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The Effect of Imide Substituents on the Excited State Properties of Perylene Diimide Derivatives

Erkan AKSOY[123*], Andrew DANOS[2], Chunyong LI[2], Andrew P. MONKMAN[2], Canan VARLIKLI[3]
[1]Solar Energy Institute, Ege University, 35100 Izmir, Turkey
[2]Department of Physics, Durham University, Durham DH1 3LE, U.K.
[3]Department of Photonics, Izmir Institute of Technology, 35430 Urla, Izmir, Turkey
*[123]erkanaksoy@iyte.edu.tr, [2]andrew.danos@durham.ac.uk, [2]chunyong.li@durham.ac.uk,
[2]a.p.monkman@durham.ac.uk, [3]cananvarlikli@iyte.edu.tr

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Abstract: Solid state optical properties of fluorescent materials are important for many photonic devices such as organic light emitting diodes, frequency down-converters or luminescent solar concentrators. Perylene diimides (PDIs) represent one of the most popular organic semiconductors which find application in such photonic device applications. In this study, photophysical properties of two dibrominated PDI (DiBrPDIs), one of which contains a branched alkyl chain (2-ethylhexyl, 2-EH) and the other with an aromatic substituent (diisopropylphenyl, DIA) at the imide positions are comparatively studied. We report their absorption and photoluminescence, lifetime and photoluminescence quantum yield (PLQY), as well as photoinduced absorption properties (PIA) examined by fs-transient absorption spectroscopy. Having the same π conjugated system, DiBrPDI-DIA and DiBrPDI-2EH exhibited identical absorption and photoluminescence (PL) spectra in chloroform (λ_{abs}:527 nm and λ_{PL}:552 nm). However, in film phase, DiBrPDI-DIA ($\lambda_{PL\text{-}DIA}$:596 nm; PLQY:73.4%) presented a shorter PL wavelength with a higher PLQY than that of DiBrPDI-2EH ($\lambda_{PL\text{-}2EH}$:649 nm; PLQY:36.7%). Bond lengths and core bending angles of PDI derivatives were calculated using Chem3D pro software. It was determined that the 2,6-diisopropylphenyl group in DiBrPDI(DIA) extends a distance of about 6.8 Å out from the imide positions, providing more effective steric protection from aggregation than the smaller 2EH group.

Key words: Solid state fluorescence, perylene diimide, fs-transient absorption spectroscopy, steric shielding.

Perilen Diimid Türevlerinin Uyarılmış Hal Özelliklerine İmid İkamelerinin Etkisi

Öz: Fluoresant malzemelerin katı hal optik özellikleri organik ışık yayan diyotlar, frekans dönüştürücü veya ışıyan güneş yoğunlaştırıcıları gibi birçok optik ve elektronik fotonik aygıtlar için önemlidir. Perilen diimidler (PDIs) bu tür fotonik aygıt uygulamalarında yer bulan en popüler organik yarı iletkenlerden birini temsil etmektedir. Bu çalışmada, biri dallı alkil zinciri (2-etilheksil, 2-EH) diğeri aromatik (diizopropilfenil, DIA) yer değiştirebilen grup içeren iki dibromlu PDI'nin (DiBrPDIs) fotofiziksel özellikleri karşılaştırmalı olarak incelenmiştir. Biz bunların soğurma ve fotolüminesans (PL), yaşam ömürü ve fotolüminesans kuantum veriminin (PLQY) ile fs-geçici absorpsiyon spektroskopisiyle incelenen foto-indüklenmiş absorpsiyon özelliklerini (PIA) rapor ediyoruz. Aynı π konjuge sistemine sahip olan DiBrPDI-DIA ve DiBrPDI-2EH, kloroformda (λ_{abs}:527 nm ve λ_{PL}:552 nm) özdeş soğurma ve PL davranışlarına sahiptir. Ancak, aynı koşullarda hazırlanan filmlerde DiBrPDI-DIA ($\lambda_{PL\text{-}DIA}$:596 nm; PLQY:73.4%), DiBrPDI-2EH'den ($\lambda_{PL\text{-}2EH}$:649 nm; PLQY:36.7%) daha yüksek bir PLQY ile daha kısa dalgaboyunda bir PL spektruma sahiptir. Chem3D pro yazılımı kullanılarak PDI türevlerin bağ uzunlukları ve körfez bükülme açıları hesaplanmıştır. DiBrPDI(DIA)'daki 2,6-diizopropilfenil grubunun imid konumlarından yaklaşık 6.8 Å'lık bir mesafeyi uzattığı ve yığılmaya karşı daha küçük 2EH grubuna göre daha etkili sterik koruma sağladığı belirlenmiştir.

Anahtar kelimeler: Katı hal fluoresans, perilen diimid, fs-geçici soğurma spektroskopisi, sterik koruyucu.

1. Introduction:

Solid state optical properties of singlet emitters are important for numerous photonic technologies due to their fast fluorescence radiative response to excitation and high photoluminescence quantum yields (PLQYs) [1–7]. Perylene diimide derivatives (PDIs) from the rylen family [8,9] (Figure 1) are one of the high performance fluorophore groups, possessing an extended π conjugation system with 2 naphthalene units substituted from the peri positions that support customisability for many photonic applications. Their excellent semiconductor properties are adjustable for specific desired application by chemical modifications of the peri or ortho positions

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[1] Corresponding author: erkanaksoy@iyte.edu.tr. ORCID: 0000-0002-0083-2574[123], 0000-0002-1752-8675[2], 0000-0002-5529-9682[3], 0000-0002-0784-8640[3], 0000-0002-1081-0803[5].

[9–11] (Figure 1), targeting material properties such as fluorescence wavelengths, highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) energy levels, and reduction potentials. The resulting materials find extensive use in organic light emitting diode (OLED) or organic solar cells (OSC) applications, with particularly valuable properties including their high emission efficiency (PLQY ≥ 90%), effective absorption of visible light ($\varepsilon \geq 10^4$ $M^{-1}cm^{-1}$), strong n type characteristic, high electron affinity and mobility, and high optical electronic and thermal stability [10,12–17].

In some photonic technologies (OLED, downconverters or fluorescence solar concentrators) which require the use of fluorescence, planar PDI structures make them susceptible to dimer formation and aggregation caused quenching (ACQ). Thus, they can lose almost all of their PLQY in film [14], limiting their successful use in these technologies. Different approaches have been reported to minimize the film phase ACQ of polycyclicaromatic compounds such as those containing the perylene or pyrene core [18,19]. One of them is direct chemical modification [14,20,21], while dispersal in an optical host material with low doping rates of emitter can also avoid ACQ [10,22]. As high concentrations are often required in applications though, the more commonly used method to reduce the aggregation of PDIs is by connecting steric groups from imide or bay positions [14,20,23–25]. Although structures attached from the imide group do not participate in π conjugation system of PDI, electron donating groups (containing amine or carbazole) can interact with the PDI core in photoinduced electron transfer processes and quench PDIs' PL by directly, affecting their photophysical properties [26,27]. Therefore, groups to be attached from imide positions should be carefully selected according to their potential applications.

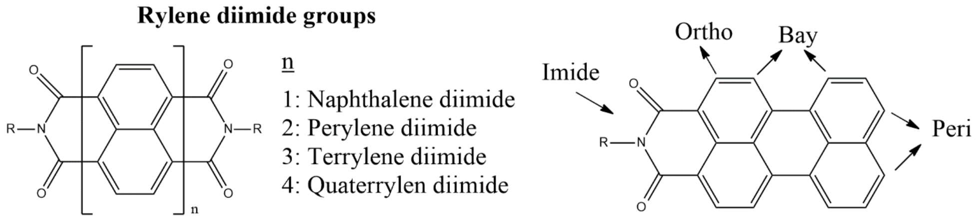


Figure 1. Some of the Rylen family members (left), and positions of Perylene for chemical modification (right).

In this work, film and solution phase photophysical properties of isomeric mixtures of 1,7 (~%83) and 1,6 (~%17) -dibromo perylene diimides [(N,N′-bis(2-ethylhexyl)-1,7(6)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DiBrPDI-2EH*)* and N,N′-bis(2,6-diisopropylphenyl)-1,7(6)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DiBrPDI-DIA), (shown in Figure 2)] were investigated. Bay-unsubstituted N,N′-bis(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic diimide (PDIref) was also used as a reference for comparison with the compounds subject to this study. DiBrPDIs exhibiting the same absorption and PL in the solution phase exhibited different PL in the film phase, due to the different steric bulk of their imide groups. PLQY measurements and computer simulations of the molecular geometries demonstrate that the DIA substituents provide superior steric protection of the PDI core from ACQ, leading to the improved film phase properties of the DiBrPDI-DIA material. The Br bay-substituents are also found to assist in preventing aggregation compared to PDIref, disrupting π-π stacking interactions by twisting the otherwise planar PDI core.

2. Experimental

2.1. Materials and instruments:

Host polymer Zeonex 480-R and 2,6-diisopropylaniline were purchased from Zeon corporation and Acros Organics, respectively. Ethanol (absolute), hydrochloric acid, bromine, iodine, hexane, chloroform ($CHCl_3$), toluene, dichloromethane, N,N-dimethylformamide, acetic acid, 1-methyl-2-pyrrolidinone, silica gel (0.040–0.063 mm) were obtained from Sigma-Aldrich and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was purchased from Fluka. Synthetic details of N,N′-bis(2-ethylhexyl)-perylene-3,4,9,10-tetracarboxylic diimide (PDIref), N,N′-bis(2-ethylhexyl)-1,7(6)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DiBrPDI-2EH) and N,N′-bis(2,6-diisopropylphenyl)-1,7(6)-dibromoperylene-3,4,9,10-tetracarboxylic diimide (DiBrPDI-DIA) (Figure 2) used in this study were previously reported [4,10,28].

Analytik Jena S 600 UV-Vis and Edinburgh Instruments FLS920P spectrophotometers were used for absorption, photoluminescence (PL), photoluminescence quantum yield (PLQY) and emission lifetime (τ) measurements (time-correlated single photon counting-TCSPC). EPL-470 model (λ_{ext}; 472.4 nm, Pulse width: 86.9 ps) laser and an integrating sphere were utilized for lifetime (ns) and absolute PLQY measurements (λ_{ext}: 492 nm), respectively.

Excited state properties of DiBrPDIs were examined by fs-TAS in 480-800 nm range. The first part of the 1030 nm output from the fs amplifier PHAROS was used as the pump for the excitation (It was used to generate 343 nm via the third harmonic generation.). The second part of the 1030 nm output was focused on a 2 mm sapphire plate to create a continuum of white light, which was used as a probe to observe the excited state behaviour of DiBrPDIs.

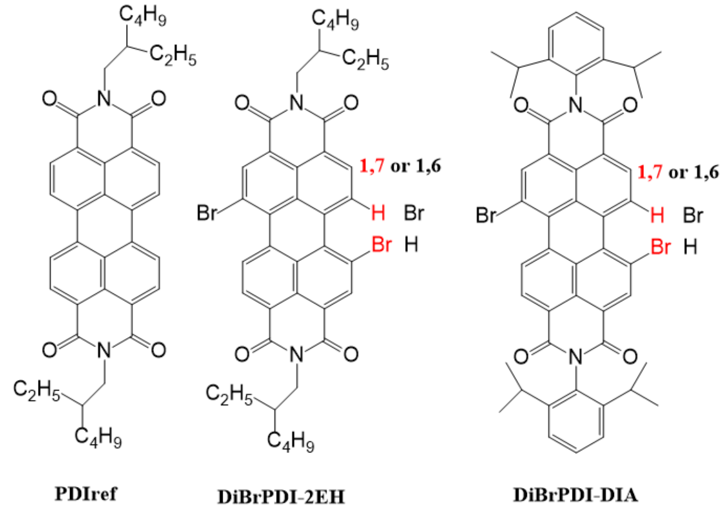


Figure 2. Molecular structure of PDIref, 1,7 (or 6) DiBrPDI(2EH) and DiBrPDI(DIA).

2.2. Preparation of neat and drop cast films

Neat films of DiBrPDIs were prepared on cleaned microscope slides by spin coating at 1500 rpm for 60 s of their solutions with the concentration of 5 mg/mL $CHCl_3$. Drop casted polymer film preparations of DiBrPDIs were started by introducing the perylene derivatives in 100 mg/mL Zeonex solution (in toluene) at different doping ratios (x: 0.25, 0.5. 1, 2, 3 and 5 wt.%) and stiring for 2 hs. Then, prepared DiBrPDIs-Zeonex solutions were drop casted on microscope slides and were dried for 30 min at 60°C.

3. Results and Discussions:

3.1 Steady state Absorption and PL properties of DiBrPDIs:

The absorption and PL spectra of PDIref, DiBrPDI-2EH and DiBrPDI-DIA (1.0×10^{-6} M in $CHCl_3$) and PL spectrum of neat films are given in Figure 3a-b. PDIref presented maximum absorption wavelength (λ_{abs}^{max}) and maximum PL wavelength (λ_{PL}^{max}) values of 526 nm and 532 nm, respectively. Although the λ_{abs}^{max} values of DiBrPDI-2EH and DiBrPDI-DIA are almost the same with PDIref, the Stokes shifts determined with these derivatives increased to 25 nm. This difference is attributed to the inductively electron donating property of the halogenic group (-Br) present at the bay positions of DiBrPDI-2EH and DiBrPDI-DIA as the N-substituents of PDIref and DiBrPDI-2EH are the same. Indeed, it is elsewhere reported that different alkyl chain or simple phenyl ring substituents (like 2EH and DIA) at the imide position have minimal effect on the properties of PDIs in dilute solution [29,30]. This contrasts strongly with the quenching effects via photoinduced electron transfer observed when using amine group-containing substituents [26,27].

Since DiBrPDI-2EH and DiBrPDI-DIA have the same π conjugation system, they present identical absorption and PL in solution phase. Their λ_{abs}^{max} and λ_{PL}^{max} are 527 and 552 nm, respectively. Despite all these similarities, the diisopropyl groups of DIA were found to prevent the π-π interaction of PDI cores more than 2EH based groups. Indeed, the DiBrPDI-DIA group displayed less evidence of aggregate formation and retained a higher energy PL than the DiBrPDI-2EH in neat film (Figure 3b). The λ_{PLmax}^{Film} of PDIref, DiBrPDI-DIA and DiBrPDI-2EH are 638, 596 and 649 nm, respectively. The PL peak of DiBrPDI-DIA in the film phase, which corresponds to the 2nd peak of the PL curve of its in the solution, suggests both excimer-dimer behaviour and significant self-reabsorption of the emitted light (dilute solution absorbance and emission spectra have some overlap). Both materials showed more evidence of aggregate PL at longer wavelengths (649 nm 2EH peak, 700 nm DIA peak) [14]. Also, the difference in their PL spectra of thin films is consistent with photographs of the pure material under UV light. DIA displayed higher energy ‘orange-red PL’, while 2EH displayed lower energy ‘red PL’ directly (Figure 3c). PDIref, on the other hand, exhibited a lower energy and broadened PL spectrum in film phase (Figure 3-a) due to the aggregation at lower energy states [14].

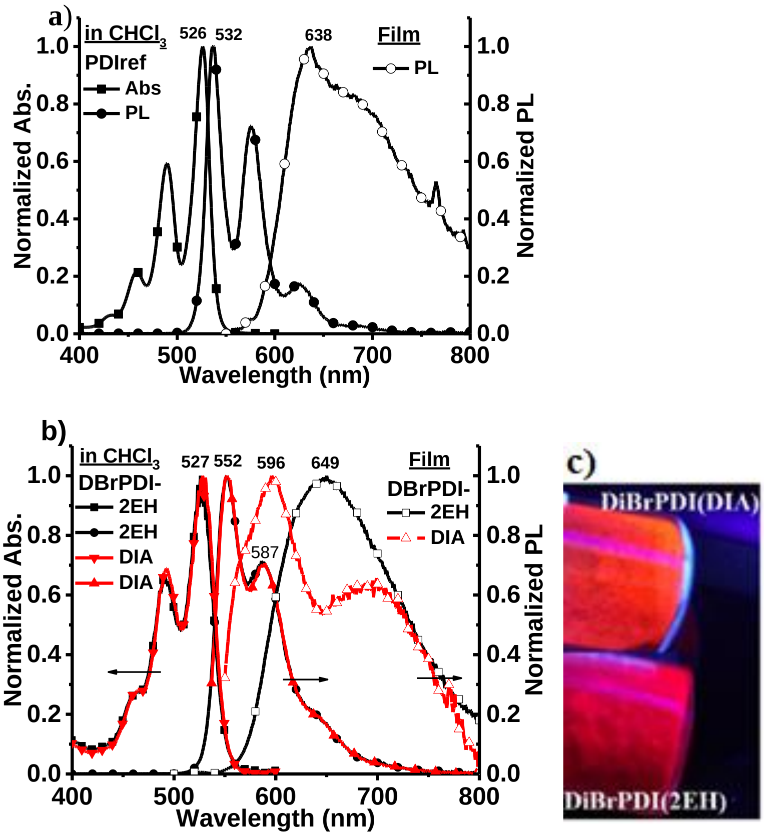


Figure 3. Absorption and PL spectrums of a) PDIref and b) DiBrPDI-2EH, DiBrPDI-DIA in dilute chloroform and neat films and c) image of orange-red (DiBrPDI-DIA) and red (DiBrPDI-2EH) powders fluorescence under UV light excition.

PDIref is well known to undergo aggregation (also named PDIref in this referenced study, [14]), and was qualitatively compared to the DiBrPDI derivatives doped with different wt.% in Zeonex (optically transparent) host material under UV light (Figure 4). Even in the 0.25% doped film of PDIref, it was found that the green-yellow PL of its monomer [PDIref PL - [13,14] was quenched (low intensity) and the PL color shifted predominantly to red-wavelength after 1% doping concentrations. DiBrPDI-2EH exhibited a fairly high PL at 1% doping rate due to sterically shielding bromines compared to planar PDIref. DiBrPDI-DIA containing both bromine and DIA was more successful at preventing aggregation and exhibited remarkably stronger PL up to 5% doping concentration. In addition to these photographs demonstrating relative PLQY under UV light excitation, quantitative measurement of the absolute PLQY of the 5% doped DiBrPDI-2EH and DiBrPDI-DIA films are found to be 36.7% and 73.4%, respectively. The resulting PLQYs combined with the observed relative emission brightness in the photographs, reveal the different aggregation tendencies of the films (Figure 4).

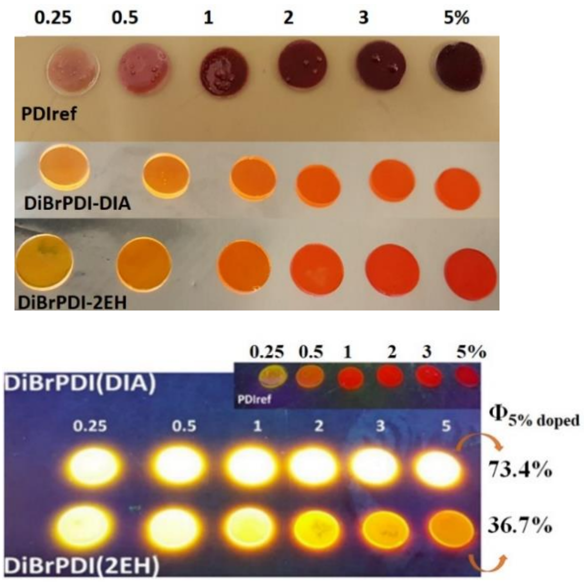


Figure 4. Images of PDIref, DiBrPDI-DIA and DiBrPDI-2EH films (in Zeonex host material with different wt.%s) under day light (upper) and UV light (lower) excitation.

PL spectra and lifetime decay of drop casted films (5 wt.%) are given in Figure 5. DiBrPDI-DIA and DiBrPDI-2EH exhibited λ_{PL}^{max} at 592 and 630 nm, respectively. In addition, average lifetime of DiBrPDI-2EH and –DIA were found to be 8.54 and 6.03 ns (Table 1), respectively. As described above (images of films in Figure 4), DiBrPDI-DIA exhibited higher energy PL (592 nm, 2.09 eV) with higher PLQY than that of DiBrPDI-2EH (630 nm, 1.96 eV) and a faster lifetime, due to its lower aggregation tendency [14].

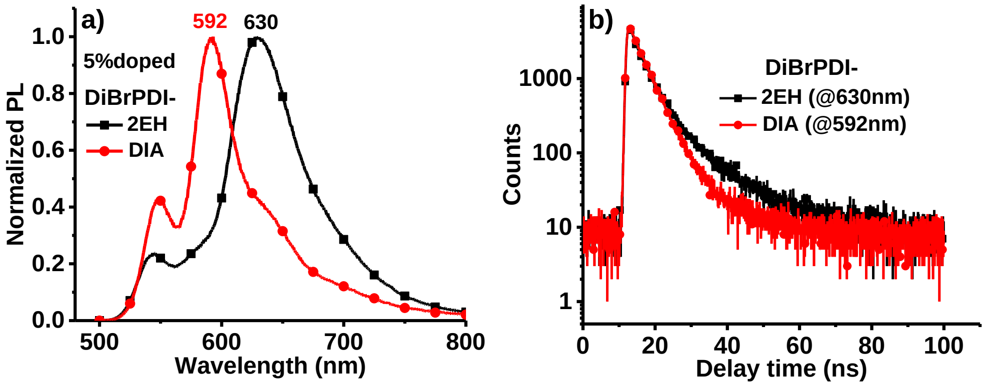


Figure 5. a) Emission spectra and b) PL lifetime (ns) decays of DiBrPDI-2EH and DiBrPDI-DIA films (5 wt. % doped in zeonex).

Table 1. Average lifetime value (τ) of DiBrPDIs at film phase (%5 doped in zeonex).

DiBrPDI-	τ_1 (ns)	%	τ_2 (ns)	%	τ_3 (ns)	%	**τ average (ns)**
2EH	1.57	8.84	4.16	69.39	13.26	21.77	8.54
DIA	3.87	95.36	16.48	4.64	-	-	6.03

3.2. 3-D study of steric shielding

In order to better explain the aggregation reducing effects of bromine and imide groups, a computational 3D study of brominated and unbrominated (-H) 2EH and DIA were carried out by using MM2 (molecular mechanics method) energy minimization in Chem3D Pro 12.0 software [10] (Table 2). In the accessible lowest-energy conformer, the DIA group occupies a volume that extends 6.8 Å perpendicular to the PDI core plane. In 2EH, this distance is only 6.0 Å. However, flexible 2EH group (alkyl group) can also rotate freely around the PDI plane, while rigid DIA groups cannot because of the presence of carbonyl groups. This causes the triisopropyl groups to stay perpendicular to the plane, providing better shielding from dimer interactions in the concentrated films.

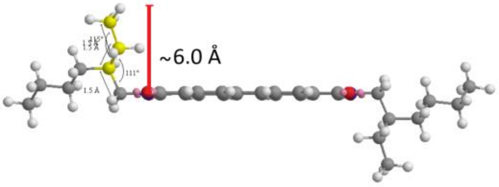
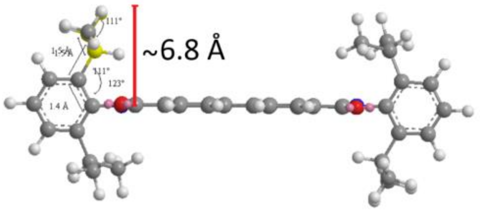
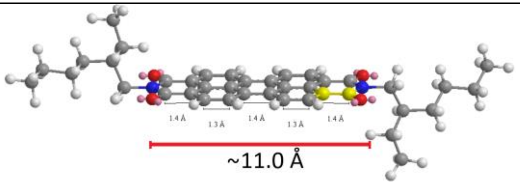
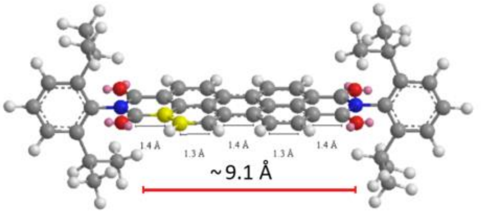
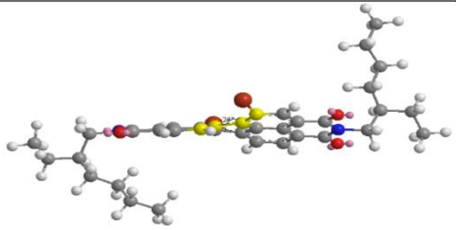
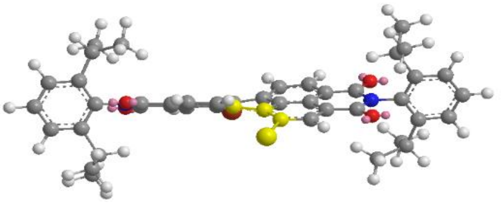
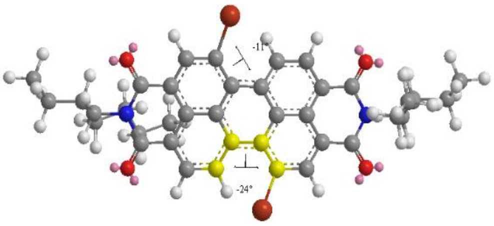
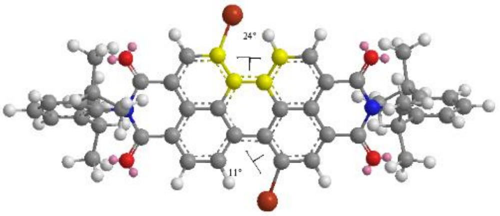
In addition to the N-substitution effect, it was observed that the PDI core twisting angle changed due to the binding of bromine atoms compared to the flat core of unsubstituted PDI. The change in core angle is also consistent with XRD results for the isolated crystal of dibromoPDI from a previously reported study [31]. This effect also caused a steric shielding among PDIs, with the twist frustrating close packing interactions. This is why the DiBr2PDI-2EH material displays better resistance to ACQ than PDIref, despite possessing the same imide group. DiBrPDI-DIA exhibited yet superior PLQY even at doping as high as 5% in films, as it has shielding due to both imide and bay groups, which provide rigid steric protection in contrast to the 2EH group.

3.3. Femtosecond Transient Absorption Properties (fs-TAS) of DiBrPDIs

Excited state properties of DiBrPDI-2EH and -DIA at 1.0 x 10^{-4} M and 1.0 x 10^{-3} M in $CHCl_3$, which exhibit similar behaviour at dilute concentrations (1.0 x 10^{-6} M, Figure 3b), were investigated. More detailed information about the pump–probe fs-TAS technique is detailed in previously reported study [14].

The TAS spectra of DiBrPDI-2EH and -DIA at different delayed time from 20 ps to 5.8 ns are summarized in Figure 6. Both DiBrPDIs exhibited only singlet state transitions at 1.0 x 10^{-4} M and 1.0 x 10^{-3} M. In summary, the DiBrPDIs showed overlap of both ground-state bleach (GSB) and stimulated emission (SE) signals at 529 nm (for -2EH), 532 nm (for -DIA), and also SE of fluorescence $S_{0-1'}$ at 575 nm (for -2EH) and 579 nm (for -DIA) at 1.0 x 10^{-4} M. Two intense PIA peaks, which were similar to each other, of DiBrPDI-2EH and -DIA were observed at 734 and 741 nm at 1.0 x 10^{-4} M, respectively. They exhibited similar features in the PIA regions (probably S1 to S2 or S3) as well as in the steady state features. Also, the PIA lifetimes of -2EH and -DIA were 4.3 and 4.6 ns, respectively (Table 3), in reasonable agreement with emission lifetimes in zeonex. These values are also similar to PDI derivatives reported with monomer structure [10,14,25]. At 1.0 x 10^{-3} M of DiBrPDIs, both PDIs' GSB-SE first overlap peaks shifted to a few nm longer wavelengths because of highly absorption of white light continuum of probe by DiBrPDIs [14] while the SE peaks did not change. No new peaks belonging to intersystem crossing transitions (which would otherwise reveal the presence of triplet states) were observed. It was observed that both DiBrPDIs were resistant to excimer-dimer at 1.0 x 10^{-3} M with no excessive increase in any PIA lifetime and no change observed at the SE peaks. The PIA lifetimes of DiBrPDI-2EH and -DIA were 5.0 and 4.8 ns, respectively (Figure 7 and Table 3), with larger values at these higher concentrations indicative of the formation of some excimer or dimer states [14].

Table 2. 3D study of brominated and unbrominated PDI-2EH and PDI-DIA.

Bay group.	PDI-2EH	PDI-DIA
-H	 =PDIref	
-H	 =PDIref	
DiBr		
DiBr		

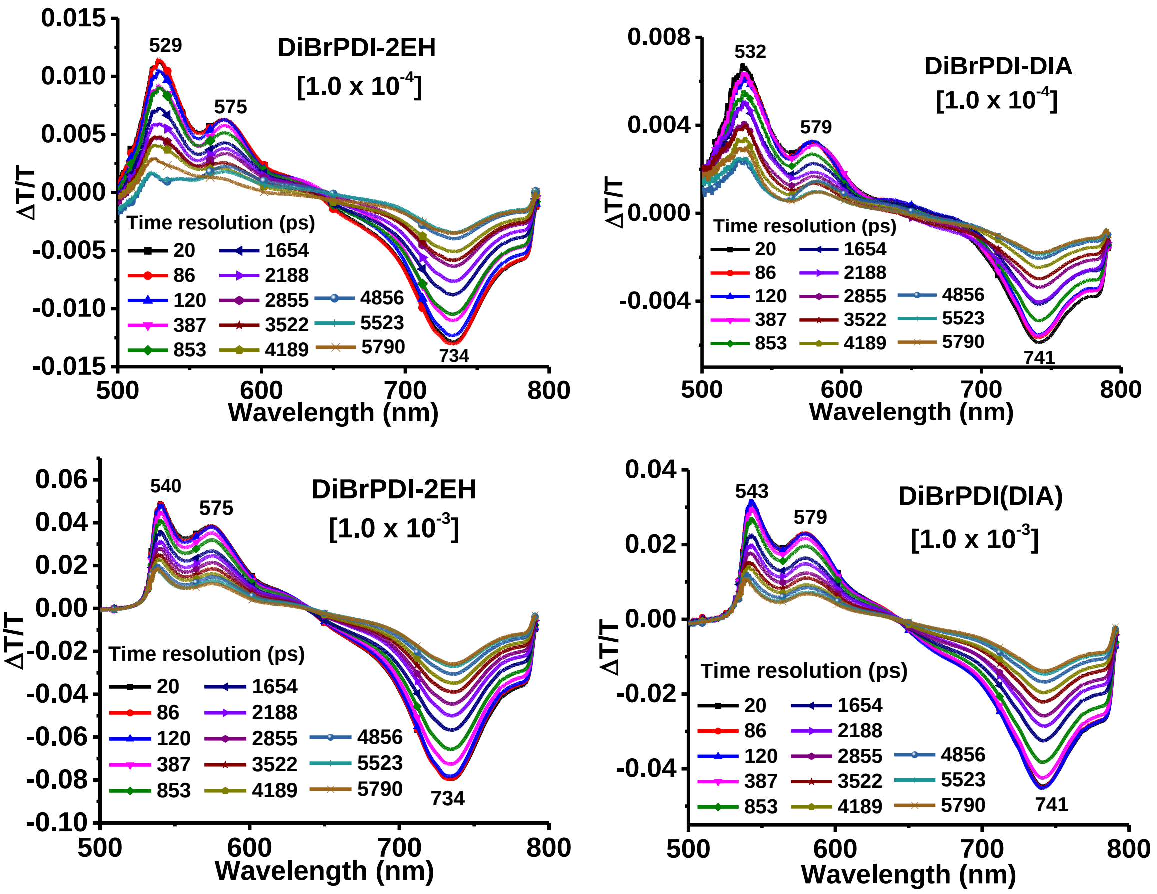


Figure 6. TAS curves of DiBrPDI-2EH and DiBrPDI -DIA at 1.0 x 10^{-4} and 1.0 x 10^{-3} M concentrations in $CHCl_3$.

Table 3. Average lifetimes (ns, weighted average of mono or biexponential fit) for PIA peaks of DiBrPDIs at 1.0 x 10^{-4} and 1.0 x 10^{-3} M concentrations.

	DiBrPDI-2EH		DiBrPDI-DIA	
Concentration	1.0 x 10^{-4} M	1.0 x [10^{-3}] M	1.0 x 10^{-4} M	1.0 x 10^{-3} M
PIA (λ_{PIA}^{max}) Lifetime (ns)	4.3 ± 0.05	5.0 ± 0.01	4.6 ± 0.01	4.8 ± 0.09

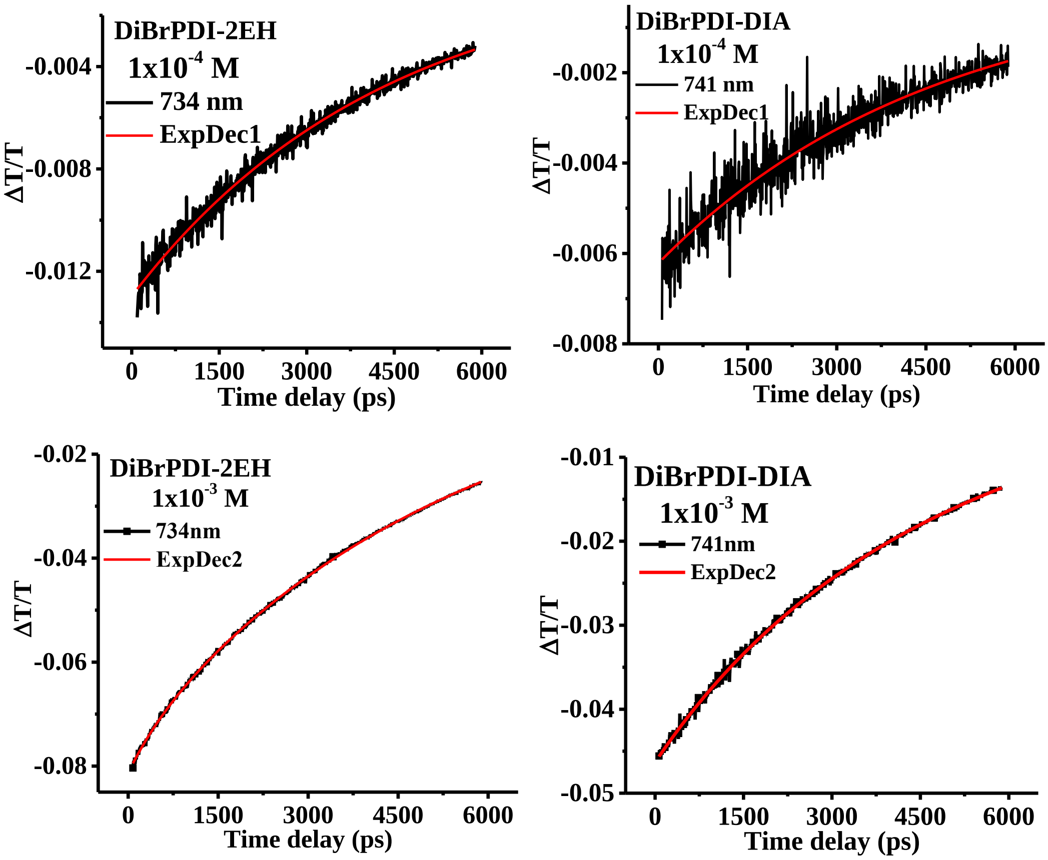


Figure 7. PIA peak decays of DiBrPDIs at 1.0 x 10^{-4} and 1.0 x 10^{-3} M concentrations in $CHCl_3$.

4. Conclusion

Unshielded planar PDIs often do not exhibit adequate photophysical properties in the film phase because of ACQ limiting many photonic applications. Especially in down-conversion studies, low rates of doping of PDIs must be made into an optical-resin in order to preserve the PLQYs of PDIs in the film phase. In this study, films and solutions of reference PDI and sterically shielded DiBrPDI derivatives with different steric imide groups were produced and compared. While both dibromoPDI derivatives exhibited very high luminescence compared to the reference at 0.25 and 5 % wt doped, DiBrPDI-DIA was able to exhibit very high PLQY even at a very high doping rate of 5 % due to the superior space filling steric protection of the DIA group. This structural property was confirmed by chemical computations. In this way, target white light downconverters may in future be produced by coating a single or several times instead of repeatedly coating from low concentrations [22], alongside enabling many other photonic applications of these materials.

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