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ARTICLE

Highly Red-Shifted NIR Emission from a Novel Anthracene Conjugated Polymer Backbone Containing Pt(II) Porphyrins

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We present the synthesis of a novel diphenylanthracene (DPA) based semiconducting polymer. The polymer is solubilised by alkoxy groups attached directly to a DPA monomer, meaning the choice of co-monomer is not limited to exclusively highly solubilising moieties. Interestingly, the polymer shows a red-shifted elecroluminescence maximum (510 nm) when compared to its photoluminescence maximum (450 nm) which we attribute to excimer formation. The novel polymer was utilised as a host for a covalently-linked platinum (II) complexed porphyrin dopant. Emission from these polymers was observed in the NIR and again showed almost a 100 nm red shift from photoluminescence to electroluminescence. This work demonstrates that utlising highly aggregating host materials is an effective tool for inducing red-shifted emission in OLEDs

Introduction

The development of solution processable near-IR (NIR) organic light-emitting diodes (OLEDs) is of great interest for many "next generation" applications, ranging from telecommunications through to wound-healing. For these applications to become reality it is necessary for chemists to develop tools for extending the emission of compounds into the NIR.[1] Several general methods of red-shifting a material's emission exist. Platinum porphyrins are extremely promising candidates for NIR OLED emitters due to their ability to phosphoresce (and hence potentially achieve 100% internal quantum efficiency) and their red to NIR emission.[2-4] The most common method to extend the emission into the NIR is the use of chemical modification of the chromophore to increase the amount of conjugation present in a sample, thus reducing the optical energy gap. Comparing the emission of **PtTPP** and **PtTPBP**, the latter is red-shifted by approximately 100 nm due to the fused benzene rings on the porphyrin core.[5-7] However, the chemistry required to synthesize these extended porphyrins is challenging and low yielding. Intermolecular aggregation is well known to induce both blue and red-shifts through a variety of mechanisms including H and J aggregates,[8] excimers,[9] and the planarization of molecular structure.[10] However, thus far the extension of the emission of a porphyrin into the NIR through intermolecular interactions has rarely been reported. Kalinowski *et al.*

demonstrated that neat films of **Pt(OEP)** displayed significantly red-shifted emission relative to blend films due to the formation of dimer triplets.[11] The observation of red-shifted PL emission from porphyrins has also been observed by other researchers.[12-14] However, the majority of these have relied on neat films of platinum porphyrin to obtain red-shifted emission, which is not practical for real use. Furthermore, porphyrin aggregation usually results in significant PL and EL quenching. In recent years, new highly efficient emissive cyclometalated platinum-complexes have been used for OLED applications.[15] Furthermore, these materials have displayed efficient emission from excimer type emissive states.[16] However, the non-porphyrinoid nature of these new complexes typically result in significantly bluer PL and EL maxima and thus are not suitable for NIR emission. Previous work has shown the utility of copolymerising a host polymer with a platinum (II) porphyrin (platinum (II) complexed 5,15-dimesityl-10,20-diphenyl porphyrin (**MPP(Pt)**)).[17] The introduction of Pt (II) complexed dopants into semiconducting polymers has been shown to result in materials with promising deep-red[18] and NIR[19-22] emitting properties.

We hypothesized that by using a highly aggregating host material it would be possible to induce a red-shift in the emission of a Pt porphyrin by the formation of intermolecular aggregates, or by the induction of conformational changes.

Anthracene and diphenylanthracene (**DPA**) are of interest in the field of organic semiconductors due to their appealing optical properties of strong absorbance and emission. In particular their solid-state aggregation is well known, and resulting excimer-like emissions has been widely reported. The use of anthracene based small molecules in organic electronics has

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been widely reported across numerous potential applications.[23-25] Disadvantages of blend systems arise from phase separation, which leads to decreased energy transfer and increased phosphorescent quenching.[26,27] Copolymerisation fixes all components of a semiconducting system at defined distances, thus suppressing thermodynamic phase separation of the various components.[28-31] The overall solubility of the system is also generally increased, allowing for low-cost solution-processed device fabrication. Despite the routine use of anthracene small molecules in optoelectronics there are very few examples of anthracene containing polymers in the literature.[32-36] Furthermore, virtually all the existing examples rely on solubilizing groups being used as co-monomers. Thus we were interested in exploring the synthesis of anthracene based conjugated polymers from a soluble anthracene based monomer, and their potential as host materials for NIR emitting OLEDs.

Here we report the synthesis of a novel anthracene based host polymer backbone, as well as its application when co-polymerised with a platinum (II) porphyrin. Solubilising oxyoctyl chains have been added to the 2,3,6 and 7 positions of the anthracene, which provide enough solubility to enable polymerisation. Excimeric green emission is observed from the conjugated anthracene backbone due to strong intramolecular interactions. Remarkably, extremely red-shifted electroluminescence of incorporated platinum porphyrins is observed demonstrating that this is a valid new tool for the development of NIR OLEDs.

Design

When designing a host-guest material for optoelectronics careful consideration of all the relevant energy levels must be considered in order to ensure that the desired energy transfer processes can occur. An estimation of the relative energy levels of the excited states of a diphenyl anthracene polymer were calculated using DFT/TDDFT B3LYP *in silico* performed using a 6-31G* basis set. It was understood that alkyl chains would be necessary in the formulation of the desired backbone of anthracene containing polymers to aid solubility. To this end, two versions of the backbone were considered; a tetrakis alkyl (approximated in all calculations as methyl) anthracene and a tetrakis alkoxy anthracene (approximated as methoxy). Effects of conjugation length on energy levels (i.e. increased conjugation length lowering bandgap) were expected to be somewhat mitigated by the large twist between phenyl moieties. The oxyoctyl moieties, being more electron donating, were expected to increase the triplet energy level of the resulting polymer and hence prevent triplet energy back transfer. It was found that the substitution of alkoxy chains for alkyl raises T_1 slightly (+ 0.10 eV) and lowers S_1 (- 0.04 eV) relative to the proposed alkyl derivative. Interestingly, the calculated singlet triplet energy gap (exchange energy, *J*) of **PDPA** is fairly large (1.22 eV) compared to most conjugated polymers, found to be around 0.7 eV.[37] The frontier molecular orbitals are shown in *figure 1*. We suggest that the significantly

larger than usual exchange energy is due to the fact that in linear anthracenes the HOMO and LUMO are largely confined to the same area, thus resulting in a significant increase in Pauli repulsion for the singlet energy level (see *figure 2*). As is clearly indicated by our theoretical calculations, the alkoxy substituted host material has superior energetic characteristics (T_1 of **PDPA** is higher than T_1 of **MPP(Pt)**) when compared to the alkyl derivative, and hence this was the focus of our synthesis.
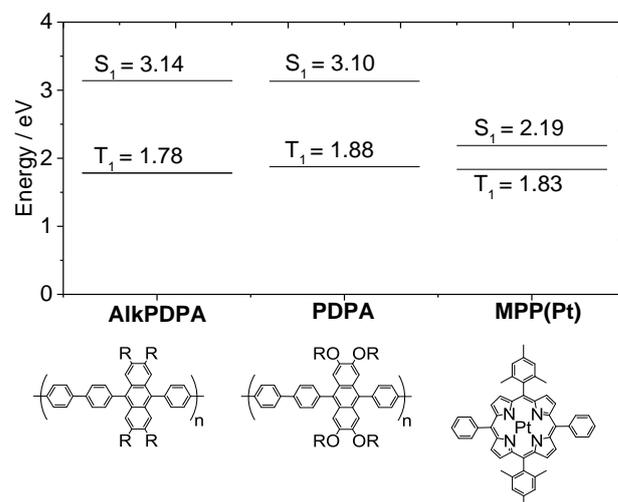
Figure 1: Calculated energy levels of anthracene polymers and MPP(Pt) using DFT B3LYP with a 6-31G* basis set. For the purposes of the calculation, R was set as methyl.

Previous work within the group has shown the utility of a platinum (II) complexed porphyrin (**MPP(Pt)**) covalently bonded in a fluorene polymer backbone.[17] The calculated energy levels of **MPP(Pt)** are also shown in *figure 1*. Encouragingly, T_1 of **MPP(Pt)** was found to be close to that of **PDPA** (-0.05 eV) so efficient energy transfer was predicted from polymer backbone to porphyrin dopant. This was expected to result primarily in phosphorescence from the porphyrin as a radiative pathway. However, as the triplet energy levels are so similar, and TD-DFT often underestimates the energetic position of these it was noted that it is possible that triplet energy back transfer, and even subsequent triplet-triplet annihilation may occur on the anthracene backbone.[38]

Synthesis

The diphenyl anthracene containing monomer, 9,10-di(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (**ODPA**), was synthesised using an analogous reaction to that of Xia.[39] Octyloxy groups have been added to the monomer to increase the overall solubility of the subsequent polymers. 1,2-dioctyloxybenzene was reacted with 4-bromobenzaldehyde in Eaton's reagent and subsequently oxidised with DDQ to yield **ODPA**, *scheme 1*.

ODPA was reacted with 1,4-Benzenediboronic acid bis(pinacol) ester in a Suzuki polymerisation using $Pd_2(dba)_3$ and $P(o\text{-}tol)_3$ as catalyst in the presence of aliquat 336 and base to form

poly[1,4-phenyl-alt-9,10-di(1,4-phenyl)-2,3,6,7-tetrakis(octyloxy)anthracene] (**PDPA**) as a white solid. The novel anthracene polymer was purified via soxhlet extraction using acetone, hexane and chloroform, before being precipitated into methanol to afford the final pure polymer, *scheme 2* and *table 1*.
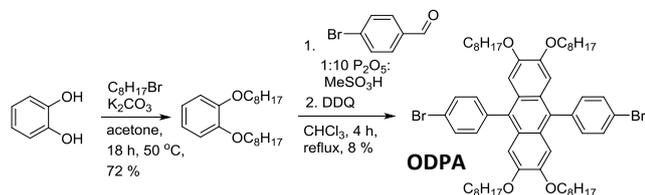
Scheme 1: Synthesis of 9,10-di(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene (**ODPA**).
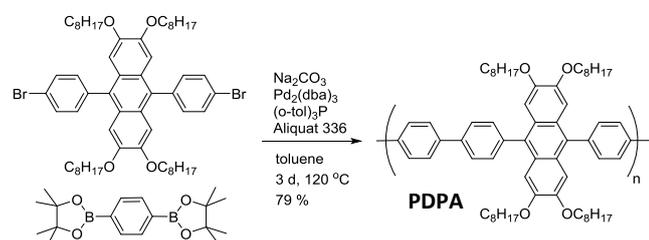
Scheme 2: Suzuki polymerisation of **ODPA** and 1,4-Benzenediboronic acid bis(pinacol) ester to form poly[1,4-phenyl-alt-9,10-di(1,4-phenyl)-2,3,6,7-tetrakis(octyloxy)anthracene] (**PDPA**).

Table 1 contains the basic physical and optical properties of the novel polymer. A relatively low molecular weight of ~8 kDa was obtained potentially due to the low solubility of the resulting polymer chain, which we believe is due to its aggregating tendency as a result of the highly planer anthracene core. The HOMO and LUMO energy levels (as measured by UV-PES and the optical energy gap) were found to be -5.48 eV and -2.60 eV respectively. These values are not too dissimilar to structurally related anthracene small molecules indicating that polymerization does not greatly affect the frontier molecular orbital energies as might be expected by the significant twist of the peripheral phenyl groups. TGA analysis shows **PDPA** is stable up to around 400 °C, shown in the supporting information. It is noted that this is exceptionally high for a semiconducting polymer and that this high thermal stability is maintained across the porphyrin copolymerised series detailed below.[40]

Figure 2 shows the HOMO and LUMO of a trimer of **PDPA**, an approximation of the entire polymer, calculated by DFT B3LYP using a 6-31G* basis set. What is most obvious is the degree of localisation of both HOMO and LUMO. The large twist in the polymer backbone between phenyl and anthracene moieties is such that conjugation across the entire molecule is broken and individual energy levels are localised. This has the likely result of decreased mobilities, but also means that the electronic characteristics of anthracene as a small molecule are only mildly affected. Both HOMO and LUMO do however show electron density on the oxygen of the alkoxy groups. This is the cause of the slightly higher T_1 of **PDPA** when compared to **AlkPDPA** (see *figure 1*).

It should be noted that the accuracy of the method employed, especially with respect to triplet excited states (TDDFT), can sometimes be uncertain and should not be considered to be precise, due to what is known as the triplet instability problem.[41,42] TDDFT does have precedent in the literature however as a convenient tool for predicting the relative levels of excited triplet states.[43,44] Due to the similar nature of the two conjugated backbones it is likely that the predicted difference in triplet energy levels is a significant difference.

PDPA LUMO
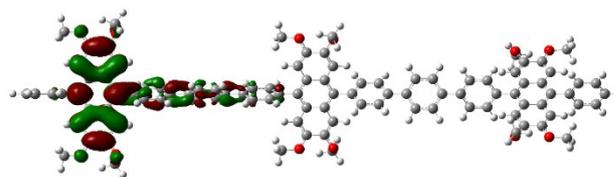
PDPA HOMO
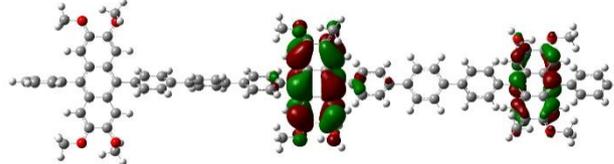
Figure 2: Calculated LUMO (top) and HOMO (bottom) of **PDPA** trimer using DFT B3LYP with a 6-31G* basis set.

Polymer	M_n[a] / kDa	M_w[a] / kDa	PDI[a]	HOMO[b] / eV	LUMO[c] / eV	Egap[d] /eV	Egap predict[e] /eV	PLQY[f] / %
PDPA	7.8	10	1.3	-5.49	-2.61	2.88	3.10	22

Table 1: Physical data and optical properties of **PDPA** polymer. **a)** Determined by SEC(PS) using PhCl eluent **b)** Determined by PESA measurements, ±0.1 eV **c)** Determined from HOMO + optical Egap **d)** Determined from thin film UV-Vis onset **e)** Determined by TDDFT B3LYP using a 6-31G* basis set **d)** Thin film PLQY determined using integrating sphere

Results and Discussion

The absorption and emission spectra of the novel polymer is shown in *figure 3*. Both in solution (chlorobenzene) and solid state (thin films spun from chlorobenzene) the novel material has a dual absorption maxima at 382 and 402 nm, with the relative ratios not changing significantly. A significant degree of scattering is present in both absorption spectra likely due to the formation of aggregates (although both solutions were filtered through 0.45 um filter before measurement). It appears that on going from solution to solid state there is a red-shift in absorption onset, potentially due to intermolecular pi-stacking interactions, but the presence of the scattering makes it difficult to quantify. Strong blue emission is observed both in solution and thin film with a slightly redder emission in the solid state, due to solid state packing effects. A relatively high thin film photoluminescence quantum yield of 22% was observed in marked contrast to other reported anthracene conjugated polymers which exhibit severe PL quenching in the solid state.[32,45]

emission peak at ~460 nm is clearly visible which corresponds well with the PL maximum. The EL emission spectra looks similar to previous reports of excimer-like emission in anthracene small molecules, indicating that solid-state aggregation is indeed occurring in this material.[46] We note the interesting difference between the PL and EL spectra. We consider this the result of two factors, namely the energy-selective nature of charge transport in organic semiconductors, and the possible effect of operation on inducing further aggregation. Regarding the first effect, we note that the PL spectra do not display much sign of aggregation, thereby providing evidence that there must be a relatively low density of aggregates/excimeric sites, thereby allowing most of the singlets to decay radiatively before migrating to aggregates or sites suitable for forming excimers. During electroluminescent operation however, charges will be transported through low-energy sites, such as those provided by the aggregates, thus favouring generation of the excitons at these very sites. In addition, we cannot rule out that mild heating of the devices during EL operation might favour additional aggregation compared to the PL experiment.

Figure 3: Normalised absorbance spectra of **PDPA** in chlorobenzene solution (black), as a thin film (red) and photoluminescence spectra in chlorobenzene solution (navy) and as a thin film (turquoise) under 350 nm irradiation. Inset shows photograph of thin film PL emission.

We fabricated OLED devices by incorporating the copolymers in LEDs with ITO/PEDOT:PSS (50 nm) anode and thermally evaporated Ca (30 nm) / Al (150 nm).[20] We deposited the active layer (90 nm) via spin coating from a 10 mg/mL chlorobenzene solution.

The electroluminescence (EL) spectra are shown in *figure 4*, and the output characteristics are shown in *table 2*. The OLEDs show bright green electroluminescence with an emission maximum at approximately 510 nm. This value is significantly red-shifted when compared to the thin-film photoluminescence (450 nm). Electroluminescence from the non-aggregated **PDPA** can be observed at 460 nm, which varies in intensity according to the processing conditions of the active layer. A maximum EQE of 0.14 % is obtained which is reasonable when considering the non-optimized nature of these single-layer devices. A small

Figure 4: a) Device structure of the OLEDs. LEDs were fabricated by using ITO/PEDOT:PSS anodes, active layer (90 nm) and Ca (30 nm)/Al (150 nm) cathodes.[47] **b)** Photoluminescence of thin film of **PDPA** (dashed) and electroluminescence of a **PDPA** device (solid).

Polymer	Max EQE / %	PL peak / nm	EL peak / nm
PDPA	0.14	450	460, 510

Table 2: PDPA OLED characteristics.

Having synthesized the novel polymer host **PDPA**, we covalently introduced a dopant into the system in order to see whether the emission spectra could be manipulated through aggregation. We have previously synthesised 5,15-dimesityl-10,20-diphenylporphyrinato platinum(II) (**MPP(Pt)**) as a constituent part of a polymer backbone.[17] **MPP(Pt)** was used as co-monomer to synthesise a series of **PDPA MPP(Pt)** polymers with various weight percentages of porphyrin loading in an analogous reaction to the non doped **PDPA** synthesis. The obtained polymeric materials all had similar molecular weights to the parent **PDPA** polymer, *table 3*.
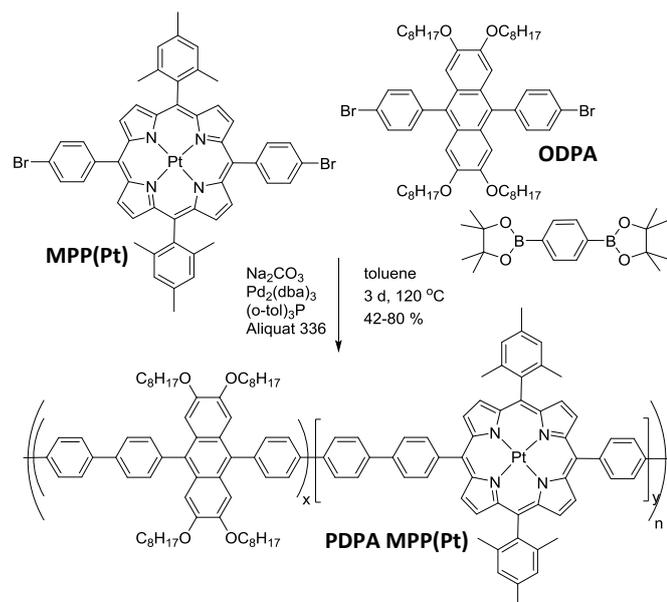
Scheme 3: Suzuki polymerisation of **ODPA**, 1,4-Benzenediboronic acid bis(pinacol) ester and **MPP(Pt)** to form various polyphenyl-9,10-di(4-bromophenyl)-2,3,6,7-tetrakis(octyloxy)anthracene **MPP(Pt)** (**PDPA MPP(Pt)**) polymers.

All polymers show good incorporation ratios of porphyrin, well in line with the desired ratios from the porphyrin feed. These values were obtained by consideration of ^{1}H NMR spectra, shown in the supporting information. A value was not obtained for **PDPA MPP(Pt) 1**, as the loading was too low to visualise the porphyrin moieties. However, consideration of the photoluminescent data clearly shows porphyrin incorporation into the polymer. The ^{1}H NMR spectra also show the high purity of the synthesised polymers. The polymers also demonstrate high thermal stability, TGA traces are shown in the supporting information.

The energy gap of the host portion of the polymers is consistent across the series, and lowered slightly for those polymers containing **MPP(Pt)**. This is due to a decrease in energy of the LUMO levels,

possibly because of increased electron density from the porphyrin moieties. PESA measurements have shown that the HOMO levels remain constant.

From *figure 5 a)*, the main absorption bands from both the anthracene and porphyrin units can be discerned. **PDPA** (0% porphyrin feed) presents two main bands peaked at 380 and 400 nm. At increasing porphyrin feed, porphyrin-related bands grow out of the polyanthracene spectrum, *table 3*. The main feature that can be observed is the appearance and progressive growth of the porphyrin Soret band (412 nm) and Q-bands (500-550 nm) at porphyrin feed > 5%. The Soret band denotes the S2←S0 transition, whereas the weak and lower energy Q bands indicate S1←S0 transitions.
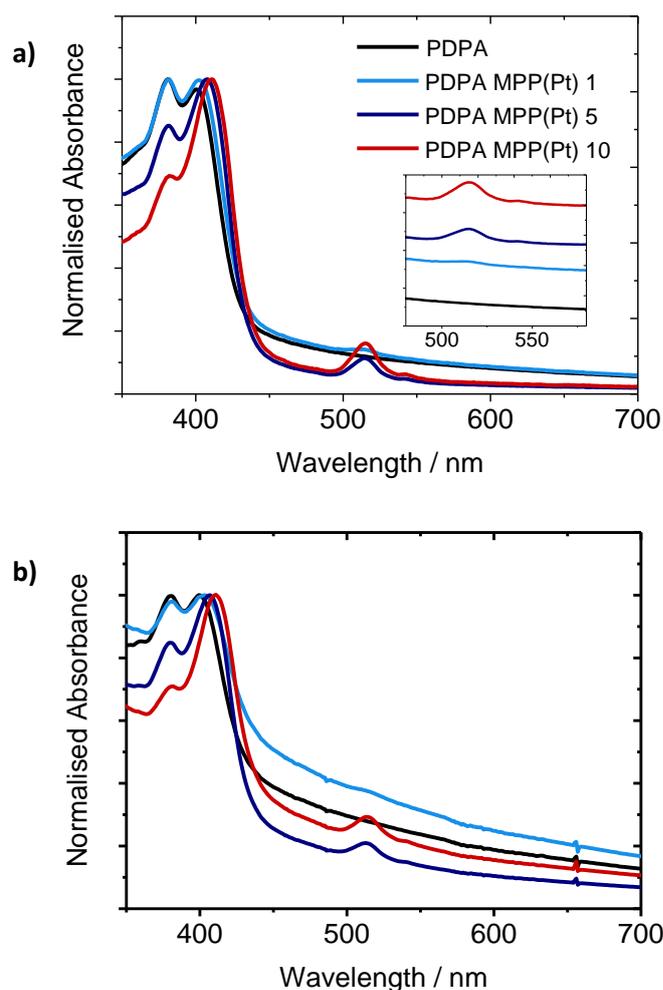
Figure 5: a) Absorption spectra of the **PDPA MPP(Pt)** polymers in chlorobenzene solution at varying porphyrin feed-ratios. Inset shows **MPP(Pt)** Q-band absorption features, the curves are stacked with Y-offset following the increase of **MPP(Pt)** content. **b)** Absorption

Polymer	Porphyrin feed / w/w %	M_n[a] / kDa	M_w[a] / kDa	PDI[a]	HOMO[b] / eV	LUMO (host)[c] / eV	Incorp Ratio[d] / w/w %	Near-IR-QY [e] / %
PDPA MPP(Pt) 1	1	8.8	12	1.4	-5.50	-2.94	≤ 1	1
PDPA MPP(Pt) 5	5	12	20	1.7	-5.48	-2.85	4	2
PDPA MPP(Pt) 10	10	11	21	1.8	-5.42	-2.79	10	2

Table 3: Physical data and optical properties of the different **PDPA MPP(Pt)** polymers. a) Determined by SEC(PS) using PhCl eluent b) Determined by PESA measurements, ±0.1 eV c) Determined from HOMO + optical Egap d) Determined from ^{1}H NMR Spectroscopy (see Supporting Information) e) Thin film PLQY determined using integrating sphere (Measured in red-NIR region >600 nm)

spectra of the **PDPA MPP(Pt)** polymers deposited onto quartz substrates from 10 mg/ml chlorobenzene solutions.

Normalised absorption spectra of the films were obtained by spin coating at 800 rpm from 10 mg/mL chlorobenzene solutions. The thin film spectra resemble the chlorobenzene solution spectra, with the exception of a further visible absorption band at 300 nm. The gradual increase of the signal at increasing energy is probably due to scattering-related effects, induced by the inhomogeneity of the solutions and films obtained, possibly as a result of poorly-dissolved aggregates with dimensions comparable to these wavelengths. We observed such effect despite filtering the solutions through a PTFE syringe filter with 0.45 μm pore size before deposition. Therefore, the aggregation is taking place immediately after filtering, possibly indicating that the solvent is not ideal.

We show the emission spectra obtained from the same films in *figure 6*.

to the excited triplet states of the Q-bands.[50,51] The photoluminescence emission efficiency from all the samples is relatively low, ~ 1-2%, with a particularly low stability under laser irradiation. The instability is indicated by a progressive quenching of the red emission from the porphyrin units upon laser irradiation. The indented peak at 600 nm is an artefact generated by the detection unit.

EL spectra are reported in *Figure 7*. These could be recorded only from **PDPA MMP(Pt) 10** (10 % porphyrin) due to device stability issues. A summary of the PLEDs performance parameters is reported in *table 4*. The EL behaviour of the PLEDs was not entirely reproducible due to the low stability of the devices. We believe this instability is likely to be a combination of the high concentrations of triplet excitons potentially generating highly reactive singlet oxygen, or from anthracene undergoing cyclisation reactions.

Figure 6: a) PL spectra and **b)** normalised PL spectra of the films obtained from the chlorobenzene solutions. PL spectra were obtained by pumping the films with a 405 nm laser diode.
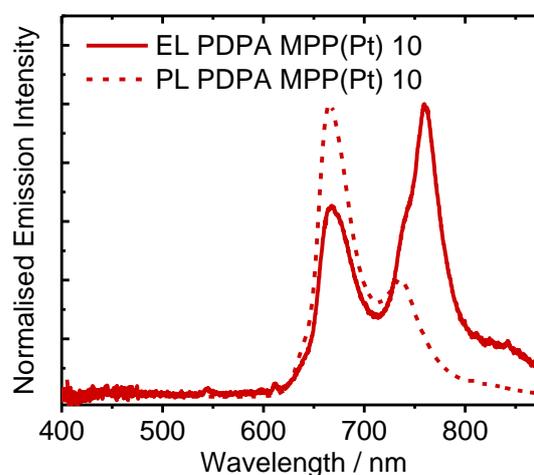
Figure 7: Normalised EL (solid) and PL (dotted) spectra of the films obtained from the chlorobenzene solutions.

Polymer	Max EQE (%)	V$_{ON}$ (V)	Max Radiance (mW/m^2)	PL peak (nm)	EL peak (nm)
PDPA MMP(Pt) 10	0.03	10	20	666, 737	666, 760

Table 4: Summary of PLEDs performance.

Efficient energy transfer from the polymer to the porphyrin units is highlighted by the quenching of the **PDPA** emission, peaked at 450 nm, and the formation of a secondary set of bands at lower energy (650-750 nm), which represents the phosphorescence from the **MPP(Pt)** units.[48,49] The two emission peaks, Q*(0,0) at 666 nm and Q*(1,0) at 737 nm are attributed

Further work on the PLED architecture, as suggested in the literature, might help to improve the EL stability and performance.[6,7,49] The emission of the **PDPA MPP(Pt) 10** sample is almost completely in the NIR region (λ > 700 nm), with an EQE of 0.03% not far from maximum values reported in literature for NIR light-emitting polymers.[20] Please note that the EQE of NIR OLEDs is generally much lower than that of OLEDs emitting in the visible range.[17-21,47,52] This is a result of different factors and in particular of the so-called "energy-gap law" (*vide infra*), and

possibly of an increased tendency towards the formation of H-aggregates, owing to a more spatially extended conjugation. H aggregates act as traps for excitons because of their lower energy compared to the unaggregated species, but emit with lower efficiency due to a vanishing dipole moment in the excited states, as clearly demonstrated by comparison of conjugated analogues in which aggregation is impeded by supramolecular engineering.[53-55] In addition, the so-called energy-gap law, suggests that the quantum efficiencies of molecular materials should decrease with the energy gap, due to vibrational overlap of ground and excited states.[56,57] This is reflected in a large body of experimental results, with only a couple of reports of relatively highly efficient NIR emitting complexes.[58] To the best of our knowledge, the highest EQEs were reported by Borek *et al* for electrophosphorescent Pt-porphyrins as emitting material, however their efficiencies reduced significantly for increasing current densities due to triplet-triplet annihilation (TTA) and reduced to ~1 % at 100 mA/cm^2. Considering their starting material had a (solution) quantum yield ~ 40 times greater than ours, our results appear to be essentially consistent with theirs (once the different PL efficiency is taken into account), despite the fact our device architecture was not optimised via incorporation of hole/electron injection as well as exciton blocking layers. In addition, we note that our emitting layer is polymeric and cannot be deposited via thermal evaporation, but is viable for spin-coating, thereby enabling fabrication via solution processing.

Figure 7 clearly shows that there is a significant red-shift between the PL max (666 nm) and the EL maximum (760 nm). The new NIR emission peak does not appear to be due to an increase in intensity of the 0,1 peak as a clear shoulder can be observed. Furthermore, it can be confirmed that this novel NIR emission is unique to the use of the novel host material, as identical porphyrins in less aggregating host materials do not display this red-shifted emission.[17] Of particular significance is that the EL maxima is at a similar wavelength to that observed for the significantly larger and fused **Pt(TPBP)** porphyrin that is often used for NIR OLEDs. Thus, our novel design strategy demonstrates that highly NIR OLEDs can be made using conventional smaller porphyrins. The origin of the red-shifted emission is currently under investigation but we tentatively propose that the increased aggregation of the novel polymer backbone induces either polymer-porphyrin or porphyrin-porphyrin aggregation to occur. This results in exciplex or excimer like behaviour in the novel material. Traditionally, aggregation in emissive porphyrins has been linked with significant emission quenching. Simultaneous uni-molecular and excimer like emission has been observed in other platinum complexes, however to the best of our knowledge we believe this is the first instance of such drastic aggregation induced red-shifted EL in a porphyrin based OLED.[16]

Conclusions

A soluble tetraoctyloxy diphenylanthracene based monomer (**ODPA**) has been synthesised and subjected to Suzuki polymerisation to form a novel semiconducting polymer (**PDPA**) with interesting emission characteristics. A photoluminescence maximum for a thin film is observed at 450 nm, whereas two peaks are observed in the electroluminescence spectra of a **PDPA** device at 460 nm and 510 nm. The peak at 460 nm is in good agreement with the photoluminescence spectra and is thought to be single molecule emission. The peak at 510 nm however has been tentatively assigned as emission from an excimer or exciplex, formed due to the highly aggregating nature of anthracene. To further investigate this effect, **PDPA** was copolymerised with a platinum (II) complexed porphyrin, **MPP(Pt)**. These polymers showed similar absorbance spectra to **PDPA** with the exception of the emergence of Q bands at 500-550 nm, but showed PL emission from the porphyrin corresponding to peaks at 666 nm and 737 nm. The Q band peaks became dominant at a 5 % w/w feed ratio of porphyrin. Electroluminescence spectra were obtained for the 10 % porphyrin loading. The emergence of a new, red-shifted peak was again observed at 760 nm as well as peaks incident with the PL spectrum. We suggest this is due to dual emission from single molecules at lower wavelengths 666 nm and 737 nm, and emission from an aggregated species at 760 nm. Aggregation of porphyrin moieties is classically associated with loss mechanisms due to emission quenching. Therefore, to the best of our knowledge, this is the first instance of an aggregation-induced red shift in platinum (II) porphyrin electroluminescence

Acknowledgements

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TOC

Anthracene backbone

Porphyrin Comonomer

PL → EL maxima shift

EL
PL

Wavelength / nm