Study of aggregation induced emission of cyano-substituted oligo (p-phenylenevinylene) by femtosecond time resolved fluorescence

Zi-Qi Yan, Zhi-Yong Yang, Hai Wang, Ai-Wu Li, Li-Ping Wang, Han Yang, Bing-Rong Gao

A R T I C L E   I N F O

Article history:
Received 12 October 2010
Received in revised form 25 January 2011
Accepted 28 January 2011

Keywords:
Aggregation induced emission
Fluorescence up-conversion
Intramolecular charge transfer state
Local excited state

A B S T R A C T

The aggregation induced emission (AIE) mechanism of the cyano-substituted oligo (p-phenylenevinylene),1,4-bis [1-cyano-2-(4-diphenylamino) phenyl] vinyl benzene (TPCNDSB) is investigated by time resolved fluorescence technique. By reconstructing the time resolved emission spectra (TRES), it is found that in solvent of low polarity, the emission is mainly from the local emission (LE) state with high quantum yield, but in high polarity solvent, the emission is mainly from the intramolecular charge transfer (ICT) state, which is a relatively dark state, with low quantum yield. In crystal form, the restriction of transfer from LE state to ICT state results in efficient AIE.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Two-photon pumped (TPP) up-converted lasing, pumping at red or near-infrared wavelength, releasing of the phase-match condition, is of great interest to make novel light source [1–4]. Recently, TPP lasing from organic crystals with low threshold was occasionally found, which is of great importance for making solid state lasing. Crystal TPP lasing and other organic devices such as organic light emitting diodes (OLED) [8–11] requires high fluorescence in solid state, however, most conjugated molecules show high fluorescence in their dilute solutions but become weakly luminescent in the solid state. In 2001, Tang and coworkers [12] occasionally found a intriguing phenomenon that the dried spot of silole compound shows much higher luminescence than its solution state, namely aggregation induced emission (AIE). Since then increasing attention has been paid to investigating new materials with high solid state luminescence and many materials have been reported that show AIE properties [13–23]. However few works have been done to deeply investigate the underlying mechanism of AIE, which is crucial for new material design. Time resolved fluorescence technique is a powerful tool to study the underlying physics of both organic and inorganic materials [24,25]. Some time resolved spectroscopy studies [26,27] of the materials with AIE properties have been conducted and concluded that AIE can be ascribed to the deactivation of nonradiative decay caused by restricted torsional motions of the molecules in the solid state. Very recently a new mechanism ‘restricted intramolecular charge transfer (ICT)’ was suggested by steady state study on AIE of boron dipyrromethene (BODIPY) derivatives [28] and time resolved fluorescence study of cyano-substituted oligo (α-phenylenevinylene) (CNDPASDB) [29]. It is generally believed now that for non-ICT systems as silole derivatives, the AIE mechanism is the restriction of the intramolecular rotation. When donor–acceptor units are introduced into the dye molecule, the mechanism becomes the restriction of the formation of the dark ICT state. Since only a few materials have been investigated by time resolved technique, it still remains a question whether these mechanisms are general and thus can be applied to other AIE materials. In this paper we study another AIE material with ICT unit to see whether the second mechanism applies.

Uniaxially oriented molecular crystal cyano-substituted oligo (p-phenylenevinylene), 1,4-bis [1-cyano-2-(4-(diphenylamino) phenyl) vinyl] benzene (TPCNDSB) (Fig. 1) was reported with enhanced emission (31% quantum yield) in crystal form and TPP lasing was observed in its crystal with threshold only one order lower compared with its single-photon pumped lasing, indicating its potential as solid state upconversion laser material [6,30]. We study the time resolved fluorescence of TPCNDSB in different solvents and crystal form. We found that the fluorescence spectra of TPCNDSB show large solvatochromism. In high polar solvents (such as dimethyl formamide (DMF) and acetonitrile), the emission is largely red shifted and the quantum yield is about 100 times lower that in toluene. Interestingly, AIE properties also sig-
and DMF solutions of TPCNDSB were prepared at the concentration of 2×10^{-5} mol/l. The crystals were prepared by solvent-exchange process at room temperature under rigorous exclusion of light. Fig. 1(b) and (c) gives the photo and emission spectra of varied solution and crystal under UV illumination.

Absorption spectra were measured by a Shimadzu UV-1700 spectrophotometer. Emission spectra were recorded with a Shimadzu RF-5301PC spectrophotometer. Nanosecond fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20 MHz) was used to excite the samples. The fluorescence was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). Time constant of the instrument response function (IRF) is about 220 ps.

Subpicosecond time resolved emission were measured by the femtosecond fluorescence upconversion method. A Nd:YVO laser (Millennia, Spectra Physics) was used to pump a Ti:Sapphire laser (Tsunami, Spectra Physics). Its output seeds a regenerative amplifier (RGA, Spitfire, Spectra Physics). The output of the amplifier of 1.5-mJ pulse energy, 100 fs pulse width, at 800 nm wavelength is split into two equal parts; the second harmonic of one beam was focused in the sample as excitation. The resulted fluorescence was collected and focused onto a 1 mm thick BBO crystal with a cutting angle of 35°. The other part of the RGA output was sent into an optical delay line and served as the optical gate for the upconversion of the fluorescence. The generated sum frequency light was then collimated and focused into the entrance slit of a 300 mm monochromator. A UV-sensitive photomultiplier tube 1P28 (Hamamatsu) was used to detect the signal. The electrical signal from the photomultiplier tube was summed by a digital oscilloscope. The relative polarization of the excitation and the gating beams was set to the magic angle. The FWHM of instrument response function was about 500 fs. All the measurements were performed at room temperature.

All the fluorescence transients were fitted to multi-exponential functions and were convoluted with the system response function by fixing the long lifetime obtained from TCSPC measurement. The fitting program is ASUFIT (available at http://www.public.asu.edu/~laserweb/asufit/asufit.html).

3. Results and discussions

3.1. Steady state spectra

To quantify the excited state dipole moment, steady state absorbance and emission spectra of TPCNDSB were measured in 9 different solvents of identical concentration. Solvents are selected with increasing polarity, and the orientational polarizability, Δf is chosen as the measure of polarity, calculated as follows [35]:

\[
\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}
\]

where \(\varepsilon\) is the static dielectric constant and \(n\) is the optical refractive index of the solvent.

The absorption and emission peaks of TPCNDSB in various solvents are listed in Table 1, including the solvent parameters. Photos and normalized emission spectra in typical solvents with increasing polarity are shown in Fig. 1(b) and (c). While the absorption spectra changes little (20 nm) with solvent polarity, the emission shows obvious solvatochromism effect, with emission peaks changing from 510 nm in hexane to 671 nm in acetonitrile, and the emission color covers from green (in hexane) to yellow (in toluene) to orange (in THF), and even to red (in DMF), which maybe hardly seen because of the low quantum yield. In n-hexane, it has clear fine structure, which becomes obscured, red shifted and slightly broadened in toluene and THF. However, in DMF, it becomes much more broadened and the spectral shape is much different from those in the other solvents. This solvatochromism can be used to determine the excited state dipole moment \(\mu_E\) [34,36,37]. The difference between the ground and excited state dipole moments can significantly change with solvent polarity. The quantum yield of the crystal form (31%) is only about 2 times of that in toluene solution (15%). However, the crystal form gives rise to almost 200 times increase comparing with that in DMF solution. This phenomenon is similar to the recent results of AIE of CNDPASDB [29], indicating that the mechanism may be the restriction of the intramolecular charge transfer (ICT) state, which is a relatively dark state with low quantum yield. The phenomenon of intramolecular charge transfer has been extensively studied before [31–34].

![Fig. 1. (a) The molecular structure of TPCNDSB; (b) photo of TPCNDSB crystal and solution in different solvent illuminated under UV light; (c) absorption spectrum in hexane (black) and fluorescence spectra in hexane (pink), toluene (blue), tetrahydrofuran (THF, red) and dimethyl formamide (DMF, green) at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)](image)
be calculated by the Lippert–Mataga equation [38,39]:

\[ \nu_a - \nu_f = \frac{2\Delta f}{\hbar c a} (\mu_E - \mu_G)^2 + \text{const} \]  

(2)

\( \nu_a \) and \( \nu_f \) represent the maximum absorbance and fluorescence wavenumbers, respectively, \( \mu_G \) and \( \mu_E \) represent the ground state and excited molecular dipole moments, respectively, and \( a \) is the Onsager solvent cavity radius. Fig. 2 shows the Stokes shifts plotted as a function of orientational polarizability, \( \Delta f(\varepsilon, n) \). It is seen that the first 7 data points can be linearly fitted, while the last two points from DMF and acetonitrile are obviously out of the line. The straight line originates from the locally excited (LE) state and the other two data points are from the intramolecular charge transfer (ICT) state. LE state possesses a charge distribution similar to that of the ground state and emits normal fluorescence. On the other hand, ICT state involves transfer of substantial charges, so that is expected to have larger dipole moment and emit more red shifted fluorescence. LE state and ICT state have different excited state dipole moments, so they show different solvent polarity dependence [34]. Since TPCNDSB molecule is symmetric in structure, so \( \mu_E = 0 \). The cavity radius is estimated to be 9 Å, and from the slope of the line, a LE state dipole moment of 22 D is obtained. Since only two data points are available, accurate dipole moment of ICT state cannot be obtained. But it obviously has a larger slope than the LE state which will result in a bigger dipole moment. This is reasonable since the ICT state has a bigger degree of charge separation and hence a bigger dipole moment.

The emission spectra of TPCNDSB crystal and its toluene and DMF solution are compared to study its AIE property. The quantum yield is only doubled in crystal than that in toluene solution. However, the crystal quantum yield is almost 200 times bigger than that in DMF solution. The full width at half maximum (FWHM) of the DMF is much broader than that in toluene and crystal [Fig. 3 inset], indicating a new emission state arises in DMF solution.

### 3.2. Time resolved fluorescence

Time resolved emission spectra (TRES) can show how fluorescence spectra evolve with time, so is a powerful tool to resolve the formation of a new state. We reconstruct the TRES for toluene and DMF solution and the crystal form of TPCNDSB. For each of them, we measured the fluorescence transients at 9–18 different wavelengths. TRES were reconstructed as reported previously [35,40,41]. Briefly, all transients are normalized so that their time-integrated values are equal to the intensity of the steady state emission at the corresponding wavelengths. In this way, the normalized fluorescence intensity is known at all times for all detection wavelengths, and thus the TRES is attained. The time dependent spectral shifts were characterized by the time-dependent first moment (or average frequency) in kK (×10^3 cm⁻¹), which is proportional to the average energy of emission. The first moment in kK is given by [35,40,41]:

\[ \tau(\lambda,t) = 10,000 \times \frac{\sum_{\lambda} I(\lambda,t)/\lambda}{\sum_{\lambda} I(\lambda,t)} \]  

(3)

#### 3.2.1. TRES in toluene

Transient dynamics at some representative wavelengths of TPCNDSB toluene solution are given in Fig. 4(a). The fitted lifetimes are given in Table 2. The intensity decays very quickly on the blue side of the emission and displays a rise on the long wavelength side. The fast decay time constant is 1.93 ps (64%) at 485 nm, 5.08 ps (49%) at 500 nm and 5.88 ps (21%) at 515 nm. The time constant is increasing with the wavelength, and the fraction of the fast component is getting smaller. The rise time constant is 9 ps (8%) at 537 nm and 9 ps (34%) at 650 nm, showing an increasing fraction with wave-
Table 2

Best-fit parameters of femtosecond fluorescence upconversion transients of TPCNDSB in various solvents with function \( I \propto \sum A_i \exp(-t/\tau_i) \). Relative weights \((A_i)\) are given in brackets.

<table>
<thead>
<tr>
<th>Detection (nm)</th>
<th>(\tau_1) (ps)</th>
<th>(\tau_2) (ps)</th>
<th>(\tau_3) (ps)</th>
<th>(\tau_4) (ps)</th>
<th>(\tau_5) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In toluene</td>
<td>485</td>
<td>1.93(0.64)</td>
<td>16.8(0.19)</td>
<td>2300(0.17)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>5.08(0.49)</td>
<td>365(0.16)</td>
<td>2300(0.35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>5.88(0.21)</td>
<td>493(0.22)</td>
<td>2000(0.57)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>537</td>
<td>9(−0.08)</td>
<td>632(0.27)</td>
<td>2000(0.73)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>9(−0.14)</td>
<td>373(0.22)</td>
<td>2000(0.78)</td>
<td></td>
</tr>
<tr>
<td>In DMF</td>
<td>560</td>
<td>0.5(0.67)</td>
<td>2.05(0.3)</td>
<td>270(0.025)</td>
<td>3000(0.0033)</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.87(0.62)</td>
<td>3.31(0.29)</td>
<td>270(0.088)</td>
<td>3000(0.0038)</td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>0.26(−0.2)</td>
<td>2.69(0.7)</td>
<td>260(0.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>670</td>
<td>0.65(−0.29)</td>
<td>3.03(0.54)</td>
<td>260(0.46)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.46(−1)</td>
<td>3.08(0.39)</td>
<td>280(0.61)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>740</td>
<td>0.53(−1)</td>
<td>280(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal</td>
<td>560</td>
<td>117(0.65)</td>
<td>1200(0.35)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>168(0.71)</td>
<td>1700(0.29)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>690</td>
<td>86(0.5)</td>
<td>1700(0.5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Fluorescence dynamics for representative wavelengths of TPCNDSB in toluene (a), in DMF (b) and crystal (c). Insets show the short time window of the dynamics.

The TCSPC measurements show that the longest lifetime is identical for all wavelengths (2000–2300 ps).

The reconstructed TRES (Fig. 5(a) and (b)) show that in the first 20 ps, the emission spectra red shifted about 10 nm, which is a typical solvation process of TPCNDSB in toluene. Then the spectra begin to decay slowly, with an average lifetime of 1.63 ns for the peak (537 nm). The time resolved first moment \(ETB(t)\) (Fig. 6) shows that the spectra have a dynamic stokes shift of 200 cm\(^{-1}\) within 20 ps. No emergence of new state indicates that the excited state dynamics in toluene is dominated by solvation process.

3.2.2. TRES in DMF

In contrast to that of toluene solution, the emission in high polarity solvent DMF decays much faster (Fig. 4(b) and Table 2). The longest lifetimes determined by TCSPC show very pronounced wavelength dependent behavior, changing from 3 ns at shorter wavelengths (500–620 nm) to 260 ps at longer wavelengths (630–740 nm). Due to the limit of the up-conversion setup, the longest wavelength that can be measured in this work is 740 nm. The reconstructed TRES (Fig. 5(a)) show that during the first 1.5 ps, accompanying the decay of the main part spectra (LE state) there arises a new spectral feature (ICT state) on the red side. The LE state decays to half of the original amplitude in only 1.5 ps, and the ICT state grows large enough to be comparable with the main part, indicating the transition from LE state to ICT state is very efficient in DMF solution. After 1.5 ps, the spectra continues to red shift and decay much faster than that in toluene (1.63 ns), the average lifetime around the peak (680 nm) is only about 130 ps, explaining the low quantum yield of DMF solution.

The time resolved first moment \(ETB(t)\) (Fig. 6) shows that the spectrum has initial fast red shift of 1850 cm\(^{-1}\) in 20 ps, which is a much larger red shift than that in toluene (200 cm\(^{-1}\) in 20 ps). All these suggest that in DMF, the spectra evolve by a two state model. The initial LE state has a longer intrinsic lifetime of 3 ns, and the ICT state has a shorter intrinsic lifetime of 260 ps. As decaying, most part of the LE state transform to ICT state in a few picoseconds, resulting in a red shift and broadening of the spectra. Then, the remaining LE state continues to decay together with the ICT state.

3.2.3. TRES of crystal

Finally, the TRES of TPCNDSB crystal are reconstructed. The representative dynamics are given in Fig. 4(c) and the characteristic times are given in Table 2. Different from the former two dynamics in toluene and DMF, all wavelengths show almost the same dynamics, suggesting no solvation or state transition occur in crystal. The average lifetime is about 550 ps, smaller than that in toluene (1.63 ns), which is caused by exciton self-quenching in crys-
The molecules are so closed in crystal that when irradiated by the focused femtosecond (up conversion) pulses, self-quenching is easily occur. If under sufficiently low excitation intensity, the average life time of the crystal should be larger than that in toluene solution.

The reconstructed TRES (Fig. 5(e) and (f)) show no obvious change of the spectra and there is no new emerging component. The time resolved first moment $\tau(t)$ (Fig. 6) shows almost no change during the decay, so the emission of crystal can be explained by a single state model, indicating only LE state emitting, without transition to ICT state.

By examining the TRES of TPCNDSB in the above three cases, we have experimentally observed an emerging excited dark state – ICT state, which is responsible for the low quantum yield in high polarity solvent. In non-polar solvents, LE is the lowest excited state and the emission comes mainly from the LE state. Since the ICT state usually has a higher dipole moment than the LE state, it is more stabilized by the solvent and the energy levels of the two states become closer to each other as the polarity of the solvent gets higher and higher. When the polarity reaches a certain value like that in DMF, the ICT state becomes even lower than the LE state so that the emission is mainly from ICT state. The conformation of ICT state is quite different from the Frank Condon ground state, so the transition rate is low and the ICT state is a relatively dark state, which explains the low emission intensity in DMF.

![Fig. 5. Reconstructed time resolved emission spectra (TRES) of TPCNDSB in toluene (a) and (b), in DMF (c) and (d), and crystal (e) and (f).](image)

![Fig. 6. The time resolved first moment $\tau(t)$ of TPCNDSB emission in toluene, DMF and crystal. The uncertainties are within ±5%.](image)
4. Conclusions

In this work, we have performed time resolved fluorescence measurement on TPCNDSB in various solvents with increasing polarity and also in crystal form. By measuring the fluorescence dynamics at various wavelengths, time resolved emission spectra have been reconstructed. It is clearly revealed that in low polarity solvent like toluene, the emission is only from LE state with high quantum yield, whereas in high polarity solvent like DMF, a fast transition from the LE state to the ICT state happens, resulting in a low quantum yield. In crystal form, the packing of the TPCNDSB molecules results in a less polar local environment and the torsional motion is restricted, so the transfer from LE state to ICT state is eliminated, resulting in an efficient AIE. The results imply that the AIE mechanism of the restriction of the ICT state is quite general for dye molecules with donor–acceptor units. This knowledge of AIE mechanism is helpful for new development of OLED and laser materials.

Acknowledgement

The authors would like to acknowledge Natural Science Foundation, China (NSFC) under grants no. 21003060, no. 20973081 and no. 61076054 for support.

References