Probing Twisted Intramolecular Charge Transfer State in Hyperbranched Conjugated Polymers

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The concepts concerning twisted intramolecular charge transfer state (TICT) are ready to be applied right now in the development of more efficient and versatile fluorescence and laser dyes and new fluorescent probes. In this paper, hyperbranched conjugated polymer functionalized in periphery with dimethylamine (HPV-MN) is characterized by means of fluorescence spectroscopy and lifetime measurements. Solvatochromic shifts, in both absorption and fluorescence spectra, and effects of solvent polarity on the fluorescence quantum yield and fluorescence lifetime have been investigated to probe the intramolecular charge transfer (ICT) state formation in HPV-MN. It is found that the emission band arising from intramolecular charge transfer (ICT) state shows red-shifted and the fluorescence quantum efficiency of HPV-MN decreases with the polarity increasing of solvent. Moreover, from the lifetime measurements, the ICT state bears shorter lifetime and relatively large amplitude in the solution with higher polarity. No clear solvatochromic shifts of the emission maxima in the long wavelength region at 77 K confirm the existence of TICT state in hyperbranched conjugated polymer. The efficiency of charge separation following the process of TICT probably reflects the integrality of HPV-MN.

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The photoinduced intramolecular charge transfer (ICT) state of various organic molecules containing an electron-acceptor and an electron-donor group has been an exciting topic for recent investigation, since the observation of dual emission by Lipert et al.1 and the introduction of the concept of twisted intramolecular charge transfer (TICT) by Grobowski et al.2 A molecular configuration change was proposed occurring upon the charge transfer, although the nature of the configuration changes is still under discussion.3,4 For p-N,N-dimethylamino benzonitrile (DABN) having a small rotating group, such as a dimethylamine group, the ICT process was found to be almost independent of viscosity up to moderate viscosities, whereas an increase in the viscosity was found to prohibit the ICT process for molecules where the rotating group was bulky.5,9 On the other hand, the photophysical and photochemical behaviors of the ICT molecule as well as the conformational changes are known to be controlled by the solvent polarity7 and the microenvironments8. The high dipole moment of the fluorescent TICT state make the fluorophores very useful in probing both the bulk and microenvironments of different media, such as supercritical fluids,9 cyclodextrins,10 micelles11 and in fluorescent sensing.12 These researches were based on the dependence on the medium polarity of the formation and emission of the ICT state. Some other simple dichromophoric organic molecules form luminescent species that display the characteristics of charge separation and therefore well-suited model systems. Research on the optoelectronic properties of conjugated polymers has created opportunities for a number of applications, such as light-emitting diodes,13 light-emitting electrochemical cells,14 solid-state lasers,15 solar cells,16 and sensors.17 In our previous work, photoinduced intramolecular charge transfer (ICT) state was investigated in alternating copolymers.18,19 Hyperbranched polymers deserve much attention as high performance polymers due to their amorphous properties with a high solvent solubility.

It is highlighted that the hyperbranched structure can provide novel properties, such as energy transfer20 or working as photophysical antenna21. To our rough knowledge, not any work concerning TICT state in hyperbranched conjugated polymers has been reported.

The aim of this work is to characterize hyperbranched conjugated polymer functionalized with dimethylamine group as the end moiety (HPV-MN). Solvatochromic shifts in both absorption and fluorescence spectra and effects of solvent polarity on the fluorescence quantum yield and fluorescence lifetime have been investigated to probe the TICT state formation in the hyperbranched conjugated polymer.

Experimental

Materials

All the solvents were commercially available and of analytical or chromatogram grade. Chloroform and acetonitrile were purchased from the Beijing Chemical Factory. The careful adjustment of the volume ratio between chloroform and acetonitrile led to mixed solvents with different polarities. Interference fluorescence was not observed under the experimental conditions.

Equipment

Absorption spectra were recorded with a Hitachi (model U-3010) UV-visible spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1 cm quartz cell. Fluorescence quantum efficiencies were determined by comparing the integrated fluorescence spectra of the sample with that of a standard (1,6-Diphenylhexatriene in cyclohexane, ϕf = 0.80). Fluorescence lifetime measurements were obtained using a time-correlated single photon counting spectrometer (model Horiba NAES-1100). The time resolution of the present system is ca. 100 ps. The decay curves were fitted with an exponential function as

\[ I(t) = \sum A_i e^{(-t/\tau_i)} \]  

(1)

where \( \tau \) is the fluorescence lifetime of the species in excited state and \( A_i \) is the preexponential factor. Unless otherwise will be stated, all measurements were made at room temperature.

Hyperbranched conjugated polymer synthesis

Scheme 1 shows the synthetic route to HPV-MN. Detail description of the synthesis are referred to our previous work.22
HPV-MN: 

Temperature at which initial loss of mass was observed. The $M_a$ and $M_d$ were determined to be 283367 g.mol$^{-1}$ and 6504 g.mol$^{-1}$ respectively by gel permeation chromatography with polystyrene as standard.

Scheme 1. Synthetic route to HPV-MN.

Results

The optical absorption and emission spectra of HPV-MN have been investigated in several solvents with varying polarities. Note that the polarity of mixed solvent is determined by the volume fraction of the two solvents. The absorption spectra in solvents with different polarities are presented in Fig. 1. The spectra display two peaks at 330 nm and 400 nm in all solvents. It is evident that the absorption band is attributed to an allowed $n\pi^*$ transition. Spectra in all the mixed solvents show almost identical except that the absorption band becomes broader and weaker, and a tail absorption band around 470 nm is seen in solutions with higher polarities.

Fig. 1. Absorption spectra of HPV-MN in mixed solvents of various polarities. The concentration of HPV-MN: 0.001 mg/mL. Chloroform-acetonitrile mixed solvent is abbreviated as $C_{x}A_{y}$. $x$ and $y$ stand for the respective volume fraction of the solvents normalized to $x + y = 10$. $C_{10}A_{0}$, $C_{0}A_{10}$, $C_{2}A_{8}$, $C_{8}A_{2}$, $C_{3}A_{7}$, $C_{7}A_{3}$, $C_{4}A_{6}$, $C_{6}A_{4}$ are denoted.

The fluorescence spectra obtained in the mixed solvents with different polarities are displayed in Fig. 2, from which it is shown that the fluorescence quantum efficiency decreases exponentially upon increasing the solvent polarity. The inset of Fig. 2 demonstrates the curve of fluorescence quantum efficiencies ($\phi_f$) versus the solvent polarity function. It can be observed that the fluorescence spectrum in chloroform bears two peaks at 460 nm and 490 nm. Interestingly, the two peaks exhibit different behavior. With increasing solvent polarity, the peak locating at 460 nm shows almost no shift, whereas the peak in the long wavelength region shifts to the red side and gains in relative intensity. Such solvatochromic shifts in the emission maxima are usually associated with a drastic change in the excited state charge distribution as compared to that in the ground state. The excited state often has ICT or TICT character. In order to correlate the solvatochromic shifts with solvent polarities, for mixed solvents, the dielectric constant ($\varepsilon_{\infty}$) and refractive index ($n_{\infty}$) were calculated as:

$$
\varepsilon_{\infty} = f_{A}\varepsilon_{A} + f_{B}\varepsilon_{B}
$$

$$
n_{\infty}^{2} = f_{A}n_{A}^{2} + f_{B}n_{B}^{2}
$$

where $f_A$ and $f_B$ are the fractions (vol/vol) of the two solvents A and B, respectively. It is proposed that ICT or TICT state often leads to the existence of excited-state dipole moment ($\mu$). For hyperbranched conjugated polymers, the excited-state dipole moment might exist at the repetition units and/or end moieties. Due to the fact that for HPV-MN the excited-state lifetime has been found to be sufficiently long ($\tau > 1$ ns) with respect to the orientation relaxation time in the solvents, the excited-state dipole moment is supposed to be determined by the fluorescence solvatochromic shift method. On basis of the assumption that a point dipole is situated at the center of the spherical cavity and neglecting the mean solute polarizability ($\alpha$) in the states involved in the transition ($\varepsilon_1 = \varepsilon_0 = \varepsilon = 0$, where $\varepsilon$ and $g$ stand for excited and ground states, respectively) one obtains:

$$
\hbar \omega_{\text{max}} = \hbar \omega_{\text{max}}(0) - [2\mu_s(\varepsilon_1 - \varepsilon_0)/\alpha_0]^{1/2}
$$

$$
\Delta \lambda = \delta \lambda - (1/2)f(n)
$$

$$
f(a) = (a-1)/(2a+1); \delta \lambda = (a-1)/(2a+1)
$$

where $\mu_s$ is the dipole moment of the solute in the ground state, $\omega_{\text{max}}$ is the solvent-equilibrated fluorescence maxima and $\omega_{\text{max}}(0)$ is the value of spectral position of the fluorescence maxima extrapolated to the gas phase, $\alpha$ is the radius of the cavity in which the fluorophore resides and $c$ and $c$ are the dielectric constant and the refractive index of the solvent, respectively.

Fig. 2. Fluorescence spectra of HPV-MN in mixed solvents of various polarities. The concentration of HPV-MN: 0.001 mg/mL. For abbreviations see Fig. 1. $C_{10}A_{0}$, $C_{9}A_{1}$, $C_{8}A_{2}$, $C_{7}A_{3}$, $C_{6}A_{4}$, $C_{5}A_{5}$, $C_{4}A_{6}$, $C_{3}A_{7}$, $C_{2}A_{8}$, $C_{1}A_{9}$, $C_{0}A_{10}$. Inset: Plot of the fluorescence quantum efficiency ($\phi_f$) in HPV-MN in different solvents against the polarity function ($\Delta \lambda$).

Fig. 3 shows the linear plot of fluorescence maxima ($\omega_{\text{max}}$) versus the solvent polarity function $\Delta \lambda$. As it is well known that charge transfer states are more stabilized in polar solvents, the linear behavior ($r = 0.991$) arises from the occurrence of the ICT state in HPV-MN. Moreover, at 77 K no clear solvatochromic shifts in the emission maxima suggests that occurrence of ICT state above may be accompanied by a specific intramolecular motion. In our case, the specific motion probably is the twisting of dimethylamine group. This evidence leads us to conclude that ICT state is formed upon the photoexcitation of HPV-MN. The emission band in the short wavelength region mainly originates from the locally excited (LE) state.
Fig. 3. Plot of the fluorescence maximum (F_{max}) for HPV-MN in different mixed solvents.

Fluorescence lifetimes of HPV-MN were measured using the time-correlated single photon counting technique. The lifetime values obtained are collected in Tab. 1. In spite of the monitoring wavelength at 460 nm or the emission maxima in the long wavelength region, the decay curves recorded in mixed solvents of varying polarity were proved to give good biexponential fitting \( \gamma^2 \) values in the range of 1-1.4. In general, the emission decay of HPV-MN exhibits a major fast-decay component (around 1.5 ns) along with a slow decay component (around 10.0 ns). The slower component is attributed to the emission from the stabilized TICT state while the faster component corresponds to the normal emission from the LE state. The former displays decreasing upon increasing the mixed solvent polarity while the latter has no remarkable changes. This probably indicates that the radiative decay rate of TICT show some clear correlation with the solvent polarity function. It is worthy to mention that at the monitoring wavelength in the red side, the relative amplitude of TICT emission increases with the solvent polarity increasing (see Tab.1). This is consistent with the solvent polarity effects on steady-state spectroscopic changes, suggesting that the TICT state of HPV-MN is more stabilized in mixed solvent of high polarity.

Discussion

In this study, the TICT state in hyperbranched conjugated polymer is characterized by varying the solvent polarity. The solvent polarity changing was followed in chloroform-acetonitrile mixtures. These solvents were chosen in order to avoid other interactions like solvent hydrogen bonding, protonation etc. Moreover, in such mixed solvents, preferential solvation of HPV-MN in chloroform solvent has been also taken into account. In such cases one would expect that the addition of acetonitrile into chloroform would affect the solvability of HPV-MN. Due to the low concentration of HPV-MN (0.001 mg/mL) used in our experiment, the linear shift in the fluorescence maximum, as polarity is varied, proves that there is no preferential solvation of HPV-MN in one of the mixed solvents in the polarity range investigated here.

As is evident from Fig. 1, the tailing absorption band appears in the mixed solvents of higher polarities although not any obvious dependence on solvent polarity function is observed. Thus, the appearance probably results from the configuration changes induced by higher solvent polarity. Simply judging from the structure of HPV-MN, the induction would not result into charge separation in ground state. Other reason for such an observation is not clear.

The slope obtained from the linear plot shown in Fig. 3 is, in fact, in coincidence with the efficiency of charge separation following the process of TICT. It is established that the motion of twisting contributes to the efficiency of charge separation. In our experiment, the slope is lower comparing to that obtained from DMABN itself in solvents of various polarities. This can be explained based on the specific structure of hyperbranched conjugated polymers. The polymer was synthesized through so-called one pot reaction, thereby the lengths of different branches in a single polymer molecule are not exactly the same. This means that the possibility of embedding of the end moiety, dimethylamine, cannot be eliminated. In this case, the twisting motion of dimethylamino group is largely prohibited (see Fig. 4).

Therewith, the efficiency of charge separation corresponding to the slope of line in Fig. 3 following the process of TICT probably reflects the integrality of HPV-MN.

Fig. 4. A possible model for microenvironment of dimethylamino groups in a hyperbranched conjugated polymer molecule.

The fact that the emission band of TICT gains in the relatively intensity and the relative amplitude of TICT component decay increases with increasing the solvent polarity demonstrates there exists a thermal equilibrium between the LE and TICT states in our system. In low-polarity solvents the LE state dominates but in relatively high-polarity solvents the TICT state tends to dominate. Since the difference of the electronic energy levels of LE and TICT states is not large, in moderate polarity solvents the two states co-exist.

Summarizing, from the solvatochromic shifts of fluorescence maxima and the solvent polarity effect on fluorescence quantum yield and fluorescence lifetimes, and also combining with the spectroscopic behavior at 77 K, it is inferred that two closely spaced electronic excited states (LE and TICT) co-exist in HPV-MN. The two states can switch over to each other depending on the solvent polarity. Due to the sensitivity of TICT state formation to the steric configuration, such a dual fluorescence consisting of two bands can be applied to probe the integrity in hyperbranched conjugated polymer. The polymer with TICT properties may also find its application in photovoltaic cells. This investigation is in progress.

Acknowledgments

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Table 1. Photophysical properties of HPV-MN in mixed solvents of different polarities.

<table>
<thead>
<tr>
<th>Solvent*</th>
<th>$\Delta f$</th>
<th>$\phi$</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>460 nm monitoring wavelength</th>
<th>LW*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_{60}$</td>
<td>0.2996</td>
<td>0.405</td>
<td>460</td>
<td>490</td>
<td>$\tau_1$ ($\times 10^3$)</td>
</tr>
<tr>
<td>$\text{C}_{70}$</td>
<td>0.3089</td>
<td>0.229</td>
<td>460</td>
<td>495</td>
<td>nd$^b$</td>
</tr>
<tr>
<td>$\text{C}_{82}$</td>
<td>0.3347</td>
<td>0.147</td>
<td>460</td>
<td>498</td>
<td>$\tau_2$ ($\times 10^3$)</td>
</tr>
<tr>
<td>$\text{C}_{85}$</td>
<td>0.3501</td>
<td>0.088</td>
<td>460</td>
<td>505</td>
<td>nd</td>
</tr>
<tr>
<td>$\text{C}_{88}$</td>
<td>0.3685</td>
<td>0.055</td>
<td>460</td>
<td>515</td>
<td>nd</td>
</tr>
<tr>
<td>$\text{C}_{90}$</td>
<td>0.3802</td>
<td>0.044</td>
<td>460</td>
<td>516</td>
<td>nd</td>
</tr>
</tbody>
</table>

$^a$SW: short wavelength;  LW: long wavelength.

$^b$not determined.

*for abbreviations see Fig. 1.

References