

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234003643>

Room-Temperature Phosphorescence From Films of Isolated Water-Soluble Conjugated Polymers in Hydrogen-Bonded Matrices

ARTICLE *in* ADVANCED FUNCTIONAL MATERIALS · SEPTEMBER 2012

Impact Factor: 11.81 · DOI: 10.1002/adfm.201200814

CITATIONS

18

READS

36

2 AUTHORS, INCLUDING:



Andy Monkman

Durham University

415 PUBLICATIONS 9,698 CITATIONS

SEE PROFILE

Room-Temperature Phosphorescence From Films of Isolated Water-Soluble Conjugated Polymers in Hydrogen-Bonded Matrices

Hameed A. Al-Attar* and Andrew P. Monkman

It is well known that luminescent conjugated polymers suffer serious loss of photoluminescence quantum yield (PLQY) in the solid state compared to dilute solution. This is due to efficient exciton migration in the solid, which enables the excitons to readily find low energy quenching sites. Here a new method to fabricate solid films with densely packed non-interacting luminescent polymer chains, which yield very high PLQY and more astonishingly room temperature phosphorescence, is reported. Using water-soluble conjugated polymers (WSCP) and polymeric surfactants such as poly(vinyl alcohol) (PVA) and poly(vinyl-pyrrolidone) (PVP), films at 1:1 wt% or higher WSCP are produced and show room temperature phosphorescence; such behavior has never been observed before and clearly shows the very high degree of chain isolation that can be achieved in these hosts. The PVA or PVP not only breaks up WSCP aggregates in solution as an effective surfactant, PVA-PVA or PVP-PVP hydrogen bond formation upon drying locks in the isolation of the WSCP, avoiding segregation and yielding long time stability to these polymer/polymer nanomixtures. The method is found to work with a wide variety of WSCPs.

1. Introduction

Water-soluble conjugated polymers (WSCPs) have drawn increasing interest due to their great potential to fabricate highly sensitive chemical and biological sensors^[1–5] and novel organic light-emitting diode (OLED), organic photovoltaic (OPV), and optoelectronic devices.^[6,7] WSCP contain ionic side chain termination groups which engender some solubility in aqueous media. However, due to the conjugated hydrophobic backbones these polymers have a high tendency to aggregate in the aqueous environment, which renders the material sparingly soluble and leads to massive emission quenching. In the solid state of all conjugated polymers, excitons are free to migrate from chain to chain such that they can readily find low energy trap states of low emission quantum yield and quenching sites. The most common methods to reduce the interchain interaction and concomitant quenching are blending the emissive polymer with

inert polymers or another active polymer.^[8] It is well known, however, that blends of dissimilar polymers undergo phase separation when cast into a thin film from solution due to the low entropy of mixing between different polymers.^[9] Other routes to maintain the chain spacing distance which reduce aggregation but not exciton migration include the introduction of long alkyl side chains,^[10] bulky pendant substituent^[11] or dendritic side groups^[12] onto the main chain of the emissive polymer. Confining a conjugated polymer in a microporous structure^[13] or containing it with a nano-porous morphology^[14] have also been used to enhance electroluminescence. These are complex and difficult to fabricate routes, and yield low density poorly isolated polymer chains in the solid state and none show room temperature phosphorescence emission indicating exciton pathways through the film still exist.

Phosphorescence in conjugated polymers is generally difficult to detect, because of the weakness of the spin-orbit coupling mechanism,^[15] which produces triplet excitons, yielding low intersystem crossing rates ($<10^7 \text{ s}^{-1}$) compared to the fluorescence rate (10^9 s^{-1}). Furthermore, efficient triplet exciton diffusion causes bimolecular annihilation of triplet states^[16] and quenching at impurities.^[17] Thus, phosphorescence is normally only observed at low temperatures using ultra-sensitive, gated emission techniques.^[16] Room temperature phosphorescence emission (RTP) can only usually be observed if an emitter contains a heavy atom which enhances spin-orbit coupling such that primary photogenerated singlet states rapidly converted to triplets and that the spin-forbidden $T_1 \rightarrow S_0$ transition becomes allowed. Prime examples are Ir centered cyclometallated complexes.^[18,19]

RTP has been observed in aqueous solution of small molecules in a micelle system which provides an appropriate rigid microenvironment to prevent triplet quenching.^[20] RTP in metal oxide, nanocomposite with SiO_2 and metal-enhanced room temperature phosphorescence have been demonstrated and used as chemo and bio-sensors platforms.^[21] Very recently, RTP in simple hydrogen and halogen bonded mixed organic crystals has been reported.^[22,23] RTP is also reported in graphene quantum dots which have a significant probability of relaxing into triplet states and emit both phosphorescence and fluorescence at room temperature due to the reduction of

Dr. H. A. Al-Attar, A. P. Monkman
Organic Electroactive Materials Research Group
Department of Physics
University of Durham
South Road, Durham DH1 3LE, UK
E-mail: h.a.al-attar@durham.ac.uk



DOI: 10.1002/adfm.201200814

the singlet-triplet splitting.^[24] However, RTP has never been observed from an intrinsic conjugated polymer, this is because isolating long polymer chains with complicated and variable conformation is extremely difficult, in addition, the strong phase segregation in blends of luminescent polymers with inert host polymers means that phosphorescence again can only be observed at low temperatures.^[17] Therefore RT phosphorescence from a polymer is the ultimate test for true individual chain isolation at the nanometer scale.

Here, we describe a new and effective method for obtaining dense isolated WSCP chains in the solid state. The fluorescence efficiency is greatly enhanced, the average singlet lifetime substantially increases and remarkably RTP emission can easily be observed. We show that the polymeric surfactant such as poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP) is an ideal host material to create such systems. The isolation efficiency depends on the preparation condition, chemical structure, molecular weight and solubility of the water soluble polymer as well as the molecular weight of the PVA or PVP. The fabrication method is very simple and compatible with all solution coating techniques making the formation of large area films possible. This is ideal for large area devices especially organic solid state lighting.^[25] In the following discussion we present the results obtained using PVA only, similar results have been obtained with PVP however and we also note that this methodology works well with many other water soluble materials and is not limited to the water soluble conjugated polymers.

It has been shown^[26,27] that surfactant interactions with WSCPs induces break-up of polymer aggregates and incorporation of the polymer chains into micelles which eliminates a high proportion of interchain and impurity quenching.^[28] However, most surfactants are low molecular weight molecules which cannot form rigid micelles that can be transformed into a thin film with high mechanical strength. To produce isolated polymer chains confined in a rigid matrix, the ideal surfactant should not only effectively break up the polymer aggregation but also form a covalently bound or cross-linked network. We have found that the polymeric surfactant PVA, a non-ionic polar water soluble polymeric surfactant, is ideal forming highly dense isolated WSCP chains in dense films. PVA is a strong amphoteric polymer and has superior initial adhesion compared with another natural water soluble polymers. The adhesion tends to increase with the degree of hydrolysis and polymerization.^[29] PVA has high tensile strength, flexibility, as well as good oxygen barrier performance. In addition to the surfactant properties of the PVA in water, it exhibits both H-bonding between hydroxyl groups between neighbouring PVA chains and H-bonding between the -OH groups of PVA and water molecules.^[30] Furthermore, at degrees of hydrolysis higher than 98%, PVA is highly crystalline and forms strong interchain or intrachain hydrogen bonding. In this form its solubility in water is strongly affected, and a solubilisation temperature above 80 °C is required to dissolve the PVA completely.

1.1. Scheme for Polymer Chain Isolation

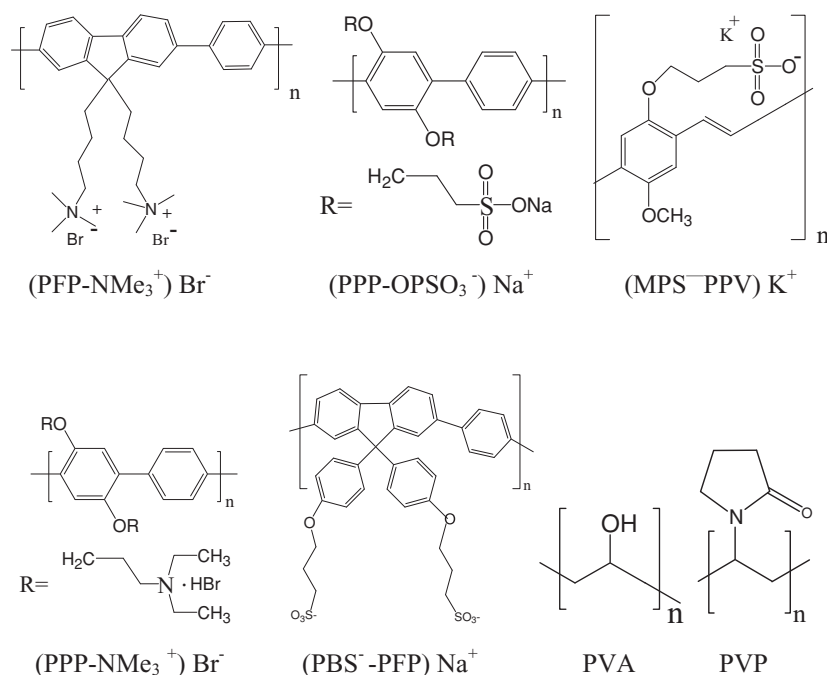
When PVA and WSCP are mixed together in water and heated to between 80–90 °C (depending on the degree of hydrolysis

and molecular weight of the PVA), the interchain and intrachain hydrogen bonding of the crystalline PVA breaks up and the PVA dissolves completely (we think of this as “opening a cage”). The surfactant properties of PVA then take effect; the PVA interacts with the hydrophobic part of the WSCP to break-up their aggregation producing free isolated conjugated polymer chains. The isolated WSCP chains are stabilized in the water via interactions with the PVA chains, the hydrophobic conjugated backbone of the WSCP associates with the hydrophobic skeleton of the PVA forming micelle like structures in the same way as the smaller molecular surfactants do. Spin-coating or drop casting of the hot PVA/WSCP solution and fast-drying of the mixture above 100 °C leads to rapid crystallisation of the PVA, “caging” the single WSCP chains in isolation within the PVA-PVA hydrogen bonding network (again, “closing the cage”). We term this technique as “thermally open-close caging” (TOCC). It is this rapid formation of PVA hydrogen bonded network that locks in the isolation of the WSCP chains without quenching emission that is key. This host network also hinders chain motion providing very rigid and compact isolated WSCP chains in extremely stable films. The isolation removes the possibility of both exciton diffusion and interchain interaction to the point where it is easy to observe RTP from the WSCP even at 1:1 WSCP:PVA wt% concentrations. Optimum WSCP concentration depends on its molecular weight compared to that of the PVA. We have found that different WSCP chemical structure, molecular weight and solubility in water required different mixing ratios for optimum chain isolation. Our preliminary investigations show that the TOCC method works very well with all WSCPs and polyelectrolyte polymers. Two water soluble polymer surfactant host PVA and PVP and five WSCPs has been tested in this preliminary investigation where chemical structures and properties are shown in **Scheme 1** and **Table 1**.

2. Results and Discussion

2.1. Photophysics of the Isolated Polymer Chains System

The absorption and emission spectra of different types of WSCPs in water or DMSO/water solution with and without PVA are depicted in **Figure 1**. In common, all WSCPs show enhancement in fluorescence quantum yield, this is ascribed to break-up of polymer aggregation induced by the surfactant properties of the PVA which produces isolated (conjugated) polymer chains. The isolated polymer chain does not exhibit strong interchain quenching leading to fluorescence enhancement.^[26] Looking to the absorption spectra the anionic WSCPs show slight absorption enhancement and red shift which is proportional to the polymer molecular weight, 25 nm for PPP-OPSO₃ (20 repeat units), 10 nm for PBS-PFP (40 repeat units), and no shift for MPS-PPV (1000 repeat units). These results indicate ion-dipole interaction^[31] between the anionic WSCP and the polar PVA where the ion-dipole force causes the two molecules to align leading to chain extension and concomitant red shift in the absorption and emission spectra of the shorter polymers. No WSCP:PVA complexation is indicated which



Scheme 1. Chemical structure of the water soluble conjugated polymers and water soluble surfactant polymers poly(vinyl alcohol) PVA and poly(vinylpyrrolidone) PVP used in the study. Poly(9,9-bis(6'-N,N,N-trimethylammonium-hexyl) fluorine phenylene) bromide (PFP-NMe₃⁺) Br⁻ (WSCP1), poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-*alt*-1,4-phenylene) PPP-OPSO₃⁻ (WSCP2), poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] potassium salt solution MPS-PPV (WSCP3), poly[(2,5-bis(2-(N,N-diethylammonium bromide)ethoxy)-1,4-phenylene-*alt*-1,4-phenylene)] (PPP-NMe₃⁺) Br⁻ (WSCP4), and poly[1,4-phenylene-9,9-bis(4-phenoxy-butylsulfonate)]fluorine-2,7-diyl]PBS-PFP (WSCP5).

would show up as a change in the absorption spectra with a signature new band. It should be noted that due to the large size of the ionic radius of the WSCP the force of interaction will be proportional to the size of the polymer chain (weaker with larger polymer size). Therefore, this conformation change depends on the polymer chain length (number of units) so the longer chain, as for PPV (1000 units), does not show significant chain extension; the force required to induce conformation change in the longer chains is too great. The expected red shift in the PL emission is not so readily observed in the anionic WSCPs, except for PBS-PFP (6 nm). This is because the break-up of the polymer aggregation induced by the surfactant action of the PVA also induces a blue shift in the emission spectra^[26] (via chain dissolution) which may balance the red shift induced

by the polymer chain extension. Upon removing the solvent (water or DMSO/water mixture) the absorption and emission spectra do not change as shown in Figure 2 for the PPP-OPSO₃ polymer as an example, which indicates that during PVA-PVA hydrogen re-bonding the isolated WSCPs chains remain isolated, intercalated and caged by the PVA-PVA hydrogen bonds.

For the cationic WSCPs, the PVA induces a reduction in the absorption band intensity and no spectral peak shift is observed. However, an increase in the emission intensity indicates break-up of polymer aggregation. The reduction in the absorption is due to enhanced transparency in the WSCP/PVA system which may related to a structural regularity obtained by self-assembly similar to that obtained by the breath-figure technique.^[32,33] The honeycomb like structure of the solid film was characterized by atomic force microscopy, which shows structural regularity over large areas consisting of 1–3 μm size void-like areas as shown in Figure 3. However, more investigation is needed to fully characterize the interaction of the cationic WSCP and PVA in water and to determine the optimum condition for perfectly shaped honeycomb structure.

Figure 4 shows the steady state absorption and fluorescence emission of WSCP1 films with and without PVA. The typical structure-

less absorption spectrum of WSCP1 films at room temperature (Figure 4a), attributed to inhomogeneous broadening,^[34] and can be explained by the dispersity of conjugation length, strong exciton vibronic coupling and disorder.^[35]

Conversely, the emission spectra from these films (Figure 4b,I) show very well structured fluorescence spectra, especially for the WSCP1/PVA system, with sharp well resolved vibronic peaks at 428, 453 nm and 487 nm, is a sign of the high degree of polymer chain isolation and increased backbone rigidity. The increase in backbone rigidity reduces vibrational dissipation and further enhancing polymer quantum yields. These emission spectra is very similar to that observed in solution at low concentration Figure 1(e'), indicating that upon transferring the WSCP1/PVA from solution to solid state, the

Table 1. Materials used in the study and the corresponding properties.

Polymer	Polyelectrolyte Type	Mw [g/mol]	Number of Units	Solvent	RT Emission
PVA	non-ionic polar	89–98 × 10 ³		water	
PVP	non-ionic polar	40 × 10 ³		water	
(PFP-NMe ₃ ⁺) Br ⁻ (WSCP1)	cationic	23 000	32	DMSO:water (1:1)	Fl, Ph
(PPP-NMe ₃ ⁺) Br ⁻ (WSCP2)	cationic	745	2	water	Fl, Ph
(PPP-OPSO ₃ ⁻) Na ⁺ (WSCP3)	anionic	8000	18	water or DMSO/water	Fl, Ph
(MPS-PPV) K ⁺ (WSCP4)	anionic	1–5 × 10 ⁵	1000	water	Fl, DF
(PBS-PFP) Na ⁺ (WSCP5)	anionic	3400	40	DMSO:water (1:3)	Fl, Ph

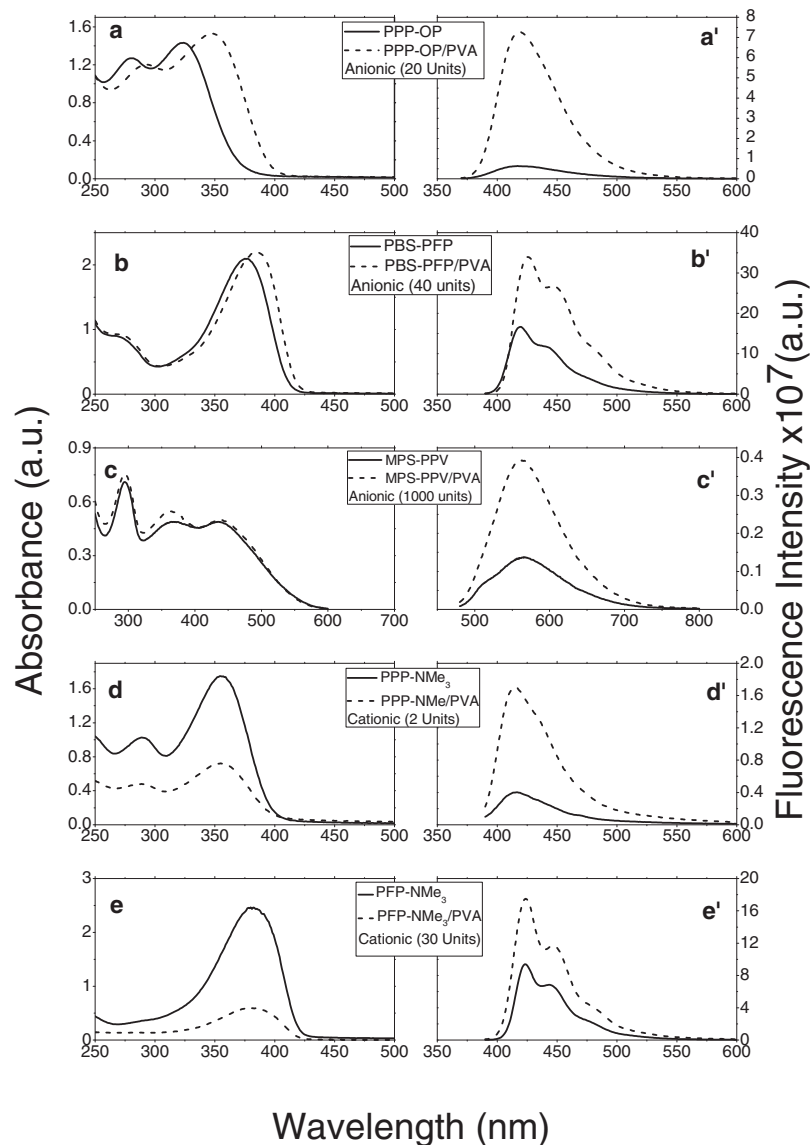


Figure 1. Absorption (a–e) and emission (a'–e') spectra for different WSCPs in solution (water or water/DMSO) with (dash) and without (solid) PVA.

PVA hydrogen bonding network has firmly locked the WSCP1 chains in place reducing the degree of chain flexibility and preserving the isolation form of the polymer chains. It can clearly be seen that the 0-0 line has much stronger intensity than the first vibronic replica (0-1) indicative of stiff conjugated segments.^[36] In thicker films, typically made by drop casting, the optical density is so high that self-absorption strongly reduces the intensity of the 0-0 line. The measured quantum yield, ϕ_{PL} , of the pure WSCP1 film was 0.075, which dramatically increases to 0.55 for WSCP1/PVA thin film, which is higher than that for WSCP1 chains in dilute solution with non-ionic surfactant pentaoxyethylene glycol monododecyl ether ($C_{12}E_5$) ϕ_{PL} , 0.24.

Quenching in the solid state has been attributed to many causes, several directly attributable to the close packing of the conjugated backbones, e.g., ground state π -stacking dimers,^[37,38] excited state excimers^[39,40] and polaron pair production^[28] the

former being characterized by a new absorption band the latter two by broader red shifted emission spectra with no vibronic structure.^[39] In addition, the overlap of a delocalized interchain excited state with the single-chain ground-state polymer wave function, leads to a weak transition dipole moment thus a long radiative lifetime of low quantum yield detected at a longer wavelength region of the emission spectra. Such states are not evident in the pure WSCP1 film and so further quenching mechanisms must be at work in this case.

2.1. Time-Resolved Analysis

Time-resolved emission spectroscopy was studied using a streak camera, **Figure 5**. The average fluorescence lifetime increases from 60 ps for the pure WSCP1 to 411 ps for the isolated chain system WSCP1/PVA. No signature of long lived species, when the decay was measured at the peak 480 nm compared to that at 430 nm was found, which indicates no π -stacking dimer or excimer emission in both WSCP1 and WSCP1/PVA systems. The reduction in quantum yield of WSCP1 therefore is due to a static quenching process potentially caused by interactions with the ionic side chain termination groups. Further, the strong absorption-emission spectral overlaps of the WSCP1 (**Figure 4a,b**) allows for significant diffusion quenching,^[41] by both Förster transfer-mediated singlet diffusion and incoherent hopping Dexter transfer of triplets^[42] to extrinsic quenching sites which can substantially reduce the polymer quantum yield.^[43]

To evaluate the difference in the degree of isolation between the pure WSCP1 and WSCP1/PVA systems, time resolved single photon counting experiments were performed

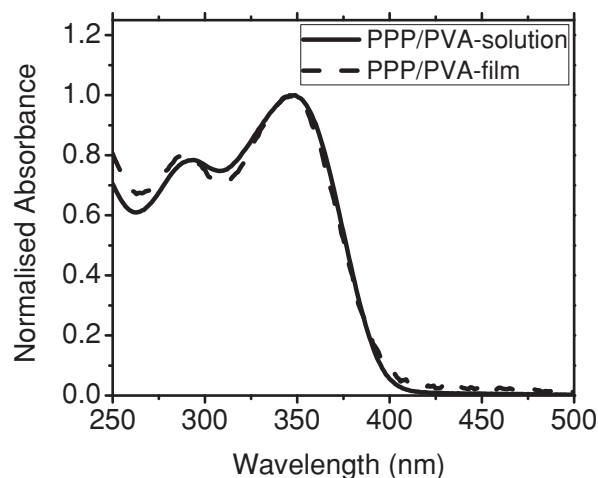


Figure 2. Normalized absorption spectra for PPP/PVA solution and film forms.

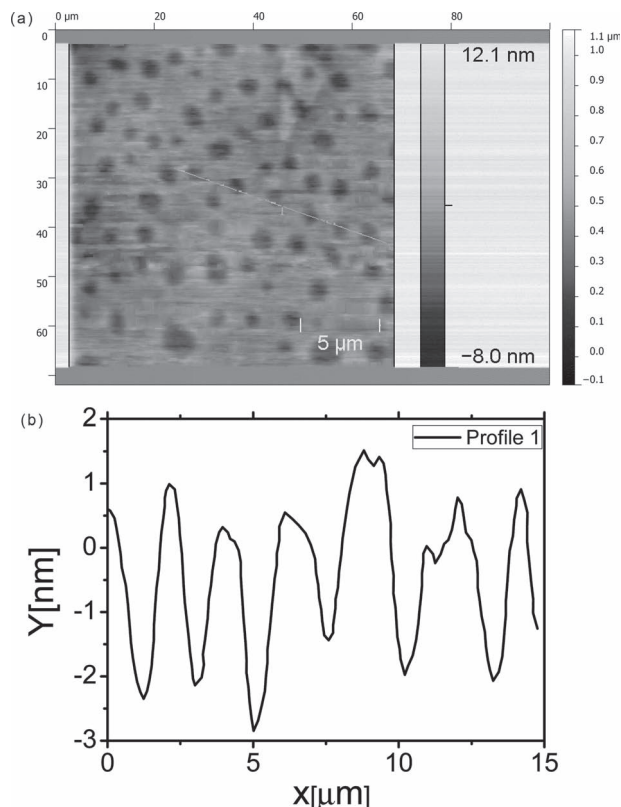


Figure 3. a) Atomic force microscopy image of cationic WSCP (PFP-NMe₃⁺)/PVA spin coated film from water solution on quartz substrate. b) Intensity profile showing the drop size and the regularity.

(Figure S1, Supporting Information). Table 2 shows the results of fitting the decay profile with three discrete exponential components. The long lifetime component of 448 ps represents fluorescence decay from the isolated polymer chain. The other two fast decay components 156 and 33 ps are related to quenching processes. Clearly PVA increases the number of the isolated single chains and hence increases the fractional contribution of this component to the steady-state parameters f_i that given by Equation (1)

$$f_i = a_i \tau_i / \sum a_i \tau_i \quad (1)$$

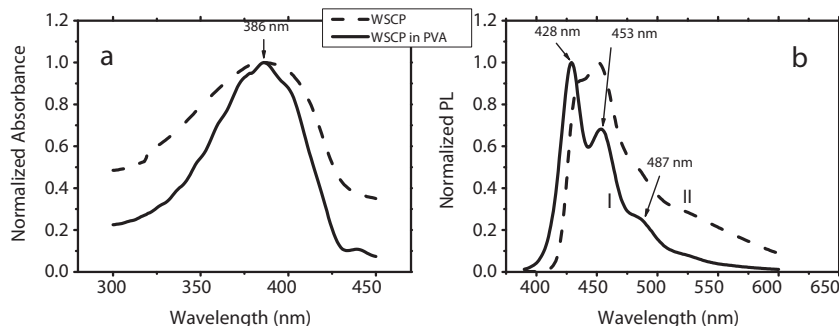


Figure 4. Absorption (a) and emission (b) spectra of the WSCP film with (I) and without (II) surfactant polymer PVA (1:4 wt% ratio, ~1:1 mol%). Excitation was at 377 nm at room temperature.

The average lifetime of the singlet (fluorescence emission) that is given by Equation (2)

$$\langle \tau \rangle = \sum a_i \tau_i^2 / \sum a_i \tau_i \quad (2)$$

extended from 60 ps for WSCP1 to 411 ps for WSCP1/PVA as shown in Table 2 due to the increase in the number of isolated polymer chains. In the WSCP1/PVA film 90% of the fluorescence emission comes from isolated chains with a life time of 448 ps compared to only 9% of the fluoresce emission comes from the isolated chains in the pure WSCP1.

The temperature dependence of the steady state fluorescence and time resolved fluorescence single photon counting measurements (Figure S2,S3, Supporting Information) indicate no singlet life time quenching or appreciable amplitude quenching of the fluorescence emission. This indicate that the dominant emissive species is the isolated polymer chains with no diffusion or interchain interaction given rise to very high solid state PLQY.

2.2. Room-Temperature Phosphorescence Emission

The true test for chain isolation can only be measured by the triplet exciton dynamics of the system. Given their very long lifetime, triplet excitons can migrate over many tens of nanometers throughout a film.^[44] This leads to them being very effectively quenched by a variety of processes. Figure 6 shows the fluorescence and phosphorescence emission at 12 K and room temperature for WSCP1/PVA drop cast film. No room temperature phosphorescence emission was observed for the pure WSCP1. A Stokes shift of 0.742 eV (149 nm) was measured which agrees with the exchange energy (singlet-triplet energy difference) for most conjugated polymers (0.7 eV).^[45] No difference in the Stokes shift between room temperature and that measured at 12 K was observed, which indicates no thermally induced conformational changes to the conjugated backbone occur, typically a blue-shift is expected as a result of thermal conformational change.^[46] This indicates the very effective nature of the PVA hydrogen bond network has in confining any relaxation of the WSCP backbone, retaining rigidity at all temperatures. The sharp, narrow fluorescence and phosphorescence spectra at 12 K with in vibrational line widths of ca 80 meV FWHM is nearly as narrow as that observed in beta-phase polyfluorene at 12 K.^[47] Figure 6 also shows a weak signature of delayed fluorescence at 12 K, which we believe originates from residual entangled polymer chains in the film that facilitate triplet interchain hopping and triplet-triplet annihilation.^[44] The observed RTP indicates that the WSCP1/PVA film contained highly concentrated but isolated single chains of the emissive polymers with very little or no exciton diffusion.

The time dependent phosphorescence decay (Figure 7a) at room temperature and at 12 K is essentially identical, which confirms the strong exciton confinement. However,

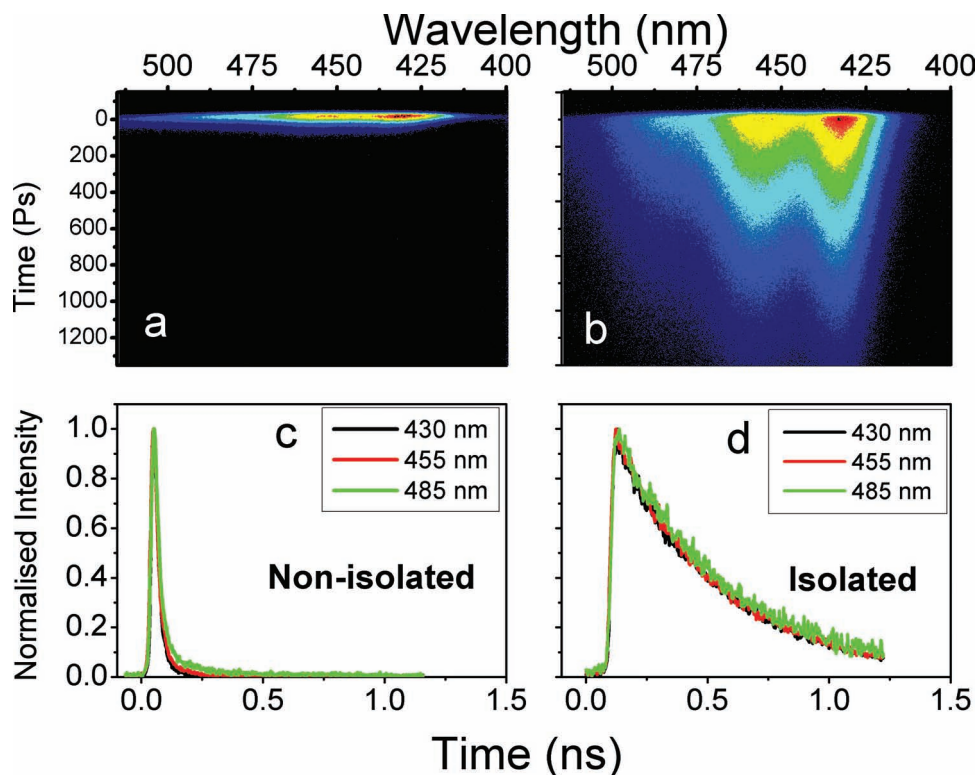


Figure 5. The streak camera images for the WSCP1 film (a) compared with the WSCP1/PVA film (1:4 wt% ratio, ~1:1 mol%) and b) laser excitation wavelength 377 nm, at room temperature. c,d) Corresponding decay profiles taken at three different emission wavelengths, 430, 455, and 485 nm.

the temperature dependent phosphorescence emission shows significant amplitude quenching for WSCP1/PVA at room temperature as shown in Figure 7b. At both RT and 12 K there is an initial rapid decay of phosphorescence followed by a much slower decay having the same time constants in both cases. This initial drop must be due to energetic triplets who manage to find some pathway to another chain or quenching site. This is more pronounced at RT as expected. Once the triplets become trapped they decay with the natural decay rate independent of temperature, thus we observe the same long time decay behavior irrespective of temperature but lower triplet population at RT due to the fact that more triplets have quenched during the initial hopping period. This type of dispersive to non-dispersive behavior is common to triplet exciton migration in conjugated polymers.^[48] It has been found that the temperature dependent phosphorescence emission depends on the preparation condition, concentration, WSCP type, solubility and molecular weight. For example, another system of isolated WSCP chains prepared from polyparaphenylene salt, WSCP3 (Mw = 8,000)/PVA which is more soluble in water shows no thermal amplitude quenching up to 180 K and then a small

drop by only 37% (Figure 7c,d), compared to the 92% drop in amplitude for WSCP1 (Mw = 23 000)/PVA at room temperature, Figure 7c. With more perfect isolation in this PPP system,

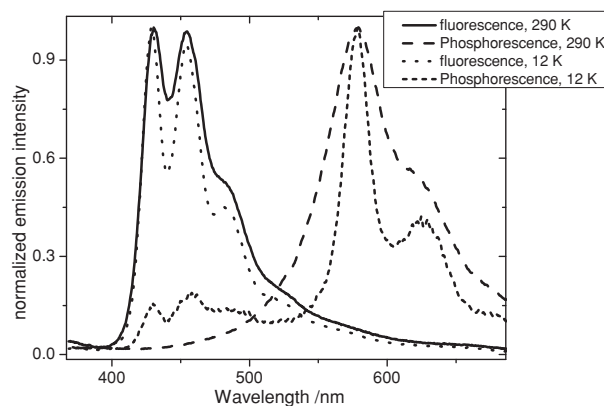


Figure 6. The normalized fluorescence and phosphorescence emission spectra for WSCP1/PVA (1:4 wt% ratio) cast film at 12 K and 290 K. The phosphorescence spectra were taken after a delay of 5 ms.

Table 2. Emission decay components of WSCP1 and WSCP1/PVA films (1:2 wt%). Where a_i , τ_i , f_i , are the amplitude, decay time [ps] and fractional contribution to the steady state respectively. χ^2 is the value of fit.

	a_1	τ_1 [ps]	a_2	τ_2 [ps]	a_3	τ_3 [ps]	f_1	f_2	f_3	$\langle \tau \rangle$ [ps]	χ^2
WSCP	1.24	383	50.7	44	178	14	0.09	0.43	0.48	60	1.13
WSCP/PVA	41	448	10.6	156	10.8	33	0.9	0.08	0.02	411	1.01

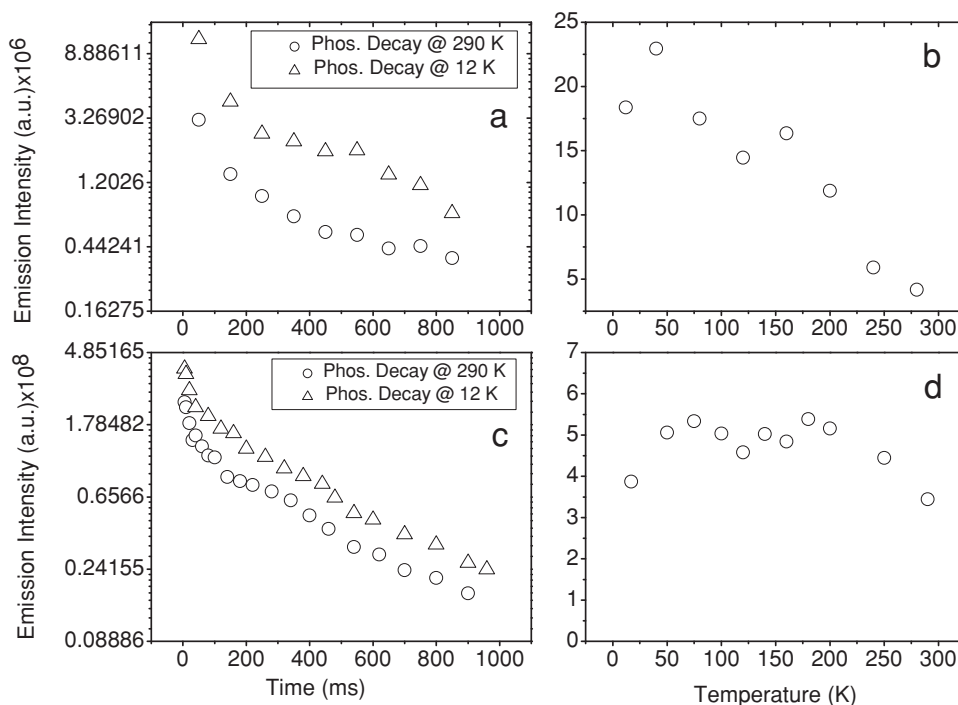


Figure 7. a) Time-dependent phosphorescence decay collected at room temperature (290 K) and at 12 K and b) temperature-dependent phosphorescence intensity for cast coated WSCP1/PVA film (1:4 wt% ratio). c,d) Similar to (a,b) but for WSCP3/PVA (1:8 wt% ratio).

we can all but stop triplet migration as well as singlet exciton migration retaining the highest possible emission quantum yields.

In order to estimate the high concentration limit for self-quenching of the WSCP, a time resolve analysis of the fluorescence (FL) and phosphorescence (Ph) emission of the WSCP3/PVA at various concentration WSCP3:PVA ratio (1:1 to 1:32) was conducted (**Figure 8**). A strong dynamic quenching of the fluorescence emission up to 95% fluorescence quenching at 1:1 WSCP3: PVA weight ratio has been observed. Room temperature phosphorescence emission was observed at all concentration ratios. Little change is observed in the decay profiles of both FL and Ph emission for ratios of 1:4 and higher. However, the observed RTP even at 1:1 ratio indicates that although the WSCP3/WSCP3 chains are typically separated by an average 1–2 nm distance the triplet quenching is not sufficient and an appreciable number of isolated WSCP chains still sustained which allow for RTP to be observed.

3. Conclusion

We have discovered and describe a novel method to achieve near perfect isolation of dense luminescent polymer chains using caging within a hydrogen bonded PVA network i.e., true nanoscale mixing of two polymers. This technique has been applied

to water soluble conjugated polymers but it is more general applicable to any water soluble materials including diblock copolymers, carbon nanotube, quantum dots, DNA, proteins, etc. The surfactant properties and the strong hydrogen bonding in the fully hydrolyzed PVA make this water soluble surfactant polymer an ideal polymer to demonstrate the concept of TOCC. The photophysics of the highly condensed isolated polymer chains shows not only that each chain is essentially independent of its neighbours, giving rise to long fluorescence lifetimes with concomitant high fluorescence quantum

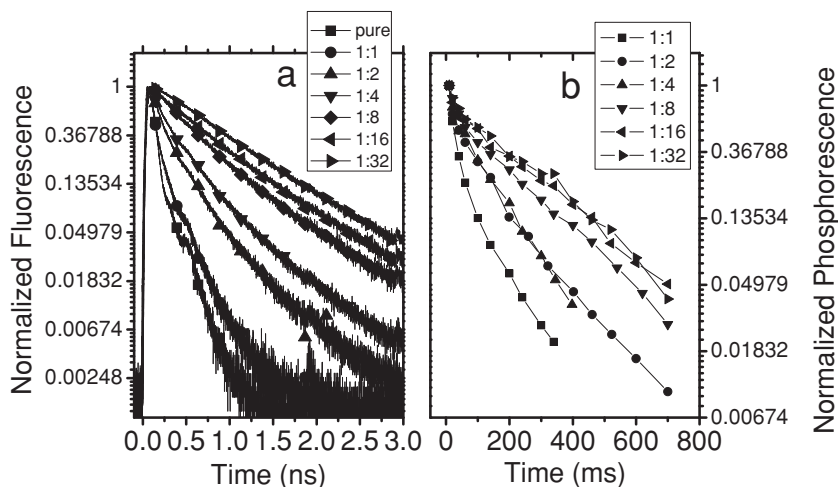


Figure 8. a) Time-resolved decay of the fluorescence and b) phosphorescence of WSCP3/PVA films at various WSCP:PVA ratios. Data in (a) were obtained using time-resolved single photon counting and data in (b) were obtained using a gate delay time-resolved technique.

yields, but also, for the first time we demonstrated room temperature phosphorescence from the water soluble conjugated polymers truly indicative of perfect chain isolation at the nano scale within a dense 1:1 wt% nanocomposite film. The WSCP/PVA films are robust and very stable which provide an ideal system to study the triplet dynamic and energy transfer in conjugated polymers. From the application point of view this system can also provide the basis for an OLED emission layer where the luminescent polymer gives its full photoluminescence efficiency which could see an immediate doubling of overall OLED electroluminescence efficiency. Having demonstrated the basic idea we now look to combine it with functionalized hydrogen bonding polymer surfactants which can aid charge transport so that this new TOCC methodology can be used effectively in OLED devices. As the water-based WSCP/PVA solution would not dissolve under lying organic soluble polymer layer and a subsequent layer could be cast on top of it from organic solution, tri-layer solution processable OLED devices become feasible. As all water soluble polymers which are sensitive to moisture, we expected PLED devices using this system will be carefully backed in vacuum to remove all water and encapsulated to reduce degradation. It is also well known^[49] that short excited-state lifetime in organic laser materials induced by chain aggregation results in an increase in the required pumping rate to maintain a population inversion and leads to exciton-exciton annihilation. Our method can overcome these limitations and provide an ideal gain medium for low threshold organic laser. The TOCC method to produce near perfect nanocomposites of isolated luminescent polymer chains will open up a new chapter in organic semiconductor research.

4. Experimental Section

Materials and Sample Preparation: The chemical structures of all water soluble conjugated polymers and PVA investigated in this study are given in Scheme 1 and Table 1. In general, a high temperature was required to dissolve PVA in water, depending on the degree of hydrolysis and molecular weight of the PVA. In this work PVA with M_w 89 000–98 000 and 99+% hydrolyzed was used, where a temperature above 80 °C was required with agitation for more than 30 min to completely dissolve the PVA. Two methods were used to prepare highly isolated polymer chains embedded in the PVA matrix. The first method was to dissolve the PVA in distilled water at a concentration of 10–20 mg/ml and also dissolve the WSCP in water separately at a concentration of 10 mg/ml. The required ratio 1:1 to 1:32 WSCP: PVA wt% was mixed as a volume ratio and agitated at 1000 rpm at 50–80 °C using an Eppendorf thermomixer for more than 1 h (the mixing temperature and time depended on the molecular weight and the solubility of the WSCP in water). Agitation at higher temperature and longer time was more important for the higher molecular weight WSCP (less soluble in water) in order to insure breaking up all the aggregated polymer chains and also to allow for PVA/WSCP chains hydrophonically associated. An alternative method was to mix the dissolved WSCP with solid PVA and mix them using agitation at 1000–1200 rpm at 80–90 °C. The later method produced better isolated polymer chains. Spin coating, drop casting, or any other solution coating technique could be used to form thin or thick film layer. The best chain isolation was obtained when the material annealed at 100–130 °C for 20 min. A full investigation of the annealing effect and optimization of the chain isolation has not been conducted as yet. Vacuum drying was also carried out at room temperature and at 40 °C but flexible films with lower chain isolation and weaker RTP intensity were obtained, which

indicated that fast crystallization of the PVA by annealing resulted in better caging of the isolated polymer chains.

Measurements: Steady state absorption and emission measurements were carried out using Shimadzu UV-3600 (UV-VIS-NIR) spectrophotometer and Jobin-Yvon FLUOROMAX spectrofluorimeter, respectively. Time-resolved fluorescence decays were collected using the picosecond time-correlated single photon counting (TCSPC) technique (IRF = 23 ps). The excitation source was a picosecond Ti:sapphire laser (MIRA) from Coherent, Inc. Emission collected was detected through a double subtractive monochromator by a microchannel plate (MCPT) Hamamatsu model R3809U-50. Signal acquisition was performed using a TCSPC module (Becker & Hickl Model SPC-630). Deconvolution of the fluorescence decays was performed using the Globals WE software package. The same laser pulses were used for time-resolved fluorescence emission spectroscopy using a Hamamatsu streak camera (C5680) setup. Temperature-dependent emission spectra and fluorescence decays were collected using a cryostat model VNF-100 from JANIS research Inc.

Phosphorescence emission spectra and decay were collected using the third harmonic of a 150 ps pulsed Nd-YAG laser (SL312, EKSPLA) operating at 1–10 Hz. The excitation wavelength was 355 nm and the energy per pulse was below 100 μ J to avoid saturation effects. All measurements were performed under a dynamical vacuum of $<10^{-4}$ Torr in a temperature-controlled (± 0.1 K) displex helium cryostat. The light emitted by the sample was dispersed by a monochromator (TRIAx 180, Jobin Yvon-Spex) and recorded by a red enhanced, gated, intensified CCD camera (4 Picos, Stanford Computer Optics).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank Professor Ullrich Scherf and Dr. Ricardo Mallavia for kindly providing some of the water-soluble conjugated polymers used in this study. Dr. Michael Hunt for providing the AFM image. The authors are also grateful to EPSRC for financial support.

Received: March 22, 2012
Published online: May 29, 2012

- [1] L. Chen, D. W. MacBranch, H. L. Wang, R. Helgeson, F. Wudl, D. G. Whitten, *Proc. Natl. Acad. Sci. USA* **1999**, 96, 12287.
- [2] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, 100, 2537.
- [3] B. S. Gaylord, A. J. Heeger, G. C. Bazan, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 10954.
- [4] H. A. Al Attar, J. Norden, S. O'Brien, A. P. Monkman, *Biosens. Bioelectron.* **2008**, 23, 1466.
- [5] M. Leclerc, *Adv. Mater.* **1999**, 11, 1491.
- [6] S. C. Change, J. Bharathan, Y. Yang, R. Helgeson, F. Wudl, M. Ramey, B. Reynolds, *Appl. Phys. Lett.* **1998**, 73, 2561.
- [7] P. K. H. Ho, J. S. Kim, J. H. Burroughes, H. Becker, S. F. Y. Li, T. M. Brown, F. Cacialli, R. H. Friend, *Nature* **2000**, 404, 481.
- [8] J. Chappell, D. G. Lidzey, P. C. Jukes, A. M. Higgins, R. L. Thompson, S. O'Connor, I. Grizzi, R. Fletcher, J. O'Brien, M. Geoghegan, R. A. L. Jones, *Nat. Mater.* **2003**, 21, 616.
- [9] M. Geoghegan, G. Krausch, *Prog. Polym. Sci.* **2003**, 28, 261.
- [10] R. Hidayat, A. Fujii, M. Ozaki, K. Yoshino, *Jpn. J. Appl. Phys.* **2001**, 40, 7103.

- [11] G. Yang, Q. H. Zhang, W. Peng, T. C. Huang, L. C. Zeng, P. F. Gu, X. Liu, *J. Lumin.* **2005**, *114*, 31.
- [12] M. Halim, J. N. G. Pillow, I. D. W. Samuel, P. L. Burn, *Adv. Mater.* **1999**, *11*, 371.
- [13] T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652.
- [14] C. J. Chiang, C. Rothe, M. Rosamond, A. Gallant, E. Ferain, R. Legras, W. B. Dave, A. Monkman, *Photonic Mater., Devices, Appl.* **2007**, *6593*, R5930.
- [15] S. M. King, C. Rothe, D. Dai, A. P. Monkman, *J. Chem. Phys.* **2006**, *124*, 234903.
- [16] C. Rothe, R. Guentner, U. Scherf, A. P. Monkman, *J. Chem. Phys.* **2001**, *115*, 9557.
- [17] C. Rothe, A. Monkman, *Phys. Rev. B* **2002**, *65*, 073201.
- [18] H. Yersin, *Top. Curr. Chem.* V241, Ch1, 1-26 Springer-Verlage, Berlin **2004**.
- [19] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4.
- [20] Y. Wang, W. J. JIN, J. B. Chao, L. P. Qin, *Chin. Chem. Lett.* **2004**, *15*, 339.
- [21] W. Na, Z. Ting, W. Jun, Y. Hongyan, X. Dan, *Analyst* **2010**, *135*, 2386.
- [22] W. Z. Yuan, X. Y. Shen, H. Zhao, J. W. Y. Lam, L. Tang, P. Lu, C. Wang, Y. Liu, Z. Wang, Q. Zheng, J. Z. Sun, Y. Ma, B. Z. Tang, *J. Phys. Chem. C* **2010**, *114*, 6090.
- [23] O. Bolton, K. Lee, H. J. Kim, K. Y. Lin, J. Kim, *Nat. Chem.* **2011**, *3*, 205.
- [24] M. L. Mueller, X. Yan, J. A. McGuire, L. S. Li, *Nano Lett.* **2010**, *10*, 2679.
- [25] K. T. Kamtekar, A. P. Monkman, M. R. Bryce, *Adv. Mater.* **2010**, *22*, 572.
- [26] H. A. Al Attar, A. P. Monkman, *J. Phys. Chem. B* **2007**, *111*, 12418.
- [27] H. D. Burrows, M. J. Tapia, C. L. Silva, A. A. C. C. Pais, S. M. Fonseca, J. Pina, J. S. de Melo, Y. Wang, E. F. Marques, M. Knaapila, A. P. Monkman, V. M. Garamus, S. Pradhan, U. Scherf, *J. Phys. Chem. B* **2007**, *111*, 4401.
- [28] M. Yan, L. J. Rothberg, E. W. Kwock, T. M. Miller, *Phys. Rev. Lett.* **1995**, *75*, 1992.
- [29] C. A. Finch, *Poly(vinyl alcohol): properties and applications*, Wiley, New York **1973**, Ch. 2.
- [30] C. Damas, T. Leprince, T. H. V. Ngo, R. Coudert, *Colloid Polym. Sci.* **2008**, *286*, 999.
- [31] X. H. Feng, P. L. Dubin, H. W. Zhang, G. F. Kirton, P. Bahadur, J. Parotte, *Macromolecules* **2001**, *34*, 6373.
- [32] G. Widawski, M. Rawiso, B. Francois, *Nature* **1994**, *369*, 387.
- [33] H. Tsai, Z. Xu, R. K. Pai, L. Wang, A. M. Dattelbaum, A. P. Shreve, H.-L. Wang, M. Cotlet, *Chem. Mater.* **2011**, *23*, 759.
- [34] M. Knaapila, F. B. Dias, V. M. Garamus, L. Almasy, M. Torkkeli, K. Leppanen, F. Galbrecht, E. Preis, H. D. Burrows, U. Scherf, A. P. Monkman, *Macromolecules* **2007**, *40*, 9398.
- [35] D. W. Bright, F. B. Dias, F. Galbrecht, U. Scherf, A. P. Monkman, *Adv. Funct. Mater.* **2009**, *19*, 67.
- [36] A. Monkman, C. Rothe, S. King, F. Dias, *Adv. Polym. Sci.*, **2008**, *212*, 187.
- [37] M. Grell, D. D. C. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. P. Woo, M. Soliman, *Acta Polym.* **1998**, *49*, 439.
- [38] J. Kim, T. M. Swager, *Nature* **2001**, *411*, 1030.
- [39] D. W. Samuel, G. Rumbles, C. Collison, *Phys. Rev. B* **1995**, *52*, R11 573.
- [40] S. A. Jenekhe, J. A. Osaheni, *Science* **1994**, *265*, 765.
- [41] R. R. Lunt, N. C. Giebink, A. A. Belak, J. B. Benziger, S. R. Forrest, *J. Appl. Phys.* **2009**, *105*, 053711.
- [42] R. R. Lunt, J. B. Benziger, S. R. Forrest, *Adv. Mater.* **2010**, *22*, 1233.
- [43] S. I. Hintschich, C. Rothe, S. Sinha, A. P. Monkman, P. S. de Freitas, U. Scherf, *J. Chem. Phys.* **2003**, *119*, 12017.
- [44] C. Rothe, A. Monkman, *J. Chem. Phys.* **2005**, *123*, 244904.
- [45] A. P. Monkman, H. D. Burrows, L. J. Hartwell, L. E. Horsburgh, I. Hamblett, S. Navaratnam, *Phys. Rev. Lett.* **2001**, *86*, 1358.
- [46] K. Kanemoto, I. Akai, M. Sugisaki, H. Hashimoto, T. Karasawa, N. Negishi, Y. Aso, *J. Chem. Phys.* **2009**, *130*, 234909.
- [47] C. Rothe, S. M. King, F. Dias, A. P. Monkman, *Phys. Rev. B* **2004**, *70*, 195213.
- [48] C. Rothe, A. P. Monkman, *Phys. Rev. B* **2003**, *68*, 075208.
- [49] D. W. Samuel, G. A. Turnbull, *Chem. Rev.* **2007**, *107*, 1272.