ORIGINAL ARTICLE

Multichromic Bis-Axially Extended Perylene Chromophore with Schiff Bases: Synthesis, Characterization and Electrochemical Studies

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Abstract In the present paper a novel way of symmetric conjugation extension along molecular axes of perylene dianhydride chromophore has been devised to achieve lengthy delocalized electronic species exhibiting red shifted absorption and emission of UV-Visible radiations. During synthetic pathway free amino Schiff bases of novel aldehydes with 4-amino acetanilide have been condensed with perylene dianhydride in quinoline at high temperature. Bis perylene diimide Schiff bases (**5a-e**) have been synthesized which showed absorption λ_{max} at 461–526 nm and emission at 525–550 nm. Structures of newly obtained compounds have been confirmed by ^{1}H and ^{13}C-NMR studies. Cyclic voltammetric analysis of these dyes exhibited oxidation and reduction peaks which provide indirect evidence for their potential utility as n-type material for sensitization of semiconductors in solar cells. LUMO and HOMO energy levels were found in the range of −4.21 to −5.20 and −6.75 to −7.57 eV, respectively.

Research Highlights
- Condensation of Schiff bases with perylene dianhydride was carried out to bis-axially extended symmetric fluorescent chromophores.
- Schiff base extended chromophores showed yellow fluorescence while extension with azo dyes produced pigments exhibiting reddish yellow fluorescence in DMSO.
- Electrochemical study of these dyes was pursued by cyclic voltammetry which showed half wave potential ($E_{1/2}$) in the range + 0.229 to −0.590 eV.
- LUMO and HOMO energy levels were found in the range of −4.21 to −5.20 and −6.85 to −7.57 eV, respectively.

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Introduction

Functional dyes have increasing importance from previous 20–30 years due to their use in high tech applications in everyday life. Perylene based dyes are well suited as functional dyes due to their wavelength span which ranges from 200 to 1500 nm. More recently, perylene molecules and their derivatives have attracted more and more attention in the past decade due to not only their outstanding thermal and photochemical stabilities [1, 2], but also their large application potential in organic opto-electronic or electronic devices [3–6], such as field effect transistors, solar cells [7–12], light-harvesting arrays [13–17] and light-emitting diodes [18–20]. Several perylene dyes have been used as sensitizers in DSSCs, however, they exhibited very low overall power conversion efficiencies [21–23]. Li and Edvinsson reported diphenylamino-substituted perylene monoanhydrides as sensitizers with power conversion efficiency 3.9 % [24], later on they reported 6.8 % power conversion efficiency with new perylene sensitizer bearing two thiophenol groups [25]. The layered growth of these planar molecules makes it possible to prepare fairly well ordered thin films of perylenes on different substrates [26, 27]. The charge transport and luminescence properties strongly depend on the structural properties of these thin films [28–30]. Perylene dyes are well known as the key chromophores among the metal-free dyes [31], which have the advantage of low cost production because they do not involve the precious rare earth metals. Their solubility, absorption, and emission behavior can be efficiently controlled using a variety of synthetic procedures, which include functionalization of peri- or bay-positions of perylene core. Systematic tuning of HOMO and LUMO levels of perylene

dyes improve both light harvesting properties and electron injection capabilities to TiO$_2$ conduction band for obtaining the high PCE [32].

Keeping in view the above importance and efficiency of rylene dyes as advanced materials we have synthesized axially bis dimides of perylenetetracarboxi-3,4,9,10-bisanhydride with Schiff bases, which have modified their hues and also made them potentially applicable for dye lasers and solar cells.

Experimental

Materials

1,6,8,12-tetrachloroperylene 3,4,9,10-dianhydride was obtained from Honest Joy Holdings Limited China. 4-Nitro-4′-hydroxy azobenzene, 4-Methoxy-4′-hydroxy azobenzene, 2-Methoxy-4′-hydroxy azobenzene, 4-Chloro-4′-hydroxyazobenzene,4-Methyl-4′-hydroxy azobenzene, 3-Nitro-4′-hydroxyazobenzene, and 4-hydroxy azobenzene-2-carboxylic acid were obtained from Sigma-Aldrich. Potassium carbonate was purchased from Daejing Korea. Solvents such as ethanol, ethyl acetate, DMF, and methanol were common laboratory grade chemicals.

Methods

All the chemicals used for analysis were of 99–100 % purity. ^{1}HNMR spectra for all the compounds were conducted on a 300 MHz Bruker NMR spectrometer in DMSO solvent. Splitting patterns were as follows: s (singlet), d (doublet), dd, (double doublet), t (triplet), m (multiplet) and br (broad). Chemical shifts were represented in δ (ppm). The FTIR spectra were taken in the 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. The data were used to calculate the molar extinction coefficients for the compounds. Whatman Filter Paper 40 was used to monitor the entirety phenolic azo dyes synthesis. TLC plate Silica Gel 60 F254 was utilized to test the progress of SJA hybrid azo dyes. Luminescence was determined by using L. S 100 m and electrochemical analysis was made by Electrochemical Analyzer CH1830C. Fluorescence quantum yields were determined using reference fluorescein having quantum yield 95 % in water.

General Procedure for Synthesis of Schiff Base and Azo Extended Perylene Chrmophores

a) Synthesis of Schiff bases

To the well stirred solution of 4-aminoacetanilide (1.52 g, 0.001 mol) in 25 ml ethanol in 250 ml round bottomed flask was added aromatic aldehyde (2a, 0.001 mol). The reaction mixture was heated at reflux temperature for 12 h in the presence of glacial acetic acid catalyst (0.5 ml). Completeness of reaction was observed by TLC (4:1, pet ether: ethyl acetate). At the completion of reaction, the reaction mixture was rotary evaporated and collected the solid residue which was further purified by recrystallization (50:50 ethyl acetate: ethanol).

Schiff base (1a) was suspended in water (30 ml) in a 250 ml round bottomed flask and was added conc. HCl (1.5 ml). Started stirring and heating at 90 °C, for 2 h, until the reaction was completed as determined from TLC of reaction mixture (4:1, pet ether: ethyl acetate). The reaction mixture was cooled and the deprotected the Schiff base was separated from water on standing for 1 h, filtered and dried in oven at 60 °C. In this way other Schiff bases were synthesized by treating aldehydes **2b-e** with p-aminoacetanilide (**1**).

b) Condensation of Schiff bases with Perylene dianhydride

Schiff base (3a, 0.002 mol) was dissolved in quinoline (20 ml) 250 ml round bottomed flask and started stirring. Then perylene dianhydride (4) (0.001 mol) was added to the above solution and the reaction mixture was heated at 165 °C. Heating was continued for 20 h for the completion of the reaction, until it was determined from its TLC (4:1, pet ether: ethyl acetate) the synthesis of perylene diimide Schiff base **5a**. On cooling the reaction mixture dye was precipitated from quinoline which filtered, dried and recrystallized from DCM. In this way other dyes **5b-e** were synthesized.

[2,9-Bis(4-((Pyren-1-Ylmethylene)Amino)Phenyl)
Anthra[2,1,9-Def:6,5,10-d'e'f']Diisoquino
Line-1,3,8,10(2H,9H)-Tetraone] (5a)

Brownish yellow crystals (67 %), m.p > 300 °C. ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm): 8.71 (s, 2H), 8.39 (2H, m), 8.35 (2H, d, J = 8.1 Hz), 8.29 (d, 4H, J = 8.6 Hz), 8.26 (d, 4H, J = 8.6 Hz), 8.20–8.04 (10H, m), 7.92 (2H, d, J = 8.1 Hz), 7.70 (d, 2H,), 7.59(d, 4H, J = 8.5 Hz), 7.56 (d, 4H, J = 8.5 Hz). ^{13}C-NMR (75 MHz, DMSO-d$_6$) δ (ppm): 167.05, 158.3, 133.6, 131.2, 130.9, 129.6, 128.4, 128.3, 126.6, 126.3, 126.1, 125.6, 125.2, 125.1, 124.0, 124.5, 124.1, 122.5, 133.3, 135.4. FTIR (Neat, cm^{-1}) ν$_{max}$: 3057, 1706, 1625, 1583, 1530, 1447, 1262, 1078, 947, 857, 842 cm^{-1}. Anal. Calcd. For C$_{70}$H$_{36}$N$_4$O$_4$ C, 84.32; H, 3.64; N, 5.62; Found: C, 84.13; H, 3.70; N, 5.43.

[2,9-Bis(4-((9H-Fluoren-9-Ylidene)Amino)Phenyl)
Anthra[2,1,9-Def:6,5,10-d'e'f']Diisoquino Line
1,3,8,10(2H,9H)-Tetraone] (5b)

Brownish yellow crystals (71 %), m.p > 300 °C. ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ (ppm): 9.24 (s, 1H), 8.58 (d, 4H, J = 8.7 Hz), 8.16 (d, 4H, J = 8.7 Hz), 8.02 (d, 4H,

$J = 8.6$ Hz), 7.94 (d, 4H, $J = 8.6$ Hz), 7.68 (d, 4H, $J = 8.6$ Hz), 7.57 (d, 4H, $J = 8.6$ Hz). ^{13}C-NMR (75 MHz, DMSO-d_6) δ (ppm): 170.31, 162.96, 146.58, 140.00, 138.74, 136.48, 135.62, 134.34, 131.18, 130.58, 129.57, 129.40, 128.39, 128.06, 125.60, 124.53, 124.29, 124.01, 122.27. FTIR (Neat, cm^{-1}) ν_{max}: 3081, 1682, 1631, 1584, 1545, 1501, 1457, 1260, 1087, 952, 868 cm^{-1}. Anal. Calcd. For $C_{62}H_{32}N_4O_4$ C, 83.02; H, 3.60; N, 6.25; Found: C, 82.97; H, 3.66; N, 6.17.

2,9-Bis(4-((4-Nitrobenzylidene)Amino)Phenyl) Anthra[2,1,9-Def:6,5,10-d'e'f']Diisoquinoline 1,3,8,10(2H,9H)-Tetraone (5c)

Yellowish red crystals (75 %), m.p > 300 °C. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 9.82 (dd, 2H), 8.29(d, 4H, $J = 8.6$ Hz), 8.11 (d, 4H, $J = 8.6$ Hz), 8.26 (d, 4H, $J = 8.5$ Hz), 8.00 (d, 4H, $J = 8.5$ Hz), 7.60 (d, 4H, $J = 8.4$ Hz), 7.54 (d, 4H, $J = 8.4$ Hz). ^{13}C-NMR (75 MHz, DMSO-d_6) δ (ppm): 177.02, 162.96, 151.75, 149.88, 140.00, 139.97, 133.99, 131.49, 130.58, 128.67, 128.06, 125.64, 125.60, 124.60, 124.53 and 124.29. FTIR (Neat, cm^{-1}) ν_{max}: 3061, 1701, 1617, 1590, 1531, 1440, 1267, 1171, 1088, 925, 863, 830, 817 cm^{-1}. Anal. Calcd. For $C_{50}H_{26}N_6O_8$ C, 71.60; H, 3.12; N, 10.02; Found: C, 71.45; H, 3.18; N, 10.00.

2,9-Bis(4-((2-Hydroxy-6-Nitrobenzylidene)Amino)Phenyl) Anthra[2,1,9-Def:6,5,10-d'e'f'] Diisoquinoline-1,3,8,10 (2H, 9H)-Tetraone (5d)

Yellowish red crystals (72 %), m.p > 300 °C. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 9.05 (dd, 2H), 8.17 (d, 4H, $J = 8.7$ Hz), 8.15 (d, 4H, $J = 8.7$ Hz), 7.94 (d, 2H, $J = 8.5$ Hz), 8.20 (t, 2H), 8.26 (t, 2H), 7.58 (d, 4H, $J = 8.6$ Hz), 7.50 (d, 4H, $J = 8.6$ Hz). ^{13}C-NMR (75 MHz, DMSO-d_6) δ (ppm): 168.52, 162.96, 151.75, 149.88, 140.00, 139.97, 133.99, 131.49, 130.58, 128.67, 125.60, 124.60, 124.53, 124.29. FTIR (Neat, cm^{-1}) ν_{max}: 3455, 3045, 1698, 1618 1585, 1537,

Table 1 Absorption maxima of perylene schiff base diimide dyes (5a-e)

S. No	Compounds	λ_{max} (Absorption)	λ_{max} (Emission)
1	5a	515	537
2	5b	487	550
3	5c	492	525
4	5d	526	Nil
5	5e	523	533

1521, 1457, 1417, 1267, 1171, 1080, 907, 870, 828, 810, 780 cm^{-1}. Anal. Calcd. For $C_{50}H_{26}N_6O_{10}$ C, 68.97; H, 3.01; N, 9.65; Found: C, 68.88; H, 3.07; N, 9.56.

2,9-Bis(4-((4-(Dimethylamino)Benzylidene)Amino)Phenyl) Anthra[2,1,9-Def:6,5,10-d'e'f'] Diisoquinoline-1,3,8,10(2H,9H)-Tetraone (5e)

Yellowish red crystals (70 %), m.p > 300 °C. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 9.21 (dd, 1H), 8.27 (d, 4H, $J = 8.6$ Hz), 8.11 (d, 4H, $J = 8.7$ Hz), 7.65 (d, 4H, $J = 8.6$ Hz), 7.53 (d, 4H $J = 8.6$ Hz), 7.56 (d, 4H, $J = 8.4$ Hz), 6.68 (d, 4H, $J = 8.4$ Hz), 2.91 (s, 12H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ (ppm): 171.02, 162.96, 155.51, 148.84, 140.28, 133.63, 131.23, 130.58, 128.67, 128.06, 125.64, 125.60, 124.53, 124.29, 122.95, 111.56, and 41.91. FTIR (Neat, cm^{-1}) ν_{max}: 3041, 2923, 1690, 1628 1582, 1541, 1511, 1457, 1262, 1088, 1011, 878, 830, 817, 791 cm^{-1}. Anal. Calcd. For $C_{54}H_{38}N_6O_4$ C, 77.68; H, 4.59; N, 10.07; Found: C, 77.53; H, 4.64; N, 10.03.
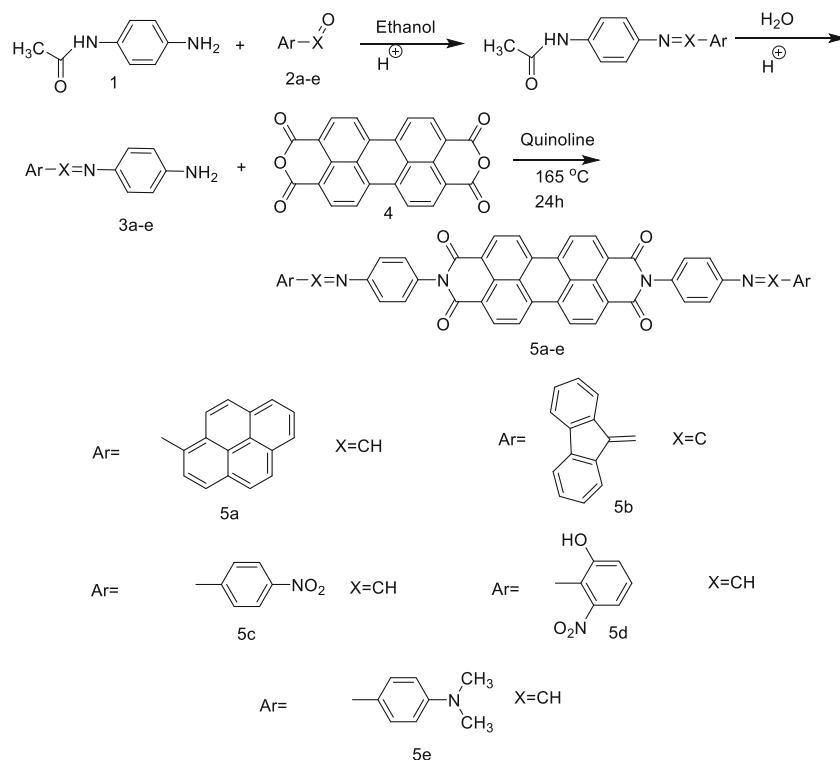
Results and Discussion

Synthesis of Perylene Schiff Base Azo Diimide Dyes (5a-e)

Synthesis of Perylene Schiff Base Azo Diimide Dyes (PDA) dyes **5a-e** has been achieved by two step procedure involving

Fig. 1 UV.visible Spectra of perylene Schiff base diimide dyes **5a-e** in DMSO
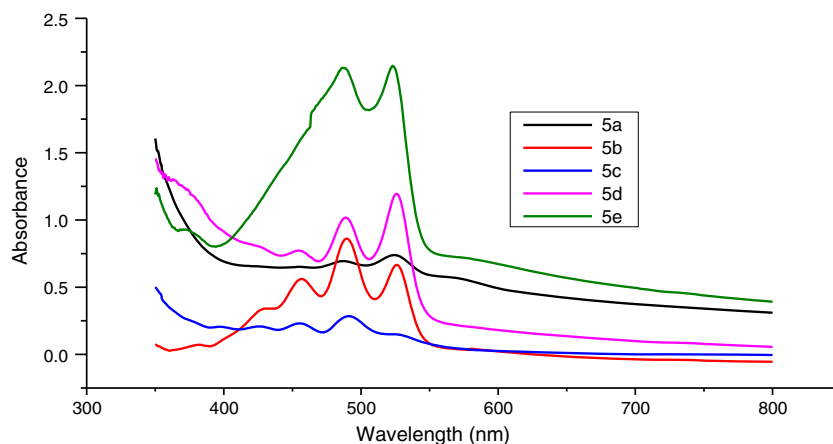
Scheme 1 Synthesis of perylene
Schiff base diimide dyes **5a-e**

the synthesis of Schiff bases and their condensation with perylene dianhydride. Schiff bases synthesis was conducted by reacting *p*-amino acetanilide (**1**) and substituted aldehydes and ketones (**2a-e**). Condensation of *p*-amino acetanilide (0.01 mol) with substituted aldehydes (0.01 mol) in ethanol was catalyzed by acetic acid. The reaction mixture was stirred for 10–12 h at reflux temperature until its completion was observed by taking the TLC of reaction mixture (4:1 Pet ether: ethyl acetate). Schiff bases were separated by rotary evaporation of the reaction mixture and then recrystallized from ethanol and ethyl acetate. In this way a series of Schiff bases **3a-e** were synthesized and purified. Deacetylation of above synthesized Schiff bases was done by hydrolysis of Schiff bases (3a-e) in aqueous solution 20 ml catalyzed by conc. HCl (4 ml). On completion of reaction deacetylated Schiff bases were separated, purified and dried. Deacetylated Schiff bases (0.01 mol) were condensed with perylene dianhydride (0.005 mol) in quinoline at temperature 165 °C and the reaction was catalyzed by zinc acetate Zn(CH$_3$COO)$_2$ (0.5 g). Reaction mixture was stirred for 24 h at this temperature, until completition of reaction was observed by TLC (pure dichloromethane). On cooling the reaction mixture, products were separated which were then filtered and dried in oven at 80 °C. In this way a series of perylene Schiff base diimides **5a-e** were synthesized [33].

Spectral Characterization of Perylene Schiff Base Azo Diimide Dyes (5a-e)

The UV, FTIR, ^{1}H-NMR and ^{13}C-NMR studies were done to elucidate the structures of newly synthesized perylene Schiff base diimide dyes. The U. V/visible absorption spectra of the dyes (1 × 10^{-5} M) were taken at room temperature in dimethyl sulfoxide (DMSO) (Fig. 1) and the selected spectral data is summarized in Table 1.

Three absorption maxima (λ_{max}), bands in UV-visible spectra of dyes (**5a-e**) were observed during electronic transition of dye molecules in DMSO, at 430–450, 470–490 and 510–530 nm. The λ_{max} for all the dyes was the result of π-π* transitions of the molecules indicative of the existence of

Table 2 Singlet energies and oscillation strengths of symmetric diimide dyes (5a-e)

Compound	λ_{max} (A^o)	E_s (kcal/mol)	ϵ_{max} (L/mol.cm)	f
5a	5150	55.5	13,880	0.091
5b	4870	58.7	17,220	0.18
5c	4920	58.1	56,800	0.11
5d	5260	54.3	23,880	0.12
5e	5230	54.6	42,940	0.15

Fig. 2 ^{1}H-NMR spectrum of **5c**
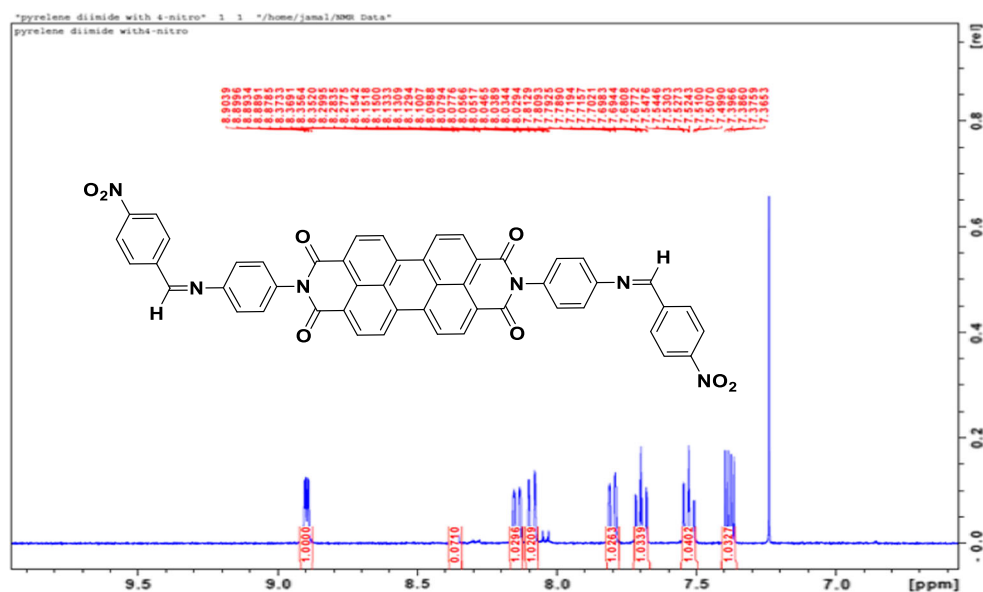
alkenic and imine linkages present in dyes. The λ$_{max}$ in range 510–530 nm is due to π-π* transitions of imine linkages C = N as well as conjugated C = C bonds of perylene ring. For dyes **5a-e** effect of substituents is not high, depicted from their λ$_{max}$ which is not too much different from one dye to another. This phenomenon was observed due to the difference in the conjugational or migrating ability of the electron lone pairs on nitrogen atoms (Scheme 1). This also indicates that the electronic behavior of the nitrogen atoms of imine group is to some extent different in different derivatives. Using the wavelength of maximum absorptions (λ$_{max}$) singlet energies of compounds **5a-e** were calculated and this was in the range 54–58 kcal/mol and oscillation strengths were also determined which varied from 0.091 to 0.15.

From the singlet energy study it is observed that there is a change of 3–4 kcal/mol in the singlet energies of compounds

(**5a-e**). Singlet energy depends upon the wavelength of maximum absorption, which is different in different derivatives as it is clear from Fig. 1 and Table 2. Oscillator strength is dependent on the half width (ν$_{1/2}$) of the selected absorption band and sharp absorption band is seen in the UV spectrum of this compound, so the oscillator strength is lowest for compound **5a** and highest for compound **5e**.

The FTIR spectra of rylene dyes **(5a-e)** exhibited absorption bands due to O-H, Ar-H, C = O of diimides, C = C and C = N, stretching and bending vibrations at 3455, 3080–3120, 1680–1690, 1585–1630, 1430–1445, 1230–1250 and 770–810 cm^{-1} respectively. In particular the peak observed at 1100–1150 cm^{-1} was as a result of C-O-C functionality. The absorption bands at 1585-1630 cm^{-1} and 770–810 cm^{-1} depicted the presence of C = C stretching and bending vibrations respectively. Schiff base linkage was con-

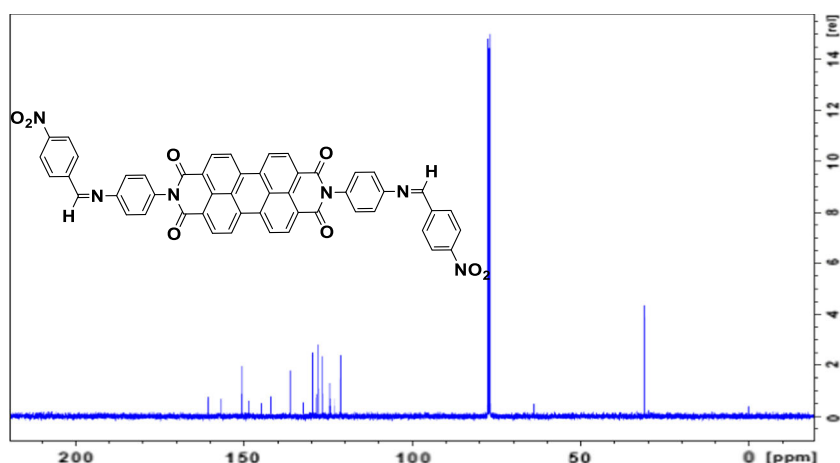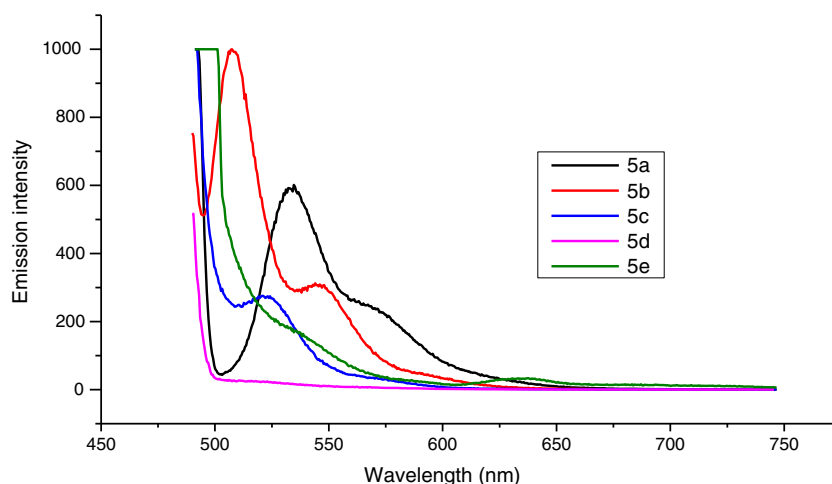**Fig. 3** ^{13}C-NMR spectrum of **5c**

Fig. 5 Cyclic Voltammogram of perylene Schiff base diimide azo dyes **5a-e** in DMSO
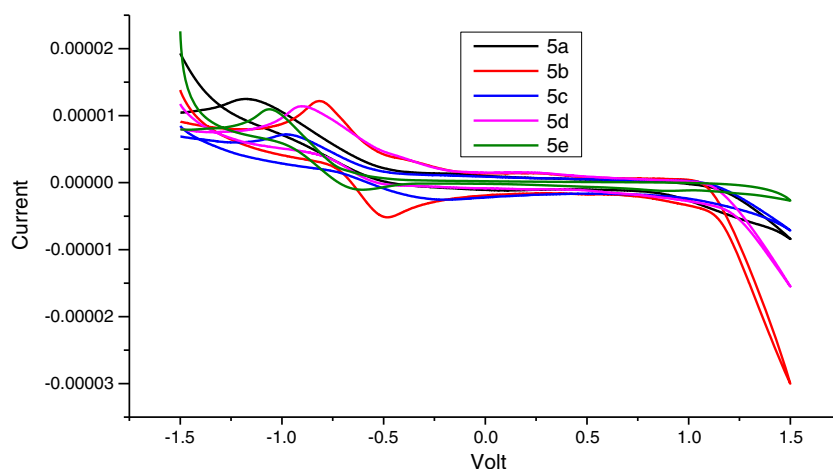
determined from their CV curves. Redox potential (E_{ox}) of dyes **5a-e** were different from each other and were in the range 0.229 to −0.590 V as shown below in the Table 4. Redox potential was highest for dye **5e** and lowest for **5a**. The E_{ox} were used to determine the energy levels of highest occupied molecular orbital (HOMO) by following the empirical Bredas equations [35].

LUMO energy levels were in −4.21 to −5.20 eV, and highest energy LUMO levels seen for **5a** dye bearing pyrene moiety and lowest were in **5e** bearing dimethylamino group at phenylene ring at imide position of perylene ring. These results were in accordance with the general phenomenon observed electrochemical studies of compounds that the electron donating groups decrease the energy gap between HOMO and LUMO levels and electron withdrawing groups increase this gap of energy. HOMO energy levels in the dyes have energy range − 6.85 to 7.57 eV and lowest HOMO levels are present in **5e** and highest for **5a** because in compound **5a** there is more availability of electrons due to highly rich pyrene ring which increases the energy of HOMO levels and thereby decreases the energy gap. Optical band gap energies were calculated by standard procedure and were in the range 2.37 to 2.64 eV. For compound **5e** lowest highest energy

gap is observed which is due dimethyl amino group at Schiff base condensed along the molecular axis, but comparison cannot be made among compounds as these have diverse Schiff bases condensed with perylene dianhydride [36–38] (Table 4).

Thermal Properties of Perylene Schiff Base Azo Diimide Dyes (5a-e)

Thermogravimetric analysis is used to evaluate the thermal stability of a material. In a desired temperature range, if species is thermally stable, there will be no observed mass change [39, 40]. Thermogravimetric study of dyes was made to determine the thermal stability of synthesized dyes **5a-e** upto 500 °C. All perylene Schiff base diimide dyes showed no considerable weight loss during the applied temperature range. From the TGA thermograms it is apparent that synthesized dyes are highly thermally stable. For all perylene Schiff base diimide dyes (5a-e) start up weight loss temperature was observed at about 450 °C and very loss occurred at this temperature as indicated from Fig. 6.

Conclusions

Synthesis of some new bis-axially extended symmetric multichromic fluorescent perylene schiff base and azo diimides chromophores was accomplished in excellent yields. Synthesized derivatives exhibited yellowish and reddish yellow fluorescence with emission peaks in the range 525–550 nm with nearly unit fluorescence quantum yields. LUMO and HOMO energy levels were found in the range of −4.21 to −5.20 and −6.85 to −7.57 eV, respectively with band gap energy 2.35– 2.69/eV. High thermal stability was shown by these dyes in

Table 4 Half wave potential ($E_{1/2}$) and LUMO energy levels of perylene Schiff base diimide azo dyes (**5a-e**)

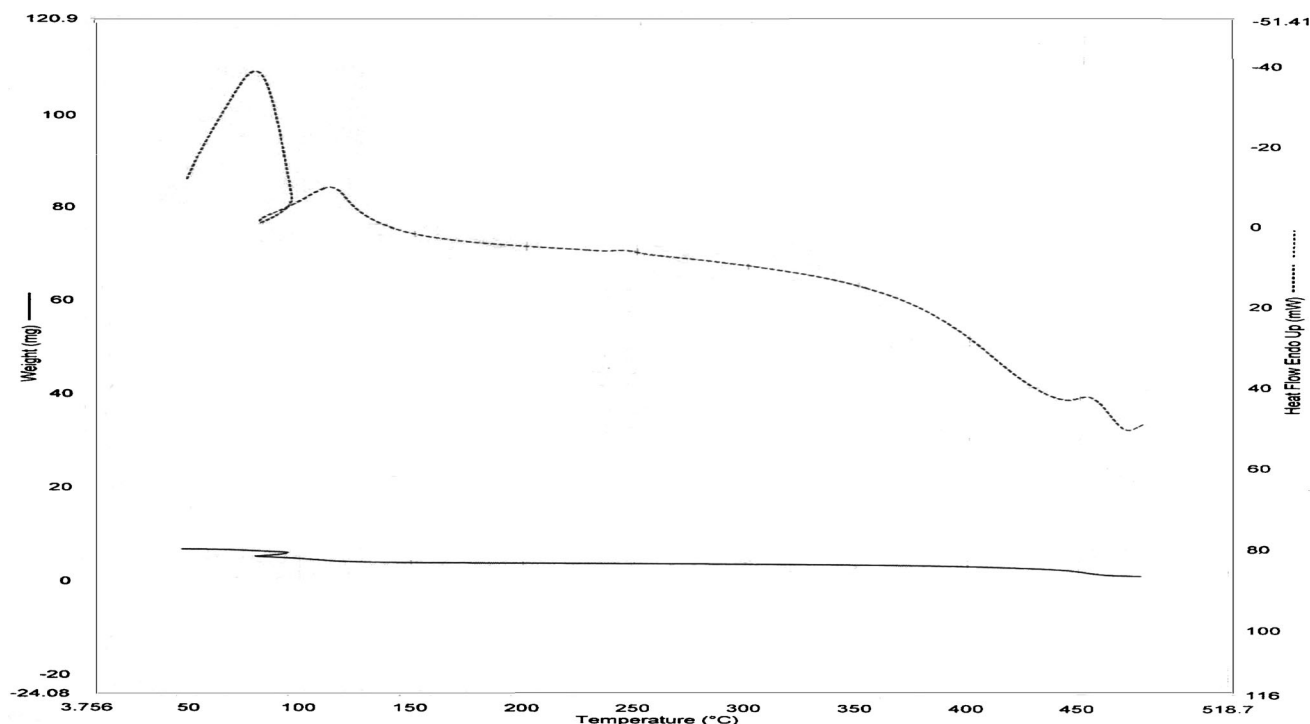| S. No.	Compounds	$E_{1/2}$ (V)	E_g (eV)	HOMO (eV)	LUMO (eV)
1	5a	-0.590	2.64	-6.85	-4.21
2	5b	-0.135	2.38	-7.04	-4.66
3	5c	+0.360	2.52	-7.68	-5.16
4	5d	+0.229	2.37	-7.37	-5.02
5	5e	+0.400	2.35	-7.57	-5.20

Fig. 6 TGA thermogram of dye (5c)

solution as well as in solid state which made them suitable for high-tech applications requiring dyes with tailor-made absorption and emission in a specific region of the visible spectrum.

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