Effects of Self-coiling of Organic Molecules on Intramolecular Exciplex Formation and Fluorescence Quenching in DX-H_2O Solvent System

CHEN, Ying-Qi*,[a](陈英奇) WANG, Xiao-Zhong[a](王晓钟) JIANG, Xi-Kui[b](蒋锡夔)
SHI, Ji-Liang[b](史济良) SHI, Min[b](施敏) LI, Zhan-Ting*,[b](黎占亭)
[a] *Department of Chemical Engineering, Zhejing University, Hangzhou, Zhejiang 310027, China*
[b] *Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Effects of self-coiling of organic molecules on intramolecular exciplex formation of compound I, in which the carbazole chromophore and terephthalic acid methylester acceptor group are linked by one $(CH_2)_{10}$ chain, and the decrease of the fluorescence intensities of compounds II, III, and IV, in which the carbazole chromophore and 3,5-dinitrobenzoate are connected by one aliphatic chain of $(CH_2)_{10}$ (II), $(CH_2)_{12}$ (III), or $(CH_2)_4$ (IV), have been studied in the dioxane(DX)-H_2O binary system. The results show that self-coiling of organic molecules in DX-H_2O facilitates intramolecular exciplex formation of I and induces the decrease of fluorescence intensities of II, because of the proximity effect brought about by self-coiling of organic molecules under hydrophobic-lipophilic interaction (HLI) between the excited carbazole chromophore and the acceptor. Since the similar effects are observed even when the concentrations of the probes are less than their CAgCs (critical aggregate concentrations) in the DX-H_2O mixture with the same ϕ values, formation of the intermolecular exciplex has been excluded. The effects are found to be strongly depended on ϕ values, indicating that they are mainly driven by HLI. The properties of the acceptors can also affect the intramolecular exciplex formation. With terephthalic acid methylester moiety as the acceptor, the carbazole chromophore exhibits the fluorescence spectra of the exciplex, while with 3,5-dinitrobenzoate moiety as the acceptor, only the fluorescence spectra of excited carbazolyl chromophore are observed.

Keywords hydrophobic-lipophilic interaction, self-coiling, intramolecular exciplex

Introduction

Hydrophobic-lipophilic interactions (HLI) play an important role in chemical and biochemical processes since water is the common medium in physiological processes.[1-4] Some recent efforts have been dedicated to studies of hydrophobic effects on photochemical and photophysical processes of organic molecules.[5-7] It has been reported that aggregation, coaggregation and self-coiling of organic molecules can affect the formation of excimers, enhance energy transfer between excited donors and acceptors[7,8] and promote electron transfer Processes.[9,10] Previously, Yamamoto[11] had reported the behavior of intramolecular exciplex emission of one D-$(CH_2)_n$-A molecule, in which one carbazole chromophore and one terephthalic acid methylester units are linked by aliphatic chains. Verhoeven[12] had also studied the intramolecular photophysics process of another D-$(CH_2)_n$-A system, in which one carbazole and one tetrachlorophthalimide are connected by an aliphatic chain. In the present work, we will report the effect of self-coiling of organic molecule on intramolecular exciplex formation and fluorescent quenching.

* E-mail: ztli@pub.sioc.ac.cn
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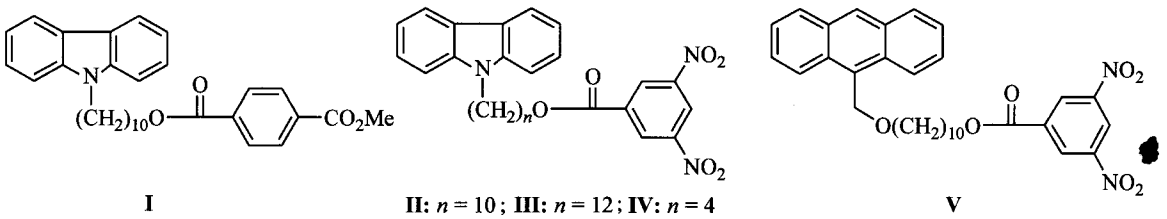
Experimental

Apparatus and materials

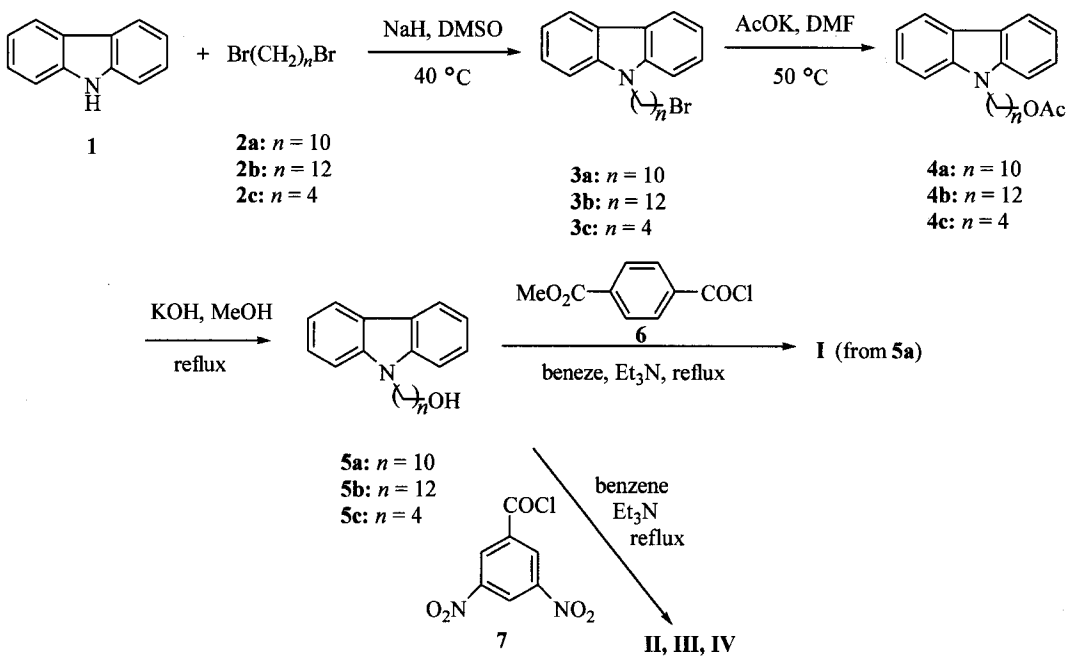
Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM 300 spectrometer with $(CH_3)_4Si$ as internal standard. Mass spectra were obtained in EI mode. Elemental analysis was carried out at the Shanghai Institute of Organic Chemistry analytical center using Element Analyzer MOD-1106. All fluorescence measurements were made using a Perking Elmer LS 50-B luminescence spectrometer. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Dioxane (DX) was purified by standard procedures. Water was deionized. The structures of the probes **I**—**V** used in this paper are shown in Scheme 1. The synthetis routes of these probes are shown in Schemes 2 and 3. All compounds have been identified by ^{1}H NMR, MS spectra and elemental analysis.

Scheme 1



I **II**: $n = 10$; **III**: $n = 12$; **IV**: $n = 4$ **V**

Scheme 2



1

2a: $n = 10$
2b: $n = 12$
2c: $n = 4$

3a: $n = 10$
3b: $n = 12$
3c: $n = 4$

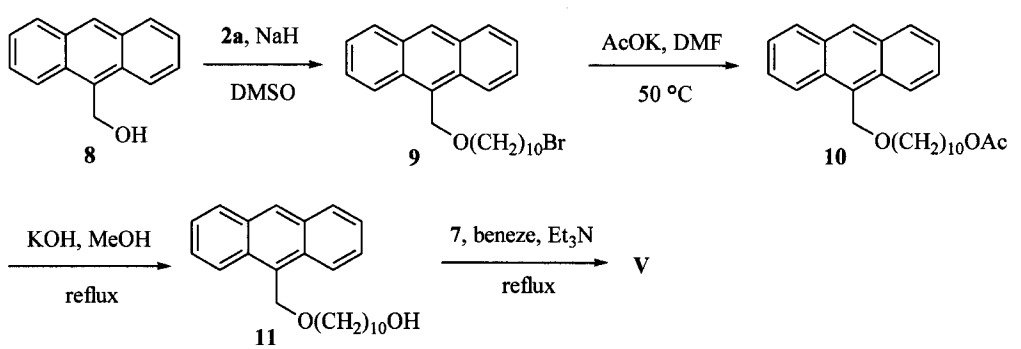
4a: $n = 10$
4b: $n = 12$
4c: $n = 4$

5a: $n = 10$
5b: $n = 12$
5c: $n = 4$

7

II, III, IV

Scheme 3



8 **9** **10** **11**

Preparation of N-(10-bromodecanyl) carbazole (**3a**)

Under a nitrogen atmosphere, NaH (0.72 g, 30.0 mmol) was added into a mixture of carbazole **1** (5.00 g, 30.0 mmol) and dried DMSO (30 mL) at room temperature. After the mixture was stirred for 2 h, the suspension was added dropwise to a solution of $Br(CH_2)_{10}$-Br (7.50 g, 25.0 mmol) in DMSO (10 mL). Stirring was continued at 40 ℃ for 1 h, the mixture was then poured into 100 g of ice. The aqueous phase was extracted with petroleum ether (200 mL × 3). The combined organic fraction was washed with water and brine, dried over $CaCl_2$, filtered, and concentrated under reduced pressure to give pale yellow oil. The material was subjected to flash chromatography (silica, petroleum ether) to afford **3a** as pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.17—1.31 (m, 12H), 1.72—1.77 (m, 4H), 3.30 (t, J = 7.71 Hz, 2H), 4.18 (t, J = 7.71 Hz, 2H), 7.18—7.2 (m, 2H), 7.30—7.40 (m, 4H), 8.06 (d, J = 8.02, 2H); MS (EI) *m/z* (%): 180 (100), 385 (68, M^+), 386 (68, M^+ + 1); Anal. calcd for $C_{22}H_{28}BrN$: C 67.59, H 7.27, N 3.62; found C 67.66, H 7.12, N 3.62.

Preparation of N-(10-carbomethyldecanyl) carbazole (**4a**)

Under a nitrogen atmosphere, a mixture of **3a** (2.77 g, 7.20 mmol), CH_3COOK (1.96 g, 20.0 mmol) and DMF (50 mL) was stirred at 90—100 ℃ for 2 h. The mixture was cooled to room temperature and poured into H_2O (100 mL) and then extracted with EtOAc (100 mL × 2). The combined organic fraction was washed with water and brine several times, and dried over Na_2SO_4. The solution was then concentrated under reduced pressure, and the resulting yellow oil was subjected to flash chromatography (silica, EtOAc/petroleum ether 1∶10) to give **4a** as light yellow oil in 99% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.25—1.37 (m, 12H), 1.60—1.63 (m, 2H), 1.86—1.88 (m, 2H), 2.03 (s, 3H), 4.03 (t, J = 7.2 Hz, 2H), 4.29 (t, J = 7.2 Hz, 2H), 7.20—7.25 (m, 2H), 7.38—7.46 (m, 4H), 8.10 (d, J = 7.7 Hz, 2H); MS (EI) *m/z* (%): 180 (100), 365 (M^+, 90); Anal. calcd for $C_{24}H_{31}NO_2$: C 79.04, H 8.49, N 4.05; found C 79.48, H 8.39, N 4.05.

Preparation of N-(10-hydroxydecanyl) carbazole (**5a**)

Compound **4a** (2.56 g, 7.00 mmol) and KOH (0.40 g, 7.00 mmol) were added into MeOH (50 mL). After stirring at 50 ℃ for 0.5 h, the solution was neutralized with CH_3COOH. The solvent was removed in vacuum and the reuslting white solid was then subjected to flash chromatography (silica, EtOAc/petroleum ether 1∶5). The title compound **5a** was obtained as white crystal in 100% yield. m.p. 70.5—70.8 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.25—1.37 (m, 13H), 1.53—1.56 (m, 2H), 1.86—1.88 (m, 2H), 3.60 (t, J = 6.6 Hz, 2H), 4.27 (t, J = 7.2 Hz, 2H), 7.20—7.25 (m, 2H), 7.40—7.47 (m, 4H), 8.10 (d, J = 7.7 Hz, 2H); MS (EI) *m/z* (%): 180 (100), 323 (M^+, 80), 324 (M^+ + 1, 20); Anal. calcd for $C_{22}H_{29}NO$: C 81.74, H 8.98, N 4.34; found C 82.02, H 8.54, N 4.60.

Preparation of 10-carbazolydecanyl-4-carbomethyloxybenzoate (**I**)

A solution of **5a** (1.30 g, 4.00 mol) in dried benzene (50 mL) was slowly added to a solution of 4-chlorocarbonylbenzoic acid, methyl ester **6** (1.00 g, 5.00 mmol) and Et_3N (2 mL) in C_6H_6 (10 mL). The suspension was refluxed for 40 min and then poured into H_2O (200 mL). The aqueous phase was extracted with C_6H_6 (200 mL × 2). The combined organic fraction was washed with water and brine, dried over Na_2SO_4. The solvent was removed *in vacuo* and the resulting pale yellow oil was subjected to flash chromatography (silica, EtOAc/petroleum ether 1∶4). Compound **I** was obtained as waxen solid, m.p. 57.5—58.3 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.28—1.42 (m, 12H), 1.73—1.78 (m, 2H), 1.85—1.90 (m, 2H), 3.95 (s, 3H), 4.28—4.35 (m, 4H), 7.21—7.27 (m, 2H), 7.40—7.49 (m, 4H), 8.10 (s, 4H), 8.10—8.12 (m, 2H); MS (EI) *m/z* (%): 180 (89), 485 (M^+, 100), 486 (M^+ + 1, 38); Anal. calcd for $C_{31}H_{35}NO_4$: C 76.7, H 7.21, N 2.88; found C 77.02, H 7.16, N 2.89.

Preparation of 10-carbazolydecanyl-3,5-dinitrobenzoate (**II**)

3,5-Dinitrobenzoic chloride (**7**) (0.37 g, 1.60

mmol) was dissolved in dried C_6H_6 (30 mL) and Et_3N (3 mL) was added, then a solution of **5a** (0.50 g, 1.50 mmol) in C_6H_6 (8 mL) was added dropwise. The mixture, after refluxing for 1 h, was poured into H_2O (200 mL), and the aqueous phase was extracted with C_6H_6 (200 mL × 2). The combined organic fraction was washed with water and brine, dried over Na_2SO_4. The solution was then concentrated. After column chromatography, the title compound was obtained as orange crystal in 83% yield. m.p. 120.5—121.9 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.12—1.36 (m, 12H), 1.77—1.91 (m, 4H), 4.35 (t, J = 7.2 Hz, 4H), 7.23 (t, J = 6.8 Hz, 2H), 7.37—7.47 (m, 4H), 8.07 (d, J = 6.8 Hz, 2H), 9.09—9.17 (m, 3H); MS (EI) *m/z* (%): 43 (100), 180 (75), 517 (M^+, 13); Anal. calcd for $C_{29}H_{31}N_3O_6$: C 67.31, H 5.99, N 8.12; found C 67.06, H 5.73, N 8.01.

Preparation of N-(12-hydroxydodecyl) carbazole (**5b**)

This compounds was prepared from carbazole and $Br(CH_2)_{12}Br$ as white crystal following the procedure for preparation of **5a**. m.p. 62.5—63.3 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24—1.34 (m, 16H), 1.53—1.57 (m, 2H), 1.84—1.89 (m, 2H), 3.63 (t, J = 6.6 Hz, 2H), 4.30 (t, J = 7.2 Hz, 2H), 7.20—7.26 (m, 2H), 7.40—7.49 (m, 4H), 8.10 (d, J = 7.7 Hz, 2H); MS (EI) *m/z* (%): 180 (100), 351 (M^+, 71).

Preparation of 12-carbazolydodecyl 3,5-dinitrobenzoate (**III**)

This compound was prepared from **5b** and **7** as orange crystal in a similar procedure as for compound **II**, m.p. 79—80.5 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz): 1.26—1.42 (m, 16H), 1.77—1.90 (m, 4H), 4.27 (t, J = 7.20, 2H), 4.43 (t, J = 6.8 Hz, 2H), 7.18—7.26 (m, 2H), 7.37—7.47 (m, 4H), 8.07 (d, J = 7.8 Hz, 2H), 9.09—9.10 (m, 2H), 9.15—9.17 (m, 1H); MS (EI) *m/z* (%): 180 (100), 545 (M^+, 57); Anal. calcd for $C_{31}H_{35}N_3O_6$: C 68.26, H 6.40, N 7.70; found C 68.32, H 6.08, N 7.57.

Preparation of N-(4-hydroxybutyl) carbazole (**5c**)

This compound was prepared from carbazole and $Br(CH_2)_4Br$ as white crystal following the procedure for **5a**, m.p. 73.5—74.8 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.59—1.68 (m, 2H), 1.93—2.05 (m, 2H), 3.64 (t, J = 6.4 Hz, 2H), 4.37 (t, J = 7.0 Hz, 2H), 7.21—7.27 (m, 2H), 7.41—7.50 (m, 4H); 8.12 (d, J = 7.7 Hz, 2H); MS (EI) *m/z* (%): 180 (79), 239 (100, M^+).

Preparation of 4-carbazolybutyl-3,5-dinitrobenzoate (**IV**)

This compound was prepared from **5c** and **7** as orange crystal following the procedure for compound **II**, m.p. 217—218.5 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.89—1.99 (m, 2H), 2.07 (m, 2H), 4.39—4.45 (m, 4H), 7.20—7.26 (m, 2H), 7.40—7.47 (m, 4H), 8.08 (d, J = 8.1 Hz, 2H), 9.04—9.05 (m, 2H), 9.21—9.25 (m, 2H); MS (EI) *m/z* (%): 180 (100), 433 (M^+, 72); Anal. calcd for $C_{23}H_{15}N_3O_6$: C 63.44, H 4.39, N 9.69; found C 63.13, H 4.45, N 9.54.

Preparation of 1-anthracenemethenoxy-10-bromodecane (**9**)

Under a nitrogen atmosphere, NaH (0.72 g, 30.0 mmol) was added to a mixture of antharacenemethol (**8**) (6.24 g, 30.0 mmol) and dried DMSO (50 mL) at room temperature. The mixture was stirred for 2 h and then was added dropwise to a solution of $Br(CH_2)_{10}Br$ (7.50 g, 25.0 mmol) in DMSO (10 mL). The mixture was stirred at 40 ℃ for 1 h and then poured into ice (100 g). The aqueous phase was extracted with petroleum ether (100 mL × 3). The combined organic fraction was washed with water and brine, and dried over Na_2SO_4. The solvent was then removed under reduced pressure and the resulting pale yellow oil was purified by flash chromatography (silica, petroleum ether) to give **9** as yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24—1.42 (m, 12H), 1.60—1.70 (m, 2H), 1.79—1.88 (m, 2H), 3.40 (t, J = 6.7 Hz, 2H), 3.67 (t, J = 6.6 Hz, 2H), 5.47 (s, 2H), 7.45—7.57 (m, 4 H), 8.02 (d, J = 8.1, 2H), 8.42 (d, J = 8.9 Hz, 2H), 8.47 (s, 1H); MS (EI) *m/z*

(%): 179 (92), 191 (100), 426 (M^+, 21); Anal. calcd for $C_{25}H_{31}BrO$: C 70.39, H, 7.29; found C 70.11, H 7.21.

Preparation of 1-*anthracenemethoxydecanyl acetate* (**10**)

Under a nitrogen atmosphere, a mixture of **9** (2.40 g, 5.70 mmol), CH_3COOK (1.96 g, 20.0 mmol) and DMF (50 mL) was stirred at 90—100 ℃ for 2 h. The mixture was poured into H_2O (100 mL) and then extracted with EtOAc (100 mL × 2). The combined organic fraction was washed with water and brine, dried over Na_2SO_4. After concentration, the resulting yellow residue was subjected to flash chromatography (silica, EtOAc/petroleum ether 1∶10). Compound **10** was obtained in 99% yield as oil. ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.22—1.32 (m, 12H), 1.56—1.65 (m, 4H), 2.03 (s, 3H), 3.66 (t, J = 7.6 Hz, 3H), 4.03 (t, J = 7.7 Hz, 3H), 5.48 (s, 2H), 7.43—7.56 (m, 4H), 8.00 (d, J = 8.1 Hz, 2H), 8.39 (d, J = 8.2 Hz, 2H), 8.44 (s, 1H); MS (EI) *m/z* (%): 179 (61), 191 (100), 192 (45), 406 (M^+, 78); Anal. calcd for $C_{27}H_{34}O_3$: C 80.06, H 8.37; found C 80.26, H 8.53.

Preparation of 1-*anthracenemethoxydecanol* (**11**)

10 (2.40 g, 5.90 mmol) and KOH (0.34 g, 6.00 mmol) were added to MeOH (50 mL). The mixture was stirred for 0.5 h at 50 ℃ and then neutralized with acetic acid. The solvent was removed *in vacuo* and the resulting solid residue was subjected to flash chromatography (silica, ether/petroleum ether/dichloromethane = 1∶5∶1) to give **11** as white crystal in 100% yield. m.p. 60.5—61.5 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.23—1.31 (m, 12H), 1.50—1.68 (m, 4H), 3.59—3.69 (m, 4H), 5.46 (s, 2H), 7.44—7.56 (m, 4H), 8.01 (d, J = 8.4 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H), 8.45 (s, 1H); MS (EI) *m/z* (%): 191 (100), 364 (M^+, 56); Anal. calcd for $C_{22}H_{32}O_2$: C 82.42, H 8.79; found C 82.63, H 8.70.

Preparation of 10-*anthracenemethoxydecanyl*-3, 5-*dinitrobenzoate* (**V**)

This compound was prepared from **11** and **7** as orange solid in the similar way as described for preparation of compound **II**. m. p. 79.5—80.1 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.26—1.42 (m, 12H), 1.62—1.66 (m, 2H), 1.78—1.81 (m, 2H), 3.66 (t, J = 6.6 Hz, 2H), 4.42 (t, J = 6.8 Hz, 2H), 5.44 (s, 2H), 7.4—7.54 (m, 4H), 7.99 (d, J = 8.4 Hz, 2H), 8.37 (d, J = 8.8 Hz, 3H), 8.43 (s, 1H), 9.09—9.15 (m, 3H); MS (EI) *m/z* (%): 191 (94), 558 (M^+, 100); Anal. calcd for $C_{29}H_{34}N_2O_7$: C 68.74, H 6.13, N 5.01; found C 68.45, H 6.00, N 4.82.

Results and discussion

The critical aggregating concentrations (CAgC) of compounds **I**—**V** in the DX-H_2O binary system with different ϕ values (ϕ is the volume fraction of organic component in aquiorgano binary solvent) were measured at 35 ℃. The results are shown in Table 1. It has been found that, if ϕ is too small, the CAgC of **V** will be so low that the fluorescence intensity of excited anthracyl group will be too weak to be measured with reasonable precision. If ϕ is too large, no aggregation of **IV** can be determined because the fluorescence intensity of **IV** moves out of the upper measure limit of the instrument.

Table 1 CAgC values of the compounds **I**—**V** in ϕ = 0.3 and 0.4 DX-H_2O solvent

Compounds	ϕ	
	0.4	0.3
I	5.37×10^{-6}	0.73×10^{-6}
II	10.85×10^{-6}	3.24×10^{-6}
III	8.24×10^{-6}	2.75×10^{-6}
IV	—	—
V	7.53×10^{-7}	—

The dependence of the fluorescence spectra of compound **I** on the ϕ values was investigated first. Fig. 1 shows the fluorescence spectra of **I** (3.1×10^{-6} mol/L) in DX-H_2O solvent system (ϕ = 0.4—0.9) at λ_{ex} = 315 nm. The shoulder at about 450 nm is the emission of the typical exciplex. The fluorescence intensity of the excited carbazolyl increases with the increase of the ϕ values [or the decrease of solvent aggregation power (SAgP)]. When ϕ > 0.5, the shoulder disappeared. Since the possibility of an intermolecular interaction can be excluded at such a low concentration, the results are ratio-

nalized as follows: at $\phi = 0.4$, the concentration of **I** (3.1×10^{-6} mol/L) is lower than that of CAgC, as shown in Table 1.[1] Since this concentration is lower than the conectration of 1×10^{-5} mol/L, the critical concentration for possible intermolecular interaction,[13] the formation of intermolecular interaction is negligible. Therefore, compounds **I** exists only in a monomeric state. It is well known that the CAgC value of the simple aggregator is increased with the increase of ϕ value of DX-H_2O solvent, therefore, the value of **I** (3.1×10^{-6} mol/L) should be less than their CAgC values for all the systems with an increasing ϕ values (0.5—0.9 in Fig. 1).

The above-mentioned results indicate that the proximity effect between the donor and the acceptor in compound **I**, driven by the self-coiling of the organic molecule under the hydrophobic-lipophilic interaction (HLI), facilitates the change of the distance between the donor and the acceptor and accelerates the formation of the intramolecular exciplex of **I**. This can be considered as the evidence for the effects of self-coiling of organic molecule on the formation of the intramolecular exciplex and the fluorescence quenching.

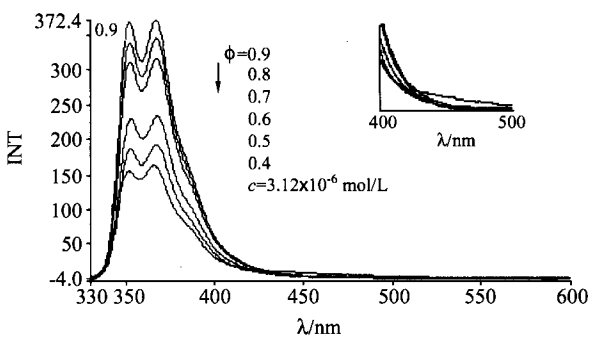


Fig. 1 Effect of gradually increasing of ϕ value of DX-H_2O solvent on the fluorescence spectra of **I** (3.1×10^{-6} mol/L) at $\lambda_{ex} = 315$ nm and $t = 35$ ℃. The values of ϕ are: 0.9, 0.8, 0.7, 0.6, 0.5 and 0.4. Insert shows the fluorescence spectra between 400 nm and 500 nm.

Fig. 2 gives the fluorescent spectrum of compound **I** in pure DX ($\phi = 1$) at $\lambda_{ex} = 315$ nm. The emission of the intramolecular exciplex at $\lambda = 450$ nm is clearly displayed, which is obviously stronger than that in the solvent systems of less ϕ values (Fig. 1). Therefore, there might be the presence of σ-bond charge-transfer process. This result is consistent with that reported by Yamamoto for the solvent 2-methytetrahydrofuran.[11] However, in the systems of $\phi = 0.5$—0.9, the emission of the intramolecular exciplex disappears as shown in Fig. 1. The result shows that the intramolecular δ-bond charge-transfer process has been destroyed by the self-coiling of **I** under HLI. In Fig. 2, the emission of the excited carbazolyl group is shown on the left side between 330 nm and 400 nm, while the intramolecular exciplex is shown on the right side at about 400 nm to 550 nm.

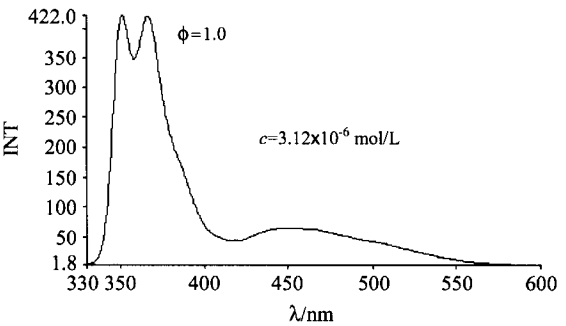


Fig. 2 Fluorescence spectrum of **I** (3.12×10^{-6} mol/L) in pure DX at $\lambda_{ex} = 315$ nm and $t = 35$ ℃.

The dependence of the fluorescence spectra of compounds **II**, **III** and **IV** on the ϕ values of DX-H_2O solvent were also investigated. Fig. 3 shows the fluorescence spectra of **II** at 5.8×10^{-6} mol/L in the $\phi = 0.5$—1.0 DX-H_2O solvent at $\lambda_{ex} = 315$ nm, while Fig. 4 shows the fluorescence spectra of **III** (6.06×10^{-6} mol/L) in the $\phi = 0.4$—1.0 DX-H_2O solvent at $\lambda_{ex} = 315$ nm. Although comparison of Fig. 3 and Fig. 4 with Fig. 1 reveals a very similar experimental phenomenon, *i.e.*, the fluorescence intensities of excited carbazolyl moiety are always increased with increasing ϕ values of the solvent, in Fig. 3 and Fig. 4, there are no emissions of exciplex at the longer wavelength, which is longer than the emission wavelength of excited carbazolyl group. In addition, the results of Fig. 3 and Fig. 4 are also different from that of Fig. 2 in pure dioxane ($\phi = 1.0$). All these results seem to suggest that intramolecular exciplex is not formed for both **II** and **III**. Instead, the ion-radical pairs[14] might be formed in these compounds, because of the stronger electron deficiency of the acceptor in **II** and **III** than that in **I**. Fig. 5 shows the fluorescence spectra of **IV** at 7.0×10^{-6} mol/L in $\phi = 0.7$—1.0 DX-H_2O solvent at $\lambda_{ex} = 315$ nm. It can be found that the fluorescence intensities are almost con-

stant with the increase of ϕ values of the solvent at the experimental uncertainty of ± 10%. In other words, the fluorescence intensity of **IV** is independent of the change of ϕ value of the solvent. For compound **IV**, with a chin of four methylene groups, it is impossible for self-coiling of the molecule **IV** to occur under HLI.[13] Thus the result can be taken an indirect evidence to support the effects of the self-coiling of **II** and **III** under HLI on the fluorescence quenching in Fig. 3 and Fig. 4.

Fig. 6 shows the fluorescence spectra of **V** at 4.68×10^{-7} mol/L in the solvents of $\phi = 0.4$—1.0 at λ_{ex} = 360 nm. The intramolecular σ-bond charge-transfer process might be retarded by the ether bond. We have reported the fluorescence quenching of the excited 9-anthrylmethyl ester of lauric acid by *p*-nitrophenyl dodecylsulfonate in DX-H_2O solvent system.[15] The ability of 3,5-dinitrobenzonate to accept an electron is stronger than that of *p*-nitrophenyl dodecylsulfonate. Therefore, the fluorescence of the excited anthryl group could be quenched by 3,5-dinitrobenzonate in the intramolecular self-coiling of **V** under HLI because of the proximity of both groups. In the experiment for **V**, no emission of the exciplex could be observed. Furthermore, the ion-radical pair might be also formed as described for compounds **II** and **III**. The results shown in Fig. 3, Fig. 4 and Fig. 6 indicate that the function of the excited anthracyl group is very similar to that of the excited carbazolyl group in the charge transfer process. However in **V** there is the effect of presence of the ether bond. It is different from the compounds **I**—**IV**.

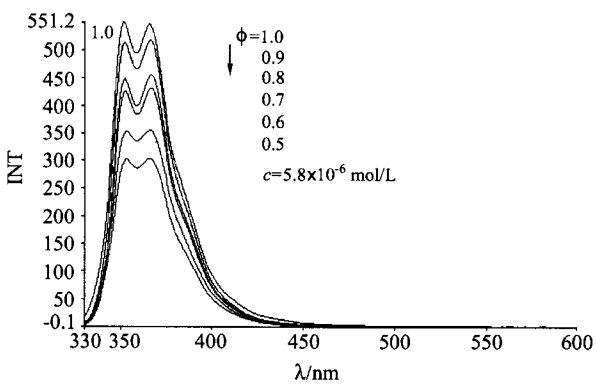


Fig. 3 Effect of gradually increasing of the ϕ value of DX-H_2O solvent on the fluorescence spectra of **II** (5.8×10^{-6} mol/L) at λ_{ex} = 315 nm and t = 35 ℃. The values of ϕ are: 1.0, 0.9, 0.8, 0.7, 0.6 and 0.5.

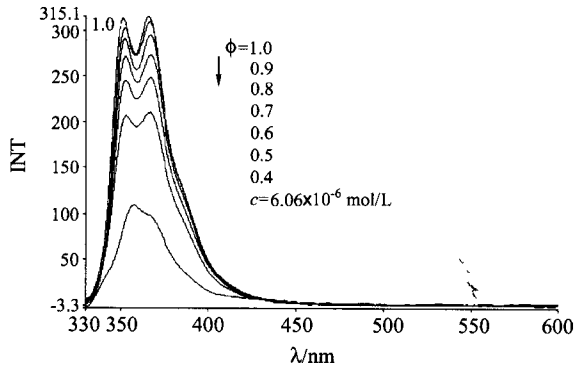


Fig. 4 Effect of gradually increasing of the ϕ value of DX-H_2O solvent on the fluorescence spectra of **III** (6.06×10^{-6} mol/L) at λ_{ex} = 315 nm and t = 35 ℃. The values of ϕ are: 1.0, 0.9, 0.8, 0.7, 0.6, 0.5 and 0.4.

Furthermore, under the above-mentioned experimental conditions, the acceptor moieties of the compounds **I**—**V** could not be excited because the absorption wavelengths of these acceptor moieties are much shorter than 315 nm (or 360 nm).

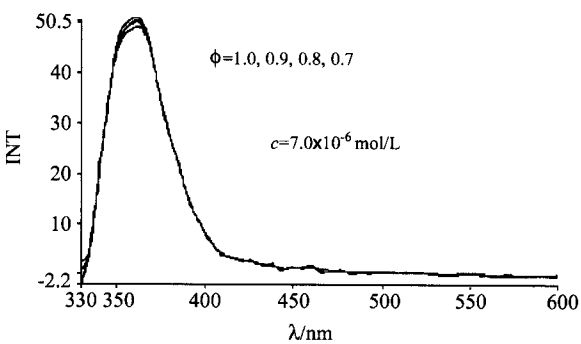


Fig. 5 Effect of gradually increasing of the ϕ value of DX-H_2O solvent on the fluorescence spectra of **IV** (7.0×10^{-6} mol/L) at λ_{ex} = 315 nm and t = 35 ℃. The values of ϕ are: 1.0, 0.9, 0.8 and 0.7.

In Fig. 1 at $\phi = 0.4$, the emission of intramolecular exciplex, brought about by self-coiling of organic molecule under HLI in polar DX-H_2O, has been observed, and Fig. 2 shows the emission of intramolecular exciplex in pure DX. In Fig. 1 from $\phi = 0.5$ to 0.9, Fig. 3 and Fig. 4, the decrease of the fluorescence intensities of excited carbazolyl with the decrease of the ϕ values is observed through self-coiling of organic molecule under HLI in DX-H_2O. For the excited an-

thracyl, Fig. 6 shows the decrease of the fluorescence intensities of excited anthracyl with the decrease of the ϕ value. It is very similar to Fig. 3 and Fig. 4.

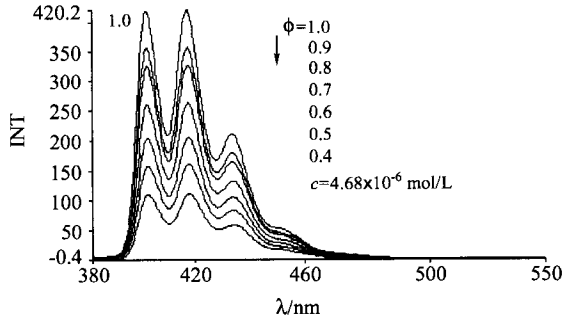


Fig. 6 Effect of gradually increasing of the ϕ value of DX-H_2O solvent on the fluorescence spectra of **V** (4.68×10^{-7} mol/L) at $\lambda_{ex} = 360$ nm and $t = 35$ ℃. The values of φ are: 1.0, 0.9, 0.8, 0.7, 0.6, 0.5 and 0.4.

In the study of intramolecular exciplex, Weller *et al.*[15] reported that at the concentration of the probe $< 10^{-5}$ mol/L the corresponding bimolecular reaction would be negligibly slow in the study on intramolecular exciplex formation and fluorescence quenching as a function of chain length in ω-dimethylaminoalkyl esters of 2-anthracenecarboxylic acid. It indicates that, at the concentration of less than 10^{-5} mol/L, the interference of intermolecular exciplex formation could be excluded in the study of intramolecular exciplex formation. Furthermore, it is well known that the concentration of the probe is less than that of CAgC and then the probe exists in its monomeric form in the organic-water binary solvent in the study of HLI.[1] Meanwhile, Weller[16] and Ottolenghi[17] pointed out that the emission of the exciplex can not be observed in a polar solvent. Ottolenghi proposed that radical-ion pairs are formed in polar solvents. However, the above-mentioned result of **I** is contrary to the fact that the emission of the exciplex can not be observed in a polar solvent. This novel finding is an explorative work and is important for further study of the effect of self-coiling of organic compounds under HLI on the information of intramolecular exciplex.

Conclusions

Under HLI, the donor and acceptor moieties approach each other by the self-coiling of the linear linkers contacting them for compounds **I**, **II**, **III** and **V**, but not for compound **IV**. The results obtained for **III** and **IV** indicate that their self-coiling tendency strongly depends on the length of the methylene chains (n). But no self-coiling behavior is observed for **IV** with a short linker. The results show that compounds **I**, **II**, **III**, and **V** are good fluorescence probes for studying the self-coiling of the organic molecule under HLI.

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