



Cite this: *Polym. Chem.*, 2021, **12**, 1830

Suppressing aggregation induced quenching in anthracene based conjugated polymers†

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Anthracene is a highly valuable building block for luminescent conjugated polymers, particularly when a large singlet–triplet energy gap (ΔE_{ST}) is desired. Unfortunately, the extended π system of anthracene imparts a strong tendency for polymer aggregation, resulting in detrimental effects on its solid state photophysics. A large decrease in photoluminescence quantum yield (PLQY, Φ_F) on going from solution to the solid state is especially common, represented in terms of a low Φ_R ($\Phi_R = \Phi_{F \text{ film}}/\Phi_{F \text{ sol.}}$). Significant and undesirable red-shifting of fluorescence in the solid state is also typical due to processes such as excimer formation. In this work a series of alkylene-encapsulated conjugated anthracene polymers is developed to overcome these challenging problems. We demonstrate a promising material which displays a good solid state PLQY that is effectively unchanged compared to solution measurements ($\Phi_R \sim 1$, $\Phi_{F \text{ film}} \sim 40\%$), alongside an identical PL 0–0 transition wavelength in solution and thin film. Such a direct transfer of luminescence properties from solution to the solid state is remarkable for a conjugated polymer and completely unprecedented for one based on anthracene.

Received 27th January 2021,
Accepted 16th February 2021

DOI: 10.1039/d1py00118c

rsc.li/polymers

Introduction

9,10-Disubstituted anthracene derivatives such as 9,10-diphenylanthracene (DPA) and 9,10-bis(phenylethynyl)anthracene (BPEA) are archetypal fluorophores. Diluted into solid hosts or solution they display photoluminescence quantum yields (PLQY, Φ_F) close to unity¹ alongside narrow Stokes shifts. They also feature large exchange energies (ΔE_{ST}). As a result, anthracenes are ubiquitous in many applications such as organic light emitting diodes (OLEDs),² organic photovoltaics (OPVs),³ chemiluminescence,⁴ triplet–triplet annihilation upconversion (TTAUC),^{5,6} singlet fission downconversion (SFDC)^{1,6} and electrochromics.⁷ Merging the advantageous photophysical properties of anthracenes with the processability of conjugated polymers should lead to highly desirable materials, and numerous works have sought to achieve this.^{8–20} Notably, the polymerization of small amounts of anthracene *via* the 9,10-positions into polyfluorenes has been shown to greatly

enhance the color stability of OLEDs due to energy transfer.^{8,9,13,14} Regioregular copolymers based on 9,10-diarylanthracenes polymerized *via* the 2,6-positions have also been reported.^{16,21–23} Additionally, some non-conjugated polymers incorporating anthracene have been investigated.^{24–26}

Despite these efforts it has been very challenging to synthesize functional conjugated anthracene polymers.^{11,12,16–18,20} This is related to the planar extended π system of anthracene, which imparts a strong tendency for aggregation. This causes the photophysical performance of anthracene-based materials to vary greatly between dispersed (*e.g.* solution) and condensed states. A common phenomenon is aggregation induced quenching (AIQ)¹⁵ in the solid state, which typically leads to a very low ratio (Φ_R) between thin film and solution PLQYs ($\Phi_R = \Phi_{F \text{ film}}/\Phi_{F \text{ sol.}}$). This is a challenging problem for polymeric and small molecule anthracene derivatives alike.^{23,27–30} For example, the near-unity solution PLQY of DPA is drastically quenched in thin films, affording $\Phi_R \sim 0.3$.³⁰ Even the polymeric examples reported by Chen *et al.*,²³ which consist of highly twisted and bulky DPA-based structures and display some of the highest reported thin film PLQYs for conjugated anthracene polymers, typically lose over half of their photoluminescence (PL) intensity in the solid state ($\Phi_R < 0.4$). Anthracene derivatives are also classic examples of molecules that undergo excimer formation in the solid state, which leads to diminished and red-shifted PL.^{17,30} A further possible PL quenching process is photodimerisation.³¹ The exact extent of

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†Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic data and additional photophysical data. CCDC 2024118. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1py00118c



each PL quenching pathway is evidently difficult to predict. Therefore, a synthetic tool to control and/or suppress aggregation in anthracene based conjugated polymers is highly desirable and would allow a previously unattainable class of materials to be accessed.

In this work we develop the synthetic chemistry required to obtain alkylene-encapsulated DPA polymers. As a result, it is possible to realize a blue emitting anthracene based conjugated polymer for which PL quenching in the solid state is essentially absent ($\Phi_R \sim 1$).

Results and discussion

Design and synthesis

Work from our group and others has shown that covalent alkylene encapsulation can increase molecular rigidity and suppress AIQ to afford highly luminescent materials that retain much of their desirable solution photophysics in the solid state.^{32–36} Kobayashi and coworkers have also proven the viability of such a tactic for preserving the photophysical performance of DPA in powder and pristine films.³⁷ However, covalent encapsulation has never been implemented in anthracene based polymers despite its clear potential to improve their photophysical performance. To achieve this new synthetic chemistry must be developed (Fig. 1).

We chose to target polymerization from the phenyl groups of encapsulated DPA as it should afford a twisted backbone, which is expected to help suppress AIQ (Fig. 1).²³ The classic synthesis of DPA derivatives involves the treatment of an anthraquinone with two equivalents of an aryl lithium or Grignard reagent to generate a bis-tertiary alcohol, which is then aromatized with SnCl_2 or NaH_2PO_2 .^{38–41} We elected to follow this methodology starting from the anthraquinone derivative **1** (Scheme 1), which was functionalized with four dodecyl chains to ensure the high solubility of the resulting polymers (Scheme S1†). The iodoaryl **Ar (a)** (Scheme 1a) was selected as a rational synthetic intermediate because the iodide is expected to undergo chemoselective Grignard for-

mation.⁴² This would allow the installation of aryl groups at the 9,10-positions of anthracene with methoxy protecting groups for encapsulation installed alongside Ar–Br functionality for polymerization. However, upon treatment of **1** at room temperature with an excess of Grignard reagent, formed through transmetalation of **Ar (a)** with iPr-MgCl ,⁴³ the expected bis-tertiary alcohol **2a** was not obtained. Instead, the product of single nucleophilic attack (**2b**) was identified by $^1\text{H NMR}$ as the predominant product alongside deiodinated **Ar (a)** (spectrum S19). A large excess of Grignard reagent (>10 eq.) and prolonged refluxing in THF failed to promote double addition to form **2a**. Attempts to improve the nucleophilicity of the organometallic through transmetalation with ‘Turbo Grignard’ (iPr-MgCl-LiCl)⁴⁴ or $n\text{-BuLi}$ rather than iPr-MgCl and addition of TMEDA were also unsuccessful, as was the addition of $\text{LaCl}_3\text{-LiCl}$ ⁴⁵ to improve carbonyl electrophilicity.

The reaction sequence was also attempted with the iodoaryl **Ar (b)** (Scheme 1a), which incorporates formally electron withdrawing methoxymethyl groups in contrast to the formally electron donating methoxy groups of **Ar (a)**. Unfortunately, the mono addition product was again solely observed by $^1\text{H NMR}$ after reaction with anthraquinone. Acidification of the crude reaction mixture and treatment with $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ also led to no appreciable blue fluorescence, which could indicate the formation of a DPA derivative. It is noted that double addition has been reported upon treatment of anthraquinone with the aryl lithium reagents generated from both 4-bromo-2,6-dimethyliodobenzene⁴⁶ and 1,3-dimethoxybenzene (**Ar (c)**).³⁷ We also observed that *ortho*-lithiated 1,3,5-trimethoxy benzene undergoes successful double addition to anthraquinone in *ca.* 80% isolated yield (Scheme S5†). Therefore, it appears that the specific combination of the ether and bromo functionalities suppresses the double addition of the organometallics of **Ar (a)** and **Ar (b)** to anthraquinones. We tentatively suggest that the additive chelating⁴⁷ and electron withdrawing⁴⁸ effects of the ether and Ar–Br functionalities, respectively, could be involved through stabilizing the organometallics and reducing nucleophilicity.

After failing to obtain a pre-functionalised polymerisable monomer, we targeted the substituted DPA **3** (Scheme 1b). It was successfully obtained in 77% overall yield upon treatment of **1** with *ortho*-lithiated **Ar (c)**, followed by aromatization of the intermediate **2c** with $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$. With DPA **3** in hand, we sought a route to install further functionality for polymerization (Scheme 1c). **3** was firstly converted into the encapsulated derivative **5** after quantitative demethylation to **4** followed by alkylation with 1,7-dibromoheptane. As the phenyl 4-positions of **5** are by far the least sterically encumbered sites on the molecule, we envisaged that they should be prone to functionalization *via* Ir-catalyzed C–H borylation, the regioselectivity of which is driven predominantly by sterics.⁴⁹ Indeed, treatment of **5** with $[\text{Ir}(\text{OMe})(\text{COD})]_2$, bis(pinacolato) diboron and 3,4,7,8-tetramethyl-1,10-phenanthroline⁵⁰ regioselectively afforded the bis(pinacol) ester **6**, the structure of which was proven unambiguously by single crystal X-ray diffr-

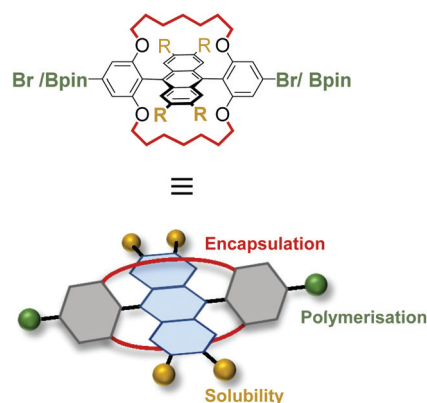
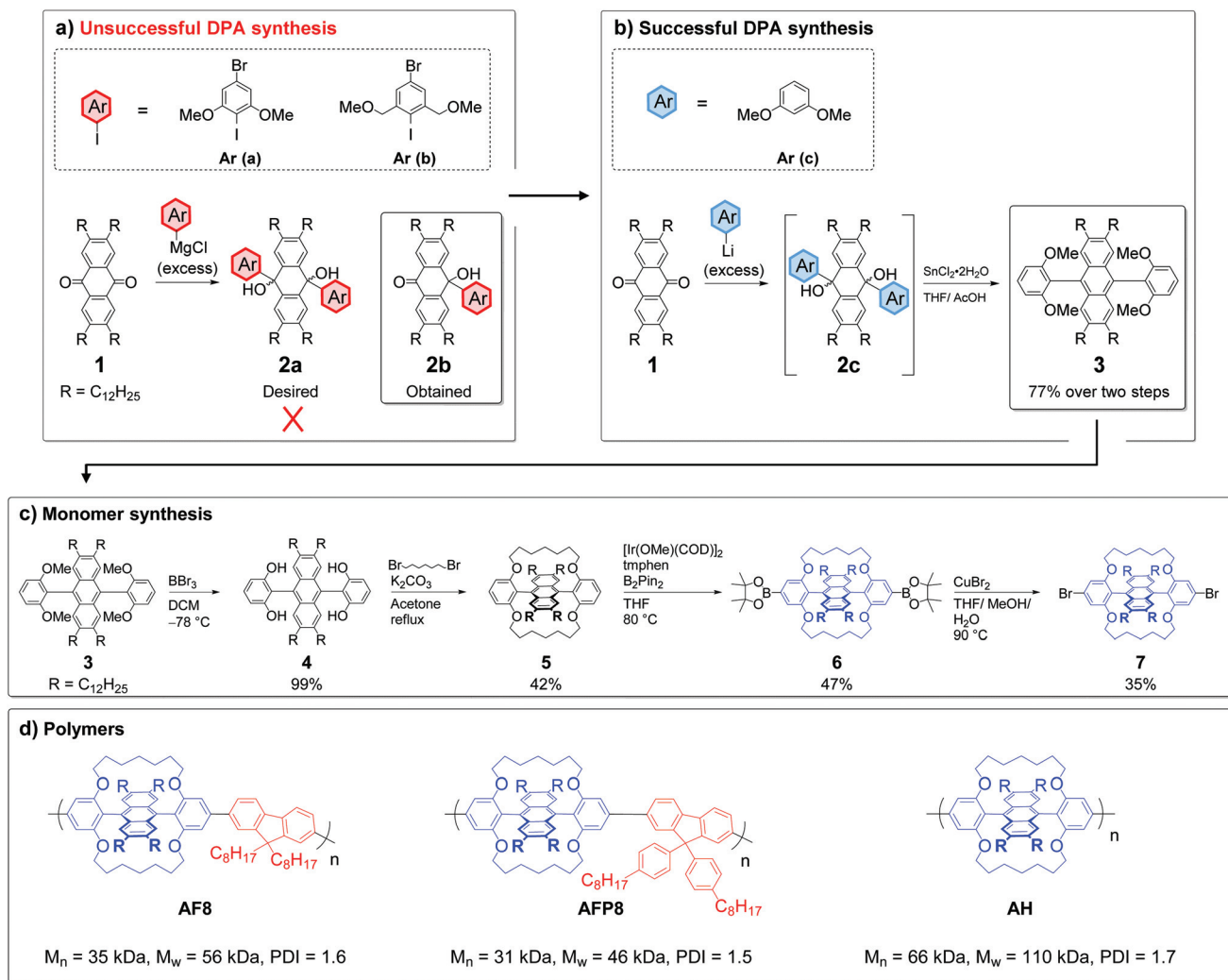


Fig. 1 Targeted monomer structural features.





Scheme 1 Synthesis of polymer precursors and polymer structures.

action (Fig. 2).[‡] Although essentially complete conversion of 5 to 6 was observed by ¹H NMR, the requirement to purify 6 by flash chromatography to obtain analytically pure material restricted the isolated yield to *ca.* 50% in our hands. Subsequent treatment of 6 with CuBr₂ in mixed solvent conditions fortunately allowed the dibromo monomer 7 to be accessed in 35% yield, despite the fact that 6 is insoluble in highly polar solvents such as MeOH.^{49,51,52} It is therefore possible to obtain encapsulated DPAs functionalized with either bromide or boronic ester groups for polymerization *via* the methodology outlined here. The encapsulated DPA 5 can be synthesized in 10 g quantities under typical laboratory conditions, highlighting the promise of obtaining the polymer

precursors 6 and 7 on scale. The obligatory high purity of 6 and 7 was confirmed by ¹H NMR and elemental analysis.

Regioregular copolymers were next synthesized through the Suzuki polycondensation of 6 with either 2,7-dibromo-9,9-(diocetylfluorene) or its arylated analogue, to obtain **AF8** and **AFP8**, respectively (Scheme 1d). They were obtained in respectable number average molecular weights and polydispersity by extraction in a Soxhlet apparatus with chloroform, after washing with acetone and *n*-hexane to remove oligomeric materials (**AF8** *M_n* = 35 kDa, PDI = 1.6, **AFP8** *M_n* = 31 kDa, PDI = 1.5). **AFP8** was investigated because 9,9-diarylfluorenes are bulkier (to suppress AIQ) and also are more stable under OLED operation than their 9,9-dialkyl analogues,⁵³ increasing the relevance of this system to optoelectronics. The homopolymer **AH** was next prepared in good molecular weight and polydispersity from 7 under microwave-assisted Yamamoto polymerization conditions followed by the same Soxhlet procedure (**AH** *M_n* = 66 kDa, PDI = 1.7) (Scheme 1d). **AF8** and **AFP8** were obtained as light yellow flakes while the higher

[‡] Crystal data. C₁₀₀H₁₆₀B₂O₈, *M* = 1511.89, monoclinic, *a* = 19.2620(7), *b* = 12.5345(5), *c* = 21.0985(8) Å, β = 110.846(2)°, *U* = 4760.6(3) Å³, *T* = 180 K, space group *P*2₁/*c* (no. 14), *Z* = 2, 37 058 reflections measured, 4996 unique (*R_{int}* = 0.089), which were used in all calculations. The final *R*1 was 0.098 (3116 data with *I* > 2σ(*I*)) and *wR*(*F*²) was 0.303 (all data).



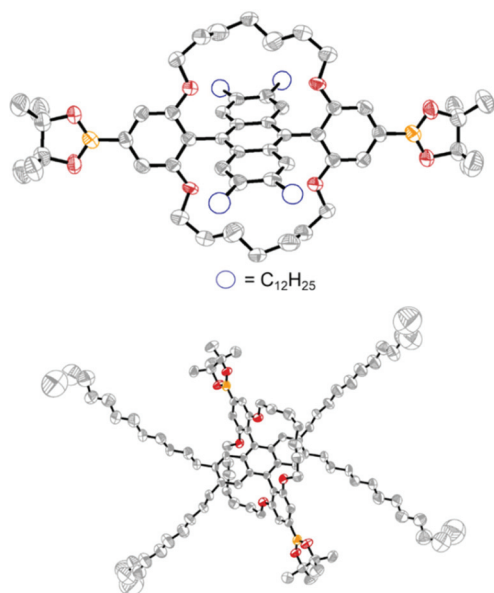


Fig. 2 X-ray crystal structure of **6**, hydrogen atoms are omitted for clarity. The molecule is situated on a crystallographic inversion centre.

molecular weight **AH** was obtained as light yellow fibres. All polymers are well soluble in common aromatic and chlorinated solvents (*e.g.* toluene, CHCl_3 and chlorobenzene).

Photophysical properties

The photophysical properties of the polymers were evaluated in toluene and 1,2-dichlorobenzene solutions and films prepared by spin coating from toluene. Absorption and emission spectra and shown in Fig. 3 and photophysical data are summarized in Table 1. In solution all polymers feature vibronically resolved absorption bands between *ca.* 370–415 nm, which are assigned to absorption by DPA. An additional band is observed for **AF8** and **AFP8** at 340 nm, ascribed to absorp-

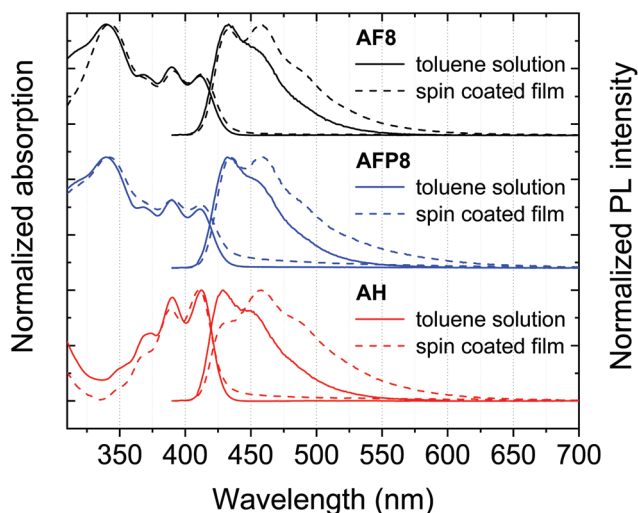


Fig. 3 Absorption and PL spectra of the polymers.

Table 1 Photoluminescence data for the polymers

Polymer	State	λ_{max} PL/nm	$\Phi_{\text{F}}^a/\%$	Φ_{R}	τ^b/ns
AF8	Solution	432	41 ± 2	~ 1	2.94
	Film	(432) 457	42 ± 2		2.28
AFP8	Solution	432	45 ± 2	0.73	2.90
	Film	(435) 459	33 ± 2		1.62
AH	Solution	429	87 ± 4	0.25	3.80
	Film	(431) 458	22 ± 1		1.52

^a Absolute PLQY measured using an integrating sphere, estimated errors correspond to a relative error of $\pm 5\%$ which is equal or larger to the observed standard error for measurements on three different films. ^b For thin films this value is the amplitude weighted average of a bi-exponential fit, full data are provided in the ESI (Fig. S1–3, Table S1†). Solution λ_{max} PL data were recorded in toluene. Solution Φ_{F} and τ values were recorded in 1,2-dichlorobenzene (DCB). The PLQY of **AF8** was equal within experimental error in toluene and DCB.

tion by their fluorene comonomers. Absorption for all polymers is clearly red-shifted compared to that of DPA (Abs 0–0 *ca.* 394 nm),³⁷ indicating that there is electronic communication between monomer units in the ground state. The position of the bands and the steepness of the absorption onsets are well retained in spin coated films for all polymers, indicating that their ground state photophysical properties are effectively unchanged in the solid state.

In solution **AF8** emits in the blue with a respectable PLQY of $41 \pm 2\%$ and a fluorescence lifetime (τ) of 2.94 ns. The solution PL of **AF8** (PL 0–0 = 432 nm) is red-shifted compared to that of DPA (PL 0–0 *ca.* 410 nm),³⁷ indicating that there is also electronic communication between monomer units in the excited state. Strikingly, on going from solution to thin film there is no red-shift in the PL 0–0 transition (432 nm) for **AF8** and the gradient of the PL onset is practically unchanged. Within experimental error, the solution PLQY of **AF8** is also completely maintained in thin film, affording an exceptional $\Phi_{\text{R}} \sim 1$. Such minimal PL quenching is in agreement with a decrease in τ of only 22% in thin film. Clearly, the detrimental effects of aggregation are essentially absent for **AF8** in the solid state. Such a direct transfer of luminescence properties from solution to the solid state is remarkable for a conjugated polymer^{54–57} and, to the best of our knowledge, completely unprecedented for one based on anthracene (Table S3†). We note a slight extension of the PL tail to longer wavelengths in thin film, which we ascribe to interchain energy transfer to lower energy trap sites in the solid state. Such a process does not constitute an additional quenching pathway compared to solution as $\Phi_{\text{R}} \sim 1$ for **AF8**.

The addition of bulkier aryl rings to the fluorene copolymer **AFP8** has a negligible effect on its solution PL properties compared to **AF8**, as expected.⁵³ However, in thin film the red tail of the PL spectrum is more greatly extended for **AFP8** than **AF8**, and the 0–0 transition of **AFP8** is red-shifted by 3 nm compared to solution. The PLQY of **AFP8** is also reduced in thin film ($33 \pm 2\%$ vs. $45 \pm 2\%$ in solution), accompanied by a 45% decrease in τ and affording $\Phi_{\text{R}} = 0.73$. While the Φ_{R} value of 0.73 for **AFP8** is very high and the best reported for a conju-



gated anthracene polymer before this work,²³ increased AIQ in **AFP8** compared to **AF8** is a surprising result, contrasting with what has been reported for polyfluorenes.⁵³ The extra bulk incorporated into **AFP8** compared to **AF8** is in the form of phenylene groups, which may provide additional π surfaces to participate in aggregation, while also introducing spiro conjugation.⁵⁸ We suggest that these factors could contribute to AIQ in the thin films of **AFP8**.

In solution the fully encapsulated polymer **AH** exhibits a high PLQY of $87 \pm 4\%$. This is consistent with its longer τ (3.80 ns) compared to the copolymers **AF8** and **AFP8**. However, in thin film the PL broadens and the PLQY is quenched significantly to $22 \pm 1\%$, corroborated by a large decrease of 60% in the τ and affording $\Phi_R = 0.25$. Significant AIQ for **AH** is an unexpected result and indicates that complete alkylene encapsulation of a conjugated polymer is not necessarily sufficient to suppress PL quenching in the solid state. In fact, **AF8**, for which AIQ is absent in the solid state, clearly incorporates a lower degree of encapsulation than **AH**. To then add a further level of complexity, the addition of sterically bulky phenylene groups in **AFP8** actually promotes AIQ compared to **AF8**, indicating that two structural features that should benefit solid state emission, encapsulation and steric bulk, are not necessarily additive. These surprising structure–property relationships raise interesting research questions that warrant further investigation in future work.

While the ability of **AF8** to retain its solution-state PL properties in thin film is highly attractive and a great advantage of our molecular design, there is room for improvement in PLQY. To determine the cause of the modest solution PLQY of **AF8** ($41 \pm 2\%$) the rates of radiative (k_r) and non-radiative (k_{nr}) decay were calculated and compared to that of **AH**, which displays a significantly higher solution PLQY. While both polymers exhibit similar values of k_r (**AF8** = $1.4 \times 10^8 \text{ s}^{-1}$, **AH** = $2.3 \times 10^8 \text{ s}^{-1}$), the rate of non-radiative decay for **AF8** is an order of magnitude larger ($2.0 \times 10^8 \text{ s}^{-1}$ vs. $3.4 \times 10^7 \text{ s}^{-1}$ for **AH**). Therefore, while copolymerization with 9,9-dioctyl(fluorene) is clearly beneficial for suppressing aggregation in the solid state, it also introduces new pathways for non-radiative decay that lower the intrinsic PLQY of **AF8**.

Conclusions

Prior to this study aggregation has heavily restricted the development of conjugated anthracene polymers, impeding their solid state photophysics by facilitating aggregation induced quenching (AIQ) and the formation of excimers. Here, new synthetic chemistry was developed to access alkylene-encapsulated DPA polymers. This provided the structural control to develop **AF8** as an anthracene polymer that eliminates AIQ and excimer formation in the solid state, displaying $\Phi_R \sim 1$ ($\Phi_R = \Phi_{F \text{ film}}/\Phi_{F \text{ sol.}}$) alongside an identical photoluminescence 0–0 transition wavelength in solution and thin film. Such a direct transfer of luminescence properties from solution to the solid state is remarkable for a conjugated polymer and, to the best

of our knowledge, completely unprecedented for one based on anthracene.

However, our results for the polymers **AFP8** and **AH** reveal that the structure–property-relationships in encapsulated polymers can be surprisingly convoluted – enhancing steric bulk and increasing the extent of encapsulation are by no means tactics guaranteed to achieve improved solid state photophysical performance. Future work should concentrate on improving our understanding of the structure–property relationships between alkylene encapsulation and the PLQYs of conjugated polymers (in both solution and thin film). This could lead to polymers with unity quantum efficiency in the solid state. An anthracene-based example would have particular promise for solid-state triplet–triplet annihilation upconversion⁵ and direct triplet injection polymer OLEDs.⁵⁹

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Andrew Danos (Durham University, UK) is acknowledged for help with the solid state PLQY measurements and helpful discussion. Aileen Congreve is acknowledged for allowing use of an integrating sphere at Durham University, UK. VG acknowledges funding from the Swedish Research Council, Vetenskapsrådet 2018-00238. This work was supported by the Engineering and Physical Sciences Research Council (grant no. EP/M005143/1) and the European Research Council (ERC). B. H. D. acknowledges support from the EPSRC Cambridge NanoDTC (grant no. EP/L015978/1).

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