

# Optical, Electrochemical and Thermoanalytical Investigations on Newly-Synthesized Perylene-3,4,9,10-Dianhydride Fluorescent Dyes

Aamer Saeed<sup>1</sup> · Ghulam Shabir<sup>1</sup> · Muhammad Arshad<sup>2</sup>

Received: 16 April 2015 / Accepted: 4 June 2015 / Published online: 18 June 2015  
© Springer Science+Business Media New York 2015

**Abstract** A series of dyes using tetrachloroerylene dianhydride as fluorescent chromophore was synthesized by the substitution of suitable aliphatic and alicyclic alcohols in alkaline medium, and evaluation of dyes was done for their optical, electrochemical and thermal properties. These dyes exhibited absorption maxima  $\lambda_{\max}$  in the range of 440–460 nm in aqueous medium due to the presence of highly-conjugated framework. Fluorescence spectra of these dyes in water showed sharp emission peaks with small bandwidths and large fluorescence rate constants, i.e.,  $1.36 \times 10^8$  to  $2.25 \times 10^8$  S<sup>-1</sup>. Redox potential  $E_{1/2}$  and band gap energy  $E_g$  were observed in the range of -0.689 to -0.784 and 2.530 to 2.610 eV, respectively. Thermal stability was noticed up to 300 °C on the basis of TG and DTA findings. The structures

of perylene-azo dyes were confirmed by FTIR and NMR spectroscopy.

**Keywords** Aliphatic alcohols · Perylene-3,4,9,10-dianhydride · Conjugated framework · Fluorescence rate constant · Redox potential · Band gap energy · Thermal stability

## Introduction

Perylene-diimides (PDIs) have been widely studied due to their stability and attractive electronic properties [1–5]. Extensive work by Wurthner et al. [6] has resulted in the synthesis of a plethora of functional supramolecular architectures engaging ionic self-assembly, hydrogen-bonding,  $\pi$ - $\pi$  interactions and metal-ligand-directed self-assembly [7, 8]. Metal-terpyridine connectivity [9] is also conducive to building functional materials due to predominant coordination, linking and easy incorporation of redox, photophysical and electrochemical properties into the resulting supramolecules. Consequently, terpyridine (tpy) coordination has permitted the exploration of diverse materials used in construction of solar devices [10]. This, along with the unique properties of perylene, provides enough to synthesize perylene-containing terpyridine (tpy) ligands [11] and their metal complexes. Recently, much attention has been paid to the design and synthesis of perylene dyes and their derivatives that can be employed in the photochemical conversion of solar energy. Essential properties of light-harvesting systems are, first the competence to absorb light over a significant part of the visible spectral region, and secondly, their chemical and photochemical stability.

Perylene dianhydride dyes display strong and tunable absorption in the visible region, bright photoluminescence with quantum yields up to unity, chemical inertness and low triplet

**Research Highlights** · Condensation of aliphatic and alicyclic alcohols with tetrachloroerylene dianhydride was carried out to prepare perylene fluorescent dyes.

- Alkylated perylene dyes exhibit greenish yellow fluorescence due to the presence of extensive conjugation and prevention of the parallel alignment of perylene chromophore.
- Electrochemical study of these dyes was pursued by cyclic voltammetry which showed  $E_p$  and  $E_{1/2}$  in the range of 0.689 to 1.400 and -0.689 to -0.740 eV, respectively.
- Newly-synthesized dyes showed stability up to 300 °C as determined by their TG and DSC analysis.
- LUMO and HOMO energy levels were found in the range of -4.010 to -4.110 and -6.230 to -6.789 eV, respectively.

✉ Aamer Saeed  
asaheed@qau.edu.pk; aamersaeed@yahoo.com

<sup>1</sup> Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

<sup>2</sup> Chemistry Division, Directorate of Science, PINSTECH, Nilore, Islamabad 45320, Pakistan

yield, and also, exceptional photostability. These dyes exhibit large fluorescence rate constant, small band gap energy, good solubility in aqueous as well as in organic media, and high thermal stability.

A lot of work was conducted on derivatization of peri positions of perylene ring with different alkyl and aryl substituents; however little efforts were made to probe the effect of different aliphatic and alicyclic chains on the optical properties of perylene dianhydride chromophore.

In this paper, synthesis, thermal stability, optical and electrochemical properties of some symmetrically alkylated (in bay area) perylene anhydride dyes are described. This study was done to see the effect of alkyl chain length on the absorption and emission properties of perylene dianhydride chromophore.

## Experimental

**Materials** All materials and reagents used for analysis were of 99 % purity. Tetrachloro perylene dianhydride was obtained from Honest Joy Holdings Limited, China. Decanol, 2-octanol, pentanol, n-butanol, propanol, ethanol, cyclopentanol and cyclohexanol were procured from E. Merck. Potassium carbonate was purchased from Daejing, Korea. Solvents such as ethyl acetate, DMF and methanol were of common laboratory grade.

**Instrumentation** Proton NMR spectra for all the dyes were recorded on a 300 MHz Bruker NMR spectrometer in DMSO- $d_6$  solvent. Splitting patterns were designated as: s (singlet), d (doublet), dd (double of a doublet), t (triplet), q (quartet), p (pentet), h (hexet), m (multiplet) and br (broad). Chemical shifts are reported in  $\delta$  (ppm). IR spectra were run on single beam Nicolet FT-IR 100. Ultraviolet–visible (UV–VIS) spectra were recorded on a double beam Perkin-Elmer Lambda 900 UV–VIS–NIR spectrophotometer. Thermogravimetric analysis was performed on TGA-3000 thermogravimetric analyzer. The gathered data were used to calculate the molar extinction coefficients for the compounds. TLC plate, coated with silica gel 60 F254, was utilized to test the progress of reaction of FDA rylene dyes.

## Synthesis of Perylene Dianhydride Dyes (3a-h)

Tetrachloroperylene dianhydride (**1**) 0.001 mol (0.53 g) was charged into 250 ml round bottom flask containing 20 ml dry distilled DMF. The flask was placed on oil bath being heated with hot plate. The reaction mixture was stirred continuously during heating. Alcohols (**2a-h**, 0.004 mol), followed by 2.0 g of  $K_2CO_3$  were added in the flask. The mixture was kept at 110 °C for 3 h. The progress of the reaction was monitored by

performing TLC intermittently in 4:1 ethyl acetate: pet ether solvent. On completion of the reaction, the mixture was filtered. The residue was dissolved in 30 mL of water and acidified with concentrated HCl, (1 mL). Precipitation occurred immediately. The contents were filtered and dried to obtain final products (3a-h) in 90–95 % yield. These dyes were coded as FDA-1, FDA-2, FDA-3, FDA-4, FDA-5, FDA-6, FDA-7 and FDA-8 (Scheme 1).

**FDA-1 (3a) 1,6,7,12-tetradecyl perylene dianhydride;** yellow crystals, m.p.>350 °C,  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 0.88 (3H, t), 1.26–1.76 (14H, m), 4.06 (2H, t), 7.81 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2975, 1828, 1772, 1620, 1580, 1584, 1549, 1438, 1367, 1110, 940, 905, 855, 810, 785, 722. Anal. Calcd. For  $C_{64}H_{88}O_{10}$  C, 75.41; H, 8.90; Found: C, 74.90; H, 8.55.

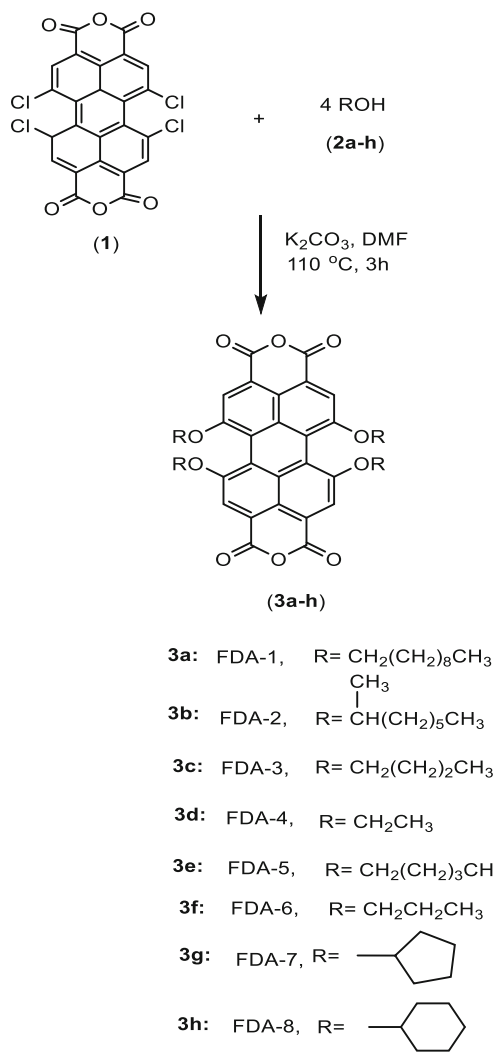
**FDA-2 (3b) 1,6,7,12-tetra-1'-methylheptyl perylene dianhydride;** yellowish orange crystals, m.p.>350 °C,  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 0.88 (3H, t), 0.96 (3H, d), 1.26–1.63 (15H, m), 3.70 (1H, sextet), 7.61 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2968, 1825, 1777, 1620, 1580, 1584, 1549, 1429, 1367, 1105, 943, 909, 865, 803, 775, 732. Anal. Calcd. For  $C_{56}H_{72}O_{10}$  C, 74.14; H, 8.22; Found: C, 73.75; H, 8.06.

**FDA-3 (3c) 1,6,7,12-tetra-butyl perylene dianhydride;** yellowish orange crystals, m.p.>350 °C.  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 0.9 (3H, t), 1.27 (2H, h), 1.62 (2H, p) 4.09 (2H, t), 7.27 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2980, 1823, 1770, 1620 1580, 1584, 1549, 1433, 1387, 1155, 968, 915, 850, 810, 780, 725. Anal. Calcd. For  $C_{40}H_{40}O_{10}$  C, 70.37; H, 6.20; O, 23.43; Found: C, 70.13; H, 6.04.

**FDA-4 (3d) 1,6,7,12-tetraethyl perylene dianhydride;** yellowish brown crystals, m.p.>350 °C,  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 1.72 (3H, t), 4.72 (2H, q), 7.27 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2925, 2855, 1813, 1775, 1620, 1580, 1584, 1549, 1435, 1382, 1135, 989, 945, 855, 820, 792, 755. Anal. Calcd. For  $C_{32}H_{24}O_{10}$  C, 67.37; H, 4.59; Found: C, 66.97; H, 4.09.

**FDA-5 (3e) 1,6,7,12-tetrapentyl perylene dianhydride;** yellowish orange crystals, m.p.>350 °C,  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 0.90 (3H, t), 1.27–1.33 (24H, m), 4.06 (2H, t), 7.27 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2905, 1810, 1772, 1620, 1580, 1584, 1549, 1420, 1387, 1115, 982, 915, 875, 850, 795, 740. Anal. Calcd. For  $C_{44}H_{48}O_{10}$  C, 71.72; H, 6.57; Found: C, 71.24; H, 6.25.

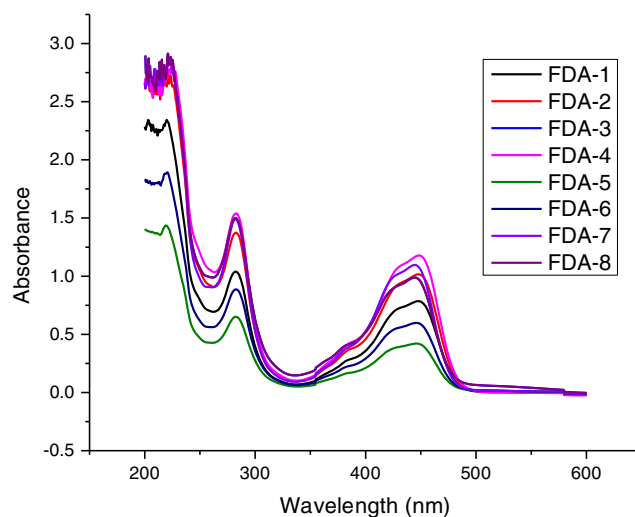
**FDA-6 (3f) 1,6,7,12-tetrapropyl perylene dianhydride;** yellowish orange crystals, m.p.>350 °C,  $^1H$ -NMR (300 MHz, DMSO)  $\delta$ : 1.3 (3H, t), 1.90 (2H, h) 4.09 (2H, t), 7.27 (4H, s). FTIR (Neat,  $cm^{-1}$ )  $\nu_{max}$ : 2925, 1818, 1762, 1620, 1580, 1584, 1549, 1425, 1395, 1145, 972, 915, 870, 825, 765, 753. Anal. Calcd. For  $C_{36}H_{32}O_{10}$  C, 69.22; H, 5.16; Found: C, 68.93; H, 4.89.



**Scheme 1** Synthetic route to tetrachloroperylene based fluorescent dyes (3a-h)

**FDA-7 (3g) 1,6,7,12-tetracyclopentyl perylene dianhydride;** yellowish orange crystals, m.p > 350 °C, <sup>1</sup>H-NMR (300 MHz, DMSO) δ: 3.71 (1H, p), 2.02 (4H, q), 1.71 (4H, t), 7.27 (4H, s). FTIR (Neat, cm<sup>-1</sup>) ν<sub>max</sub>: 2935, 1815, 1765, 1620, 1580, 1584, 1549 1427, 1385, 1145, 950, 933, 867, 838, 785, 758. Anal. Calcd. For C<sub>44</sub>H<sub>40</sub>O<sub>10</sub> C, 72.51; H, 5.53; O, 21.95; Found: C, 72.11; H, 5.35.

**FDA-8 (3h) 1,6,7,12-tetracyclohexyl perylene dianhydride;** yellowish orange crystals, m.p > 350 °C, <sup>1</sup>H-NMR (300 MHz, DMSO) δ: 3.64 (1H, p), 1.95 (4H, q), 1.53 (4H, p), 1.46 (4H, p), 7.27 (4H, s). FTIR (Neat, cm<sup>-1</sup>) ν<sub>max</sub>: 2950, 1805, 1757, 1620, 1580, 1584, 1549, 1440, 1380, 1160, 962, 905, 877, 828, 795, 750. Anal. Calcd. For C<sub>48</sub>H<sub>48</sub>O<sub>10</sub> C, 73.45; H, 6.16; Found: C, 73.08; H, 5.90.



**Fig. 1** UV-Visible absorption spectra of FDA perylene dyes

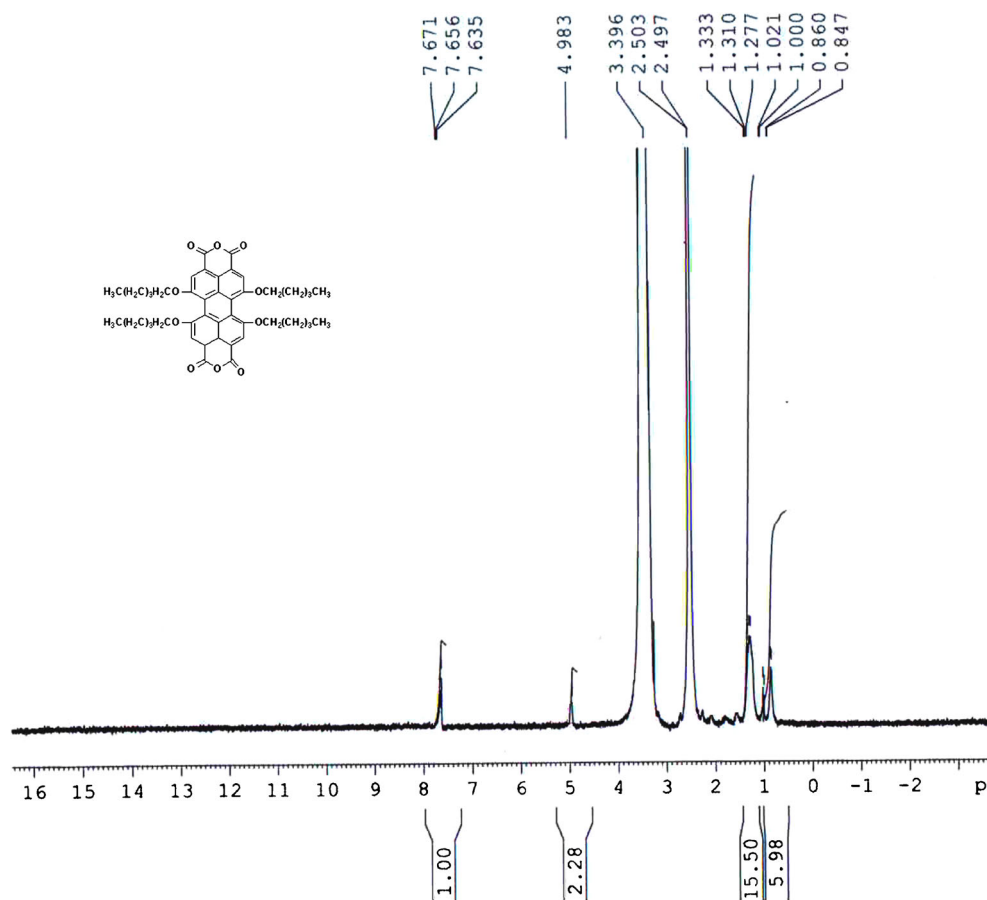
## Results and Discussions

Synthesis of FDA perylene dyes derivatives (3a-h) was accomplished by condensation of tetrachloroperylene dianhydride with different alcohols (2a-h) in the presence of potassium carbonate and dry distilled DMF at 110 °C. Reaction completed in three hours of continuous heating and stirring [12]. Temperature was not allowed to exceed 110 °C to avoid the decomposition of DMF, which may result in the substitution of ring oxygen by nitrogen. A molar ratio of 1:4 for tetrachloroperylene dianhydride and different aliphatic and alicyclic alcohols was applied for the substitution of all four chloro groups by an addition-elimination mechanism. The addition of excess potassium carbonate was meant to enhance the nucleophilic character of different alcohols to complete the reaction quickly and to neutralize the acid generated within the reaction mixture to prevent the hydrolysis of dianhydride. The solids were filtered, dissolved in a minimum amount of water and acidified to afford the base free products (Scheme 1).

**Table 1** Wavelength of maximum absorption λ<sub>max</sub> of FDA Perylene dyes in water (FDA-1 to FDA-8)

Dye	λ <sub>max</sub> (nm)
FDA-1	282, 446.6
FDA-2	282, 445.4
FDA-3	282, 447.5
FDA-4	282, 448
FDA-5	282, 448
FDA-6	282, 448.5
FDA-7	282, 446
FDA-8	282, 445.5

**Fig. 2**  $^1\text{H}$  NMR spectrum of FDA-5 perylene dye (3e)



### UV-Visible, FTIR and NMR Studies of FDA Rylene Dyes

The structures of newly-synthesized perylene derivatives were elucidated by UV-Visible, FTIR and NMR spectroscopy. The solvatochromic behavior was observed for these dyes which was due to change in their dipole moment which occurred during transitions between two electronic states ( $\pi$  to  $\pi^*$ ) with differential solvent polarity. The UV-visible absorption spectra of the FDA perylene dyes ( $1 \times 10^{-4}$  M) were taken at room temperature in aqueous medium (Fig. 1) and the selected spectral data are summarized in Table 1.

The electronic transition of UV-visible spectra of dyes in water gave rise to two absorption maxima ( $\lambda_{\text{max}}$ ), first at 282 nm and the other at 445–448 nm, respectively. The  $\lambda_{\text{max}}$  for all the compounds at 445–448 nm is the result of  $\pi$ - $\pi^*$  transition of the compounds due to the presence of C=C, characteristic of perylene motif. Difference in  $\lambda_{\text{max}}$  of the synthesized dyes follows a narrow range for different alkyl substituents. All FDA dyes have maximum  $\lambda_{\text{max}}$  in water when compared with that in non-polar solvents. From UV results, it is revealed that all perylene derivatives show approximately identical  $\lambda_{\text{max}}$ . This evidence indicates that chain length of alkyl groups at bay positions of perylene ring does not affect

much the  $\lambda_{\text{max}}$  of dyes. Moreover, the solvent effect on UV-visible absorption spectra of FDA dyes strongly depends on the nature of the substituent on the perylene nucleus, whether the substituents' interact with solvent molecules or not. Solvent effect is more pronounced for substituents intermolecular interaction with solvent molecules. This solvent effect has also been observed for many perylene derivatives.

The FTIR spectra of FDA dyes give absorption bands due to C-H, C=O (for dianhydride), C=C and C-O, stretching and bending vibrations in the range of 2900–2980, 1805–1828,

**Table 2** Molar extinction coefficients of perylene dyes (FDA-1 to FDA-8)

Dyes	$\lambda_{\text{max}}$ (nm)	A	$\epsilon_{\text{max}}$ (L mol $^{-1}$ cm $^{-1}$ )
FDA-1	446.6	1.5060	30,120.38
FDA-2	445.4	1.5432	30,865.1
FDA-3	447.5	0.7859	15,719.28
FDA-4	448	1.016	20,331.98
FDA-5	448	0.9863	19,727.46
FDA-6	448.5	1.178	23,564
FDA-7	446	1.09674	21,934.8
FDA-8	445.5	0.9887	19,774.94

**Table 3** Fluorescence values of FDA perylene dyes in water (FDA-1 to FDA-8)

Dye	Excitation wavelength\ (nm)	Emission wavelength (nm)	Emission Height	Stoke Shift (nm)
FDA-1	455	502	720	78
FDA-2	455	510	698	59
FDA-3	460	503	4859	81
FDA-4	490	515	12.58	25
FDA-5	460	513	1894	49
FDA-6	455	470	1070	30
FDA-7	455	480	1070	40
FDA-8	455	490	1070	50

1757–1777, 1150–1100 and 723–750  $\text{cm}^{-1}$ , respectively. In particular, the peak observed in the range of 1150–1100  $\text{cm}^{-1}$  was as a result of C–O–C functionality. The absorption bands at 1618 and 750  $\text{cm}^{-1}$  depict the presence of C=C stretching and bending vibrations, respectively. Azo linkage was confirmed by absorptions in the range of 1540–1510  $\text{cm}^{-1}$ . All these stretching and bending bands identify perylene derivatives (FDA-1 to FDA-8).

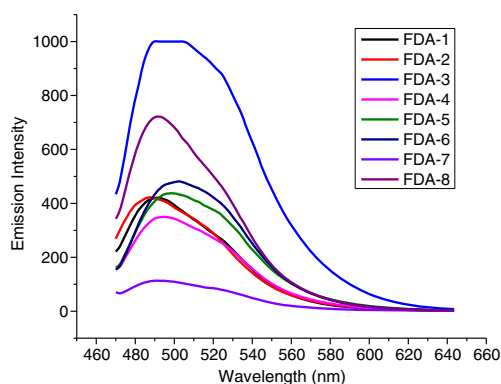
The  $^1\text{H}$  NMR spectrum of FDA-1 exhibits a high field triplet peak due to  $\text{CH}_3$  group at 0.88 ppm, a multiplet due to methylene envelope in the zone of 1.26–1.76 ppm and a triplet at 4.06 ppm due to  $\text{CH}_2$  group adjacent to oxygen atom in the decyl chain by the de-shielding caused by oxygen. Due to perylene ring there is singlet peak in the range of 7.27–7.81 ppm, common in all compounds. For FDA-2 there are one triplet and one doublet at 0.88 and 0.96 ppm, respectively, due to two  $\text{CH}_3$  groups present in 2-octyl chain, attached in bay region of perylene. These are highly shielded protons due to rich electron density around them. Hexet at 3.70 ppm is ascribed to the proton adjacent to oxygen atom and a multiplet arises due to methylene envelope in the range of 1.26–1.63 ppm. In FDA-3 dye, 3H triplet, 2H hexet, 2H pentet and 2H triplet found at 0.90, 1.27, 1.62 and 4.09 ppm, respectively, are attributed to butyl chain symmetrically attached to

perylene ring. One triplet at 1.72 ppm and a quartet at 4.72 ppm appear due to the presence of ethyl chain in case of FDA-4. FDA-5 exhibits a triplet due to  $\text{CH}_3$  (adjacent to  $\text{CH}_2$  group) at 0.86 ppm and a broad multiplet at 1.27–1.33 ppm owing to methylene envelope in the n-pentyl chain. A triplet at 4.95 ppm points at  $\text{CH}_2$  adjacent to oxygen atom. FDA-6 evinces triplet, hexet and triplet at 1.3, 1.90 and 4.09 ppm, respectively. These include  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}_2$  protons in the propyl segment. FDA-7 and FDA-8 (cyclopentyl and cyclohexyl attached to perylene ring) manifest 1H pentet (each) at 3.71 and 3.74 ppm, respectively, while other protons in these compounds exhibit multiplet in aliphatic region in the range of 1.46 to 2.02 ppm. All chemical shifts prove the substituent's identity and existence of the perylene ring chromophore in these derivatives (3a–h) Fig. 2.

## Optical Properties

### Maximum Extinction Coefficients ( $\epsilon_{\text{max}}$ )

The maximum extinction coefficient is a measurement of how strongly a chemical species absorbs light at a given wavelength depending upon the presence or absence of certain

**Fig. 3** Fluorescence spectra of perylene dyes (FDA-1 to FDA-8)**Table 4** Singlet energies of dyes (FDA-1 to FDA-8)

Dye	$\lambda_{\text{max}}$ (Å)	$E_s$ (kcal/mol)
FDA-1	4466	64.3
FDA-2	4454	64.2
FDA-3	4475	63.91
FDA-4	4480	62.5
FDA-5	4480	62.5
FDA-6	4485	63.7
FDA-7	4460	64.1
FDA-8	4455	64.34



**Table 5** Oscillator strengths of perylene dyes (FDA-1 to FDA-8)

Dye	$\Delta V_{1/2}$ (cm <sup>-1</sup> )	$\epsilon_{\max}$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	Oscillator strengths f
FDA-1	3449	30,120.38	0.448
FDA-2	3847	30,865.10	0.512
FDA-3	4603	15,719.28	0.312
FDA-4	3755	20,331.98	0.329
FDA-5	3660	19,727.46	0.311
FDA-6	3424	23,564.00	0.348
FDA-7	3481	21,934.80	0.329
FDA-8	4294	19,774.94	0.366

functionalities in the molecule. It is an intrinsic property which depends upon the actual absorbance (A), path length (l) and the concentration (c) of the species (Beer-Lambert law) i.e.,  $A = \epsilon_{\max} cl$ . Molar extinction coefficient of perylene dyes is presented in Table 2.

Absorption in UV- visible region by FDA perylene dyes is higher for those dyes which have longer alkyl chains substituted on perylene dianhydride chromophore and higher value of molar extinction coefficients are linked to/associated with high absorption intensity. It can be generalized that branched chain and long-chain alkyl groups substituted perylene chromophores have high molar extinction coefficients than shorter chain substituted perylene as it is evidenced from high molar extinction coefficients of FDA-1 and FDA-2 as compared with other FDAs.

### Fluorescence Investigation

Fluorescence data of these dyes are reproduced in Table 3. Fluorescence spectra were recorded by selecting different excitation wavelengths of the source as excitation spectrum is dependent on emission intensity at single wavelength upon various excitation wavelengths [13] (Fig. 3). The fluorescence spectra of these dyes display only one fluorescence peak at 500–513 nm when excited by different wavelengths in the concentration range of  $10^{-4}$  to  $10^{-5}$  M. All dyes exhibit nearly

**Table 6** Theoretical radiative lifetime of perylene dyes (FDA-1 to FDA-8)

Dyes	$\Delta V_{1/2}$ (cm <sup>-1</sup> )	$\epsilon_{\max}$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	$V_{\max}$ (cm <sup>-1</sup> )	$\tau_0$ (ns)
FDA-1	3449	30,120.38	25,918	4.98
FDA-2	3847	30,865.10	25,773	4.43
FDA-3	4603	15,719.28	26,012	5.49
FDA-4	3755	20,331.98	26,093	6.73
FDA-5	3660	19,727.46	25,768	7.30
FDA-6	3424	23,564.00	25,725	6.55
FDA-7	3481	21,934.80	25,737	7.04
FDA-8	4294	19,774.94	25,242	6.46

**Table 7** Fluorescence rate constant of perylene dyes (FDA-1 to FDA-8)

Dye	$\tau_0$ (ns)	$k_f$ (10 <sup>8</sup> /s)
FDA-1	4.98	2.00
FDA-2	4.43	2.25
FDA-3	5.49	1.82
FDA-4	6.73	1.48
FDA-5	7.30	1.36
FDA-6	6.55	1.52
FDA-7	7.04	1.42
FDA-8	6.46	1.54

identical emission, which showed the little effect of chain length on emission intensity. Emission peak of high intensity at 500–513 nm for different dyes corresponds to absorption peak in the range of 445–448 nm. This observed phenomenon of absorption and emission verifies the mirror image rule [13].

Fluorescence of these dyes is maximum in water and minimum in other solvents. In water high fluorescence is due to non-aggregation of dye molecules affected by high polarity and small size of water molecules. While other solvents have larger molecular size, they cannot penetrate and solvate completely the individual molecules of dyes with bulky structures. Self association of dye molecules occurs in solvents like ethanol, methanol and consequently, fluorescence decreases [14].

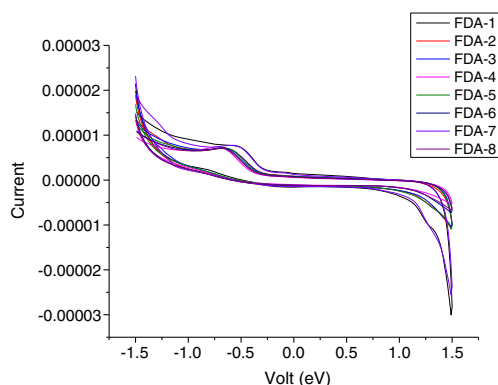
### Singlet Energies (E<sub>s</sub>)

Singlet energies were calculated by using the equation,  $E_s = 2.86 \times 10^5 / \lambda_{\max}$  [15]. The data is represented in Table 4.

From this study, it is concluded that there is small change in the singlet energies of perylene dyes. Singlet energy depends upon the wavelength of maximum absorption, which does not fluctuate largely. In order to notice bigger changes in wavelength of maximum absorption there must be delocalization of electrons through alternating single and double bonds. Since energy difference decreases between HOMO and LUMO energy levels, singlet energies reduce consequently.

**Table 8** Redox potential (E<sub>1/2</sub>) of perylene dyes (FDA-1 to FDA-8)

Compounds	E <sub>pa</sub> (V)	E <sub>pc</sub> (V)	$\Delta E_p$ (mV)	E <sub>1/2</sub> (V)
FDA-1	-0.0390	-1.4390	1.400	-0.739
FDA-2	-0.3445	-1.0335	0.689	-0.689
FDA-3	-0.3495	-1.0485	0.699	-0.699
FDA-4	-0.3745	-1.1235	0.749	-0.749
FDA-5	-0.2490	-1.4390	1.190	-0.696
FDA-6	0.0790	-1.4390	1.360	-0.759
FDA-7	-0.1290	-1.4390	1.310	-0.784
FDA-8	-0.3595	-1.0785	0.719	-0.719



**Fig. 4** Combined cyclic voltammogram of perylene dyes FDA-1 to FDA-8

**Oscillator Strengths (f)**

Oscillator strengths were calculated by the reported procedure using the equation,  $f = 4.32 \times 10^{-9} \Delta V_{1/2} \epsilon_{\max}$  [16]. The results are shown in Table 5.

It is observed that oscillator strength varied from 0.311 to 0.512 and is highest for FDA-2, which has tetra-substituted 2-octyl chains on the perylene dianhydride. In FDA-2, since the molar extinction coefficient is higher than other derivatives, so its oscillator strength is high. This may also be attributed to larger absorption by branched chain alkyl group on perylene ring. Same pattern is also observed for FDA-1, which has second highest fluorescence rate constant in the present series. This can be generalized that oscillator strength is dependent upon the molar extinction coefficient.

**Theoretical Radiative Lifetimes ( $\tau_0$ )**

Theoretical radiative lifetimes ( $\tau_0$ ) depend upon molar extinction coefficient ( $\epsilon_{\max}$ ), mean frequency ( $V_{\max}^2$ ) and half-width of the selected absorption ( $\Delta V_{1/2}$ ). Molar extinction coefficient ( $\epsilon_{\max}$ ) of these dyes is high for longer alkyl chains substituted on perylene dianhydride chromophore and varies from 4.43 to 7.30 (ns) (Table 6). FDA-1 and FDA-2 have larger  $\epsilon_{\max}$  value and smaller values of the radiative lifetime

**Table 9** LUMO energy of perylene dyes (FDA-1 to FDA-8)

Compounds	$E_{1/2}$ (V)	LUMO (eV)
FDA-1	-0.739	-4.010
FDA-2	-0.689	-4.110
FDA-3	-0.699	-4.100
FDA-4	-0.749	-4.050
FDA-5	-0.696	-4.104
FDA-6	-0.759	-4.041
FDA-7	-0.784	-4.016
FDA-8	-0.719	-4.081

**Table 10** Band gap energy of perylene dyes (FDA-1 to FDA-8)

Dye	Cut-off $\lambda$ (nm)	$E_g$ (eV)
FDA-1	482	2.572
FDA-2	484	2.561
FDA-3	490	2.530
FDA-4	479	2.588
FDA-5	488	2.540
FDA-6	480	2.583
FDA-7	475	2.610
FDA-8	485	2.555

( $\tau_0$ ). From data, it can be gathered that those perylene derivatives, which have larger absorptions in UV-visible region, possess lower values of the radiative lifetime ( $\tau_0$ ). Calculated theoretical radiative lifetimes are shown Table 6.

**Fluorescence Rate Constants ( $k_f$ )**

The results of fluorescence rate constants of dyes are represented in Table 7. The values for these dyes vary from  $1.36$  to  $2.25 \times 10^8 \text{ s}^{-1}$ , with FDA-2 displaying the highest value, which has tetra-substituted 2-octyl chains on the perylene dianhydride. In FDA-2, the radioactive life time is very low, so it has a high fluorescence rate constant. This may also be attributed to space interaction of the branched chain alkyl group with perylene electrons that decreases the radiative life time and increases the fluorescence rate constant. The same pattern is also observed for FDA-1 which has a second highest fluorescence rate constant in this series.

**Electrochemical Properties**

The electrochemical characterization of these dyes was studied by Cyclic Voltammetry using water having 0.1 M TBAPF6 as a supporting electrolyte. All redox potentials, HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and band gap energies ( $E_g$ ) were calculated from this technique.

**Table 11** HOMO energy of perylene dyes (FDA-1 to FDA-8)

Compounds	$E_g$ (ev)	HOMO (eV)
FDA-1	2.572	-6.582
FDA-2	2.561	-6.672
FDA-3	2.530	-6.630
FDA-4	2.588	-6.638
FDA-5	2.540	-6.644
FDA-6	2.583	-6.624
FDA-7	2.610	-6.623
FDA-8	2.555	-6.630

**Table 12** TG and DTA data of dyes(FDA-1 to FDA-8)

Dye	Temperature TG, °C (T <sub>o</sub> )
FDA-1	218
FDA-2	195
FDA-3	193
FDA-4	214
FDA-5	198
FDA-6	189
FDA-7	190
FDA-8	194

### Redox Potentials (E<sub>1/2</sub>)

For reversible processes, reduction potentials were calculated from cyclic voltammograms according to reported procedure  $E_{1/2} = [E_{\text{HOMO}} + E_{\text{LUMO}}]/2$  [17, 18]. Redox potentials of dyes are shown in Table 8 Fig. 4.

### Lowest Unoccupied Molecular Orbital (LUMO)

In order to calculate the absolute energies of LUMO level with respect to the vacuum level, the redox data were standardized to the ferrocene/ferricenium couple which has a calculated absolute energy of  $-4.8$  eV,  $E(\text{LUMO}) = E(\text{HOMO}) + E_g$  [18]. The data related to LUMO level energies of dyes are presented in Table 9.

It is inferred from energy range of  $-4.010$  to  $-4.110$  eV that there is no appreciable difference between different aliphatic and alicyclic chains used for substitution on perylene ring. It is concluded that the effect of chain length of alkyl groups is same for all dyes. The energy of LUMO levels can be varied only by increasing the delocalization of electrons through alternating single and double bonds and it is noticed that energy difference decreases with increasing conjugation and vice versa [18].

### Band Gap Energy (E<sub>g</sub>)

The optical band gap values are calculated using the standard procedure [19] using the equation given below.

$$E_g = 1242 \text{ eVnm}/\lambda$$

The band gap energy is the span of energies that lies between the valence and conduction bands for insulators and semiconductors. Every solid has its own characteristic energy-band structure and is related to absorption maxima of compounds. For compounds which have higher  $\lambda_{\text{max}}$  the HOMO and LUMO levels become close to each other having smaller values of band gap energies [19]. The band gap energy of dyes is given in Table 10. No significant difference is evident for different aliphatic and alicyclic chains substituted on

perylene ring and it is clear that the chain length of alkyl group doesn't affect the band gap energy. Band gap energy can be varied only by increasing the delocalization of electrons through alternating single and double bonds and the energy difference decreases with increasing conjugation and vice versa.

### Highest Occupied Molecular Orbital (HOMO)

Highest occupied molecular orbital energy levels were calculated using the standard reported procedure [19, 20] following the Bredas equation and energy span for HOMO levels is given in Table 11.

$$E(\text{HOMO}) = -(E_{\text{ox}} + 4.8) \text{ eV (Bredas equation)}$$

Considering the energy range from  $-6.582$  to  $-6.672$  eV for these dyes, no large difference for various aliphatic and alicyclic chains substituted on perylene ring is observed. It is concluded that there is a minor effect of chain length of alkyl groups on HOMO energy levels. The HOMO energy levels can be changed only by increasing the delocalization of electrons through alternating single and double bonds. The energy difference decreases with increasing conjugation and vice versa.

### Thermal Properties

Thermo gravimetric measurement of dyes was carried out to check the thermal stability [21, 22] using inert atmosphere. The results are reproduced in Table 12. On the basis of TG, perylene dyes demonstrate high thermal stability. The stability is attributed to the presence of rigid ring structure. When T<sub>o</sub> (temperature at which first mass-loss is detected) is taken into account from TG results it is seen that it occurs at temperature range  $189 - 218$  °C for FDA-1 to FDA-8 and major weight loss occurs above  $300$  °C. It is observed from TG thermograms that these dyes will not be affected structurally by higher temperatures if the applications demand thermal stability.

### Conclusions

New perylene dyes were synthesized via a short route with high per cent yields. These dyes are soluble in water as well as in polar solvents. The dyes absorb in the range of  $440 - 450$  nm and appear yellow. The absorption maxima ( $\lambda_{\text{max}}$ ) of all dyes was found to be the highest in water, which was in accordance with the general rule that polar solvents shift  $\pi - \pi^*$  to higher wavelengths. These dyes exhibit remarkably high fluorescence, especially in water. The dyes show excellent thermal stability (up to  $300$  °C) for potential high-tech applications



which require dyes with tailor-made absorption and emission in a specific region of the visible spectrum. HOMO and LUMO levels of these dyes are in the range of  $-6.623$  to  $-6.670$  and  $-4.010$  to  $-4.110$  eV, respectively. These values impart them the characteristics to act as p-type materials for sensitization of semiconductors.

**Acknowledgments** We gratefully acknowledge a research grant from higher Education Commission of Pakistan under the project No.4-279/PAK-US/HEC 2010–917 (Pakistan-US Science & Technology Cooperation Program).

## References

- Zhan X, Tan Z, Domercq B, An Z, Zhang X, Barlow S, Li Y, Zhu D, Kippelen B, Marder SR (2007) A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells. *J Am Chem Soc* 129:7246–7247
- Sadrai M, Hadel L, Sauers RR, Husain S, Krogh-Jespersen K, Westbrook JD, Bird FR (1992) Lasing action in a family of perylene derivatives: singlet absorption and emission spectra, triplet absorption and oxygen quenching constants, and molecular mechanics and semiempirical molecular orbital calculations. *J Phys Chem* 96:7988–7996
- Ego C, Marsitzky D, Becker S, Zhang J, Grimsdale AC, Müllen K, MacKenzie JD, Silva C, Friend RH (2003) Attaching perylene dyes to polyfluorene: three simple, efficient methods for facile color tuning of light-emitting polymers. *J Am Chem Soc* 125:437–443
- O'Neil MP, Niemczyk MP, Svec WA, Gosztola D, Gaines GL, Wasielewski MR (1992) Pico second optical switching based on biphotonic excitation of an electron donor-acceptor-donor molecule. *Science* 257:63–65
- Fedorov IA, Zhuravlev YN, Berveno VP (2013) Structural and electronic properties of perylene from first principles calculations. *J Chem Phys* 138:094509–094510
- Wurthner F, Bauer C, Stepanenko V, Yagai S (2008) A black perylene bisimide super gelator with an unexpected J-type absorption band. *Adv Mater* 20:1695–1698
- Saeed A, Shabir G (2014) New fluorescent symmetrically substituted perylene-3, 4, 9, 10-dianhydride-azohybrid dyes: synthesis and spectroscopic studies. *Spectrochim Acta A Mol Biomol Spectrosc* 133:7–12
- Wang ZY, Qi Y, Gao JP, Sacripante GG, Sundararajan PR, Duff JD (1998) Synthesis, characterization, and xerographic electrical characteristics of perylene-containing polyimides. *Macromolecules* 31:2075–2079
- Holtrup FO, Müller GR, Uebe J, Müllen K (1997) Benzoylperylenedicarboximides: functional dyes with attractive optical and electronic properties. *Tetrahedron* 53:6847–6860
- Nagao Y, Misono T (1984) Synthesis and properties of N-alkyl-N'-aryl-3, 4: 9, 10-perylenebis (dicarboximide). *Dyes Pigments* 5:171–188
- Seybold G, Wagenblast G (1989) New perylene and violanthrone dyestuffs for fluorescent collectors. *Dyes Pigments* 11:303–317
- Naidu JJ, Bae YJ, Jeong KU, Shin S, Lee MH (2009) Color tuning of perylene based lyotropic chromonic liquid crystal. *Bull Korean Chem Soc* 30:224–226
- Gryko DT, Piechowska J, Gałezowski M (2010) Strongly emitting fluorophores based on 1-azaperylene scaffold. *J Org Chem* 75:1297–1300
- Atilgan S, Ekmekci Z, Dogan AL, Guc D, Akkaya EU (2006) Water soluble distyryl-boradiazaindacenes as efficient photosensitizers for photodynamic therapy. *Chem Commun* 42:4398–4400
- Adamovich VI, Cordero SR, Djurovich PI, Tamayo A, Thompson ME, D'Andrade BW, Forrest SR (2003) New charge-carrier blocking materials for high efficiency OLEDs. *Org Electron* 4:77–87
- Mohanty J, Nau WM (2004) Refractive index effects on the oscillator strength and radiative decay rate of 2, 3-diazabicyclo [2.2. 2] oct-2-ene. *Photochem Photobiol Sci* 3:1026–1031
- Ishii H, Hayashi N, Ito E, Washizu Y, Sugi K, Kimura Y, Niwano M, Seki K (2004) Kelvin probe study of band bending at organic semiconductor/metal interfaces: examination of Fermi level alignment. *Phys Status Solidi* 201:1075–1094
- Wurthner F, Thalacker C, Diele S, Tischierske C (2001) Fluorescent J-type aggregates and thermotropic columnar mesophases of perylene bisimide dyes. *Chem Eur J* 7:2245–2253
- Leonat L, Sbarcea G, Branzoi IV (2013) Cyclic voltammetry for energy levels estimation of organic materials. *UPB Sci Bull Ser B* 75:111–118
- Zagranyarski Y, Chen L, Jansch D, Gessner T, Li C, Müllen K (2014) Toward perylene dyes by the hunsdiecker reaction. *Org Lett* 16:2814–2817
- Arshad M, Masud K, Arif M, Saeed A (2014) Mechanistic study of thermal behavior of poly (vinyl acetate) blended with aluminum tribromide: an investigation aided by IR and Py-GC-MS techniques. *J Therm Anal Calorim* 115:759–769
- Arshad M, Masud K, Saeed A (2012) The impact of AlBr<sub>3</sub> on the thermal degradation of P(S-co-MMA)-A study by using contemporary techniques. *Iran Polym J* 21:143–155