[20]
	21K	 (45%)	13±4CR				
	21K	 (55%)	2±0.5CR				
PG modified with  (25%)	Total 6.4K	Dihydroxyl groups	0.50pyrene; 0.15nimodipine	PM	High dilution		[23]
 (25%)	Total 6.6K	Dihydroxyl groups	0.29pyrene; 0.41nimodipine				
 (23%)	Total 6.8K	Dihydroxyl groups	0.72pyrene; 0.21nimodipine				

Table 1. contd….

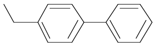
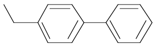
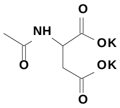
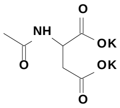
Hyperbranched Polymer Core	M_n of Core	Shell (and DF)	Guest [a]	Solution Property	Release Method	Remark	Ref.
 (25%)	Total 6K	Dihydroxyl groups	0.80pyrene; 0.18nimodipine				
 (44%)	Total 6.9K	Dihydroxyl groups	0.193pyrene; 0.85nimodipine				
PG	5K	No shell	0.0016pyrene; 0.0096 tamoxifen		Addition of NaCl solution	Pyrene spread in both PEG and PEI.	[24]
	5K	2×(PEG5000) [d]	0.0058pyrene; 0.123tamoxifen				
	5K	3×(PEG3400+Folate)	2.48tamoxifen				
Polythreitol	11.8K	Trityl groups (15.7%)	0.5RB	Aggregates	Suspended in a phosphate buffer solution (pH =7.4)	Rapid release and large amount of release	[25]
	11.8K	Trityl groups (23.8%)	1.4RB	UIM		Slight release	
	11.8K	Trityl groups (38.7%)	1.3RB				
	47.9K	Trityl groups (23.2%)	4.9RB				
	47.9K	Trityl groups (43.2%)	4.4RB				
	47.9K	Trityl groups (61.0%)	4.3RB				
Poly(3,4-epoxycyclo - hexanemethanol)	10.3K	 (22%)	1.2Reichardt's dye	PM			[26]
Poly(3,4-epoxycyclo - hexanemethanol) (linear analogue)	25.1K	 (31%)	0.1Reichardt's dye				
PAMAM	8.3K	benzoyl groups	3.7 CR				[27]
	8.3K	C16	11.9CR				
	8.3K	No shell	Not available				
	3.4K	methoxyl groups	0.012CR				
PSA	Total 11.2K	C16 (65%)	41.8CR; 19.4MO		Washing with water	Reversible encapsulation	[28]
		C9 (65%)	23.4CR; 15.5MO				
		C5 (65%)	12.4CR; 12.7MO				
PAMAM	Total 10.8K	C16 (61%)	5.26MO; 0.90MB; 9.08MO/0.45MB [h]			Synergistic encapsulation	[29]
PSA	Total 11.2K	C16 (65%)	16.7MO; 0.05MB; 17.2MO/2.04MB				

Table 1. contd….

Hyperbranched Polymer Core	M_n of Core	Shell (and DF)	Guest [a]	Solution Property	Release Method	Remark	Ref.
PAMAM	Total 10.8K	C16 (61%)	5.26MO; 3.09RB; 3.18PB; 1.81EY; 0.73FS; 0.90MB; 0.00MO/3.26RB; 0.00MO/3.14PB; 2.77MO/0.68EY; 3.60MO/0.00FS; 9.08MO/0.45MB			Competitive encapsulation	[30]
PSA	Total 11.2K	C16 (65%)	16.70MO; 3.16RB; 2.47PB; 1.09EY; 0.10FS; 0.05MB; 0.00MO/3.14RB; 0.00MO/2.51PB; 2.31MO/0.96EY; 1.37MO/0.00FS; 17.21MO/2.04MB				
PEI	10K	C16 (60%)	14.4EY; 7.0FS; 25.6MO; 16.9CR	UIM			[31]
	25K	C16 (60%)	38.4EY; 14.2FS; 57.4MO; 44.5CR				
PEI (40% quaternized)	10K	C16 (60%)	41.2EY; 12.2FS; 56.6MO; 49.3CR				
PEI (40% quaternized)	25K	C16 (60%)	71.4EY; 41.7FS; 153MO; 90.1CR				
PEI (linear analogue)	15K	C16 (60%)	4.2EY; 0.9FS; 5.3MO; 0.0CR				
PEI	10K	C16 (30%)	67.6MO; 38.3EY; 15.9FS	UIM			[32]
	10K	C16 (60%)	62.3MO; 25.8EY; 14.2FS				
	10K	C16 (73%)	51.9MO; 25.2EY; 10.3FS				
	25K	C16 (73%)	132MO; 63.5EY; 23.3FS				
	10K	C12 (73%)	9.0MO; 8.4EY; 0.7FS				
PEI (27% quaternized)	10K	C16 (73%)	87.4MO; 45.6EY; 24.6FS				
	25K	C16 (73%)	211MO; 107EY; 66.7FS				
PEI	10K	PEG450 (54%)	Pyrene	PM	Addition of NaCl solution	Pyrene spread in both PEG and PEI.	
	10K	C12 acid	8.5MO; 3.3MO	IM	Reduction of pH value	Electrostatic interaction between core and shell	[33]
	10K	C16 acid	8.6MO; 2.9MO				
	25K	C12 acid	21.4MO; 7.2CR				
PEI (linear analogue)	15K	C12 acid	1.2MO; 0.0CR				

Table 1. contd….

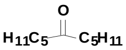
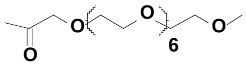
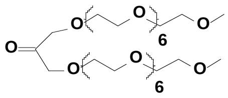
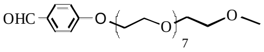
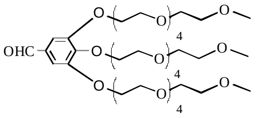
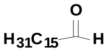
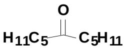
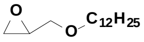
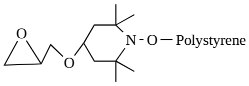
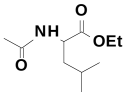
Hyperbranched Polymer Core	M_n of Core	Shell (and DF)	Guest [a]	Solution Property	Release Method	Remark	Ref.
PEI	1.8K	30×(PCL1100) [e]	1.2MO	IM			[34]
PEI (quaternized)	1.8K	30×(PCL1100)	1.9MO				
PEI	1.8K	30×(PCL2500)	1.5MO				
PEI (quaternized)	1.8K	30×(PCL2500)	7.8MO				
PEI	10.5K	No shell	0.054CR			pH-Sensitive linkages	[36]
	10.5K	 $H_{11}C_5C(=O)C_5H_{11}$ (100%)	0.35CR				
	10.5K	 (100%)	0.44CR				
	10.5K	 (42%)	0.35CR				
	10.5K	No shell	1.37RB; 0.03CR; 6.03TB		Reduction of pH value	pH-Sensitive linkages	[37]
	10.5K	 (>99%)	11.7RB; 0.06CR; 5.27TB				
	10.5K	 (>99%)	19.6RB; 0.19CR; 21.2TB				
	25K	No shell	0.02±0.005CR		Reduction of pH value	pH-Sensitive linkages	[20]
PEI	25K	 $H_{31}C_{15}C(=O)H$ (33%)	0.6±0.1CR				
	25K	 $H_{11}C_5C(=O)C_5H_{11}$ (53%)	0.2±0.05CR				
	10K	PBLG25000	21.4MO	UIM	Release occurs at pH<2.3 or pH>10.3.	pH-Sensitive linkages	[38]
	3.6K	C18+PEG300 (70%) [f]	ca. 10 Dox and Mtx; 6-8ITCC			Aggregation causes a reduction on the C_{load} for NR.	[39]
	3.6K	C18+PEG450 (70%)	ca. 10 Dox and Mtx;				
	10.5K	C18+PEG450 (50%)	Not available for Dox and Mtx				
PEI (acetylated)	10.5K	C18+PEG300 (70%)	ca. 1-3 Dox and Mtx				

Table 1. contd….

Hyperbranched Polymer Core	M_n of Core	Shell (and DF)	Guest [a]	Solution Property	Release Method	Remark	Ref.
PEI	10K	 (15%)	9MO	Aggregates of IMs		Aggregation causes a reduction on C_{load}. The larger concentration, the lower C_{load}.	[40]
	10K	2-Dodecyloxymethyl -oxirane (30%)	75MO				
	10K	2-Dodecyloxymethyl -oxirane (60%)	69MO				
	10K	2-Dodecyloxymethyl -oxirane (86%)	71MO				
	10K	2-Dodecyloxymethyl -oxirane (15%) and propylene oxide (85%)	11MO				
	10K	2-Dodecyloxymethyl -oxirane (30%) and propylene oxide (70%)	85MO				
PEI	10K	2-Dodecyloxymethyl -oxirane (60%) and propylene oxide (40%)	81MO				
	10K	2-Dodecyloxymethyl -oxirane (86%) and propylene oxide (14%)	72MO				
	10K	 (15%)	ca.8MO	UIM			
	10K	Polystyrene (30%)	ca.13MO				
	10K	Polystyrene (60%)	ca.17MO				
Polyphenylene	3.8K	Carboxyl groups	MR; MO [g]				[2]
Poly(D-Glucan)	70.6K	 (68.7%)	0.0CR; 8.7RB/15.5 Thymol blue; 17.6RB/11.5AY	UIM		Size-selective encapsulation	[43]
Poly(ester amide)	5.8K	52×(PCL350)	0.95CR; 0.0MO; 0.0BB	UIM			[47]
	5.8K	52×(PCL830)	6.94CR; 6.35MO; 3.47BB				
	5.8K	52×(PCL1500)	22.6CR; 22.0MO; 8.79BB				
Poly(ester amine)		C18	MO		Release under basic condition		[48]
Polyacrylate		No shell	Rhodamine 6G				[50-54]

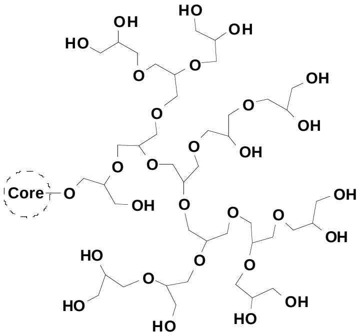
[a] Average number of loaded dye molecules per macromolecules. [b] C16: alkyl chain with 16 carbon atoms. [c] Total: M_n contains both the M_n of shell and core. [d] 2×(PEG5000): each core was modified with two PEG (M_n=5000) chains on average. [e] 30×(PCL1100): each core was modified with thirty PCL (M_n=1100) chains on average. [f] C18+PEG300: inner shells are C18 alkyl chains; outer shells are PEG300 chaines. [g] The solubility of MR was enhanced 30 times; the solubility of MO was enhanced twice. [h] 9.08MO/0.45MB: double-dye host-guest encapsulation.

2.1. Encapsulation Properties of Hyperbranched Polymer-Dye Host-Guest Complexes

2.1.1. Polyether Polyol

Polyglycerol

Frey *et al.* described the use of core-shell amphiphilic hyperbranched polyglycerol (HPG) (see Scheme **2**) for encapsulating guest molecules for the first time [14, 15]. In the contribution, HPG was prepared via ring-opening multibranching polymerization of glycidol under slow monomer addition and partially esterified with hydrophobic alkyl chains to form amphiphilic polymers. The chloroform solutions of the obtained amphiphilic polymers can extract dyes such as Congo red (CR) and Rose Bengal (RB) from aqueous solution into the organic phase. Once the saturation concentration of dye in the organic phase was reached, the adsorption did not go on. The loading capacity (C_{load}) depends on four factors: the molecular weight of HPG, the length of alkyl chains, the degree of functionalization (DF) and the structure of dye molecules. The encapsulation is irreversible and the entrapped dyes cannot be released unless the linkage between the core and the shell is destroyed. Dynamic light scattering (DLS) measurements confirmed that the amphiphilic polymers acted as UIM in organic solvents. The linear counterpart of the amphiphilic HPG cannot extract any dyes from aqueous solution, suggesting that the dendritic topology is crucial to render the encapsulation property to HPs [16]. When all the hydroxyl groups were esterified with alkyl chains, the polymer could not encapsulate any dyes, implying that it is the hydroxyl groups which mainly create the polar environment for the encapsulation behavior through hydrogen bonding [17].



Scheme 2. Chemical structure of hyperbranched polyglycerol (HPG).

Frey and coworkers successfully introduced pincer-platinum (II) complexes into the core-shell HPG nanocapsule [18]. It was found that the princer complex with a carboxylic group could not be encapsulated, while the one with a sulfonic group could be, indicating that high affinity between host and guest is necessary for the encapsulation. The C_{load} increases with the molecular weight of the HPG core. The formed supramolecular complex showed catalytic activity in a dual Micheal addition. They also prepared a series of HPG-*star*-poly(2-hydroxyethyl methacrylate)s (PHEMA) and modified them with alkyl chains to afford amphiphilic polymers [19]. Three methods can be used to enhance the C_{load}s of water-soluble dyes: decreasing the polarity of outer part by increasing the length of alkyl chain, slightly increasing the thickness of the inner part by slightly decreasing the amount of alkyl chain and tremendously increasing the polarity of the inner part by converting the hydroxyl groups into quaternary amines. The C_{load}s can reach an amount of 84.6 of MO and 31.6 of CR per polymers by combination of the three methods.

HPs-based pH-responsive nanocapsules were developed by Haag *et al.* [20, 21]. HPG was used as core, alkyl chains were employed to form the hydrophobic shells and between them there were acid-sensitive linkages. The encapsulation experiments revealed that the optimal encapsulation capacity was obtained with the DF of about 45-50%, higher or lower than this range would cause the decrease of capacity. The number average diameter of the dye-loaded particles was larger than the unloaded particles in the atomic force microscopy (AFM) measurements, implying that the guest molecules swelled the core. The calculation values of particle size according to force-field theory are consistent with the practical value, suggesting that the core-shell nanocapsules are present as UIM in dilute solution ($<10^{-4}$ M). The nanocapsules possess high C_{load}, but cannot hold any cationic dyes, indicating polar anionic dyes have a high affinity with the HPG core. Titration of dyes of higher affinity with the core can substitute the encapsulated dyes of lower affinity, implying the encapsulation process is a dynamic equilibrium process and the encapsulation mechanism has an enthalpic component. The pH-sensitivity test showed that the acid-sensitive linkages gradually broke up in acid media after a period of time and thus the core-shell structure was gradually destroyed, resulting in the release of the entrapped dyes.

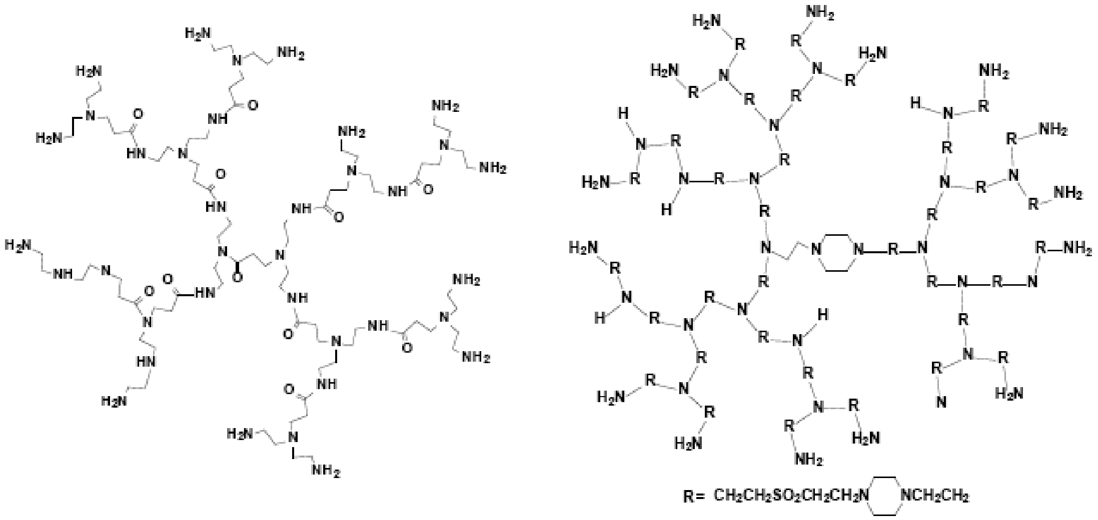
The encapsulation properties of the nanocapsules with HPG or polyethyleneimine (PEI) core and extremely nonpolar perfluorinated shell were investigated as well [22]. The nanocapsules can transport dyes from water into the fluorous phase. The polymers with PEI core exhibited better transport capacity than the ones with HPG core, indicating stronger interaction between PEI and anionic dyes.

Haag *et al.* prepared a series of nanocapsules composed of hydrophobic cores and hydrophilic shells, which acted as PMs and transported hydrophobic guests into water [23]. The inner hydroxyl groups of HPG were modified with several biphenyl derivatives to generate the hydrophobic cores, and the terminal hydroxyl groups formed the hydrophilic shells. The C_{load} of nimodipine based on hydrophobic host-guest interactions can be enhanced by increasing the DF and by the presence of special π-π interaction between the biphenyl groups and nimodipine as revealed by ultraviolet/visible (UV/Vis) spectroscopy. DLS measurements, transmission electron microscopy (TEM) analysis and critical aggregate concentration (CAC) measurements revealed that both the unloaded polymer and the loaded polymer complex formed aggregates in water. Interestingly, the sizes of the loaded polymer complexes are smaller than the sizes of the unloaded polymers, might be resulted from the attractive interaction between the biphenyl groups and guest molecules. The release of guest molecules occurred by high dilution.

Paleos *et al.* prepared polyethylene glycol (PEG)-functionalized HPG [24]. The C_{load} for hydrophobic anticancer drug tamoxifen in water was larger than that of the control HPG, which was ascribed to additional solubilization of tamoxifen in the PEG chains. The release could be achieved by adding NaCl to cationize the PEG moiety.

Other Polyether Polyol

Satoh *et al.* prepared hyperbranched polythreitol with trityl groups as shells and tested the encapsulation properties for RB [25]. Increasing the molecular weight of hydrophilic polythreitol led to the enhancement of the C_{load}. The optimal DF with trityl groups was about 23%, and lower or larger than this value resulted in the lower C_{load}. It was judged that high DF caused a decrease in the hydrophilic core space. The C_{load} of the nanocapsule with sufficient DF



Scheme 3. Chemical structures of hyperbranched poly(amido amine) (HPAMAM, left) and hyperbranched poly(sulfone-amine) (HPSA, right).

increased proportionally with increasing the polymer concentration, which could also be called concentration-independent, implying the polymer existed as UIM. When the DF was reduced to 15.7%, the polymer could not hold RB molecules. Only if the polymer concentration increased over a certain value where large aggregates had formed, the polymer aggregates were capable of encapsulating RB. Nevertheless, the aggregates were not as stable as UIM. The encapsulated RB molecules could be rapidly released from the aggregate and the amount of released molecules was 55%, while the released amount from the UIM was less than 10%. They also prepared a hydrophobic hyperbranched polyether polyols by cationic ring-opening polymerization of 3, 4-epoxycyclohexanemethanol and converted the outer hydroxyl groups into potassium carboxylates [26]. The obtained polymer had a hydrophobic core and a hydrophilic shell, and thus the PM could accommodate the hydrophobic Reichardt's dye in water. Its linear counterpart showed a much lower capacity, suggesting that the dendritic topology is crucial in supramolecular encapsulation.

2.1.2. Poly(amido amine) and poly(sulfone-amine)

Liu *et al.* reported the synthesis of a series of hyperbranched poly(amido amine)s (HPAMAMs) (see Scheme **3**, left) by condensation of methyl acrylates and various amines [27]. Different feed radios of methyl acrylates to amines afforded HPs with terminal methoxyl groups of different densities. It was found that the polymers with dense terminal hydrophobic methoxyl groups could encapsulate some dye molecules such as CR, while the polymers with few terminal methoxyl groups could not hold any. When hydrophobic benzoyl or palmitoyl groups were employed to end-cap the amino groups of HPAMPAM to generate a core-shell structure, the C_{load} for dye molecules was enhanced dramatically. As shown in Table 1, the macromolecules end-capped with benzoyl and palmitoyl groups could hold an average maximum of 3.7 and 11.9 CR molecules, respectively. It was concluded that the presence of hydrophobic shell plays a crucial role in the encapsulation of the HP host.

Another series of amphiphilic polymers composed of highly hydrophilic hyperbranched poly(sulfone amine) (HPSA) (see Scheme **3**, right) as cores and hydrophobic alkyl chains of different length as shells were also prepared [28]. Phase-transfer experiments showed that these nanocapsules possessed very high capacity of holding water-soluble dyes (see Table **1**). This could be attributed to the dense and highly hydrophilic sulfonyl and amino groups. By increasing the length of hydrophobic alkyl chains, the polarity difference between the core and the shell was enlarged and thus, the C_{load} was enhanced. Especially, the polymer capped with palmitoyl groups reached C_{load} of 41.8 CR and 19.4 methyl orange (MO) molecules per macromolecule. By washing the chloroform solution of dye-loaded nanocapsules with pure water, some of the entrapped dye molecules could be transferred from the cavities in the polymers to aqueous phase. This reversibility was ascribed to the lower density of the hydrophobic shells which allowed the entrapped dye molecules to go outside.

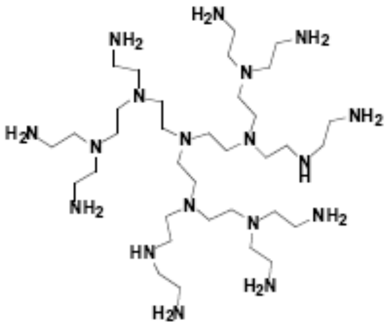
The authors further investigated the double-dye host-guest encapsulation for core-shell amphiphilic HPs and reported a novel synergistic effect [29]. Two kinds of palmityl chloride-modified HP, PAMAM10K-C16 and PSA11K-C16, were used as the hosts, and water-soluble dyes such as MO and methyl blue (MB) were selected as the corresponding guests. Three types of experiments were carried out: single-dye encapsulations, one-step double-dye encapsulations and gradual double-dye encapsulations. With the cooperation of MB, the C_{load} of MO could be doubled for the PAMAM10K-C16. For the PSA11K-C16, the C_{load} of MB could be increased to a 96-fold level of single-dye encapsulation with almost no loss of MO. By changing the encapsulating sequence, two types of processes were found. The synergistic encapsulation for HPAMAM10K-C16 was a parallel-type process because the sequence had no significant impact on the loading capacity of each dye, while the case of HPSA11K-C16 was a cascade-type process since the results with different encapsulating order were different. In addition, pH value did not have significant influence on the synergistic encapsulation capacity. The synergistic effect was found simultaneously in the supramolecular encapsulation of two hosts, indicating this effect is not limited to a peculiar dendritic polymer.

Then, a systematical investigation on double-dye encapsulation was performed using the same host HPs of PAMAM10K-C16 and PSA11K-C16 by Wu *et al.* [30]. In the double-dye encapsulation, three kinds of interactions existed: the binding force between the host and each guest and the interaction between the two guests. Different pairs of dyes resulted in different interactions, and led to four different results: (1) C_{load} of MO decreased significantly in the presence of the other one (MO & RB, MO & phloxine B (PB)), (2)

C_{load}s of both dyes decreased (MO & eosin Y (EY)), (3) C_{load} of MO decreased and that of the other dye almost decreased to zero (MO & fluorescein sodium (FS)), and (4) C_{load} increased for one or both of the pair dyes (MO & MB). Four models of double-guest supramolecular encapsulations were proposed: competitive, random, synergetic and negative. A new parameter (relative selectivity constant) was proposed to measure the competitive abilities.

2.1.3 Polyethyleneimine

Stiriba *et al.* prepared a core-shell nanocapsule with hyperbranched polyethyleneimine (HPEI) (see Scheme **4**) as hydrophilic core and alkyl chains as hydrophobic shell via amidation [31, 32]. They found the C_{load} for water-soluble dyes could be enhanced significantly by increasing the sizes of cores, optimalizing the DF, increasing the length of the alkyl chains and quaternizing the core with MeI. The latter two methods were also explained as increasing the core-shell polarity difference.



Scheme 4. Chemical structure of hyperbranched polyethyleneimine (HPEI).

Almost all of the core-shell amphiphilic nanocapsules based on HPs contain covalent linkages between cores and shells. Stiriba *et al.* developed a supramolecular nanocapsule from non-covalent assembly of HPEI and fatty acids [33]. The nanocapsule showed encapsulation property for CR and MO. Reducing pH to 2 led to the cleavage of electrostatic interaction linkage, and thus, the disassembly of nanocapsules and the release of dyes into aqueous phase.

Chen *et al.* carried out a ring-opening polymerization of ε–caprolactone with hyperbranched PEI as initiator to afford a core-shell amphiphilic polymer [34]. The polymer showed encapsulation property for MO, and the C_{load} could be further improved by quaternizing the tertiary amines with hydrochloride. Haag *et al.* prepared analogical nanocapsules via ring-opening polymerization of lactide and the obtained polymer also exhibited encapsulation property [35].

The preparations of a series of pH-sensitive nanocapsules based on hyperbranched PEI were reported by Haag *et al.* [20, 36, 37]. pH-Sensitivity was achieved by forming the acid-labile linkage between core and PEG shell, which was a C=N bond generated by the reaction of primary amino end groups in the PEI core with carbonyl groups in the shells. It is worthy pointing out that because the secondary amino groups cannot react with carbonyl groups, the interior of the nanocapsule was kept intact. This is an advantage compared with amidation which involves secondary amino group. The authors found that increasing the DF with PEG from 0% to 100% can enhance the C_{load}. The rapid release of encapsulated molecules was found by reducing the pH to 5-6 to cleave the C=N bond linkage.

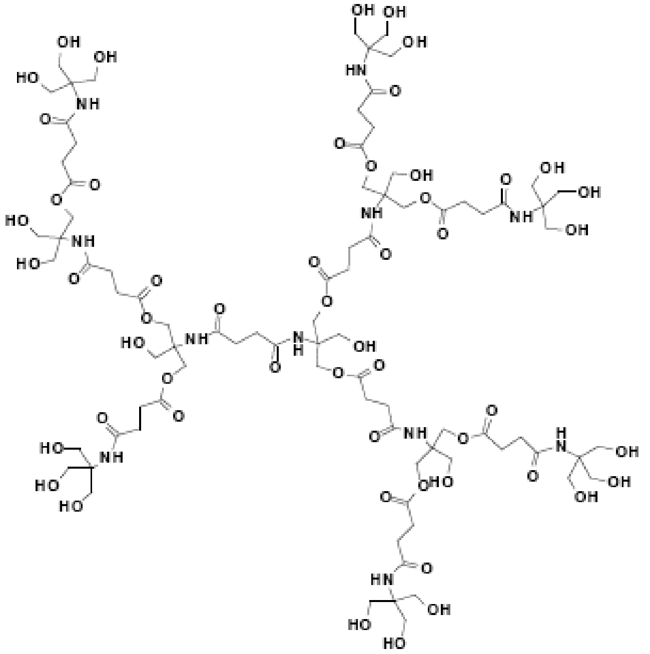
Chen *et al*. prepared hyperbranched, amphiphilic multiarm biodegradable PEI –poly(g-benzyl-l-glutamate) (PBLG) nanocapsules and examined the encapsulation properties [38]. They found the pH-sensitivity of the nanocapsules is different from the one discussed above: in the pH range of 2.3 to 10.3, MO could be extracted into organic phase; out of this range, the release of MO took place. So the encapsulation could be reversible.

The encapsulation properties of nanocapsules with core-multishell architecture were studied by Haag *et al.* [39]. The nanocapsule contained a hydrophilic PEI core, a hydrophobic C18 alkyl chain inner shell and a hydrophilic PEG outer shell. The results of the encapsulation for antitumor drugs Doxorubicin (Dox) and Methotrexate (Mtx) indicated that the existence of the hydrophilic core and the hydrophobic inner shell was essential in the supramolecular encapsulation. The amount of encapsulated Nile red (NR) dye molecules reached the maxium value at the CAC, but the encapsulation decreased with further increasing the concentration. The explanation is the aggregates formed above the CAC only allow them to collide with guest molecules at the interface and the differential migration kinetics of guest molecules from shell to core caused the observed drop of encapsulation as a function of polymer concentration.

Wan *et al.* studied the encapsulation properties of three sets of nanocapsules in details [40]: A) the PEI alkylated with 2-dodecyloxymethyloxirane; B) The PEI alkylated with 2-dodecyloxymethyloxirane and further with propylene oxide; C) The PEI alkylated with mono-epoxy group terminated polystyrene (see Table **1**). The shells of Group **C** are much thicker than the shells of Group **A** and **B**, and consequently, Group **C** acts as UIMs in solution, while Group **A** and **B** are present as IM aggregates in solution. The C_{load} of the UIMs formed by Group **C** is concentration-independent; by contrast, the C_{load} of the IM aggregates formed by Group **A** and **B** are concentration-dependent, that is, the C_{load} decreases with increasing the concentration.

2.1.4 Other Hyperbranched Polymers

After functionalizing hyperbranched polyphenylene with terminal carboxyl groups, the polymer became water-soluble and could make naphthalene soluble in water and improve the solubility of methyl red (MR) and MO in a phosphate buffer solution by 30 and 2 times, respectively [2]. A facile and efficient synthesis of wholly aliphatic hyperbranched polyester was reported by Kumar *et al.* and the polymers showed irreversible encapsulation property for MO, although the polymers did not possess a typical core-shell structure [41]. Ramakrishnan *et al.* prepared PMs and UIMs based on hyperbranched polyether [42]. Satoh *et al.* prepared three types of hydrophilic hyperbranched polysaccharide-based nanocapsules, hyperbranched D-glucan as core and L-leucine ethyl ester as shell [43], hyperbranched poly(D-glucopyranose) as core and L-leucine ethyl ester as shell [44], and hyperbranched D-mannan as core and polylactide as shell [45]. These nanocapsules showed the encapsulation properties for water-soluble dyes. Smet *et al.* synthesized hyperbranched poly(arylene oxindole)s with DB of 100% by condensation of isatin moieties and aromatic groups in the AB_2 monomers [46]. The modification with the functional groups of different polarity could be carried out independently at the nitrogen atoms in the interior and the terminal isatin moieties, affording PMs in water and IMs in nonpolar solvents. These two micelles showed the encapsulation property for hydrophobic dye, 3,5-dichloro-BODIPY, and hydrophilic dye, RB, respectively. Li *et al.* prepared hyperbranched poly(ester amide)-*star*-poly(ε-caprolactone) (PCL) polymers (see Scheme **5**) and studied the encapsulation property [47]. Increasing the PCL chain length led to an improvement in C_{load}, which is in agreement with the results reported by Chen *et al.* [34]. Alkyl chains-modified hyperbranched poly(ester amine) prepared by Tang *et al.* could extract more MO molecules at lower pH, and release them in a basic media [48, 49]. A series of hyperbranched polyacrylates were prepared by Sato *et al.,* which could encapsulate water-soluble Rhodamine 6G dye in toluene solution directly [50-54]. Amphiphilic HP of very high molecular weight with polystyrene as hydrophobic core and a polyvinyl ether hydrophilic shell showed a great C_{load} for metallo-porphyrins, such as MTPP and Hemin, up to several thousands of guest molecules per macromolecule [55].



Scheme 5. Chemical structure of hyperbranched poly(ester amide) [47].

2.1.5. Influence Factors on Encapsulation Property of Inverse Micelle

Dendritic topology and amphiphilic core-shell structure are essential to render polymer an encapsulation capability.

Table **2** gives a brief summary on the general influence factors for the encapsulation capacity of IM, which could be used in turn to design novel host-guest systems with tailor-made properties.

2.2. Applications of Hyperbranched Polymer-Dye Host-Guest Complexes

Host-guest complexes of HPs and dyes could combine both functions and supramolecular encapsulation via noncovalent bond, which saves efforts on time-consuming synthesis and purification associated with covalent bonding. Since the knowledge on encapsulation property was understood, the corresponding application had been tried (see Table **4**).

The combination of supramolecular encapsulation and self-assembly of HPs for the facile fabrication of multifunctional thin films was reported for the first time by Liu *et al.* [56]. HPAMAM modified with palmitoyl chloride was employed as core-shell polymer host in this study. By means of breath-figure-templated assembly, honeycomb-patterned films were prepared on various substrates such as mica, quartz, silicon wafer, glass, gold and carbon within a wide range of relative humidity (30-72%) at room temperature, and the depth of honeycomb cells could be adjusted by changing the concentration of the polymer solution from only 65 nm at 0.05 g/L to 1.4 μm at 2 g/L. The dye-containing honeycomb-patterned films could be obtained in the same way from the dye-loaded HPAMAM. The emission wavelength could be tuned easily by the fluorescent dyes loaded into the PAMAMs, opening up a straightforward approach to multifunctional supramolecular materials.

Haag *et al.* used pH-sensitive PEG functionalized HPG nanocapsule in delivery of anticancer agent Dox [57]. The authors also used this pH-sensitive HPG nanocapsule and the PEI based multishell nanocapsule to complex with tetrasulfonated indotricarbocyanine (ITCC) dye, and then successfully applied in *in vivo* tumor imaging [39, 57]. Hyperbranched poly(siloxysilane)s with carboxyl groups and quaternary ammonium groups synthesized by Prasad *et al.* were also tried to encapsulate two two-photon-absorption dyes, TPDTT-3 and b-CBS-TP, and used in *in vitro* bioimaging [58].

The selective encapsulation property of nanocapsule can be applied in the separation of double-dye mixtures [59]. The PEI based

Table 2. Summary of Influence Factors on Encapsulation Property of IM

Components	Factors	Encapsulation Capacity
Dye	Size ↑	↓
	Polarity (or affinity with core) ↑	↑
Hyperbranched polymer core	Size (or M_n) ↑	↑
	Polarity ↑	↑
Hydrophobic shell	DF ↑	first ↑, and then ↓ [a]
	Hydrophobic chain length ↑	↑
Core and shell	Polarity difference ↑	↑
UIM	Concentration ↑ or ↓	Independent
	In some cases, aggregation forms	↓ and slow

↑: increase; ↓: decrease

[a] It is in most of cases, because at first the higher DF leads to higher encapsulation stability, but the overmuch functionalization also results in a decrease in binding sites and spaces. Nevertheless, if the functionalization has no effect on the inner sites, the higher DF the better the encapsulation capacity [37].

Table 3. Encapsulation of Dendrimers to Dyes

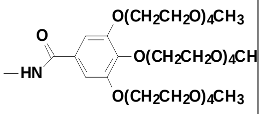
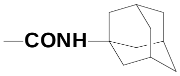
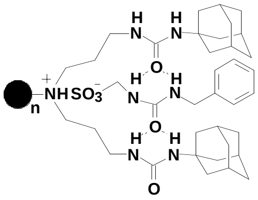
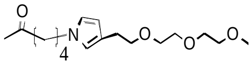
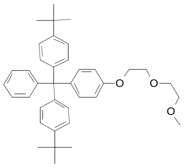
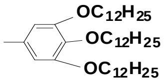
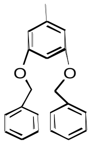
Dendrimer Core	Shell	Guest	Solution Property	Release Method	Remark	Ref.
PPI	tBoc groups protected amino acid	TCNQ; RB ; EPR probe 3-carboxyproxyl			Encapsulation occurred during the coupling reaction. Irreversible encapsulation.	[13]
	tBoc groups protected amino acid	RB; New coccine; Methylene violet 3RAX; Nitrophenol; EPR probe		Cleavage by hydrolysis	Encapsulation occurred during the coupling reaction. Irreversible encapsulation. Selective release by partly opening the shell.	[123]
	C16	RB	UIM	Addition of toluene	Encapsulation occurred by mixing the host and guest in ethanol followed by precipitation of the complex.	[124]
	C16	RB; FS; Erythrosin B; 4,5,6,7-Tetrachloro -fluorescein			The first example for liquid-liquid extraction. The extraction occurs at low pH, but not at high pH.	[125]
		RB; 4,5,6,7-Tetrachloro -fluorescein			Dye molecules prefer to accumulate in the dendritic moiety of the host molecules.	[126, 127]
		Pyridinium (3-benzyl-ureido) methane sulfonate			One-to-one complexation 	[128]
PPI (quaternaized)	C8 and PEG150	Reichardt's dye; pyrene				[129]
PPI	PEG5000	Pyrene; BV; BD		High dilution	Pyrene is solubilized by both the dendrimer and the PEG.	[130]
PPI		NR				[131]
PAMAM	Hydroxyl groups	Benzoic acid				[132, 133]
	No shell	Ibuprofen			Electrostatistic interaction between the NH_2 groups of dendrimer and the carboxyl group of ibuprofen	[134]
	$HSCH_2CHNHCO\text{-}PEG$	RB			Oxidation-reduction sensitivity. The formed disulfide bonds lead to a reduction in C_{load}.	[135]
	No shell	Phenol blue				[136]
	Octadecyl acrylate	Acid red 1	UIM			[137]
Poly(PAMAM dendrimer) with linear PEI as backbone	Hexyl acrylate	Rhodamine 6G			Increasing the generation leads to a more densely packed structure which increase difficulty for the entrance of dye and thus, C_{load} is decreased.	[138]
Crosslinked PAMAM	No shell	MO				[139]

Table 3. contd…

Dendrimer Core	Shell	Guest	Solution Property	Release Method	Remark	Ref.
PAMAMs included in a microcapsule					Microcapsules were prepared by layer-by - layer deposition of poly(allylamine·HCl) and poly (vinyl sulfate) on $CaCO_3$ particles.	[140]
PEG-b-Poly(L-lysine) linear-dendron polymer	Perfluorooctanoyl or tBoc groups	Orange-OT				[141, 142]
Poly(L-lysine)	tBoc groups	Proflavine hydrochloride; Aurin tricarboxylic acid				[143]
poly (glycerol succinic acid)	Hydroxyl groups or carboxylate anions	Reichardt's dye; 10-hydroxycamptothecin				[144]
Polyphenylene	Carboxyl groups	Pinacyanol				[145]
Polyphenylene (with internal COOH)		Proflavine hydrochloride		Contact with water		[146]
Oligo(phenylene)	Two PEG dendrimers and one C22 chain	NR	Aggregates			[147]
Poly(aryl ether)		Reichardt's dye; Proflavine hydrochloride	UIM in toluene; aggregates in water		These polymers exhibited both polar and apolar nanocontainer characteristics	[148]
Poly(phenyl silyl ether)	Phenolic hydroxyl groups	Disperse red 1	Aggregates			[149]
Polyviologen		EY			One-to-one complexation	[150, 151]
Poly(quaternized amine)	 or 	MO				[152, 153]

nanocapsule was able to selectively capture MO, RB, CR and CR from the four double-dye mixtures, MO/Methylene blue (MeB), RB/MeB, CR/MeB and MO/CR, respectively, and the separated dyes were left in the water phase.

Chen *et al.* attached HPAMAM to cotton fiber and found that the modified fiber exhibited enhanced color strength and the dyed fiber displayed better washing fastness, rubbing fastness and levelling properties [60, 61].

3. HYPERBRANCHED POLYMER AND METAL-CONTAINING GUESTS

Besides the organic molecules, HPs can also be used to load inorganic compounds or used as templates to fabricate organic-inorganic hybrid nanomaterials. The inorganic guests mainly include metal nanoparticles, metal ions, and quantum dots (QDs). Started by Mecking *et al.* [62], preparations and applications of HP-encapsulated metal-containing guests have gained remarkably research interest. Metal nanoparticles and QDs are generally prepared by sequestering metal ions within HP cores which are usually coated with hydrophobic shells, followed by *in-situ* chemical reaction to yield the corresponding nanoparticles. The sizes of such particles are dependent on the number of metal ions initially adsorbed by the HPs. In some cases, it is also possible for amphiphilic HPs to extract preformed nanoparticles via phase-transfer, affording hybrid nanomaterials. These materials have potential applications in catalysis, antibacterial surface, and bioimaging, etc.

3.1. Preparations and Applications of Metal Nanoparticles

3.1.1. Polyglycerol

Mecking *et al.* applied amphiphilc HPG to prepare metal nanoparticles [62, 63]. They esterified 60%-67% of hydroxyl groups of the HPG with C15 alkyl chains and subsequently used the polymers to solubilize $PdCl_2$ or $Pd(OAc)_2$. After reduction with H_2 or heating, Pd nanoparticles formed without deposition. In contrast, precipitation occurred immediately upon reduction in the absence of the amphiphilic polymers. The sizes of the nanoparticles could be enhanced by increasing the HPG molecular weight and the polymer/metal feed radio. TEM observations clearly showed that the sizes of nanoparticles on the polymer scaffold of M_n=4.7 K were 5.2±1.8 nm, in the magnitude of unimolecular micelles. The colloidal solution was stable in air for at least several months at room temperature, and the dried solid could be redissolved in olefinic substrates to yield clear dark solutions again. The catalytic activity of the Pd particles on hydrogenation of cyclohexene was better than Pd/C catalyst and could be recovered by ultrafiltration and recycled used [64]. When CO reduction was introduced, Pd particles of hexagonal platelet structure with the sizes from 30 to several hundred nanometers were formed, rather than the spherical particles produced by other methods [65]. When linear PG was used, precipitates were usually obtained, indicating that dendritic structure plays a crucial role in the metal nanocrystal preparation. Frey *et al.* reported that $NaBH_4$ reduction yielded smaller Pd nanoparticles compared with H_2 reduction and the nanoparticles were successfully applied on the catalytic Heck reaction [66].

Wan *et al.* prepared amphiphilic thioether-containing core-shell HPGs and used them as templates for *in-situ* synthesis of Au nanoparticles [67]. Frey *et al.* prepared Au nanoparticles coated with thermosensitive poly(N-isopropylacrylamide) (PNIPAM) brushes and pH-sensitive hyperbranched polyelectrolyte [68, 69]. The water-soluble gold nanoparticles exhibited readily controllable lower critical solution temperature (LCST) in a very broad temperature range of 25-55°C.

3.1.2. Polyethyleneimine

Mecking *et al.* used core-shell HPEI as templates to prepare Ag nanoparticles *in-situ* from $AgNO_3$ [70]. Contrast variation experiments by means of small-angle neutron scattering (SANS) measurements revealed that for the higher molecular weight polymer, the Ag particle is homogeneously distributed within the polymer, whereas for the lower molecular weight polymer the particle located on the periphery of the aggregates. HPEI-Ag nanoparticle hybrids could be used in preparing environmentally friendly antimicrobial surface coatings [71, 72]. HPEI with fluorinated shells could be used as templates for preparing Pd and Ag nanoparticles in supercritical CO_2 [73].

HPEI-poly(propylene oxide) (PPO)-HPEI dumbbell-like copolymers and HPEI coated with glycidol, gluconolactone, or lactobionic acid were used as support materials in the preparation of Au, Pt and Cu nanoparticles [74-76]. The Pt nanoparticles showed catalytic activity for the hydrogenation of isophorone [76]. Zhang *et al.* coated Au substrate with HPEI thin film and then prepared Pt nanoparticles by electrochemically reduction of $PtCl_6^{2-}$ in the film. The hybrid film showed excellent electrocatalytic activity for O_2 reduction [77]. Voit *et al.* used oligosaccharide-modified PEI as templates to prepare Au nanoparticles [78]. They demonstrated that tertiary amino groups were inactive during reduction, secondary amino groups were the major reducing components, and primary amino groups stabilized the particles and influenced the particle shape.

By phase-transfer extraction, amphiphilic core-shell HPEI could also entrap citrate-protected Au nanoparticles from water into chloroform phase directly [79].

3.1.3 Polyester

Polyester (PE) terminated with carboxyl and hydroxyl groups was employed to prepare Ag nanoparticles with sizes of 3-19 nm by UV irradiation with the assistance of aliphatic phosphate surfactant [80]. Tsukruk *et al.* prepared Ag nanoparticles of 2-4 nm by using a Langmuir-Blodgett (LB) monolayer as template which was formed by amphiphilic HPE with part of primary amine groups [81, 82]. Liu *et al.* functionalized the Boltorn H40 PE with PNIPAM chains and then used the polymer to *in-situ* synthesize Ag nanoparticles [83]. The relative spatial distances between neighboring Ag nanoparticles could be reversibly adjusted by heating/cooling cycles. Similarly, Au nanoparticles were prepared and displayed the thermosensitivity [84].

3.1.4 Poly(amido amine)

Marty *et al.* compared the use of HPAMAM as template to prepare Au nanoparticles with the use of PAMAM dendrimer and found that the open structure of HPAMAM facilitated the interactions between metal ions and binding sites [85, 86]. The authors also prepared Pt nanoparticles of about 1.8 nm and found them effective and robust for hydrogenation reaction [87].

HPAMAM prepared by polymerization of N,N'-methylene bisacrylamide and N-aminoethyl piperazine was used as templates to prepare Ag nanoparticles [88, 89, 90]. Yan *et al.* investigated the antimicrobial property of these hybrids [91, 92]. They also prepared polymeric hollow spheres using PAA and HPAMAM by complex self-assembly process in aqueous solution, and employed the spheres as templates to prepare Au, Ag and Pd nanoparticles [93].

In-situ generation of Ag nanoparticles on carbon nanotubes decorated with PAMAM showed higher antimicrobial activity than control carbon nanotubes [94].

3.1.5. Other Hyperbranched Polymers

Hyperbanched polyaramids prepared by Russo *et al.* were used as supporting materials to prepare Pd nanoparticles with sizes of 2-3 nm by reducing $PdCl_2$ through $NaBH_4$ or bubbling H_2 [95]. The Pd nanoparticles exhibited high catalytic activity for the selective hydrogenation of various unsaturated substrates and the activity and selectivity could be adjusted by varying the polarity of solvents [96]. The authors also prepared solution and melt blends composed of hyperbranched aramids and polyamide 6, and employed the blends to prepare Pd nanoparticles of several nanometers [97].

Bipyridyl group terminated poly(phenylene vinylene) (PPV) was coated with the Au nanoparticles at the periphery by *in-situ* reduction and its fluorescence could be significantly quenched due to the electron transfer and energy transfer to the Au nanoparticles [98].

Soluble hyperbranched acrylate copolymers obtained by the copolymerization of divinylbenzene and ethyl acrylate using dimethyl 2,2-azoisobutyrate initiator was used to support Ag nanoparticle [50]. TEM images showed that the nanoparticles were not only entrapped in the polymer's void, but also connected multiple macromolecules.

Au nanoparticles *in-situ* generated in hyperbranched polystyrene was employed to fabricate a single-layered organic electrical bistable device by spin-coating [99]. Ag nanoparticles encapsulated in hyperbranched polyamine showed antibacterial activity related with the concentration of the Ag nanoparticles [100, 101]. Lu *et al.* prepared hyperbranched poly(amine-ester) by condensation of N,N-diethylol-3-amine methylpropionate to template the formation of Au and Ag nanoparticles [102,103]. Wei *et al.* used similar polymer to support Cu nanoparticles [104].

3.2. Other Guests

3.2.1. Quantum Dots

Thioether-modified HPG was used to template the formation of CdS or CdSe nanocrystals [105]. Bai *et al.* immersed PPV into $CdCl_2$ solution to *in-situ* synthesize the CdS nanoparticles with the diameter of about 4 nm in the presence of H_2S [106]. Shi *et al.* prepared PbS/HPE nanocomposite hollow spheres with external diameter of about 50–70 nm and the wall thickness of about 10–20 nm by using the modified HPE as templates [107, 108]. Core-shell and multilayered nanoparticles such as CdS/ZnS, ZnS/CdS and CdS/ZnS/CdS in the presence of PEI was prepared by a sequential feed of two metal chloride solutions and Na_2S [109].

Nie *et al.* used PEG grafted PEI to encapsulate luminescent QDs of CdSe/CdS/ZnS via direct ligand-exchange reactions [110]. The coated QDs could penetrate cell membranes and disrupt endosomal organelles in living cells due to the positive charges and a "proton sponge effect" related with multivalent amine groups. The PEG outlayer was crucial in reducing the cytotoxicity of PEI. This work is important toward the design and development of nanoparticle agents for intracellular imaging and therapeutic applications. PEG grafted HPAMAM could transfer CdSe and Fe_3O_4 nanoparticles into water via ligand exchange process [111]. Nann *et al.* employed amphiphilic HPEI to transfer CdSe@ZnS QDs into apolar solvents [112].

3.2.2. Metal Ions

Hyperbranched polymer with PEG units was used as polymer electrolyte to complex with lithium metal salts, $LiCF_3SO_3$ and $Li(CF_3SO_2)_2N$ [113]. The complex with $Li(CF_3SO_2)_2N$ showed higher conductivity.

Tang *et al.* prepared cobalt–polymer complexes by reaction of cobalt carbonyl with hyperbranched poly(ferrocenylphenylenes) and then ceramized them to afford soft ferromagnetic ceramics with high magnetizability and low coercivity [114].

Hyperbranched polyesters by polymerization of 2,2-bis(hydroxymethyl)propionic acid could extract some specific ions [115]. Grafting the polymer onto attapulgite nano-fibrillar clay afforded practically useful materials for metal ion extraction [116]. Application of HPAMAM-grafted silica-gels in this aspect was also studied [117].

Besides the metal ion extraction, complexation of metal ions with HPs has been found applications on metal ion detection. Fluorescent hyperbranched aromatic polyamines containing a number of coordinating sites exhibited much better selective quenching for Cu^{2+} ion than for other cations, such as Zn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} [118]. HPs containing triphenylamine and divinyl bipyridyl units displayed no quenching for alkali metal ions, earth alkali ions and Hg^{2+} ions, partially quenching for Cr^{2+}, Mn^{2+}, Fe^{3+} and completely quenching for Co^{2+}, and Ni^{2+}[119].

3.2.3. Other Metal Compounds

Qian *et al.* used hyperbranched polyurethane as template to prepare β-Ag_2S nanoparticles of 4-10 nm by *in-situ* reaction with thioacetamide and prepare Ag nanoparticles by *in-situ* photochemical reduction [120, 121]. Ludwigs *et al.* prepared ZnO nanoparticles with sizes of several nanometers by the slow decomposition of Et_2Zn in presence of HPG coated with C17 alkyl chains [122]. In contrast, attempt to prepare ZnO nanoparticles in the presence of low molecular weight alcohols or esters failed, indicating the core-shell structure plays a key role.

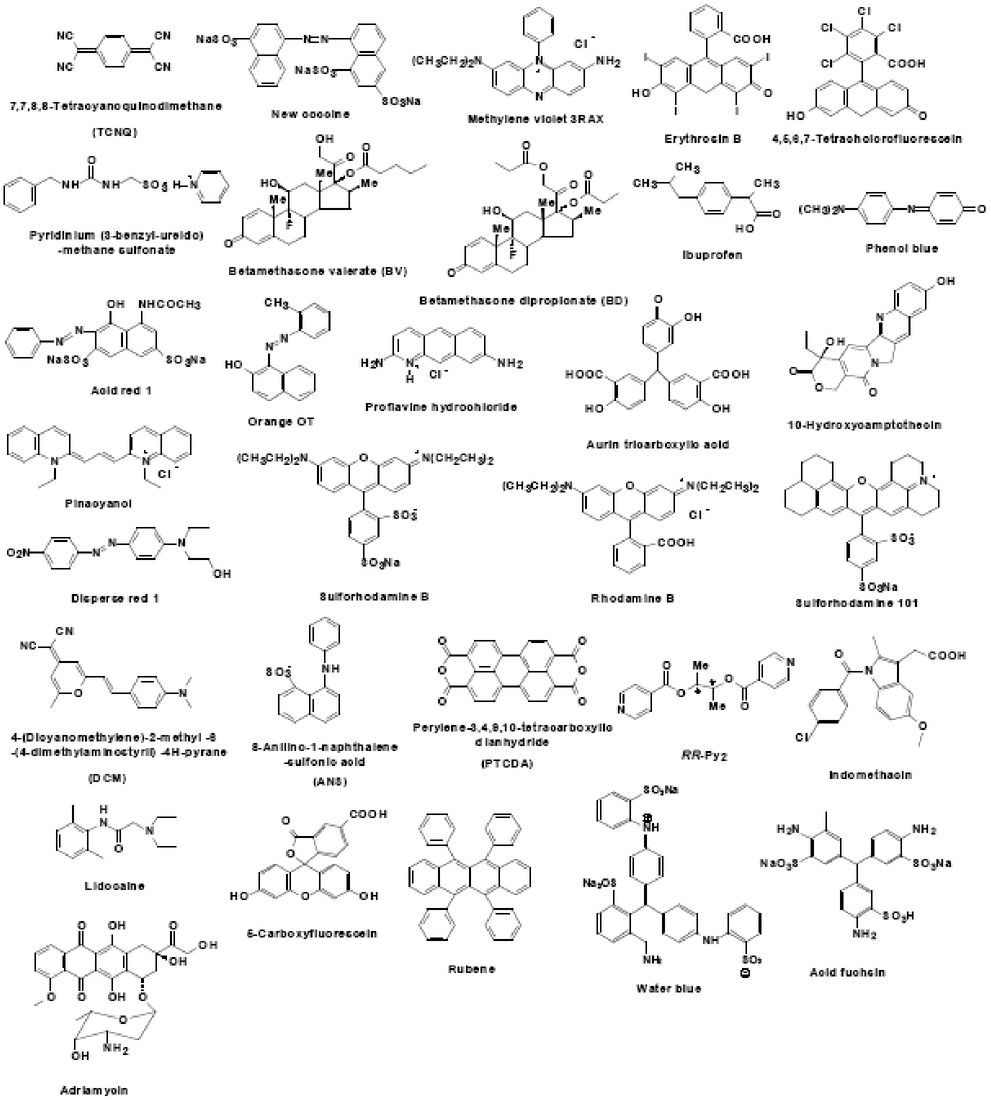
4. DENDRIMER AND DYE

Dendrimers are a class of macromolecules characterized by a well-defined highly branched structure, a compact shape, a large number of end groups, and room for guests. The guests used for dendrimer encapsulation are summarized in Scheme **6**. Although the investigation on encapsulation property of dendrimer-dye host-guest complexes is not as extensive and systematic as the cases of HP-dye host-guest complexes, it was carried out earlier and has gained great success for their applications in aspects such as extraction, dendrimer structure detection, nanodevice for capture and transfer of photon energy, and facile laser media.

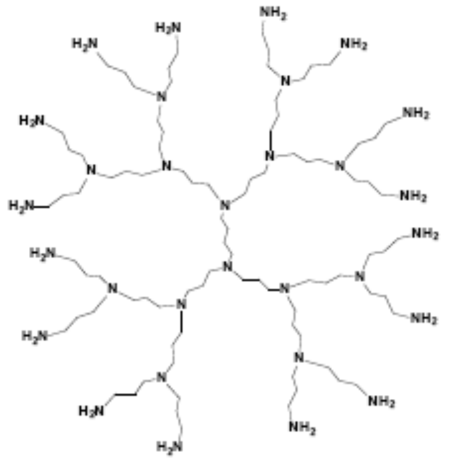
4.1. Encapsulation Properties of Dendrimer-Dye Host-Guest Complexes

In 1994, Meijer *et al.* reported the encapsulation of guest molecules into a dendritic box and then carried out a series of fundamental researches in this area [13, 123-126]. In the beginning, encapsulation was achieved by coupling the poly(propylene imine) (PPI) dendrimers (see Scheme **7**) with a chiral shell of protected amino acids in the presence of guests [13]. Then, complex can be prepared by dissolving dendrimer and dye in co-solvent and followed by precipitation [124]. Finally, successful application of encapsulation property to liquid-liquid extraction established this phase-transfer process as a convenient and general method for preparing dendritic polymer-dye host-guest complex [125]. The encapsulation was confirmed by encapsulating an electron paramagnetic resonance (EPR) probe guest in the dendritic box and studying the EPR spectra [13]. Investigation on radius of gyration (Rg) values obtained from small angle X-ray scattering (SAXS) analysis led to a conclusion that dye molecules preferred to accumulate in the dendritic moiety of the host molecules [126]. The line broadening in ^{13}C nuclear magnetic resonance (NMR) spectrum and the increase in spin-lattice relaxation implied that the dense shell of higher generation polymers acted as an almost solid-phase, made the complexes very stable and as a result, the encapsulated dyes could not get out readily without destruction of the shell [13]. Accordingly, shape-selective release of entrapped dyes could be achieved: the smaller dyes could be released by partially perforating the shell, while the larger dyes remain in the dendritic box [123]. The investigation on the solution property of a PPI dendrimer modified with hydrophobic C15 alkyl chains by DLS measurements suggested the presence of the dendritic box as UIM in nonpolar solvent [124].

By now, various kinds of dendrimers have been employed as dendritic hosts to prepare dendrimer-dye host-guest complexes (see Table **3**). The encapsulation properties of dendrimer-based complexes were also studied and similar results to that of HP-based complexes were found. So the influence factors on encapsulation



Scheme 6. Chemical structures of the guest molecules used for dendrimer encapsulation.



Scheme 7. Chemical structure of three-generation (G3) poly(propylene imine) dendrimer (PPI).

property of HP-based IM shown in Table **1** are compatible for dendrimer cases to some extent.

4.2. Applications of Dendrimer-Dye Host-Guest Complexes

The fundamental knowledge of encapsulation properties of dendrimers grounded their applications. Researches on applications based on guests-loaded dendrimers are much more extensive than those of HP-based complexes and have achieved great success, which are described as follows (see Table **4**).

4.2.1. Photon Energy Transfer System

Meijer *et al.* prepared PPI dendrimers modified with an oligo(*p*-phenylene vinylene)s (OPV) periphery that could extract dye from water [154]. On account of the overlap between the emission spectrum of the OPV and the absorption spectrum of the entrapped dyes, the energy transfer from the OPV periphery to the entrapped dyes could be detected, that is, the fluorescence of OPV was quenched and the emission of the entrapped dyes was found if excited at the excitation wavelength of OPV moiety. The energy transfer is quite efficient in solid state and the emission wavelength can be tuned by encapsulating various dyes. The supramolecular complex can be used to funcationalize the PPV thin films due to their good compatibility.

Table 4. Applications of Dendritic Polymer-Dye Host-Guest Complexes

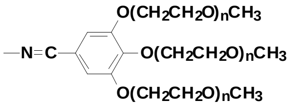
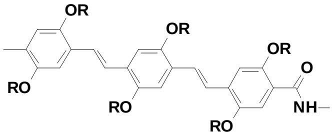
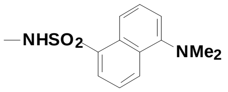
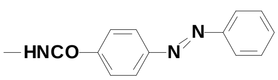
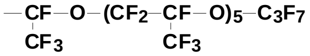
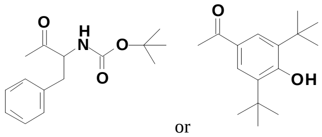
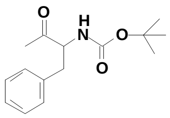
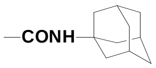
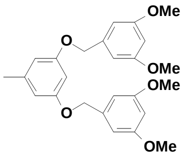
Core	Shell	Guest	Application	Ref.
HPAMAM	$-HNCO(CH_2)_{14}CH_3$	FS; PB; RB; CR	Functionalization of self-assembly films	[56].
	No shell	Reactive brilliant yellow A-4GLN; Reactive brilliant red A-EF	Enhancement of dyeing property of cotton fibre	[60,61]
HPG		Anticancer agent, Dox; Near-infrared imaging dye, ITCC	Delivery of therapeutic and diagnostic agents. (pH-sensitive)	[57]
HPEI	$-O(CH_2)_{11}CH_3$	MO; CR; MeB; RB	Dye separation promoted by electrostatic molecular recognition	[59]
	Inner shells are Cn chain; outer shells are PEG.	ITCC	*In vivo* tumor imaging	[39]
Hyperbranched polysiloxysilane	$CH_2CH_2SCH_2COOH$ or $CH_2CH_2SCH_2N(CH_3)_3I$	TPDTT-3; β-CSB-TP	*In vitro* two-photon bioimaging	[58]
PPI dendrimer		Sulforhodamine B; Rhodamine B; Rhodamine 6G; Sulfordamine 101	Photon Energy transfer system; Functionalization of poly(*p*-phenylene vinylene)s thin films by incorporating the complex	[154]
		FS; RB; EY	Photon Energy transfer system	[155,157-160]
		EY	Photon Energy transfer system	[156]
	 $-\underset{CF_3}{CF}-O-(CF_2-\underset{CF_3}{CF}-O)_5-C_3F_7$	MO	Extraction from water into supercritical CO_2	[189]
	$-NH_2$	PB	Dye probe for detecting the physical and chemical properties of the dendrimers	[169]
PPI dendrimer	 or	Rubene	Protection for encapsulated dye from photodegradation	[190]
	$-NH_2$	RB; Erythrosin B; 4,5,6,7-Tetrachloro -fluorescein; FS; Methylene violet 3RAX; Rhodamide B; New coccine	Functionalization of PPI monolayer by adsorption of dyes	[185]
		CR	Modulation of the luminescence properties of encapsulated CR by electronic confinement effect	[191]
		RB; FS	Functionalization of β-CD molecular printboards with dye-loaded complexes	[184]
PPI dendrimer (quaternized)	No shell; with C12 shell; with PEG100 shell	BB; Thymol blue; MO; FS; EY	Dye probe for studying the nature of cationic dendrimer	[175]
PPI dendrimer	C18 shell	Acid blue 344	Enhancement of dyeing property of poly(propylene) fibre	[187]
	C9 shell	Reactive blue 163	Enhancement of color strength of cotton fabric	[188]

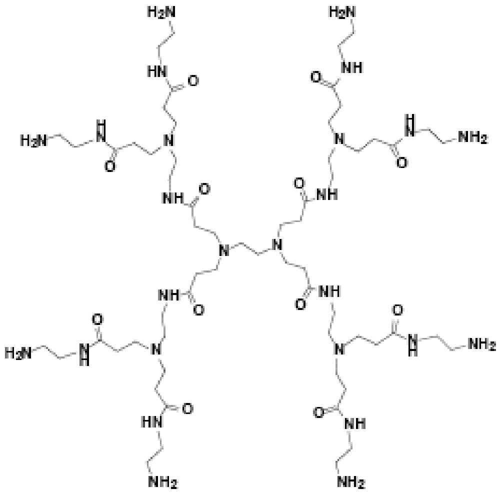
Table 4. contd….

Core	Shell	Guest	Application	Ref.
PAMAM dendrimer	Carboxylate anions	Pyrene; MB	Dye probe for studying the surface property of dendrimer	[171-173]
PAMAM dendrimer ($NH_2CH_2CH_2NH_2$ or NH_3 core)	-NH_2	MB	Dye probe for revealing the surface difference of the two dendrimers	[174]
PAMAM dendrimer (C12 core or C2 core)	-NH_2	NR	Dye probe for studying the structure of the two dendrimers	[194]
PAMAM dendrimer	-NH_2	Ibuprofen	Drug delivery and sustained release	[134]
	PEG550 or PEG2000	Adriamycin; Mtx	Drug delivery and sustained release	[195]
	-NH_2	Phenol blue	Dye probe for detecting the physical and chemical properties of the dendrimers	[170]
	-NH_2	DCM	High optical gain media for laser emission	[161]
	-NH_2	5-Carboxyfluorescein	Functionalization of ultrathin and multilayered polyelectrolyte/dendrimer films	[186]
	-NH_2	ANS	Fluorometric assay for detection and quantitation of polyamidoamine dendrimers	[176-178]
	-NH_2	Water blue; Acid fuchsin	Decolorisation of dye solution	[192,193]
Poly (glycerol succinic acid) dendrimer	-OH	DCM	High optical gain media for laser emission	[162-165]
Poly(aryl ether) dendrimer	PEG700	Indomethacin	Sustained release	[181]
Poly(biaryl ether) dendrimer		Pyrene; PTCDA	Sensing metalloproteins by generating fluorescence response patterns	[179]
Polycarbosilane dendrimer		FS; Rhodamine B	High optical gain media for laser emission	[166-168]
Poly(zinc porphyrins)		*RR*-Py$_2$	Cooperative chiroptical sensing	[180]
Star poly(lauroyl ester) (12 arms)	3×PEG5000	Lidocaine	Drug delivery and sustained release	[182,183]

Balzani and Vogtle *et al.* prepared PPI dendrimers functionalized with dansyl groups or photoisomerizable azobenzene groups and studied their transfer of photon energy to a series of entrapped dyes, which were also remarked by two minireviews [155,156]. By means of femtosecond transient absorption spectroscopy, Aumanen *et al.* studied excitation energy transfer process in dansylated PPI-eosin complexes [157]. The result indicated that non-covalent bonding of eosin dye in complex led to a faster relaxation process than eosin dye in its own solution. The structures and the properties of these dansylated PPI-dye complexes were also studied theoretically by Zerbetto *et al.* using molecular dynamics [158-160].

4.2.2. Facile Laser Media

Yokoyama *et al.* used PAMAM dendrimer (see Scheme **8**) to encapsulate the conventional laser-dye, 4-dicyanomethylene-2-methyl-6-4-dimethylaminostyril-4H-pyrane (DCM), and studied the laser emission from the methanolic solution containing the PAMAM/laser-dye complex [161]. The encapsulation greatly enhances the concentration of the dye in solution and limits the aggregation and intermolecular energy transfer. Consequently, the loss effect on the laser emission caused by scattering and self-quenching is inhibited, the optical-gain is greatly enhanced and the threshold intensity required for lasing is dramatically reduced. Similar results were obtained by employing hydroxyl group terminated polyester dendrimer as host [162]. Modification of the polyester dendrimer with terminal acrylate groups and followed by laser-dye complexation and UV polymerization, afforded solid-state material which still showed improvement on optical-gain [163-165]. Alternatively, Duan *et al.* used polycarbosiloxane dendrimer as host for laser-dye encapsulation and improved the optical-gain [166-168].



Scheme 8. Chemical structure of two-generation (G2) poly(amido amine) dendrimer.

4.2.3. Dye Probe for Detecting Host Properties

The physical and chemical properties of PPI dendrimer was studied by employing a solvatochromic probe phenol blue [169]. It was found that the vast majority of dye stayed in the interior near the core. The increase of dendrimer generation would lead to the decrease of a microenvironment polarity, and the polarity remained constant when the generation>3. A comparison study of PPI dendrimer to PAMAM dendrimer was carried out [170]. The PPI dendrimer has a slightly less polar microenvironment than the PAMAM dendrimer because of its chemical functionality. Moreover, the PPI dendrimer shows a more rapid transition to higher binding constants and a more rapid increase of anisotropy values.

Investigation on surface structure employing pyrene probe suggested that the structure of the PAMAM dendrimer with terminal carboxylate groups could be divided into two parts: earlier generations (0.5-3.5) and later generations (>4.5) [171]. The earlier generations have hydrophilic and curved surfaces, and the adsorption of the cationic surfactant molecules on the surface is noncooperative and random; the later generations possess more hydrophobic and dense surfaces, and the adsorption is initially noncooperative and random, subsequently cooperative. Investigation on the adsorption of cationic dye MB with the same dendrimer implied that MB aggregates stacked perpendicularly to the surface of the dendrimer [172, 173]. By using a number of probes, the surface properties of nitrogen core and ethylenediamine core of PAMAM dendrimers were proved to be similar [174].

The effects of cationized PPI dendrimers' solution on acid-base equilibria and reaction kinetics were studied using dye probes and compared with those of cationic surfactant solution [175]. The similarities are the effects on the protolytic equilibria and the spectra of the dyes. The differences are: (1) the rate of reaction with hydroxide ion is faster in cationic surfactant micelles, (2) bromophenol blue (BB) dye faded in the dendrimer solution, but did not in the cationic surfactant solution.

4.2.4. Sensing

Viologen units of polyviologen dendrimers could form one-to-one strong host-guest complexes with the red dye eosin and showed potential application on sensing [150, 151]. The fluorescence of dye could be completely quenched by the host-guest complexation, and recovered by addition of chloride ions and quenched again by precipitating chloride ions with silver cations.

Sharma *et al.* utilized the electrostatic interaction between the PAMAM dendrimers and the fluorescent acid dye, 8-anilino-1-naphthalene-sulfonic acid (ANS), to establish a qualitative and quantitative method for the analysis of PAMAM in solution [176]. The fluorescence intensity of the dye displayed a linear relationship with dendrimer concentration. The interaction was further studied by Klajnert *et al.* [177, 178].

Thayumanavan *et al.* prepared poly(aryl ether) dendrimers containing many carboxyl groups and C10 alkyl chains [148]. They employed these polymers to encapsulate pyrene and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) to generate fluorescent micelles and used them for sensing metalloproteins [179]. The sensing mechanism is that different proteins can induce different degree of fluorescence quenching.

Aida *et al.* reported a cooperative effect on chiroptical sensing of asymmetric guests [180]. Each zinc porphyrin unit in the 12-unit dendrimer showed enhanced contribution on chiroptical response towards *RR*-Py_2, compared with that in the 2-, 4- and 24-unit dendrimers.

4.2.5. Drug Delivery and Sustained Release

Unmodified PAMAM dendrimer could electrostatically interact with a carboxyl acid drug, ibuprofen, resulting in the formation of complex [134]. The maximum C_{load} approached 78 molecules per macromolecule. The drug-loaded PAMAM could get into the cells much more rapidly than the uncomplexed drug, and the complex could slow down the *in vitro* release of the drug, indicating that PAMAM could be a promising drug carrier. Dendritic poly(glycerol succinic acid)s with terminal hydroxyl or carboxyl groups were tried to encapsulate an anticancer drug, 10-hydroxycamptothecin [144]. The tests for cytotoxicity showed that the drug remained active. Amphiphilic polymers with dendritic poly(aryl ether) core and PEG shells prepared by Frechet *et al.* showed sustained *in vitro* release property of a drug, indomethacin [181]. Polymer with hydrophobic alkyl chains as core and hydrophilic PEG shells slowed down the release of a hydrophobic drug, lidocaine [182, 183].

4.2.6. Functionalization of Films

Encapsulation of dyes into dendritic polymer films could be regarded as a "dyeing process", which could be used for fabrication of functional films. Ravoo *et al.* applied the encapsulation property of dendritic box to the coloration of a molecular printboard [184]. They used dye-filled dendritic boxes with adamantyl terminals to colorize β-cyclodextrin monolayer via supramolecular microcontact printing. When cross-printing was employed, alternating patterns of two dyes could be obtained. Jiang *et al.* immobilized the PPI dendrimer monolayer onto a self-assembled monolayer (SAM) surface and investigated the adsorption of dye on the monolayer [185]. Caruso *et al.* prepared multilayered films consisting of negatively charged poly(styrenesulfonate) and positively charged PAMAM on planar supports and colloid particles, respectively, and functionalized the films with an acidic dye, 5-carboxyfluorescein [186].

4.2.7. Other Applications

Host-guest encapsulation can also be used for solving the difficulty in dyeing poly(propylene) fibres on account of the hydrophobic nature. Froehling *et al.* prepared fibers by blending hydrophobic alkyl-modified PPI dendrimer with poly(propylene), and then dyed the fibers by contacting with the dye solution [187]. Burkinshaw *et al.* treated cotton fabric with the similar PPI dendritic box and found that both the color strength and the yield were enhanced [188].

PPI dendrimers with fluorinated shell were successfully used to transport a CO_2-insoluble dye MR from water into CO_2 [189]. PPI dendritic box with a tert-butyloxycarbonyl (tBOC)-L-Phenyl shell could protect the entrapped dyes, rubrene, from photodegradation by singlet oxygen [190]. The bleaching of entrapped rubrene was 50 times less effective than that of rubrene alone. Adjustment of solvent polarity could tune the fluorescence emission of encapsulated CR by affecting the conformation and the aggregation of the dendrimer host which directly act on the dye through electronic confinement effect [191]. PAMAM dendrimer was also tried in decolorisation of aqueous solution containing Water blue or Acid fuchsin [192, 193].

5. DENDRIMER AND METAL-CONTAINING GUESTS

Since many relevant reviews have been published from 2001 to 2008 [196-208], we omitted this topic herein.

6. CONCLUSION AND PERSPECTIVES

As outlined in this paper, the encapsulations for the hosts of HPs and dendrimers with multiple guests have greatly further the progress of supramolecular chemistry. Once functionalized with shielding shell of opposite polarity, HPs and dendrimers can act as PM or IM to form stable complexes with various guests. The noncovalent integration of functions of both polymer and guests presented a facile and cost-effective avenue to multifunctional nanoobjects. The applications of the host-guest chemistry have achieved plentiful fruits in nanotechnology (e.g. templating nanoparticles, and fabrication of nanodevices), materials science (e.g. functionalization of polymer materials, and laser media), and biotechnology (e.g. bioimaging, and sustained release).

From our point of view, the following directions deserve special attention in the near future: (1) realization of desired multifunctions which were originally achieved covalently through noncovalent encapsulation, (2) development of hyperbranched polymer-based host-guest systems into industrial applications, and (3) improvement of the selectivity and specificity for dendritic polymer encapsulations and extension of their applications in nanotechnology and biomedicine.

ACKNOWLEDGEMENTS

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NOMENCLATURE

(H)PAMAM = (hyperbranched) poly(amido amine)
(H)PE = (hyperbranched) polyester
(H)PEI = (hyperbranched) poly(ethyleneimine)
(H)PG = (hyperbranched) polyglycerol
(H)PSA = (hyperbranched) poly(sulfone-amine)
AFM = atomic force microscopy
ANS = 8-anilino-1-naphthalene-sulfonic acid
BB = bromophenol blue
BD = betamethasone dipropionate
BV = betamethasone valerate
CAC = critical aggregate concentration
C_{load} = loading (or transport) capacity
CR = Congo red
DB = degree of branching
DCM = 4-dicyanomethylene-2-methyl-6-4 - dimethylaminostyril-4H-pyrane
DF = degree of functionalization
DLS = dynamic light scattering
Dox = doxorubicin
EPR = electron paramagnetic resonance
EY = eosin Y
FS = fluorescein sodium
HP = hyperbranched polymer
IM = inverse micelle
ITCC = tetrasulfonated indotricarbocyanine
LB = Langmuir-Blodgett
LCST = lower critical solution temperature
MB = methyl blue
MeB = methylene blue
M_n = number-average molecular weight
MO = methyl orange
MR = methyl red
Mtx = methotrexate
NMR = nuclear magnetic resonance
NR = Nile red
OPV = oligo(*p*-phenylene vinylene)s
PB = phloxine B
PBLG = poly(g-benzyl-l-glutamate)
PCL = poly(ε-caprolactone)
PEG = polyethylene glycol
PHEMA = poly(2-hydroxyethyl methacrylate)
PM = micelle
PNIPAM = poly(N-isopropylacrylamide)
PPI = poly(propylene imine)
PPO = poly(propylene oxide)
PPV = poly(phenylene vinylene)
PTCDA = perylene-3,4,9,10-tetracarboxylic dianhydride
QD = quantum dot
RB = Rose Bengal
Rg = radius of gyration
SAM = self-assembled monolayer
SANS = small-angle neutron scattering
SAXS = small angle X-ray scattering
tBOC = tert-butyloxycarbonyl
TCNQ = 7,7,8,8-tetracyanoquinodimethane
TEM = transmission electron microscopy

UIM = unimolecular inverse micelle
UV/Vis = ultraviolet/visible spectroscopy

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