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Characterization of novel perylene diimides containing aromatic amino acid side chains

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Abstract

Perylene diimide derivatives have attracted initial interest as industrial dyes. Recently, much attention has been focused on their strong π - π stacks resulting from the large PDI aromatic core. These PDI stacks have distinct optical properties, and provide informative models that could mimic light-harvesting systems and initial charge transfer typical of photosynthetic systems. The absorption property of PDI derivatives may be tuned from visible to near-infrared region by peripheral substitution. We have studied a new class of PDI derivatives with aryl substituents derived from the side chains of aromatic aminoacids (Tyrosine, Tryptophan and Phenylalanine). We have investigated their absorption and the fluorescence properties in a set of organic solvents and established their different tendencies to aggregate in solution despite their solubility. Most aggregation appears to be unordered. One PDI analogue (the one formed from Tyr) in Methanol, however, appears to form J-type aggregates. Based on our results the compounds appear to be promising for future investigations regarding the interaction of these dyes with biomolecules.

Keywords

Perylene diimides; Fluorescence; Aggregation; Fluorescence decay

1. Introduction

Perylene diimides (PDI) have attracted substantial interest for their chemical and photophysical versatility [1–7]. For instance, thermal and light stability as well as a relatively facile synthesis are attractive properties that have been exploited to yield analogues capable of absorbing light over a large portion of the visible spectrum [8]. In addition, PDIs showed increase solubility in solvents and matrices facilitating the development of operational organic semiconductors and photovoltaic materials [2,9–13]. PDIs are attractive options for these applications because they offer the possibility of modulating intra- and intermolecular charge transfer between the typically electron poor

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perylene ring and the peripheral substituents. The π - π^* transition in perylenes has been used as a model for many photophysical studies [8,14–16]. We had previously investigated the properties of a group of 3,9-disubstituted perylenes in organic solvents as well as in aqueous environment in the presence of globular proteins [15]. These analogues, however, presented challenges in terms of solubility and the results led to the conclusion that they did not provide suitable candidates for either organic semiconductor or as fluorescent ligands for biomolecules [15].

This study characterizes a novel class of PDI and the effect that the aromatic amino acids substituents [17] (Phenylalanine, F, Tyrosine, Y and Tryptophan, W) produce on the photophysical properties of PDIs. For comparative purposes, the isobutyl amino acid (Leucine, L) PDI analogue was also examined. Compared to the 3,9-substituted perylenes that were previously investigated [15], the PDIs show significantly higher solubility in polar solvents, thus providing the potential for more widespread application not only as organic photovoltaic materials but also for potential biophysical applications. One of the motivations for investigating these novel compounds is that the presence of amino acid side chains may increase their interaction with biomolecules, in particular proteins. An increased interaction with biomolecules would, in turn, provide potential applications in optoengineered materials [18] and biophysics. Improved solubility is also an important factor in the use of these compounds for the development and future fabrication of devices for solar energy conversion [2,19]. The novelty of the compounds, however, requires a basic characterization of their photophysical properties. We have recorded absorption and emission spectra as well as the fluorescence lifetimes of these compounds in various polar solvents. Our measurements revealed that the derivatives have the characteristic absorption and fluorescence features of the unsubstituted PDI with transition energies that are lower by ~ 0.35 eV (or 50–60 nm) compared to the 3,9-disubstituted compounds that were characterized previously [15] and would potentially complement them in absorbing visible radiation. In other words, a mixture of the two types of compounds would cover a range of wavelengths between ~ 400 and 530 nm. We also characterized the emission properties and estimated the change in dipole moment between the ground and excited state, which remains quite small as expected for symmetrically substituted compounds. We demonstrated that the interaction between the aromatic substituents and the solvents influences the aggregation of the compounds.

2. Experimental methods

2.1. Chemicals

PDI-Phenylalanine (PDIF), PDI-Leucine (PDIL), PDI-Tryptophan (PDIW) and PDI-Tyrosine (PDIY), (Scheme 1) were synthesized as described below. Acetone, Dimethyl Sulfoxide (DMSO), Ethanol, Pyridine, Tetrahydrofuran (THF), and Methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification.

2.2. Synthesis of PDIs derived from amino acid with aryl side groups and Leucine

As mentioned in the introduction perylene diimide derivatives PDIF, PDIW, PDIY, and PDIL, which were derived from aryl amino acids Phe, Trp, and Tyr, and isobutyl amino acid

Leu, respectively, were prepared using a modified procedure reported for the preparation of PDI analogues [20].

Each amino acid (2.2 Eq) was added to perylene tetracarboxylic acid dianhydride (250 mg) with imidazole (1 g) and the mixture was melted and stirred at 120 °C for 30 min. After cooling to room temperature, the mixture was dissolved in water and filtered. The filtrate was acidified (6 M HCl) and washed with EtOH (5–10 washes) to remove residual imidazole, as detected in ^1H NMR spectra. The samples were dried under high vacuum to obtain products in modest to excellent yields (36–97%). The products appeared as reddish/burgundy colored amorphous solids. Upon examination by ^1H NMR spectroscopy (DMSO- d_6), each product exhibited a characteristic methine proton at 5.4–6.1 ppm, in addition to other signals expected for the PDI analogues. Thus, PDIF exhibited the appropriate ^1H NMR signals, but those of the perylene core were broadened, concealing the expected spin–spin splitting (Supplemental Material Figure S1A). PDIY exhibited the expected aryl signals, but the methylene proton signals of the side chain were apparently hidden under the solvent signal at 3.9 ppm. Addition of two drops of D_2O to the sample induced shifting of the methylene proton signals to 3.3 and 3.5 ppm, and eliminated the phenolic OH signal at 9.6 ppm (Supplemental material Fig. S1B). PDIW exhibited highly broadened perylene ^1H NMR signals and they were shifted upfield of the typical positions, presumably due to stacking-induced aggregate formation. The perylene signals of this sample emerged upon warming to 65 °C (Supplemental material Fig. S1C). PDIL exhibited the expected ^1H NMR signals including the downfield doublets for the perylene core (8.4 and 8.7) ppm. These latter signals also exhibited adjoining shoulders, probably also a consequence of aggregation in the sample (Supplemental material Fig. S1A).

2.2.1. PDIF—Yield: 82%; Mp > 300 °C, ^1H NMR (DMSO- d_6): δ = 8.52 (bs, 4H), 8.34 (bs, 4H), 7.21 (d, J = 7.40, 4H), 7.13 (t, J = 7.60, 4H), 7.09 (t, J = 7.30, 2H), 5.92 (dd, J = 5.50, 9.75, 2H), 3.61 (d, J = 5.40, 2H), 3.58 (d, J = 5.30, 2H). ^{13}C NMR (DMSO- d_6): δ = 171.1, 162.4, 138.4, 133.4, 131.0, 129.5, 128.6, 128.1, 126.9, 124.9, 123.1, 121.84, 56.5, 34.7. IR (cm^{-1}): 1693, 1652, 1590, 1574. HRMS–ESI (m/z) calcd for $\text{C}_{42}\text{H}_{26}\text{N}_2\text{O}_8$ [$\text{M}-\text{H}^+$] $^-$ 685.1616 found 685.1616.

2.2.2. PDIY—Yield: 36%; Mp > 300 °C, ^1H NMR (DMSO- d_6): δ = 9.06 (bs, 4H), 8.28 (bs, 4H), 7.01 (d, J = 8.1, 4H), 6.54 (d, J = 8.3, 4H), 5.89 (dd, J = 5.6, 10.1, 2H), 3.49 (dd, J = 5.3, 14.3, 2H), 3.35 (dd, J = 5.2, 14.2, 2H). IR (cm^{-1}): 1752, 1728, 1590, 1505, 1405. HRMS–ESI (m/z) calcd for $\text{C}_{42}\text{H}_{26}\text{N}_2\text{O}_{10}$ [$\text{M}-\text{H}^+$] $^-$ 717.1515 found 717.1517.

2.2.3. PDIW—Yield 96%; Mp (dec) 273 °C. ^1H NMR (DMSO- d_6 ; 65 °C): δ = 8.03 (d, J = 7.6, 4H), 7.68 (bs, 4H), 7.15 (m, 4H), 6.90 (m, 2H), 6.02 (dd, J = 6.1, 9.4, 2H), 3.70 (m, 4H). ^{13}C NMR (DMSO- d_6): δ = 171.4, 162.5, 136.4, 133.4, 131.2, 128.2, 127.9, 125.1, 122.0, 121.4, 118.9, 111.8, 110.5, 54.0. IR (cm^{-1}): 1730, 1687, 1650, 1592, 1574, 1455, 1435. HRMS–ESI (m/z) calcd for $\text{C}_{46}\text{H}_{28}\text{N}_4\text{O}_8$ [$\text{M}-\text{H}^+$] $^-$ 763.1834 found 763.1831.

2.2.4. PDIL—Yield: 97%; Mp > 300 °C, ^1H NMR (DMSO- d_6): δ 8.70 (d, J = 5.84, 4H), 8.45 (d, J = 7.36, 4H), 5.58 (dd, J = 5.10, 8.70, 2H), 2.10 (m, 4H), 1.59 (m, 2H), 0.98 (d, J = 6.45, 6H), 0.91 (d, J = 6.49, 6H). ^{13}C NMR (DMSO- d_6): δ = 172.3, 162.2, 134.3, 130.9,

128.4, 124.4, 123.2, 122.0, 22.1, 38.7, 23.3, 25.6. IR (cm^{-1}): 1695, 1646, 1591, 1434. HRMS–ESI (m/z) calcd for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_8$ $[\text{M}-\text{H}^+]^-$ 617.1929 found 617.1929.

2.3. Sample preparation

Although the NMR spectra indicate a large degree of aggregation at room temperature, we were able to obtain concentrated stock solutions of the compounds in the organic solvents used in this study. Solubility of these compounds in moderately to highly polar solvents was certainly much larger than for the 3,9-disubstituted perylenes studied previously [15] which did not dissolve at all. The increased solubility of the compounds was judged by the presence of well-structured absorption and emission spectra (see “Results and discussion”) whereas the 3,9-disubstituted perylenes did not yield any noticeable absorption spectrum [21] in polar solvents. All samples were prepared and handled under dim light conditions by dissolving the solid perylene analogues into a known volume of each solvent of interest to form a stock solution which was left equilibrating for 30 min. A small volume of the stock was diluted in the same solvent before recording the absorption spectrum. For fluorescence experiments, the concentration of each sample was adjusted as to yield an optical density at the excitation wavelength <0.15 in order to ensure a uniform light distribution within the 1 cm optical path-length of the quartz cells and prevent nonlinear effects arising from changes in the geometry of the detection.

2.4. Absorption spectroscopy

Absorption spectra were recorded using a dual beam Agilent Cary 100 spectrophotometer (Agilent Technologies Inc., Santa Clara, CA) at 2 nm resolution and 600 nm/min speed. Spectra, corrected for the baseline, were recorded in the 350–700 nm interval. Baseline absorbance spectra for all solvents were recorded and subtracted from the corresponding spectra of the perylene analogue solutions to obtain corrected absorption spectra. The absorption spectra were recorded after each dilution using 3.5 ml quartz cells (NSG Precision Cells, Farmingdale, NY).

2.5. Fluorescence spectroscopy

Steady-state fluorescence spectra of PDIF, PDIL, PDIW, and PDIY in various solvents were recorded using an AB2 double-monochromator fluorimeter (Thermo Scientific, Waltham, MA) at 1 nm/s and 4 nm bandpass in excitation and emission. The high voltage to the photomultiplier was set in the range of 780–850 V and was kept constant throughout each experiment. The excitation wavelength was set at 457 nm, which in these compounds corresponds to the vibronic band ($0 \rightarrow 2$) of highest energy. This λ_{ex} was selected for two reasons: i) it enables us to collect the emission spectrum of all the vibronic levels of the $S_1 \rightarrow S_0$ transitions and ii) it corresponds to the wavelength of the pulsed source used for fluorescence lifetime experiments. Fluorescence spectra were recorded from 465 nm to 700 nm, in order to avoid the contribution of the stray light from the excitation source.

2.6. Fluorescence lifetime decay

Fluorescence decay lifetimes were measured using a time-correlated single photon counting instrument (Fluorocube, Horiba JobinYvon, Edison, NJ) with a 457 nm pulsed LED

(NanoLED-293, Horiba JobinYvon, Edison NJ) light source having a 1 ns pulse width and 1 MHz repetition rate. Decays were recorded at the emission maximum of each PDI with a 32 nm bandwidth.

3. Data analysis

3.1. Transition dipole moment

The magnitude of the excited-state dipole, which is indicative of the intramolecular charge distribution, was established using the Lippert–Mataga method [22]. The theory predicts a linear relationship between the Stokes shift (i.e., the difference between the frequency of the maximum in absorbance and the one in emission, $\bar{\nu}_A - \bar{\nu}_E$, of the lowest vibrational transition) and the orientation polarizability function $\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$ (where ε is the dielectric constant of the solvent and n is the index of refraction) according to the following equation:

$$\bar{\nu}_A - \bar{\nu}_E = \frac{2(\Delta\mu)^2}{hca^3} \Delta f + \text{constant} \quad (1)$$

where μ , is the change in electric dipole moment of the molecule between the excited state and the ground state, h is the Planck's constant, c is the speed of light in vacuum and a is the Onsager cavity radius [23]. Eq. (1) establishes that μ can be estimated from the slope of the plot of $\bar{\nu}_A - \bar{\nu}_E$ vs. Δf by measuring the absorption and emission spectra of a molecule in various solvents and using tabulated values for the dielectric constant and the index of refraction of the solvents.

3.2. Fluorescence lifetime decay

The fluorescence decay lifetime of the protein was analyzed using the deconvolution software DAS6 (Horiba Scientific). Without entertaining a detailed discussion which can be found elsewhere [24,25], the software uses an iterative re-convolution of the source time profile of the instrument, $G(t)$ or prompt, with the theoretical fluorescence decay which is modeled as a sum of exponentials

$$F(t) = \sum_i A_i e^{-\frac{t}{\tau_i}} \quad (2)$$

where A_i is the weighted amplitude (fractional value between 0 and 1) and τ_i is the lifetime of the i -th fluorescent component. $G(t)$ is recorded from a scattering sample that does not fluoresce (in this case a 1 mg/ml suspension of glycogen in DI water). Both $F(t)$ and $G(t)$ are recorded at a sampling rate $<2.0\%$ of the repetition rate of the pulsed source in order to avoid non-linear effects in the acquisition [24]. The convolution of $F(t)$ and $G(t)$ is fitted to the experimental decay curve, $I(t)$, by iterative change of the amplitude and lifetime parameters, using the least-squares method to optimize the fitting parameters. The quality of the fit is determined by ensuring that the χ^2 statistical parameter is between 1 and 1.5 and the Durbin–Watson parameter is between 1.8 and 2.0 [25].

3.3. Fluorescence quantum yield (Φ_f)

Fluorescence quantum yields were calculated using the direct method which calculates Φ_f by comparison with the emission of a reference molecule of known fluorescence quantum yield [24]. In order to obtain more accurate results, the calculation of Φ_f with this method typically requires the use of a reference compound with absorption, emission and solubility characteristics as close as possible to the one of the chromophore that one wants to characterize. In this case, unsubstituted perylene diimide provides the best option as it has been used as a reference chromophore for several decades [26] and has absorption and emission spectra similar to those of the PDIs. Using this method Φ_f is calculated as

$$\Phi_f = \Phi_R \frac{I_f n_f}{I_R n_R} \quad (3)$$

where Φ_R is the fluorescence quantum yield of the reference, I is the fluorescence intensity calculated as the area of the fluorescence spectrum after normalization for the optical density at the excitation wavelength, and n is the refractive index of the solvent.

4. Results and discussion

4.1. Absorption spectroscopy

The UV-vis spectra of PDIF, PDIL, PDIW, and PDIY (Fig. 1), in most solvents, show the typical features of perylene [27] absorption with three peaks (associated with the $0 \rightarrow 0$, $0 \rightarrow 1$ and $0 \rightarrow 2$ vibrational modes of the perylene ring [27]) separated, in this case, by ~ 1 , $370 \pm 80 \text{ cm}^{-1}$ with decreasing intensities ($I_{0 \rightarrow 0} > I_{0 \rightarrow 1} > I_{0 \rightarrow 2}$, Table 1). These features indicate negligible effects of the substituents and a visible spectrum dominated by the perylene diimide moiety.

As a function of aryl-substitute and solvent, the spectra show similarities and some interesting differences. All compounds show consistently large and well-structured absorption in THF and DMSO with the former being the most blue-shifted spectrum and the latter the most red-shifted. The position of the peaks (Table 2) correlates with the dielectric constant which for this series of solvents is largest ($\epsilon = 46.7$) for DMSO and smallest ($\epsilon = 7.56$) for THF [28]. Previous experimental and computational research indicated that values of $\frac{I_{0 \rightarrow 0}}{I_{0 \rightarrow 1}} > 1.5$ are consistent with the presence of monomers [29]. This is certainly the case, for all PDIs discussed here, in THF and DMSO as well as in other solvents (Table 1), with few exceptions that are going to be discussed below. The presence of narrow peaks is also an indication of monomerization [30]. Thus the width of the $0 \rightarrow 0$ peak was calculated as the ratio between the full-width at half-maximum (FWHM) of the peak determined through direct calculation (or through spectral fitting) and the optical density of the peak ($I_{0 \rightarrow 0}^{max}$).

One can see that in THF and DMSO as well as other solvents where $\frac{I_{0 \rightarrow 0}}{I_{0 \rightarrow 1}}$ near or above 1.5 the value $\frac{FWHM}{I_{0 \rightarrow 0}^{max}} < 10^4$. The correlation between the two values (Table 3) leads us to conclude that when the above conditions are met, the spectra indicate the almost exclusive contribution of monomeric PDIs.

As mentioned earlier there are few interesting exceptions to this behavior (Table 3). PDIF in Pyridine yields $\frac{I_{0 \rightarrow 0}}{I_{0 \rightarrow 1}} = 1.14$ (thus significantly smaller than 1.5) and $\frac{FWHM}{I_{0 \rightarrow 0}^{max}} = 2.48 \times 10^4$ (thus $> 10^4$) which strongly indicate the substantial contribution of aggregation. In Acetone, although $\frac{I_{0 \rightarrow 0}}{I_{0 \rightarrow 1}} > 1.5$, the $0 \rightarrow 0$ peak is significantly broader ($\frac{FWHM}{I_{0 \rightarrow 0}^{max}} = 4.27 \times 10^4$) which suggests aggregation in this solvent as well. Similar parameters in Pyridine are also shown by PDIY and PDIW (Table 3) and indicate a substantial aggregation. PDIY duplicates the same trend in Acetone. Overall the data are consistent with aggregation of the aryl-PDIs in Pyridine and in Acetone (with the exception of PDIW). PDIL, on the other hand does not show any indication of the formation of aggregates in any of the solvents used in this study. Aggregation can be explained by more than one mechanism. Since only the PDIs with aromatic substituents appear to aggregate, it is likely that the interaction among the aromatic residues as well between them and the core perylene ring could be driving the aggregation [31]. On the other hand, several reports on amino acid-substituted PDIs provide evidence for the formation of a network of hydrogen bonds that favors the formation of aggregates [32,33]. A separate discussion should be reserved for PDIY in Methanol (Fig. 1d, insert). Table 1 shows that $\frac{I_{0 \rightarrow 0}}{I_{0 \rightarrow 1}}$ reverses (i.e., becomes < 1) for such mixture. In addition two other unique features (compared to all other spectra reported here) appear: i) the peaks are substantially shifted to lower wavelengths (Table 2) and ii) an additional broad and less intense peak appears with a maximum around 605 nm. As a result of these features the data for PDIY in Methanol are not listed in Table 3 since there is no correspondence with the spectra of the other compounds. An absorption spectrum similar to the one in the insert of Fig. 1d was observed for other PDIs and was attributed to J-type aggregates [34]. The data suggest that in the case of PDIY the formation of the J-aggregates may be possible due to the network of hydrogen bonds that could involve the hydroxyl group of the Tyr residue and the carboxyl group of the core PDI [33]. It is still unclear why this effect manifests only in Methanol.

Based on absorption spectra one can conclude that the aryl compounds have the propensity to aggregate, albeit in different solvents, whereas PDIL appears to be monodispersed in all solvents. With the exception of PDIY in Methanol, the aggregates do not seem to present clear evidence for H- or J-type aggregates whereas PDIY shows features typical of the formation of J-aggregates.

Compared to unsubstituted perylene as well as the 3,9-analogues that we discussed in the past [15], the chromophores presented here show a substantial (50–80 nm) red-shift of the absorption spectrum. The red-shift is consistent with other perylene diimides, thus suggesting that the photophysical properties are dominated by the effects of the two imides groups and is not affected by the aryl substituents. In other words, there does not appear to be electronic coupling among the aromatic rings at the center and at the periphery of the molecule.

4.2. Fluorescence spectroscopy and fluorescence lifetime

Emission spectra of PDIF, PDIL, PDIW, and PDIY were recorded upon excitation at various wavelengths within the absorption spectrum. The emission spectra were not substantially

affected by the excitation wavelength as predicted by the Kasha–Vavilov rule [35] and indicate that the structure of the absorption spectrum is indeed caused by vibrational modes of the same electronic excited state. Therefore, all fluorescence measurements were carried out using $\lambda_{ex} = 457$ nm, which ensures the detection of all the emission vibrational bands (Fig. 2) and is the wavelength of the pulsed source used for the fluorescence lifetime experiments. Overall, the emission spectra have many similarities. The vibronic structure ($0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ transitions) is clear in all spectra, with the last one being often detected as a shoulder at longer wavelengths. Acetone and THF yield the most blue-shifted spectra, whereas Pyridine and DMSO (with the exception of PDIY) yield the most red-shifted spectra for all compounds. Quite surprisingly for the conditions where the absorption spectra indicated the presence of aggregates (PDIF and PDIY in Pyridine and Acetone, PDIW in Pyridine), the fluorescence spectra yield the features expected for monodispersed perylenes. This indicates that the aggregates do not contribute to the emission and only the residual monomeric PDIs do, which suggests the formation of unstructured and large non-emitting aggregates. Normalization for the optical density at $\lambda_{ex} = 475$ nm yields a different intensity which may be representative of differences in fluorescence quantum yield, however because of the likely presence of aggregates and their unknown role in the quenching of the fluorescence of the monodispersed molecules a correlation between the intensities shown in Fig. 2a–c and the quantum efficiency cannot be drawn. Nevertheless, we estimated the fluorescence quantum yield Φ_f using Eq. (3) and unsubstituted perylene as a reference with $\Phi_f = 0.97$ [26]. From the results summarized in Table 4 one notices that the value of Φ_f varies remarkably for the various compounds in the different solvents. The same variability of Φ_f has been reported for other PDIs [29] indicating the influence of solvents on the $S_1 \rightarrow S_0$ transition. From Table 4 one can observe that, on average, the lowest value occurs consistently in DMSO ($\Phi_f = 0.13 \pm 0.06$). The result would be consistent with the efficient fluorescence quenching of the sulfur in the solvent. Conversely, the largest value of Φ_f for all aryl-PDIs as well as PDIL occurs in Pyridine ($\Phi_f = 0.79 \pm 0.17$). This is in contrast with the apparent larger level of aggregation in the former solvent (Table 3) but is consistent with our interpretation that the aggregates do not contribute to the emission spectra (Fig. 2) because: i) their absorption at 457 nm is probably negligible and ii) their size might be too large and unordered to yield the excitonic emission which is known to occur from H-, J- or other types of aggregates [36]. Surprisingly, the emission spectrum of PDIY in Methanol (whose absorption spectrum is an outlier, Fig. 1d) does not reflect the presence of exciton emission expected for J-type aggregates and yields a very large quantum yield.

Stokes shifts were calculated from absorption and emission spectra using the frequencies of the peaks corresponding to the $0 \rightarrow 0$ vibronic transition. The results (Table 5) show a correlation with the dielectric properties of the solvents. On average PDIF exhibited the smaller Stokes shift across the various solvents while PDIY showed the largest Stokes shift (367 ± 21 cm⁻¹ vs. 450 ± 35 cm⁻¹). The Lippert–Mataga method applied to the spectroscopic data yields a relatively linear relationship (with $R^2 > 0.75$) between Stokes shift (ν) of the PDI in different solvents versus the orientation polarizability (f) of solvents (Fig. 3, Table 5). From Eq. (1) an estimate for the value of μ is obtained assuming an approximate Onsager radius of 7 Å for the perylene diimides which is in agreement with previous calculations [37]. As seen in Table 6 the difference in dipole moment between the

ground and the excited state for each compound is relatively small as expected for symmetric molecules such as the ones investigated here [38]. The largest value appears to be the one for PDIW. Therefore, although the indications derived from the absorption spectra and the fluorescence quantum yields do not appear to exactly correlate with f , the Stokes shifts do obey the Lippert–Mataga model. This evidence suggest that the aggregation pattern is not correlated with the dielectric properties of the solvents, but that the monomeric portion of the compounds in each solvent does behave as if it was solvated uniformly by the solvent as expected by the Lippert–Mataga model.

4.3. Fluorescence decay

Fluorescence decay experiments of PDIF, PDIL, PDIW and PDIY show that in all solvents, the decay of emission is monoexponential (Fig. 4) and does not depend on the emission wavelength as expected since the emission proceeds through transitions among different vibrational states of the same electronic states. The deconvolution of the decays using Eq. (2) yields a broad set of values for the emission lifetime. On average the decay in DMSO is faster for all compounds, consistent with the smaller steady state fluorescence (Fig. 2A–D) and likely explained by the strong fluorescence quenching property of the sulfur atom compared to the other solvents [39,40]. Particularly short (<1 ns) is the fluorescence decay of PDIF in DMSO. Particularly long-lived, instead is the decay of the same compound in Pyridine, which is the only one yielding a lifetime >5 ns. All other compounds present lifetimes in the 3.0–4.5 ns. Remarkable is, once again, the lack of correlation with the apparent presence of aggregates. For instance, whereas the absorption spectrum of PDIY (Fig. 1d) in Methanol suggests the presence of aggregates, the emission lifetime is one of the longest recorded (Table 7). This, however, can be explained by the fact that the source used for the lifetime experiments (457 nm) may not excite a sufficient amount of aggregates.

5. Conclusions

We have characterized the absorption and emission properties of a novel set of perylene diimides with aryl substituents and compared it with a non-aryl substituted one. The results indicate a larger solubility in polar solvents than, for instance, 3,9-disubstituted perylenes. Data however also show that the aryl-substituted compounds still form aggregates especially in Pyridine and Acetone. PDIF and PDIY show a greater tendency to aggregate than PDIW. The reason for this tendency is still unclear and it might involve the formation of a hydrogen bond network. The indole in PDIW might be less inclined to form hydrogen bonds than the benzyl in PDIY. PDIF on the other hand could have aggregation driven by the stacking of the highly hydrophobic side chain and the core perylene ring. We have undertaken both molecular dynamic simulation and electron microscopy studies to characterize the aggregates and we hope to provide a detailed model in the near future. The NMR data indicate a large degree of aggregation in DMSO that is not observed in optical measurements, probably because of 3 orders of magnitude dilution of the samples investigated optically. None of the aggregates appears to be structurally organized (i.e., J- or H-type), with the exception of PDIY in Methanol that shows the characteristics of J-aggregation for PDI molecules. The lack of contribution of the aggregates in emission suggests that the aggregates are fairly large so that any absorbed light is redistributed

through internal conversion within the aggregates. The pattern for aggregation as well as the peculiar formation of J-aggregation in PDIY is unclear and currently being investigated with computational models.

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Fig. 1.

(a) Visible absorption spectra of PDIF in various solvents. Absorption intensity of PDIF in Pyridine and Acetone has been increased by a factor of four for a better comparison. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (b) Visible absorption spectra of PDIL in various solvents. Absorption intensity of PDIL in Ethanol and Acetone has been reduced by a factor of two for a better comparison. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (c) Visible absorption spectra of PDIW in various solvents. The inset graph shows a closer look at the PDIW in Pyridine with the same wavelength range as the main graph. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (d) Visible absorption spectra of PDIY in various solvents. The inset graph shows a closer look at the PDIY in Pyridine, Acetone and Methanol with the same wavelength range as the main graph. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2.

(a) Visible emission spectra of PDIF in various solvents. Emission intensity of PDIF in DMSO has been increased by a factor of four for a better comparison. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (b) Visible emission spectra of PDIL in various solvents. Emission intensity of PDIL in DMSO has been increased by a factor of four for a better comparison. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (c) Visible emission spectra of PDIW in various solvents. The inset graph shows a closer look at the PDIW in DMSO, Ethanol, and Methanol with the same wavelength range as the main graph. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (d) Visible emission spectra of PDIY in various solvents. The inset graph shows a closer look at the PDIY in THF, DMSO, and Ethanol with the same wavelength range as the main graph. THF (Black Dashes), Pyridine (Red Dashes), DMSO (Blue Dashes), Acetone (Black Dots), Ethanol (Red Dots), and Methanol (Blue Dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Lippert plots for PDI in various organic solvents. (a) PDIF, (b) PDIL, (c) PDIW, (d) PDIY.

Fig. 4.

Representative fluorescence lifetime decay of PDIF (Black), PDIL (Red), PDIW (Blue) and PDIY (Pink) in acetone. The linearity of the decay in this logarithmic scale is an excellent indicator of the monoexponential decay of the dyes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Scheme 1.

Schematic representation of the PDI derivatives. The amino acid residues are represented in the insert.

Table 1

Vibronic peak ratios.

	THF	Pyridine	DMSO	Acetone	Ethanol	Methanol
<i>Absorption peak ratios</i>						
F	0 → 10 → 0	1.67	1.14	1.64	1.86	1.64
	0 → 20 → 1	3.04	2.44	2.80	7.00	2.89
L	0 → 10 → 0	1.61	1.45	1.62	1.65	1.57
	0 → 20 → 1	2.56	2.59	2.69	2.83	2.46
W	0 → 10 → 0	1.58	1.05	1.58	1.63	1.44
	0 → 20 → 1	2.54	2.67	3.03	2.22	2.14
Y	0 → 10 → 0	1.62	1.25	1.58	1.37	1.58
	0 → 20 → 1	2.57	2.78	2.66	2.66	2.66
<i>Emission peak ratios</i>						
F	0 → 10 → 0	2.48	2.09	2.25	2.68	2.27
L	0 → 10 → 0	2.48	2.61	2.59	2.36	2.18
W	0 → 10 → 0	1.31	2.14	1.25	1.78	1.54
Y	0 → 10 → 0	2.48	2.09	2.39	2.69	2.29

Table 2

Summarized absorption and emission peaks of the PDIs in various solvents.

		Dielectric constant	Absorption (nm)	Emission (nm)
F	THF	7.58	456	487
			456	523
			487	532
			487	571
			487	588
L	Pyridine	12.4	465	495
			465	529
			495	539
			495	583
			495	583
W	DMSO	46.7	463	493
			463	530
			493	541
			493	583
			493	583
Y	Acetone	20.7	452	484
			452	520
			484	531
			484	570
			484	570
Y	Ethanol	24.5	457	487
			457	523
			487	534
			487	574
			487	574
Y	Methanol	37.7	456	486
			456	522
			486	533
			486	573
			486	573
Y	THF	7.58	455	486
			455	523
			486	532
			486	572
			486	572
Y	Pyridine	12.4	462	494
			462	531
			494	541
			494	583
			494	583
Y	DMSO	46.7	461	492
			461	530
			492	541
			492	583
			492	583
Y	Acetone	20.7	454	485
			454	520
			485	531
			485	570
			485	570
Y	Ethanol	24.5	456	487
			456	522
			487	536
			487	573
			487	573
Y	Methanol	37.7	454	486
			454	522
			486	534
			486	573
			486	573
Y	THF	7.58	457	488
			457	523
			488	527
			488	562
			488	562
Y	Pyridine	12.4	458	504
			458	525
			504	533
			504	575
			504	575
Y	DMSO	46.7	463	494
			463	530
			494	540
			494	576
			494	576
Y	Acetone	20.7	455	486
			455	522
			486	532
			486	561
			486	561
Y	Ethanol	24.5	456	489
			456	524
			489	540
			489	579
			489	579
Y	Methanol	37.7	459	487
			459	523
			487	538
			487	576
			487	576
Y	THF	7.58	456	486
			456	522
			486	532
			486	568
			486	568
Y	Pyridine	12.4	458	489
			458	523
			489	534
			489	573
			489	573
Y	DMSO	46.7	462	493
			462	529
			493	543
			493	579
			493	579
Y	Acetone	20.7	458	481
			458	515
			481	529
			481	560
			481	560
Y	Ethanol	24.5	457	487
			457	522
			487	536
			487	573
			487	573
Y	Methanol	37.7	458	472
			458	509
			472	532
			472	573
			472	573

Table 3

FWHM and peak O.D. values for PDI F, L, W, and Y.

	THF	Pyridine	DMSO	Acetone	Ethanol	Methanol
F	FWHM (cm ⁻¹)	644	748	555	755	544
	O.D. _{peak}	0.026	0.21	0.013	0.27	0.30
	FWHM _{Peak}	2.07 · 10 ³	3.56 · 10 ³	4.27 · 10⁴	2.80 · 10 ³	1.81 · 10 ³
L	FWHM (cm ⁻¹)	803	777	715	682	799
	O.D. _{peak}	0.13	0.14	0.30	0.44	0.13
	FWHM _{Peak}	5.67 · 10 ³	5.55 · 10 ³	2.38 · 10 ³	1.55 · 10 ³	6.15 · 10 ³
W	FWHM (cm ⁻¹)	2437	799	704	792	799
	O.D. _{peak}	0.50	0.62	0.14	0.16	0.45
	FWHM _{Peak}	1.42 · 10 ³	1.29 · 10 ³	5.03 · 10 ³	4.95 · 10 ³	1.78 · 10 ³
Y	FWHM (cm ⁻¹)	927	894	693	774	ϕ
	O.D. _{peak}	0.41	0.59	0.071	0.46	ϕ
	FWHM _{Peak}	1.60 · 10 ³	1.52 · 10 ³	9.76 · 10³	1.68 · 10 ³	ϕ

The values in bold are the ones consistent with the presence of aggregates in solution.

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Table 4

Fluorescent quantum yield calculated values for PDI F, L, W, and Y.

	THF	Pyridine	DMSO	Acetone	Ethanol	Methanol
F	0.81	0.86	0.11	0.95	0.63	0.51
L	0.92	0.54	0.17	0.90	0.66	0.86
W	0.78	0.91	0.25	0.57	0.40	0.52
Y	0.42	0.88	0.06	0.51	0.33	0.92

Table 5

Stokes shift for the perylene diimides in various solvents.

	<i>f</i>	F	L	W	Y
$\nu(\text{cm}^{-1})$					
THF	0.20	323.5	323.5	145.1	360.1
Pyridine	0.21	350.7	348.1	285.9	393.9
DMSO	0.26	383.6	383.6	349.4	487.4
Acetone	0.28	391.3	398.4	378.5	513.9
Ethanol	0.29	393.9	500.4	565.5	500.4
Methanol	0.31	395.4	430.5	533.1	849.4
Avg Stokes shift		373.1	397.4	376.2	517.5

Table 6

Lippert–Mataga plot fit variables.

	m	$\mu(\text{D})$	R^2
F	627.0	1.74	0.87
L	893.1	2.47	0.97
W	3230	8.95	0.80
Y	1655	4.59	0.79

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Table 7

Fluorescent lifetime of nanosecond decay component of the PDI measured in different solvents.

	F (ns)	L (ns)	W (ns)	Y (ns)
THF	4.1 ± 0.1	4.0 ± 0.1	4.3 ± 0.1	4.0 ± 0.1
Pyridine	5.7 ± 0.2	3.9 ± 0.1	3.8 ± 0.1	3.9 ± 0.1
DMSO	0.52 ± 0.1	3.0 ± 0.1	4.0 ± 0.1	3.5 ± 0.1
Acetone	4.1 ± 0.1	4.2 ± 0.1	4.4 ± 0.1	4.3 ± 0.1
Ethanol	3.9 ± 0.1	4.0 ± 0.1	4.1 ± 0.1	3.3 ± 0.1
Methanol	4.1 ± 0.1	4.8 ± 0.1	4.4 ± 0.1	4.4 ± 0.1