Chapter VI

Soluble Fluorescent Derivatives of Poly(Phenylenevinylene) in Solution and in Supramolecular Assemblies
6.1 Introduction

In Chapter I, it was pointed out that the PPV polymer, despite having novel properties like fluorescence and electrical conductivity, has an inherent problem of solubility. This severely hinders the preparation of PPV solutions or films, thus restricting its usage for practical purposes. To circumvent this problem, soluble PPV derivatives have been developed in recent times, mainly by introducing suitable side-groups into the ring that promote solubility in a variety of solvents, without seriously compromising the core optoelectronic properties of pure PPV. Following this strategy, we have synthesized two soluble fluorescent PPV derivatives: mehPPV and mcpPPV, which are depicted in Figure 1. In this Chapter, we delve into the photophysical studies carried out on these two derivatives.

![Structure of mehPPV and mcpPPV](image)

**Figure 1:** Structure of mehPPV and mcpPPV.

mehPPV is probably the most well-known among the soluble PPV derivatives, and its physico-chemical properties are well-documented [1-22]. For mehPPV, the presence of alkoxy side-groups in its phenylene unit dramatically improves its solubility in a number of non-aqueous solvents over a wide range of dielectric constants. The polymer solubility results from favorable solvent-segment interactions that dominate over segment-segment interactions. Moreover, different solvents exhibit different degrees of interaction with different types of segments [23-25]. For example, solvents like chlorobenzene, xylene and toluene preferentially solvate the main phenylenevinylene backbone, while solvents like THF and chloroform preferentially solvate the lateral substituents. These interactions are usually determined by parameters like molecular architecture, aromaticity, and solvent polarity. A good solvent such as chloroform allows the polymer chain to adopt an extended conformation, while in poor solvents such as aliphatic alkanes and alkyl alcohols, the polymer chain collapses, and several polymer chains
may come together to form aggregates [26,27]. A schematic view of the polymer conformations in these two kinds of solvents is offered in Figure 2.

![Figure 2: Schematic view of the polymer conformations in two different kinds of solvents (see text for details).](image)

Although the polymer backbone consists of alternating single and double bonds, there are several means by which the conjugation can be interrupted [28]:

i) Presence of structural defects like saturated carbon centres resulting from random synthetic errors or oxidation of double bonds.

ii) Rotation around the single bonds which disrupts the planarity of the $\pi$-electron orbitals and thus hinders unrestricted $\pi$-electron delocalization along the entire main chain length.

Due to these factors, the effective conjugation length of the polymer is drastically reduced. Thus, in realistic terms, a schematic representation of a conjugated polymer molecule should be a random, linear sequence of conjugated segments of varying lengths, punctuated by centres where the conjugation is destroyed, as depicted in Figure 3.
The shorter conjugated segments (blue sticks in Figure 3) absorb and emit at relatively shorter wavelengths (i.e., higher energies) in comparison to the longer conjugated segments (red sticks in Figure 3), which absorb and emit at relatively longer wavelengths (i.e., lower energies). Each of these segments behave as independent fluorophores, so that a conjugated polymer chain is essentially a set of different fluorophores having different ranges of absorption and emission bands. Such a situation favors energy transfer when the absorption of a long-conjugated segment overlaps with the emission of a short-conjugated segment.

Under this situation, the polymer conformation plays a crucial role in defining its photophysics [4,5,7,11,14,19-21]. On the one hand, in good solvents, where a more extended conformation predominates, the polymer segments are surrounded by solvent molecules and prevented from approaching too close to each other. This hinders energy transfer, ensuring that a larger proportion of blue-emitting shorter segments survive without losing their energy non-radiatively. As a result, the overall emission spectrum is blue-shifted. On the other hand, in poor solvents, one or more polymer chains collapse to form a tight coil or aggregate, expelling the solvent molecules. This draws the conjugated segments to close vicinity, promoting both intra-chain and inter-chain energy transfer, enhancing the population of long-conjugated segments at the cost of the short-conjugated segments. As a result, the overall emission spectrum is red-shifted.
During the preparation of polymer films from polymer solutions, the conjugated polymer molecule usually retains its solution conformation even in the film state [7,13,18,29-31]. This structural memory effect underlines how important it is to make the proper choice of solvent while processing a given conjugated polymer.

For mehPPV, the absorption and emission spectra have been shown to depend on the nature of the solvent, allowing the classification of good and poor solvents [2-5,9,15,16]. In this Chapter, our objective is to extend the scope of mehPPV photophysics into supramolecular assemblies like AOT-based organogels and aqueous micelle solutions. Here we point out that mehPPV is insoluble in pure water. Thus, solubilization in a micelle – if possible – will afford a means to introduce it into a predominantly aqueous environment.

The second PPV derivative that we studied - mcpPPV – carries carboxylic acid bearing side-groups. These not only promote its solubility in water, but deprotonation of these groups at a suitable pH range turns the mcpPPV into a fluorescent conjugated polyelectrolyte. In other words, the presence of the carboxylic moieties allows the polymer to be launched into a water-based platform without the use of a micelle-like carrier. This in turn, may open up the possibility of utilizing PPV fluorescence properties in a biological environment.

In contrast to mehPPV, reports on conjugated polyelectrolytes like mcpPPV are rare [32-38]. While some of these works dwell upon films cast from solutions of ionic PPV derivatives [35,36], others have focused on fluorescence quenching [33] and charge transfer processes [34]. Very recently, composites between water soluble PPV derivatives and PbS nanocrystals have been reported [38]. However, to our knowledge there are still no reports on the detailed photophysics of such PPV derivatives in solvents, which are capable of affording a wide variety of environments that might modify the fluorescence properties of the polymers.

Keeping this mind, we have taken up the photophysical studies of mcpPPV in water as well as in a number of non-aqueous solvents. In water, we have also examined the effect of basic pH, which causes deprotonation of the carboxylic acid groups, turning mcpPPV into an anionic polymer. We have also incorporated the polymer in aqueous micelle solutions as well as in sol gel glasses to probe the effect of confinement.
6.2 Experimental Details

6.2.1 Chemicals

Solvents used for spectroscopy were purchased from Merck, India and were of either UV or HPLC grade. They were freshly distilled before conducting spectroscopic measurement. Tetraethyl orthosilicate (TEOS) for sol-gel glass synthesis, Pluronic F68 amphiphilic triblock copolymer and surfactants CTAB, SDS, TX-100 were purchased from Sigma-Aldrich. Surfactant AOT (Sigma) was dried in vacuum for 10-12 hours before use was purchased from Aldrich.

6.2.2 Sample preparation

a) PPV polymers

The synthesis, isolation, purification and characterization of the PPV derivative mehPPV and mcpPPV are described in details in Chapter II [Section 2.2, Scheme 3 and 4, along with related discussions].

b) AOT organogel

Organogels were prepared [39, 40] taking m-xylene as solvent and adding AOT and p-chlorophenol (PCP). PCP and AOT were dissolved separately in m-xylene containing dissolved mehPPV. The initial concentrations of both PCP and AOT were maintained at 0.4 M. When these pregel solutions were mixed at 1:1 ratio at room temperature, immediate gelation was observed. The mixture was then heated up to 80 °C in a water bath to obtain an isotropic solution. The solution was removed from the water bath and cooled down to room temperature, whereupon a solid AOT organogel containing entrapped mehPPV was obtained.

c) Sol-gel glass

These were prepared following the usual method [20, 41] of room temperature acid hydrolysis of TEOS followed by alcohol condensation. The mcpPPV was added in situ during the synthesis. The polymer-laden glass samples were dried in oven (60 °C) for three days before study.

6.2.3 Spectroscopy

Absorption and fluorescence spectra were measured in a HITACHI UV spectrophotometer (U-3501) and Perkin Elmer LS55B fluorimeter, respectively. For fluorescence dynamics studies in the nanosecond time-scales, a picosecond time correlated single photon counting (TCSPC) system of JobinYvon Horiba was used, employing a picosecond diode laser operating with $\lambda_{ex} = 450$ nm and pulsewidth of ~80 ps.
6.3 Results and Discussion

6.3.1 Steady state spectra of mehPPV

The absorption and emission spectra of mehPPV in different solvents are shown in Figure 4. Emission spectra were recorded at $\lambda_{\text{ex}} = 450$ nm, although changing $\lambda_{\text{ex}}$ along 450 nm to 500 nm produced no change in the emission peak position for any of the media under study.

On the basis of spectral peak positions, the solvents can be clearly divided into two distinct groups. On the one hand, in dioxane, THF, chloroform and toluene, the absorption bands are narrow, with sharp peak positions nearly coinciding at $\sim 500$ nm. The emission peaks appear around 550 nm, with a shoulder at $\sim 600$ nm. On the other hand, in solvents acetonitrile, DMF and aliphatic alcohols from methanol to 1-decanol, the absorption bands extend into longer wavelengths, with considerably broader peaks. Moreover, the emission spectra in these solvents are noticeably red-shifted, with peaks appearing around 600 nm, and shoulders at $\sim 640$ nm. Such type of behavior has been previously reported for mehPPV [2-4,6-7,16-18].

Following the discussion in the Introduction section, the spectral characteristics helps us to distinguish between good solvents and poor solvents for mehPPV. Thus, as far as solubility of
mehPPV is concerned, dioxane, THF, chloroform and toluene behave as good solvents, whereas acetonitrile, DMF and the aliphatic alcohols behave as poor solvents.

Next, we examined the fluorescence properties of mehPPV in AOT organogels and aqueous micelle solutions. While mehPPV could be readily incorporated into the AOT organogel, it was found to be insoluble in micelle solutions of ordinary surfactants like CTAB, SDS or TX-100. However, mehPPV could be solubilized in aqueous micelle solutions of the Pluronic F68 triblock copolymers, which behave like surfactants owing to their amphiphilicity.

The emission spectra of mehPPV in organogels and pluronic micelle solutions are appended to Figure 4. The spectral peak positions immediately suggest that the organogels cluster with the good solvents, while the pluronic micelles cluster with the poor solvents. When we closely compare the emission spectra of mehPPV in m-xylene, AOT/m-xylene reverse micelle solutions and AOT/PCP/m-xylene organogels, we find that the first two nearly coincide, while the third one undergoes a small but definite red-shift, as shown in Figure 5. This clearly indicates that entrapment of mehPPV in the organogels perturbs its local environment in comparison to that in pure m-xylene solution, although the environment still resembles that of a good solvent.

6.3.2 Picosecond Time-resolved Spectroscopy of mehPPV

Time-resolved experiments were done with $\lambda_{ex} = 450$ nm. The resulting transient emission curves are shown in Figure 6. For each solvent, transients were recorded at different
emission wavelengths across the emission spectrum. However, the curves do not display any notable dependence on emission wavelength.

Figure 6: Picosecond transient emission curves of mehPPV in different solvents.
For the emission curves of mehPPV in the good solvents, a mono-exponential fit was sufficient, yielding a decay time-constant of ~0.3 ns. In contrast, a double-exponential decay was necessary to fit the transients in the poor solvents, yielding a major component of ~0.2 ns and a minor component of ~0.8 ns. Thus, the difference in solvent environment is also reflected in the picoseconds dynamics of mehPPV. However, the average time-constant in poor solvents is nearly similar to that in good solvents, i.e., ~0.3 ns.

Transient emission curves for mehPPV in AOT organogels and pluronic micelles are shown in Figure 7. The curves in organogels comply to a simple mono-exponential decay of time-constant ~0.3 ns, similar to the time-constant of ~0.28 ns in pure m-xylene. In pluronic micelles, a double-exponential fit with time-constants of 0.18 ns (90%) and 1.0 ns (10%) was necessary. In other words, the emission dynamics of mehPPV in organogels and aqueous micelle solutions resemble those in good solvents and poor solvents, respectively.

Figure 7: Picosecond transient emission curves of mehPPV in organogels and pluronic micelles.
6.3.3 **Steady state spectra of mcpPPV**

The absorption and emission spectra of mcpPPV in different solvents and micelles are shown in Figure 8. Emission spectra were recorded at $\lambda_{ex} = 450$ nm, although changing $\lambda_{ex}$ across the visible absorption band from 400 nm to 500 nm produced no change in the emission peak position for any of the media shown in Figure 8.

![Figure 8: The absorption and emission spectra of mcpPPV in different solvents and supramolecular assemblies.](image-url)
In the pure solution, the emission spectra of mcpPPV definitely depends on the nature of the solvent. The spectrum in dioxane is most blue-shifted, followed by methanol. In water at pH = 7, the spectrum is distinctly red-shifted. However, in water at pH = 12, a prominent blue-shifted shoulder appears at ~525 nm, approximately coinciding with the peak in dioxane. These results suggest that although mcpPPV is soluble in water, the latter still behaves as a poor boxylic solvent. As a result, the polymer in aqueous solution adopts a coiled conformation which favors energy transfer from the blue-emitting short conjugated segments to the red-emitting long conjugated segments, causing the overall emission spectrum to be red-shifted. However, at basic pH, the carboxylic groups of mcpPPV ionize, so that the polymer chain becomes anionic. This produces strong electrostatic repulsion between the carboxylate anions that pushes the segments apart. In other words, the polymer coil swells up and energy transfer is diminished as the average segment-segment distance becomes longer.

In the aqueous micelles, the mcpPPV appears to experience a good solvent-like environment. This contrasts to what we observed in mehPPV, where the environment in aqueous micelles decidedly resembled that in a poor solvent. In fact, mehPPV could not be solubilized in aqueous micelles of common surfactants like CTAB, SDS or TX-100, but required micelles of the amphiphilic block copolymer Pluronic F68. The absence of polar groups in mehPPV prevents its solubility in polar solvents like water. Hence inside the micelle, it preferably occupies the hydrophobic core region rather than the hydrophilic shell. However, due to the nano-dimensional size of the micelle core, mehPPV is forced to adopt a tightly coiled conformation in the micelles. This facilitates segment–segment energy transfer, producing a red-shifted emission even when the local environment of mehPPV is non-polar.

On the other hand, mcpPPV is soluble in water, and highly soluble in methanol. Hence, in micelle solutions, it partitions preferentially into the hydrophilic surface region of the micelles particles. The surface region is rich with interfacial water molecules, creating a local polarity that is lower than that found in of pure, bulk water. Thus, the local environment at the micelle surface is similar to that in moderately polar solvents like methanol where mcpPPV is highly soluble. This leads to favorable solvent-segment interactions, causing the polymer chain to open up. Consequently, the emission spectrum is blue-shifted.

Finally, the spectra of mcpPPV entrapped in sol-gel glass is shown in Figure 9. Here, we observe an unusual blue-shift of both the absorption as well as emission spectra of mcpPPV.
Figure 9: The absorption and emission spectra ($\lambda_{ex} = 370$ nm) of mcpPPV in glass.

compared to all of the other solvents/ supramolecular assemblies probed. The emission spectrum in water is also appended to Figure 9 in order to highlight the extent of the blue-shift.

This unusually large blue shift does not conform to the usual explanation based on good/ poor solvent. Moreover, we note that, once mcpPPV was embedded in the silicate glass, it could not be extracted by treatment with any of the solvents, including methanol. This suggests that the mcpPPV molecule entrapped within the pores of the silicate glass becomes cross-linked, which drastically decreases the average conjugation length. This may account for the extreme blue shift of the spectra in Figure 9.

6.3.4 Picosecond Time-resolved Spectroscopy of mcpPPV

Time-resolved experiments were done with $\lambda_{ex} = 450$ nm. The resulting transient emission curves for mcpPPV in the solvents are shown in Figure 10. For each solvent, transients were recorded at different emission wavelengths at 10 nm intervals across the emission spectrum. In water at pH = 7, the emission decay is extremely fast and does not display any notable dependence on emission wavelength. However, in the non-aqueous solvents, the emission decay becomes remarkably faster at longer emission wavelengths. This effect is most pronounced in the good solvent methanol and dioxane. In contrast to water at pH = 7, the transient emission curves of mcpPPV in water at pH = 12, shown in Figure 11, exhibit an emission wavelength dependence similar to that in the non-aqueous solvents in Figure 10.
Figure 10: Picosecond transient emission curves of mcpPPV in different solvents.
The transient emission curves for mcpPPV in the micelles are shown in Figure 12. Considering the data from both steady-state and time-resolved spectroscopy, we can safely conclude that mcpPPV in aqueous micelle solutions find themselves in a local environment that is quite different from that in bulk water, but rather resembles moderately polar solvents like methanol. As discussed above, a substantial proportion of mcpPPV polymers are embedded in the polar shell region of the micelles.

The transient emission curves in figures 10 to 12 were fitted with a poly-exponential decay function of the form:

$$F(t) = \sum_j [a_j \times \exp(-t/\tau_j)]$$

For mcpPPV in aqueous solutions (pH=7), a double exponential fitting with time-constants of ~120 ps (97%) and ~700 ps (3%) was adequate. In the micelles, the decay time-constants were 120 ps and 800±200 ps, with the shorter component dominating at longer emission wavelengths. In bulk water at pH = 12, the trends are similar, only the time-constants being 120 ps and 1 ns ± 200 ps. The results confirm what we inferred from the steady state spectra. In aqueous micelle solutions, the mcpPPV samples a heterogeneous local environment: the 120 ps component is identified with the environment in the bulk, outside the micelle solutions, while the longer component can be associated with a location which is markedly different from bulk water. The latter is most probably the polar surface of the micelles.
Figure 12: Picosecond transient emission curves of mcpPPV in different aqueous micelles.
6.3.5 Time-resolved Emission Spectra of mcpPPV

The results obtained from the time-resolved emission studies can be summarized as follows:

i) The transient emission curves in each case show a monotonic poly-exponential decay, with no growth-like feature.

ii) In solvents other than water, the decay rate depends on the emission wavelength. Remarkably, the decay rate becomes faster at longer emission wavelengths. The same holds true in the micelle solutions of SDS and TX-100.

Emission wavelength dependence of decay rate often indicates the occurrence of solvation dynamics, as described in Chapters III and IV. However, in that case, the decay rate is supposed to become slower at longer wavelengths, and is associated with a time-dependent Stokes shift. However, for mcpPPV in solvents and micelle solutions, we observe exactly the opposite. Thus, solvation dynamics can be ruled out for these types of systems. On the other hand the conspicuous absence of single-exponential decay suggests that the excited state of mcpPPV in these solvents and micelles may not involve only one single emissive species. In such a situation, construction of the Time-resolved Area Normalized Emission Spectra or TRANES serves as a convenient tool for elucidating the nature of the excited emissive state [42-44]. The TRANES analysis has already been utilized in Chapter V to deal with the emission of the Pterin molecules. We follow the same method here for mcpPPV in the three solvents: Water at pH =12, Acetonitrile, Methanol and Dioxane.

For mcpPPV in any of these solutions, the Time-resolved Emission Spectra (TRES) were first constructed using the fitting parameters for the transient emission curves.

\[
I(v,t) = \frac{I_{ss}(v) \times \sum_j [a_j(v) \times \exp(-t/\tau_j)]}{\sum_j [a_j(v) \tau_j]}
\]

The procedure of constructing TRES has already been described in detail in Chapter III. Next, TRANES were constructed by normalizing the area under the TRES curve such that the area of the spectrum at time \( t \) is equal to the area of the spectrum at \( t = 0 \).

The TRANES for mcpPPV in some of the solvents are shown in Figure 13.
Figure 13: The TRANES for mcpPPV in Water at pH =12, Acetonitrile and Dioxane, over a time-delay from 100 ps to 5 ns.
Each of the TRANES curves in Figure 13 reveal a depletion of the red-shifted emission intensity, along with a concomitant rise of the blue-shifted emission intensity, at longer time-delays. However, the most remarkable feature of the TRANES curves in Figure 13 is the unambiguous presence of an isoemissive point in each solvent. For mcpPPV in water at pH =12, Acetonitrile and Dioxane, the isoemissive points appear at 18100, 18230 and 19250 cm$^{-1}$, respectively. This fact clearly indicates that the excited state of mcpPPV in these solvents comprise of two distinct emissive species [42-44].

It should be noted that the TRANES method does not allow us to identify the nature of the two emissive species involved. It also cannot clarify whether these two species are in equilibrium or not. Nevertheless, the clear evidence of two distinct emissive species in a complicated molecule like mcpPPV – a high polymer capable of assuming virtually endless number of conformations – is itself remarkable. To our knowledge this is the first instance in which the TRANES method has been successfully applied in unraveling the nature of the emitting states of a fluorescent conjugated polymer.

The TRANES of mcpPPV in water at pH = 7 could not be constructed since the transient emission curves in this case did not show any significant dependence of the emission wavelength. On the other hand, for methanol, the TRANES could be constructed at different time-delays, but no clear isoemissive point was found. The reason for this is not very clear at the moment. One possibility is that methanol may form strong intermolecular H-bonds with the polar side-groups of mcpPPV, which perturb the energy levels of the emissive state. Hence, two distinct emissive species cease to exist, and are instead replaced by a range of emissive states with closely spaced energy levels. Consequently, no unique isoemissive point appears in the TRANES.

6.4. Conclusions

In this chapter of the thesis, we have addressed the problem of photophysics of two soluble derivatives of PPV, the well known conjugated polymer, namely – mehPPV and mcpPPV. The spectral characteristics of mehPPV in the solution state could be interpreted in terms of the conformation state of the polymer in solution, which allowed us to distinguish between what could be regarded as good solvents or poor solvents for mehPPV. In the former, segment-solvent interactions were favorable, driving the polymer chain to adopt a more open
conformation which minimized energy transfer between the short conjugation length segments and long conjugation length segments of the chain. As a result, the overall emission spectrum of the polymer tends to be blue shifted, because a higher proportion of blue-emitting short conjugation length segments survive without losing their excitation via non-radiative energy transfer to the red-emitting long conjugation length segments. On the other hand, in the poor solvents, segment-solvent interactions are less favorable, so that the polymer chain tends to collapse into a tight coil, wherefrom the solvent molecules are largely excluded. This brings the polymer segments into close vicinity to each other, promoting energy transfer from high-energy to low-energy segments. Consequently, the overall emission spectrum tends to be red shifted, because energy transfer ensures that a large number of red-emitting long conjugation length segments are generated at the cost of blue-emitting short conjugation length segments.

We specifically explored the photophysics of mehPPV in two supramolecular assemblies: AOT organogels and aqueous micelle solutions of Pluronic block copolymers.

In the organogels, the fluorescence spectral behavior of mehPPV was similar to that in the precursor solution, where the solvent is m-xylene, regarded as a good solvent. Although gelation did modify the spectral characteristics of mehPPV, the change in its conformational state appears not to be too significant.

In the aqueous micelles, the spectroscopic data suggests that mehPPV experiences a poor solvent like environment. mehPPV is itself insoluble in water, so that in a micelle solution, it should be exclusively localized inside the micelle nano-particle and not in the bulk aqueous dispersion phase. The forced confinement of the high polymer inside the nano-dimensional volume of the micelle particle naturally induces coiling of the polymer chain. As a result, its spectral properties resemble that found in poor solvents.

The other PPV derivative – mcpPPV – stands out because of its solubility in water. Although the solubility is not extremely high, it is considerably higher than that of the water-insoluble mehPPV, allowing the formation and study of aqueous solutions of mcpPPV. Nevertheless, water still behaved as a poor solvent for this polymer along with solvents like acetonitrile, while dioxane and methanol appeared to behave as good solvents. Interestingly, at basic pH, the emission spectrum of mcpPPV in water suggests the onset of good solvent-like environment. We explained this in terms of the deprotonation of the carboxylic side groups of the polymer at basic pH. This generates negatively charged centres along the polymer chain,
which opposes the collapse of the polymer due to electrostatic repulsion between like-charged segments. Consequently, the polymer is forced to adopt an elongated conformation even in water.

In aqueous micelle solutions, the mcpPPV was found to partition between the aqueous phase and the micelle particles, where it occupied the polar outer shell of the micelle.

The transient emission curves of the polymer in the non-aqueous solvents show that the emission decay rate depend strongly on the emission wavelength. However, in stark contrast to well-known phenomena like salvation dynamics, here the decay rates become faster at longer wavelengths. This, along with the utter absence of mono-exponential decay of the emission dynamics, strongly suggested that the excited state of mcpPPV in these solvents involves more than one emissive species. To probe this issue, we applied the TRANES analysis. For mcpPPV in solvents acetonitrile, dioxane and water at pH =12, the TRANES curves clearly reveal the clear presence of isoemissive points, indicating the presence of two emissive species in the excited state.

However, no unique isoemissive point was obtained for mcpPPV in methanol. Although the reason for this is not very clear to us, intermolecular H-bonding between mcpPPV and methanol solvent may create a large number of emissive species with closely spaced energy levels, obscuring any signature of a definite isoemissive point.

6.5 References

Chapter VI