

High-Pressure Tuning of Excited States: Distinguish the Emission of the Exciplexes in the Intramolecular Electron Transfer Compound

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The fluorescence spectra of the intramolecular electron-transfer compound, N-(1-pyrenylmethyl)-N-methyl-4-methoxyniline (Py-Am), have been studied at different pressures. There are three emitting species in the excited molecules of Py-Am for the neat sample, local excited state of pyrene group for monomer emission, intermolecular exciplex, and intramolecular exciplex. The exciplexes are difficult to characterize at ambient pressure. Pressure tuning for the electronic states shows its powerful ability to distinguish the different properties of the states. Under the effect of pressure, the intermolecular and intramolecular exciplexes are observed clearly with different tendencies to change their emission intensity at significantly different wavelengths.

Introduction

Excimers or exciplexes provide an important and common way for energy relaxation in the excited state of molecules. The formation of the excimer or exciplex is not only affected by the intrinsic properties of its donor and acceptor^{1–6} but also by its environment.^{7–10} For intramolecular electron donor–acceptor (D–A) systems, the effect of environment is more conspicuous. It has been reported that valence carbon chain-linked aryl and amine systems have different spectrum behavior in various solvent polarity, viscosity, and temperature.^{11–16} In general, when no carbon chain is present and the donor and the acceptor is connected directly, a twisted intramolecular charge transfer conformation is favorable in the solvents with higher polarity. With a longer chain in the compound between the donor and the acceptor, it is possible to form a planar sandwich-like exciplex, and the polarity of the solvent influences the emission of the exciplex significantly. However, the compounds with one carbon connection usually take a V-like conformation due to the methylene structure. In this case the conformation of the compounds could change in different solvents with the movement of the two end groups.

For the neat sample of intramolecular D–A compound, the fluorescence is relatively complicated because there could be several excited species to emit in the system. One is the intramolecular exciplex between the donor and the acceptor, similar to that in solutions. Another is the intermolecular exciplex between different molecules because the close packing of the molecules in crystal. Meanwhile, an intramolecular excimer formed by the donor or acceptor between two molecules may also exist and give its emission. When the sample is irradiated, it is not easy to characterize the emission band, especially for the sort of exciplex or excimer emission.

Pressure is a good tool for tuning the environment and the electronic states of molecules.¹⁷ With different structures and

different environments in the excited state, the emitting species could have different sensitivities for pressure tuning. Thus pressure could be used for distinguishing the different species from the fluorescence spectra.

The intramolecular D–A compound is a good candidate for the studies in the dynamics and kinetics of complicated emission in the neat sample and crystal. Here we use N-(1-pyrenylmethyl)-N-methyl-4-methoxyniline (Py-Am) as our object compound. In this compound the electron donor is an aniline group (N-methyl-4-methoxyaniline) and the acceptor is the pyrenyl group. Because of the interaction between the donor and the acceptor from different ways in the crystal there could be exist the intramolecular exciplexes, intermolecular exciplexes and intermolecular excimers. Blend film of Py-Am in PMMA is as the model sample. In the blend film, the Py-Am molecules are dispersed molecularly and only the intramolecular interactions between the donor and the acceptor could influence the emission. With the pressure tuning, the emission from different excited species gives different behavior and the reason for the different effects are discussed preliminarily in this paper.

Experiments

Py-Am was synthesized in our lab according to the method in previous work.¹⁸ Pyrene and poly(methyl methacrylate) (PMMA, medium molecular weight) were purchased from Aldrich. The PMMA was used after redeposition before using. Spectral-grade chloroform was used as the solvent to dissolve Py-Am, and PMMA for the film preparation.

For the preparation of the blending film of Py-Am in PMMA, PMMA and Py-Am were dissolved in chloroform and the solution was poured in a glass dish to form a blend film after the solvent evaporated at room temperature. The film was then put in a vacuum oven for a few days at 45 °C. Transparent blend film (about 35 μ m in thickness) was obtained with low concentration (<0.01% for Py-Am) and was optically clear without phase separation.

For fluorescence measurements a Merrill-Bassett diamond Anvil Cell (DAC) was used to generate high pressure. The hole

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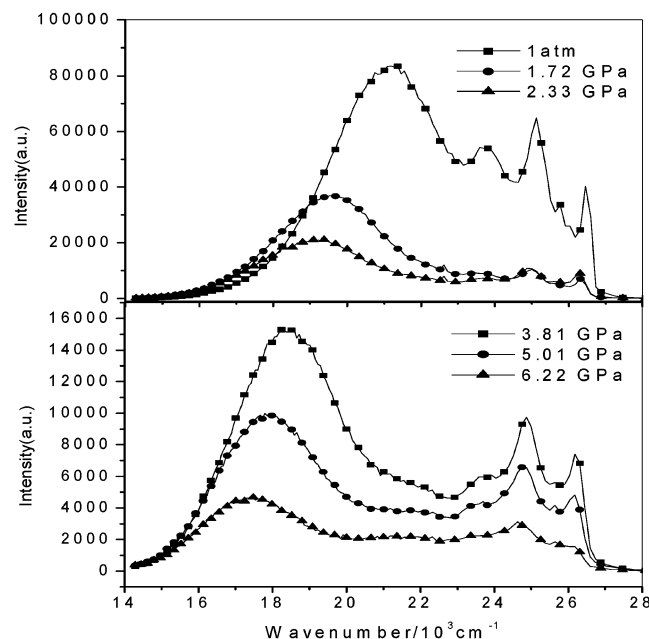


Figure 1. Pressure-dependent fluorescence spectra of Py-Am powder.

diameter of the gasket to hold the sample was about 300 μm with thickness about 90 μm . A small chip of ruby was put in the hole to calibrate the pressure by measuring its fluorescence red shift.^{19,20} Light mineral oil was served as a pressure medium. For the emission detection, a CW He–Cd laser (325 nm, Omnichrom) was used as the excitation source. The fluorescence spectra were dispersed with a 0.3 m spectrometer and a photo multiplier (PMT) coupled to a 32 bit microprocessor-based data acquisition and spectrometer controller module (NCL Electronics Interface, Acton-Research Corporation) and computer. The details of the setups are described in another paper.²¹

Results and Discussion

Figure 1 shows typical pressure-dependent fluorescence spectra of Py-Am powder. At 1 atm, there are two different emission bands. The first one locates at 24–27 cm^{-1} , and it includes several sharp peaks, which present the local excited state emission of the pyrene group in Py-Am molecule. With the increase in pressure, the intensity of the emission of pyrene group is quenched quickly. This can be understood as the pressure effects: under pressure the distance between molecules decreases, but the interactions between the molecules intensify. One of the results is that the thermovibration of the crystal lattice and the radiationless decay becomes intense and the emission is decreased. Meanwhile, it can be seen that the peak location of this band changes slightly with pressure. Another band is much more strong and broad. At 1 atm, the maximum of this band is at about 21.2 cm^{-1} . With the increase of pressure to 1.72 GPa, the peak maximum quickly red shifts to about 19.5 cm^{-1} , and a new broad band arises at around 22 cm^{-1} . When the pressure is up to 6.22 GPa, the former (band A) shifts to about 17.5 cm^{-1} , and the latter (band B) gradually emerges relative to band A and shifts to about 21.5 cm^{-1} . These two bands might be the intermolecular or intramolecular exciplexes of the aniline with pyrene, or the intermolecular excimer of the pyrene groups.

The fluorescence data are fitted by peakfitting, and the results are presented in Figure 2. At 1 atm, the higher-energy emission from the excited pyrene group can be fitted with five peaks, according to the five peaks of pyrene at ambient pressure,²²

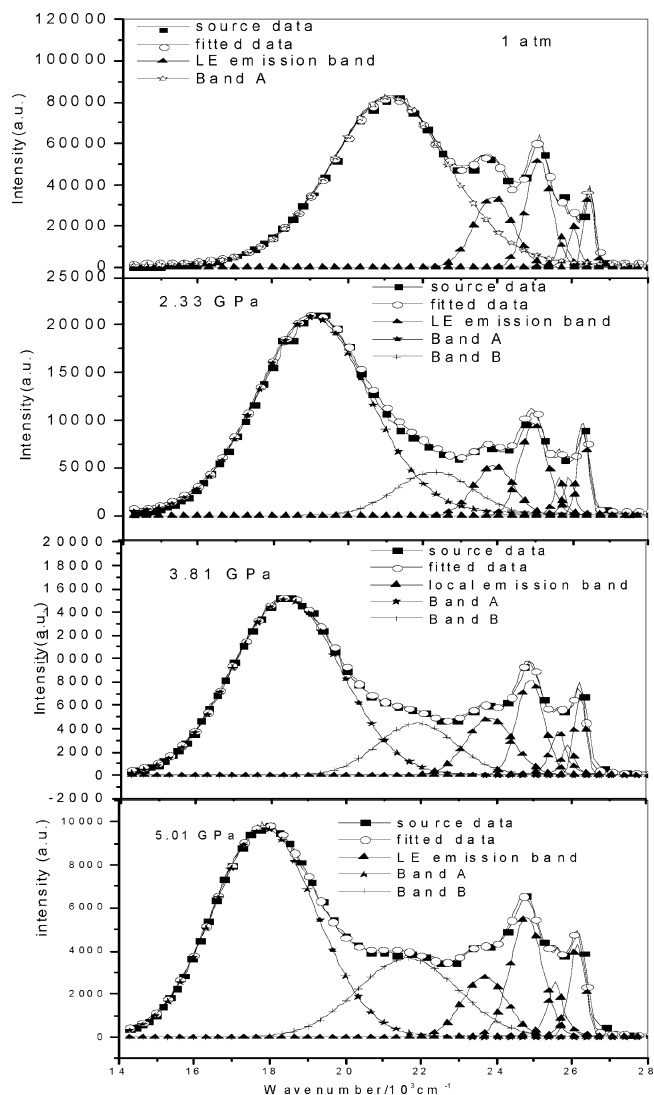


Figure 2. The fitting results of the fluorescence of Py-Am powder at different pressures.

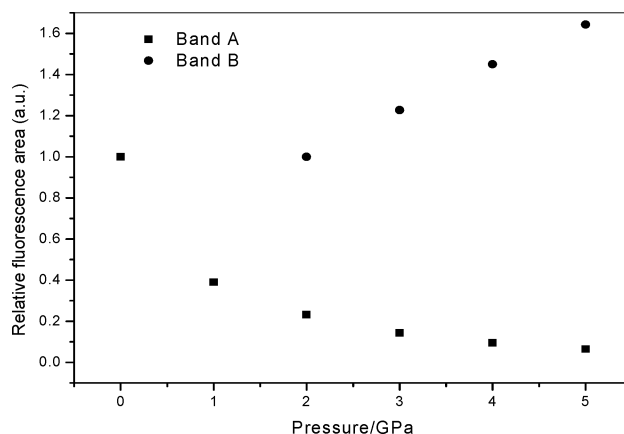


Figure 3. Relative fluorescence area of the two exciplex bands (averaged by two measurement runs).

and at this time band B is covered by band A. With the increase of pressure, band B appears, and both of them shift to red side. According to the normalized fluorescence intensity of these two bands, the pressure dependence of the emission bands (averaged by two measurement runs) is present in Figure 3.

It is clearly illustrated that after the band B is observed (about 2.0 GPa), its emission intensity increases with the increase of

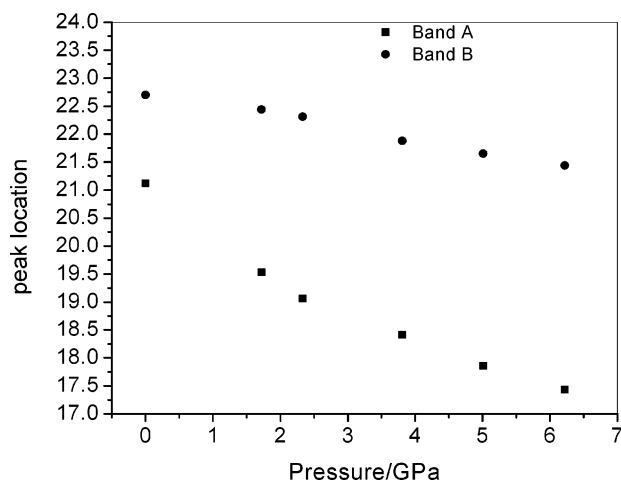
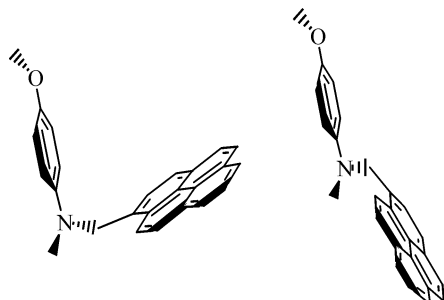


Figure 4. The peak maximum of the two exciplex bands at different pressures.

SCHEME 1: The Stable Conformations of Py-Am cCompound



the pressure. When pressure rises to 5.0 GPa, the relative fluorescence area becomes 1.64 times of that at 2.0 GPa. At 2.0 GPa the emission of band A drops quickly to 23% of that at 1 atm and then decreases slowly to 0.07% at 5.0 GPa. One of the main reasons comes from the adjusting of intermolecular interactions by high pressure, which leads to the great increase of the radiationless decay of the excited molecules. This induces the emission band B at the excited state.

The emission maximum for different bands with pressure is shown in Figure 4, according to the fitting results of the emission. In Figure 4 the peak location of the band B at 1 atm is obtained from the linear extension of the peak location data at other pressures, because at 1 atm band B is covered by the band A and cannot be observed clearly. From Figure 4, it is evident that with the increase of pressure band A and band B have different red shift rates. The maximum of band A shifts from 21.12 k cm^{-1} at 1 atm to 17.43 k cm^{-1} at 6.22 GPa, and the maximum of band B shifts from 22.75 to 21.44 k cm^{-1} at the same pressure range. Band A moves much faster than band B with pressure. That means the energy level of band A decreases much faster with pressure than that of band B. This decrease of the energy level is also another reason of the quick and large drops of the emission intensity of band A (seen in Figure 3), because the reducing of the energy level would lead to the enhancement of the efficiency for the radiationless decay.

Py-Am has two stable conformations according to the results of semiempirical method calculation (PM3), shown in Scheme 1. In the neat Py-Am sample, the extended conformation cannot induce the intramolecular exciplex due to the distance between the donor and the acceptor. The intermolecular exciplex or excimer could exist with this conformation. For another stable conformation (V-like), except to the intermolecular interactions

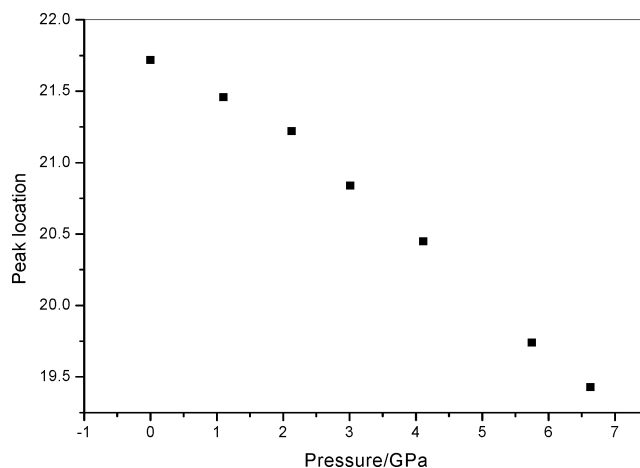


Figure 5. The peak maximum of pyrene powder at different pressures.

between the donor and acceptor in different molecules, there would be additional intramolecular interactions between the π orbital of the donor and the acceptor, to form the intramolecular exciplex.

Neat pyrene is used as the model sample because the pyrene molecules would form excimer at excited state and produce the excimer emission. The fluorescence spectra of the neat pyrene have been detected at different pressures, and with peak-fitting the pressure-dependent band maximum of the excimer is obtained as shown in Figure 5.

The peak maximum of the pyrene excimer emission locates at 21.75 k cm^{-1} at 1 atm that is quite different from the peak maximum of band A of Py-Am powder that is 21.12 k cm^{-1} in Figure 3. With the increase of pressure, the maximum of the excimer band red shifts to 19.46 k cm^{-1} at 6.63 GPa at a rate of 0.34 $\text{k cm}^{-1} \text{ GPa}^{-1}$. As shown in Figure 3, band A of neat Py-Am red shifts to 17.43 k cm^{-1} at 6.22 GPa at a rate of 0.59 $\text{k cm}^{-1} \text{ GPa}^{-1}$. The beginning maximum, ending maximum with pressure and the change trend of the excimer emission of the neat pyrene and band A emission, are totally different. So it means that the band A in Py-Am does not come from the intermolecular excimer of the pyrene group, and it comes instead from the exciplex (intramolecular or intermolecular) between the pyrene group and the aniline group in Py-Am molecule.

We have dispersed the Py-Am in PMMA with low concentration to determine the peak maximum of the intramolecular exciplex band. When the concentration is low enough, the Py-Am is dispersed molecularly in PMMA, and there would not be intermolecular exciplexes between the molecules. In this case only the emissions from the monomer of pyrene and intramolecular exciplex could be observed. Figure 6 shows the pressure-dependent fluorescence spectra of Py-Am and model compound pyrene dispersed in PMMA at different pressures.

At 1 atm, the emission of Py-Am consists of multi-peaks, with maxima at around 25000 cm^{-1} due to the local excited-state emission, just like the characteristic multi-peak bands of the pyrene group. Meanwhile, an emission tail at a lower-energy region (around 18 000–22 500 cm^{-1}) is clearly observed. At higher pressures, a significant broad emission band emerges in the lower-energy region corresponding to the tail at 1 atm. Because the sandwich-like exciplex has an almost perfect face-to-face structure and in the Py-Am the electron donor and electron acceptor are nearly perpendicular in its V-like conformation, the emission around 18 000–22 500 cm^{-1} is attributed to the emission from an intramolecular exciplex of the molecule by partial electron transfer from the aniline group to the pyrene

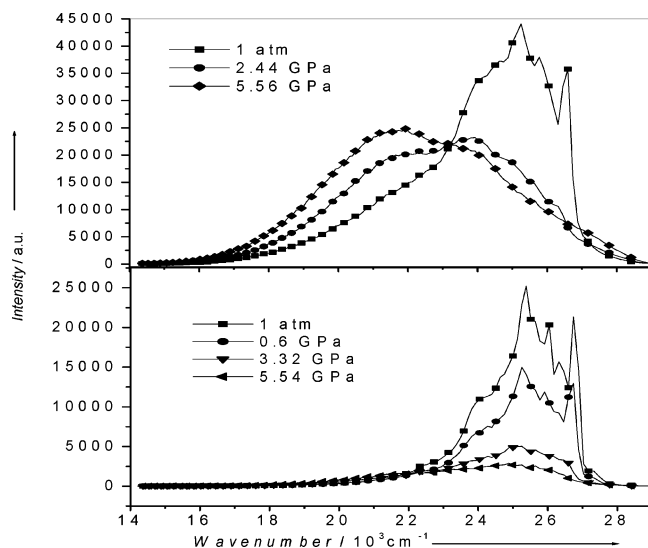


Figure 6. Typical fluorescence spectra of Py-Am in PMMA (up) and the model compound pyrene in PMMA (down) at different pressures.

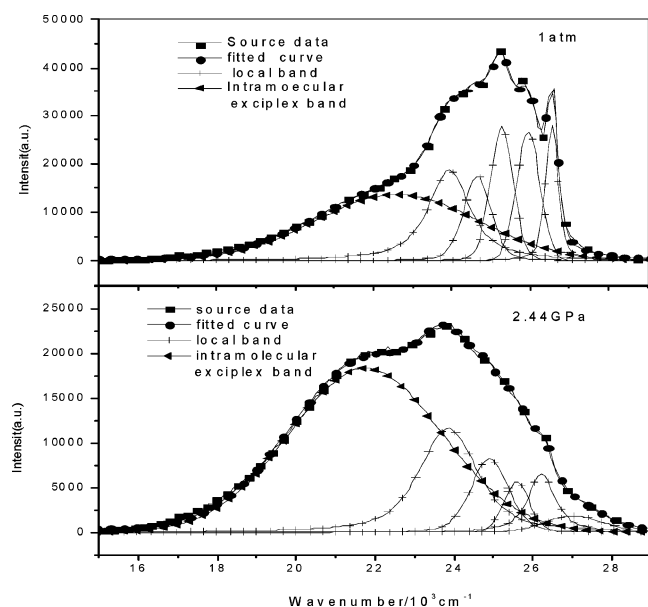


Figure 7. The typical peak fitting results of the fluorescence spectra of Py-Am in PMMA at 1 atm and 2.44 GPa.

group. With the increase of pressure, the intensity of the local excited emission band (LE emission band, monomer emission of pyrene group) decreases, and the intramolecular exciplex emission band increases. This indicates that more and more intramolecular interactions occur when pressure is increasing. The formation of the intramolecular exciplex corresponded almost directly to the reduction of the pyrene monomer because of an observed equal luminescent point.

The fluorescent peaks of Py-Am in PMMA at different pressure are fitted with two bands, the LE emission band and the intramolecular exciplex emission band. Typical results are shown in Figure 7. Five peaks are used to fit the LE emission band, and a broad peak is used for the intramolecular exciplex emission band fitting at all pressures due to its nonstructure emission.

The emission maximum of the intramolecular exciplex emission band is obtained from the fitting results and shown in Figure 8. In Figure 8, it should be noted that the peak maximum of the intramolecular exciplex emission band of the Py-Am red

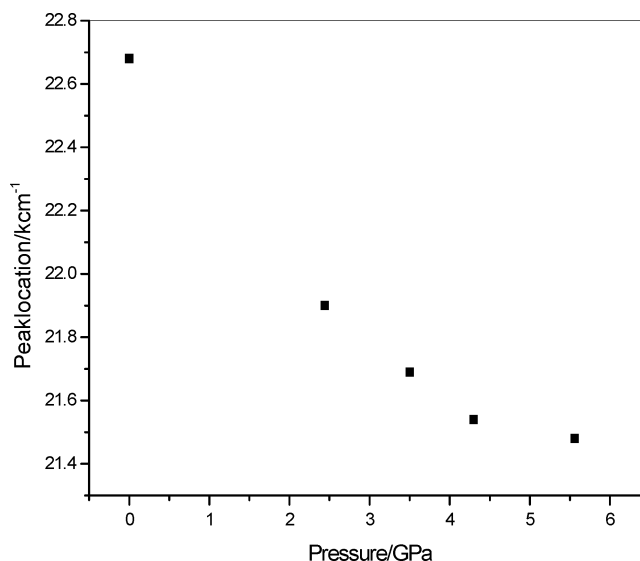


Figure 8. The pressure-dependent peak location of the Py-Am in PMMA at different pressures.

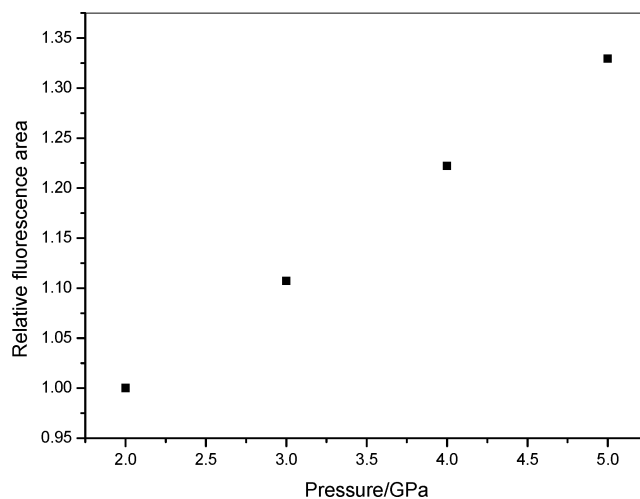


Figure 9. The relative fluorescence area of Py-Am intramolecular exciplex in PMMA at different pressures.

shifts from 22.68 to 21.48 km^{-1} between 1 atm and 6.11 GPa. It is quite similar to that of the band B in Figure 3, where the peak maximum of the exciplex band B has a red shift from 22.75 to 21.44 km^{-1} from 1 atm to 6.22 GPa and both shifts in almost linear mode. According to the fitting result for Figure 6, the pressure-dependent relative fluorescence area of the intramolecular exciplex is obtained and shown in Figure 9. The relative fluorescence efficiency of the intramolecular exciplex band in PMMA increases linearly and reaches about 1.34 times of that at 2.0 GPa when the pressure is at 5.0 GPa. The change trend is also quite similar to that of the band B in Figure 3. So, it can be concluded that the exciplex band B emission in the Py-Am neat sample comes from the intramolecular exciplex between the pyrene group and the aniline group.

From the results and discussion above, it can be seen that when the neat Py-Am sample is irradiated, there are several species formed that could emit. At 1 atm the emission from intramolecular exciplex is too weak and too close to that of the intermolecular exciplex, so it could be covered by the emission from the intermolecular exciplex. The pressure is favorable for the intramolecular exciplex emission, and at high pressure the intramolecular exciplex emission can be observed clearly.

TABLE 1: ΔG of the Inter- and Intramolecular Exciplex with Pressure (ΔG_{inter} and ΔG_{intra} , Averaged by Two Runs)

pressure/ GPa	$E_{0,0}$ / k cm ⁻¹	interexciplex maximum/k cm ⁻¹	intraexciplex maximum/k cm ⁻¹	$\Delta G_{\text{inter}}/$ ev	$\Delta G_{\text{intra}}/$ ev
0	26.81	21.12	22.75	-0.71	-0.50
1	26.53	20.11	22.54	-0.80	-0.50
2	26.32	19.33	22.32	-0.87	-0.50
3	26.11	18.74	22.11	-0.92	-0.50
4	25.91	18.22	21.90	-0.96	-0.50
5	25.64	17.84	21.69	-0.97	-0.49

TABLE 2: The Percentages (R) of the Emission Area from Each Excited Species in the Total Fluorescence Area at Different Pressures (Averaged by Two Runs)^a

pressure/GPa	$R_{\text{inter}}/\%$	$R_{\text{intra}}/\%$	$R_{\text{LE}}/\%$
1	77.1	—	22.9
2	83.6	3.6	12.8
3	76.3	7.7	16.0
4	65.7	11.7	22.6
5	57.3	15.7	27.0
6	49.0	19.7	31.3

^a R_{inter} , R_{intra} , and R_{LE} are the percentages of the emission for intermolecular exciplex, intramolecular exciplex, and the local excited state (LE, monomer emission of pyrene group), respectively.

From the energy point of view, these processes are controlled by the relative energy change between the referred excited species for not only the neat powder sample but also the sample blending in PMMA. Some empirical treatments could be used to estimate the energy change in these processes from the spectrum data^{23,24}

$$\Delta G = E^{\text{re}} - E^{\text{ox}} - \Delta - E_{0,0} \quad (1)$$

and

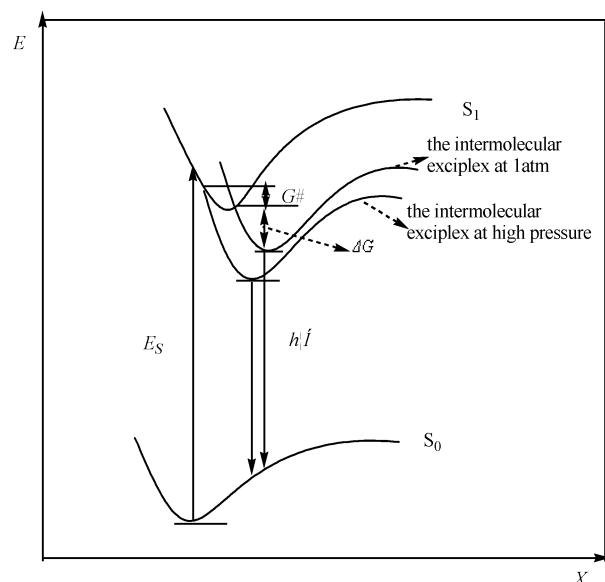
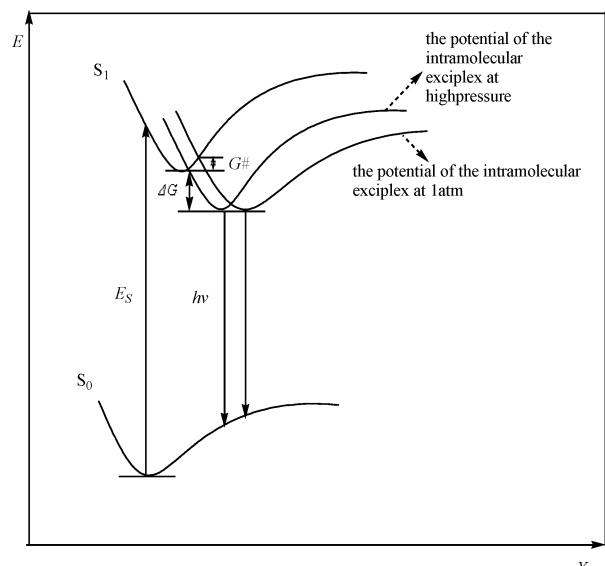
$$h\nu_{\text{max}} = E^{\text{re}} - E^{\text{ox}} - \Delta \quad (2)$$

where the ΔG is free energy change of the electron-transfer process, ν_{max} is the fluorescence peak center of the exciplex, E^{re} and E^{ox} are the reduction potential of the acceptor group and the oxidation potential of the donor group, respectively, $E_{0,0}$ is the absorption zero-zero band energy, and Δ presents the Coulomb and solvation energies. From eq 1 and eq 2 we get

$$\Delta G = h\nu_{\text{max}} - E_{0,0} \quad (3)$$

According to eq 3 we can estimate the energy changes in the process of the photophysics for the neat sample with pressure, listed in Table 1.

In Table 1 it is shown that the value of the ΔG_{inter} becomes more and more negative from -0.71 to -0.97 eV, but ΔG_{intra} changes slightly. It is also shown that the $E_{0,0}$ value of Py-Am neat sample red shifts from 26.81 to 25.64 k cm⁻¹ linearly at the rate of 0.23 k cm⁻¹/GPa, the emission maximum of the intermolecular exciplex red shifts from 21.1 k cm⁻¹ to 17.84 k cm⁻¹ at the rate of 0.66 k cm⁻¹/GPa (also see Figure 4). So the energy of the excited state of the intermolecular exciplex decreases much faster than that of the LE state (S_1). The emission of the intramolecular exciplex red shifts from 22.75 to 21.69 k cm⁻¹ linearly at the rates of 0.21 k cm⁻¹ GPa⁻¹ (also see Figure 4). It means that the energy of the excited state of the intramolecular exciplex has the similar rate of decrease with that of the S_1 excited state. It is interesting that for the intermolecular exciplex when the driving force ΔG is increasing with pressure, the emission efficiency is reducing, but for the intramolecular exciplex when the driving force changes slightly with pressure, the emission efficiency is enhanced a lot. So the

**Figure 10.** The configuration coordination model for the Intermolecular exciplex at 1 atm and high pressure.**Figure 11.** The configuration coordination model for the intramolecular exciplex at 1 atm and high pressure.

photophysical processes of the formation and the emitting of the exciplexes might also be controlled by other factors except ΔG , such as the activation energy G^\ddagger and the structure of the excited state.

For the emission of the excited states, the percentage of the emission for each excited species in the total emission (R) at different pressures is also important. It implies the relative quantum yield and that is presented in Table 2.

At the beginning, the emission from the intermolecular exciplex is the main part, 77.1%. When pressure is around the range of 1–2 GPa, it is boosted to 83.6%. At the same time, the local excited state (LE) emission has a quick decrease from 22.9% to 12.8%, and the emission from the intramolecular exciplex becomes manifest. Then the emission from the intermolecular exciplex is depressed and the value of R_{inter} reduced from 83.6% at 2.0 GPa to 49% at 6 GPa. After the quick drop, the value of R_{LE} increases from 2.0 GPa and reaches to 31.3% at 6.0 GPa. The intramolecular exciplex emission increase all along with pressures to 19.7% at 6.0 GPa.

Configuration coordination model can be built to understand these photophysical processes, shown in Figure 10 and Figure 11. Because the polarizability of the ground state is much smaller than that of the excited states, the S_0 state could be considered as independent to pressure in this system. Meanwhile, the local excited band red shifts slightly with pressure, and the movement of the S_1 state could also be ignored in the compressing process.

With the increase of pressure, as the distance between the molecules is diminished, the potential energy curve of the intermolecular exciplex at high pressure moves to left to some extent along the configuration coordinate, as shown in Figure 10. In Table 2, it is noted that the emission from the intermolecular exciplex dominates at 1 atm. This indicates that the crossing from S_1 state to the intermolecular exciplex is of high efficiency and the activation energy for the formation is relatively small at 1 atm. It is also noted in Table 2 that R_{inter} increases slightly at pressures from 1 to 2 GPa. This means that the crossing point of the potential curves of the S_1 and the intermolecular exciplex is very close to the bottom and on the right side of the S_1 state. At lower pressure the G^\ddagger is relatively small. Upon compressing, ΔG becomes more negative, and the crossing point between the potential curves of the S_1 excited state and the intermolecular exciplex goes downward along the S_1 potential energy curve to the bottom, which results in the reduction of G^\ddagger and the increase of R_{inter} at 1–2 GPa and also partially in the quick reduction of R_{LE} . Then with the increase of the pressure, ΔG becomes more negative, and the crossing point goes upward along the left side of the S_1 potential curve. At the same time, the G^\ddagger value increases, which leads to the difficulty of molecules at S_1 excited-state overcoming the energy bar and to the reduction of R_{inter} after a short-lived increase before 2 GPa. The quick decrease of the energy level of the intermolecular exciplex is also favor for the enhancement of radiationless decay.

The configuration coordination model for the intramolecular exciplex is quite different from that of the intermolecular exciplex, shown in Figure 11. The relative energy change between the S_1 and intramolecular exciplex excited states is ignored because ΔG_{intra} hardly changes. The change in energy level is not the main reason for the enhancement of the intramolecular exciplex emission. In this case, the structure change of the excited molecular under pressure could be considered to influence the emission of the intramolecular exciplex. With the increase of pressure, the acceptor and the donor approach each other, and the potential curve of the intramolecular exciplex moves horizontally to the left, as shown in Figure 11. The cross point between the potential curves of S_1 and the intramolecular exciplex goes downward along the S_1 potential curve. So the activation energy decreases, which could lead to the increase of the crossing from S_1 to the intramolecular exciplex and result in the increase of the emission from the intermolecular exciplex.

Corresponding to the increased values of R_{inter} and R_{intra} at 1–2 GPa, the value of R_{LE} drops quickly. The reason is illustrated in Figures 10 and 11: G^\ddagger for the formation of the inter- and intramolecular exciplex is reduced with pressures in this range. After 2 GPa, the value of R_{inter} decreases as G^\ddagger for the intermolecular exciplex begins to rise, after the crossing point of the potential of S_1 and the intermolecular exciplex goes over the bottom of the potential of S_1 and then upward in Figure 10. So the crossing from S_1 to the intermolecular exciplex is suppressed. Meanwhile, R_{LE} begins to increase with pressure.

Conclusion

In this paper we have studied the fluorescence spectra of the electron transfer compound Py-Am at different pressures. Pressure tuning for the electronic states shows its powerful ability to distinguish the different properties of the states that are difficult to characterize at 1 atm. There are three emitting species in the excited molecules of Py-Am for the neat sample, local excited state of pyrene group (for monomer emission of pyrene group), intermolecular exciplex, and intramolecular exciplex. At 1 atm the emission from the intermolecular exciplex is much larger than that from other two species. With the increase of pressure, the donor and the acceptor get much closer, and the emission of the intermolecular exciplex red shifts greatly, the relative efficiency drops significantly. Meanwhile, the intramolecular exciplex increases with pressure and gives relatively higher fluorescence efficiency with a slight shift in its energy level. At higher pressure, the intermolecular and intramolecular exciplexes are observed with the emission at significantly different wavelength ranges. Although the total emission quickly diminishes with pressure, the relative percentage of the emission from the intermolecular exciplex among the total emission has a short increase when pressure is at 1–2 GPa and then decreases. At the same time, the intramolecular exciplex emission is enhanced by the increase of pressure.

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