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Concentration effects on emission of bay-substituted perylene diimide derivatives in a polymer matrix

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ABSTRACT

Reduction of emission quenching in a gain medium based on a dye-doped organic matrix at high doping concentrations is of crucial importance for achieving efficient lasing with a low threshold. In this study, concentration effects on emission properties of bay-substituted perylene diimide derivatives, considered to be promising for lasing application, are reported. Dynamics of emission spectra, quantum yield, lifetime, amplified spontaneous emission, amplified spontaneous emission threshold and photostability of the bromo-, 2,4-di(trifluoromethyl)phenyl- and 4-pyridyl-substituted perylene diimide derivatives in polystyrene films are explored in a wide range of diimide concentrations from 0.06 wt % to 8 wt %. For comparison, emission properties of an unsubstituted perylene diimide derivative are also investigated. An importance of the bay substitution in the perylene diimides is emphasized through i) reduction of emission concentration quenching, which allows for 3–4 times higher doping levels as compared to the doping with an unsubstituted perylene diimide, ii) observation of amplified spontaneous emission at one order of magnitude higher concentrations with reasonable thresholds (up to 200–300 kW/cm^2), and iii) high photostability, which is one order of magnitude higher than that of other bay-substituted perylene diimides and various organic compounds. The results imply potential of the perylene diimide substitution at the bay position for tailoring molecular packing and emission properties via steric hindrance effects, and suggest the bay-substituted perylene diimides may be useful as active media for lasing applications.

1. Introduction

Perylene tetracarboxylic acid diimide, in short, perylene diimide (PDI) derivatives are among the most widely investigated organic dyes. Due to their chemical inertness, photo- and thermal stability as well as excellent tinctorial properties, PDIs initially received a lot of interest as potential dyes and pigments, meanwhile after 1950 they found high grade industrial applications, particularly as automotive dyes [1,2]. Furthermore, owing to their well expressed π-electron conjugation, PDI derivatives attracted much attention as organic electronic materials [3–7]. For the development of electronic applications, solubility of the chromophores became an important issue, and therefore, various strategies dealing with the incorporation of solubility-increasing groups into various positions of the perylene structure have been proposed [8,9]. Nowadays PDI derivatives constitute one of the most widely studied molecular systems, which, owing to a unique combination of physical properties found applications in almost all areas of organic optoelectronics. Based on their high stability, optical and redox properties PDI derivatives are employed in electrophotography (xerographic photoreceptors) [10] and photovoltaics [11,12]. High electron affinity of rylene diimide dyes and close chromophore packing in the solid state make them one of the best organic electron-transporting materials for thin film transistor applications [13,14]. Recently, air-stable thin film transistors have been demonstrated [15]. Additionally, extended π-conjugation and rigid molecular structure of the PDI core results in a high fluorescence quantum yield (QY), thus making PDI derivatives attractive as laser dyes [4,16–21], e.g. famous perylene orange and red dyes, fluorescent light collectors and labels [22,23], fluorescence sensors [24] as well as emitters in organic light emitting diodes (OLED) [7,25,26]. It is important to note that PDIs are among the most photostable organic electronic materials reported in the literature, which is

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advantageous for optoelectronic applications, in particular for laser applications [3,21]. When considering the PDI derivatives studied in this work, the latter application is at our primary focus.

PDI-based compounds specifically designed for emissive layers of light-emitting devices are expected to show high fluorescence QY, and preferably, tunability of the emission wavelength. Although the imide nitrogen substituted PDI derivatives demonstrate excellent thermal- and photo- stability, and show superior fluorescence QY (up to 100%), they have negligible spectral tunability [9]. Moreover, a planar structure of the PDI core facilitates formation of H-type (face-to-face stacked) aggregates in concentrated solutions and the solid state, which generally results in significant fluorescence quenching. An alternative way for tuning the absorption/emission wavelength either by modification of the diimide groups or by substitution at the perylene core (bay-substitution) have been proposed [9,21]. The modifications of the diimide group via the ring opening of the imide moiety, replacement of the carbonyl groups by imino groups and their incorporation into a six-membered rings [9], alteration of the ring sizes, enabled reasonable spectral tuning through extended conjugation and in some cases yielded luminescence efficiency close to 100%. However, efforts in achieving amplified spontaneous emission from the derivatives with modified diimide group were unsuccessful [21]. PDI derivatives substituted at the bay positions of the perylene core (Fig. 1) using C—O, C—C and C—N coupling are considered to be promising [27], owing to the fact that the steric hindrance and perylene core twisting induced by the bay substituents could prevent π—π stacking [28], and thus, reduce luminescence quenching.

Organic materials targeted for laser applications must have high QY, enhanced photostability, short radiative lifetimes and negligible absorption in the spectral region of stimulated emission ensuring low stimulated emission threshold [29]. Unfortunately, the vast majority of the chromophores do not show stimulated emission in their neat form or at high concentration in a polymer matrix because of the deteriorated film quality, decreased photostability or concentration quenching effects. There are a few reports on the novel molecular systems expressing low-threshold amplified spontaneous emission in the form of neat films [30], however, photostability of the neat films of the materials employed still remains as one of the most important challenges. Thus optimization of the chromophore concentration in the matrix and the concentration effects on the amplified spontaneous emission threshold as well as on the photostability are of crucial importance for laser application and need to be thoroughly investigated.

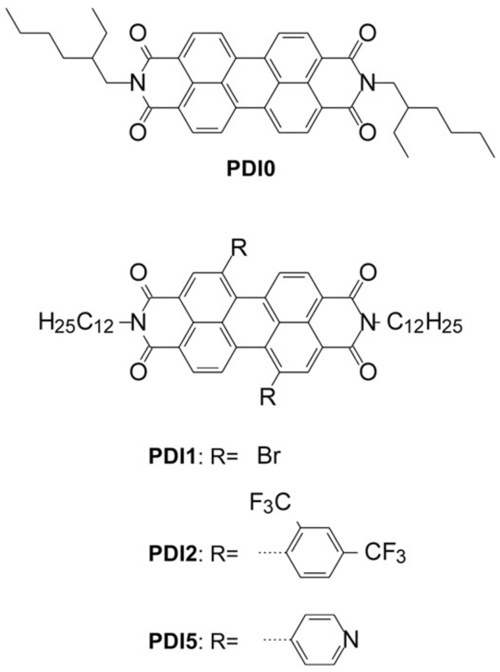

Fig. 1. Chemical structures of the PDI derivatives.

Recently, we reported on the synthesis and thermal and optical properties of a novel series of PDI derivatives with various electron-accepting substituents at the bay positions of the perylene core [31]. The bay substitution-induced effects on the photophysical properties of the PDIs in dilute solutions and neat films were investigated in great detail. In this work, we focus on the emission properties of the analogous series of bay-substituted PDIs dispersed in a rigid polymer (polystyrene) matrix placing a special emphasis on the chromophore concentration effects. For comparison the properties of unsubstituted (at the bay position) PDI dispersed in polystyrene are also investigated. By taking into account absorption and fluorescence spectral properties of the PDIs, we discuss the bay substitution-induced steric hindrance, which predetermines intermolecular packing, resulting exciton coupling and migration properties. We also examine the impact of different bay substituents on the concentration dependence of the amplified spontaneous emission (ASE), ASE threshold, emission wavelength and photostability in PDI-doped polymer films.

2. Experimental details

2.1. Materials and methods

Detailed synthesis of the perylene diimide derivatives under study with electron-deficient bromo (PDI1), 2,4-di(trifluoromethyl)phenyl (PDI2), and 4-pyridyl (PDI5) bay substituents (see Fig. 1) were described elsewhere [31]. The commercially available unsubstituted compound (PDI0) was explored as a reference. The chromophore concentration effects on emission properties were studied by dispersing the PDI derivatives in a solid polystyrene (PS) matrix at different concentrations ranging from 0.06 to 8 wt %. The PDI-doped polystyrene (PDI/PS) films were prepared by dissolving the PDIs and PS at appropriate ratios in toluene solutions and casting the solutions on quartz substrates.

Absorption and fluorescence spectra of the PDI/PS films were measured using back-thinned CCD spectrophotometer PMA-11 (Hamamatsu). Fluorescence of the films was excited by 150W xenon arc lamp coupled to monochromator to produce emission at 520 nm with a full width at half maximum of 13 nm. Fluorescence QY of the films was estimated by using integrating sphere (Sphere Optics) coupled to the CCD spectrometer [32,33]. Fluorescence transients of the films were measured using time-correlated single photon counting system PicoHarp 300 (PicoQuant GmbH). Pulsed excitation at 1 MHz repetition rate was provided by picosecond diode laser with the pulse duration of 70 ps and the emission wavelength of 375 nm. ASE measurements were carried out by exciting the films with 150-μm wide laser stripe focused on the film surface near its edge by using a cylindrical lens [34]. Spontaneous emission amplification, which occurred due to population inversion created along the excitation stripe was determined from the superlinear increase in the emission intensity measured from the sample edge as a function of excitation power density. Frequency-doubled (532 nm wavelength) radiation of Nd^{3+}:YAG laser with pulse duration of 5 ns and pulse repetition rate of 10 Hz served as an excitation source in the ASE experiments. To determine the ASE threshold the excitation power density was varied by several orders of magnitude from 1 to 6000 kW/cm^2.

3. Results and discussion

3.1. Origin of the excited states

Polymer films doped with dye molecules constitute nontrivial objects with optical properties varying from those of molecular-like to crystal-like depending on doping concentration [21,35,36]. Strong concentration effects might occur as a result of various excitation energy-transfer processes that can be critical for the dye performance in a device [19,37,38]. To disclose molecular and exitonic spectral properties of the PDI-doped polymer films, absorbance and fluorescence spectra of the PDI0/PS, PDI1/PS, PDI2/PS and PDI5/PS films at relatively low 0.06–0.5 wt % and high 8 wt % doping concentrations were investigated (Fig. 2). 0.06 wt % doped PDI0/PS film exhibits spectral behavior typical of single perylene diimide molecules, which have a narrow 0–0 absorption band at 531 nm accompanied by well-resolved set of vibrational satellites (spaced by 0.17 eV) originating from several internal breathing modes [39]. Corresponding fluorescence bands appear as a mirror-image of the absorption bands and are Stokes-shifted by only 5 nm. This indicates high rigidity of the PDI molecular structure. Similarly, absorption spectra of the PDI1/PS, PDI2/PS and PDI5/PS films doped with the bay-substituted PDIs at low concentration closely resemble those obtained for dilute THF solutions with non-interacting PDI molecules [31]. A small red shift (of about 5 nm) of the PDI/PS spectra in respect to the PDI solution spectra can be attributed to the different surrounding media of the PDI molecules. Generally, the bay substitution with electron-withdrawing groups causes only slight modifications to the spectral properties of isolated PDI molecules, and consequently, only a minor reduction of photoluminescence QY in dilute solutions [31,40]. On the other hand, the bay substitution was reported to have dramatic effect on the spectral properties of the PDIs in a solid state [40]. Indeed, absorbance and fluorescence spectra of highly doped PDI1-5/PS films (solid lines in Fig. 2) demonstrate remarkable modifications of the spectral profiles and maxima positions. The modifications of the excitonic properties are mainly related to different molecular packing caused by the steric hindrance effects. The substitution at the bay position induces two major changes to the planar geometry of the unsubstituted PDI. The first is a twisting of the perylene core by 14-36 degrees depending on a bay-substituent, which generally reduces intermolecular interaction [40], whereas the second geometry modification, i.e. large torsions of the bay substituents in respect to the core, arises from the steric hindrance at the bay regions. Large torsion angles (~70°) between the planes of the perylene core and aromatic bay substituents revealed by DFT calculations inhibit close packing of the PDI2 and PDI5 molecules thus also diminishing intermolecular coupling in a solid state [31]. Meanwhile, owing to the planar geometry of PDI0, the highly doped PDI0/PS film shows a very broad absorption spectrum with a significantly red shifted lowest energy band at about 625 nm indicating strong excitonic coupling. We attribute this band to J-like (Jelley–Scheibe) aggregates in accordance with the previous reports, where the absorption band located in the range of 621–629 nm for similar PDI derivatives with ethyl-heptyl groups at the imide nitrogen position were attributed to the J aggregates [41,42]. Similarly to changes in absorption, the fluorescence spectrum of the PDI0/PS film also exhibits pronounced red shift of the emission maximum from 536 nm to 652 nm followed by increase in the chromophore concentration from 0.06 to 8 wt % confirming strong excitonic coupling. The emission spectrum is Stokes-shifted by 27 nm and shows a well-expressed vibronic structure typical for excitonic spectrum. It is well-known that the bay substitution of PDIs leads to significant transformation of the excitonic interaction. Incorporation of bromine at the 1,7 position of the PDI (compound PDI1) was shown to result in the core twisting by about 24 degrees and reduction of excitonic coupling [31,40]. This is evidenced from the less broadened absorption spectrum and blue shifted lowest-energy absorption band (at about 585 nm) as compared to that due to aggregates of planar PDI0 (see Fig. 2a,b). Bulky 2,4-di(trifluoromethyl)phenyl bay substituents in the PDI2 give rise to both geometrical modifications (PDI core twisting and torsions of the bay-substituents) of the molecule resulting in even stronger suppression of the excitonic interaction. The absorption spectrum of highly doped PDI2/PS film is similar to the molecular spectrum obtained at low chromophore concentration and shows just a slight broadening (Fig. 2c). Correspondingly, the main fluorescence band of highly doped PDI-2/PS film experiences much smaller red shift in respect to the lightly doped PDI-2/PS film as compared to the red shifts of the rest films and a continuous trend of fluorescence band shifting from 625 nm (for PDI0/PS) to 589 nm (for PDI2/PS) can be observed (see solid lines in Fig. 2a–c). Increase of the doping concentration in PDI5/PS film with dopant PDI5 having less polar 4-pyridyl bay substituents also causes a slight broadening of the absorption spectrum with the lowest-energy band at about 560 nm (Fig. 2d), which is attributed to the face-to-face or rotationally displaced face-to-face molecular packing (H-type aggregates) [40]. The fluorescence spectrum of highly doped PDI5/PS film is strongly Stokes-shifted and features a broad unstructured band at about 659 nm. This signifies remarkable lattice reorganization leading to exciton self-trapping, which is commonly observed for face-to-face packing of large aromatic molecules [39,43].

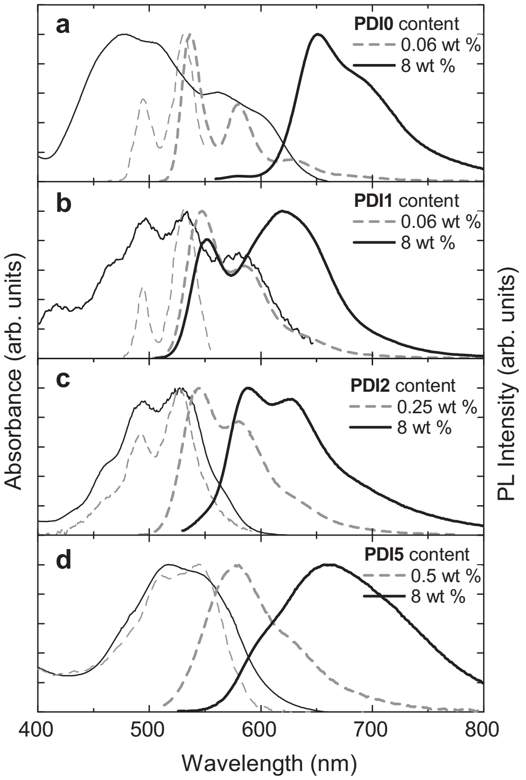

Fig. 2. Normalized absorption and fluorescence spectra of a) PDI0/PS films, b) PDI1/PS films, c) PDI2/PS films and d) PDI5/PS films with relatively low 0.06–0.5 wt % (dashed lines) and high 8 wt % (solid lines) PDI-doping concentrations.

3.2. Fluorescence quenching

Increase in the PDI concentration causes formation of aggregates leading to remarkable fluorescence quenching of the PDI/PS

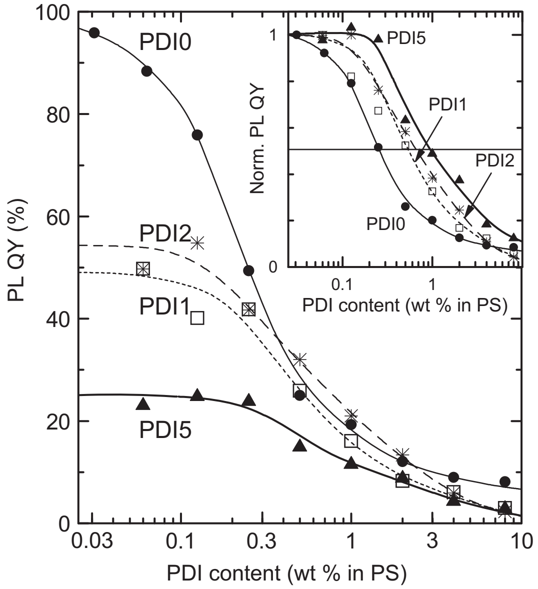

Fig. 3. Fluorescence quantum yield of the PDI0/PS films (dots), PDI1/PS films (rectangles), PDI2/PS films (stars) and PDI5/PS films (triangles) as a function of PDI-doping concentration. Lines are guides for the eye. Inset depicts normalized PL QY results of the PDI/PS films vs PDI content.

films. Fluorescence QY dependences of the PDI0/PS, PDI1/PS, PDI2/PS and PDI5/PS films on the PDI content for the 0.06–8 wt % range are depicted in Fig. 3. At low PDI concentration the reference film PDI0/PS attains QY of 96% that is similar to the value obtained for non-interacting PDI0 molecules in dilute solutions. On the other hand, the films doped with the bay-substituted PDIs (PDI1, PDI2 and PDI5) at low concentration express somewhat lower QY values as compared to those obtained in their solutions. Note that the QY values ranging from 73% to 47% were obtained for the PDI1–PDI5 compounds, respectively, in their dilute solutions [31] and the values from 56% to 26% were estimated for the same compounds in PS films at low doping concentration (Fig. 3). This discrepancy of the QY values in solution and polymer film at low doping level might be attributed to the sensitivity of the bay-substituted PDIs to the polarity of the surrounding media as was reported for the bromine bay-substituent [44]. Generally, the reduction of fluorescence QY with incorporation of bay-substituents in dilute media is known to originate from intramolecular charge-transfer induced by the difference in a polarity of the PDI core and the bay-substituents [31,44].

All the studied PDI derivatives dispersed in a polymer matrix at high concentration display very low PL QY (2–8%) (Fig. 3). This decrease of PL QY with increase of the doping concentration suggests formation of aggregate states acting as molecular emission quenchers. Obviously, fluorescence quenching is dependent on the bay-substituents, which govern the molecule arrangement in solids via the steric hindrance effects. As it can be seen from the inset of Fig. 3 half of the fluorescence intensity of the unsubstituted planar PDI0 molecules quenches already at 0.24 wt % doping content, whereas fluorescence concentration quenching for the bay-substituted non-planar PDI1, PDI2 and PDI5 compounds occurs at about 0.6 wt %, 0.6 wt % and 0.9 wt % doping content, respectively. The quenching at the 3–4 times higher doping levels for the polymer films doped with the bay-substituted PDIs is a result of reduced intermolecular interaction due to the less tight packing of the films.

To reveal the dominating excited state relaxation processes and to support fluorescence QY decrease due to concentration quenching effects, fluorescence transients of the PDI/PS films at various PDI concentrations were measured. At low PDI doping concentrations (<0.5 wt %) the transients could be fairly well approximated by using single-exponential decay model, whereas at high PDI concentration at least two decay components were required to fit the data. Correspondingly, only the average fluorescence lifetime (τ_{avg}) for high PDI content of 8 wt % is given in Table 1. Based on measured fluorescence lifetime and QY results radiative (τ_{rad}) and nonradiative (τ_{nrad}) decay time constants for the PS films with low PDI content were evaluated. Fluorescence lifetimes of the bay substituted PDI1–PDI5 compounds embedded in a PS matrix were found to be slightly longer (see Table 1) than those obtained for the same compounds in THF solution [31]. The radiative relaxation rate was clearly dominant for the isolated molecules of the reference PDI0 compound and this rate determined the character of the excitation relaxation processes in the bay-substituted PDI/PS films at low PDI concentration. At high doping concentration fluorescence lifetime is affected by the nature of exciton-vibronic coupling and exciton transfer processes. Interestingly, an increase in the PDI-doping concentration resulted in the 2-fold shortening of the fluorescence lifetime for the PDI1/PS and PDI2/PS films, meanwhile in more than 2-fold extension of the lifetime for PDI0/PS and PDI5/PS films. The result can be clarified by the differences in molecular packing of the aggregates indicating the presence of self-trapped excitons in more tightly packed PDI0/PS and PDI5/PS films as it was previously revealed from the excitonic spectral features (see Fig. 2).

3.3. *Amplified spontaneous emission*

Alteration in intermolecular coupling caused by the electron-withdrawing bay-substituents of the PDI compounds severely influences ASE properties of the PDI/PS films. Fig. 4 depicts excitation power dynamics of the edge emission of PDI0-PDI5/PS films in the “thin-stripe” geometry [34]. All the PDI/PS films demonstrate broad spontaneous emission spectra structured with vibronic modes, particularly well-resolved for PD0/PS film, at the lowest pump density. Note that the maxima of spontaneous emission spectra measured from the edge are located at the first vibronic replica if compared with the spectral maxima peaked at the zeroth vibronic mode, which are measured in the usual backscattering configuration. This is caused by the reabsorption of the short-

Table 1
Optical properties of the bay-substituted PDI derivatives (PDI1, PD2 and PDI5) and unsubstituted reference PDI compound (PDI0) dispersed in polystyrene film at low and high doping concentration.

	PDI content in PDI/PS film 0.06–0.5 wt %					PDI content in PDI/PS film 8 wt %			QY_{max}	I_{ASE}^{th} (kW/cm^2)	$t_{0.7}$ (pump pulses)
	λ_{abs} (nm)	λ_{em} (nm)	τ (ns)	τ_{rad} (ns)	τ_{nrad} (ns)	λ_{abs} (nm)	λ_{em} (nm)	τ_{avg} (ns)			
PDI0	495, 531	537, 579	4.9	5.1	123.3	474, 508, 560, 605	650	11.51	0.96	20@0.03 wt %	120×10^3@40 kW/cm^2
PDI1	494, 532	547, 585	6.6	13.4	12.9	496, 534, 580	552, 619	3.10	0.49	69@0.25 wt %	120×10^3@200 kW/cm^2
PDI2	493, 526	545, 581	6.1	11.0	13.4	495, 528	589, 628	2.93	0.55	166@0.5 wt %	25×10^3@300 kW/cm^2
PDI5	510, 545	579	6.7	27.0	9.0	517, 552	662	16.88	0.25	816@0.5 wt %	10×10^3@1600 kW/cm^2

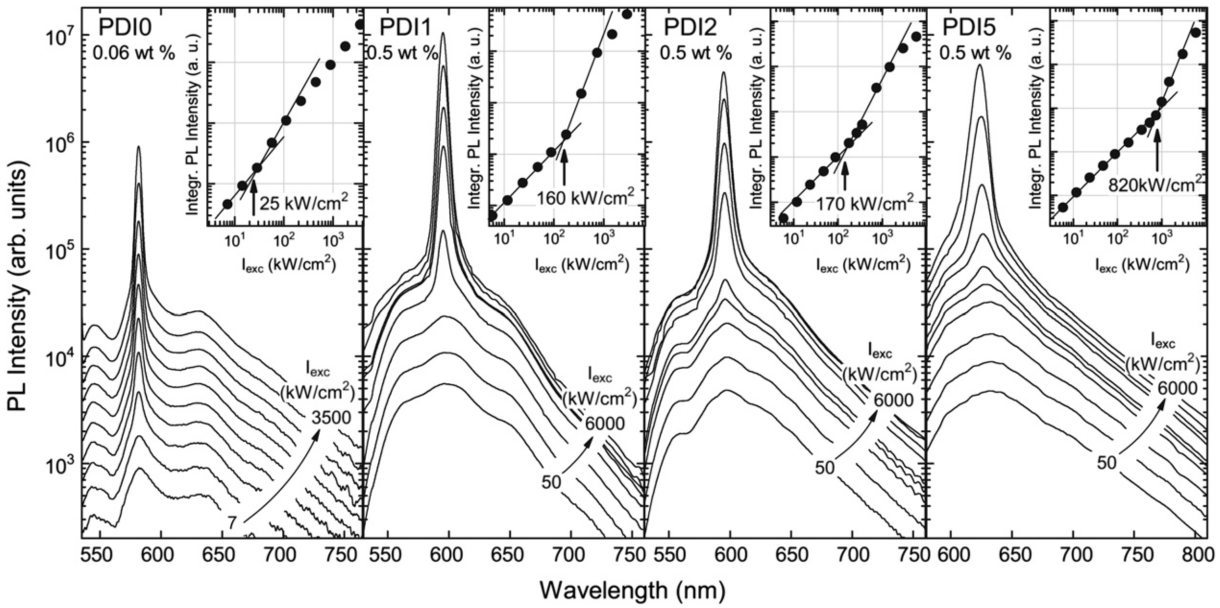

Fig. 4. Excitation power dependence of the edge emission spectra of (a) PDI0/PS film, (b) PDI1/PS film, (c) PDI2/PS film and (d) PDI5/PS film doped with 0.06, 0.5, 0.5 and 0.5 wt % of the PDI, respectively. Insets show integrated fluorescence intensities as functions of excitation power densities. The arrows indicate onset of ASE.

wavelength tail of the emission band. Increase in the excitation power density of the PDI/PS films at a certain point results in the emission band narrowing indicating an onset of ASE. The ASE band emerges at the spectral position of the first vibronic replica, i.e. at the emission band maximum, which is a typical situation for PDI derivatives since absorption in the spectral region of the zeroth vibronic replica is relatively strong [21]. All of the studied bay-substituted PDI derivatives demonstrate pronounced ASE behavior. Substitution at the bay position enables tuning of the ASE wavelength from 581 nm (for unsubstituted PDI0) to 624 nm (for PDI5). Additionally, some tuning of the ASE peak can be accomplished by changing the dye concentration in the PDI/PS films. For example, variation in the PDI5 content from 0.06 wt % to 4 wt % can shift the ASE peak from 596 nm to 626 nm.

The onset of the ASE can also be verified from the integrated fluorescence intensity dependence on the pump density (see insets of Fig. 4). A sudden change in the intensity dependence from linear to superlinear clearly signifies the onset of the ASE and enables estimation of the excitation intensity threshold values (I_{ASE}^{th}) of the ASE for each PDI/PS film at various doping concentrations. I_{ASE}^{th} value is an important parameter describing the feasibility of the material to be employed in lasing systems as an active media. Evidently, an active material featuring lower I_{ASE}^{th} will require lower operating current density, which is critical for the device formation [29,45].

Since the molecule arrangement plays a major role in obtaining high fluorescence QY and stimulated emission in a solid state, detailed investigations of the ASE performance as a function of the concentration of the active material is of great importance. Moreover, these investigations are indispensable for determination of the optimal concentration for laser operation [21]. Essentially, the ASE performance of the PDI derivatives is rather sensitive to the chromophore concentration. PDI derivatives substituted at the imide nitrogen position were reported to show ASE for concentrations ranging from 0.25 to 5 wt % [21,46], whereas the derivatives additionally substituted at the bay position by tert-butylphenoxy or tert-octylphenoxy groups expressed ASE for concentrations ranging from 1.5 to 3 wt % [30,47].

PDI concentration dependencies of the I_{ASE}^{th} of the bay-substituted PDI1–PDI5/PS films as well as unsubstituted PDI0/PS film are depicted in Fig. 5. All of the studied PDI/PS films demonstrate nontrivial ASE behavior with increasing PDI content. At low PDI content I_{ASE}^{th} decreases, while at higher chromophore concentration it increases. Since non-interacting PDI molecules usually exhibit higher fluorescence QY as compared with that of their solids, the onset of ASE initially occurs for the single molecular states. This is also confirmed by the ASE spectral behavior observed in the PDI/PS films with low PDI content (Fig. 4). Increasing PDI content reduces intermolecular separation and thus diminishes optical losses causing lowering of the I_{ASE}^{th}. However, further increase in the PDI concentration results in the formation of aggregated states with absorption in the emissive region of single PDI molecules. As shown in Fig. 3, aggregates of the PDI0–PDI5 derivatives also act as quenchers of molecular emission, and

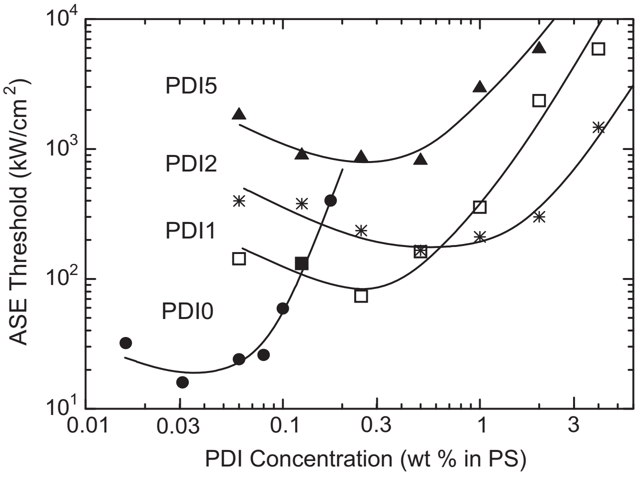

Fig. 5. ASE threshold of the PDI0–PDI5/PS films as a function of PDI-doping concentration. Lines are guides for the eye.

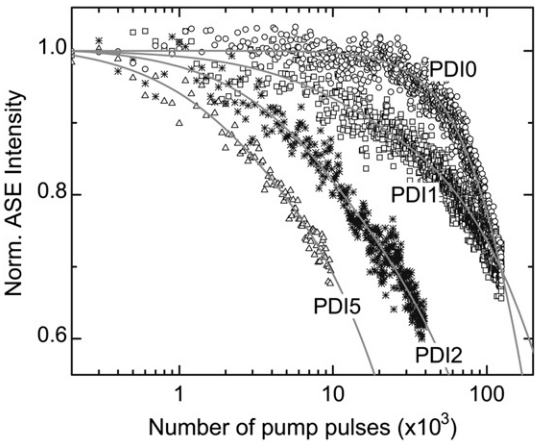

Fig. 6. Normalized ASE intensity dependence on the number of pump pulses for PS films doped with PDI0, PDI1, PDI2 and PDI5 at optimal doping concentration of 0.03, 0.25, 0.5 and 0.25 wt%, respectively. The excitation power densities were 40, 200, 300, and 1600 kW/cm^2, respectively.

consequently, lead to an increase of the $I_{\mathrm{ASE}}^{\mathrm{th}}$. This implies the presence of some optimal chromophore concentration range in the PDI0–PDI5/PS films, where favorable conditions for ASE and minimal $I_{\mathrm{ASE}}^{\mathrm{th}}$ value can be attained. This optimal concentration range for the reference compound PDI0 was determined to be between 0.01 and 0.25 wt %, whereas the minimal $I_{\mathrm{ASE}}^{\mathrm{th}}$ value was estimated to be as low as 20 kW/cm^2. Note that a similar ASE threshold value (15 kW/cm^2) has been reported for the PDI substituted at the imide nitrogen [21]. Although the bay-substituted PDI1–PDI5 derivatives demonstrate remarkably higher $I_{\mathrm{ASE}}^{\mathrm{th}}$ values, they also feature a wider concentration range (0.06–4 wt %) favorable for ASE observation, which is shifted by more than one order of magnitude to higher concentrations (see Fig. 5). The minimal $I_{\mathrm{ASE}}^{\mathrm{th}}$ values of 70 kW/cm^2, 165 kW/cm^2 and 860 kW/cm^2 were obtained for PDI1/PS film doped with 0.25 wt % of bromo-substituted PDI dopant, PDI2/PS film doped with 0.5 wt % of 2,4-di(trifluoromethyl)phenyl-substituted PDI dopant and PDI5/PS film doped with 0.25 wt % of 4-pyridyl-substituted PDI dopant, respectively. $I_{\mathrm{ASE}}^{\mathrm{th}}$ values estimated in previous ASE studies were 300 kW/cm^2 for tert-butylphenoxy and 1500 kW/cm^2 for tert-octylphenoxy bay-substituted PDIs dispersed in polystyrene [21,30,47]. It is worth noticing that the obtained ASE threshold values of PDI1 and PDI2 compounds are the lowest threshold values observed for the bay-substituted PDIs. Although the minimal $I_{\mathrm{ASE}}^{\mathrm{th}}$ is significantly lower for the unsubstituted reference compound PDI0, the ASE is rapidly quenched for the chromophore concentration exceeding 0.25 wt %. 2,4-di(trifluoromethyl)phenyl-substituted perylene diimide derivative (PDI2) can be distinguished by the smallest intermolecular coupling due to the bulky bay-substituents resulting in the greatly extended range of doping concentrations (0.06–4 wt %) favorable for the ASE observation. The latter result infers realization of spontaneous emission amplification in the PDI2/PS films for the PDI2 concentrations up to 2 wt % at reasonably low $I_{\mathrm{ASE}}^{\mathrm{th}}$ values of 200–300 kW/cm^2. High doping levels are required for efficient lasers where dye-doped organic matrices are used as the gain medium.

3.4. Photostability

One of the most attractive properties of perylene diimides is their unique photostability [30]. This property is especially important for practical lasing applications, where sufficiently high photon flux must be maintained. The photostability of the PDI0–PDI5/PS films was investigated by recording the integral ASE intensity as a function of the number of pump pulses at constant pump intensity (see Fig. 6). Twice as high pump intensity as the minimal $I_{\mathrm{ASE}}^{\mathrm{th}}$ for each of the PDI/PS film was used in the photostability measurements. A general tendency of the photodegradation evidenced from a decrease of the total ASE output was observed for all the PDI/PS films. To compare the stability of lasing PDI/PS films it was defined as the number of pump pulses at which the ASE intensity decayed by 30% of its initial (maximal) value. Very good stability lifetime ($t_{0.7}$) of 120×10^3 pump pulses was obtained for the reference compound PDI0 as well as for the bromo-substituted PDI1 compound. These results are comparable to those obtained for commercially available perylene orange laser dye dispersed in various matrices, like organically modified silica (ORMOSIL) [17] or PMMA [20]. On the other hand, PDI2/PS and PDI5/PS films with the bay-substituted PDI dopants degraded remarkably faster with $t_{0.7}$ of 25×10^3 and 10×10^3, respectively, mainly because of the considerably larger ASE thresholds (see Table 1). Despite their weaker photostability, our bay-substituted PDI derivatives (PDI1 and PDI2) demonstrate at least an order of magnitude higher photostability as compared to various other organic compounds including other bay-substituted PDIs such as phenoxy-substituted PDIs [30,47].

4. Conclusions

Concentration effects on the emission properties of the bay-substituted PDI derivatives dispersed in polystyrene matrix at various concentrations were thoroughly explored. Considerable impact of the electron-withdrawing bay substituents on the strength of the excitonic interaction and coupling to the lattice (vibrational modes) was elucidated by studying PDI-concentration dependent spectral dynamics of the PDI/PS films. Bay-substitution-induced significant reduction of the excitonic coupling was attributed to the twisting of the perylene core as well as to the out-of-plane twisting of the bay substituents, which prevented close packing of the neighboring π-electron systems of the perylene core. The bay-substitution was also found to lessen emission concentration quenching of PDI/PS films by allowing 3–4 times higher doping levels (as compared to the doping with unsubstituted PDI) at which half of the initial emission efficiency was still preserved.

Importantly, all of the investigated bay-substituted PDI derivatives doped in polystyrene matrix demonstrated pronounced ASE behavior with the minimal ASE threshold of 70 kW/cm^2 for bromo-substituted PDI, 170 kW/cm^2 for 2,4-di(trifluoromethyl)phenyl-substituted PDI and 820 kW/cm^2 for 4-pyridyl-substituted PDI at an optimal doping concentration of 0.25–0.5 wt %. Although obtained ASE thresholds were significantly higher as compared to that of the unsubstituted PDI (20 kW/cm^2), the bay-substitution favored observation of ASE at one order of magnitude higher concentrations and for a wider concentration range (0.06–4 wt %). Additionally, the bay-substituted PDI derivatives (PDI1 and PDI2) demonstrated about an order of magnitude higher photostability as compared to other various organic compounds including other bay-substituted PDIs. The results demonstrate the potential of the bay-substituted PDI derivatives to be exploited as active media for lasing applications. The bay substitution creates an opportunity for the trade-off between ASE threshold, photostability and charge carrier transfer via modification of molecular properties and packing.

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