

Photoluminescence Characteristics of p-Phenylene Vinylene and Its Derivatives in Solution and in Nanoaggregates

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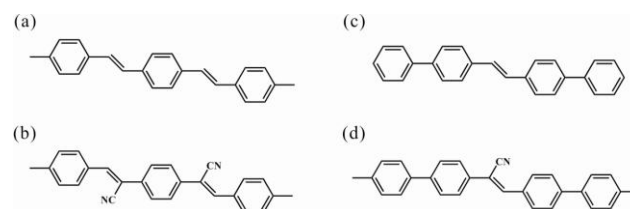
ABSTRACT: Oligomers of p-phenylene vinylene and its derivatives have drawn much attention due to their unusual emission characteristics of showing increased emission when they form into nanoparticles. We have investigated the optical properties of the oligo-(p-phenylene vinylene) and its cyano-substituted derivatives in solution and in nanoaggregate media by femtosecond and picosecond time resolved fluorescence as well as stationary spectroscopies. All the spectroscopic data are consistent with the conclusion that the cyano substitution on the β -position of oligo-(p-phenylene vinylene) leads to breakage of the otherwise planar structure of cyano-unsubstituted molecules, which opens up an extremely efficient, as fast as 100 fs, non-radiative relaxation channel of the excited state. Formation of the nanoaggregates reverts the effect to make the molecules planar and to block the non-radiative relaxation channel. Therefore, concerning the applications in organic electroluminescent devices and organic light emitting diodes, substitution by the cyano group is not advantageous, although such modification should be useful in respect of controlling fluorescence intensity in different media.

Poly(p-phenylene vinylene) (PPV) and conjugated polymer based materials have been studied extensively particularly concerning their optical properties, as their luminescence property can be utilized to fabricate electroluminescent devices and organic light emitting diodes.¹ Much efforts have been given to increase the emission quantum yield and to tune the transition energy and electron affinity of the conjugated polymers.²⁻⁵ Oligomers of p-phenylene vinylene and its derivatives are the useful model compounds for the study of their physical and optical properties.⁶

Organic nanoparticles provide distinct advantages in applications because they allow much variety and flexibility in materials synthesis compared to the inorganic counterparts.⁷ Nanoaggregates of organic molecules including the oligomers of p-phenylene vinylene have drawn considerable interest in part due to their enhanced emission property.⁷⁻¹⁴ In this work, we have investigated the fluorescence properties of nanoaggregates of oligomers of p-phenylene vinylene homologues and their cyano-substituted derivatives, 1,4-bis(4'-

methylstyryl)benzene (DS), 1,4-bis(β -cyano-4'-methylstyryl)benzene (DCS), trans-4,4'-diphenylstilbene (DPST), and 1-cyano-trans-1,2-bis-(4'-methylbiphenyl)ethylene (CN-MBE). Structures of the molecules are shown in Scheme 1. These molecules form spherical nanoaggregates in THF/water emulsion, and the cyano derivatives show enhanced emission in nanoaggregates.⁸ To examine this attractive optical property, stationary and time-resolved fluorescence (TRF) of the molecules in solution and their nanoaggregates in THF/water emulsion were investigated.

Scheme 1. Molecular structures of (a) DS, (b) DCS, (c) DPST, and (d) CN-MBE.



DPST (Lancaster, 99%) was purchased commercially and used as received. Synthesis of the molecule has been reported elsewhere.⁸ Nano-sized aggregates were prepared by the solvent-displacement process.¹⁵ Distilled water was added to the THF (Aldrich) solution of each molecule to form nanoaggregate. Concentrations of the molecules in both the THF solutions and THF/water suspensions were 20 μ M. All the experiments were performed at ambient temperature.

Time resolved experiments were performed by using a home-built Kerr-lens mode-locked cavity-dumped Ti:sapphire laser that generates 20 fs pulses centered at 760 nm with a repetition rate of 380 kHz. Pump pulses at 380 nm was generated by the second harmonic generation in a β -barium borate (BBO) crystal. Picosecond TRF was measured by a time correlated single photon counting (TCSPC) method and a microchannel plate photomultiplier tube, which gave instrumental response function having full width at half maximum (FWHM) of 50 ps. Polarization of the excitation pulse was rotated by a $\lambda/2$ plate located next to an input polarizer for the anisotropy measurement. Fluorescence upconversion by sum frequency generation (SFG) was used for the femtosecond TRF. Details of the setup has been reported previously.¹⁶ A 500 μ m thick

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BBO crystal was employed for the SFG in type I phase matching. Time resolution of the TRF apparatus estimated by the SFG of the scattered pump and the gate pulses was 160 fs (FWHM).

UV/VIS Absorption spectra of the molecules in THF solutions (supporting information, Figure S1) are peaked at 350–360 nm with small redshifts for the cyano-substituted molecules, DCS and CN-MBE. The effect of cyano-substitution on the transition energy was reported by Brédas and coworkers.^{2,17} The cyano-substitution leads to overall stabilization of the HOMO and LUMO levels because of its strong electron withdrawing nature. Upon formation of the nanoaggregates effective conjugation length increases, which manifests in the broadening of the spectral width with the appearance of a small shoulder in the 375–425 nm region for all molecules (Figure S1).

Fluorescence spectra of the solutions and aggregates, scaled by their estimated extinction coefficients, are shown in Figure 1. Fluorescence spectra of the unsubstituted species (DS and DPST) show vibration progressions of $\sim 1300\text{ cm}^{-1}$, which may be associated with the C=C stretching and C-H bending motions of the vinyl group,¹⁰ whereas clear vibrational structure is absent for the cyano-substituted molecules in THF. This is a strong indication that DS and DPST are in planar structure in excited state, but the cyano-substitution makes the molecules not planar. Excitation spectra are also recorded for nanoaggregates. The excitation spectra shown in Figure 1(d) are similar to the absorption spectra, although the small band around 400 nm for the aggregates are prominent in the excitation spectra. The shape of the fluorescence spectrum including the 400 nm peak is invariant upon change of the excitation wavelength, which strongly suggests that the 400 nm band is a part of the vibronic progression in aggregates.

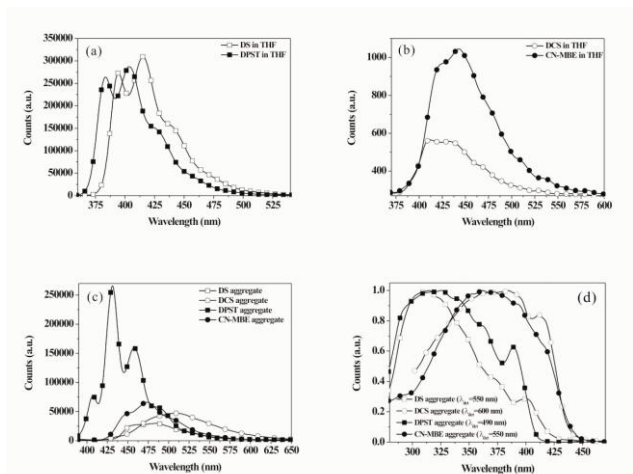


Figure 1. Fluorescence spectra of (a) DS and DPST in THF, (b) DCS and CN-MBE in THF, and (c) their nanoaggregates. ($\lambda_{\text{exc}} = 350\text{ nm}$). (d) Excitation spectra of nanoaggregates detected at the respective fluorescence wavelengths.

In THF solutions, the relative intensities of cyano-substituted molecules are ca. 400 times weaker than those of the unsubstituted molecules. This is consistent with the fluorescence spectra, where the cyano-substituted molecules do not show the vibrational structure indicating flexible non-planar structure in the excited state. Upon formation of nanoaggregates, the unsubstituted molecules show reduced fluorescence intensities by factors of 30 and 5 for DS and

DPST, respectively. In contrary, the cyano-substituted molecules show increased fluorescence intensities by as much as 50 and 60 times for DCS and CN-MBE, respectively, upon formation of nanoaggregates. It should also be noted that DPST, which is not cyano-substituted, shows the highest fluorescence intensity among all four nanoaggregates. Therefore, the stationary spectra in THF solution and in nanoaggregates suggest that the increased fluorescence intensity of cyano-substituted molecules in nanoaggregate is the recovery, not the enhancement, of the lost fluorescence intensity due to the cyano-substitution, which most likely causes the rotation of the dihedral angle between the benzene (naphthalene) rings to result in the loss of fluorescence intensity by the non-radiative process in non-planar flexible structure. This suggestion can be proved unambiguously by TRF measurements.

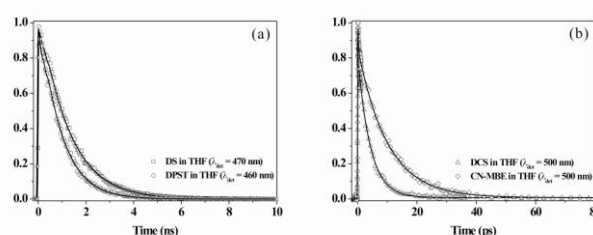


Figure 2. TRFs of THF solutions of (a) DS and DPST by TCSPC and (b) DCS and CN-MBE by fluorescence up-conversion methods.

Table 1. Exponential fit parameters for the TRFs of the molecules in THF.

	A_1	τ_1 (fs)	A_2	τ_2 (ps)	A_3	τ_3 (ns)
DS					1	1.2
DPST					1	0.9
DCS	0.69	90	0.31	4.2		
CN-MBE	0.40	130	0.6	10		

Table 2. Exponential fit parameters for the TRFs of nanoaggregates detected at 470 nm. Time constants are in nanoseconds.

	A_1	τ_1	A_2	τ_2	A_3	τ_3	$\langle \tau \rangle$
DS	0.29	0.45	0.57	1.8	0.14	5.0	1.9
DPST	0.32	0.17	0.56	0.7	0.12	2.7	0.77
DCS	0.45	0.08	0.32	1.6	0.23	7.4	2.2
CN-MBE	0.32	0.11	0.6	0.5	0.15	1.3	0.53

We have performed both TCSPC and fluorescence up-conversion experiments for the THF solutions of all four molecules to further understand their fluorescence behaviors, and they are shown in Figure 2. TRFs of the nanoaggregates (Figure S2) were measured only by TCSPC because of the interference from strong scattering of the nanoparticles. The TRF decay profiles were fitted to a sum of exponentials and the results are listed in Tables 1 and 2.

The TRFs of unsubstituted molecules in THF show a single exponential decay with $\sim 1\text{ ns}$ time constant, and the lifetime is not sensitive to the detection wavelengths indicating that the emissions come from a single excited state and that radiative relaxation is a

significant relaxation pathway. As implied from the stationary spectra, the cyano-substituted molecules in THF show ultrafast decay. The ultrafast decay rates are even faster than the values estimated from the stationary fluorescence intensities. Therefore, it can be concluded that the cyano-substitution does not alter the nature of the emitting state, but opens up an extremely efficient ~100 fs non-radiative relaxation channel.

Although TRFs of the unsubstituted molecules in THF solution show single exponential decay, TRFs in nanoaggregates show multi-exponential decay. In addition to the fast ~100 ps component (τ_1), all the nanoaggregates show a nanosecond component (τ_3). In particular, nanoaggregates of cyano-substituted molecules show a significant nanosecond component, which are absent in the TRFs in THF solutions. The average lifetimes of all four nanoaggregates listed in the last column are all close to 1 ns. In fact, the TRFs of nanoaggregates of all four molecules are rather similar suggesting that both intra- and inter-molecular structures in nanoaggregates are also similar for all four molecules. The vibrational structures in stationary fluorescence spectra of nanoaggregates suggest that they are in planar geometry, and the optimized geometry of the unsubstituted molecules are also close to planar.

Fluorescence intensity difference between the cyano-substituted and unsubstituted molecules in THF solutions may arise from the difference of molecular geometry. DFT calculations showed that the dihedral angles between the vinylene and phenyl groups are zero for the oligomers of p-phenylene vinylene, giving planar structures.¹⁸ We obtained comparable results from the semi-empirical calculations by PM3 Hamiltonian. DS and DPST have planar C_2 geometries, although the outer phenyl rings of DPST are tilted around 47° to the stilbene plane because of the ortho-hydrogen steric hindrance. However, the cyano-substituted DCS and CN-MBE show twisted geometries; cyano groups made 8° with the middle ring and 50° with the outer rings in DCS, and all ring units in CN-MBE made ~47° to the adjacent groups. Accordingly, the cyano-substituted molecules show low fluorescence quantum yields via the torsion induced nonradiative deactivation.¹² When the molecules in poor solvent make aggregate spontaneously, molecular environment become different from normal solution. Distances between molecules are getting closer and packed. Molecular geometry will be changed during the aggregate formation. Levitus et al. suggested such aggregation scheme from their studies on 1,4 - bis(phenylene ethynyl)benzene,¹⁹ which is called aggregation-induced planarization. Consequently, the torsional nonradiative relaxation is effectively suppressed.

In conclusion, we have shown by stationary and pico- and femto-second time-resolved fluorescence that the introduction of the cyano group to the oligomers of p-phenylene vinylene opens up a non-radiative relaxation channel by the rotation of the dihedral angle of the phenyl groups. The resulting fluorescence quenching is extremely efficient to make the fluorescence decay ultrafast in 100 fs. The formation of nanoaggregates induces planarization to block the non-radiative relaxation channel and to increase the fluorescence quantum yields. The molecules without the cyano group remain planar in solution and in nanoaggregates to give strong fluorescence in both media. Thus, in respect to the applications in organic electroluminescent devices and organic light emitting diodes, substitution by the cyano group is not advantageous. In the respect of

control of the fluorescence intensity in different media, however, such modification should be useful.

KEYWORDS: p-phenylene vinylene, nanoaggregates, time-resolved fluorescence

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