Spectroscopic Characteristics and Intermolecular Interactions of Thiophene/Phenylene Co-Oligomers in Solutions

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Thiophene/phenylene co-oligomers that include the thiophenes and phenylenes with various arrangements in the molecule were investigated spectroscopically in solutions and compared with oligothiophenes and oligophenylenes. The electronic spectra are influenced by both the molecular size and the difference in the thiophene/phenylene arrangements. In the dilute regime ($\sim10^{-5}$ M) monomeric emissions prevail. Quantum efficiencies of the fluorescence emissions of the co-oligomers are estimated in this regime. High quantum efficiencies of 0.79 and 0.74 were recorded for 4,4′-bis(2-thienyl)biphenyl (T2P) and 1,4-bis(5-phenylthiophene-2-yl)benzene (AC5), respectively. The experimental data in the dilute regime are compared with the results of the quantum chemical calculations at semiempirical levels. Intermolecular interactions increasingly play a role for higher concentrations. The spectroscopic characteristics in this regime are closely inspected using 2,5-diphenylthiophene (P1T), 5,5′-diphenyl-2,2′-bithiophene (P2T), and 1,4-bis(2-thienyl)benzene (T1P). By increasing the concentration, these co-oligomers show well-structured emissions that are red-shifted relative to the monomeric emissions. New absorption shoulders appear in the longer wavelengths region due to the intermolecular interaction. These features are assigned to the intermolecular ground-state complexes with fully overlapped $\pi-\pi$ groups. Besides the above spectral features, T1P exhibits a long tail toward ~700 nm in the absorption spectra at higher concentrations and a broad emission band around 520 nm replaces the strong band at 450 nm. We referred these features to the intermolecular charge-transfer from a thiophene to a phenylene ring. The fluorescence emissions of the co-oligomer thin films are also red-shifted relative to the monomeric emissions. The origin of these emissions in the solid state is briefly discussed.

1. Introduction

Organic semiconductors typified by conjugated polymers and oligomers have been investigated intensively in the past few decades because of their unusual electrical and optical properties. Of special interest are electroluminescence, photoconductivity, photovoltaic effects, and the electrical conductivity of oxidized or reduced materials.[1−6] Moreover, the nonlinear optical effects of these materials have been studied in detail and their response is found to be much faster than that of any other semiconductors.[7−9] These aspects make the organic semiconducting materials applicable to electronic and photonic devices such as field-effect transistors and light-emitting diodes. Oligothiophenes and oligophenylenes are typical of those materials.[10−17]

Of these, the oligothiophenes permit color tuning through the control of the π-conjugation length. Because of the planar molecular structure, they show a strong redshift in the electronic spectra by increasing the repeat units in the molecules.[13,18−24] This planar structure, on the other hand, causes aggregation of the molecules and weakens the quantum efficiency of fluorescence.[22,23] Meanwhile, the oligophenylenes have higher quantum efficiencies owing to the suppression of such aggregation. A

quantum efficiency even up to 1.0 was observed.[25] Nonetheless, highly twisted molecules limit the π-delocalization and, hence, increase the optical transition energy.[25−28]

Thus, from the point of view of the optical device applications, it is difficult in these two classes of materials to obtain both high quantum efficiency of fluorescence and wide spectral range of emissions. To circumvent these drawbacks, amorphous molecular compounds based on oligothiophenes have recently been proposed and synthesized as novel light-emitting materials.[29−31] These compounds had an improved quantum efficiency of electroluminescence compared to conventional oligothiophenes. Hotta and Lee[32] used thiophene/phenylene co-oligomers in which the total ring number of thiophenes and phenylenes and their mutual arrangement were suitably changed. This allows a variation of the π-conjugation extension in the molecule, leading to a wide spectral range of fluorescence (blue to orange).[33]

In the present paper we investigate spectroscopic features in solution for various thiophene/phenylene co-oligomers with different ring numbers and arrangements, trying to establish how the molecular size and the arrangement of the thiophenes and phenylenes influence the spectra. To this end, the absorption and fluorescence spectra were recorded both in the dilute regime ($\sim10^{-5}$ M) and at higher concentrations according to whether intermolecular interactions play a role. The experimental results in the dilute regime are interpreted in light of the semiempirical

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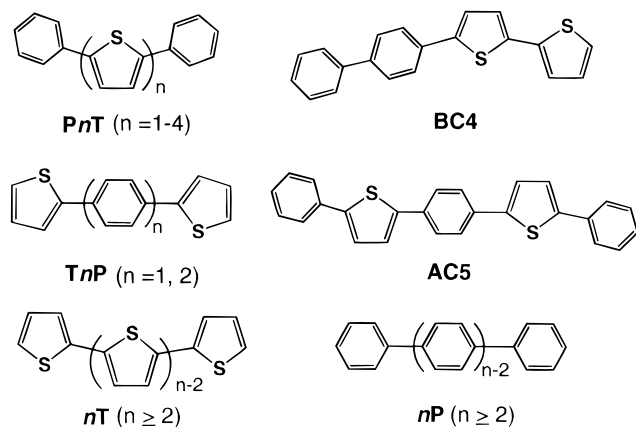‡ Joint Research Center for Harmonized Molecular Materials.

Figure 1. Chemical structures of a series of thiophene/phenylene co-oligomers; phenyl-capped oligothiophenes (PnT), thienyl-capped oligophenylenes (TnP), a block co-oligomer (BC4), and an alternating co-oligomer (AC5). The chemical structures of oligothiophenes (nT) and oligophenylenes (nP) are depicted for comparison.

calculations. Solvent and concentration effects on the electronic spectra were examined to study molecular interactions. The spectra of thin films were measured and compared with those in solutions to elucidate the origin of the solid-state fluorescence.

2. Materials and Methods of Measurements and Calculations

Figure 1 shows chemical structures and abbreviated notations of the thiophene/phenylene co-oligomers. These include phenyl-capped oligothiophenes (PnT), thienyl-capped oligophenylenes (TnP), a block co-oligomer (BC4), and an alternating co-oligomer (AC5). The molecular structures of the oligothiophenes (nT) and oligophenylenes (nP) are depicted for comparison. Thin films (0.5 μm in thickness) were prepared either by evaporating the materials in a vacuum or by casting dichloromethane solutions onto the quartz glasses at room temperature. The detailed synthetic and purification methods of the co-oligomers and the preparation methods and conditions for the thin films can be seen elsewhere.[33,34]

UV−vis absorption spectra and steady-state fluorescence spectra were measured at room temperature using a Shimadzu UV-2500PC spectrophotometer and a Jasco FP-777 spectrofluorometer, respectively. Lifetimes of the fluorescence emissions (τ_F) were measured in chloroform solution using a Horiba NAES-700. N$_2$ laser pulses of a 337 nm wavelength were used as an excitation light source. Quantum efficiencies of fluorescence (Φ_F) were measured by the comparative method[35] against standard samples of quaterthiophene ($\Phi_F = 0.18$)[13] and anthracene ($\Phi_F = 0.22$)[36,37] dissolved in ethanol. Spectroscopic grade chloroform, dichloromethane, acetonitrile, and ethanol provided by Tokyo Kasei Co., were used as solvents without further purification. The spectroscopic results of the co-oligomers were compared with those of quaterthiophene (4T) and quaterphenylene (4P).

Quantum chemical calculations at semiempirical levels were performed using a WinMOPAC Ver2.0 package (Fujitsu) for Windows 95. Preliminarily, we chose the PM3[38] (in MOPAC97) as the calculation method and optimized the geometry using 4P and 4T as model compounds. The optimized geometry reproduced those of the existing molecules; the twisting angle of 47° for 4P is consistent with that of oligophenylenes[25,39] and the planar S-trans conformation for 4T represents the crystallographically determined structure.[40] Therefore, we determined the optimum geometry of the co-oligomers on the basis of the
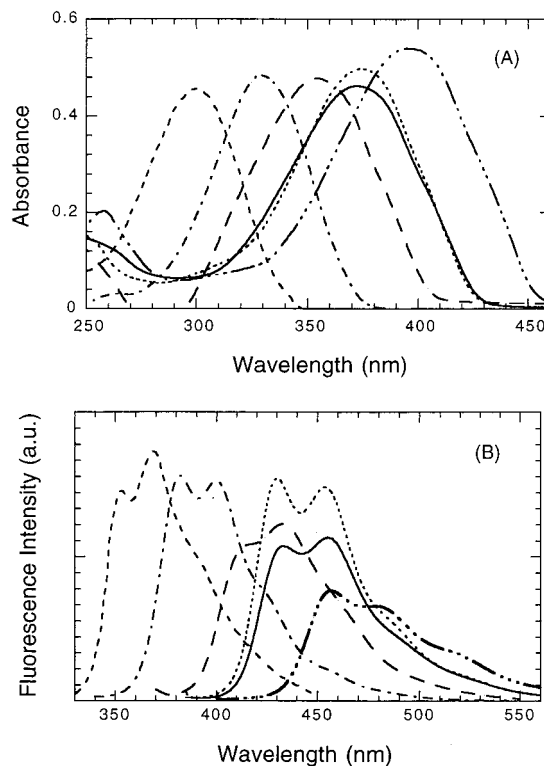

Figure 2. Arrangement effect of thiophenes and phenylenes on the absorption and fluorescence spectra of the co-oligomers and their homooligomers, 4P and 4T, measured in 10^{-5} M chloroform solutions. (A) The absorption spectra. (B) The fluorescence emission spectra are excited at each absorption maximum. 4P(- - -), T2P($- \cdot -$), BC4 ($- - -$), AC5($\cdots$), P2T($-$), and 4T ($- \cdot\cdot$).

PM3 method. The electronic spectra and related physical quantities were calculated using the CNDO/S[41] method in a MOS−F Ver4[42] software (Fujitsu).

3. Results and Discussion

3.1. Arrangement and Size Effects in the Co-Oligomers. Figure 2 represents the absorption and fluorescence spectra of several co-oligomers and their parent homooligomers 4T and 4P, measured in chloroform solutions in the dilute regime (10^{-5} M). The absorption spectra reflect a variety of electronic structures due to different mutual arrangements of thiophenes and phenylenes in the molecules [Figure 2A]. The progressive redshift in the $\pi-\pi^*$ transition maxima reflects the π-delocalization increasing in the order of T2P, BC4, AC5, and P2T, whose absorption maxima are peaked at 328, 355, 374, and 376 nm, respectively. The homooligomers 4P and 4T show the absorption bands at 299 and 396 nm, respectively, located on either side of the spectral range of the above four co-oligomers.

The fluorescence emission spectra also reflect the arrangement effect as shown in Figure 2B. These spectra show well-structured emission maxima and a shoulder. The emission maxima related to the 0−0 bands are located at 380, 412, 430, and 433 nm for T2P, BC4, AC5, and P2T, respectively. The corresponding emission maxima of 4P and 4T are observed at 354 and 454 nm, respectively, also located on either side of the spectral range of the co-oligomers. As one of the arrangement effects, P2T and BC4 show more red-shifted absorption and fluorescence emission spectra than T2P.

To examine the molecular size dependence of the electronic spectra, we show in Figure 3 A,B the absorption and fluorescence spectra, respectively, for PnT and TnP measured in chloroform solutions (10^{-5} M). The absorption spectra of PnT

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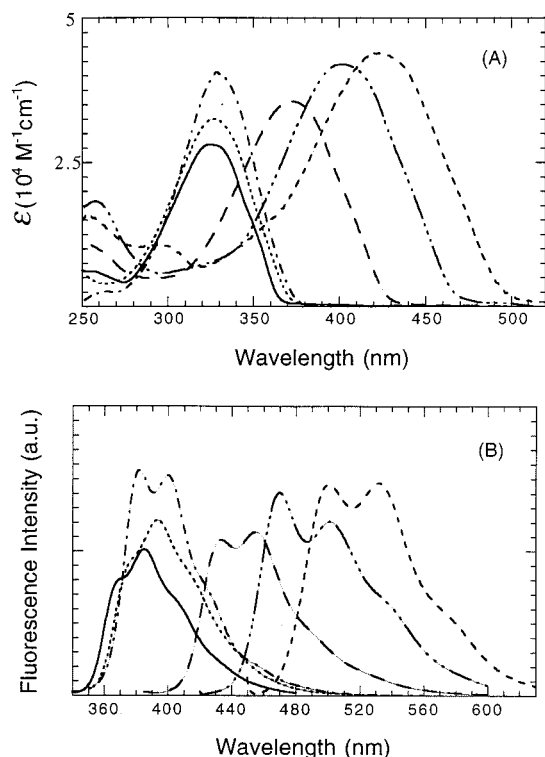*J. Phys. Chem. A, Vol. 104, No. 9, 2000* **1829**

Figure 3. Size dependence on the absorption and fluorescence spectra for PnT and TnP, measured in 10^{-5} M chloroform solutions. (A) The absorption spectra. (B) The emission spectra are excited at each absorption maximum. T1P(—), T2P(— ·—), P1T(···), P2T(— — —), P3T (— ··), and P4T(- - -).

are shifted to longer wavelengths in accordance with the extension of the π-conjugation length and show the $\pi-\pi^*$ absorption bands at 326, 376, 404, and 423 nm for $n = 1, 2, 3$, and 4, respectively. In Figure 3B the fluorescence emission spectra of PnT also show that the emissions are red-shifted as the number of repeat units is increased. The fluorescence emissions of PnT are well-structured with two peaks and a shoulder. Of these, the 0−0 bands are observed at 378, 433, 470, and 500 nm for $n = 1, 2, 3$, and 4, respectively. By contrast, the electronic spectra of TnP are not shifted significantly to longer wavelengths when the number of repeat units is increased from 1 to 2. The absorption bands are peaked at 325 and 328 nm for T1P and T2P, respectively [Figure 3A]. Their fluorescence spectra also show small shifts with the emission maxima at 368 and 385 nm for T1P, and 380 and 400 nm for T2P. The results for PnT and TnP agree well with those for a series of

nT[30,31,43,44] and nP,[45] respectively, when one views the band shift as a function of n.

Table 1 summarizes the spectroscopic results of the co-oligomers measured in the dilute regime. These include the theoretical values of absorption maxima and ionization potentials (I_P). The thin films data are listed for comparison. The fluorescence emissions are attributed to the monomeric emissions in the dilute solution, because the fluorescence excitation spectra correspond to the absorption spectra (see Table 1). This implies that the molecular interactions do not take place in the ground state or excited states. The fluorescence emissions of the co-oligomers decay with a single exponential, whose lifetime is a good measure of the extension of the π-conjugation length. As an example, the lifetimes of the emissions for a series of PnT are progressively elongated from 0.72 ns for P1T to 1.02 ns for P4T (Table 1). This agrees with the results observed by Becker et al.[13] and Grebner et al.[43,44]

As compared with homooligomers, all the thiophene/phenylene co-oligomers exhibit higher quantum efficiency than 4T and lower than 4P. The quantum efficiencies decrease in the order of 4P ($\Phi_F = 0.8$), T2P (0.79), AC5 (0.74), BC4 (0.54), P2T (0.29), and 4T (0.18). Exceedingly high quantum efficiencies are observed in T2P ($\Phi_F = 0.79$) and AC5 (0.74). AC5 can be regarded as a molecule that is formed by inserting a phenylene into the molecular center of P2T. Quite interestingly, the quantum efficiency can be improved from 0.29 (for P2T) to 0.74 (for AC5) by this molecular manipulation. Meanwhile, if one notices the related spectral data of P2T and AC5 in Table 1, this manipulation turns out to keep the π-conjugation extension unchanged. Moreover, if one compares the spectral data of T2P and AC5, AC5 exhibits the $\pi-\pi^*$ absorption maximum at 374 nm red-shifted by 46 nm relative to that for T2P, while retaining a high quantum efficiency comparable to that of T2P. These aspects indicate that the extended π-conjugation and the high quantum efficiency of fluorescence emissions are not at all mutually exclusive. This can be counted among specific effects that are produced by appropriately arranging thiophenes and phenylenes in the co-oligomers.

The results of the theoretical calculations explain the experimentally observed data appreciably well except for P4T to which the molecular geometry could not be optimized (see Table 1). In particular, the accordance in the absorption maxima between the experiments and theory is satisfactory for T1P, T2P, and P1T. Although the discrepancy is somewhat large for other co-oligomers, yet the theoretical data reflect the redshift that is enhanced in the order of BC4, AC5, P2T, and P3T. Regarding the former three compounds, the planar molecular structure was

TABLE 1: Experimental and Theoretical Spectroscopic Data of the Thiophene/Phenylene Co-Oligomers and Homooligomers (4P and 4T)[a]

	abs max, λ_{max}/nm							thin film	
sample	experiment ($\epsilon/10^3$ M^{-1} cm^{-1})[b]	theory (f)[c]	ex max (λ_{max}/nm)	em max (λ_{max}/nm)	Φ_F	τ_F/ns	I_p [theory (eV)]	abs max (λ_{max}/nm) (0-0)	em max (λ_{max}/nm)
4P	299 (39.4)[d]	289 (1.73)	300[d]	354,[d] 367[d]	0.8[d]	0.7[d]	8.67	365[d]	419[d]
4T	396 (31.5)	461 (1.59)	398	454, 484	0.18[e]	0.53[e]	8.49	455	555, 600
T1P	325 (28.0)	338 (1.28)	328	368, 385	0.56	0.77	8.73	361	450, 470
T2P	328 (40.6)	340 (1.88)	330	380, 400	0.79	0.84	8.39	383	455, 485
P1T	326 (32.5)	337 (0.82)	330	378, 393	0.24	0.72	8.69	375	455, 470
P2T	376 (35.5)	423 (1.53)	376	433, 455	0.29	0.85	8.44	440	515, 550
P3T	404 (41.9)	471 (1.87)	400	470, 500	0.32	0.89	7.14	476	540, 575
P4T	423 (43.8)	[f]	424	500, 530	0.33	1.02	[f]	506	575, 620
BC4	355 (28.7)	399 (1.53)	360	412, 433	0.54	0.52	8.46	411	515, 545
AC5	374 (41.5)	412 (2.06)	376	430, 453	0.74	0.82	8.36	445	530, 560

[a] The spectra were measured in dilute chloroform solutions (10^{-5} M). [b] Molecular extinction coefficient. [c] Oscillator strength. [d] Reference 25. [e] Reference 13. [f] Molecular geometry was not optimized.

reached after the geometry optimization. The three thiophene rings of P3T also have the planar (S-trans) structure, even though one of the two adjacent thiophene/phenylene pairs exhibits a twist angle of 48°. Such planar structures, however, are difficult to retain in the solution and the resulting ring twisting causes a blue shift in the electronic spectra on account of the segmentation of the π-electronic wave function.[46] Consequently, if the ring twisting had appropriately been taken into account, the theoretical values would have been closer to the experimental results. As for T1P, T2P, and P1T, on the other hand, the number of rings which the planar structure encompasses is not more than two. The ring twisting up to 49° is predicted for one of the adjacent thiophene/phenylene pairs of these three molecules and for an adjacent phenylene/phenylene pair of T2P. In other words, the segmentation of the wave function is thought to have already taken place. This is expected to resemble an actual situation in the solution, rendering the theory reliable.

3.2. Intermolecular Interactions in the Co-Oligomers. In the previous subsection, we dealt with the spectroscopic results in the dilute regime where the intermolecular interactions are suppressed to the smallest possible extent. In this subsection, we study the molecular interactions in solution by inspecting effects of concentration and solvent species on the electronic spectra.[47] Intermolecular interactions increase with solution concentrations. Even if there are no interactions between electronic systems in the ground states, it is possible that various interaction processes arise in the excited electronic states. This is because the electron affinity of a molecule is larger and its I_P is smaller in the electronically excited state than in the ground state.[48] The electron donor−acceptor interaction, i.e., the charge-transfer (CT) interaction, is a typical example.[48,49] Here we present the spectroscopic data and discuss their physicochemical implications for P1T, P2T, and T1P.

Examining the concentration and solvent effects on the electronic spectra is also useful in elucidating the origin of the solid-state fluorescence emissions in the co-oligomers. In this context we mention briefly the spectroscopic features of thin films. Of these, PnT films show a strong red shift as a function of n in the electronic spectra, e.g., the 0−0 bands of the fluorescence emissions are observed at 455, 515, 540, and 575 nm for $n = 1, 2, 3$, and 4, respectively.[33] On the other hand, TnP films exhibit small shifts in the electronic spectra; the fluorescence emissions peak at 450 and 455 nm for $n = 1$ and 2, respectively. This trend agrees with that observed for the solutions. The co-oligomer films show the red-shifted fluorescence emissions relative to the monomeric emissions, probably resulting from intermolecular interactions.

(i) Formation of Intermolecular Ground-State Complexes. Figure 4 represents the concentration dependence of the absorption spectra of P1T in chloroform (6.6×10^{-6} to 1.2×10^{-2} M). In the dilute regime, the $\pi−\pi^*$ absorption band is positioned at 326 nm with an absorption edge at 375 nm. With increasing concentration, however, a new absorption shoulder appears around 400 nm and grows gradually with the edge shifted to 430 nm. This absorption shoulder is attributed to the ground-state complexes formed by intermolecular interactions because it is not observed in the dilute regime.[47] The presence of the intermolecular interaction is more evident in the fluorescence spectra, since it occurs easily in the electronically excited state.[48] Figure 5A displays the fluorescence emission and excitation spectra of P1T at a low concentration of 6.6×10^{-6} M. The fluorescence excitation maximum is observed at 330 nm correspondingly to the absorption band. The fluorescence emission spectrum has two structured peaks at 378 and 393 nm
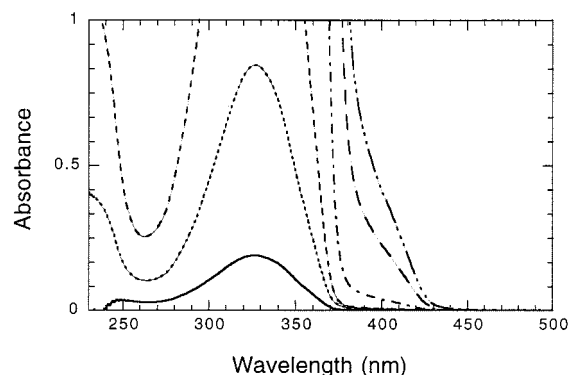

Figure 4. Concentration effect on the absorption spectra of P1T measured in chloroform. 6.6×10^{-6} M(—), 2.6×10^{-5} M(···), 6.6×10^{-5} M(- - - -), 6.6×10^{-4} M(− · −), 6.6×10^{-3} M(− − −), and 1.2×10^{-2} M(− ··).
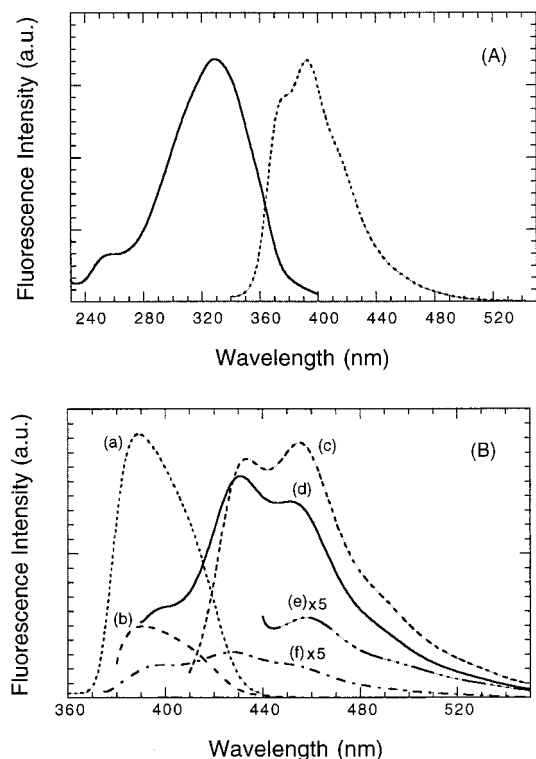

Figure 5. Fluorescence excitation and emission spectra for P1T in chloroform, measured in low and high concentrations. (A) In the low concentration (6.6×10^{-6} M), the fluorescence excitation spectrum was monitored at 400 nm (—) and the fluorescence emission spectrum was excited at 330 nm (···). (B) In the high concentration (1.2×10^{-2} M), (a) and (b) are the fluorescence excitation spectra monitored at 450 and 500 nm, respectively. (c)−(f) are the fluorescence emission spectra excited at 400, 380, 430, and 370 nm, respectively.

(the monomeric emissions). A shoulder is noticeable at around 410 nm. Figure 5B shows the fluorescence excitation and emission spectra of P1T of a high concentration (1.2×10^{-2} M). Strong fluorescence emissions at 430 and 455 nm with a shoulder around 490 nm [excited at 400 nm; see (c)] are red-shifted relative to the above-mentioned monomeric emissions. Note that the monomeric emission is only observed around 395 nm as a shoulder with weak intensity [excited at 370 (f) and 380 nm (d)].

The fluorescence excitation spectra are useful in elucidating the fluorescence emission species. A strong excitation peak is observed at 388 nm [(a) and (b) in Figure 5B] and its tail is extended to 440 nm correspondingly to the new absorption shoulder in the ground state (Figure 4). Therefore, the afore-
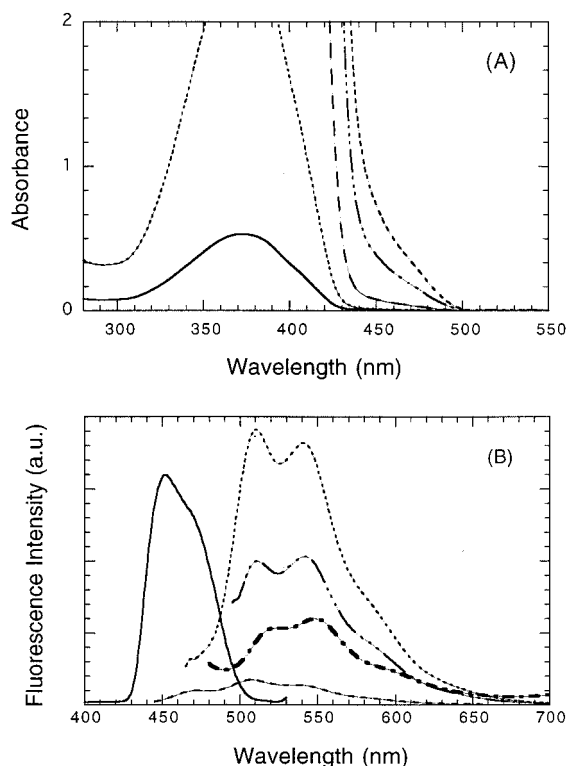
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Figure 6. (A) Concentration effect on the absorption spectra of P2T measured in chloroform. 1.5×10^{-5} M (—), 1.5×10^{-4} M (···), 1.5×10^{-3} M (– – –), 6.5×10^{-3} M (– ··), and 1.2×10^{-2} M (- - -). (B) Fluorescence excitation and emission spectra of P2T in chloroform solution, measured in a high concentration 1.2×10^{-2} M. The excitation spectrum is monitored at 550 nm (—). The emission spectra are excited at 430 (- - -), 450 (···), and 480 nm (– ··). The emission spectrum of the 0.5 μm film, excited at 440 nm (– · —), is shown together.

mentioned emissions at 430 and 455 nm are assigned to ground-state complexes formed between π-conjugated groups, as in oligothiophene thin films.[19,20] The well-structured fluorescence emissions with a strong intensity and the new absorption shoulder indicate that the ground-state complexes are due to the fully overlapped groups by π–π stacking.[50] The fluorescence emissions for the P1T film at 455 and 470 nm (Table 1) are more red-shifted than those of the ground-state complexes in solution (430 and 455 nm). Nevertheless, the close resemblance between the fluorescence emission spectra of the film and concentrated solutions (i.e., two well-structured peaks and a shoulder on the longer wavelengths side) implies that the fluorescence emission spectra of the P1T film are also due to intermolecular ground state complexes of the same origin as mentioned above. The close-packing of the molecules in the film is probably responsible for the additional redshift in this state.[33]

Figure 6A shows the concentration dependence of the absorption spectra for P2T in chloroform solution (1.5×10^{-5} to 1.2×10^{-2} M). The π–π* absorption band of P2T is observed at 376 nm at a low concentration. With increasing concentration, a new absorption shoulder occurs at around 460 nm. In a concentrated solution (1.2×10^{-2} M), the fluorescence emission peaks are shifted from 433 and 455 nm [Figures 2B and 3B] to 510 and 542 nm with a shoulder around 590 nm [see Figure 6B]. The new fluorescence emissions with well-structured peaks are independent of the excitation wavelengths. On the other hand, the monomeric emission is only observed as a weak shoulder at around 470 nm (excited at 430 nm). The excitation maximum at 450 nm with a shoulder at around 470 nm (monitored at 550 nm) corresponds to the absorption
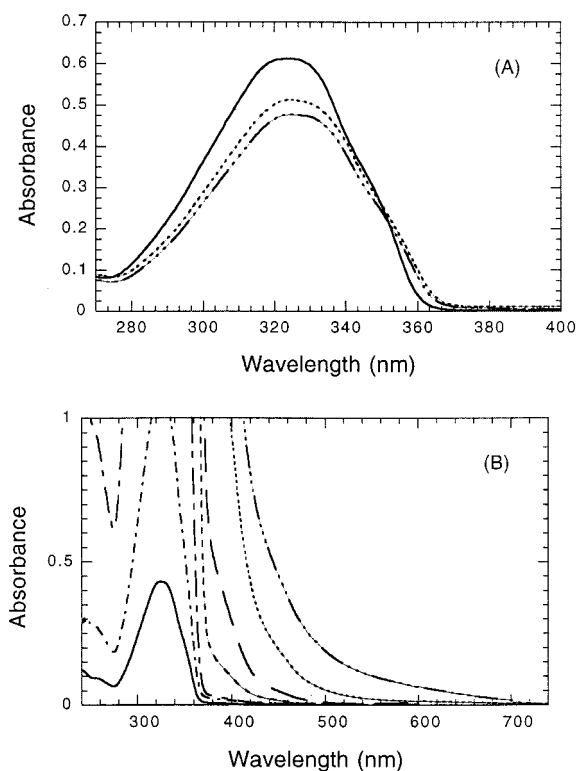

Figure 7. (A) Solvent effect on the absorption spectra of T1P solutions. The concentration was 10^{-5} M in dichloromethane (– ··), acetonitrile (—), or chloroform (···). (B) Concentration effect on the absorption spectra of T1P measured in chloroform. 1.5×10^{-5} M (—), 6.6×10^{-5} M (– · —), 1.5×10^{-4} M (– - –), 6.6×10^{-4} M (- - - -), 1.5×10^{-3} M (– – –), 6.6×10^{-3} M (···), and 1.5×10^{-2} M (– ··).

shoulder in the ground state, again indicating that the above emissions at 510 and 542 nm are due to the intermolecular ground-state complexes comprising the fully overlapped molecules. The fluorescence emissions of the P2T film are observed at 515 and 550 nm with a shoulder at around 600 nm. Although these peaks are slightly red-shifted relative to the emission maxima for the solution of 1.2×10^{-2} M, the spectral profiles are closely related to each other [Figure 6B]. As a consequence, the fluorescent species of P2T are most likely of the same origin in both the film and concentrated solution, as in the case of P1T.

(ii) Formation of Intermolecular Charge-Transfer (CT) Complexes. CT complexes are often formed by the intra- or intermolecular interaction, especially in π-conjugated molecules and occur easily between the electronically ground and excited states.[47] Figure 7A displays the absorption spectra for T1P measured in dilute solutions (10^{-5} M) of chloroform, dichloromethane, or acetonitrile. Each absorption spectrum shows the maximum at 325 nm with a shoulder slightly varied around 350 nm by changing the solvents. An additional solvent effect on the absorption spectra is observed at the longer wavelengths around 360 nm, more red-shifted in chloroform and dichloromethane than in acetonitrile, suggesting some molecular interactions.[47]

Figure 7B shows the concentration dependence on the absorption spectra for T1P, measured in chloroform (1.5×10^{-5} to 1.5×10^{-2} M). In the dilute regime, the absorption band is observed at 325 nm with a tail extended to 360 nm. This absorption tail is gradually shifted to the longer wavelengths with increasing concentration and eventually extended to even 720 nm in a 1.5×10^{-2} M solution. This red-shifted tailing is far larger than that for P1T and P2T. It indicates that the
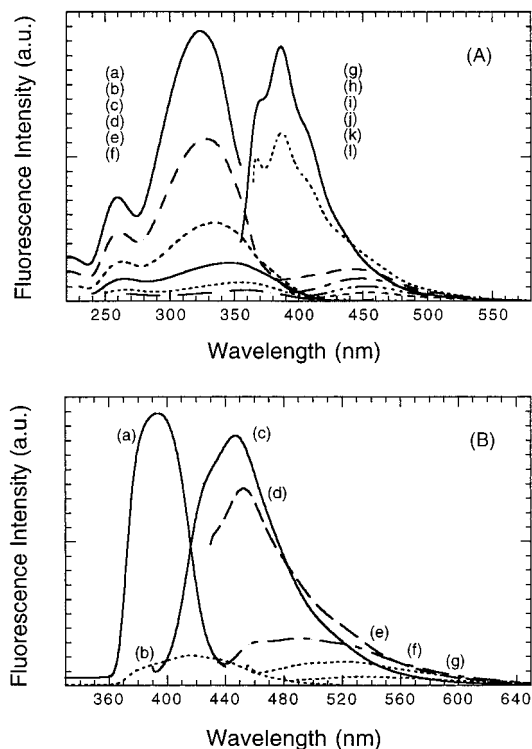
Figure 8. Fluorescence excitation and emission spectra of T1P in chloroform, measured in low and high concentrations. (A) For a 1.5×10^{-5} M solution (a)−(f) are the excitation spectra (starting from the top) monitored at 390, 430, 450, 470, 490, and 510 nm, respectively. (g)−(l) are the emission spectra (starting from the top) excited at 330, 360, 370, 380, 390, and 400 nm, respectively. (B) For a 1.5×10^{-2} M solution (a) and (b) are the excitation spectra monitored at 450 and 550 nm, respectively. (c)−(g) are the emission spectra (starting from the top) excited at 380, 410, 430, 450, and 470 nm, respectively.

absorption spectra result from the formation of the $\pi-\pi$ CT complexes.[48,49] In this context Lee et al.[48a] and Viallat et al.[49] have reported a similar concentration dependent redshift in absorption tails for pyridinium ions coexistent with an electron donor of hexamethylbenzene and soluble poly(ether imides), respectively.

Figure 8A represents the fluorescence spectra of T1P in chloroform (1.5×10^{-5} M). Their spectral profiles are not simple even in dilute solution because of well-structured emissions and the broad emissions in the longer wavelengths region. The structured fluorescence emissions at 368 and 385 nm (the monomeric emissions) are retained for the excitation wavelengths up to 360 nm [(g) and (h) in Figure 8A]. However, this structured emission profile rapidly collapses and becomes broad, and the peak position is red-shifted with longer excitation wavelengths [excited at 370 nm (i) to 400 nm (l)]. The excitation maximum is also red-shifted gradually with increasing monitoring wavelengths from 325 nm [monitored at 390 nm (a)] to 370 nm [monitored at 510 nm (f)]. Figure 8B shows the fluorescence spectra of T1P in a concentrated solution (1.5×10^{-2} M). A strong emission is observed at 450 nm [excited at 380 nm (c)]. This emission becomes again broad and red-shifted gradually by exciting with longer wavelengths and is eventually replaced with a featureless band around 520 nm [excited at 470 nm (g)]. The peak shift and broadening provide a striking contrast to the behavior of P1T and P2T in which the well-structured fluorescence emission maxima are quite persistent and their positions are independent of the excitation wavelengths [compare Figure 8B with Figures 5B and 6B]. The difference between P1T and T1P in the concentration dependent fluores-

cence emissions shown in the present studies thus constitutes one of interesting arrangement effects of the thiophene/phenylene co-oligomers.

The coexistence of the structured strong emission and the broad emission in T1P means that two different chromophores are responsible for the fluorescence emissions of T1P in solution. One associated with the strong fluorescence at 450 nm is attributed to the ground-state complexes due to the overlapped $\pi-\pi$ groups. The other representing the red-shifted broad emission spectra is assigned to the intermolecular $\pi-\pi$ CT complexes.[48] The presence of the former species is also evident from the fluorescence excitation spectrum that shows a strong peak at 393 nm [(a) in Figure 8B] when monitored at 450 nm. This peak is also replaced with a broad excitation band around 420 nm when monitored at 550 nm (b). A longer tail extended to 520 nm in this broad band corresponds to the red-shifted absorption tails and, hence, indicates the presence of the $\pi-\pi$ CT complexes in the ground state. Similar results were reported by other researchers, who referred related red-shifted absorption tails and fluorescence emissions to intra- or intermolecular CT complexes formed either in the ground state or in the excited state.[48,49,51]

Transition energy and I_P of the molecules are important to explain molecular interactions. Varsányi et al.[52] have investigated these quantities for several five-membered heterocycles, and reported a low I_P of 5.8 eV for thiophene. Garcia et al.[53] have reported the intramolecular CT band from thiophene rings to the end nitro groups in end-substituted oligothiophenes. Also, the appearance of an intermolecular CT band in oligothiophenes solutions on addition of electron acceptors has been reported.[54−56] Matsuoka et al.[45] have pointed out that oligophenylenes generate a radical anion by a charge-transfer from tetraethyleneamine to the oligophenylenes. Judging from those findings we assume that the associated CT complexes of T1P are very likely formed between the thiophenes and phenylenes both in the ground state. The charge-transfer is expected to take place from the former (an electron donor) to the latter (an electron acceptor). In T1P film, the strong emissions are observed at 450 and 470 nm by exciting at 360 nm (Table 1). The fluorescence spectra of the T1P film are also broad and red-shifted depending upon the excitation wavelengths. This indicates that the intermolecular $\pi-\pi$ CT complexes again play a role in its fluorescence emissions.

Conclusion

We have investigated the spectroscopic characteristics of the thiophene/phenylene co-oligomers in which the number of thiophenes and phenylenes and their mutual arrangement in the molecules are varied. To study the effects of the molecular size and arrangement on the electronic spectra, we first measured and compared the spectra of the co-oligomers in the dilute regime ($\sim10^{-5}$ M) in which the intermolecular interactions are minimized. Phenyl-capped oligothiophenes (PnT) are better conjugated than other co-oligomers, resulting in the strong redshift both in the absorption and fluorescence emission spectra by increasing the number of thiophenes in the molecules. Thienyl-capped oligophenylenes (TnP) and an alternating co-oligomer (AC5) show higher fluorescence quantum efficiencies. In particular, AC5 exhibits both a high quantum efficiency and an extended π-conjugation and provides an interesting example as the light-emitting material. The experimental results were compared with those of the quantum chemical calculations and the theory interpreted the experimental data recorded in the dilute regime pretty satisfactorily.

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Next, we discussed the spectroscopic features of the co-oligomers in the concentrated regime where intermolecular interactions increase with the solution concentrations. There we focused on the behavior of P1T, P2T, and T1P. In this regime, an absorption shoulder appears at longer wavelengths and grows with the concentration. The fluorescence emission spectra are characterized by the well-structured peaks that are red-shifted relative to the corresponding monomeric emission bands. These absorption and emission features are attributed to the ground-state complexes formed between the fully overlapped $\pi-\pi$ groups. Among the above three compounds, T1P displays an exceedingly long tailing toward ~700 nm in its absorption spectra and a broad featureless band around 520 nm in the fluorescence emission spectra. These result from the intermolecular ground-state $\pi-\pi$ CT complexes. The emission spectra of the thin films of P1T, P2T, and T1P were related to those of the concentrated solutions in both the peak positions and spectral profiles. This indicates that the fluorescence emissions of the co-oligomer films originate mainly from the above-mentioned complexes as well.

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