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Intramolecular photoinduced electron-transfer in azobenzene-perylene diimide*

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This paper studies the intramolecular photoinduced electron-transfer (PET) of covalent bonded azobenzene-perylene diimide (AZO-PDI) in solvents by using steady-state and time-resolved fluorescence spectroscopy together with ultrafast transient absorption spectroscopic techniques. Fast fluorescence quenching is observed when AZO-PDI is excited at characteristic wavelengths of AZO and perylene moieties. Reductive electron-transfer with transfer rate faster than 10^{11} s^{-1} is found. This PET process is also consolidated by femtosecond transient absorption spectra.

Keywords: electron-transfer, femtosecond, AZO-PDI, transient absorption
PACC: 3425, 3320K, 3350D

1. Introduction

Perylene derivatives such as perylene-3, 4:9, 10-bis(dicarboximide) [perylene-diimide (PDI)] dye are very interesting molecular systems, which were intensively investigated for their excellent photophysical properties including broadband absorption from visible to near-infrared, intense photoluminescence with near unity quantum yields, and remarkable n-type semiconductivity.[1−9] In many of these derivatives, PDI works as a remarkable electron-acceptor with fast electron-transfer. Photoinduced electron-transfer (PET) rate is a very important parameter for these dyads. This rate is affected by many factors, such as the match of energy levels between donor and acceptor, the configuration of the molecules, the length and conjugation of the bridges, and solvent environment. The PET rate from fluorene to perylene in 2, 7-bis(N-(1-hexylheptyl)-3, 4:9, 10-perylene-bisimide-N'-yl))- 9, 9-didodecylfluorene (PFP) molecule strongly depending on mediums was reported, and varies more than 2 orders of magnitude (10^8–10^{10} s^{-1}).[1] Intramolecular electron-transfer rates also vary significantly for two different donors in 20-phenyl-substituted Chlorophyll (ZCPh)-PDI and zinc 5,10,15-tri(n-pentyl)-20-phenylporphyrin (Z3PnPh)-PDI system because the change of charge density.[2] When different moieties of the dyads are excited, the competition of excited-state energy-transfer and intramolecular electron-transfer may happen and transfer rates are affected. The effect was reported in several dyads containing PDI as acceptors.[3−6] Oligo (p-phenylene vinylene) (OPV)-perylene compounds were investigated and their electron-transfer rates depended on the configuration of molecules,[7,8] the length of the saturated spacer connecting the OPV and perylene units plays key role on Gibbs free energy of electron transfer and then affects the transfer rate. From all the systems studied, perylene derivatives have almost no ground state coupling with the donor moieties, whose absorption bands are shorter than perylene derivatives.

For the application of future organic solar cells and photosynthetic systems, the free energy of PET should be negative and small enough, then energy barrier would be very small and transfer rate would

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be large to improve conversion efficiency.[1] However, most donor–accepter systems containing PDI can not fulfill the requirement. Current research focuses on this problem and looks for a probable way to solve it. As we know, AZO is a molecule with large extinction coefficient from 300 nm to 420 nm. When its end group is substituted by NH_2, AZO turns to be an electron-rich moiety and becomes an appropriate electron donor. The combination of AZO and perylene will extend the light harvesting in blue side absorption of perylene. However, the efficiency of photo-induced charge separation at donor excitation depends not only on the absorption cross-section of the donor moiety, but also on the electron-transfer rate to perylene. For most dyads, the donor and acceptor are connected by conjugated bridges. However, the bridge may increase the distance between two moieties and decrease transfer efficiency. If the conjugation of donor and acceptor at excited-state is strong enough, direct connection without bridge would be better for electron transfer systems. Here we report the photophysical processes in such a model carrying AZO as donor and PDI as acceptor. The donor and acceptor moieties are directly linked through imides nitrogen atom, with charge transfer along the direction of long symmetric axis of PDI.

2. Experimental section

The synthetic details and chemical characterization of AZO-PDI were published elsewhere.[10] For AZO-PDI, hydrogen of PDI is substituted by AZO-NH_2 at one end and by C_{12} alkyl chain at the other end. The molecular structure of the sample is shown in Fig.1. The AZO-PDI is dissolved in polar and non-polar solvents with concentration diluted to 5.0×10^{-5} M. Absorption and emission spectra of the sample were measured with an Agilent 8453 UV–Vis photodiode array spectrophotometer and a Hitachi F-2500 fluorescence spectrophotometer.

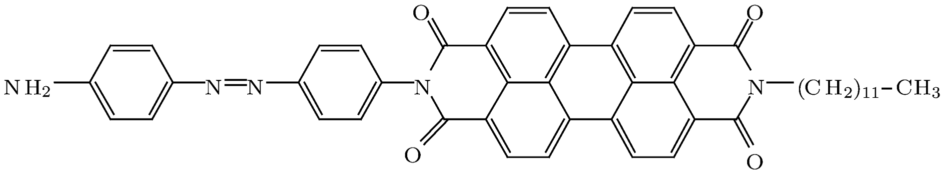

Fig. 1. The Molecular structure of AZO-PDI.

Picosecond time-resolved fluorescence spectra were measured by using a streak camera system. The samples, filled in a revolving spinning cell, were excited by 120 fs pulses at 390 nm and 458 nm, frequency doubled from output of a Ti:sapphire oscillator (Mira 900F, Coherent, USA). Fluorescence was collected at the magic angle to the excitation polarisation, and finally detected with a Hamamatsu C5680 synchroscan streak camera attached to a C5094 imaging spectrograph. The time windows applied were 160 ps and 2.2 ns with 4 ps and 20 ps instrument responses limits, respectively.

Femtosecond transient absorption investigations were carried out by using an ultrafast pump-probe spectrometer detecting in the visible region. Pulse train of 120 fs at 830 nm with a repetition rate of 1 kHz were obtained from a Ti:sapphire regenerative amplifier (Spitfire, Spectra Physics). The output of the laser beam was frequency doubled to generate pump pulse. The probe beam was generated by injecting the rest of the fundamental pulse into a flowing water cell. The optical dispersion was corrected by varying the optical delay line at corresponding wavelength. Photodiode was used for signal detection and reference white light beam was also detected for comparison. The energy of excitation pulse was 200 $\mu J/cm^2$.

3. Results and disscussion

The UV/Vis absorption spectrum and emission spectrum excited by 458 nm of AZO-PDI dissolved in room-temperature dichloromethane (DCM) are shown in Fig. 2. The absorption spectrum presents a structured absorption band between 420 nm and 550 nm, which is the $S_0 \rightarrow S_1$ transition of the PDI chromophore with maximum intensity at 526 nm. The well-resolved vibronic structure can be ascribed to the breathing vibration of the perylene skeleton which coupled strongly with the electronic transition polarised along the long axis of the molecules.[3,11] The energy intervals between the adjacent absorption peaks of vibronic band are 0.175 eV. The aggregation effect can be neglected in dilute solution, since no significant shift of absorption peak is found in comparison with its aggregation form,[3] as observed in Fig. 2. Another absorption band is located around 380 nm, which is accordant to the absorption of AZO moiety. The emission spectrum also presents the vibronic structure of PDI at 530 nm and 570 nm as shown in Fig. 2. The emission spectra of AZO and PDI monomers are also detected. The emission spectrum of PDI is same as that of AZO-PDI, which consolidates that the emission is from PDI moiety. The emission intensity of AZO is only 1% of PDI emission and can be neglected.

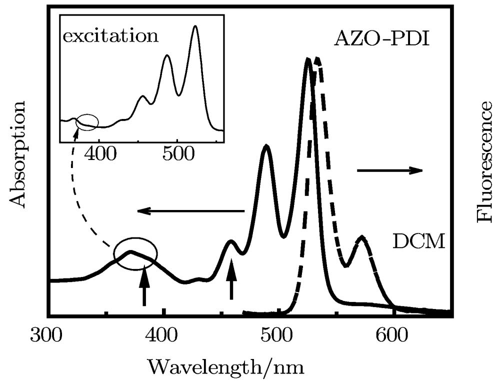

Fig. 2. The UV/Vis absorption spectrum and emission spectrum excited at 458 nm. Inset: Excitation spectrum of AZO-PDI observed at 570 nm.

The fluorescent quantum yield (FQY) is 0.22 for excitation at 458 nm and 0.06 at 373 nm, respectively. The FQY of PDI and its derivatives has been studied by many groups. Icli *et al.* found that the FQY of perylene 4-carboxylphenyl-bis-diimide dissolved in $CHCl_3$ is 0.87.[12] Nagao presented similar results of PDI derivatives from 0.6 to 0.9.[13] Flors *et al.* verified the FQY of PDI again with the value of 0.9–1.0.[14] The sample of AZO-PDI shows significant lower FQY at various excitation wavelengths, which usually indicates a special mechanism for fluorescence quenching in the molecule. The molecular excitation spectra are detected at emission of 530 nm and verified at 570 nm, as shown in inset of Fig. 2. The excitation spectra at both observed wavelengths are almost the same, which confirms that these two peaks are from same electronic excited state. Another characteristic is that the absorption band of 380 nm is missing in excitation spectra, which means that the band has little contribution to fluorescence emission from PDI moiety. This absorption band correspond to $\pi \rightarrow \pi^*$ transition of AZO, with weak ground state coupling to PDI moiety. The excitation spectra uncover another absorption (excitation) band shorter than 400 nm, which originates from S_0 to S_2 transition of PDI according to the study of the Wasielewski group.[15]

Figure 3(a) shows the picosecond fluorescence decay of the AZO-PDI at the peak of 530 nm excited at 458 nm and 390 nm. All decays are reconstructed with a sum of two exponentials convoluted with instrumental response function. The fitting results employing a least-squares fitting procedure are acquired by using Fluofit, a global fluorescence decay data analysis software. When AZO-PDI is excited, the quick decay component of fluorescence is 9.6 ps (49%) and the slow process is 2.5 ns. The later process is regarded as the excited state lifetime of PDI. According to the study of Flors *et al.*[14] and Kirmaier *et al.*,[16] only nanosecond decay from 3.6 ns to 3.8 ns exists in the singlet excited state of PDI derivatives, while the ultrafast decay process is not observed in these molecules.

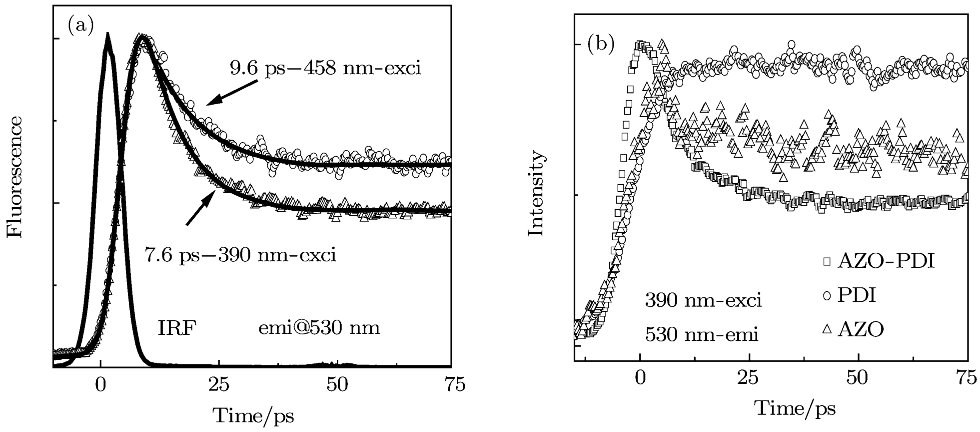

Fig. 3. Time-resolved emission of: (a) AZO-PDI dissolved in DCM observed at 530 nm excited at 458 nm and 390 nm; (b) AZO and PDI monomer in DCM observed at 530 nm excited at 390 nm.

For the emission of PDI monomer, there is no ultrafast component in fluorescence decay, which consolidates the ultrafast decay of AZO-PDI originated from electron transfer, as shown in Fig. 3(b). In our compound, AZO moiety plays a key role in the ultrafast fluorescence quenching process. This fast decay component may correspond to intramolecular energy-transfer or electron-transfer process. However, at 458 nm excitation, photoinduced energy-transfer from PDI to AZO could be neglected due to two reasons: (i) the absorption cross-section of AZO is quite small in visible range; (ii) the emission of PDI and the absorption of AZO are mismatched. Thus, only the electron-transfer process could take place in the system. The energy level scheme of intramolecular electron transfer is shown in Fig. 4(a). For the electron acceptor moiety PDI, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are −6.03 eV and −3.71 eV, respectively.[3] The energy gap is 2.32 eV. The molecular orbital of electron donating group, azobenzene, are π, n and π^*, at −6.34 eV, −5.3 eV and −2.9 eV, respectively.[17,18] The HOMO and LUMO levels correspond to n and π^* orbital. When PDI is excited from HOMO to LUMO by 458 nm, HOMO electrons of AZO will transfer to empty HOMO of PDI, which produces fluorescence quenching as fast as 9.6 ps. This process is defined as reductive electron transfer and is further proved by the transient absorption spectroscopy (see below). Intramolecular electron-transfer rate can be calculated by equation $k_{\text{et}} = 1/\tau_{\text{et}}$ and the result is 1.0×10^{11} s^{-1} for AZO-PDI. This rate varies in one order of magnitude in perylene derivatives. Neuteboom and his fellows studied PFP molecule, electron-transfer rate from fluorine to perylene is $\sim9\times10^{9}$ s^{-1},[1] and the charge separation rate k_{CS} from pentathiophene to PDI ranges from 10^{10} s^{-1} to 10^{11} s^{-1}.[6] Faster charge separation rate higher than 10^{12} s^{-1} could be found in aggregates such as OPV-perylene.[19] From these reports, AZO-PDI is proved to be one of the most effective electron donor-acceptor systems and can provide a relatively high intramolecular transfer rate. This could be due to the short distance between the moieties. Photo-induced isomerization of AZO is also checked. Alternative irradiation at 360 nm and 480 nm are applied and no evidence of isomerization can be found. The isomerization process of AZO-PDI from trans to cis was reported by the first one minute ultraviolet irritation.[10] The AZO-PDI possesses a small amount of cis-AZO groups in the photostationary state and the experiments carried out in current research are for AZO-PDI in photostationary state.

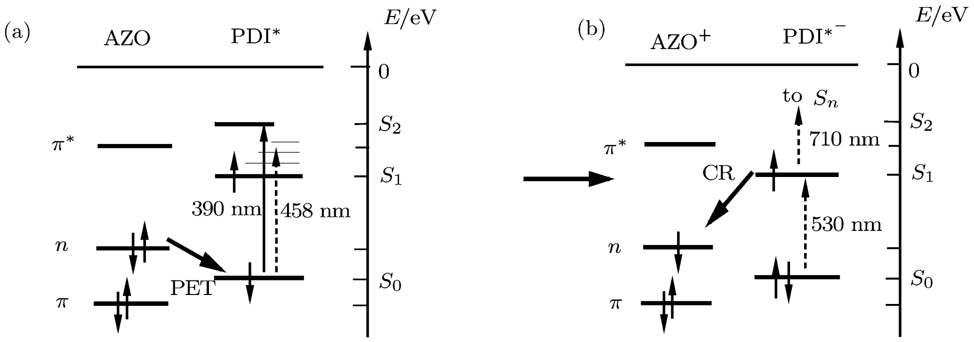

Fig. 4. Schematic diagram for (a) PET and (b) charge recombination.

When AZO-PDI is excited at 390 nm, electrons of AZO are excited from π to π^*, time-resolved emission spectrum also displays an ultrafast and a long time decay. No rising component in fluorescence dynamics, corresponding to the energy-transfer from AZO to PDI, is found. This is consistent to the excitation spectra and quantum yield results as listed earlier. The latter one of 2.1 ns is again the lifetime of the excited state of PDI, which is similar to the excitation at 458 nm. The time scale of ultrafast decay is 7.6 ps (71%). Though slightly faster and larger in amplitude, this quick decay does not show significant difference considering these two excitation wavelengths target to two different moieties. In addition, we expect that the emission again comes from the excitation of PDI itself, but to higher vibration sub-state.

Then the electron transfer can happen again at this excitation wavelength. The enhanced ultrafast decay of 7.6 ps is faster than the corresponding decay excited at 458 nm. This phenomenon may be due to the fact that electrons after higher energy excitation (at 390 nm) are easier to get across the energy barrier of charge transfer than electrons after lower energy excitation (at 458 nm). Another probable reason is the mixing of the AZO fluorescence decay, which can be observed in time-resolved emission spectrum in ultrafast time scale.[20] According to the emission of AZO monomer, an ultrafast decay is observed (Fig. 3(b)), although the emission intensity is much lower than PDI, which explains why the fast decay component of AZO-PDI excited at 390 nm is faster than that excited at 458 nm.When excited at 458 nm, there is no fluorescence emission for AZO monomer. One of the interesting energy-transfer/electron-transfer mixed mechanism is suggested by Majima who claimed that the excitation aimed to donor group would first transfer its energy to the acceptor group, followed by the electron-transfer process similar to the perylene excitation at 550 nm.[6] However, considering the excitation spectrum, low quantum yield, in addition to the data from transient spectra, we can conclude that the energy transfer process is not significant in our system when the AZO moiety is selected to be excited. The reason can be assigned to the fast excited-state decay of AZO, which has been extensively investigated.[21] This efficient energy relaxation process strongly competes with the intramolecular energy-transfer. Therefore the energy-transfer from the excited state of AZO to PDI is largely reduced.

As published in literatures, the intramolecular PET process is extremely sensitive to the solvent environment.[1−3] In order to understand the dependence distinctly, we observed the PET process in AZO-PDI dissolved in several solvents with increasing polarity. Three solvents, toluene, DCM, and tetrahydrofuran (THF) are chosen. The time-resolved fluorescence emission spectra in these solvents are shown in Fig. 5. The decay time and solvent parameters are listed in Table 1. The results reveal that PET process is strongly affected by solvent polarity. With the increase of the solvent polarity, the ultrafast process is faster and the amplitude is enhanced correspondingly. The decay time of 9.3 ps (25%) in toluene reduces to 5.1 ps (67%) in THF. The rate constants of electron-transfer process are determined by the energy barrier of PET.[22,23] As the polarity of solvent increases, the free energy of electron transfer decreases, and then the electron transfer rate increases. That is the reason why intramolecular electron-transfer of AZO-PDI is faster and the decay proportion is larger in THF than in toluene.

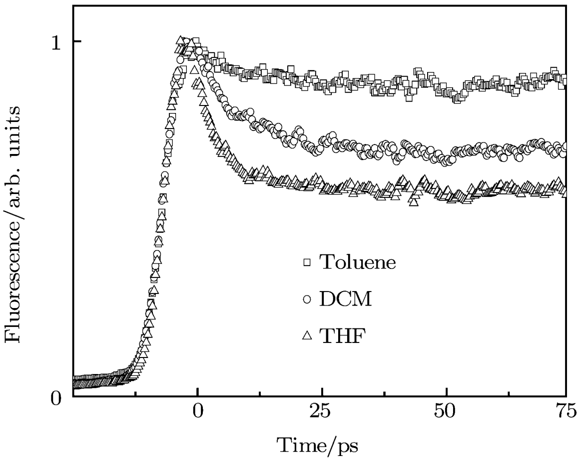

Fig. 5. The time-resolved fluorescence emission spectra of AZO-PDI in several solvents excited by 458 nm.

Table 1. The picosecond fluorescence decays depending on solvent polarities and excitation wavelengths.

solvents	polarity/10^{-30} C·m	fast decay/ps (amplitude)			
		458 nm exc.	FQY	390 nm exc.	FQY
toluene	1.23	9.3(25%)	0.29	8.0(18%)	0.08
DCM	3.80	9.6(49%)	0.22	7.6(71%)	0.06
THF	5.70	5.1(67%)	0.38	4.5(72%)	0.10

The PET process was directly observed by ground state recovery of PDI through femtosecond transient absorption studies with 415 nm pulses. The AZO moiety has very tiny absorption at 415 nm and only PDI moiety is excited. The transient absorption spectra of AZO-PDI in solvent THF are shown in Fig. 6, which presents the characteristic bands and their kinetics. Two absorption bands correspond to the photophysics products. The first band from 440 nm to 560 nm is ground state bleaching, which presents similar fine structure to the static absorption spectra. The initial ultrafast recovery of kinetics at 530 nm (see Fig. 6) confirms the reductive electron transfer from AZO to ground state energy level of PDI, with time constant of 4.6 ps. This is consistent to the fluorescence decay in THF, excited at 390 nm (see Table 1). It should be noticed that another broad absorption band centred at 710 nm corresponds to the absorption from PDI^{*-} state to higher excited state, $S_1 \rightarrow S_n$, according to the research of Wasielewski group.[24] This is proved by the research of Anh *et al.*,[25] the absorption of PDI anion at the band centred at 710 nm, which overlaps with the PDI singlet excited state. The research of Hippius *et al.* about three different types of perylene bisimide chromophores (orange, red,and green PDIs) consolidates the PDI anion absorption at around 700 nm.[26]

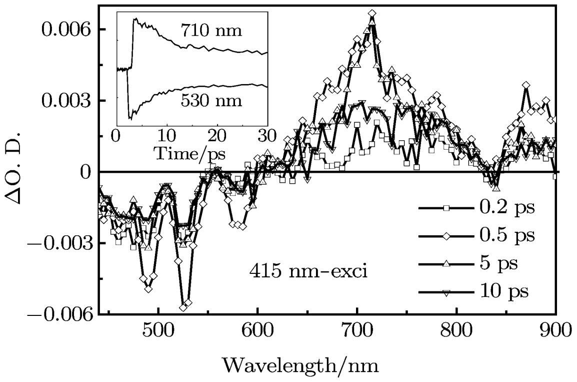

Fig. 6. The femtosecond transient absorption spectra of AZO-PDI in solvent THF. Inset: the kinetics of absorption at 530 nm and 710 nm.

The absorption of AZO$^+$ cation is not observed because the electron transfer in AZO-PDI is reductive electron transfer and AZO moiety is not excited. Therefore, after electron transfer, the AZO$^+$ cation is still on the ground state, the absorption peak of AZO is shorter than 400 nm, according to the steady-state absorption spectrum in our experiment. The researches of Yamaguchi *et al.*[27] and Ho *et al.*[28] proved that the absorption peaks of trans-AZO and cis-AZO are 350 nm and 430 nm respectively. Meanwhile, the observed wavelength range of transient absorption spectrum is between 430 nm to 900 nm, so the absorption of AZO$^+$ cation can not be observed, which is different from some previous researches. Nevertheless, the ground state bleaching from 440 nm to 560 nm and the absorption of PDI^{*-} have proved intramolecular electron transfer The kinetics of 710 nm shows an ultrafast decay with time constant of 7.5 ps, confirmed to be 7.4–10.8 ps at various wavelengths between 580 nm and 780 nm. This ultrafast process may be due to the fast electron backward transfer (recombination) from AZO$^+$-PDI^{*-} to AZO-PDI, as shown in Fig. 4(b). This recombination was also found in perylenebisimide dimmers.[22]

4. Conclusions

Steady-state absorption and femtosecond transient absorption spectra together with time-resolved fluorescence decay are used to study the photophysical processes of compound molecule AZO-PDI. Intramolecular electron-transfer occurs when the molecule is excited at different wavelengths. When AZO-PDI is irradiated, PDI is excited from S_0 to S_1 and electrons on HOMO of AZO transfer to S_0 of PDI. This is a solvent enhanced fast electron-transfer process, and $k_{\rm CS}$ is higher than 1.0×10^{11} s^{-1}. The electron transfer rate is accelerated as the increase of solvent polarity. When the sample is selectively excited at the wavelength of AZO absorption, there is no evidence for efficient energy-transfer from excited AZO group to PDI group. From the high electron-transfer rate, we can deduce that the distance between AZO and PDI is very small. Our study indicates that AZO-PDI holds efficiently fast electron-transfer property. It is also helpful to understand the importance of energy transfer process and efficiency within PDI derivatives.

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