

Silylethynyl Substitution for Preventing Aggregate Formation in Perylene Diimides

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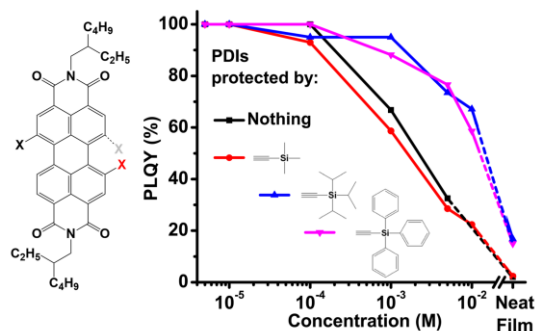
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ABSTRACT

Ethynylene bridged perylene diimides (PDIs) with different sized silane groups have been synthesized as a steric blocking group to prevent formation of non-radiative trap sites e.g. strong H-aggregates and other dimers or excimers. Excited singlet state exciton dynamics were investigated by time-resolved photoluminescence and ultrafast pump-probe transient absorption spectroscopy. The spectra of the excimer or dimer aggregates formed by the PDIs at high concentrations were also determined. Although the photophysical properties of the bare and shielded PDIs are identical at μM concentrations, more shielded PDI2 and PDI3 exhibited resistance to aggregation, retaining higher PLQY even at 10 mM concentration and in neat films. The PDIs also exhibited high photostability (1 hour of continuous excitation), as well as electrochemical stability (multiple cycles with cyclic voltammetry). Prevention of dimer/aggregate formation in this manner will extend the uses of PDIs in a variety of high concentration photonics and optoelectronics applications, such as OLEDs, organic photovoltaics, and luminescent solar concentrators.

TOC graphic (7.16×4.45cm)



Introduction:

Perylene diimides (PDIs) are one of the important chromophore groups, with extended π -conjugation systems leading to many optical and optoelectronic applications. Of particular usefulness in applications are their high absorption coefficients ($\epsilon > 10^4$) in the visible region, strong electron affinities, high electron mobilities, and photoluminescence quantum yields (PLQY or Φ , typically near 100%). PDIs also frequently exhibit excellent optical, thermal, and electronic stability.¹⁻⁷ Combined with their n-type charge transport characteristics and singlet emission, PDIs are commonly applied in organic or perovskite solar cells, organic light-emitting diodes (OLEDs), and organic transistors.⁸⁻¹³ Due to their large and chemically tuneable ϵ in the blue-green region (400-550 nm), they can also be used to obtain white light with downconverters^{4,14,15} for lighting applications, or in organic luminescent solar concentrators¹⁶⁻¹⁸ for hybrid photonic devices.

The superior optical properties of PDIs and other flat polycyclic aromatic hydrocarbon molecules in solution phase are often not preserved in film phase due to aggregation caused quenching (ACQ).^{19,20} The same is also true for regular perylenes,²¹ which are often used as blue emitters and for triplet-triplet annihilation applications.^{22,23} The transitions associated with the lowest energy excitonic states are critical to the performance of organic photonic devices,^{19,24,25} with deactivation and quenching by dimer^{26,27} or excimer^{28,29} states able to outcompete many desired processes - such as charge transfer and transport³⁰, exciton diffusion³¹ and intersystem crossing.^{26,27,32} PDIs that form such excimer, dimer, or aggregate states also often exhibit significantly different photophysical properties compared to isolated molecules, making understanding and developing device applications complicated at higher concentrations³³. For example, red shifted photoluminescence (PL) spectrum, increased fluorescence lifetime, and losses in PLQY are all commonly reported.^{19,34-36} The deleterious effects of high-concentration multimolecular interactions and ACQ are further amplified in systems where dyes are anchored at high loading onto nanoparticle²⁸ surfaces as ligands, with such dye-particle composite materials generating strong interest for light-harvesting and photon conversion applications.^{37,38}

Avoiding the formation of these quenching states is therefore important for improving the performance of PDI devices, with several molecular design strategies already reported towards protecting this and other optically active cores from interactions with neighbouring molecules.^{1,39-44} One of the popular strategies for preventing π - π aggregations of PDIs is to modify the bay positions with large steric groups, such as tert-butylphenoxy.^{16,31,44-49} This

approach can either directly block the approach of neighbouring molecules, or twist the backbone of the PDI making it less planar and therefore also less susceptible to π -stacking interactions.⁴⁶ In recent studies this approach has been shown to preserve excellent PLQY values upwards of 90% in crystals⁴⁴ and 60% in neat films.⁴⁹ However, as the linking ether bridges do not fully isolate the PDI core from the electronic system of the shielding groups, this strategy also introduces slight changes in the absorption and emission spectra of the sterically shielded materials even in dilute solutions. Indeed, the degree of spectral redshift increases with the size of the shielding groups,⁴⁹ while in other systems these groups can directly interact with the PDI core to form charge transfer states⁴⁸ or influence electron transport properties.⁵⁰ Elsewhere, fused systems can lengthen the π -conjugation system without causing the PDIs to twist, which facilitates exciton diffusion and improves charge transport.^{50,51} The redshifting effect of increased bay-substituent bulk is not as pronounced in similar studies of imide-substituted PDIs though,¹ indicating different levels of electronic communication through that site.

Inspired by the electronically insulating properties of silyly-containing spacer materials in TADF exciplex blends,^{52,53} in this study a reference PDI (PDIref) and three bay-substituted ethynyl-bridged PDIs (PDI1, PDI2, and PDI3) with bulky silane groups were synthesized (**Figure 1**) and their exciton dynamics investigated at high and low concentrations. Sonogashira coupling of acetylene-bridged derivatives with sp hybrid structure to the bay positions of the PDI^{4,54,55} is found to expand the electronic system of the PDI core, although the high PLQY in dilute solution is preserved.^{4,56} Crucially, no further spectral changes are observed as the bulk of the shielding groups is varied beyond the silicon atom.

At higher concentrations, complicated dynamics involving excimer and higher-order aggregate states were revealed in the PDIs using time-resolved spectroscopy. The excited state properties of PDIs were also compared by fs-transient absorption spectroscopy (TAS) and PLQY measurements at different concentrations. The extent of PDI interactions and ACQ decreased as the silane steric size increased from PDI1 to PDI2 but with no additional protecting effect as it was further increased from PDI2 to PDI3.

Methods:

Full description of all synthetic methods and structural, electrochemical, and optical characterisation methods are included in the Supporting Information.

Results and Discussions:

Synthesis

Previously reported PDIref⁵⁷ was used as a reference in this study due to its planar aromatic structure and its predisposition to form molecular interactions. In order to compare with shielded PDIs modified with different volumes of steric groups, previously reported PDI2⁵⁶ as well as newly prepared PDIs 1 and 3 were synthesised (**Figure S1**) following the Sonogashira coupling synthetic process in the literature.^{56,58} The new materials PDI1 and PDI3 were additionally characterized by NMR and HRMS spectroscopy.

The first of the two most well-known examples of these regioisomer synthesis methods starts with the synthesis of perylenetetraester (PTE) and dibromoperylene-tetraester (DBrPTE), and then conversion of the 1,7-isomeric DBrPTEs obtained by crystallization of the mixed-isomer 1,6 and 1,7-DBrPTE derivatives to 1,7-dibromoperylene-tetracarboxylic dianhydride (DBrPTCDA).^{59,60} In the second method 1,6 and 1,7-regio isomers of diBrPDIs are synthesized from specific alkyl-amine derivatives and purified by column chromatography. The purified 1,6 or 1,7-DBrPDI derivatives are then hydrolysed in basic medium and converted back into the DBrPTCDA derivatives. The target regioisomer is then obtained by re-imidization reaction with the desired functional group.^{61,62} However, the reaction conditions provided here to obtain 1,6 and 1,7 acetylenyl bonded PDI2 may guide researchers wishing to synthesize the individual isomers (to obtain isomer purity acetylene bridges or fused system⁶³) without needing to separate a mixture. It is quite efficient to subsequently remove the silane groups under basic reaction conditions.

First, brominated PDIs of 1,7-func. (87% isomeric purity, the remainder being 1,6 brominated) were prepared⁵⁶ and degassed in triisopropylamine (base medium) to remove oxygen. Then [Pd(PPh₃)₄] and CuI catalysts and acetylene sources [(trimethylsilyl)acetylene for PDI1, (triisopropylsilyl)acetylene for PDI2 and (triphenylsilyl)acetylene for PDI3] were added at room temperature (RT), with a resulting change in color. The reactions continued for 3 days at room conditions, after which PDI1 and PDI2 were obtained with high yield (84% and 93%, respectively) and subsequently purified [column chromatography, chloroform: hexane (1:1 to 1.5:1)]. PDI3 was obtained in 50% yield (silica gel, chloroform:hexane 1:1 to 2:1). The 1,7-isomers of PDI1 and PDI2 were then purified, although the PDI3 isomers could not be purified by column chromatography. As a result, the as-syntheses mixtures of 1,7 and 1,6 isomers of

PDI 1-3 were investigated in this work. Full Synthetic details are given in **SI** and in **Figure S2-S9**.

Steady state Absorption and PL properties of dilute solutions

The absorption and PL spectra of PDIref, PDI1, PDI2, and PDI3 in chloroform (CHCl_3 , one of the well-known solvents with the best solubility of PDIs) at 10^{-6} M concentration are shown in **Figure 2**. The high solubility solvent and low concentrations were used to ensure measurements corresponded to isolated molecules. PDIref has an absorption maximum peak (π - π^*) at 526 nm with lower intensity vibronic peaks (S_{0-1} and S_{0-2}) at 490 and 458 nm (**Figure 2a**). The absorption maximum peak of PDIs 1-3 functionalized with acetylene bridges was 552 nm, redshifted 26 nm compared to PDIref due to their expanded aromatic system. Similar lower intensity vibrational peaks of PDI1-3's main absorption were red-shifted and found at about 512 (S_{0-1}) and 480 nm (S_{0-2}) (**Figure 2b**). Molar extinction coefficients were calculated for the main absorbance peak of each material (**Figure S10**) and were all in the range of $4\text{-}8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. PDIs 1-3 exhibited identical maximum PL peak at 568 nm, demonstrating that the silyl group prevents electronic communication between the steric groups and the common core unit.

Electrochemical properties and optical stability

Cyclic voltammetry measurements were carried out to investigate the effect of silane groups on reduction potentials and LUMO levels (**Figure 3**). While the PDI derivatives did not show any oxidation potential in the positive region, they exhibited double reduction potentials in the negative region as expected.⁶⁴ The ethylene bridging group actively participates in the conjugation system, increased the potential of the first half reduction wave compared to PDIref (**Table S1**). The first half-wave reduction potentials of PDIref, PDI1, PDI2, and PDI3 are -0.61, -0.55, -0.58, -0.52 V, respectively. The effect of the triphenyl containing silane group in PDI3 was greater than the shift due to the silane groups containing trimethyl and triisopropyl (PDI1 and PDI2) due to the inductively electron donating phenyl group (**Table S1**).

The LUMO energy levels of the PDIs were calculated according to the formula ($E_{\text{LUMO}} = -[(E_{\text{red}} - E_{\text{Fc}}) + 4.8 \text{ eV}]$) from the 0.45 eV oxidation potential of Fc/Fc^+ and with reference to the vacuum level. Optical band gaps (ΔE_{opt}) were calculated from the energy of the absorption onset. Finally, the HOMO levels were calculated according to the formula ' $E_{\text{HOMO}} = E_{\text{LUMO}} - \Delta E_{\text{opt}}$ ' with all values summarized in **Table S1**. While PDIref exhibits a bandgap of 2.28 eV, PDIs 1-3 exhibit smaller but uniform optical bandgaps of around 2.15 eV, consistent with their redshifted but otherwise identical absorption spectra. It is known that sp hybridized groups such

as acetylenyl bridges reduce LUMO energy levels and increase the electro negativities of PDIs.⁶⁵ The decrease in reduction potentials of PDI1-3 substituted by acetylenyl bridges from the bay position showed that the electron affinities increased compared to PDIfref. To summarize briefly, they can serve as electron acceptors in organic solar cell applications.

In addition, multicycle CV results of all PDIs demonstrated excellent electrochemically stability (**Figure S11**). Analogous photostability characterizations were completed by applying continuous excitation for 1 hour and monitoring the PL intensity (**Figure S12**). In both tests the PDIs were found to be highly stable, a desirable property for their applications in optical-electronic devices. Moreover, the HOMO and LUMO energy levels of the PDIs are compatible with other materials commonly used in optoelectronic devices. This includes hole (e.g. poly(N-vinyl carbazole) (PVK), 4,4'-bis(9-carbazolyl)biphenyl (CBP)) and electron transport (e.g. (4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine) B3PYMPM) or host materials (PVK) used in OLEDs.⁶⁶⁻⁶⁸ In addition, these PDIs are likely to be compatible with perovskites or other donor materials in solar cells.^{9,10,69}

Time-resolved photoluminescence

The concentration dependent time-resolved PL behaviour of the PDIs (collected with pulsed laser excitation and iCCD camera with gated detection in chloroform solution) are given in detail in **Figure S13-S16**, and summarized in **Figures 4a-d**. Solutions at low and high concentrations reveal the types of excimer and aggregates formed, and how these are impacted by the different volumes of protecting silane groups.

First, PDIfref is susceptible to aggregation since it does not have any steric shielding group. When the time-resolved PL spectra of PDIfref solutions prepared from concentrations 10^{-6} to 5×10^{-4} M were examined, they exhibited the typical vibrationally resolved emission band (S_{0-0} , S_{0-1} and S_{0-2}) at low concentrations consistent with the steady state spectra (**Figure S13a**). The PL spectra changes up to a concentration of PDIfref 10^{-5} M, with the loss on intensity from the $0-0'$ peak likely due to inner filter effects (self absorption) (**Figure S13b**). At higher PDIfref concentrations (10^{-4} M), the PL peak at 537 nm of monomers disappears, leaving only the lower energy vibronic bands. In addition, a new low-energy aggregate-like emission band appears at 616 nm (**Figure S13c**). Since no associated change is observed in the absorbance spectrum as the concentration is increased, we attribute this new peak primarily to excimer formation.²⁹ At the maximum concentration of PDIfref the PL spectrum is of an even lower energy (possibly multi-molecular) aggregate-like species, which continued emitting up to 21.7 ns at 629 nm

(**Figure S13d**). The spectra of the new species that are formed depending on concentration are summarized in the **Figure 4a**.

PDI1 exhibited similar concentration dependent behaviour as PDlref (**Figure S14a**). At 10^{-5} M and 10^{-4} M of PDI1 the PL is dominated by the monomeric species with some inner filter effect modulating the PL spectrum shape (**Figure S14b**). At 10^{-3} and 10^{-2} M new broad spectra were observed at 632 and 662 nm at longer times (2.2 ns) (**Figure S14c and d**). As with PDlref we attribute these to excimer emission and aggregate forms of the PDI1 material. The similarity in behaviour for PDlref and PDI1 suggests that the smallest methylsilyl protecting groups do not offer adequate steric bulk to prevent aggregation. What is clear from the time evolution of the emission spectra at high concentrations is that a new long lived emitting species remains after all the monomeric singlet excitons have decayed (**Figure S14c and d**) showing that the change of the emission band is not simply due to increasing self absorption at higher concentrations.

PDI2 and PDI3 show similarities in the formation paths of concentration-dependent new PL features species as PDI1, although these do not become apparent until a concentration of 10^{-2} M is reached (**Figures S15 and S16**). The monomeric emission also persists at higher concentrations in these materials, whereas it becomes fully suppressed in PDlref and PDI1. As the steric shielding groups are larger in PDI2 and PDI3, they are likely more effective at preventing excimer formation at the lower concentrations, with excimer emission only becoming apparent at much higher concentrations. We also do not observe the lowest energy 660 nm excimer band displayed by PDI1 in either PDI2 or PDI3 at the investigated concentrations, consistent with their steric shielding preventing the formation of higher-order aggregates.

Concentration-dependent PLQY measurements

ACQ effects of silylethynyl substitution on PDIs were also investigated by concentration-dependent PLQY measurements (absolute method in integrating sphere). The excitation wavelengths were 490 nm for PDlref and 512 nm for PDIs 1-3, respectively (**Figure S17 and TOC graphic**). All PDI derivatives exhibited $\Phi_s > 90\%$ and above up to 10^{-4} M, indicating high efficiency for isolated molecules. At 10^{-3} M concentration PDlref and PDI1 suffer significant ACQ due to the formation of aggregates and excimers identified by time-resolved PL, with Φ decreasing to $\sim 60\%$. More shielded PDI2 and PDI3 are not as affected, showing resistance to aggregation at these concentrations and retaining PLQYs above 85%. At a very high concentration of 10^{-2} M, the steric shielding of PDI2 and PDI3 still performed quite effectively,

retaining Φ values of 67% and 58% respectively. In contrast, PDIref was insoluble at 10mM, while PDI1 at this concentration gave Φ of only 22%. Interestingly from these results, we note that the shielding performance of PDI2 and PDI3 are very similar. This indicates that the larger triphenyl shielding offers no additional benefits compared to triisopropyl groups.

Investigating this steric protection in the extreme limit, PLQYs of neat films were also investigated - prepared by spin coating (for PDIs 1-3; 2500 rpm, 10 mg/mL) (for PDIref; 2500 rpm, 5 mg/mL). PDIref and PDI1 exhibited PLQY of only 2.1 and 2.4%, respectively in the neat films. More protected PDI2 and PDI3 instead gave 16.8% and 15%, respectively. The PLQYs of the films clearly decreased compared to the solution phase, as the total removal of solvent strongly promotes molecular aggregation and excimer formation. The formation of such multi-molecular states is apparent from the change in absorption and PL spectra displayed by the neat films (**Figure S18**), although with PDI2 and PDI3 less severely affected. Almost total ACQ was observed in PDIref and PDI1 due to the lack effective steric protection and thus their potential to form closely-spaced coplanar structures.¹⁹ The more substantial steric shielding in PDI2 and PDI3 prevent this interaction, allowing them to retain higher PLQYs in the neat films. The fact that the triisopropylsilane and triphenylsilane groups result in similar outcomes for these two materials (as was observed in solution measurements) demonstrates that they have reached the limit of diminishing returns as it concerns protecting group size and prevention of ACQ. Although these neat film PLQYs are lower than what can typically be achieved by embedding the material in an optically transparent host,⁵⁶ such values can still be suitable for applications as emitters in high-luminance OLEDs, with the enhanced solubility of the PDIs potentially supporting improved solution processing applications.^{70,71}

Femtosecond-Transient Absorption Spectroscopy (fs-TAS) properties of PDIs

TAS measurements of different concentration chloroform solutions of the PDIs were performed in the 480-800 nm range. Part of the 1030 nm output from the femtosecond amplifier PHAROS was used to generate 343 nm via third harmonic generation, which is used as the pump to excite the PDIs. Another part of the 1030 nm output was focused on a 2-mm sapphire plate to generate white light continuum, which was used as a probe to observe the excited state behaviour. More detailed information about the pump-probe fs-TAS technique is detailed in the SI.

The induced absorption spectra of each PDI at 80 ps delayed time are summarized in **Figure 5**. TAS measurements of PDI solutions at 5×10^{-5} to 5×10^{-4} M showed only singlet state dynamics. The PDIref at 5×10^{-5} M exhibited ground state bleach (GSB) and stimulated emission (SE)

signals at 537 nm and also SE of the S_{0-1} fluorescence transition at 574 nm, following the steady state and 2 ns time-resolved PL spectra as a function of concentration extremely closely. A photoinduced absorption (PIA) peak of PDIref was seen at 711 nm (**Figure 5a**), which likely corresponds to S_1 to S_2 absorption. Changes in TAS spectra were observed with a controlled increase of PDIref concentration. The intensity of the SE at 537 nm decreased (likely due to inner filter effects and increased self-absorption), while the SE at 574 nm increased its intensity due to increased pump beam absorption in the sample. In the PIA region, shifts to short wavelengths of a few nm were detected and exhibited PIA with a maximum peak at 706 nm at 5×10^{-4} M (**Figure 5a**). Throughout the TAS measurements we observe no indication of the formation of triplet states, which is consistent with low intersystem crossing in these materials and their high intrinsic PLQYs. More importantly, we neither observe the appearance of a new instantaneous PIA feature at high concentration that could be associated with states resultant from ground state interactions such as dimers and small aggregates. This further points to the main intermolecular interaction at high concentration being excimeric in nature.

The concentration-dependent TAS spectra of PDIs 1-3 are illustrated in **Figure 5b-d** (at 80 ps). Although this delay time is before the emergence of excimer PL from the time-resolved emission measurements, no further change in the TAS spectral shape was observed at any other later time for any material at any concentration, up to ~ 5 ns for these measurements (**Figure S19**). Since the solubilities of PDIs 1-3 were higher, measurements were also completed at higher concentrations such as 10^{-2} M. PDI1 exhibits longer wavelength GSB and SE due to extension of its aromatic system with the ethynyl bridges in line with the steady state measurements, found at 515 nm (GSB), 555 nm (GSB), 578 nm (SE) and 615 nm (SE) respectively (at 5×10^{-5} M). At higher concentrations the GSB was not always observed due to the high absorption, while SE was evident at 578 nm and 615 nm at 10^{-3} M. The PIA peak at all concentrations was determined to be about 733 nm (**Figure 5b**). PDI2 and PDI3 exhibited similar TAS properties as PDI1, confirming their similar optoelectronic properties but revealing little about the aggregate or excimer state from the available range of wavelengths and timescales. (**Figure 5c**).

Excited state lifetimes of PDIs 1-3 were determined by exponential fitting of the TAS signal decay (amplitude weighted average of biexponential fit). The excited state lifetime of PDI1, 2, and 3 at 10^{-4} M were 4.4, 5.2 and 12.2 ns respectively, although we suggest that the value for PDI3 may be an outlier due to low optical density at this concentration. At 10^{-3} M concentrations, the lifetimes increased to 7.4 and 7.58 ns for PDI1 and PDI2, while for PDI3 it

appeared to decrease to 8.5 ns (**Table S3**). These excited state lifetimes were also comparable with the ~8 ns lifetimes observed for the emission decays of PDIs 1-3 (**Figure S20-S22**), with a longer-lived component emerging at higher concentrations attributed to excimer emission.

Finally, we note that the best PLQY values we are able to achieve in neat film (15 and 17%) are significantly lower than some recently reported using dendritic ether-bridged PDI bay substituents (up to 60% PLQY, or 90% in crystals^{44,49}). Nonetheless the use of electronically insulating silyl groups is able to fully decouple the electronic systems of the PDI core and the shielding groups. This leads to more stable absorption and emission spectra as the shielding group size increases. Our PLQYs are instead similar to those achieved using dendritic steric groups attached to the imide position (21 and 29%¹).

The different PLQY values achieved with these shielding strategies are likely due to the different structural shapes associated with each. X-ray analysis shows that dendritic ether-linked shielding groups at the bay positions are able to wrap around the PDI core and provide 360-degree protection.⁴⁴ The very similar shielding groups employed at the imide position are able to protect the plane of the PDI core from above and below, but not as effectively from the side.¹ This difference probably accounts for the differences in neat-film PLQYs reported in those two works. The ethynyl-silyl groups here are instead expected to provide dumbbell-like protuberances, preventing other molecules from approaching in the plane of the PDI core but not perpendicular to it – completely the opposite of the imide-substituent strategy. Clearly the fully enwrapped PDI is the most resilient to ACQ, although alternate shielding strategies such as the one presented here may prove to be more effective at preserving the electronic properties of PDI, which would likely be disrupted by the same shielding that protects against ACQ. The directionality of the shielding strategy is also likely to be critical in surface-bound applications, where ACQ and excimer formation happens at predictable molecular geometries.²⁸

Conclusions

Due to the large planar aromatic systems of PDIs, they are prone to form aggregates and dimers or excimers at high concentration that negatively impact their optoelectronic performance. In this study, we have synthesized three different silylethynyl-substituted PDIs to investigate the effects of their differently-sized silane groups relevant to ACQ and aggregation behaviour. PDI1, 2, and 3 exhibited the same photophysical properties at low concentrations, while the larger volumes of silane groups bestowed PDI2 and PDI3 with greater solubility and resistance to excimer formation than PDI1 (with smaller steric groups) and PDIref (with no protection).

Time-resolved PL measurement revealed the formation of excimer or multi-molecular aggregates, which PDI2 and PDI3 are not susceptible to even at very high concentrations. Steady-state and transient absorption measurements further establish the formation of excimer species rather than ground-state dimers. Both PDI3 and PDI2 consequently retain high PLQY even at very high concentrations, and retain more of this performance in neat films compared to PDIref and PDI1. This strategy for preventing aggregation formation therefore has the potential to be applied for a wide range of organic electronic materials that suffer aggregation effects at high concentrations.

CONFLICTS OF INTEREST

There are no conflicts of interest to declare

SUPPORTING INFORMATION

Full description of all methods, including synthesis of PDIs and their structural, electrochemical, and optical characterisations; additional time-resolved emission and transient absorption spectra; PLQY data and optical spectra of neat films; decay fitting of time-resolved emission and transient absorption signal decays.

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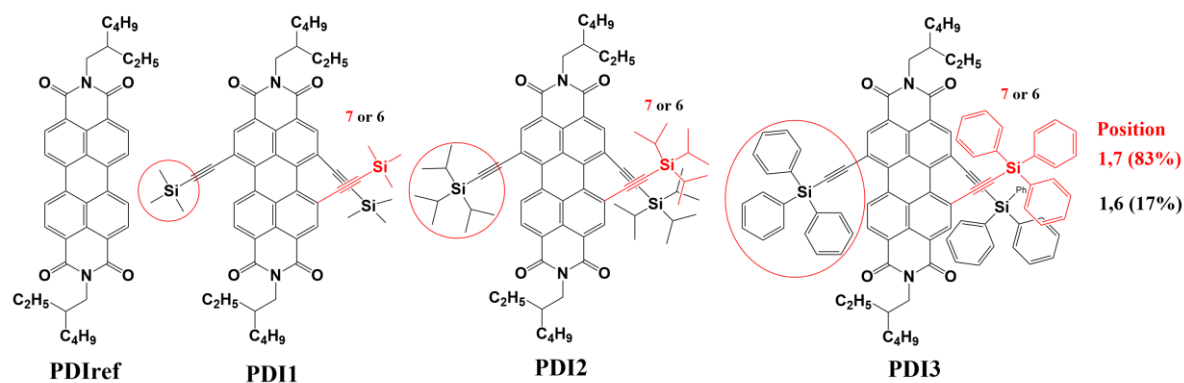
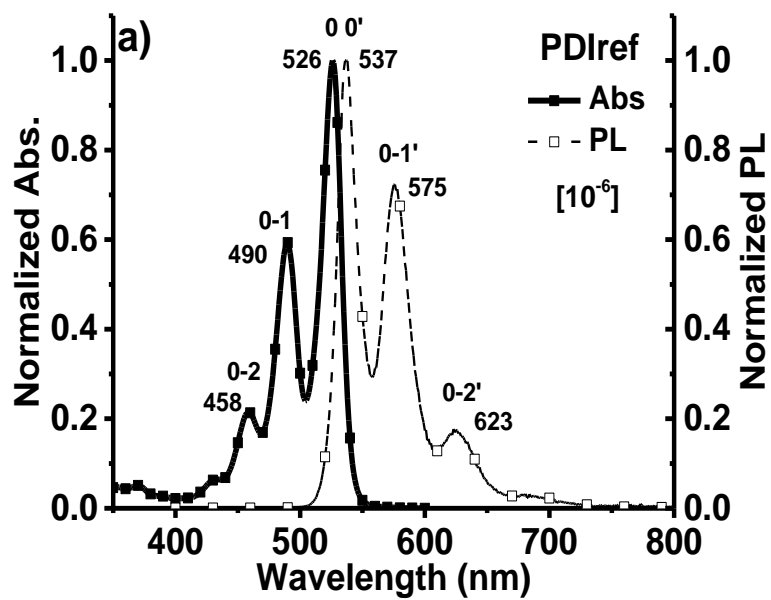


Figure 1: Synthesized Perylene derivatives.



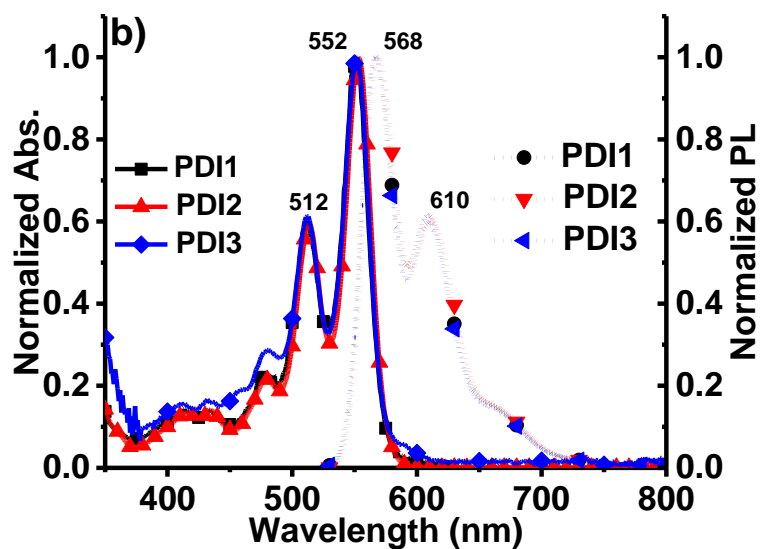


Figure 2: Normalized steady-state absorption and PL of *a*) PDIfref and *b*) PDIs 1-3 in chloroform (10^{-6} M). Excitation wavelengths of PDIfref and PDI1-3 are 490nm and 512nm, respectively (i.e. using their 0-1 absorption vibronic bands).

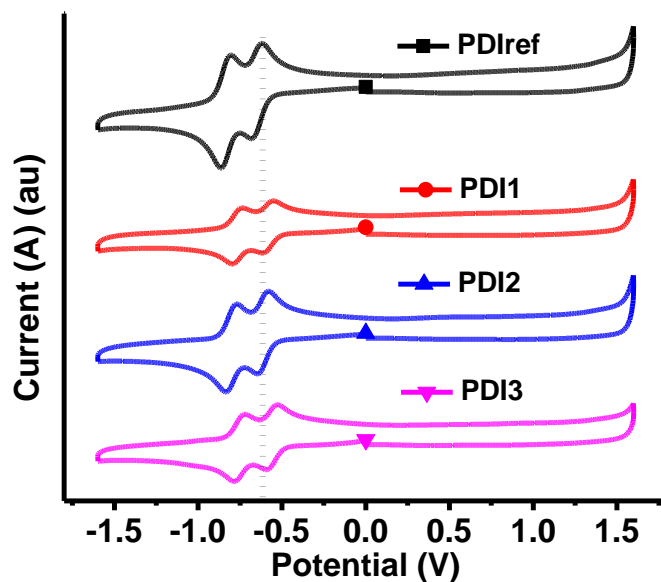


Figure 3. Voltammogram curves of solutions of PDIs with 0.1 M TBAPF6 in dichloromethane.

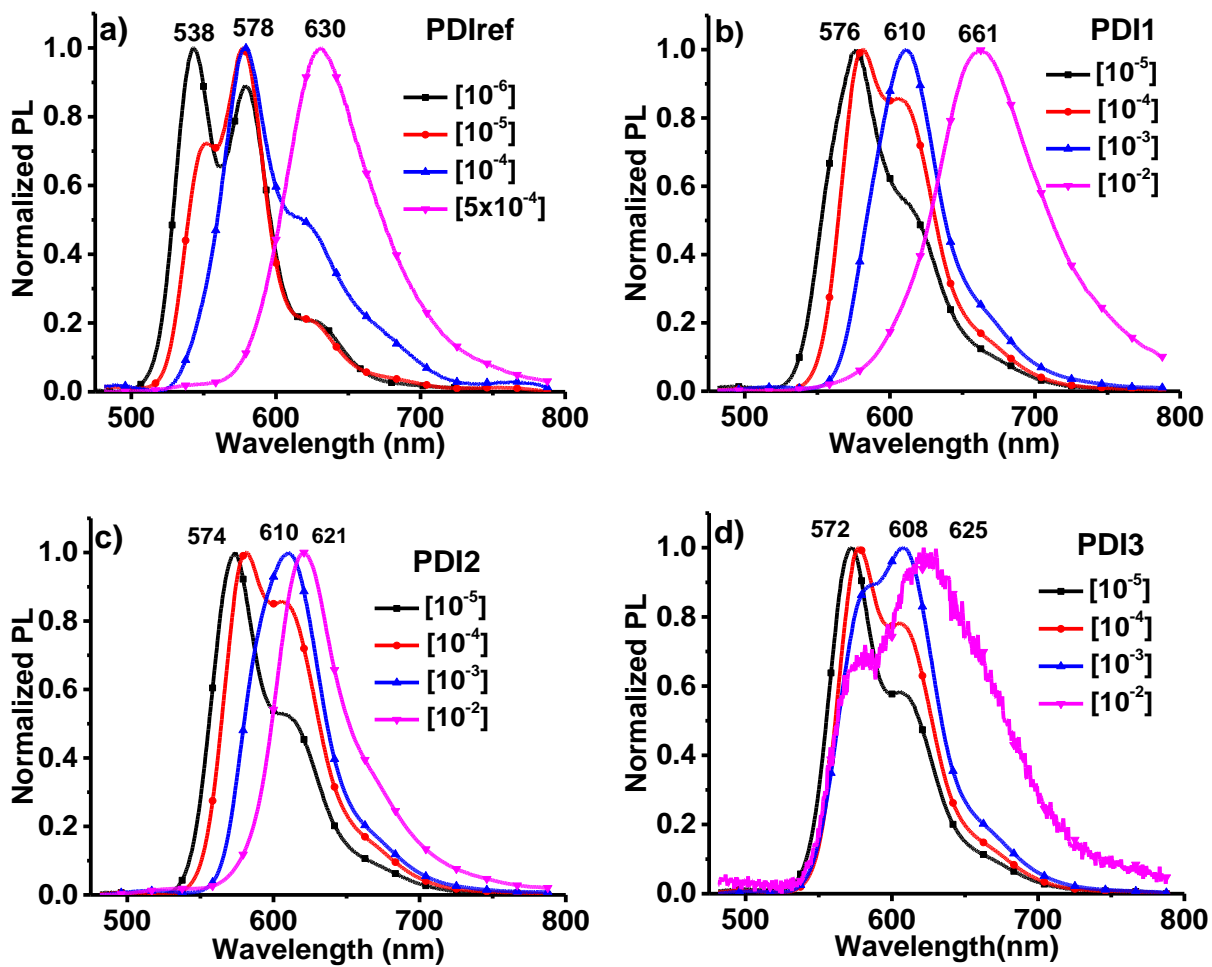


Figure 4: Time-resolved PL spectra at 4.3ns of PDIref, PDI1 PDI2 and PDI3 at different concentrations in chloroform.

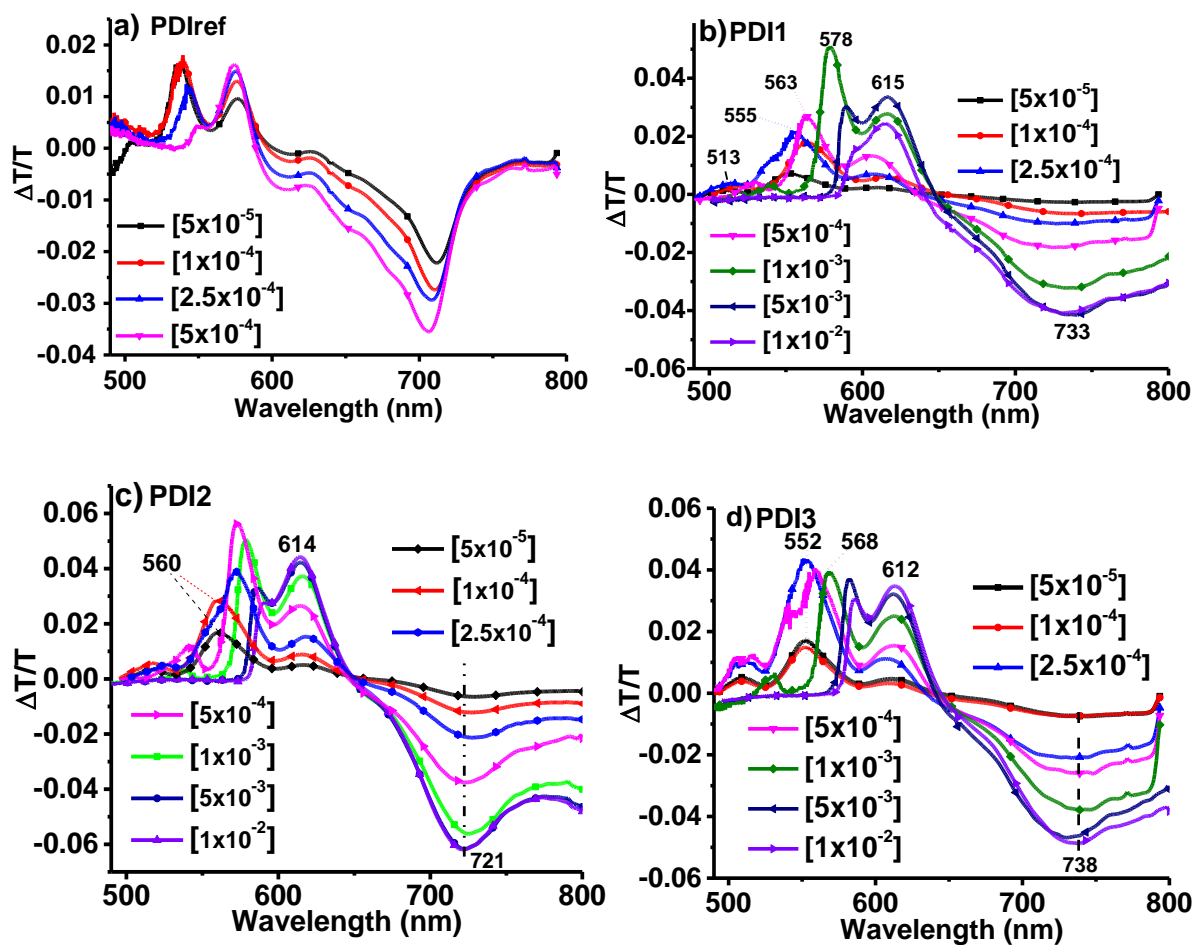


Figure 5: TAS curves of PDIref, and PDIs 1-3 at different concentrations in chloroform (80ps delayed time).