Molecular Encapsulation of Naphthalene Diimide (NDI) Based \(\pi\)-Conjugated Polymers: A Tool for Understanding Photoluminescence

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Abstract: Conjugated polymers are an important class of chromophores for optoelectronic devices. Understanding and controlling their excited state properties, in particular, radiative and non-radiative recombination processes are among the greatest challenges that must be overcome. We report the synthesis and characterization of a molecularly encapsulated naphthalene diimide-based polymer, one of the most successfully used motifs, and explore its structural and optical properties. The molecular encapsulation enables a detailed understanding of the effect of interpolymer interactions. We reveal that the non-encapsulated analogue P(NDI-2OD-T) undergoes aggregation enhanced emission; an effect that is suppressed upon encapsulation due to an increasing \(\pi\)-interchain stacking distance. This suggests that decreasing \(\pi\)-stacking distances may be an attractive method to enhance the radiative properties of conjugated polymers in contrast to the current paradigm where it is viewed as a source of optical quenching.

Introduction

\(\pi\)-Conjugated polymers are an important class of semiconductors with unique and tunable optoelectronic properties, which hold great promise for the development of solution-processible and low-cost sustainable energy applications, such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), sensors and energy storage devices\(^[1,2]\).

In particular, naphthalene diimide (NDI) based \(\pi\)-conjugated polymers are among the most interesting electron-transporting semiconductors given their remarkable track record as high-performance non-fullerene acceptors (NFAs) in OPVs\(^[2–5]\) and high mobility n-channel semiconductors in OFETs\(^[2,6]\). NDI’s excellent device performance and many favorable properties (e.g., appropriate energy levels, facile synthesis, low synthetic cost, good electron mobility, high solubility as well as thermal and (photo)chemical stability) have therefore made this electron-depleted core extremely popular in plastic electronics\(^[2–7,9]\). However, since NDI-based polymers such as N2200 [P(NDI-2OD-2T)] or PCE8 [P(NDI-2OD-T)] are based on quite large aromatic units, they have a great propensity to aggregate in both solution and as thin films\(^[5]\). This can directly affect the conjugated polymer properties (both optical and electronic) as well as their miscibility with other polymers and hence greatly influences their device performance. Gaining greater synthetic control over the intermolecular interactions of these materials is therefore very important but remains challenging.

Recently, it has become apparent that one of the most important obstacles that must be overcome in conjugated polymer design is the suppression of non-radiative decay in narrow band gap conjugated polymers.\(^[10]\) Numerous recent studies have revealed that the high non-radiative voltage loss encountered in organic photovoltaics (OPVs), which holds back their efficiency, is primarily a consequence of the low solid state photoluminescence quantum yields (PLOQYS) of the blend materials\(^[11,12]\). Hence, increasing the PLOY of narrow band gap conjugated polymers is essential for next generation OPV, as well as being appealing for light emitting diodes and biological imaging. It is commonly assumed that the close packing of conjugated polymers results in the creation of additional non-radiative decay pathways. Therefore, the most promising strategy to increase the solid-state PLOY of conjugated polymers is to molecularly isolate the...
chains either through covalent or non-covalent encapsulation.\textsuperscript{[13–21]} Polymer dilution in a host matrix can also be used to increase PLOY but this cannot suppress intramolecular interactions, or even intermolecular in some cases.\textsuperscript{[22]} Herein, we report the synthesis and characterization of a novel encapsulated conjugated NDI polymer and report the resulting effect of molecular encapsulation on its optical properties. For our study we chose to encapsulate a P(NDI-T) derivative as it is one of the most successful n-type conjugated polymers used in organic photovoltaics.\textsuperscript{[31]} Thus, our findings are applicable and of relevance to virtually all polymer-polymer solar cell devices. We present a novel synthetic methodology which represents a significant advance in the functionalization of NDI-based monomers and allows for a much wider use of solubilizing/bulky functional groups on the N-atom of the naphthalene diimide. This strategy enables the tuning of intermolecular interactions in NDI-based polymers in an unprecedented fashion, and thereby allows invaluable fundamental insight into their solid-state optical properties. Our key finding is that upon increasing conjugated polymer interstrand separation, the photoluminescence is quenched due to the suppression of an AIEE (aggregation induced enhanced emission) type phenomena which is present in the parent polymer.

**Results**

**Synthesis**

The preparation of the encapsulated NDI monomer (E-NDI-T) commenced with the synthesis of Br$_2$-NDA (Figure 1). Br$_2$-NDA can be obtained by brominating 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) using dibromoisoocyanuric acid (DBI)\textsuperscript{[23,24]} bromine and catalytic iodine\textsuperscript{[25,26]} or 1,3-dibromo-5,5-dimethylhydantoin (DBH)\textsuperscript{[27,28]} in oleum or concentrated sulfuric acid. In our hands, the use of DBH in sulfuric acid was the most reliable, leading to a mixture of brominated products (44 % yield); of which the 2,6-isomer (Br$_2$-NDA) was the predominant product. Next, Br$_2$-NDA was treated with 2,6-dimethoxy-4-tridecylaniline (DMTAn) in an attempt to prepare Br$_2$-NDI-OMe. However, despite the use of acidic conditions, DMTAn did not attack the carbonyls of the anhydride. Instead, nucleophilic aromatic substitution (S$_\text{N}$Ar) occurred, thereby displacing the bromines with DMTAn. This was quite surprising considering that similar anilines, such as 2,6-diisopropylaniline,\textsuperscript{[29]} 2,4,6-trimethylaniline\textsuperscript{[30]} and a few other para-functionalized anilines\textsuperscript{[31–33]} had been used successfully before. Therefore, unless the oxygen lone pairs (on the methoxy groups) make DMTAn bulkier than 2,6-diisopropylaniline, steric encumbrance is likely not the underlying reason. Instead, we suggest that the

![Figure 1. Synthesis of the encapsulated NDI monomer (E-NDI-T).](image-url)
electronics of DMTAn disfavor nucleophilic attack at the anhydride carboxylic(s) via either hydrogen-bonding interactions or inductive withdrawal from the methoxy groups. Therefore, in this study we propose an alternative strategy that should allow access to a larger variety of phenyl-substituted NDI molecules by avoiding potential S_N_Ar pathways.

Here, Br_2-NDA was first converted into Th_2-NDA through a traditional Stille cross-coupling reaction and subsequently functionalized with a more versatile aniline, such as DMTAn (Figure 1). Our methodology therefore allows for a much wider use of solubilizing/functional groups at the imide nitrogen positions, which would not be possible via the traditional route (indicated in the middle). Th_2-NDA was obtained in 93% using commercial Br_2-NDA or 39% from the “home-made” mixture of brominated products. The presence of other, unwanted brominated products in the “home-made” Br2-NDA sample therefore affords a lower yield upon isolation/purification. Next, Th_2-NDA was reacted with DMTAn, leading to the formation of Th_2-NDI-OHe in 34% yield. Subsequent treatment of Th_2-NDI-OHe with excess sodium ethane thiolate successfully generated the crude demethylated product (Th_2-NDI-OH), which was encapsulated with 1,12-dibromododecane to give the encapsulated NDI monomer (E-NDI-T) in a two-step yield of 34%.

The structure of the encapsulated NDI monomer; E-NDI-T, was determined by X-ray crystallography (single crystals grown via the layering technique using chloroform and methanol), which confirmed that the straps indeed shield the NDI core (Figure 2). Analysis of the packing shows minimum distances of ≈12 Å between the centroids of the NDI cores (see Supporting Information), with the closest intermolecular separations being between the alkyl chains, of the order of 4 Å. Analysis of the packing shows minimum distances of ≈12 Å between the centroids of the NDI cores (see Supporting Information), with the closest intermolecular separations being between the alkyl chains, of the order of 4 Å. In contrast, non-encapsulated NDIs often show close π-π stacking distances in the region of ≈3.3 Å, demonstrating the ability of the macrocycle to spatially separate the chromophores effectively.

The molecule is centrosymmetric in the crystal structure, with dihedral angles of ≈40° between the NDI and thiophene units. This is consistent with other reports on NDI-T based polymers, which indicate a large degree of non-coplanarity between the thiophene and the naphthalene core.[35–37]

The conjugated polymers (Figure 3) were prepared through a direct arylation polymerization (DArP) procedure, using N,N’-bis(2-octyldodecyl)-2,6-dibromo-1,4,5,8-naphthalene diimide (Br_2-NDI-2OD) as the co-monomer. DArP was chosen as the preferred method for this study since it is an emerging, green approach that enables the direct coupling of aryl halides (Ar-X) and (hetero)aryls (Ar-H), while avoiding toxic side products.[38–42] Furthermore, recent studies have demonstrated that polymers prepared via DArP can achieve very similar molecular masses (M_n and M_w) and device performances compared to traditional methods.[39–42] As observed, the polymer series consists of the reference polymer P(NDI-2OD-T), an in-between, bulky dimethoxyphenyl polymer P(NDI-DMP-T), and lastly the encapsulated P(E-NDI-T) polymer. All polymers were obtained in similar number average molecular weights (M_n) of approximately 15 kDa (Table 1) and display good solubility in various solvents.

The HOMO energy levels were measured using PESA.

Table 1: Physical properties of the conjugated NDI polymers. The HOMO energy levels were measured using PESA.

| Polymer    | M_n [kg mol^{-1}] | M_w [kg mol^{-1}] | Dispersity | HOMO [eV] |
|------------|-------------------|-------------------|------------|-----------|
| P(NDI-2OD-T) | 16.1             | 42.2              | 2.62       | −5.8      |
| P(NDI-DMP-T) | 16.3             | 29.5              | 1.81       | −5.75     |
| P(E-NDI-T)  | 14.6             | 38.4              | 2.46       | −5.75     |
Optical Properties

The solution and thin film absorption and emission spectra of the three NDI polymers are shown in Figure 4 and summarized in Table 3. As observed, the spectral profiles of the solution absorption spectra are relatively featureless and nearly identical for all polymers, having \( \lambda_{\text{max}} \) values of 545 nm, 549 nm, and 546 nm for P(NDI-2OD-T), P(NDI-DMP-T) and P(E-NDI-T), respectively. The thin film absorption spectra, on the other hand, show a much clearer difference between the different polymers. For P(NDI-2OD-T), \( \lambda_{\text{max}} \) is significantly red-shifted (by 51 nm) to 596 nm on going from solution to solid state. In contrast, P(NDI-DMP-T) and P(E-NDI-T) display only minor redshifts of 3 and 1 nm, respectively. In other words, with increased shielding of the polymer backbone, the formation of lower energy species is increasingly suppressed, with a concomitant retention of the absorption profile when going from solution to thin film. This trend is consistent with previous studies on encapsulated conjugated materials.[13,14,43]

Similarly, the photoluminescence (PL) of the three polymers in solution is almost identical, with a \( \lambda_{\text{max}} \) at \( \approx 636 \) nm. This suggests that, in solution, the emission originates from isolated chains. In thin film, on the other hand, the spectra are again progressively red-shifted according to the “exposure” of the polymer chains to one another. For P(NDI-2OD-T), the \( \lambda_{\text{max}} \) red-shifts from 636 nm to 725 nm when going from solution to solid state. For P(NDI-DMP-T) instead, the PL maximum is only red-shifted by 31 nm (from \( \lambda_{\text{max}} = 639 \) nm to 670 nm) in film compared to solution, thus indicating some remnant interstrand interaction. The discrepancy with the absorption results, which hint instead at a more significant suppression of interpolymer interactions, confirms the higher sensitivity of luminescence vs. absorption spectroscopy. Importantly however, the P(E-NDI-T) PL spectrum remains essentially identical when going from solution to the solid state, with the \( \lambda_{\text{max}} \) only red-shifted by 5 nm (from 635 nm to 640 nm). This observation confirms effective suppression of solid-state interactions and thus lower energy states in P(E-NDI-T).

Film Microstructure

Grazing incidence wide-angle X-ray scattering (GIWAXS) was performed on all three polymers to elucidate the origins of the observations from the optical spectroscopy. Figure 5 shows the two-dimensional scattering data and the corresponding radial integrals, with Table 2 containing the extracted d-spacings of the novel polymeric materials.

The GIWAXS data for the parent polymer P(NDI-2OD-T) exhibits three prominent scattering features, a Debye-Sherrer-ring at 0.26 Å\(^{-1}\), a partial ring scattering ring at 0.62 Å\(^{-1}\), and a Debye-Sherrer-ring at 1.4 Å\(^{-1}\). These features are consistent with previous reports of closely related polymers,[5,44–46] and as-such, the observed scattering features may be ascribed to typical 100 lamellar packing with a distance of 25 Å (\( Q = 0.26 \) Å\(^{-1}\)) and 010 interchain stacking with

![Figure 4. Normalized absorption and photoluminescence spectra of P(NDI-2OD-T) (top), P(NDI-DMP-T) (middle) and P(E-NDI-T) (bottom) in a 0.01 g L\(^{-1}\) chloroform solution (solid line) and \( \approx 100 \) nm thin film on spectrosil substrates, not corrected for reflectivity (dash-dot line).](image)

![Figure 5. GIWAXS scattering data of a) P(NDI-2OD-T), b) P(NDI-DMP-T), and c) P(E-NDI-T), and their respective radial integrations (below).](image)

| Table 2: Summary of the extracted d-spacings in P(NDI-2OD-T), P(NDI-DMP-T) and P(E-NDI-T). |
|---------------------------------|-----------------|---|---|---|
| \( Q_x (\text{Å}^{-1}) \)       | \( d \) (Å)     | 100 | 001 | 100 | 001 | 100 |
| P(NDI-2OD-T)                  | 0.26            | 0.62 | 1.39 | 24.169 | 10.121 | 4.51 |
| P(NDI-DMP-T)                  | 0.25            | NA   | 1.37 | 25.316 | NA   | 4.59 |
| P(E-NDI-T)                    | 0.26            | NA   | 1.33 | 24.169 | NA   | 4.72 |
Photoluminescence

To further investigate the effects of the interchromophore interactions, the PLQYs of the three different polymers in both solution and solid state were also measured. The results are summarized in Table 3. As observed, the solution PLQYs of all polymers are relatively low, with 3.6%, 4.1% and 3.2% for P(NDI-2OD-T), P(NDI-DMP-T) and P(E-NDI-T), respectively. However, surprisingly, the thin film PLQYs for both P(NDI-2OD-T) and P(NDI-DMP-T) are enhanced considerably, reaching 9.2% and 6.1%, respectively, while P(E-NDI-T) only exhibits a small increase, going from 3.2 to 3.7%. The increase in PLQY for both P(NDI-2OD-T) and P(NDI-DMP-T) can therefore be associated with aggregation-induced enhanced emission (AIEE), whereas P(E-NDI-T) mostly suppresses intermolecular interactions and hence retains its PLQY at higher concentrations (i.e., in thin films).

PL lifetimes and rate constants for radiative ($k_r$) and non-radiative ($k_{nr}$) decay provide further insight (Table 3). In line with the PLQYs, for all polymers the weighted-average PL lifetimes ($\tau_{AVG}$) are very similar in solution, yielding comparable values of $k_r$ and $k_{nr}$. Combined with the near-indistinguishable profiles of their solution PL spectra, it can be concluded that the PL properties of the isolated chains of P(NDI-2OD-T), P(NDI-DMP-T) and P(E-NDI-T) are very similar.

For all polymers, the values of the average lifetime $\tau_{AVG}$ are lower in solution than in thin films. For P(NDI-2OD-T), both solutions and thin films follow a similar bi-exponential decay, in which the fast-decaying component ($\tau_f$) dominates exciton deactivation. As seen, the PL lifetime increases from $\tau_f = 0.31$ ns (or $\tau_{AVG} = 0.43$ ns) in solution to 0.89 ns (or $\tau_{AVG} = 1.16$ ns) in film. This is manifested in a near three-fold decrease in $k_{nr}$ in films of P(NDI-2OD-T) ($k_{nr} = 7.86 \times 10^8$ s$^{-1}$) compared to the solution value ($k_{nr} = 22.47 \times 10^8$ s$^{-1}$). In contrast, $k_r$ is effectively unchanged on going to the solid state. The absence of any additional fast-decaying PL components in thin film, and the near identical values of $k_r$ for P(NDI-2OD-T) in solution and thin film suggest that J-aggregation is likely not responsible for its enhanced PL in the solid state.$^{[47,48]}$

For P(NDI-DMP-T), a similar trend is observed. However, the difference between solution and thin films is much smaller due to partial suppression of interchromophore interactions. The average lifetimes for P(NDI-DMP-T) are 0.47 ns in solution and 0.65 ns in thin film, again closely matching the difference in PLQYs (4.1% in solution vs. 6.1% in thin film). This is similarly due to a decrease in $k_{nr}$ in thin film compared to solution, albeit a smaller one than for P(NDI-2OD-T) (14.45 $\times 10^8$ s$^{-1}$ in thin film vs. 20.40 $\times 10^8$ s$^{-1}$ in solution). There is again no significant change in $k_r$. In contrast, when going from solution to thin films the PL characteristics of P(E-NDI-T) remain relatively unaffected due to the suppression of intermolecular interactions by molecular encapsulation. This translates to a $\tau_{AVG}$ of 0.44 ns in solution and 0.45 ns in thin film, which is comparable to the small difference in PLQYs (3.2% in solution versus 3.7% in thin film). Hence, $k_r$ and $k_{nr}$ are effectively unchanged.

| Sample          | $\lambda_{max,abs}$ [nm] | $\lambda_{max,em}$ [nm] | $\%$ | PL lifetimes [ns] | Average PL lifetime [ns] | $k_r^{AVG}$ [s$^{-1}$] | $k_{nr}^{AVG}$ [s$^{-1}$] |
|-----------------|---------------------------|-------------------------|------|-------------------|--------------------------|------------------------|-------------------------|
| P(NDI-2OD-T) in CHCl$_3$ | 545 | 636 | 3.6 $\pm$ 0.3 | $r_f = 0.31$ (97.0%) | $r_f = 4.26$ (3.0%) | $\tau_{AVG} = 0.429$ | 0.84 | 22.47 |
| P(NDI-DMP-T) in CHCl$_3$ | 549 | 639 | 4.1 $\pm$ 0.1 | $r_f = 0.29$ (78.2%) | $r_f = 0.61$ (19.6%) | $\tau_{AVG} = 0.470$ | 0.87 | 20.40 |
| P(E-NDI-T) in CHCl$_3$ | 546 | 635 | 3.2 $\pm$ 0.2 | $r_f = 0.27$ (22.2%) | $r_f = 0.57$ (25.4%) | $\tau_{AVG} = 0.444$ | 0.72 | 21.80 |
| P(NDI-2OD-T) film | 596 | 725 | 9.2 $\pm$ 0.3 | $r_f = 0.89$ (92.1%) | $r_f = 4.26$ (7.9%) | $\tau_{AVG} = 1.156$ | 0.80 | 7.86 |
| P(NDI-DMP-T) film | 552 | 670 | 6.1 $\pm$ 0.3 | $r_f = 0.23$ (35.5%) | $r_f = 0.61$ (61.0%) | $\tau_{AVG} = 0.65$ | 0.94 | 14.45 |
| P(E-NDI-T) film | 547 | 640 | 3.7 $\pm$ 0.2 | $r_f = 0.20$ (63.1%) | $r_f = 0.57$ (34.0%) | $\tau_{AVG} = 0.446$ | 0.83 | 21.59 |

[a] Excitation at 520 nm, [b] Fluorescence lifetimes measured at 375 nm, and percentage weights are reported between parentheses. [c] Rate constants for radiative ($k_r$, 10$^8$ s$^{-1}$) and non-radiative decay ($k_{nr}$, 10$^8$ s$^{-1}$) were calculated from the $\%$ and $r$ values according to the formulae $k_r = \%/r$ and $k_{nr} = (1-\%)/r$, where $r$ corresponds to the weighted average of the lifetimes.

Angew. Chem. Int. Ed. 2021, 60, 25009–25012 © 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH www.angewandte.org 25009
To summarize, as the interactions between polymer chains are increased in the order P(E-NDI-T) \(\rightarrow\) P(NDI-DMP-T) \(\rightarrow\) P(NDI-2OD-T) an enhancement of solid-state PL is observed due to an improved suppression of non-radiative decay pathways. The combined photophysical and crystallographic characterisation clearly shows that the substantial decrease in non-radiative decay for P(NDI-2OD-T) in thin film is a consequence of stronger intermolecular interactions between polymer chains.

**Discussion**

It is commonly assumed and observed that conjugated polymers undergo substantial photoluminescence quenching on going from solution to the solid state. Our combined morphological and photophysical results show the surprising result that i) the extremely well-known polymer P(NDI-2OD-T) undergoes strong aggregation induced enhanced emission and ii) this phenomenon originates from the interchain packing. We (and others) have previously shown that molecular encapsulation allows a polymer to retain, to some extent, solution properties when in the solid state.[13,14] In this work, we find the same concept applies to P(E-NDI-T) as both the absorption and emission shapes, yields and lifetimes are almost identical. However, in contrast to almost all other reported conjugated polymers, the emissivity of the non-encapsulated derivative increases in the solid state (as opposed to decreasing), resulting in a relatively high emission PLQY for this wavelength region. The phenomenon of aggregation induced enhanced emission is well known and has been reported in numerous conjugated polymer systems, including those containing naphthalene diimide units.[49] Crucially however, in virtually every example of conjugated polymers AIEE-specific groups (such as vinylenes or TPEs), that are well known to imbue AIEE-like properties, are introduced for this reason.[50–55] There are almost no examples of a “conventional” conjugated polymer undergoing aggregation induced enhanced emission. Moreover, it is remarkable that it has not been previously observed in P(NDI-2OD-T), which have been extensively studied. In fact, we can find only one other example of AIEE in a conventional (i.e., without the inclusion of AIEE-specific groups) conjugated polymer, where emission efficiency was enhanced through the formation of close contacts between adjacent polymer chains.[56]

To determine the origin of the observed AIEE in this system it is useful to consider all the possible mechanisms through which it could be occurring. NDI-based small molecules have previously been shown to undergo enhanced emission in the solid state predominantly through J-aggregation.[57–61] However, the \(\pi\)-stacking distance as measured by GIWAXS for P(NDI-2OD-T) is \(\approx 4.5\) Å, which is considerably longer than those reported for small molecule NDIs displaying J-aggregates \(<4.5\) Å. We also do not observe a sharpening of the absorption spectrum or an enhancement in \(k_s\) in the solid state, which are common spectroscopic signatures of J-aggregation. Furthermore, the red-shifted emission of NDI-T based polymers has been demonstrated to originate from the crystallization induced planarization of the conjugated backbone rather than J-aggregates.[62] We observe a stepwise reduction in AIEE when going from P(NDI-2OD-T) to P(NDI-DMP-T) and P(E-NDI-T) films, which correlates extremely well with the increased 010 distances interlayer separation. Thus, the crystallization of the \(\pi\)-conjugated faces of the polymer results not only in a planarization, but also in the suppression of non-radiative decay pathways, and thereby a substantially increased photoluminescence efficiency. We believe that this is the first observation of this effect in a non-vinylene containing conjugated polymer and suggest that it could provide a novel design strategy for obtaining good emissive efficiency in narrow band gap conjugated polymers—a major hurdle that must be overcome to increase the efficiency of OPV devices.[10] Finally, we note that P(NDI-2OD-T) and related polymers are the most successful conjugated polymers used in all-polymer solar cells[63] and this previously unreported AIEE may provide a clue as to why they have performed so well.

**Conclusion**

This article reports the synthesis of molecularly encapsulated, naphthalene diimide based conjugated polymers through the development of new synthetic pathways. The encapsulated polymer allows us to determine the exact effect of interpolymer interactions on the optical properties of the conjugated polymer. Surprisingly, in the solid state, the encapsulated polymer has a higher energy, but lower photoluminescence quantum yield compared to the naked reference polymer, which is in contrast to the current conventional wisdom and a violation of the energy gap “law”.[64,65] Instead, this work reveals a previously unrecognized aggregation induced enhanced emission phenomena in one of the most well studied conjugated polymers P(NDI-2OD-T). Structural characterization confirms that this AIEE is due to the crystallization of the \(\pi\)-conjugated faces of the polymer chains. Therefore, we believe that understanding and having control over the crystallization and solid-state behavior of conjugated polymers may be key to enhance their emissive properties. Our results conclusively demonstrate that solid state photoluminescence in conjugated polymers can actually be enhanced through closer packing (which is often beneficial for charge transport) suggesting that high PLQY and high charge carrier mobility may not be as mutually exclusive as is commonly believed.

**Acknowledgement**

We gratefully acknowledge funding by EPRSC (Grants EP/P007767/1, EP/S003126/1, and EP/P006280/1), Qatar National Research Grant NPRP 12S0304-190227, U.S. Office of Naval Research Contract N00014-20-2116, the Royal Society (Newton International Fellowship to K.G.), and the Winton Programme for the Physics of Sustainability. This work was
carried out with the support of Diamond Light Source, instrument I07 (proposal SI23587-1).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** conjugated polymers · encapsulation · macrocycles · organic electronics · photoluminescence
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Manuscript received: July 29, 2021
Revised manuscript received: August 31, 2021
Accepted manuscript online: September 14, 2021
Version of record online: October 18, 2021