

Magnetic field effect on exciplex-forming organic acceptor/donor system: a powerful tool for understanding the preferential solvation

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ABSTRACT

Many acceptor/donor systems can form excited-state charge-transfer complexes (exciplexes) in photo-induced electron transfer reactions. Exciplex can be detected by their luminescence. In addition, the exciplex luminescence is magneto-sensitive. Here, we employ an approach based on the magnetic field effect on the exciplex of 9,10-dimethylantracene/*N,N*-dimethylaniline pair in micro-homogeneous and micro-heterogeneous binary solvents to investigate the effects of the preferential solvation processes on solute molecules in solutions. Micro-homogeneous solvent mixtures of propyl acetate

(PA)/butyronitrile (BN) allow for a systematic variation of the static dielectric constants, ϵ_s , in the range from 6.0 to 24.6. The mixtures of toluene (TO)/dimethylsulfoxide (DMSO) with varying the ϵ_s values in the range from 4.3 to 15.5 are used as micro-heterogeneous binary solvents. In micro-heterogeneous environment, DMSO molecules get preferentially favoured in the solvation shell, forming micro-clusters surrounding the solute molecules. This solvation effect is reflected in the altered magnetic field effects, lifetimes and dissociation rate constants of the exciplexes.

Key words: Exciplex, magnetic field effect, photo-induced electron transfer, radical ion pair

INTRODUCTION

Exciplexes, excited-state charge-transfer complexes, are formed in bimolecular photo-induced electron transfer (PET) reactions of excited electron acceptor (A^*) and electron donor (D) [1]. Fig. 1 depicts a scheme of the PET reaction in a typical exciplex forming acceptor/donor system. Here, the vertical axis refers to free energy and the abscissa expresses a reaction coordinate involving the distance between A^* and D [2, 4]. The exciplex is formed

when the contact distance of A^* and D is 6.5 Å while the distance of 10 Å refers to radical ion pair (RIP). In general, exciplexes can be monitored by their emission, which is spectrally well separated from the locally-excited emission of A^* [5-7]. In addition, the exciplex population can react to a weak external magnetic field [2-4, 8-12]. This effect originates from the so-called radical pair mechanism [13, 14].

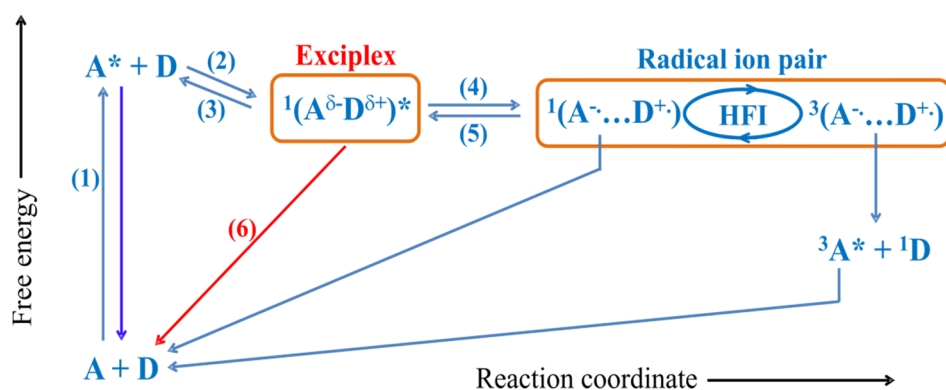


Fig. 1. Species and reactions involved in a photo-induced electron transfer reaction. Exciplex occurs as an intermediate in reaction. Photo-excitation (1), exciplex formation (2), exciplex dissociation into locally-excited acceptor (3), exciplex dissociation into radical ion pair-RIP (4), singlet-triplet conversion by hyperfine interaction (HFI), re-formation of the exciplex from the singlet RIP (5), exciplex emission (6). The blue and red arrows give the decay processes of either the locally-excited acceptor or the exciplex. $3A^*$ denotes the triplet products.

Magnetic field effect (MFE) on exciplex results from the inter-conversion of the singlet and the three triplet states of the RIP in equilibrium with the exciplex. Fig. 2 depicts the effect of an external magnetic field on singlet-triplet conversion according to the hyperfine coupling mechanism (HFC). Due to the Zeeman interaction, an external magnetic field will remove the degeneracy of the three triplet sublevels (T_0 and T_{\pm}) of spin-correlated RIPs generated via photo-induced electron transfer in solution. When the energy separation between three triplet states exceeds the size of the mixing interaction, T_{\pm} cannot mix with the singlet state, S. Thus, the external magnetic field reduces the

probability of intersystem crossing and, therefore, changes the relative concentrations of both singlet and triplet states [14-17]. Due to reversibility of the singlet RIP and the exciplex, the change of the concentration of singlet RIP can be detected through the emission of the exciplex. In other words, the exciplex luminescence is also magneto sensitive. Note, that the spin mixing between S and T_0 occurs when the electron exchange interaction, $J(r)$, depending exponentially on the distance between radical ions and the determination of the energy gap between the S and T_0 levels is negligible [17].

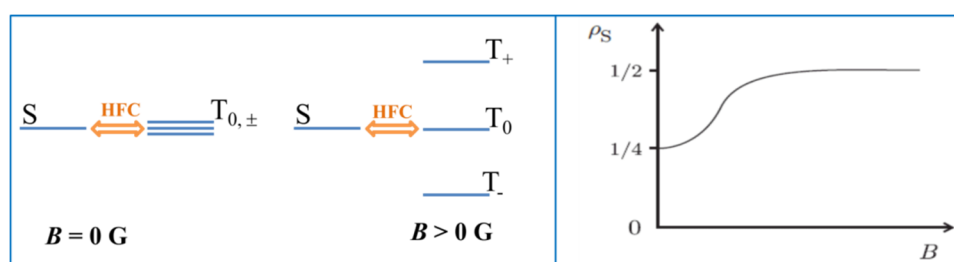


Fig. 2. Left panel refers to energy separations of singlet (S) and three triplet ($T_{0,\pm}$) states in the absence and presence of an external magnetic field, B . The dependence of singlet RIP probability, ρ_S , on the external magnetic field is shown in the right panel. Before reaching the saturating value, ρ_S increases with increasing the magnitude of B .

MFEs of the exciplexes strongly depend on solvent polarity [1-7]. In particular, the presence of polar micro-domains in binary solvents may affect the preferential solvation process of radical ion pairs (RIPs). This results in some interesting phenomena. The $B_{1/2}$ values (the field at which the delayed exciplex emission reaches half of its maximum intensity relative to that at zero field) show either a decrease in micro-heterogeneous solvents or remain constant in micro-homogeneous solutions with increasing polarity [8]. These results demonstrated that any factors imposed on the RIP dynamics may affect on the MFE of the exciplex and this effect is a powerful tool to investigate the specific solvation processes.

The paper is structured as follows: In section 2 we show the apparatuses to measure the absorption and fluorescence spectra of acceptor/donor pair of 9,10-dimethylantracene/*N,N*-dimethylaniline before the reader is fully acquainted with the preparations of micro-homogeneous (propyl acetate/butyronitrile) and micro-heterogeneous (toluene/dimethylsulfoxide) binary solvents with varying different static dielectric constants. The properties of solvent mixtures, e.g., viscosities (η), static dielectric constants (ϵ_s) are shown in this part as well. Thereafter, we continue by presenting an experimental method to measure the MFEs on the exciplexes of 9,10-dimethylantracene/*N,N*-dimethylaniline system based on steady-state measurements in micro-homogeneous and micro-heterogeneous solutions. In section 3, we then show the solvent property dependence of MFEs (χ_E), lifetimes (τ_E) and dissociation rate constants (k_d) of the exciplexes, and a discussion of the effect of the preferential solvation of polar components in

binary solvents on the χ_E , τ_E and k_d . Finally, we close with conclusions in section 4.

MATERIALS AND METHODS

Absorption spectra of the studied systems are recorded on Shimadzu UV-3101-PC UV-Vis-NIR spectrophotometer. The fluorescence spectra are measured on a thermostatted Jobin Yvo Fluoromax-2 spectrofluorimeter, sampling time: 1s nm⁻¹. The temperature for fluorescence measurements is held $T = 295$ K with the control of a Haake F3 thermostat. For MFE steady-state measurements, a detailed description of the experimental procedure and the apparatuses used is depicted in refs 2, 4. The concentration of donor is 0.06 M, while that of the acceptor is 2.10^{-5} M. Samples are prepared in septa-sealed quartz cuvettes with 1 cm path length. In order to remove dissolved oxygen, all solutions are sparged with nitrogen gas for 15 minutes prior to addition of the donor. The cuvette is immersed between two magnets. MFEs on exciplexes from steady-state measurements are recorded using a thermostated cell (295 K) coupled to a Jobin Yvon FluoroMax2 fluorescence spectrometer via light guides. The liquid donor is added directly through the septum using a Hamilton syringe. The exciplex lifetime, τ_E , is determined from the exciplex emission spectrum based on Time-Correlated Single Photon-Counting (TCSPC) technique in the absence of a saturating external magnetic field. TCSPC apparatus is described in details in ref 2. The exciplex formation is efficient when the excited acceptor and donor can be positioned into a sandwich-like conformation [18]. Thus, we have studied the dependent MFE on the 9,10-dimethylantracene (Acceptor-A)/*N,N*-dimethylaniline (Donor-D) system in binary solvents. Chemical structures of acceptor and donor are depicted in Fig. 3.

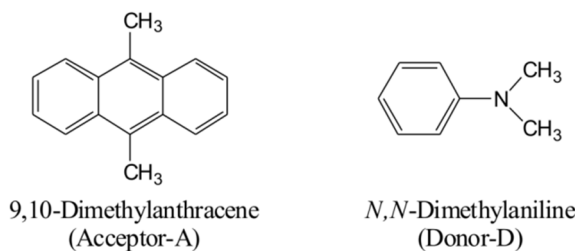


Fig. 3. Chemical structures of acceptor and donor have been used in the present work

The solvent medium strongly affects on the magnetic field effect of the exciplex. Here, we have designed two binary solvents in terms of micro-homogeneity and micro-heterogeneity. Mixtures of propyl acetate (PA, $\epsilon_s = 6.0$, $\eta = 0.58$ cP)/butyronitrile (BN, $\epsilon_s = 24.6$, $\eta = 0.58$ cP) varying the static dielectric constants, ϵ_s , in the range from 6 to 24.6 are selected as micro-homogeneous binary solvents. The different ϵ_s values are prepared according to: $\epsilon_s(w_1) = w_1\epsilon_1 + (1-w_1)\epsilon_2$ with ϵ_i and w_i denoting the dielectric constant and weight fraction of component i [2]. In these mixtures, the viscosity ($\eta = 0.58$ cP), and thus, the diffusion coefficients are nearly constant [4]. The refractive index ($n = 1.383$) is likewise almost invariant with solvent composition [2]. The Pekar factor ($1/n^2 - 1/\epsilon_s$) of PA/BN mixtures, which governs the outer-sphere electron transfer reorganization energy and, thus, the rate of ET processes, varies by only $\pm 5\%$ in the studied ϵ_s -range [19, 20].

The bulk dielectric constants, ϵ_s , of micro-heterogeneous toluene (TO, $\epsilon_s = 2.4$, $\eta = 0.55$

cP)/dimethylsulfoxide (DMSO, $\epsilon_s = 50.0$, $\eta = 2.2$ cP) mixtures vary in the range from 4.3 to 15.5 via: $\epsilon_s = 62.5\exp[-(1-x_{\text{DMSO}})/0.78]-15.6$ with x_{DMSO} giving the DMSO mole fraction in micro-heterogeneous mixture [8]. The solvent viscosity η (γ) and Pekar factor (γ) increase with increasing the DMSO concentration in TO/DMSO mixtures [8, 21]. MFEs on exciplexes from steady-state measurements are recorded in the absence and presence of a saturating external magnetic field at 295 K. All fluorescence signals have been background corrected.

RESULTS AND DISCUSSION

Fig. 4 depicts the absorption and emission spectra of 9,10-dimethylanthracene (DMAnt) in the absence and presence of *N,N*-dimethylaniline (DMA). The acceptor is excited at 375 nm to be sure that the donor is not excited at excitation wavelength of the acceptor. The emission spectrum of acceptor is directly accessible from the spectrum in the absence of donor. A model is employed to extract the exciplex emission [22, 23].

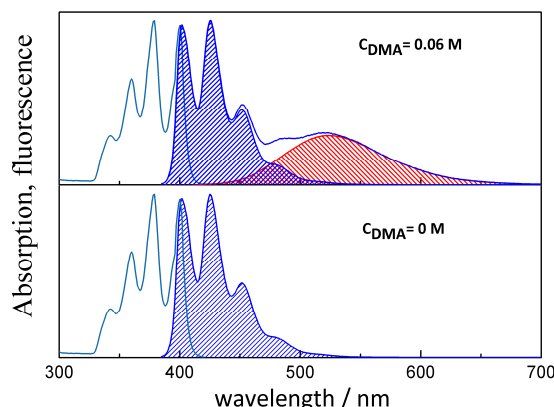


Fig. 4. Absorption and fluorescence spectra of 9,10-dimethylanthracene in the absence (bottom) and presence (top) of *N,N*-dimethylaniline ($C_M = 0.06$ M) in PA/BN mixture with a static dielectric constant of $\epsilon_s = 12.0$. The fluorescences of the excited acceptor and the exciplex are shaded in blue and red, respectively.

As shown in Fig. 4, the emission spectrum of the exciplex is separated from the fluorescence spectrum of the excited acceptor A^* . When applying a saturating external magnetic field ($B_0 = 62$ mT), the emission intensity of the exciplex increases. Fig. 5 refers to the time-dependent MFE on the DMAnt/DMA exciplex emission in steady-state measurements. The exciplex emission is detected at 550 nm for 60 s, time

constant of 1 s. At each time, three measurements are accumulated, there by alternating zero ($B_0 = 0$ mT) and saturating magnetic field ($B_0 = 62$ mT). As noted above, an external magnetic field changes the relative populations of singlet and triplet RIPs. The singlet RIP population increases, and the exciplex is in equilibrium with the singlet RIP. This causes an increase of the exciplex population.

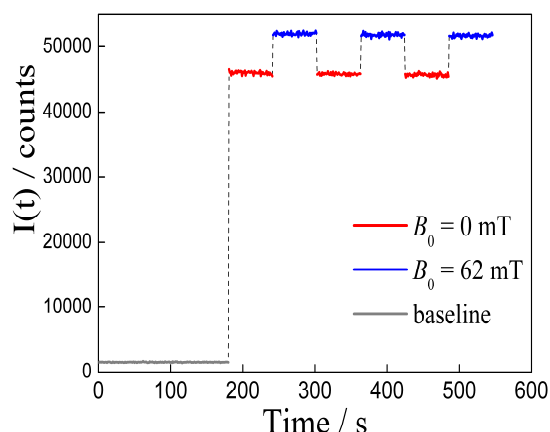


Fig. 5. Time-dependent magnetic field effect on the exciplex emission of the 9,10-dimethylanthracene/*N,N*-dimethylaniline system from steady-state measurements in the absence and presence of an external magnetic field. The exciplex emission is observed at 550 nm. Mixture of TO/DMSO at $\epsilon_s = 11.5$ is used as solvent.

Time scans at the emission wavelength ($\lambda_{em} = 550$ nm) of the exciplex are used to evaluate the MFE on the exciplex, χ_E , given by:

$$\chi_E = \frac{I(\lambda_{em}, B_0 = 62 \text{ mT}) - I(\lambda_{em}, B_0 = 0 \text{ mT})}{I(\lambda_{em}, B_0 = 0 \text{ mT})} \quad (1)$$

Here, $I(\lambda_{em}, B_0 = 62 \text{ mT})$ and $I(\lambda_{em}, B_0 = 0 \text{ mT})$ are the mean intensities of the exciplex at $\lambda_{em} = 550 \text{ nm}$ in a saturating and in the absent magnetic field. All emission intensities are baseline extracted. Fig. 6 refers to the solvent

dependence of the MFEs of the exciplexes of the DMAnt/DMA pair determined by eq 1 in micro-homogeneous and micro-heterogeneous binary solvents.

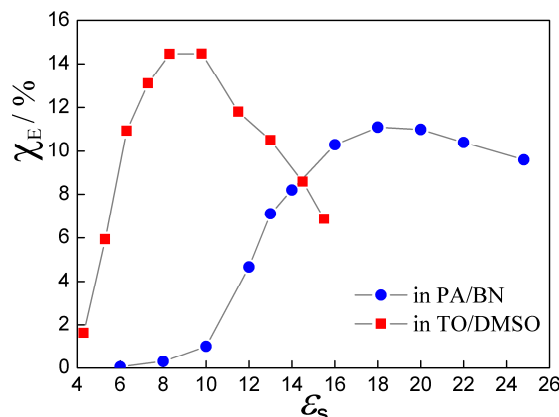


Fig. 6. Steady-state MFEs of the exciplexes (χ_E) in PA/BN (blue circles) and TO/DMSO (red circles) mixtures with varying the dielectric constants, ϵ_s .

MFE features have been analyzed in terms of $\epsilon_{s, \text{onset}}$, $\epsilon_{s, \text{max}}$ (ϵ_s values showing the onset and maximum of MFEs, respectively), x_{onset} , x_{max} (mole fraction values of polar component in binary solvent showing the onset and maximum of MFEs) and χ_{max} (the maximum MFE obtained). Table 1 gives the above parameters in two binary solvents. The onset and maximum of MFEs obtain at smaller ϵ_s values in TO/DMSO mixtures. The maximum MFE value ($\chi_{\text{max}} = 14.6\%$) appears at $\epsilon_s = 8.3$ in micro-

heterogeneous solutions while that obtains at $\epsilon_s = 18$ ($\chi_{\text{max}} = 11.4\%$) in micro-homogeneous ones. As mentioned above, RIP dynamics may reflect altered MFEs. The environment around RIP changes with the change in the composition of the solvent mixtures. According to suppan's model, the polar micro-domains (DMSO or BN) around solute species (RIP or exciplex) are produced via ion-dipole and dipole-dipole interactions of solute molecules with the polar components [24, 25].

Table 1. The parameters used to analyse the MFEs of the DMAnt/DMA exciplexes in micro-homogeneous and micro-heterogeneous binary solvents

Solvent	$\epsilon_{s, \text{onset}}$	x_{onset}	$\epsilon_{s, \text{max}}$	x_{max}	$\chi_{\text{max}}(\%)$
PA/BN	8.0	0.15	18.0	0.72	11.4
TO/DMSO	4.3	0.10	8.3	0.25	14.6

In micro-heterogeneous environment, DMSO molecules get preferentially favoured in the solvation shell, forming micro-clusters surrounding the RIPs [25-30]. The results have been published in ref 8, the authors used the dielectric continuum model suggested by Basilevsky et al [31] to simulate the local concentration of DMSO, $y(r)$, surrounding RIP in TO/DMSO mixtures (r is inter-radical separation). The polar micro-domains are surrounding radical ions and the space in between two radical ions. Irrespective of DMSO mole fraction in mixtures, the ions are covered by a layer of DMSO with a local DMSO concentration, $y(r) = 1$. This solvation effects on RIP lifetimes and induces an effective compromise between separation and recombination in geminate RIPs [8]. Thus, MFEs appear and reach the maximum value at smaller ϵ_s in TO/DMSO solutions.

After reaching the maximum value, MFEs decrease with increasing the solvent polarity. The effect of solvent polar components reaches saturation with increasing their mole fraction in mixture. At high ϵ_s values, i.e., high mole fractions of BN and DMSO in the corresponding mixtures, the separation of the two radicals in RIP is favourable, but the radical reencounter

probability in the geminate cage is not sufficient due to the prevention from solvent polar components (BN or DMSO) in solution. This results in a decrease in MFEs.

The dependence of the exciplex lifetime, τ_E , on solvent polarity is depicted in Fig 7. The exciplexes exponentially decay. Their lifetimes are obtained by fitting a combination of exponential functions to the experimental TCSPC measurements [2]. The exciplex lifetimes decrease with increasing the mole fractions of BN or DMSO in micro-homogeneous and micro-heterogeneous solutions. These results can be explained by the effect of the environment around the exciplex. The local BN or DMSO concentrations increase with increasing their mole fractions in mixtures. The micro-cluster formation of polar molecules surrounding the charge-transfer dipoles (exciplexes) governs the exciplex lifetime. As mentioned above, the exciplex is formed in a contact distance between excited acceptor (A^*) and donor (D). The dipole-dipole interaction increases with increasing the BN or DMSO concentrations in solvation shell surrounding exciplexes. This causes the exciplex to dissociate into RIPs, i.e., the exciplex lifetime decreases.

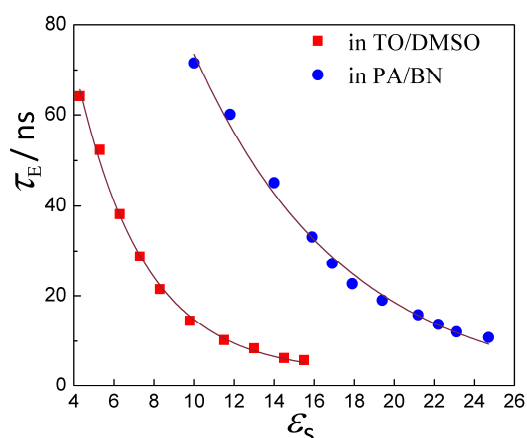


Fig. 7. Solvent polarity dependence of the exciplex lifetimes of the DMAnt/DMA system in PA/BN (blue circles) and TO/DMSO (red squares) mixtures

The exciplex kinetics is evaluated through the rate of exciplex dissociation, k_d , into RIP (pathway 4 in Fig. 1). The k_d values are extracted by least-squares fitting to time-resolved MFE data of the exciplex [2, 4]. The time-resolved MFEs of exciplexes are measured based on TCSPC technique in the absence and presence of a saturating external magnetic field [2, 4]. The plot of k_d as a function of solvent polarity is

described in Fig. 8. The k_d increases with increasing the solvent polarity, i.e., the exciplexes dissociate into RIPs faster. The enrichment of polar components (BN or DMSO) in solvation shell surrounding solute exciplex mainly governs the separation of the exciplex into the ions. That is reflected in the trend of k_d with increasing the mole fractions of polar components in solvent mixtures.

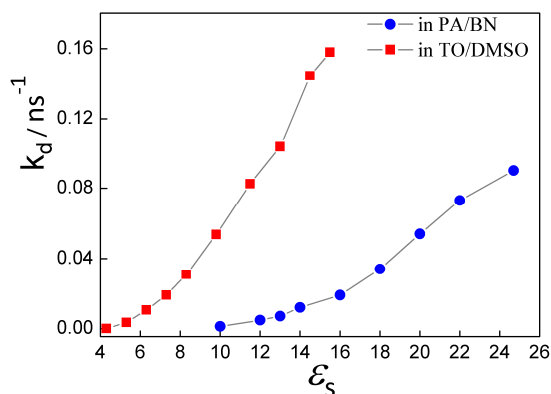


Fig. 8. The plot of exciplex dissociation rate constants, k_d , as a function of solvent polarity of the DMAnt/DMA exciplexes. Mixtures of PA/BN (red squares) and TO/DMSO (blue circles) are used as micro-homogeneous and micro-heterogeneous binary solvents

CONCLUSION

By using the MFEs on the exciplexes of DMAnt/DMA system in micro-homogeneous and micro-heterogeneous binary solvents with systematically varying the static dielectric constants, ϵ_s , we have been able to demonstrate that the MFE on the exciplex-forming organic acceptor/donor system is a powerful tool to investigate the preferential solvation effects. The onset and maximum MFEs of the exciplexes occur at smaller ϵ_s values in micro-heterogeneous solutions TO/DMSO in comparison to micro-homogeneous mixtures PA/BN. The exciplexes

dissociate into RIPs faster with increasing the mole fractions of polar components of BN or DMSO in mixtures. As a consequence, the exciplex lifetimes decrease in more polar solutions. All these results can be attributed to the preferential solvation of polar components (BN or DMSO) in mixtures. They form a polar cluster around solute molecules (RIPs or exciplexes) due to dipole-dipole interaction. In particular, with the presence of the high polar component DMSO in the polar cluster, the effects on the resulting observations are more significant.

Ảnh hưởng của từ trường lên trạng thái kích thích của hệ cho/nhận hữu cơ: một công cụ hiệu quả để tìm hiểu quá trình dung môi hóa

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TÓM TẮT

Nhiều hệ cho/nhận electron có thể hình thành các phức trao đổi điện tích ở trạng thái kích thích (exciplex) trong các phản ứng trao đổi electron giữa chất nhận ở trạng thái kích thích và chất cho ở trạng thái nền. Exciplex có thể được phát hiện qua phổ huỳnh quang. Hơn nữa, sự phát huỳnh quang của exciplex bị ảnh hưởng bởi từ trường ngoài. Trong nghiên cứu này, chúng tôi dựa vào ảnh hưởng của từ trường ngoài lên exciplex của cặp cho/nhận electron *N,N*-dimethylaniline (chất cho)/ 9,10-dimethylantracene (chất nhận) trong các hệ hỗn hợp 02 dung môi đồng thể và dị thể để nghiên cứu các ảnh hưởng của quá trình dung môi hóa

lên các chất tan trong dung dịch. Hằng số điện môi, ϵ_s , của hệ hỗn hợp 02 dung môi đồng thể propyl acetate (PA)/butyronitrile (BN) thay đổi trong khoảng 6,0 đến 24,6. Hỗn hợp 02 dung môi dị thể toluene (TO)/dimethylsulfoxide (DMSO) có hằng số điện môi thay đổi trong khoảng 4,3 đến 15,5. Trong môi trường dị thể, các phân tử DMSO dung môi hóa ưu thế các chất tan trong dung dịch bằng cách tạo một vi đám DMSO xung quanh chất tan. Tất cả những ảnh hưởng của quá trình dung môi hóa được thể hiện qua sự thay đổi về từ trường, thời gian tồn tại và động học của exciplex.

Từ khóa: Exciplex, ảnh hưởng từ trường, trao đổi electron nhờ hấp thụ năng lượng UV-Vis, cặp gốc ion

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