Conjugated Polymers

Counting Chromophores in Conjugated Polymers[**]

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The development of novel materials for organic optoelectronics based on conjugated polymers (CPs) has been paralleled by the quest to understand the nature of the fundamental emitting species.[1] CPs can have molecular weights of hundreds of thousands, comprising thousands of repeat units, yet the delocalization of π electrons is thought to be limited by structural and chemical defects on the chain and leads to the formation of "isolated" chromophore units on the CP. Although this idea is generally upheld, there is little direct evidence for this model; the evidence reported until now is derived mainly from site-selective fluorescence investigations.[2] The size of the emitter has also been widely debated in the literature as the size defines the key difference between polymeric and small-molecule organic semiconductors.[1–6] A simple way to assess the size of the chromophore is to study model oligomeric compounds and establish the critical oligomer length for which absorption and emission spectra correspond to the polymeric analogue.[1,4] However, electron–hole correlations are very strong in conjugated systems, thus this approach only provides insight into the delocalization or coherence length of the exciton but not the so-called diagonal length; that is, the actual length of the conjugated segment over which the electron–hole pair may move.[6] These two physical quantities can be very different, such as in the case of defect-free polydiacetylene.[7]

Single-molecule (SM) detection and spectroscopy (SMS) are powerful tools to help to construct an understanding of the basic electronic properties of molecules.[8] SMS has

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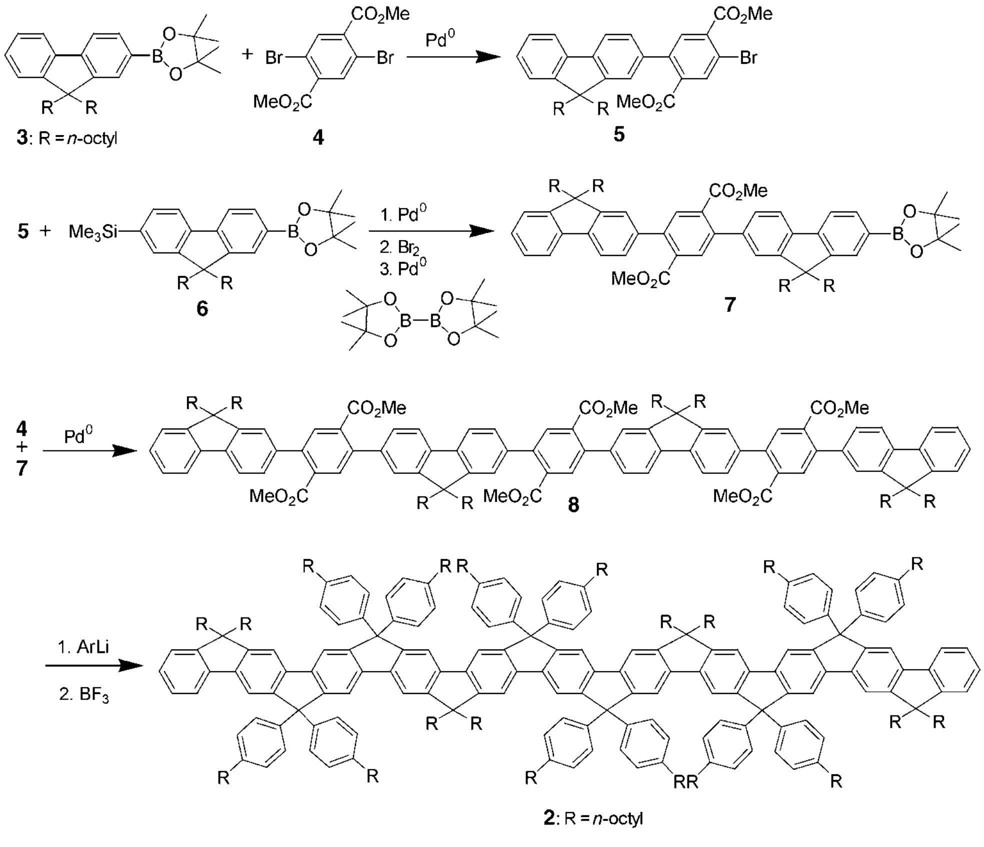
yielded insight into the nature of emission in a number of well-defined multichromophoric assemblies[9–11] as well as demonstrating that the emission from CPs can occur from trap states which can be reversibly quenched.[12–17] We recently showed that SMS can provide unique information on the presence of chromophores in CPs and may be used to investigate intramolecular interchromophoric couplings.[18–21] Single chromophores exhibit universal photophysical properties independent of the details of the materials chemistry, thus enabling the derivation of universal structure–property relationships.[21] Herein we address the fundamental issue of how the number of chromophores varies with molecular size (i.e. the number of repeat units) and present the first study by high-resolution SMS on model oligomeric compounds. The complexity of the SM emission spectra varies with chain length and results from the contribution of individual spectral features of single chromophores. Comparison of these data with those of oligomeric compounds allows a direct differentiation between the single-charge carrier and exciton confinement lengths. Most importantly, we demonstrate that a single CP molecule can support multichromophoric emission, which is not trap-state limited.

As a suitable polymer we chose methyl-substituted poly(*para*-phenylene) (MeLPPP, **1**), and as a model oligomer we chose a ladder-type undecaphenylene **2**, which is one of the longest poly(*para*-phenylene) oligomers reported thus far and which was specifically synthesized to clarify the nature of emission in CPs. The synthetic pathway to undecaphenylene **2** is shown in Scheme 1. The key intermediate in the preparation of **2** is a singly end-functionalized pentaphenylene prepared by a modification of existing routes to pentaphenylenes.[22] Starting with 2,5-dibromodimethylterephthalate **4**, two sequential Suzuki couplings generated a pentaphenylene diester bearing a trimethylsilyl group at one end. This group was converted through the bromide to a boronic ester group to produce the end-functionalized pentamer intermediate **7** in an overall yield of 14% from **3**. The corresponding deboronated compound (arising from addition of two equivalents of **3** to **4**) was present as a major (≈33 mol%) contaminant in all the earlier steps but could be removed by chromatography only at this stage. The problem in removing this contamination together with the low overall yield of **7** illustrate the difficulties inherent in the synthesis of defined ladder-type oligomers. Another Suzuki coupling of **7** with **4** gave the undecaphenylene hexaester **8** (68%), which upon addition of excess aryllithium followed by Lewis acid catalyzed Friedel–Crafts alkylation was converted into the undecamer **2** (56% yield from **8**, 3% overall yield based on **3**). The oligomer **2** was characterized by microanalysis, NMR, UV/Vis absorbance, and photoluminescence (PL) spectroscopy, and mass spectrometry. Full details of the synthesis and characterization of **2** are given in the Supporting Information.

We studied the PL spectra of single molecules of the rigid rod ladder-type CP **1** and the undecamer model compound **2** dispersed in a polystyrene matrix. Figure 1 shows spectra recorded both in solution at room temperature and as single molecules at 5 K. The spectra of the undecamer are blue-shifted by 8 nm with respect to the CP, but are otherwise rather similar with maxima at around 450 nm. The spectra of the SM are substantially narrower (1–2-nm width) than those



Scheme 1. Synthesis of the ladder-type undecamer **2**.

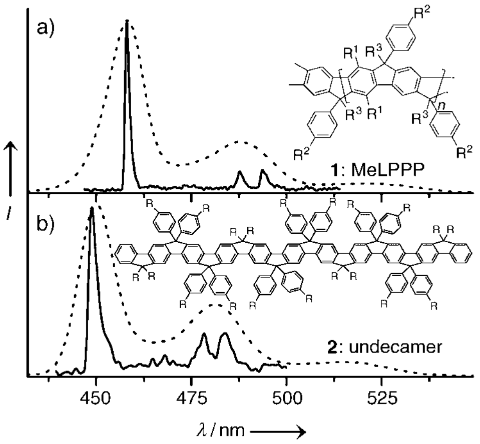


Figure 1. Single-molecule (SM) photoluminescence spectra at 5 K of a) the conjugated polymer (CP) MeLPPP (**1**) and b) the model oligomer **2**. Dotted lines (•••••) show PL spectra of the ensembles in solution at room temperature.

of the solution ensemble and reveal a distinct splitting of the vibronic 0–1 transition around 480 nm. SMS shows a significantly higher spectral resolution which allowed us to pinpoint the nature of emission on the polymer chain. To do this, the chain length of the CP was varied from approximately 62 to around 165 phenylene units ($M_r \approx 25$ kDa to $M_r \approx 67$ kDa; polydispersity ratio (PD) = 1.8–4.7), with the larger CPs displaying a somewhat higher polydispersity ratio.

The different single CPs were compared directly with the undecamer model compound. Figure 2a shows the 0–0 transition of a typical PL spectrum of a single oligomer. In comparison, a characteristic PL spectrum of the short-chain CP is presented in Figure 2b. One clear peak is identified in both cases. The maximum of the short-chain CP is red-shifted by a few nm and is somewhat narrower (≈1 nm) relative to that of the oligomer, but otherwise they are similar in shape. The ensemble spectrum of the CP is found to be virtually independent of molecular weight (not shown). The SM spectrum of the long-chain CP in Figure 2c, however, is more complex. We identify 5 distinct peaks, all of which have the same shape and width as the single peak in panel b, and for better comparison the PL peak of the short-chain CP is superimposed on each of the 5 lines (dotted curves). We conclude that the emitting species is similar in all cases and is almost independent of chain length, which simply controls the number of emitting units. The histograms in Figure 2d show a statistical analysis of peak positions and line widths for a total of 161 SMs that exhibit resolvable peaks in the PL spectra. The distribution in peak energies is closely matched by the ensemble spectra recorded at 5 K (solid lines). The spectra of the single undecamer are on average twice as broad as the CP spectra and are blue-shifted by 10 nm. There is a certain overlap between the histograms of the CPs and the oligomers, so that a few spectra of CPs are indistinguishable from those of the oligomers. This suggests that the emitting species can indeed be identical in the undecamer and the CP; that is, a subunit on the chain which consists of 11 benzene rings makes up the conjugated segments. It should be stressed that although the line widths of the spectra of the SMs are broader for the oligomer than those for the CP, the distribution in peak positions is considerably narrower as a direct consequence of the monodispersity of the oligomer.

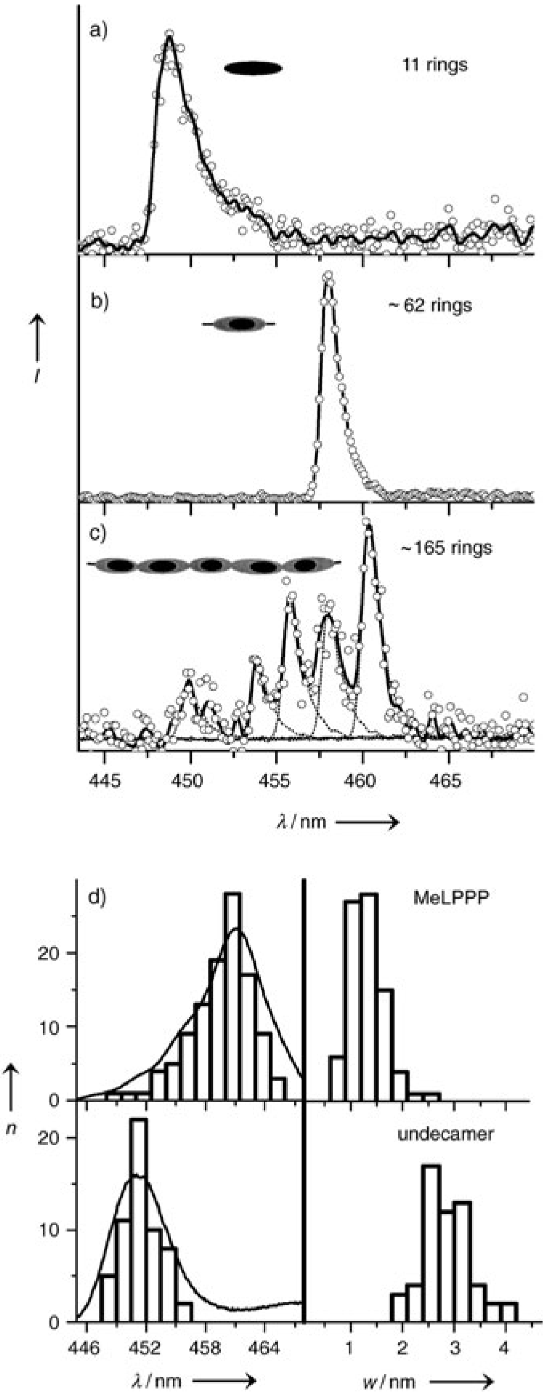


Figure 2. Single-molecule PL emission spectra at 5 K of the the model oligomer and the conjugated polymer MeLPPP: a) the undecamer, b) a short-chain CP ($M_r \approx 25$ kDa), and c) a long-chain CP ($M_r \approx 67$ kDa). Each of the individual peaks in the emission from the long-chain CP is identical in shape to the single peak in the emission from the short-chain CP (this single peak is superimposed for each peak in part c; •••••). The sketches indicate the difference between exciton size (black) and conjugation length (gray). d) The distribution of peak energies (λ) and line widths (*w*) for the short-chain CP and the model oligomer, with ensemble spectra overlaid (——; *n* = occurrence).

Note that in contrast the spectra of the ensemble at room temperature are equally broad and thus do not provide a measure of disorder.

Evidently, segments as short as 11 rings can constitute the emitting species in CPs. The chain may be over 13 times as long as this, so that a single chain should support multiple chromophores emitting simultaneously. The number of units should therefore depend on the chain length. Figure 3 shows the variation in the number of emission lines, that is, chromophores, with chain length which were extracted from a total of 200 SMs. Note that the data point at a chain length of 138 rings was determined for a phenyl-substituted rather than a methyl-substituted LPPP, which otherwise has identical fluorescence properties.[23] A monotononic increase in the number of units was observed which provides clear evidence for a disruption of the π-electron system along the chain and the formation of more-or-less isolated conjugated subunits. The average PL intensity per chromophore line (circles) is also indicated. This is virtually independent of chain length, but increases almost tenfold upon going from the oligomer to the CP. The PL intensity is both a measure of the absorption and the emission efficiency. As the fluorescence yields of the ensemble are comparable for the two materials, this difference in intensity can only be an effect of a difference in absorption. The emitting unit on the CP must be comparable to the undecamer in size, but the remainder of the conjugated segment apparently leads to a substantial increase in oscillator strength and absorption.

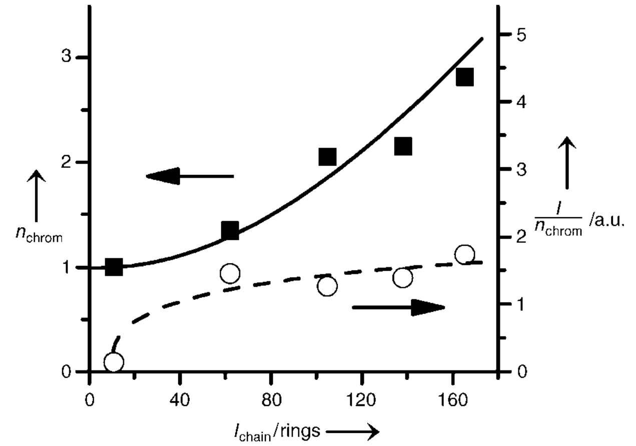


Figure 3. ■: Variation of the average number of peaks (chromophores) in the PL spectra (n_{chrom}) with chain length (l_{chain}, number of benzene rings). ○: The average intensity per peak for a total of 108 molecules (I/n_{chrom}).

The effective conjugation length for absorption thus increases with chain length but not the effective conjugation length for emission. This effect may in part be explicable by efficient light harvesting on the CP chain by ultrafast energy transfer between adjacent chromophore units, which we were recently able to identify by studying the polarization of absorption and emission of single chains.[18] However, the conjugation length (marked in gray in the sketch in Figure 2)—the distance over which an excitation may move coherently—may be substantially larger than the actual size of the excitation (black). This effect has been studied in detail by using quantum-chemical models,[6] but has so far been hard to assess experimentally. Our data suggest that the absorbing unit should be larger than the emitting unit. Above a length of 11–12 benzene rings, the Coulombic interactions as well as phonon-mediated self-trapping are so strong that the exciton size remains independent of the length of the conjugated segment. The conjugation length may therefore substantially exceed the exciton size. For a chain length of 165 rings, we find 2.8 lines on average which provides an upper estimate of the conjugation length of 59, approximately five times the size of the exciton. Even if we account for the possibility of the chain containing structural defects that lead to a branching of the rigid rod structure and to different polarizations of the individual conjugated segments,[18] which would not all be excited by the linearly polarized laser light used, at most 50% of the conjugated units on the chain would escape excitation. The effective length of the optically active segment on the chain is therefore at least twice the size of the exciton. As the number of chromophores varies approximately linearly with chain length, we propose that the exciton localization length in this class of materials is generally at least twice the exciton coherence size of roughly 12 phenylene units.

This conclusion is compatible with previous observations in highly ordered and virtually defect-free polydiacetylenes.[7] The huge optical non-linearities, which can be well-described by a phase–space-filling model of one-dimensional excitons[7c] as well as by ultrafast intramolecular migration of excitation energy in single chains,[7b] are signatures of extended π conjugation with limited exciton size. Evidence for conjugated units that are larger in absorption than in emission is also seen in more-disordered materials for which the red shift in fluorescence saturates considerably sooner with increasing chain length than the red shift in absorption.[4g] This effect, which is in part related to structural relaxation (although this is very weak indeed in the ladder-type polymers[19]), has also been investigated theoretically,[24,25] as a precise knowledge of the size of the emitting and absorbing unit is imperative for understanding and modeling intramolecular energy transfer.[25]

The conclusion of extended conjugations naturally raises the question of the origin of static disorder, which gives rise to a distribution in chromophore energies and the associated inhomogeneous broadening witnessed in Figure 2d. The common notion is that topological defects lead to a confinement of the excitation and thus to a modification in transition energy. Our data suggest that the origin of disorder is more subtle, although clear scissions of the π system do occur. Instead, we propose that the dielectric environment of the individual chromophores, that is, both the surrounding matrix and the remaining chain, leads to an effective potential-energy landscape, which is different for each chromophore and which slightly modifies the transition energies between different chromophores. This situation is conceptually similar to the description of energetic disorder in single dye molecules for which a comparably large degree of disorder is observed despite the absence of a distribution in conjugation lengths.[8,9] Further evidence for this picture comes from the fact that the line widths in the PL spectra of the single-molecule oligomer are substantially greater than those of the CP. As the undecamer is just of the length where the exciton is still slightly confined by the limited π-electron delocalization, a conclusion is that confinement of the exciton wavefunction by complete disruption of the π system leads to line broadening in similar fashion to J-aggregates, for example.[1] The distribution in emission wavelengths in the CP is therefore most likely not a direct consequence of the distribution in conjugation lengths, which should lead to substantial line broadening.

Finally, to highlight the relevance of our conclusions to bulk materials for devices, we demonstrate that the ensemble photophysical properties of **1** and **2** are also consistent with the picture of polymeric chromophores substantially exceeding the size of oligomers. Figure 4a shows a direct comparison of the PL spectra of **2** and the CP (≈ 25 kDa) in solution at room temperature. The spectra are very similar in shape. The PL spectrum of the oligomer is also shown red-shifted by 8 nm and superimposed (dashed line) on that of the CP (dotted line) for comparison. The spectral width of the monodisperse oligomer and the polydisperse CP are almost identical, in agreement with our conclusion that the CP spectrum is not primarily broadened owing to a distribution of different conjugation lengths. The CP spectrum does exhibit a slight broadening to shorter wavelengths relative to the oligomer which may indeed be an indication of the presence of conjugated segments with effective lengths equal to or shorter than the oligomer. The similarity in the PL spectra of the CP and the oligomer is even more striking in the case of spin-coated bulk films, which are compared in Figure 4b. Besides the reduced intensity of the vibronic sideband in the case of **1** and the blue shift of 10 nm, the spectra are identical to within 1 nm, thus suggesting that **2** may indeed be an excellent model for **1** in the bulk phase.

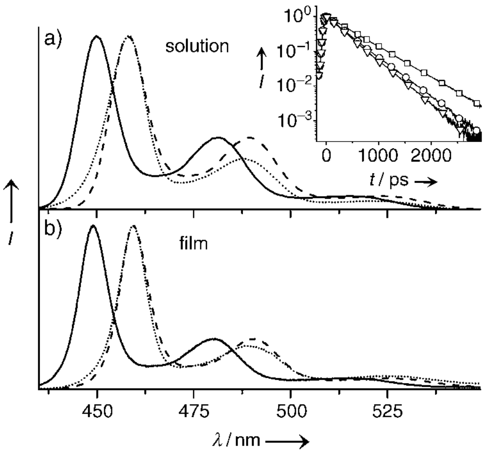


Figure 4. a) Ensemble fluorescence spectra of the undecamer (——) and polymer (•••••) in dilute solution in toluene. The spectrum of the oligomer is shown as recorded as well as shifted by 8 nm to overlap that of the polymer (-----) for better comparison. Inset: The PL decay of the oligomer (□) and two conjugated polymers ($M_\text{r}\approx 25$ kDa (○); $M_\text{r}\approx 67$ kDa (▽)). b) Fluorescence spectra of the oligomer (——) and the polymer (•••••) in the solid state, again with the spectrum of the oligomer shifted and superimposed (-----).

Time-resolved measurements pinpoint a substantial difference in the fluorescence from the oligomer and the CP. Figure 4 inset shows three PL lifetime measurements recorded for **2** and two CPs (with $M_\text{r}\approx 25$ kDa and $M_\text{r}\approx 67$ kDa). The oligomer has a PL lifetime of 490 ps, whereas this is reduced significantly to 360 ps in the short-chain CP. Increasing the chain length by a factor of 2.5 leads to a 10% decrease in the lifetime to 330 ps. Although the size of the π-conjugated segment occupied by the exciton in the CP must be of the order of the dimensions of the oligomer (i.e. 11 to 12 phenylene units) as the transition energies of **1** and **2** are virtually equal, the remainder of the CP chain clearly affects spontaneous emission. This is in part caused by highly efficient intramolecular energy transfer[20] and the presence of singlet scavenging defects, which have been shown to lead to a chain-length-dependent decrease in the lifetime in polyfluorenes.[26] However, the change in lifetime is much smaller upon increasing the length of the CP than in going from the oligomer to the CP. The conjugation length of the CP must substantially exceed the undecamer size, which in turn is a measure of the actual size of the excitation rather than of the conjugated length. Whereas the excited state on the oligomer has the nature of a molecular excitation, the emission from the CP has excitonic character[1] as it arises from coherently coupled conjugated segments extending further than the effective spatial delocalization of the excited state. A consequence of this is that vibrational coupling is weaker in the CP than in the oligomer, which is clearly seen in the reduced intensity of the 0–1 transition. Whereas molecular excitations display very strong vibrational coupling, excitations in coherently delocalized systems such as J-aggregates or highly conjugated polydiacetylenes couple only weakly to vibrations.[7] Furthermore, extension of the π-electron system also leads to an increase in oscillator strength and consequently to a reduction in fluorescence lifetime, in agreement with the substantial acceleration in the emission rate observed in the CP. These ensemble observations are fully consistent with our results on counting the number of chromophores in single CP chains and relating this to the dimensions of oligomers.

In summary, we have correlated the number of lines observed in the fluorescence spectra from single CP molecules directly with the average chain length. Our data suggest that the origin of disorder in CPs is not caused by a statistical distribution of defects confining the exciton but rather the polarizing influence of the local environment. Understanding the nature of the chromophores, the origin of disorder, and in particular the interactions between chromophores on a chain is absolutely vital to optimizing both electroluminescent and photovoltaic CP devices. Our results provide strong evidence that chromophoric emission is intrinsic to the nature of extended π-electron systems and not directly controlled by defects, which would be detrimental to device operation.

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