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Synthesis of fluorescent polycarbonates with highly twisted *N*,*N*-bis(dialkylamino)anthracene AIE luminogens in the main chain†

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A synthetic route to embed aggregation-induced-emission-(AIE)-active luminophores in polycarbonates (PCs) in various ratios is reported. The AIE-active monomer is based on the structure of 9,10-bis(piperidyl)anthracene. The obtained PCs display good film-forming properties, similar to those observed in poly(bisphenol A carbonate) (Ba-PC). The fluorescence quantum yield (Φ) of the PC with 5 mol% AIE-active monomer was 0.04 in solution and 0.53 in solid state. Moreover, this PC is also miscible with commercially available Ba-PC at any blending ratio. A combined analysis by scanning electron microscopy and differential scanning calorimetry did not indicate any clear phase separation. These results thus suggest that even engineering plastics like polycarbonates can be functionalized with AIE luminogens without adverse effects on their physical properties.

Introduction

The production of polymeric organic light-emitting diodes (OLEDs) requires luminophores whose luminescence efficiency does not decrease due to concentration quenching.[1] In recent years, the aggregation-induced emission (AIE) phenomenon has received substantial attention on account of its potential applications in OLEDs.[2,3] AIE describes a phenomenon in which organic chromophores exhibit efficient luminescence in aggregated states or under conditions where molecular motions are restricted, while their luminescence is suppressed in dilute solutions.[4] This phenomenon is thus the opposite of aggregation-caused quenching (ACQ), which is encountered in most organic chromophores. The most outstanding advantage of AIE luminogens (AIEgens) is their bright solid-state luminescence. This feature arises from the weak excitonic interactions between these chromophores even in the solid state.[5]

Over the last two decades, AIEgens have been extensively investigated in the context of materials[6] and analytical[7] science. However, the structural diversity of typical AIEgens is limited. These molecules are usually sterically demanding and contain multiple rotating axes.[8] When such AIEgens are employed to fabricate polymeric thin films, their physical properties, such as the glass transition temperature (T_g) and the toughness are usually affected negatively. Structurally simple AIEgens are therefore desirable in order to apply AIEgens in *e.g.* OLEDs and luminescent polymers. Moreover, structural simplicity would make AIEgens (i) easy to synthesize and (ii) susceptible to further modifications.[6a]

In a previous report, we have discovered *N*,*N*-dialkylaminoarenes as a new class of unique AIEgens,[8–10] which do not depend on axis rotation to display the AIE phenomenon. These structurally simple dyes are easier to synthesize than the aforementioned bulky AIEgens and display superior fluorescence in the solid state. Moreover, they exhibit the same color in solution and in the solid state. Our mechanistic study of these unusual AIEgens opened up a new design avenue for structurally simple AIEgens, which has been corroborated by theoretical calculations.[9] Our design strategy consists of introducing strong electron donors to polycyclic aromatic hydrocarbons (PAHs) so that a S_1/S_0 crossing (or minimum energy conical intersection (MECI)) with large amplitude modes becomes readily accessible in dilute states. This large motion is suppressed in the solid state, which leads to pronounced AIE phenomena.

By modifying these AIE dyes into bifunctional monomers, application of these AIE dyes as building blocks in polymer science becomes possible. As reported in our previous report,

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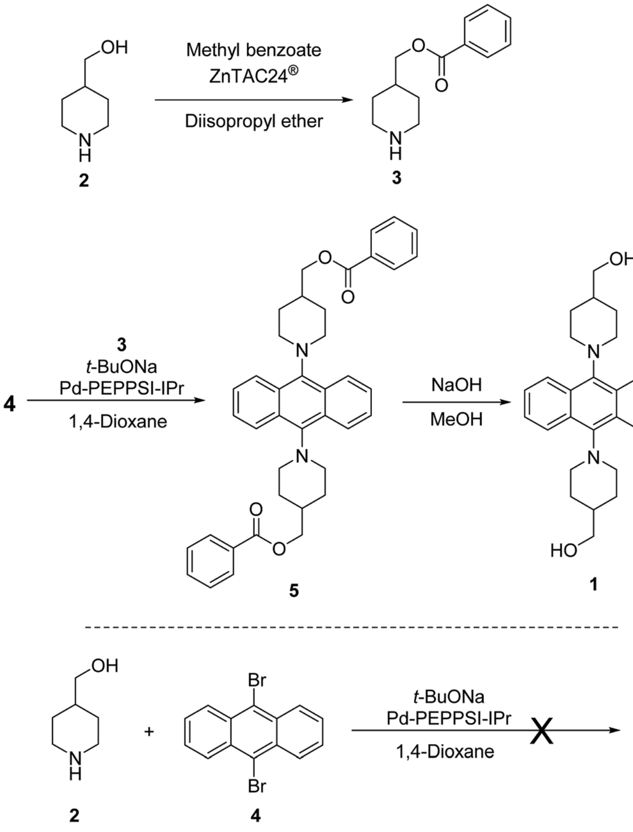
we have already synthesized AIE-active diamine monomers and AIE-active polyamides.[11] However, the application of AIEgens in OLEDs requires the introduction of these dyes in transparent optical materials such as polymethylmethacrylates (PMMAs) and polycarbonates (PCs),[12] which has not yet been accomplished. Incorporation of the AIEgen in the polymer chain has many advantages compared to making doped polymers with the AIEgen, such as the synthesized polymer not being affected much by factors such as physical ageing of the polymer, *etc.*

In this study, we synthesized a new type of fluorescent PCs that contain *N*,*N*-dialkylaminoarene chromophores as AIEgens in the main chain. The AIEgen was synthesized from an anthracene derivative and a piperidine derivative with a hydroxyl group. The bifunctional diol monomers were synthesized by a selective transesterification process to protect the hydroxyl group using the Ohshima–Mashima zinc cluster catalyst (ZnTAC24®),[13] followed by a C–N cross-coupling reaction[14,15] and a simple deprotection step. Using this bifunctional diol monomer, PCs with varying AIE-active monomer ratios were synthesized. The PCs were then cast into thin films in order to determine the transparency of these films. The miscibility of these PCs were determined by mixing them with commercially available poly(bisphenol A carbonate) Ba-PC. The optical properties of the PCs were then studied.



Scheme 1 Synthesis of AIE-active monomer 9,10-bis(4-hydroxymethylpiperidyl)anthracene (**1**).

Results and discussion

Monomer synthesis

Synthesis of 9,10-bis(4-hydroxymethyl)piperidylanthracene (**1**) was done by introducing a reactive group into the previously reported AIEgens based on 9,10-bis(piperidyl)anthracene (**BPA**).[8] Diol monomer **1** was synthesized according to Scheme 1. Initially, we attempted a direct synthesis using 9,10-dibromoanthracene **4** and 4-piperidinemethanol (**2**) with Pd-PEPPSI-IPr[14] as a catalyst. This reaction was not successful, most likely due to the interference of the hydroxyl group with the C–N coupling reaction. One plausible explanation for this failure is that the hydroxyl group might coordinate to the palladium atom, which could stop the catalytic cycle. Therefore, the reaction scheme was altered to include the protection of the hydroxyl group and a final deprotection step. In this case, ZnTAC24®[13] was used, given that it efficiently catalyzes the selective *O*-acylation. This is due to the fact that the chemoselective *O*-acylation using zinc clusters can be carried out under mild conditions, similar to enzymes, which allows the preservation of sensitive functional groups. Therefore, we used ZnTAC24® as a catalyst to selectively protect the hydroxyl group of 4-piperidinemethanol (**2**) to afford **3** in 43% yield through a transesterification process with methyl benzoate (Scheme 1). For the C–N cross-coupling reaction, we used Pd-(PEPPSI-IPr)[14] or Pd(BINAP)[15] as the catalyst, considering that Pd catalysts with N-heterocyclic carbene ligands are known for their high tolerance towards sterically congested systems.[9] Ultimately, Pd-PEPPSI-IPr afforded better results compared to Pd-BINAP.[§,16] The final step, *i.e.*, a deprotection with sodium hydroxide, afforded **1** as a yellow solid in 41% yield.

Monomer **1** was characterized by ^{1}H and ^{13}C NMR spectroscopy as well as FT-IR spectroscopy and high-resolution mass spectrometry (HRMS) (Fig. S2–S4†). Usually, anthracene rings with identical moieties at the *para*-position of the central aromatic ring, such as 9,10-bis(*N*,*N*-dimethylamino)anthracene, are expected to produce NMR spectra that exhibit doublets of doublets in the aromatic region. However, the aromatic region of the ^{1}H NMR spectrum of **1** shows three types of peaks. Moreover, the ^{13}C NMR spectrum shows more peaks in the aromatic region than what should be expected of **1**. Variable-temperature (VT) ^{1}H and ^{13}C NMR experiments revealed that indicates that **1** has more than one isomer at room temperature. (Fig. S14†) In particular, measurement of ^{13}C NMR (DMSO-d_6) at 20.5 shows at least 14 peaks in aromatic region (carbon of anthracene ring). On the other hand, that of 140 °C shows 4 peaks (carbons a–d: minimum number of anthracene ring) in the aromatic region, as shown in Fig. 1. Some possible isomers of **1** include an isomer in which both hydroxyl groups are facing the same direction, and an isomer in which the hydroxyl groups are facing opposite directions. In order to unequivocally determine the precise structure of **1**, a single-crystal X-ray diffraction analysis would be required; however, this is beyond the scope of this study. The FT-IR spectrum indicates the presence of a hydroxyl group, and the observed *m*/*z* value matches the calculated *m*/*z* value measured by HRMS.

[§] The choice of the catalyst depends on the substrate. The Buchwald–Hartwig C–N coupling reaction may proceed even with the presence of hydroxyl groups by choosing a different ligand and base. However, in this study, we followed the synthetic condition that was successful in our previous studies.

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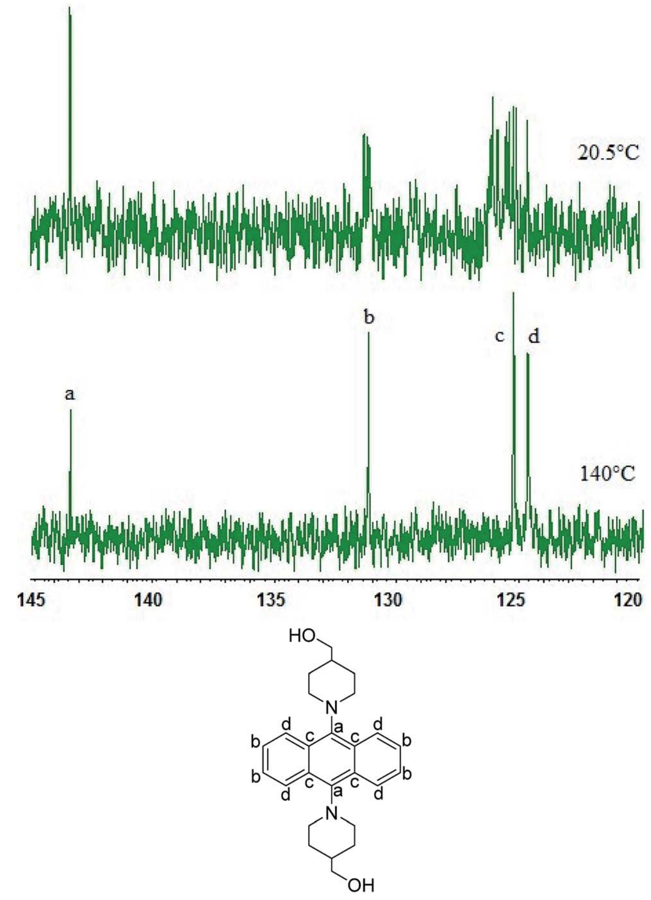
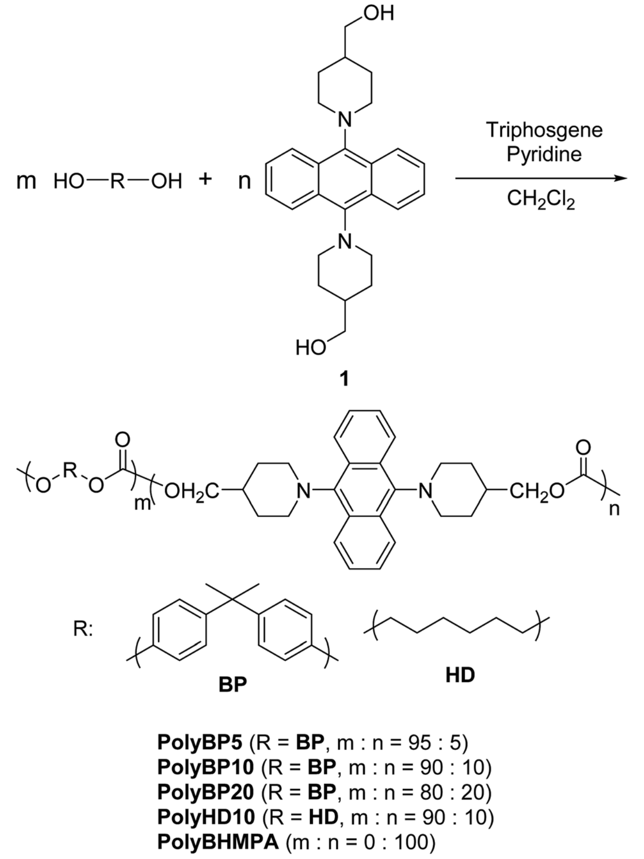


Fig. 1 Magnified view of the aromatic region of the ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of **1** at 20.5 °C (top) and 140 °C (bottom).



Scheme 2 Synthesis of PCs with varying AIEgen ratios.

Polymer synthesis

To capitalize on the excellent transparency, strength, and film-forming properties of Ba-PC, a novel design of copolymers with low AIEgen content is required. Numerous polymers have been synthesized through condensation polymerization with luminescent units in the polymer chain, which contain small doses of dyes.[17] In this study, we decided to use various ratios of AIEgens in the copolymerization of triphosgene and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) as shown in Scheme 2. For comparison, PCs containing only the AIEgen or utilizing 1,6-hexanediol were also synthesized.

The synthesis of all PCs was carried out at low temperatures in solution. The concentration of the diol monomers in dry pyridine was set to 1.0 mol L^{-1}. Triphosgene was dissolved in dichloromethane at a concentration of 0.40 mol L^{-1}, and added dropwise to the monomer solution at 0 °C. The reaction mixture was then allowed to stir for 30 minutes at 0 °C, and then for another 30 minutes at room temperature. Subsequently, dichloromethane was added to dissolve the precipitate formed during the reaction. The reaction mixture was then added dropwise to methanol at 0 °C in order to induce reprecipitation. The precipitate was filtered and dried *in vacuo*. Furthermore, in some cases, the amount of dry pyridine was increased due to the low solubility of **1**. The obtained copolymers were well soluble in good solvents for Ba-PC, *e.g.* dichloromethane and THF.

The structures of the obtained PCs were determined by ^{1}H NMR spectroscopy (Fig. S5 and S7–S10†). The ^{1}H NMR spectra show that the ratios of bisphenol A to monomer **1** in the synthesized PCs are approximately identical to the starting ratios.

The yields of the synthesized PCs, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (PDI) are summarized in Table 1. The molecular weight and the degree of polymerization (DP) were determined either by gel permeation chromatography (GPC) in THF or by ^{1}H NMR spectroscopy. The obtained results suggest that the molecular weight increases with a decreasing ratio of monomer **1** to bisphenol A. In the case of **1**, decomposition did not occur during the synthesis and the purification of the PCs. Therefore, the reduction of the molecular weight of the PC due to the decomposition of **1** is highly unlikely. In the case of **PolyBHMPA**, the low molecular weight was therefore attributed to its low solubility during the polymerization.

Subsequently, copolymer **PolyBP5** was chosen for the analysis of its physical properties given that it is the only copolymer among the synthesized PCs with properties similar to engineering plastics, *i.e.*, **PolyBP5** exhibits a suitable molecular weight, film strength, and stability of its melting point. Therefore, it is possible to generate transparent films of **PolyBP5** from spin coating or casting from dichloromethane solution.

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Table 1 Yield and physical properties of the synthesized PCs

PC	Yield (%)	M_n	M_w	PDI
PolyBP5	92	32 000	100 000	3.1
PolyBP10	78	18 000	45 000	2.5
PolyBP20	48	5900	15 000	3.0
PolyHD10	72	7200	27 000	3.8
PolyBHMPA	30	[a]	[a]	[a]

[a] **PolyBHMPA**: DP = 4; calculated based on the ^{1}H NMR spectrum.

Polymer blends

Apart from the use of the polymer films of fluorescent PCs, the use of polymer blends is also important for applications in advanced optical materials. To study the miscibility of **PolyBP5** with Ba-PC, we employed differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

PolyBP5 was mixed with commercially available Ba-PC (typically: $M_w = 64\,000$; Sigma-Aldrich) in a dichloromethane solution (1 : 1, w/w). The mixture was stirred until the polymers were completely dissolved before the polymer solution was added dropwise into methanol at 0 °C in order to induce reprecipitation of the polymer. The precipitate was filtered and dried under reduced pressure. This precipitate was then dissolved in 1,4-dioxane and used to generate a polymer blend film (thickness: ~10 nm; measured by a Dektak surface profiler) using a spin coater.

This polymer blend exhibited a jump in heat capacity ascribed to the glass transition at 127 °C. This glass transition temperature (T_g) lies between that of the commercially obtained Ba-PC ($T_g = 150$ °C) and that measured for **PolyBP5** ($T_g = 119$ °C). The observed single intermediate glass transition indicates that the polymers were mixed evenly (Fig. 2).

The polymer blend film was then characterized by SEM in order to examine the morphology of the film. The SEM images show a clear image without any visible polymer domains (Fig. 3), which is consistent with the DSC data, that the formed film is structurally uniform. The results of the SEM and DSC measurements thus suggest the absence of any phase separation between **PolyBP5** and Ba-PC. Based on these results, **PolyBPs** with small AIEgen ratios (5 mol%) seem ideal candidates for polymer blends, in view of their good solubility, film-forming properties and transparency, which are comparable to those of Ba-PC.

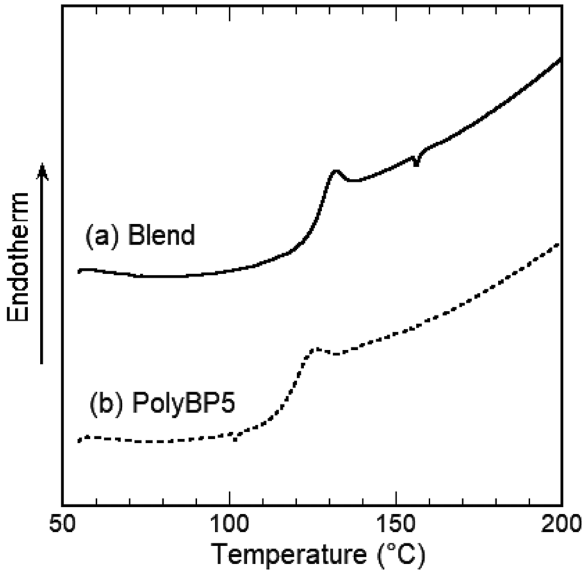

Fig. 2 DSC thermograms of **PolyBP5** and a 1 : 1 (w/w) polymer blend of **PolyBP5** and Ba-PC.

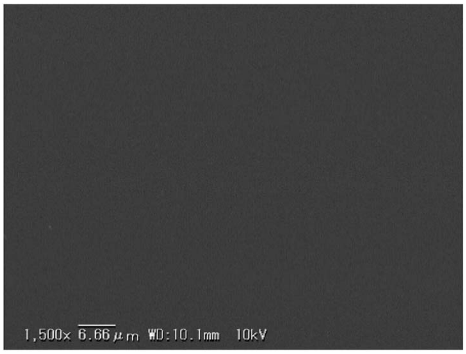

Fig. 3 SEM analysis of a 1 : 1 (w/w) polymer blend of **PolyBP5** and Ba-PC.

Optical properties

The optical absorption and fluorescent properties of the PCs synthesized in this study are summarized in Table 2 together with those of the reference compound **BPA**. Fig. 4a and b show the UV-vis absorption and fluorescence spectra of the PCs together with those of **1**. Fig. 5 shows the UV-vis absorption and fluorescence spectra of monomer **1** and the reference compound **BPA**.

The absorption and fluorescence spectra of **1** do not differ from those of previously reported **BPA**. However, **1** shows a similar quantum yield in solution, and a lower quantum yield than **BPA** in the solid state. The presence of the hydroxyl groups in **1** makes it difficult to remove all impurities from the sample. The decreased quantum yield in the solid state might be caused

Table 2 Optical properties of **1** and the PCs synthesized in this study

Compound	λ_{abs} [nm]	λ_{fl} [nm]	Φ_{THF}[a]	Φ_{solid}[b]
1	399	528	0.03	0.57
PolyBP5 (bulk)	399	522	0.04	0.53
PolyBP5 (film)	407	516	—	0.62
PolyBP10	399	519	0.04	0.54
PolyBP20	399	524	0.04	0.47
PolyHD10	399	524	0.04	0.23
PolyBHMPA	399	520	0.04	0.17
PC blend film	400	510	—	0.51
1&Ba-PC blend	410	510	—	0.74
BPA[c]	399	528	0.02	0.86

[a] Measured in THF (10^{-4} M) to obtain Φ at 293 K; excitation wavelength: 399 nm. [b] Bulk sample; excitation wavelength: 400 nm. [c] 9,10-Bis(piperidyl)anthracene (**BPA**).

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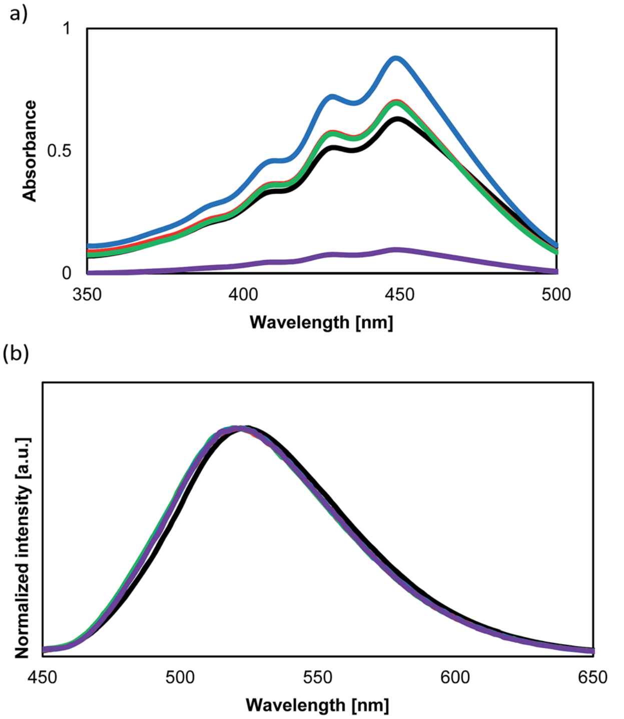

Fig. 4 (a) Absorption spectra of monomer **1** (black), as well as copolymers **PolyBP5** (red), **PolyBP10** (green), **PolyBP20** (blue), and **PolyBHMPA** (purple). All spectra were measured in THF (10^{-4} M). (b) Fluorescence spectra of monomer **1** (black), as well as copolymers **PolyBP5** (red), **PolyBP10** (green), **PolyBP20** (blue), and **PolyBHMPA** (purple). All spectra were measured in THF (10^{-4} M).

by these impurities. Unfortunately, it is currently not possible for us to purify **1** further with the equipment available to us.

Dispersing **1** in Ba-PC at a concentration of 0.5 wt% creates a dispersion which shows a slightly higher quantum yield compared to **1** in bulk. The dispersion solution produced a polycarbonate film which is mostly clear, indicating that the individual AIEgens are mixed evenly throughout. The higher quantum yield might be due to the fact that factors such as charge transfer cannot occur easily in the dispersion, and also the fact that there is less contamination when compared to the synthesized polycarbonates.

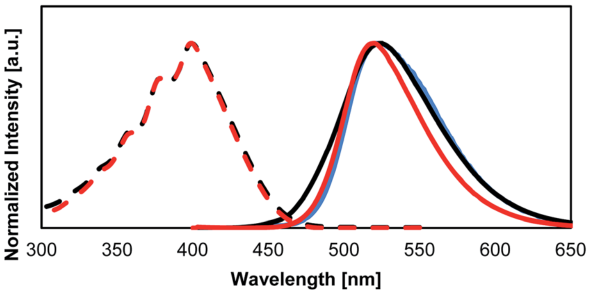

Fig. 5 Absorption and fluorescence spectra of **1** and **BPA**. Solid fluorescence of **1** (blue), as well as solution fluorescence of **1** (black) and **BPA** (red) (dashed lines: absorption spectra; solid lines: fluorescence spectra). The intensities of the spectra were normalized. All spectra were measured in THF solution (10^{-4} M).

All the PCs display *Φ* values of *ca.* 4% in dilute solution, which is identical to that of **1** and **BPA**.[8] Therefore, it can be concluded that in dilute solution, mobility of the luminophore units are not affected by the polymer chain of PCs. Hence, the luminophores in these PCs should undergo rapid non-radiative transitions *via* their S_1/S_0 MECI, which is stabilized by *N*,*N*-dialkylamino functional groups and consistent with our previous report.[9]

The quantum yield of **PolyBP5** and **PolyBP10** in solution and the solid state is comparable to that of **1**. However, when the concentration of the AIEgen is increased to 20% (**PolyBP20**), the quantum yield in the solid state decreases to 47%. This phenomenon could be explained by contamination from the polymerization, given that the absorption band of **PolyBP20** is broader than that of the other copolymers. Such impurities might also absorb the excitation beam, thus affecting the quantum yield.

As **PolyHD10** is a viscous liquid at room temperature ($T_g = -51$ °C), the micro-Brownian motion of the polymer chain is less restricted than that of the PCs synthesized from bisphenol A. The unrestricted movement could make the S_1/S_0 MECI of the **BPA** luminophore easily accessible, which would result in efficient quenching.

PolyBHMPA shows the smallest *Φ* value in the solid-state (0.17). The absorption spectrum suggests that this might be due to a potential contamination of the sample, similar to the case of **PolyBP20**.

The photophysical properties of PC films of **PolyBP5**, which were generated using a spin coater, showed an average *Φ* of 0.62, which is similar to that of **PolyBP5** in the bulk state. The PC blend film also showed a similar quantum yield of 0.51. The emission and fluorescence spectra are also comparable to those in the bulk. The fluorescence lifetime was found to be

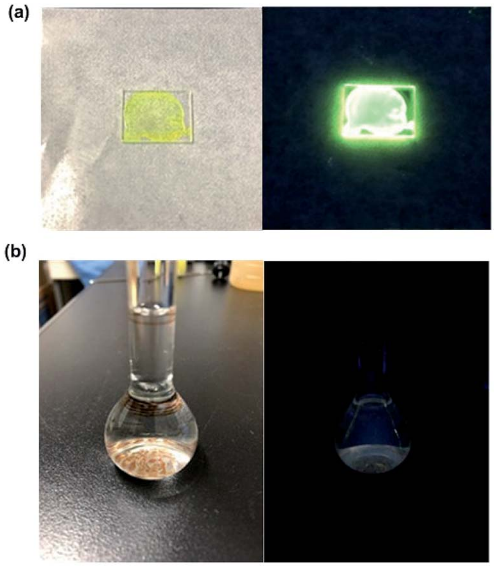

Fig. 6 (a) **PolyBP5** film under ambient light (left) and under exposure to a UV lamp ($\lambda_{ex} = 365$ nm) (right). (b) **PolyBP5** in THF solution under ambient light (left) and under exposure to a UV lamp ($\lambda_{ex} = 365$ nm) (right).

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approximately 11.7 ns. The k_f was calculated to be $4.8 \times 10^7\ s^{-1}$, and the k_{nr} was found to be $4.6 \times 10^7\ s^{-1}$. In comparison, **BPA** shows a fluorescence lifetime value of 9.9 ns in THF solution, and 12.1 ns (k_f was calculated to be $6.7 \times 10^7\ s^{-1}$, and the k_{nr} was found to be $1.8 \times 10^7\ s^{-1}$) in colloidal suspension in a mixture of THF and water. These values indicate that non-radiative deactivation is faster, most likely due to the remaining molecular movement or the contamination in the sample (Fig. 6).

Conclusions

AIE-active PCs with varying AIE-active monomer ratios were synthesized. The photophysical properties of these PCs show that PCs with 5 mol% or 10 mol% AIE-active monomers achieve optimal luminescence. These PCs also form miscible blends with commercially available Ba-PC. The synthesized PCs exhibit good film-forming properties, which renders them suitable for applications in *e.g.* luminescent polymers. Embedding small ratios of AIEgens in PCs do not seem to negatively affect the physical properties of the films, and the unique properties of the AIEgen is retained in the films. Currently, we are investigating AIEgens that exhibit the three basic colors; *i.e.* blue, red and green in order to produce a PC with white fluorescence.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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