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Aqueous highly emissive host-guest systems by host enhanced intramolecular charge transfer



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Keywords: Supramolecular assembly Cucurbit[n]uril Fluorescent dye Host-guest chemistry	Highly emissive host-guest systems have been an emerging topic which combines dynamic supramolecular system with fluorescent dyes. In this work, we report the host-guest interactions between (<i>E</i>)-1-benzyl-4-(2- (pyren-1-yl)vinyl)pyridin-1-ium bromide (PVP) and cucurbit[n]uril (CB[n], $n = 7$, 8), which were investigated in aqueous solution by ¹ H NMR, UV/Vis, fluorescence spectroscopic techniques and isothermal titration calorimetry (ITC). The results indicate the simultaneous formation of 1:1 inclusion complexes between CB [7] and PVP with the binding constant as $4.97 \times 10^6 \text{ M}^{-1}$. Meanwhile a 2:2 homoternary inclusion complex CB [8]- PVP with a binding constant of $2.49 \times 10^5 \text{ M}^{-1}$ was detected. The two macrocycles are found to effectively increases the fluorescence efficiency <i>via</i> the bost-enhanced intramolecular charge transfer (ICT) effect. This system provides a		

distinct strategy to construct high-quantum-yield fluorescent systems.

1. Introduction

The supramolecular host-guest complexes with macrocycles and fluorescent dyes plays a vital role in supramolecular materials. The classical water-soluble macrocyclic hosts included cyclodextrins [1], calix[n]arenes [2], Pillar[n]arenes [3], Cucurbit[n]urils [4] and other macrocycles [5]. Due to the advantages of the binding interactions of high affinity [6], high selectivity of binding [7] and low toxicity in vivo or vitro, cucurbit[n]urils as the common supramolecular macrocyclic molecules facilitate biologically relevant applications [8] and also contribute to nanotechnology [9] and dynamic self-assembly system [10]. Water-soluble fluorescent dyes as molecular containers (nanocavities) have been found particularly useful to monitor the formation of discrete host-guest complexes with macrocyclic structures [11]. Pyrene is a typical water-soluble aromatic fluorescent dye and intramolecular charge-transfer (ICT) fluorophore with an electron acceptor (A) and an electron donor (D) exhibit a broad and structure-less fluorescent emission [12]. To improve the emissive properties and ease charge transfer between the donor and acceptor parts in the excited state, several π - π conjugated systems including benzene, thiophene and furan rings generally have been incorporated into pyrene dyes as π -linkers [13]. The great efforts have been devoted to the structural modification of pyrene

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to avoid aggregation and to suppress the quenching effect of the $\pi\text{-}\pi$ interactions.

Herein, we explore the host-guest interactions between the CB[n] (n = 7, 8) and the chromophoric monomer (*E*)-1-benzyl-4-(2-(pyren-1yl)vinyl)pyridin-1-ium bromide (PVP). Because of the tendency to form the fluorescent π - π stacking, the fluorescence emission of this kind of fluorophores has remained low in aqueous solution. Therefore, the aggregation behavior of ICT compounds can be controlled by the movement of macrocyclic components [14]. To efficiently suppress aggregation, we establish a supramolecular approach to prevent PVP dyes from aggregating by forming a strong host-guest inclusion complex with the macrocyclic host; cucurbit[n]urils (n = 7, 8). CB [7] can form 1:1 complexes with a range of PVP which efficiently suppress aggregation of PVP. In this case, the PVP dye encapsulation resulted in profound changes in the emission wavelength and quantum yield, as well as increased photostability. Compared with CB [7], CB [8] has the increased volume of its cavity, the uniqueness of CB [8] as molecular receptor is expanded by the very nature of its hollow structure [15]. Based on the research of Scherman and Biedermann [16], CB [8] is a unique hydrophobic molecular receptor, its polar cavity can stabilize charge-transfer interactions between two guests of complementary nature, such as aromatic electron acceptors and donors [17]. In this case,

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Fig. 1. Partial ¹H NMR spectra (400 MHz, 293K) of **PVP** (0.05 mM) with addition of molar equivalents of CB [7]: a) 0; b) 0.3; c) 0.5; d) 0.7; e) 0.8; f) 1.0 in DMSO-*d*₆/DCl (50:1, v/v) at 25 °C.

while **PVP** dyes encapsulated by CB [8], the charge-transfer interaction is enhanced between pyrene and bipyridinium moieties of **PVP**. Designing **PVP** dyes with structural and functional diversity and tailorability is a promising means of fabricating well-formed supramolecular architectures with functions as well as understanding their self-assembly processes [18].

2. Experimental section

2.1. Materials and reagents

Parts of chemicals were used as received from Adamas-beta, Acros, Aldrich, or Merck. CB [7] and CB [8] were synthesized and separated according to the reported literature [19]. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. D₂O or DCl/D₂O was used as solvent in ¹H NMR and ¹³C NMR experiments.

2.2. Instrumentation

All absorption and fluorescence measurements were performed in quartz cuvettes ($1 \text{ cm} \times 1 \text{ cm} \times 4.5 \text{ cm}$). The UV/Vis absorption spectra were recorded on an Agilent Technologies Cary 60 UV–Vis spectro-photometer. The fluorescence spectra were obtained on a Varian Cray Eclipse fluorescence spectrophotometer. The excitation and emission bandwidths were both set at 10 nm. ¹H NMR and ¹³C NMR spectra were carried out on a Bruker AM400 and AM600 spectrometer. The MS spectra were recorded on a 4800 Plus M-TOF/TOF analyzer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The binding constant were tested by NANO ITC instrument. All measurements were performed at room temperature.

2.3. Synthesis of the guest

The intermediate compound **1** was prepared by the routes in Scheme 2, the detailed characterization data are deposited in supporting information (Scheme S1, Fig. S1).

Compound PVP: Piperidine (36.65 mg, 0.43 mmol) was added dropwise into a methanol (10 mL) solution of pyrene-1-carbaldehyde (100 mg, 0.43 mmol) and Compound 1 (136.52 mg, 0.51 mmol), the reaction solution was stirred for 48 h at 60 $^\circ C$ and the reaction mixture was allowed to cool to room temperature. Then, methanol $(3 \times 20 \text{ mL})$ was added to the mixture. The resulting precipitate was separate by filtration and the filtrate was concentrated and washed successively with methanol $(3 \times 20 \text{ mL})$ to give crude **PVP** as an orange solid (154 mg, 75%). ¹H NMR (400 MHz, DMSO- d_6 , 298K) δ 9.14 (d, J = 6.6 Hz, 2H), 9.09 (d, J = 16.0 Hz, 1H), 8.93 (d, J = 9.4 Hz, 1H), 8.63 (d, J = 8.3 Hz, 1H), 8.53 (d, J = 6.6 Hz, 2H), 8.38 (td, J = 7.7, 3.2 Hz, 4H), 8.22-8.29 (m, 2H), 8.12 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 16.0 Hz, 1H), 7.57 (d, J = 6.9 Hz, 2H), 7.51–7.43 (m, 3H), 5.80 (s, 2H). ¹³C NMR (600 MHz, DMSO-d₆, 298K) & 153.72, 144.70, 137.77, 135.19, 132.84, 131.35, 130.75, 130.11, 130.01, 129.74, 129.43, 129.29, 129.08, 127.87, 127.22, 126.78, 126.52, 126.09, 125.94, 125.10, 124.75, 124.63, 124.21, 123.59, 62.74. HRMS (ESI) (m/z): $[M - Br]^+$ calcd for $C_{30}H_{22}N$, 396.1747; found, 396.1733. (For details, see Support Information, Figs. S2-S5).

3. Results and discussion

3.1. The formation of inclusion complexs

To get an insight into the structure of host-guest complexes, ¹H NMR titration experiment of **PVP** dyes were performed by adding of varied amounts of CB [7] and CB [8] and the ¹H NMR assignments were ascertained by 2D NMR technique ROESY(Figs. S8–S9).



Fig. 2. Partial ¹H NMR spectra (400 MHz, 293K) of **PVP** (0.05 mM) with addition of molar equivalents of CB [8]: a) 0; b) 0.6; c) 1.0; d) 1.4; e) 1.5; f) 1.9 in DMSO-*d*₆/DCl (50:1, v/v) at 25 °C.



Fig. 3. UV/Vis absorption (a, b) spectra and PL (c, d) spectra of PVP (0.2 mM) in H₂O upon addition of CB [7] (a, c) and CB [8] (b, d) in H₂O. The insets show the corresponding absorbance and PL intensities with increasing CB [7] and CB [8] concentration.

Compared with the ¹H NMR spectrum of the free **PVP** (Fig. 1a), most protons of **PVP** with the increasing addition of CB [7] were found distinctly upshifted. Upon addition of 1.0 equiv of CB [7], the signals for proton H_e and H_f on pyridine group underwent upfield shift ($\Delta \delta = -0.09$ ppm and $\Delta \delta = -0.13$ ppm, respectively). The proton signals for H_a, H_b and H_c of benzene units moved upfield slightly. In general, the hydrophobic cucurbit[n]uril cavity inner protons of guest undergo shielding effect, and those near the carbonyl rim are hardly affected [20]. That suggests that these protons were encapsulated into CB [7] cavity and the methylene-linked benzene rings can rotate into CB [7] cavity spatially.

As a comparison, while adding 1.0 equiv of CB [8] (Fig. 2c), the pyridine proton H_e and the methylene proton H_d experienced a downfield-shift ($\Delta \delta = + 0.01$ ppm; $\Delta \delta = + 0.03$ ppm). Continue to add CB [8], the pyridine proton and other protons almost show a trend of upfield shift. It obviously means that the dynamic process of **PVP** dyes



Scheme 1. Schematic representation of the complex formation of CB [7]-PVP and CB [8]-PVP.



Scheme 2. Synthetic routes of PVP.

encapsulation into CB [8] cavity can be clearly observed by the change of ¹H NMR and the aromatic protons encapsulated by CB [8] were placed near the inter-pyridinium moiety owing to the stacked intermolecular interactions in CB [8] cavities.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) results, gave a response of 1:1 complex formation for CB [7]-**PVP** and CB [8]-**PVP** (Figs. S6–S7). The coexistence of pyrene and bipyridinium moieties in the cavity of CB [8] was further indicated by the red-shifted absorption peak observed in UV/Vis spectra, indicating the formation of charge-transfer interaction in CB [8]-**PVP** complex [21].

3.2. Spectral properties

The photophysical properties of **PVP** were investigated by UV/Vis absorption and photoluminescence (PL) intensity in water. UV/Vis absorption titration experiments were carried out to better understand the interaction between Cucurbit[n]uril (n = 7, 8) and guests. The results demonstrated the existence of binding modes between the host and guest, which was consistent with ¹H NMR data. Fig. 3 shows changes in the optical properties upon complexation of **PVP** with CB [7] and CB [8].

The absorption intensity of CB [7]-**PVP** in H_2O undergoes a slight hypsochromic shift (from 606 to 568 nm) which provide the spectral signature for the deaggregation of the **PVP** chromophore upon addition

of CB [7]. and the maximum absorption peak in 438 nm was reduced from 0.38 to 0.34 when the chromophore was encapsulated into the cavity of the CB [7] (Fig. 3a).

The fluorescence intensity of CB [7]-**PVP** was significantly increased and the color of the solution changed from orange to bright yellow (Scheme 1). When 1.0 equiv of CB [7] was added to the system, the fluorescence intensity of **PVP** in 600 nm increased by about 800%. Moreover, the fluorescence emission spectra of it were blue shifted from 607 nm to 569 nm (Fig. 3c). In most cases, the fluorescence emission has remained low, likely on account of π - π stacking. However, some derivatives can become highly fluorescent under the deaggregating conditions of high dilution [22]. Apparently, the pyrene units tend to form π - π stacking in the polar solution and the CB [8] efficiently suppress aggregation of **PVP** dyes in water.

In this context, our host-guest combination strategy offers a much more straightforward approach to protect the **PVP** dye from selfaggregation than synthetic modifications of the molecule. Different from the CB [7]-**PVP** system, the absorption maximum of CB [8]-**PVP** showed shorter red-shifts from 437 nm to 464 nm and the maximum absorption peak in 437 nm is reduced from 0.38 to 0.31 (Fig. 3b). The ICT fluorophore in solution exhibits significant emission wavelength changes by altering the excited state [23] and the ICT fluorophores suffer from a very low fluorescence efficiency [24] due to the characteristic of forbidden electronic transition. In our case, considering the pyrene moiety in **PVP** as strong electron-rich group, the broad

Table 1

Excitation maxima (λ_{ex}), emission maxima (λ_{em}), stokes shift ($\Delta\lambda$) and fluorescence quantum yield (Φ_f) values for PVP, CB [7]-PVP system and CB [8]-PVP system (0.2 mM PVP with addition of 1 equivalents of CB [7] and CB [8] determined in H₂O, 25 °C).

System	λex/nm	λem/nm	$\Delta\lambda/nm$	Φf (%)
PVP	437	600	163	9.22
CB [7]- PVP	430	570	140	35.68
CB [8]- PVP	464	600	136	16.78



Fig. 4. Job's plot for the complexation of CB [7]-PVP (the total concentration of CB [7] and PVP is 0.04 mM).

absorption band centered at 463 nm could be contributed to the charge-transfer interaction with the electron-deficient pyridinium unit in water. The phenomenon is probably the result of the enhancement of intramolecular charge-transfer caused by the deshielding effect to the

pyridinium unit when the two binding sites are encapsulated by CB [8]. Remarkably, the bathochromic shift also explained that the stacking occurred after **PVP** dyes enter CB [8] cavity.

Interestingly, after mixing with CB [8] or CB [7], the absorbance of **PVP** both decreased due to the formation of inclusion complex. The different self-assembly forms result in an opposite spectral shifts. During the gradual increase of CB [8], the fluorescence intensity first decreases slightly (Fig. 3d). However, compared with CB [7]-**PVP**, the color brightness of the CB [8]-**PVP** system enhanced but there was no obvious color change. The structure of CB [8]-**PVP** system has not been further calculated. Therefore, we assume a stacking form of CB [8]-**PVP** to roughly represent the difference from the CB [7]-**PVP** complex (Scheme 1).

Combining the UV/Vis absorption and fluorescence emission spectrum of **PVP** (0.2 mM in water with 1.0 equiv CB [7] or CB [8]), the fluorescence quantum yields of CB [7]-**PVP** and CB [8]-**PVP** complexes were calculated as 35.68% and 16.78%, respectively (Table 1).

Stoichiometric binding ratio of CB [7]-**PVP** were verified to be 1:1 by Job's plot (Fig. 4) and ITC studies (Fig. S10). Applying a modified Benesi-Hildebrand equation (Table S1) fit the experimental data presented at 430 nm, the binding constants K_a value was estimated as $4.97 \times 10^6 \text{ M}^{-1}$. Otherwise, CB [8] has a larger cavity than CB [7], it can synchronously bind two planar aromatic molecules [25]. Due to the poor solubility of CB [8], the Job's plot titration was not successful. The CB [8]-**PVP** complex appears to be the 1:1 as measured by ITC and the binding constants K_a value was estimated as $2.49 \times 10^5 \text{ M}^{-1}$ (Fig. S11).

To further confirm the co-conformations of CB [7]-**PVP** and CB [8]-**PVP** and approve our host-guest encapsulation strategy offered a much more straightforward approach to protect the **PVP** dyes from self-aggregation than arduous synthetic modifications of the dyes, the stronger binding ammonium hydrochloride (AD) was used [26]. Whether it is CB [7]-**PVP** or CB [8]-**PVP** systems, when 1.0 equiv of AD is gradually added, the UV/Vis showed the opposite trend. With addition



Fig. 5. UV/Vis absorption (a, b) spectra and PL (c, d) spectra for CB [7]-**PVP** and CB [8]-**PVP** (2×10^{-4} M) upon addition of ammonium hydrochloride (AD) (0–1.0 equiv) in water.



Fig. 6. a) The digital photographs of using free **PVP** dyes as the printing material; b) The digital photographs of using CB [7]-**PVP** as the printing material; c) The Digital printing picture of CB [7]-**PVP** placed for one week. (The power of UV lamp is 8 W, and the wavelength is 420 nm).

of AD to CB [7]-**PVP** and CB [8]-**PVP** in water, the decrease in the CB [7]-**PVP** solution absorption was observed as well as a red shift on 439 nm and the CB [8]-**PVP** solution undergoes a slight blue shift from 465 nm to 447 nm. The CB [8]-**PVP** solution also shows the contrary phenomena compared with the black CB [8]-**PVP** system(Fig. 5). This phenomenon suggests that adding AD can make self-assembling system return to the state without cucurbit[n]uril (CB[n], n = 7, 8).

3.3. Application of cucurbit [7] uril enhanced fluorescence encryption printing technology

Interestingly, encrypting printing technology with chemical language simplifies the encryption process and provides a new way of simple encryption [27]. It is possible to generate a library of potentially different fluorescent color combinations. Compared to ordinary fluorescent dyes, the encrypted information printed using the **PVP** inks can be verified.

When the **PVP** dye was added to the print cartridge, the printed "Peace Dove" and "Chinese Totem" were not displayed under day light. Under the illumination of 365 nm UV light, there was also only a shallow fluorescent pattern (Fig. 6). However, when adding CB [7] to the original **PVP** dyes, it could be clearly seen that the pattern fluorescence has a strong enhancement effect (Fig. 6). In order to ensure good stability of the luminescent mode of CB [7]-**PVP** fluorescent inks. We took the photographs of "Chinese Totem of Fu" patterns as an example exposed for different time to study the photostability. As shown in Fig. 6, the photographs printed by using CB [7]-**PVP** ink showed almost no changing after one week later. That indicated that the adding CB [7] luminescent inks can enhance the photostability. However, the actual use of CB [8]-**PVP** ink did not significantly enhance the fluorescent printing effect, it is probably due to the precipitation of part CB [8] in the process of adding CB [8]-**PVP** ink.

4. Conclusions

The fluorescent dye molecule **PVP** has good red fluorescence properties and the macrocyclic hosts, cucurbit[n]uril (CB[n], n = 7, 8), can encapsulate **PVP** inside its cavity, leading to a dramatic increase in the fluorescence quantum yield of the dye while ensuring high photochemical and chemical stability of the **PVP** dye. CB [7] and CB [8] bind to **PVP** to form host-guest inclusion complexes with different 1:1

binding modes. CB [7]-**PVP** system is demonstrated a facile supramolecular approach to eliminate the self-aggregation of fluorophores in aqueous and while the CB [8]-**PVP** can be the example as enhancement of intramolecular charge-transfer fluorophore complex system.

Furthermore, the **PVP** dye molecules encapsulated in the cucurbit[n] uril(n = 7, 8) have good optical stability as fluorescent printing materials. This approach provides an attainable method to prepare luminescent materials, which could be a simple encryption printing technology widely applied in identification, information storage, markers, writing, and printing.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107919.

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