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Hydrophobic Acceleration of Electron Transfer Processes

Ji-Liang Shi,* Xin Chen, and Xi-Kui Jiang*

Shanghai Institute of Organic Chemistry, 354 Fenglin Lu, Shanghai 200032, China

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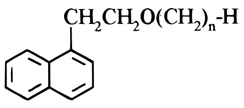
Electron transfer processes between 1-α-naphthyl-3-oxa-alkanes (**1**-*n*, *n* = 1, 8, 12, 16) and 2-alkyl-3,5,6-trichloro-1,4-benzoquinones (**2**-*n*, *n* = 8, 12, 16) facilitated by hydrophobic−lipophilic interactions (HLI) have been investigated by means of fluorescence spectroscopy in dioxane−H_2O systems of different ψ values, where ψ is the volume fraction of the organic component of an aquiorgano mixture. Three lines of evidence, namely, EPR, UV−vis, and fluorescence quenching, indicate that electron transfer between **1**-12 and **2**-12 has occurred. Furthermore, both UV−vis evidence and the near constancy of the life time τ of **1**-12* in the presence of different concentrations of the quencher **2**-12 show that the electron transfer is preceded by preassociation, i.e., the quenching process is static. Therefore, the extent of HLI-driven coaggregation (preassociation) between the donors and the acceptors may be assessed from the Stern−Volmer slopes (Ksv). The chain-length effect, and possibly also a chain-foldability effect, has been observed. A notable observation is the importance of solvent aggregating power (SAgP) effect, which is indicated by the surge of Ksv values at $\psi \leq 0.40$ (dioxane−H_2O) for monomeric **1**-12.

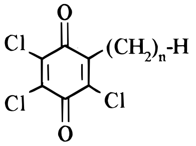
Hydrophobic−lipophilic interactions (HLI) play an important role in chemical and biochemical processes such as conformational changes of biopolymers, the binding of a substrate to enzyme, the formation of living cells from biological molecules, etc.[1−3] On the other hand, studies on photophysical and photochemical processes in organized assemblies have also attracted much attention.[4−6] Since aggregates of electrically neutral organic molecules are formed almost solely by HLI, some recent efforts have been dedicated to studies of hydrophobic effects on photochemical and photophysical processes.[6−9] It has been reported that aggregation, coaggregation, and self-coiling of organic molecules affect the formation of excimers[7,8] and enhancement of energy transfer between excited donors and acceptors.[10,11] However, electron transfer processes facilitated by the HLI-driven formation of simple aggregates have not yet been studied in detail.

Electron transfer is one of the very active topics in chemical research.[12] It is well-known that the medium effects, such as solvent polarity and the addition of the salts, have an important influence on the behavior of photoinduced electron transfer between the donor and the acceptor in solution.[12] On the basis of previous studies of aggregating tendencies of organic molecules[13,14] and hydrophobic effects on photophysical properties of fluorescence probes,[7−10] we have now extended our study to the electron transfer process facilitated by HLI-driven aggregation.

In the present work, 1-α-naphthyl-3-oxa-alkanes (**1**-*n*) with different chain lengths (*n* = 1, 8, 12, 16) were used as the donor and fluorescence probe and 2-alkyl-3,5,6-trichloro-1,4-benzoquinones (**2**-*n*, *n* = 8, 12, 16) as the acceptor and quencher. They were synthesized by reactions shown in Scheme 1.



1-n (donor)
(n = 1, 8, 12, 16)



2-n (acceptor)
(n = 8, 12, 16)

The occurrence of electron transfer between our donor and acceptor results in the fluorescence quenching of the excited donor **1**-*n** by **2**-*n*. There are two possible pathways leading to the fluorescence quenching of the excited state donor.[15] The best-known and commonly investigated pathway involves the collisional or diffusion-controlled encounter between ground-state quencher and excited fluoropher molecules. This process is refered to as diffusional quenching and is characterized by a time-dependent rate constant.[6,16] Another possible process is the static quenching that occurs with fluorophers already associated with the quencher in the ground state.[6] The static quenching process is characterized by an invariant fluorescence lifetime.[6] In the present work, the HLI-driven electron transfer between **1**-*n** and **2**-*n* of certain chain lengths has been found to proceed by the latter pathway.

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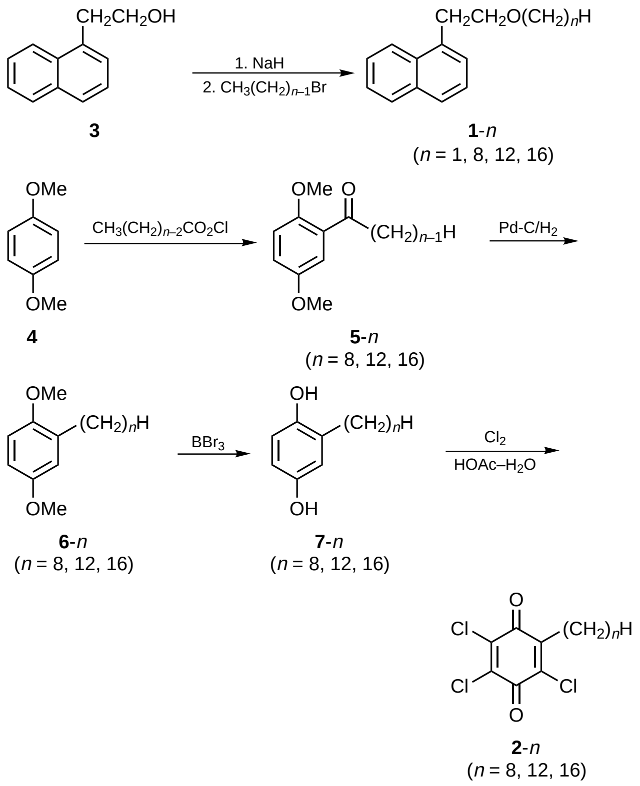
Scheme 1



Molecules may associate in solution for a variety of reasons, e.g., van der Waals forces, collision-induced weak CT interactions, etc. However, both contributions are quite small.[17] On the other hand, previous works have established that preassociation of chromophores greatly facilitates excimer formation.[6,7,18] We speculate that enhancement of fluorescence quenching might also be facilitated by HLI-driven coaggregation of a donor and an acceptor at very low concentrations (ca. 10^{-5} M). Furthermore, the efficiency of fluorescence quenching should depend on the chain length of the substituent groups of the acceptor quenchers (**2**-*n*) or the donor probes (**1**-*n*) and on the solvent aggregating power (SAgP)[13] of the reaction media. These speculations have been found to be true.

Experimental Section

Reagents and Substrates. ^{1}H NMR spectra were obtained at 200 and 90 MHz on Varian XL-200 and FX-90Q spectrometers, with TMS as an internal standard. Chemical shifts are expressed in ppm (δ), and coupling constants (J) are quoted in hertz (±0.3 Hz). Mass spectra (MS) were taken on a Finnigan-4201 spectrometer (EI, 70 eV or FAB). Flash column chromatography was performed on silica gel with petroleum–EtOAc as the eluent. 1-α-Naphthyl-3-oxa-alkanes (**1**-*n*) are known compounds.[7] The general procedures for the synthesis of 2-alkyl-3,5,6-trichloro-1,4-benzoquinones (**2**-*n*) are shown in Scheme 1 and described as below.

2-Alkanoylhydroquinone Dimethyl Ethers (5-*n*) and **2-Alkylhydroquinone Dimethyl Ethers (6-*n*)** were prepared from hydroquinone dimethyl ether by the method of Dawson.[19] Spectral data of **5**-*n* and **6**-*n* prepared in this laboratory are given below.

5-8. ^{1}H NMR (CDCl$_3$): δ 7.22 (1H, d, J = 4.0), 7.00 (1H, dd, J = 9.0, 4.0), 6.90 (1H, d, J = 9.0), 3.87 (3H, s), 3.80 (3H, s), 2.97 (2H, t), 1.66 (2H, br), 1.26 (8H, m), 0.89 (3H, t). MS (EI): m/z (relative intensity) 265 $(M + 1)^+$ (85.2), 264 $(M)^+$ (24), 165 (100).

5-12. ^{1}H NMR (CDCl$_3$): δ 7.23 (1H, d, J = 4.0), 7.01 (1H, dd, J = 10.0, 4.0), 6.91 (1H, d, J = 10.0), 3.87 (3H, s), 3.80 (3H, s), 2.98 (2H, t), 1.68 (2H, br), 1.27 (16H, m), 0.90 (3H, t). MS (EI): m/z (relative intensity) 321 $(M + 1)^+$ (92.2), 320 $(M)^+$ (23.4), 165 (100).

5-16. ^{1}H NMR (CDCl$_3$): δ 7.21 (1H, d, J = 4.0), 7.01 (1H, dd, J = 8.5, 4.0), 6.90 (1H, d, J = 8.5), 3.87 (3H, s), 3.80 (3H, s), 2.97 (2H, t), 1.65 (2H, br), 1.25 (24H, m), 0.89 (3H, t). MS (EI): m/z (relative intensity) 377 $(M + 1)^+$ (20.2), 180 $(M)^+$ (32.3), 165 (100).

6-8. ^{1}H NMR (CDCl$_3$): δ 6.72 (3H, m), 3.78 (3H, s), 3.77 (3H, s), 2.56 (2H, t), 1.57 (2H, br), 1.25 (10H, m), 0.90 (3H, t). MS (EI): m/z (relative intensity) 250 $(M)^+$ (100), 152 (64.5).

6-12. ^{1}H NMR (CDCl$_3$): δ 6.71 (3H, m), 3.78 (3H, s), 3.76 (3H, s), 2.57 (2H, t), 1.56 (2H, br), 1.25 (18H, m), 0.88 (3H, t). MS (EI): m/z (relative intensity) 306 $(M)^+$ (100), 152 (68.7).

6-16. ^{1}H NMR (CDCl$_3$): δ 6.75 (3H, m), 3.79 (3H, s), 3.78 (3H, s), 2.58 (2H, t), 1.58 (2H, br), 1.26 (26H, m), 0.90 (3H, t). MS (EI): m/z (relative intensity) 362 $(M)^+$ (100), 151 (72.8), 137 (30.2).

2-Alkylhydroquinones (7-*n*). A solution of **5** (5 mmol) and boron tribromide (15 mmol) in dichloromethane (30 mL) was stirred at −20 °C for 1 h and then for an additional 3 h at rt. The mixture was hydrolyzed with water (10 mL) and extracted with ether. The solvent was then removed in vacuo, and the products (52.3–61.7%) were separated by flash column chromatography on silica gel with petroleum–EtOAc (8:2) as the eluent.

7-8. ^{1}H NMR (CDCl$_3$): δ 6.70 (1H, d, J = 8.0), 6.66 (1H, d, J = 4.0), 6.51 (1H, dd, J = 4.0, 8.0), 4.30 (2H, br, OH, D$_2$O exchangeable), 2.55 (2H, t), 1.61 (4H, br), 1.28 (8H, m), 0.90 (3H, t). MS (EI): m/z (relatively intensity) 222 $(M)^+$ (57.2), 124 (100).

7-12. ^{1}H NMR (CDCl$_3$): δ 6.68 (1H, d, J = 8.0), 6.65 (1H, d, J = 4.0), 6.57 (1H, dd, J = 4.0, 8.0), 4.35 (2H, br, OH, D$_2$O exchangeable), 2.56 (2H, t), 1.62 (4H, br), 1.28 (16H, m), 0.91 (3H, t). MS (EI): m/z (relatively intensity) 279 $(M + 1)^+$ (66.1), 278 $(M)^+$ (35.9), 124 (100).

7-16. ^{1}H NMR (CDCl$_3$): δ 6.65 (1H, d, J = 8.0), 6.60 (1H, d, J = 4.0), 6.48 (1H, dd, J = 4.0, 8.0), 3.24 (2H, br, OH, D$_2$O exchangeable), 2.55 (2H, t), 1.60 (4H, br), 1.29 (24H, m), 0.90 (3H, t). MS (FAB): m/z (relatively intensity) 334 $(M)^+$ (42), 123 (45), 41(100).

2-Alkyl-3,5,6-trichloro-1,4-benzoquinones (2-*n*). A suspension of **6** (2 mmol) in glacial acetic acid (80% aqueous, 35 mL) was refluxed under chlorine gas for 5 h. A yellow solid was formed, and the product (7.2–9.1%) was separated by flash column chromatography on silica gel with petroleum–EtOAc (100:1) as eluent.

2-8. ^{1}H NMR (CDCl$_3$): δ 2.73 (2H, t), 1.69–1.24 (12H, m), 0.90 (3H, t). MS (EI): m/z (relatively intensity) 324 $(M + 2)^+$ (19.1), 225 (100). Anal. Calcd for $C_{14}H_{17}O_2Cl_3$: C, 51.95; H, 5.30. Found: C, 52.13; H, 5.42.

2-12. ^{1}H NMR (CDCl$_3$): δ 2.73 (2H, t), 1.70–1.25 (20H, m), 0.90 (3H, t). MS (EI): m/z (relatively intensity) 380 $(M + 2)^+$ (4.7), 225 (30.7), 43(100). Anal. Calcd for $C_{18}H_{25}O_2Cl_3$: C, 56.93; H, 6.64. Found: C, 57.06; H, 6.81.

2-16. ^{1}H NMR (CDCl$_3$): δ 2.71 (2H, t), 1.67–1.24 (28H, m), 0.91 (3H, t). MS (EI): m/z (relatively intensity) 436 $(M + 2)^+$ (13.3), 227 (100). Anal. Calcd for $C_{22}H_{33}O_2Cl_3$: C, 60.59; H, 7.62. Found: C, 60.90; H, 7.39.

Electronic Spectra. All aquiorgano solutions used for spectroscopic measurements were prepared from deionized water and dioxane (DX) that was purified by a standard

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procedure.[20] Stock solutions of **1**-*n* and **2**-*n* were prepared and diluted as needed. The EPR spectrum was recorded on a Varian E-112 spectrometer, and the UV−vis absorption spectrum was recorded on a Perkin-Elmer Lambda-5 spectrometer. The lifetimes of excited **1**-12 were measured by utilizing the time-correlated single-photon counting technique on a Horiba NAES-1100 spectrometer, with the degassed solutions of **1**-12 excited at 285 nm and the monomer fluorescence observed at 337 nm. Fluorescence emission spectra of nondegassed aquiorgano solutions (DX−H_2O) of **1**-*n* were recorded in the absence and presence of varying amounts of **2**-*n* by a Perkin-Elmer LS-50 spectrometer at 298 K. The relative fluorescence intensity measurements were determined at the emission maxima of 337 nm for the monomer of **1**-n^*, and an excitation wavelength of 285 nm was used. The error in the fluorescence intensity measurements was less than ±5%.

Results and Discussion

Previous works have proved that HLI facilitates the formation of intermolecular excimers of **1**-*n*, a fluorescence probe.[7] In order to keep the fluorescence probe **1**-*n* from forming excimers with itself, it must be kept at the monomeric state in solvent systems used. Therefore, the critical aggregate concentrations (CAgC) of **1**-*n* were measured by previous reported methods.[7,13,21] In the dioxane (DX)-H_2O solvent system of $\psi = 0.40$, where ψ represents the volume fraction of the organic component of the aquiorgano mixture, the CAgC value for **1**-8 was found to be greater than 3.0×10^{-5} M, the CAgC value for **1**-16 was smaller than 0.1×10^{-5} M, and no CAgC value could be found up to 3.0×10^{-5} M for **1**-1. Finally, for **1**-12, the CAgC value was smaller than 0.02×10^{-5} M at $\psi = 0.25$, the CAgC values were found to be 0.10×10^{-5} M at $\psi = 0.30$, 0.24×10^{-5} M at $\psi = 0.35$, 0.60×10^{-5} M at $\psi = 0.40$, 2.5×10^{-5} M at $\psi = 0.45$, and greater than 3.0×10^{-5} M at $\psi = 0.50$, 0.55, and 0.60. Furthermore, it was necessary to ascertain that the presence of the acceptor **2**-*n* did not interfere with fluorescence intensity measurements of **1**-n^*. Our experiments showed that when **2**-*n* in the DX−H_2O solvent systems was excited at 285 nm, there was no fluorescence emission of **2**-n^* in the spectral range from 300 to 550 nm, in which **1**-n^* emits. Therefore, it is possible to study the emission spectra of **1**-n^* fluorescence probes in DX−H_2O solutions containing **2**-*n* at the excitation wavelength of 285 nm. In other words, HLI facilitated electron transfer processes between **1**-*n* and **2**-*n* can be investigated by the evaluation of **1**-n^* concentration quenching constants or Stern−Volmer slopes (Ksv values) at **1**-*n* concentrations below their CAgC values in the presence of the quencher (**2**-*n*) when the solution was irradiated at 285 nm. Results of these Ksv measurements at $\psi = 0.40$ and some other ψ values of the DX−H_2O solvent systems are summarized in Figure 1−3.

At this juncture, we would like to present the lines of evidence for the quenching mechanism.

First, at $\psi = 0.40$, the ground state charge-transfer complex formation between **1**-12 and **2**-12 in DX−H_2O solution was demonstrated by identification of our EPR spectrum of the anion radical of **2**-12 with the EPR of chloranil anion radical.[22] The CT complex formation was also indicated by the temporary appearance of the UV−vis absorption band of the charge-transfer complex at 570 nm, even though it was not possible to evaluate the association constant because the intensity of the CT band (also, the EPR signal) quickly decreased with time after the mixing of **1**-12 and **2**-12. Finally, it is notable that

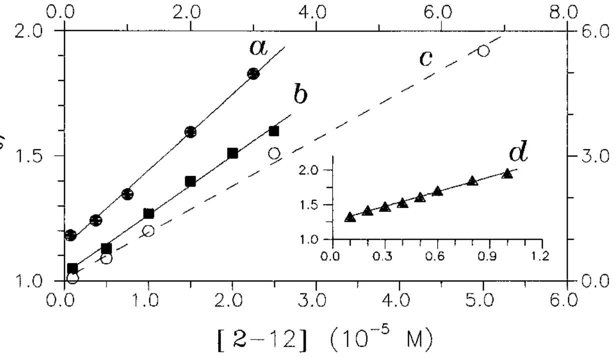

Figure 1. Stern−Volmer plots for the quenching of **1**-12^* (line a), **1**-8^* (b), **1**-1^* (c), and **1**-16^* (d) by **2**-12. Molar concentration units on the botton are for lines b and c and that on the top is for line a; I_0/I ratio units on the left are for lines b and c, and that on the right is for line a.

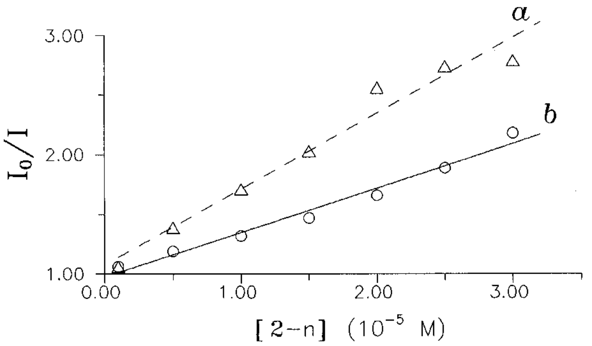

Figure 2. Stern−Volmer plots for the quenching of **1**-12^* by **2**-16 (line a) or **2**-8 (b).

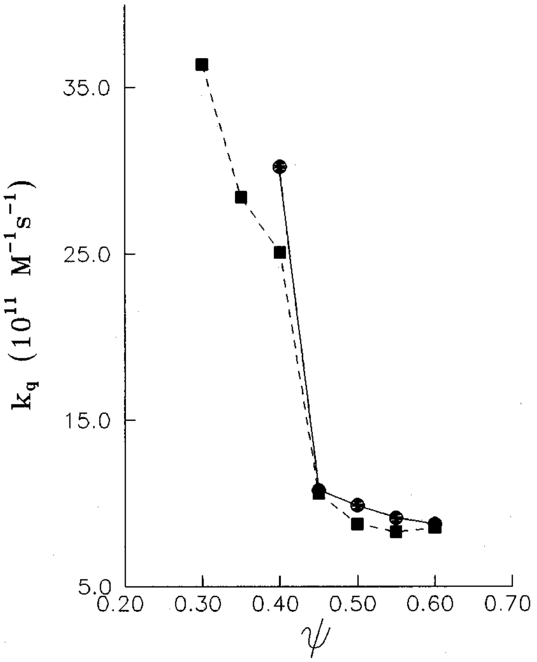

Figure 3. Dependence of Ksv on ψ in the quenching of **1**-12^* by **2**-12. Solid lines are for [**1**-12] = 0.5×10^{-5} M and dashed lines are for [**1**-12] = 0.2×10^{-5} M.

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different degrees of fluorescence quenching of all **1**-*n* fluorophers have been observed when **2**-*n* is added. All the above-mentioned observations are in accord with the proposition that electron transfer and fluorescence quenching occur after preassociation of the doner **1**-*n* with the acceptor **2**-*n*.

When one of the molecules is in its excited state, the free energy change of the electron transfer quenching in polar solvents between the donor and the acceptor can be given by the Weller equation,[23] $\Delta G = E(\mathrm{D/D^+}) - E(\mathrm{A^-/A}) - E(\mathrm{oo})$, where $E(\mathrm{D/D^+})$ is the oxidation potential of the donor, $E(\mathrm{A^-/A})$ is the reduction potential of the acceptor, and $E(\mathrm{oo})$ is the excitation energy of the excited molecule. If we use the oxidation potential of naphthalene (1.54 V)[24] for **1**-12, the reduction potential of 2,3,5,6-tetrachloro-1,4-benzoquinone (0.02 V)[25] for **2**-12, and the energy of naphthalene singlet excited state (92 kcal/mol)[26] for that of **1**-12, then the ΔG can be approximately evaluated to be 23.06 (1.54−0.02) kcal/mol −92 kcal/mol = −57 kcal/mol. The negative sign of ΔG suggests that electron transfer between **1**-*n** and **2**-*n* can occur easily.[27]

The second line of evidence for ground state association is the near constancy of the lifetime (τ) of the excited monomer **1**-12* in the DX−H$_2$O solution (ψ = 0.40) in the absence and presence of **2**-12, i.e., τ = 44.4 ns ([**2**-12] = 0), τ = 44.2 ns ([**2**-12] = 0.1 × 10^{-5} M), τ = 43.7 ns ([**2**-12] = 0.5 × 10^{-5} M), τ = 43.2 ns ([**2**-12] = 1.0 × 10^{-5} M), and τ = 44.7 ns ([**2**-12] = 5.0 × 10^{-5} M). This is consistent with the value (40 ns) of the naphthalene monomer lifetime in H$_2$O.[27] In contrast, if we let I_0 and I respectively represent the fluorescence intensities of excited fluoropher in the absence and presence of the quencher, then the I_0/I ratios for **1**-12 will show linear dependence on the quencher concentration (cf. line a in Figure 1). These results show that the lifetimes of **1**-12* are not affected by the addition of different amounts of **2**-12; meanwhile, the fluorescence intensity of **1**-12* decreases, i.e., the ratio I_0/I increases, when the quencher **2**-12 is added. Consequently, all lines of evidence mentioned above indicate that the quenching mechanism is static.[6] In other words, HLI-driven preassociation precedes electron transfer,[7] as shown below

$$\mathbf{1}\text{-}n + \mathbf{2}\text{-}n \xrightarrow{\text{HLI}} \underset{\text{preassociation}}{[\mathbf{1}\text{-}n\cdots\mathbf{2}\text{-}n]} \xrightarrow{\text{ET}}$$

$$\underset{\text{CT complex}}{[\mathbf{1}\text{-}n^{+}\cdots\mathbf{2}\text{-}n^{-}]} \xrightarrow{h\nu} \text{quenching products}$$

Notably, on the basis of the above-mentioned considerations, the quenching yields are expected to reflect the coaggregation tendency of quencher **2**-*n* with the donor **1**-*n*. This expectation is materialized by a comparison of the quenching of **1**-12* and **1**-1* with **2**-12. The effective quenching of the long-chained **1**-12* by **2**-12 is clearly illustrated by Figure 4, which shows that the fluorescence intensity of **1**-12* decreases quickly with increasing amounts of the quencher **2**-12. On one hand, it has been experimentally observed that the intensity of **1**-1* is affected very little by the addition of **2**-12. In other words, the near absence of fluorescence quenching between **1**-1* and **2**-12 is a consequence of the fact that the short-chained **1**-1 does not effectively coaggregate with **2**-12,[13,14] while extensive preassociation of **1**-12 and **2**-12 leads to highly effective quenching. The above-mentioned preassociation was also extensively confirmed by the analysis of the fluorescence intensity data in terms of Stern−Volmer slopes (Ksv).

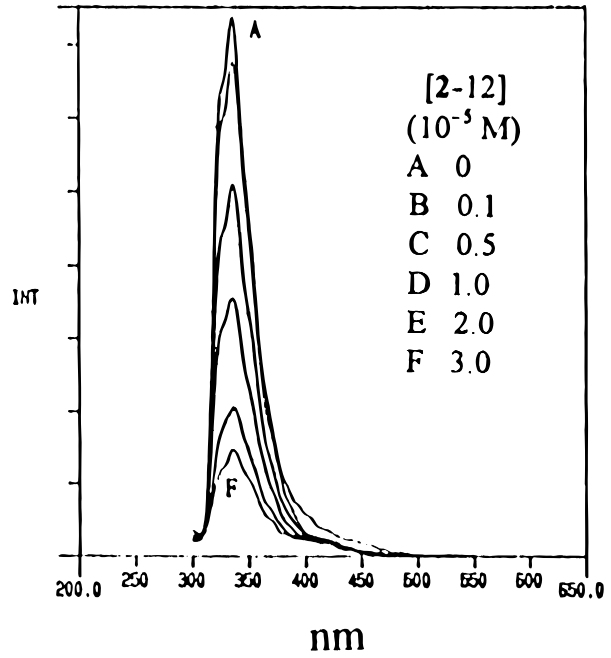

Figure 4. Effect of **2**-12 concentration on the fluorescence intensity of **1**-12* (0.5 × 10^{-5} M). ψ = 0.40 DX−H$_2$O, λ_{ex} = 285 nm.

Table 1. Ksv Values (×10^4 mol^{-1} L) for the Fluorescence Quenching of 1-*n* ([1-*n* = 0.50 × 10^{-5} mol^{-1} L) by 2-12 and for the Fluorescence Quenching of 1-12 ([1-12 = 0.50 × 10^{-5} mol^{-1} L] by 2-*n* of Different Chain Lengths in DX−H$_2$O, with ψ = 0.40

1-*n*	Ksv	**2**-*n*	Ksv
1-1	1.86	**2**-8	3.73
1-8	2.36	**2**-12	13.7
1-12	13.7	**2**-16	6.37
1-16	7.03		

On the basis of our I_0/I data, the Ksv values can be evaluated from the Stern−Volmer plots. Figure 1 shows the I_0/I *vs* [**2**-12] plots at a fixed concentration of **1**-1, **1**-8, **1**-12 and **1**-16 ([**1**-*n*] = 0.5 × 10^{-5} M) in the ψ = 0.40 DX−H$_2$O mixture. The Ksv values derived from the slopes of these plots are for the **2**-12/**1**-1 combination, 1.86 × 10^4 M^{-1}; for the **2**-12/**1**-8 combination, 2.36 × 10^4 M^{-1}; for the **2**-12/**1**-12 combination, 13.7 × 10^4 M^{-1}; and for the **2**-12/**1**-16 combination, 7.03 × 10^4 M^{-1}. (see Table 1). Figure 2 shows the I_0/I *vs* [**2**-8] and I_0/I *vs* [**2**-16] plots at a fixed concentration of **1**-12 ([**1**-12] = 0.5 × 10^{-5} M) in the same solvent mixture. The Ksv value thus obtained for the **2**-8/**1**-12 combination is 3.73 × 10^4 M^{-1}, and that for the **2**-16/**1**-12 combination is 6.37 × 10^4 M^{-1} (see Table 1). A larger Ksv value, of course, signifies a more effective quenching of the donor (**1**-*n**) by the acceptor.

The results indicate that the order of decreasing Ksv values for the quenching of the **1**-*n** monomer by **2**-12 is **1**-12 > **1**-16 > **1**-8 > **1**-1, whereas the order for the quenching of the **1**-12* monomer by **2**-*n* is **2**-12 > **2**-16 > **2**-8.

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The above-mentioned orders clearly show that in the quenching process between **1**-*n* and **2**-*n* (1) there is a chain-length effect for the Ksv values, i.e., **1**-12 > **1**-8 > **1**-1 and **2**-12 > **2**-8 (in other words, molecules with longer hydrocarbon chains have a higher coaggregating tendency)[13,14] and (2) there may be a chain-foldability effect, i.e., flexible hydrocarbon chains with more than about 16 CH_2s have a greater tendency to fold on itself than those with 12 CH_2s, and consequently, the aggregating tendency of a 16-carbon chain becomes smaller than that of the 12-carbon chain.[13,14,28] In other words, with the same acceptor **2**-12, **1**-16 < **1**-12, and with the same donor **1**-12, **2**-16 < **2**-12.

Solvent aggregating power (SAgP) is an inherent solvent property[13,14] expected to exert an effect on the efficiency of fluorescence quenching. In a given aquiorgano solvent system, the SAgP can be raised by decreasing the ψ value. In Figure 3, at two constant concentrations of **1**-12, i.e., [**1**-12] = 0.5×10^{-5} M (solid line) and 0.2×10^{-5} M (dashed line), the Ksv values are plotted against ψ. As a whole, Ksv values increase with decreasing ψ values as expected from the fact that within a limited range of ψ values SAgP and ψ are almost linearly related.[11,12,29] Interestingly, at approximately $\psi \leq 0.40$, there appears to be a surge of Ksv for both of the two curves. This might be a consequence of factors (e.g., change of solvent structure) which we do not yet understand.

Finally, we have a few words of comment on Ksv values. Our Ksv values are also in harmony with the static (preassociation) mechanism viewed from a different perspective. For diffusional quenching, it is generally known that Ksv is equal to $kq\tau_0$, where kq is the bimolecular rate constant and τ_0 is the monomer lifetime of **1**-12* in the absence of quencher. If we take the case of **1**-12 at $\psi = 0.40$, together with the τ_0 value of 44.4 from the list of our experimentally measured τ_0 values at graded ψ values, i.e., the τ_0 value is 44.4 ns at $\psi = 0.40$, 48.7 ns at $\psi = 0.45$, 50.4 ns at $\psi = 0.50$, 51.1 ns at $\psi = 0.55$, and 52.5 ns at $\psi = 0.60$, then $kq = (13.7 \times 10^4\ M^{-1})/(44.4 \times 10^{-9}\ s) = 3.0 \times 10^{12}\ M^{-1}\ s^{-1}$. This calculated kq value is certainly much larger than the diffusion-limited kq value (ca. $10^{10}\ M^{-1}\ s^{-1}$) of the diffusion-controlled quenching process.[30] In other words, a diffusional fluorescence quenching mechanism is very unlikely.

In conclusion, we have demonstrated that HLI-driven coaggregation of a donor and an acceptor can very effectively facilitate the electron transfer processes between that donor and acceptor because they become preassociated inside the coaggregate species.

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