# Aggregating Properties of Compounds Cz-C-n in DMSO-H<sub>2</sub>O Binary Solvent

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**Abstract:** The aggregating properties of Cz-C-n (n = 3, 6, 10) have been investigated by means of fluorescence method in DMSO-H<sub>2</sub>O binary solvent. The measured CAC and C  $\Phi$  values indicate that the aggregating tendency of the amphiphilic compounds Cz-C-n containing crown ether increases with the length of alkyl chains, similar to that of carbazole compounds with long alkyl chains.

Keywords: Aggregate, fluorescence method, amphiphilic compounds Cz-C-n, crown ether.

## Introduction

It is well known that hydrophobic-lipophilic interaction, together with other forces, creats aggregates, micelles, vesicles and living cells from organic molecules in aggregating media<sup>1</sup>. In general aggregation is driven by hydrophobic-lipophilic interaction and is an important phenomenon in the life process<sup>2</sup>. Many reports focused on the aggregation of hydrophobic molecules containing chromophores and long alkyl chains<sup>3-5</sup>. However, relatively few works on the aggregating behaviours of amphiphilic molecules were reported. Here we extend our study to the aggregation behaviour of bis(carbazolyl) substituted diaza-18-crown-6 ethers in DMSO-H<sub>2</sub>O binary solvents. The structure of Cz-C-n is shown in **Scheme 1**.

#### Experimental

The synthetic details of the target compounds Cz-C-n (n = 3, 6, 10) have previously been reported<sup>6</sup>. DMSO is spectroscopy trade. Water is deionized and distilled three times. Absorption spectra were recorded on a PE Lambda 20 UV/VIS spectrometer. Fluorescence spectra were measured on a PE LS 50B luminescence spectrometer.  $\Phi$  stands for the volume fraction of water in the mixed solvent. The critical aggregation concentration (CAC) is the concentration of the aggregator at the onset of aggregation under a certain  $\Phi$ .

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Jiu Yan LI et al.



## **Results and Discussion**

**Figure 1** shows the fluorescence spectra of Cz-C-6 in DMSO-H<sub>2</sub>O at  $\Phi = 0.6$ . It is noted that the fluorescence spectra changed dramatically with increasing Cz-C-6 concentration. At low concentration of Cz-C-6, only the monomer emission was observed. Increasing the concentration of Cz-C-6 led to a decrease in the monomer emission at  $\lambda = 355$  and 371 nm with a development of low energy excimer emission at  $\lambda = 410$  nm<sup>5</sup>. The excitation spectra for the Cz-C-6 excimer and monomer emission were measured. The general features of the two speatra are similar, but the spectrum for the excimer red-shifted about 8 nm compared with that for the monomer, suggesting that the excimer originated from pair of carbazolyl groups which exist prior to excitation.

The ratio of  $I_e/I_m$  ( $I_e$  and  $I_m$  represent the fluorescence intensities of the carbazolyl excimer emission at  $\lambda = 410$  nm and monomer emission at  $\lambda = 355$  nm respectively) of Cz-C-n in DMSO-H<sub>2</sub>O at  $\Phi = 0.6$  was measured and shown in **Figure 2**. The plot of  $I_e/I_m$  vs [Cz-C-6] displays a break, which is a typical behaviour of aggregation. We attribute the increase in the excimer emission to intermolecular aggregation, which induces the enhancement of local chromophore concentration. The concentration corresponding to the break point is the critical aggregation concentration (CAC). At the concentration below CAC, Cz-C-6 exists only in its monomeric form.





## Aggregating Properties of Compounds Cz-C-n in DMSO-H<sub>2</sub>O 173 Binary Solvent

Above the CAC, the degree of aggregation increases with [Cz-C-6]. Thus  $L/I_m$  is dependent on the concentration of Cz-C-6. At high enough concentration, the excimer emission dominates the fluorescence spectra.

Compounds Cz-C-3 and Cz-C-10 reveal similar aggregating behaviors under the same condition, as shown in **Figure 2**. The CAC of these compounds are given in **Table 1**. It was noted that the Cz-C-n with longer chains have smaller CAC values and greater slops of the lines at concentrations above CAC. These observations indicate that Cz-C-n with longer chains are expected to undergo greater hydrophobic interaction and possess higher aggregation ability.

Table 1 The CAC values of Cz-C-n in DMSO-H<sub>2</sub>O with  $\Phi = 0.6$  at 25°C

	Cz-C-3	Cz-C-6	Cz-C-10
CAC (mol/L)	4.13×10 <sup>-5</sup>	3.20×10 <sup>-5</sup>	0.29×10 <sup>-5</sup>

To investigate the effect of solvent component on the aggregating properties of Cz-C-n, the fluorescence spectra of Cz-C-n (4×10<sup>-5</sup> mol/L) in DMSO-H<sub>2</sub>O under different  $\Phi$  were measured. **Figure 3** clearly shows the variation of fluorescence spectra of Cz-C-6 at different  $\Phi$ , which is typical of the other Cz-C-n in DMSO-H<sub>2</sub>O studied in this work. As  $\Phi$  was increased, the monomer emission at  $\lambda = 355$  and 371 nm was decreased and the excimer emission at  $\lambda = 410$  nm of Cz-C-6 was gradually enhanced. The cross point of  $\Phi$  obtained by the plot of Ie/Im *vs*  $\Phi$  is defined as C $\Phi$ . Generally, a lower value of C  $\Phi$  represents a stronger aggregating ability under the same condition<sup>7</sup>. From **Table 2**, we can infer the aggregating tendency for Cz-C-n is Cz-C-3 < Cz-C-6 < Cz-C-10. This observation is in agreement with that drawn from the above study of CAC.

Figure 3 Fluorescence spectra of Cz-C-6 ( $4 \times 10^{-5}$  mol/L) in DMSO-H<sub>2</sub>O under different  $\Phi$  at 25°C ( $\lambda_{ex} = 300$  nm)



**Table 2** The C $\Phi$  values of Cz-C-n (4×10<sup>-5</sup> mol/L) in DMSO-H<sub>2</sub>O at 25°C

	Cz-C-3	Cz-C-6	Cz-C-10
СΦ	0.6	0.42	0.14

## Jiu Yan LI et al.

In summary, we have demonstrated that the amphiphilic compounds Cz-C-n can aggregate in aquiorgano binary solvent by fluorescence method, and their aggregation behaviours are rather similar to that of carbazole compounds with long alkyl chains<sup>8</sup>.

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