

# Comparative Time-Resolved Study of Two Aggregation-Induced Emissive Molecules

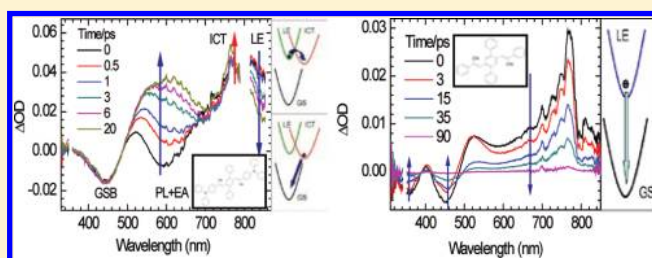
Bing-Rong Gao,<sup>†</sup> Hai-Yu Wang,<sup>\*,†</sup> Zhi-Yong Yang,<sup>†,‡</sup> Hai Wang,<sup>†,‡</sup> Lei Wang,<sup>†,‡</sup> Ying Jiang,<sup>†</sup> Ya-Wei Hao,<sup>†,‡</sup> Qi-Dai Chen,<sup>†</sup> Yu-Peng Li,<sup>§</sup> Yu-Guang Ma,<sup>§</sup> and Hong-Bo Sun<sup>\*,†,‡</sup>

<sup>†</sup>State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, and

<sup>§</sup>State Key Laboratory on Supramolecular Structures and Materials, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China

<sup>‡</sup>College of Physics, Jilin University, 119 Jiefang Road, Changchun 130023, People's Republic of China

**ABSTRACT:** Femtosecond time-resolved measurements are conducted on two aggregation-induced emissive molecules: cyano-substituted oligo-( $\alpha$ -phenylenevinylene)-1,4-bis(*R*-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (CNDPASDB) and cyano-substituted oligo(*p*-phenylenevinylene) (CNDPDSB). By examining whether the photoluminescence decay is accompanied by ground state bleaching recovery, different mechanisms for their low emission in solution state are revealed. For CNDPASDB with donor/acceptor group, the interconversion from the highly emissive local excited state to the relatively dark intramolecular charge transfer state results in the low emission. For CNDPDSB without electron donor group, there is no intermediate dark state, and the low emission is caused by the efficient vibrational/torsional nonradiative relaxation.



## 1. INTRODUCTION

Organic devices such as organic light emitting devices (OLEDs) and lasers usually function in solid state, in forms of spin-coated films or engineered crystal plates. However, most molecules highly luminescent in solution state emit weakly in solid state because of the emission quenching effect.<sup>1</sup> Consequently, increasing attention has been paid to enhance the solid state emission efficiency of luminescent materials. Many groups such as Tang's,<sup>2–9</sup> Park's,<sup>10</sup> and Ma's<sup>11–15</sup> have successfully synthesized various kinds of molecules possessing the property of aggregation-induced emission (AIE). It has been revealed by time-resolved spectroscopic studies that for molecules without donor/acceptor groups such as the typical AIE molecule silole,<sup>16–18</sup> lifetime elongation of the photoluminescence (PL) has been induced by aggregation, solution thickening, and cooling. It is suggested that in solvents with low viscosity at room temperature, the intramolecular vibrational and torsional motions<sup>3</sup> lead to the fast nonradiative relaxation and reduced fluorescence quantum yield. While in solid state (or in thick solvent, at low temperature), the rigorous restriction of these free motions deactivates the nonradiative pathways and results in high luminescence. For AIE molecules with donor/acceptor groups such as CNDPASDB<sup>19</sup> and TPCNDSB,<sup>20</sup> a fast interconversion from the highly emissive local excited (LE) state to the low emissive intramolecular charge transfer (ICT) state<sup>21–24</sup> is revealed in high polar solvents like DMF. In low polar solvent like toluene or in solid state, this transition is restricted, resulting in a high luminescence from the LE state.

If for molecules with donor/acceptor group in high polar solvents, a relatively dark state accounts for the low luminescence efficiency, we raise the question whether a similar dark state is

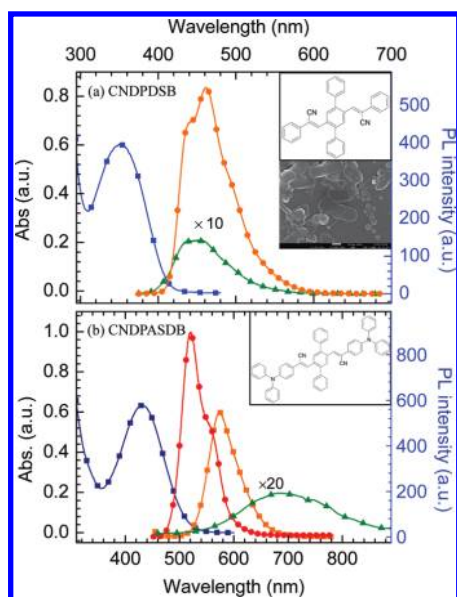
also present in the molecules without donor/acceptor group that is responsible for the low emission in solution state? We know that both the vibrational/torsional nonradiative pathway and the transition to a relatively dark state lead to a shortening of the PL lifetime. Therefore, solely examining the PL lifetime cannot distinguish these two mechanisms. Ren<sup>17</sup> et al. also mentioned the possibility of the existence of a nonfluorescent state for silole in solution state. While the PL dynamics reflects the population of the excited state, the transient absorption measurements detect the ground state bleaching (GSB) recovery dynamics, which exhibits the refilling of the ground state. Comparison of the dynamics of the GSB recovery with the PL dynamics can reveal whether a dark state exists.

Here in this report, we conducted transient absorption measurements for two AIE molecules, with and without donor/acceptor groups, to comparatively study their AIE mechanisms. Cyano-substituted oligo-( $\alpha$ -phenylenevinylene)-1,4-bis(*R*-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (CNDPASDB, referred to as ASDB in the rest of the text) possesses electron donor (diphenylamine) and electron acceptor (cyano) groups in its molecule structure and shows high fluorescence yield ( $\phi_f \sim 30\%$ ) in solid state.<sup>14</sup> Interesting phenomena such as two-photon absorption up-conversion emission<sup>25–28</sup> and pumping wavelength dependent ASE peak wavelength<sup>29</sup> have been found for ASDB crystal. Our previous work has demonstrated the existence of the dark ICT state in its DMF solution by reconstructed

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**Figure 1.** Steady state absorption (left axis) and PL spectra (right axis). (a) DSB absorption in THF (blue square), PL in THF (green up-triangle, multiplied by 10), and PL of the aggregate state (orange circle). The upper inset is the molecular structure of DSB, and the lower inset is the SEM image of DSB aggregate; the scale bar is 100 nm. (b) ASDB absorption in DMF (blue square), PL in *n*-hexane (red circle), PL of aggregate state (orange square), and PL in DMF (green up-triangle, multiplied by 20). The inset is the molecular structure of ASDB.

time-resolved emission spectrum (TRES). In the current research, we will further explore how this dark state could be revealed by the transient absorption experiment. Cyano-substituted oligo(*p*-phenylenevinylene) (CNDPDSB, referred to as DSB in the rest of the text)<sup>13,30</sup> is reported showing almost no fluorescence ( $\phi_f < 1\%$ ) in solution state, but its crystal exhibits very strong blue emission with  $\phi_f$  up to 80%, demonstrating a typical AIE behavior. DSB has similar molecular structure with ASDB, but without the electron donor group of diphenylamine locating at the two ends of the molecule. We compare its transient absorption results with that of ASDB to reveal whether a dark state is responsible for its low fluorescence in solution.

## 2. EXPERIMENTAL SECTION

ASDB and DSB were synthesized by a typical Knoevenagel condensation method.<sup>14,31</sup> DMF solution of ASDB and THF solution of DSB were prepared at a concentration of  $5 \times 10^{-5}$  mol/L. The aggregate state of DSB was prepared by slowly injecting its concentrated THF solution into a THF/water mixture of 90% volume fraction of water when the latter is being stirred. The concentration of the final solution is  $5 \times 10^{-5}$  mol/L. The scanning electron microscopic (SEM) image shows particles ranging from tens to hundreds of nanometers in size (Figure 1a, lower inset).

Absorption spectra were measured by a Shimadzu UV-1700 spectrophotometer at 0.2 nm resolution. Emission spectra were recorded with an AvaSpec-2048 fiber optic spectrometer at 0.6 nm resolution.

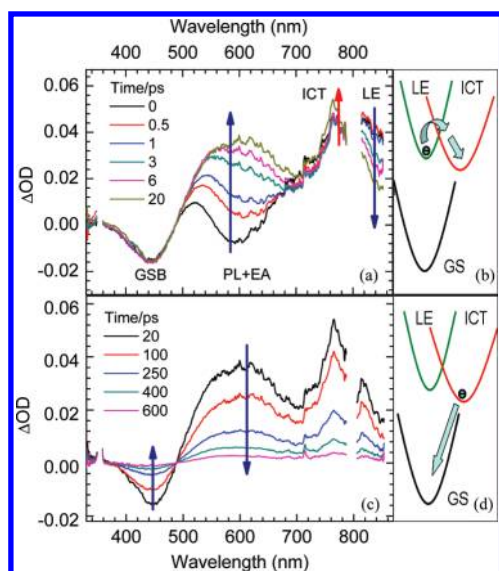
The femtosecond transient absorption spectroscopy was performed as follows.<sup>32</sup> The output of a Ti:Sapphire laser (Tsunami, Spectra Physics) pumped by a Nd:YVO laser (Millennia, Spectra Physics) was amplified in a regenerative amplifier (RGA, Spitfire,

Spectra Physics). The output of the amplifier of 1.5 mJ pulse energy, 100 fs pulse width, at 800 nm wavelength with a repetition rate of 250 Hz was split into two parts. One of them (800 nm) was then used to generate a white light continuum as the probe beam by focusing the beam into a 2 mm water cell (for ASDB measurements) or CaF<sub>2</sub> crystal (for DSB measurements). The other was either used to pump OPA to generate excitation pulse at 345 nm or sent to a 1 mm thick BBO to get the double frequency of 400 nm excitation pulses, which were then sent to a delay line and modulated by a synchronized optical chopper (Newport Model 75160) with a frequency of 125 Hz as the pump beam to excite the sample. Time-resolved transient absorption spectra were recorded with a highly sensitive spectrometer (Avantes AvaSpec-2048  $\times 14$ ). The dynamics traces were obtained by controlling the relative delay between the pump and the probe pulses with a stepper-motor-driven optical delay line (Newport M-ILS250CC). The relative polarization of the excitation and the probe beams was set to the magic angle for all the measurements. The group velocity dispersion of the whole experimental system was compensated by a chirp program. The intensities of the pump pulses were measured with a laser power meter (Sanwa LP1). The excitation spot is about 300  $\mu\text{m}$  in diameter. All the measurements were performed at room temperature.

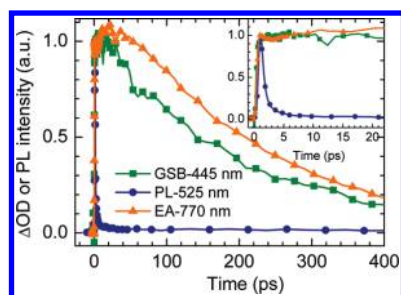
Subpicosecond time-resolved emissions were measured by the femtosecond fluorescence up-conversion method as reported previously.<sup>19</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Steady State Properties of DSB and ASDB.** Both DSB and ASDB show high luminescence in their crystal form. DSB emits blue light, and ASDB emits orange light. The reasons for the strong luminescence in crystal form are the same for both molecules. First, the strong supramolecular interactions (C—H...N hydrogen bonds) fix the double bond and the peripheral ring to prevent the free twisting motions around the double bonds; second, the twisted molecular structure prevents face-to-face  $\pi$ — $\pi$  stacking interaction by the bulky cyano and phenyl substituents.<sup>13</sup> However, in solution state, the two molecules show different behaviors. DSB exhibits low quantum efficiency in all solvents of varied polarities ( $\phi_f \sim 1\%$ ),<sup>13</sup> whereas ASDB shows solvent polarity dependent emission intensity. It has relatively high emission ( $\phi_f \sim 9\%$ ) in low and medium polar solvents from *n*-hexane to THF, but much lower emission for high polar solvents such as dimethyl formamide (DMF).<sup>19</sup> Their absorption and PL behaviors are also different (Figure 1). The absorption peak of DSB in THF is 345 nm and its PL peaks at 450 nm, without much change in solvents of different polarity and crystal form. However, both the absorption (434 nm) and PL spectra of ASDB red-shifted relative to DSB and show large solvatochromism effect: the emission peaks range from 520 nm in *n*-hexane to 685 nm in DMF.<sup>19</sup> We want to point out that the PL spectra measured here are different from that in our previous report which peaks at about 580 nm.<sup>19</sup> The reason is that the Shimadzu RF-S301PC spectrometer we used before is not sensitive to PL beyond 600 nm. In this work, we use an AvaSpec-2048 fiber optic spectrometer instead, which is much more sensitive to light of wavelengths from 600 to 800 nm and gives more reasonable PL spectra, peaking at 685 nm. (Note that the improper measurements of the steady state PL spectra only affect the spectral shape of the time-resolved emission spectra but do not affect the basic dynamical process. The conclusion in the previous paper still holds true.) For DSB, the molecule without the



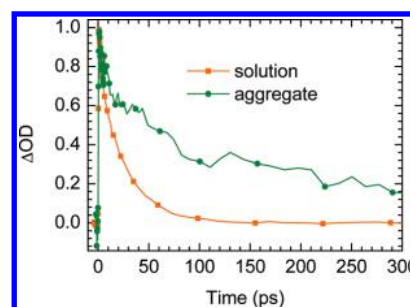
**Figure 2.** Transient absorption spectra of ASDB in DMF recorded at delay times (a) of the first 20 ps and (c) after 20 ps. (b) Illustration of LE  $\rightarrow$  ICT interconversion and the following conformation relaxation and (d) illustration of decay of ICT state to ground state.



**Figure 3.** ASDB dynamics of ground state bleaching of 445 nm (green square), ICT excited state absorption of 770 nm (orange up-triangle), and PL dynamics of 525 nm measured by fluorescence up-conversion (blue circle). The inset is the same dynamics in a 20 ps time window.

electron donor group, the real mechanism for the low emission in solution is still unclear. So we focus on comparative study of the origin of the low emissions of the two molecules in solution state to reveal whether there is a dark state for DSB in solution state.

**3.2. Time-Resolved Study of ASDB.** Transient absorption study of ASDB in the high polar solvent DMF was performed under excitation of 345 nm with a pump power of 20 nJ/pulse. Transient absorption spectra at different delay times are shown in Figure 2. The initial spectra consist of a GSB peaking at around 440 nm, a stimulated emission (SE) around 600 nm, and the excited state absorption (EA) ranging from 500 nm to over 840 nm, which overlaps with the SE. Note that SE here is much bluer than the steady state PL spectra in DMF peaking at 685 nm, but it is very similar to the PL of the aggregate peaking at about 600 nm (Figure 1b). It indicates that the origins of the SE and the steady state PL in DMF are different; they are not from the same excited state. In the first 20 ps, the SE decays very fast, leaving an EA peaking at 600 nm at the end of 20 ps. However, even though much change has occurred for the excited state, the GSB remains unchanged; it does not recover with the SE decay. Since the SE is



**Figure 4.** Comparison of PL dynamics of DSB aggregate (green circle) and its THF solution (orange square). The excitation wavelength is 345 nm; the detecting wavelength is 450 nm.

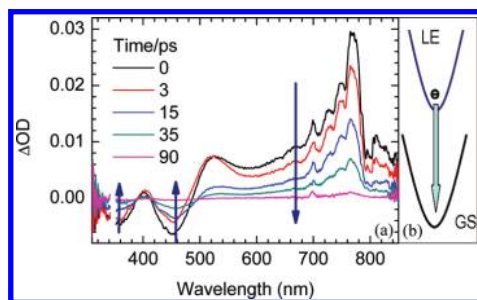
strongly overlapped with the EA in transient absorption measurements, it is hard to obtain a pure PL dynamics. So we conducted a fluorescence up-conversion experiment to measure the pure PL decay of 525 nm, which is the blue side of the LE emission with little influence from the ICT emission. The comparison of the GSB recovery and the PL dynamics (Figure 3) shows that for the first few picoseconds, the PL of 525 nm quickly decays out, but the GSB of 445 nm shows a flat curve, without any recovery. If the PL decay is not accompanied by a recovery of the GSB, it implies that there must exist an intermediate state where the excited state electrons go to, instead of going back to the ground state. It is consistent with the existence of a relatively dark ICT state in the ASDB of solution state.<sup>19</sup> A quick interconversion from the LE state to the ICT state happens, leaving the ground state unchanged. Now we can safely assign the SE peaking at 600 nm to the local excited (LE) state emission, which is much bluer than the ICT state emission (700 nm). The LE emission is strong, so the initial SE can be clearly seen in the transient absorption measurements; however, the ICT state is a relatively dark state, and its SE appears only as a small dip overlapped with the EA. The transient spectra from 500 to 840 nm are a mixture of the stimulated emission, the excited state absorption of the LE state and ICT state, so pure dynamics of any state cannot be found from the transient results. However, we can still find some clues of each state. If we check the EA at around 770 nm (Figure 3), a little initial decay followed by a rise component is revealed. The initial decay should come from the LE state, and the decay rate is consistent with the previous work.<sup>19</sup> The following rise component may come from the conformation relaxation to the bottom of the ICT energy surface, resulting in a red-shift of the stimulated emission spectra. The dip caused by the SE gradually red-shifts from 600 nm to about 700 nm, which becomes more like the steady state PL in DMF solution (Figure 2a). During this conformation relaxation, the ground state remains unchanged to about 20 ps. The LE  $\rightarrow$  ICT interconversion and the following conformation relaxation is depicted in Figure 2b. After 20 ps, spectra at all wavelengths decay with time (Figure 2c). The GSB also starts to recover with the decay of the EA. The EA after 20 ps are mainly caused by the ICT state because most of the LE state interconverts to the ICT state. The following decay is from the ICT state to the ground state, which is illustrated in Figure 2d. The time constant of the ICT decay of about 200 ps is much shorter than that of the LE state of 3 ns,<sup>19</sup> which indicates that the ICT state is a relatively dark state, explaining the low luminescence efficiency in DMF solution.

**3.3. Time-Resolved Study of DSB.** For DSB, we first conducted fluorescence up-conversion measurements of its tetrahydrofuran

**Table 1.** Best-Fit Parameters of Fluorescence Up-Conversion Transients of ASDB in DMF and DSB in THF and Aggregate State with Function  $I \propto \sum_i A_i \exp(-t/\tau_i)^a$ 

	detection (nm)	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ps)	$\tau_4$ (ps)
ASDB in DMF	525	0.65(0.87)	3.4(0.12)	6300(0.008)	3800(0.002)
DSB in THF	450	1.4(0.39)	23(0.61)		
DSB aggregate	450	2(0.43)	20(0.35)	142(0.2)	2770(0.02)

<sup>a</sup>Relative weights ( $A_i$ ) are given in parentheses.

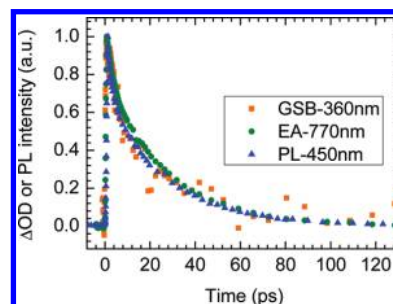


**Figure 5.** (a) Transient absorption spectra of DSB in THF recorded at various delay times. (b) Illustration of the decay of the excited state to the ground state.

(THF) solution and aggregate state. The excitation and detecting wavelengths were 345 and 450 nm, respectively. The excitation power is 20 nJ/pulse. The PL dynamics are shown in Figure 4. It is obvious that the PL lifetime of the aggregate is much longer than that of the solution state (Table 1), which explains the high luminescence in aggregate form. It is a similar result with that of the silole AIE study:<sup>17</sup> the aggregation of the molecules restricts the intramolecular motion and results in high luminescence. However, this PL lifetime shortening in solution state may come either from the vibrational/torsional nonradiative decay or from a fast transition from the LE state to a dark intermediate state. Therefore, it is hard to tell the real processes that happened in its solution from only the PL lifetime measurements.

From the transient absorption study of ASDB in DMF, we know that if there is an intermediate dark state, the GSB will not recover with the PL decay. The same approach can be used to further examine whether there is also a dark state in the solution state of DSB.

Transient absorption experiments were conducted on the THF solution of DSB under excitation of 345 nm, with a pump power of 20 nJ/pulse. The spectra consist of a GSB peaking at 350 nm, a SE peaking at 450 nm, and a broad EA from 500 to 840 nm. Both the GSB and SE spectra resemble the steady state absorption and PL spectra, respectively. Unlike the complicated spectra evolution of ASDB, all parts of the spectra of DSB decay at the same time (Figure 5). Again, because SE measured with transient absorption could be overlapped by EA, we use the PL dynamics of 450 nm obtained from the fluorescence up-conversion measurements to compare with the GSB recovery of 360 nm. Figure 6 show that the dynamics of the two are almost the same, the decay of the excited state corresponding to a recovery of the GSB. So the electrons from the excited state directly go back to the ground state, without going through any intermediate state (Figure 5b). The dynamics of the EA of 770 nm is also the same as the GSB recovery and the PL



**Figure 6.** DSB THF solution dynamics of the ground state bleaching recovery of 360 nm (orange square), the excited state absorption of 770 nm (green circle), and the PL decay measured with fluorescence up-conversion (blue up-triangle).

dynamics (Figure 6). All these prove that there is no intermediate nonluminescent state in DSB. Now we can conclude that the low luminescence in DSB solution is caused by the fast vibrational/torsional nonradiative decay, and there is no existence of nonfluorescent state.

#### 4. CONCLUSION

Transient absorption experiments have been performed on DMF solution of ASDB and THF solution of DSB to comparatively study the mechanisms of the low fluorescence in solution state. Fluorescence up-conversion measurements of their PL dynamics are also provided to compare with the transient absorption dynamics. For ASDB with donor/acceptor group, it is found that the rapid initial decay of the PL is not accompanied with the recovery of the GSB; instead, the GSB remains constant for the first 20 ps. It indicates the existence of an intermediate state, ICT state. Rapid LE  $\rightarrow$  ICT state interconversion happens, followed by the conformation relaxation, which results in the red-shift of the ICT emission. After 20 ps, the ICT state decays back to the ground state, resulting in a similar rate of 200 ps for the ICT decay and the GSB recovery. So the mechanism for the low fluorescence of ASDB solution is the interconversion from the highly luminescent LE state to a relatively dark ICT state. For DSB without donor/acceptor group, the decay of the PL and the EA are accompanied with a GSB recovery at the same rate, indicating no existence of an intermediate nonfluorescent state. So the mechanism for the low luminescence for DSB solution is the rapid vibrational/torsional nonradiative relaxation.

#### AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: haiyu\_wang@jlu.edu.cn (H.-Y.W.); hbsun@jlu.edu.cn (H.-B.S.).

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