ORIGINAL PAPER

Synthesis, Characterization and Fluorescence Studies of Novel Tetrachloroperylene-Azo Hybrid Dyes

Aamer Saeed · Ghulam Shabir

Abstract Novel rylene-azo hybrid dyes have been synthesized by condensation of azo-dyes with tetrachloroperylene dianhydride, possessing stupendous thermal, chemical and photochemical stability. Phenolic azo dyes are used for the nucleophilic replacement of chlorine substituents at 1,6,7,12-positions of perylene 3,4,9,10-dianhydride system. The absorption maxima ($Λ_{max}$) of these dyes have been determined in diverse solvents such as water, ethanol, methanol, ethyl acetate and N, N-dimethylformamide. Fluorescence spectra are taken in water and highest fluorescence was exhibited by dyes containing carboxylic groups. The $Λ_{max}$ and fluorescence of these dyes is greatly affected by polarity of solvents. The structures of newly synthesized rylene-azo hybrid dyes have been confirmed by UV, FTIR and ^{1}HNMR spectroscopy.

Keywords Tetrachloroperylene dianhydride · Azo dyes · Fluorescence · UV-visible spectra

Introduction

Perylene dianhydrides (PDAs) are important representatives of the perylene ring system. Highly fluorescent PDA derivatives are widely been employed as dyes and pigments due to their exceptional chemical and thermal stability and photochemical inertness [1, 2]. These are used in the field of paints and lacquers particularly in car industry and as key chromophores for highly technical applications such as reprographic processes, fluorescent solar collectors, optical switches [3]

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and dye lasers [4]. Since PDA derivatives enjoy high electron nobilities, these have been fabricated to high efficiency organic photo voltaic devices by using a blend of electron accepting PDAs and hole accepting hexabenzocoronene as well as polymeric TPA blends respectively [5]. The higher homologues have played a key role in single molecule spectroscopy and as NIR (Near Infra Red) absorbers [6].

PDAs based pigments demonstrate high thermal stability, having decomposition temperature is up to 350 °C [7]. They are used to stain polymers such as polyethylene as well as various copolymers. A further advantage of perylene pigments is their broad range of colors which can be controlled by using different substituents for imidization of PDAs. The reason for large differences in colours is veiled in the small differences of the imide substituents, and the influence of the respective crystal structure on the light absorption. One way to convert the perylene pigments into dyes is by imidization of perylene dianhydride with aromatic as well as aliphatic primary amines with bulky substituents. Bulky substituents on imide structure of perylene diimides (PDIs), suppress the parallel stacking of the aromatic systems in space which is a basic requirement of perylene based pigments. If more bulky substituents are present, then parallel stacking of PDIs is completely avoided resulting in dyes instead of the pigments. Another way to transform perylene chromophores into dyes is to introduce phenoxy substituents in the bay region of PDA. This substitution pattern prevents the aggregation of chromophores in solution, resulting in a remarkable increase in solubility in different organic solvents and bright colours with strong fluorescence.

Solubility in aqueous medium is achieved by introduction of sulfonyl or carboxyl groups in the phenolic units in the bay position of dianhydride [8] (Fig. 1a). The soluble derivatives of PDA exhibit brilliant orange to red colours as well as intensive yellowish green fluorescence with nearly 100 % quantum yield. Functionalization of the bay positions also

enables an effective shielding of the chromophore which otherwise exhibits a high tendency toward Π stacking. High quantum yields with respect to fluorescence make perylene based dyes widely applicable [9]. In addition to colouration these compounds are being used in various fields, especially as functional dyes. Their absorption maximum is restricted to a relatively narrow range, with maximum near 530 nm. Even trimeric perylene dyes absorb marginally longer wavelength of 544 nm. Mullen and coworker nevertheless could find a way of extending the chromophoric system of perylene dyes by which near IR absorbing dyes can be obtained, diimides of quarter rylene 3,4,13,14- tetracarboxylic acid, having absorption maximum 764 nm which is 200 nm more than relative to the parent perylene compound [10, 11] (Fig. 1b). The extinction coefficient of these, quaterrylene 3,4,13,14- tetracarboxylic acid diimides, increases from 80,000 to 162,000 M^{-1} cm^{-1}. Perylene dyes can be functionalized by a variety of organic reactions to control their solubility, absorption and emission behavior [12].

In the past few decades, the level of interest in domain of fluorescence is increasing towards the development of fluorescent chemosensers for various ions [13]. In this regard fluorescence spectroscopy has played a vital role to achieve this task. Moreover, photoactive molecular sensors are being developed for the detection of anions which have considerable importance in biological systems [14]. Anion-induced fluorescence sensors are particularly attractive because of the simplicity and high spatial and temporal resolution of fluorescence [15].
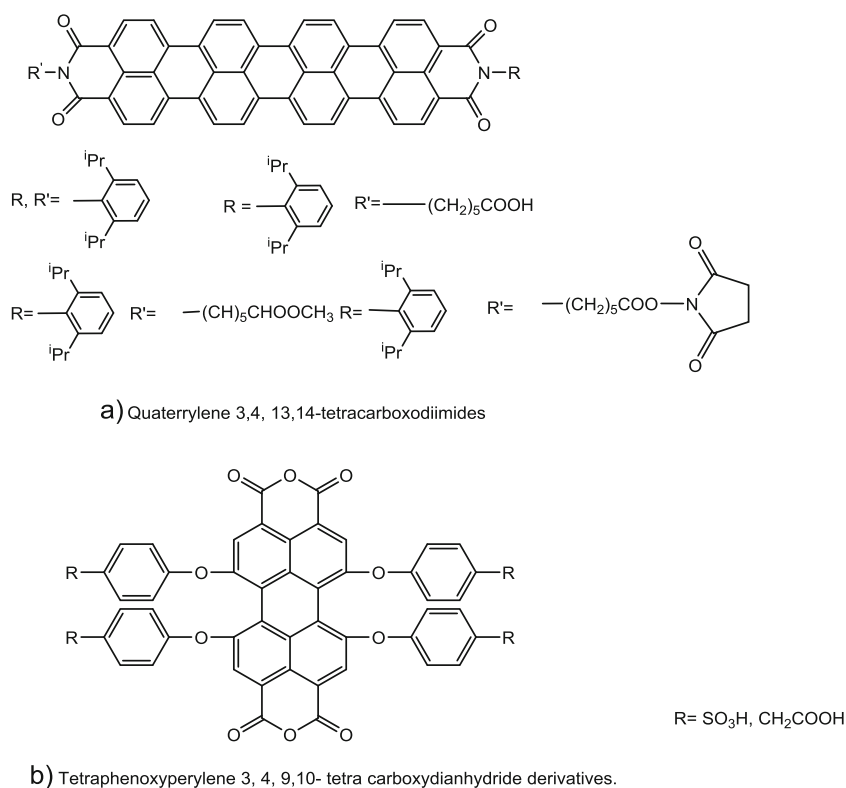
Keeping in view the individual importance of azo-dyes and tetrachloroperylene dianhydride, the aim of present work was to synthesize new fluorescent rylene-azo dyes leading to compounds with enhanced absorptions and emissions properties. Moreover, the effect of substituents on absorptions and emissions of rylene-azo dyes was also studied.

Experimental

Materials Tetrachloroperylene dianhydride was obtained from Honest Joy Holdings. 4-Nitro-4′-hydroxyazobenzene, 3-Nitro-4′-hydroxyazobenzene, 4-hydroxyazobenzene-4-sulfonic acid, 4-hydroxyazobenzene-4-carboxylic acid, and 4-hydroxyazobenzene-2-carboxylic acid were prepared according to known procedures. Solvents such as ethanol, ethyl acetate, DMF, and methanol were analytical grade purchased from Merck.

Methods All raw materials and reagents used for analysis were of 99 % purity. Melting points were recorded using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are uncorrected. ^1H NMR spectra for all the compounds were recorded on a 300 MHz Bruker NMR spectrometer using D_2O as solvent. Splitting patterns notations follows: s

Fig. 1 Some diimide and tetraphenoxyperylene derivatives reported in literature

a) Quaterrylene 3,4, 13,14-tetracarboxodiimides

R= SO₃H, CH₂COOH

b) Tetraphenoxyperylene 3, 4, 9,10- tetra carboxydianhydride derivatives.

(singlet), d (doublet), dd, (double doublet), t (triplet), m (multiplet) and br (broad). Chemical shifts are reported in δ (ppm). The IR spectra were run 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. Thin layer chromatography (TLC) was conducted on 0.25 mm silica gel plates (60 F254, Merck). Visualization of chromatograms was made with UV at 365 and 254 nm.

Synthesis of 1,6,7,12-Tetra-(arylazophenoxy) perylene dianhydrides. General Procedure

Suitable 4-hydroxyazobenzene derivative (2a-e)(0.004 mol) was added to a stirred solution of tetrachloropyrelene anhydride (1, 0.001 mol) (0.53 g) dissolved in 20 ml of freshly distilled dry DMF. Anhydrous potassium carbonate (2.0 g) was added and the reaction mixture heated at a constant temperature of 110 °C for 3 h. The progress of reaction was monitored by TLC using solvent system (4:1 ethyl acetate: pet ether). Filtered the reaction mixture and the residue was dissolved in 30 ml of water. On acidification with conc. HCl (1 ml), precipitation occurred immediately, which was filtered and dried to afford the products (3a-e) in 90–95 % yields. Dyes were named as TPA-1, TPA-2, TPA-3, TPA-4, and TPA-5 are represented in scheme 1.

1,6,7,12-Tetra-(4′-sulfophenylazophenoxy) perylene dianhydride (3a;TPA-1); yellow crystals, m.p>350 °C, ^{1}H-NMR (DMSO): 8.17 (d, 2H), 8.11(d, 2H=R$_3$), 7.86 (d, 2H), 7.84 (d, 2H), 8.62(s, 4H), 2.0 (br singlet 1H) ppm. FTIR (Neat) 1774, 1694, 1607, 1589, 1495, 1430, 1360, 1217, 1025, 852, 754 cm^{-1}.

1,6,7,12-Tetra-(4′-carboxyphenylazophenoxy) perylene dianhydride (3b;TPA-2); yellowish orange crystals, m.p>350 °C, ^{1}H-NMR (DMSO): 8.20 (d, 2H), 8.14(d, 2H), 7.76 (d, 2H),7.83 (d, 2H), 8.62(s, 4H), 10.48 (br singlet 1H) ppm. FTIR (Neat) 3500–3000, 1777, 1685, 1589, 1558, 1494, 1420, 1357, 1227, 1020, 961, 862, 752 cm^{-1}.

1,6,7,12-tetra-(2′-carboxyphenylazophenoxy) perylene dianhydride (3c;TPA-3); yellowish orange crystals, m.p>350 °C ^{1}H-NMR (DMSO): ^{1}H-NMR (D$_2$O): 8.11–8.17 (m, 4H), 7.65–7.80 (m, 4H), 8.62(s, 4H), 10.49 (br singlet 1H) ppm. FTIR (Neat) 3417, 1780, 1683, 1590, 1557, 1495, 1427, 1303, 1229, 1022, 962, 894, 758 cm^{-1}.

1,6,7,12-tetra-(4′-nitrophenylazophenoxy) perylene dianhydride (3d;TPA-4); yellowish brown crystals, m.p>350 °C ^{1}H-NMR (DMSO): 8.39 (d, 2H), 8.19 (d, 2H), 7.76
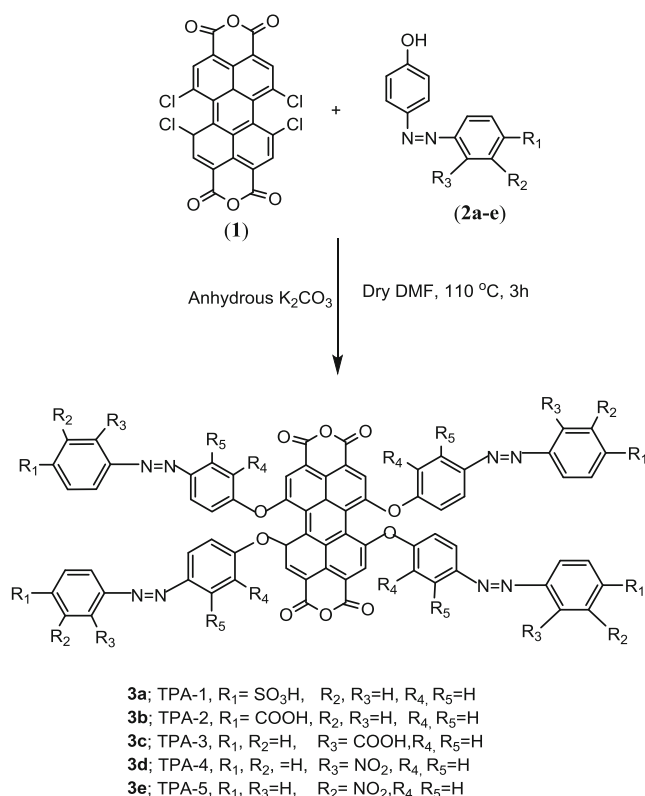
(d, 2H), 6.93 (d, 2H), 8.62(s, 4H), ppm. FTIR (Neat) 1775, 1683, 1585, 1556, 1495, 1425, 1362, 1338, 1308, 1135, 1021, 845, 753, 669 cm^{-1}.

1,6,7,12-tetra-(3′-nitrophenylazophenoxy) perylene dianhydride (3e;TPA-5); yellowish orange crystals, m.p>350 °C, ^{1}H-NMR (DMSO): 8.39 (m, 1H), 8.86 (s, 1H), 7.72 (m, 1H), 8.32 (m, 1H), 7.76 (d, 2H), 6.93 (d, 2H), 8.62(s, 4H) ppm. FTIR (Neat) 1773, 1651, 1584, 1548, 1519, 1392, 1357, 1124, 1060, 789, 702, 671 cm^{-1}.

Results and Discussions

Synthesis

The synthesis of rylene-azo hybrid dyes (TPA-1 to TPA-5) was carried out according to synthetic route sketched in scheme 1. Accordingly tetrachloroperylene dianhydride (1) was treated with suitably substituted 4-hydroxyazobenzene derivatives (2a-e) in 1:4 M ratio in dry distilled DMF solvent at 110 °C in presence of anhydrous potassium carbonate to afford the corresponding TPA fluorescent dyes (3a-e) in excellent yields. The substituted 4-hydroxyazobenzene derivatives (Fig. 2a–e) were prepared according to known literature

3a; TPA-1, R$_1$= SO$_3$H, R$_2$, R$_3$=H, R$_4$, R$_5$=H
3b; TPA-2, R$_1$= COOH, R$_2$, R$_3$=H, R$_4$, R$_5$=H
3c; TPA-3, R$_1$, R$_2$=H, R$_3$= COOH,R$_4$, R$_5$=H
3d; TPA-4, R$_1$, R$_2$, =H, R$_3$= NO$_2$, R$_4$, R$_5$=H
3e; TPA-5, R$_1$, R$_3$=H, R$_2$=NO$_2$,R$_4$, R$_5$=H

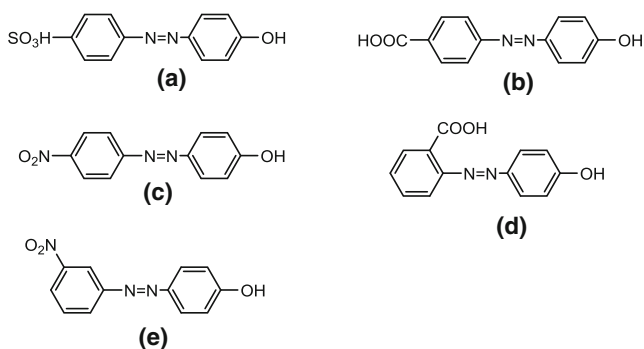**Scheme 1** Synthetic route to tetrachloroperylene based azo dyes (TPA-1 to TPA-5)

Fig. 2 4-Hydroxyazobenzene derivatives used as nucleophile for replacement of chlorine atoms from TPD pigment

procedures. The maintenance of temperature at 110 °C was found to be important as an increase beyond this temperature leads to the decomposition of DMF which may result in substitution of nitrogen in the ring instead of oxygen [16, 17]. The use of molar ratio of (1:4) for anhydride and 4-hydroxyazobenzene derivative was necessary for the replacement of all the four chloro groups of the perylene ring system (scheme 1). The replacement involves an addition elimination mechanism. Anhydrous potassium carbonate was added in excess to increase the nucleophilic character of 4-hydroxyazobenzene derivatives thereby decreasing the reaction time and neutralizing the HCl generated during reaction to avoid the hydrolyze the dianhydride ring system. Reaction mixture was filtered to isolate the products followed by dissolution in minimum amount of water and acidification to reprecipitate the products.

UV, IR, NMR Studies of rylene-azo Dyes (TPA-1 to TPA-5)

The structures of newly synthesized dyes were elucidated by IR, UV, NMR, and mass spectral studies. The strong solvatochromic behavior was observed for dye molecules with large dipole moment changes during transitions between two electronic states. The solvatochromic behavior resulted in the shift of absorption wavelength due to the interaction between the solute and solvent molecules. The U.V. visible absorption spectra of the TPA dyes (1×10^{-5} M) were obtained at room temperature in various organic solvents with different dipole moments (Fig. 3). The selected spectral data is also summarized in Table 1.

UV-visible spectra of dyes were taken in water, ethanol, methanol and DMF. The electronic transition of UV-visible spectra in water gave rise to two absorption maxima (λ_{max}), one ranging from 250 to 270 nm and other ranging from 440 to 450 nm. The first wavelength (λ_{max}) for all the compounds in the range between 250–270 nm was the result of π-π^* transition of the compounds, which showed the presence of C=C, peculiar to benzene and other aromatic nuclei in the dyes. This is in agreement with earlier report by Mielgo et al.,

as per benzenoid UV-visible absorption [18]. The λ_{max} of all dyes in range 440–450 nm was due to π-π^* transitions of azo linkages N=N. Difference in λ_{max} of the synthesized dyes was not too much high. There was difference of 2 to 4 nm in o, m and p-substituted anilines with same substituents. TPA-1 dye shows λ_{max} at 442.6 which is lowest of all the dyes. This is due to highly polar group at p-position of azobenzene, which establishes the attractive interactions with water, decreasing the possibility of π-π^* transitions, so its λ_{max} is lowest. TPA-4 dye having a NO_2 group at p-position of azobenzene, shows the highest λ_{max} at 448 nm. There is no possibility of H-bonding in case of NO_2 with water. The nitro group has highly delocalized charge; it develops very little attractive interactions with water, which does not affect the λ_{max} too much. When NO_2 is at m-position as it is in TPA-5, its inductive effect decreases the λ_{max} about 4 nm. In case of carboxyl group at p-and o-positions of azobenzene, λ_{max} of o-substituted derivative is higher than p- substituted derivative because it is not free to form H-bonding with water, so it has 2 nm higher λ_{max} than p-substituted derivative. The absorption maximum in the range in 350–390 nm in ethanol and methanol is due to π-π^* of N=N transitions, which confirm the presence of azo linkage in the structure of dyes. λ_{max} of hybrid azo dyes is high as these contain a highly conjugated system of single and double bonds and also due to solvent polarity effect which stabilizes the π^* orbitals and shift λ_{max} to higher wavelength compared with non polar solvent systems.

Results obtained show that the solvent effect on UV/vis absorption spectra of investigated TPA azo dyes is very complex and strongly depends upon the nature of the substituent on the aromatic rings. This phenomenon is caused by the difference in the conjugational or migrating ability of the electron lone pairs on nitrogen atoms and azo-hydrazo tautomerism of azo dyes. These results are in accordance with structure of these dyes, (Table 1). This also indicates that the electronic behavior of the nitrogen atoms of azo group is somewhat different between derivatives with electron-withdrawing substituents.

The infrared spectra of the synthesized TPAs azo dyes showed absorption bands due to Ar-H, C=O of dianhydride, C=C and N=N, stretching and bending vibrations at 3,160-3,448, 1,780, 1,680 cm^{-1}, 1,589-1,637, 1,230–1,250 and 723–750 cm^{-1} respectively as shown in Fig. 4 and Fig. 5. Specifically the peak observed at 1,230–1,020 cm^{-1} was a result of C-O-C functionality. The absorption bands at 1,608 cm^{-1}, 1,584, 1,548 and 750 cm^{-1} depicted the present of C=C stretching and bending vibrations respectively. Azo linkage was confirmed by the peak at 1,508-1,495 cm^{-1}. Here the two peaks of dianhydride group have been shifted to lower frequency owing to extended conjugation in molecule. Due to high conjugation carbonyl groups have their character in between single and double bonds instead of pure double bond, so the carbonyl peaks are shifted to lower frequency.
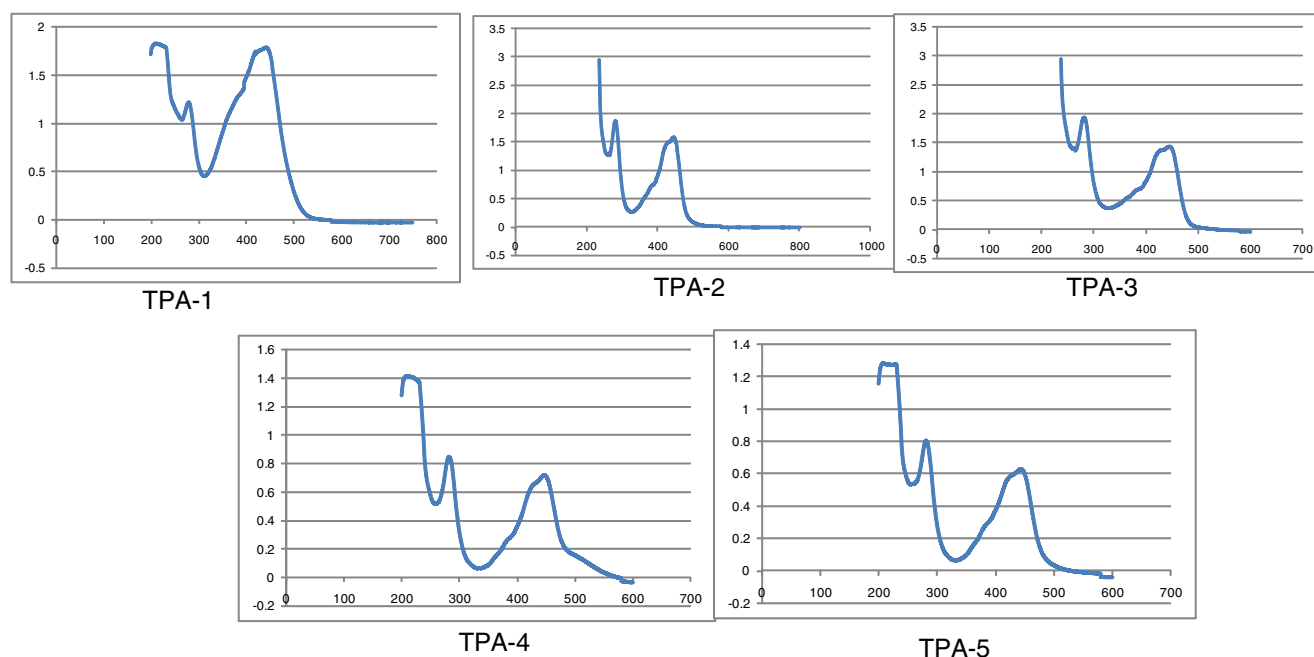
Fig. 3 U.V Visible spectra of TPA-1, TPA-2, TPA-3, TPA-4 and TPA-5

Table 1 Wave length of maximum absorption λ_{max} of TPA Dye in different solvents

Dye	Solvent	λ_{max} (nm)
TPA-1	Water	442.6
	Ethanol	346
	Methanol	349
	DMF	353
	Ethyl acetate	343
TPA-2	Water	444
	Ethanol	351
	Methanol	356
	DMF	370
	Ethyl acetate	341
TPA-3	Water	446
	Ethanol	344
	Methanol	350
	DMF	343
	Ethyl acetate	337
TPA-4	Water	448
	Ethanol	387
	Methanol	390
	DMF	396
	Ethyl acetate	366
TPA-5	Water	443.6
	Ethanol	350
	Methanol	353
	DMF	360
	Ethyl acetate	340

The ^{1}HNMR spectrum of TPA-1 showed signals downfield in the aromatic region of the TMS scale which was between δ 8.1–8.2 due to azobenzene ring and at 2.0 broad singlet due to O-H of SO_3H and 6.79–6.77 ppm as one proton doublet each with coupling constant of 8 Hz. Perylene dianhydride ring system gave singlet peak at 8.62(s) ppm due to four symmetrical protons which is common in all TPA dyes as represented in Fig. 6. Perylene ring peaks of these hybrid dyes are not affected by different azo dyes replacing the chlorine groups of tetrachloroperylene dianhydride molecule. TPA-2 showed 1H broad singlet at 10.48 ppm due to COOH group in the molecule and 4H d, 2H d at 7.89 and 8.11 ppm due to azobenzene ring attached to carboxyl group and 2H d at 6.98 ppm due to benzene ring having oxygen atom attached. Two proton at ortho to azo linkage have signal at the same position at 7.89 ppm.TPA-3, showed four different signals in the range 8.11–8.17 ppm having COOH group at o-position of aromatic ring and 2H, 2H doublets at 7.76 and 6.95 ppm due to benzene ring having oxygen atom attached. Difference from p-COOH is that here four signals are observed; in that case two symmetrical signals are observed. TPA-4 showed peaks at 8.39 and 8.19 due to two different types of proton of benzene ring attached with NO_2 group and 2H, 2H d at 7.76 and 6.93 ppm due to benzene ring having oxygen atom attached. TPA-5 showed four different signals due to non symmetrical protons attached to benzene ring having nitro group at m-position, and 2H, 2H d at 7.76 and 6.93 ppm due to benzene ring having oxygen atom attached. Other prominent signals include one proton doublet each at δ 8.24–8.22 and 8.07–8.05; two proton doublets at 7.65–7.63; two proton triplet at δ 7.74–7.70 and one proton triplet each at δ 7.88–7.82, 7.51–7.47 and 7.30–
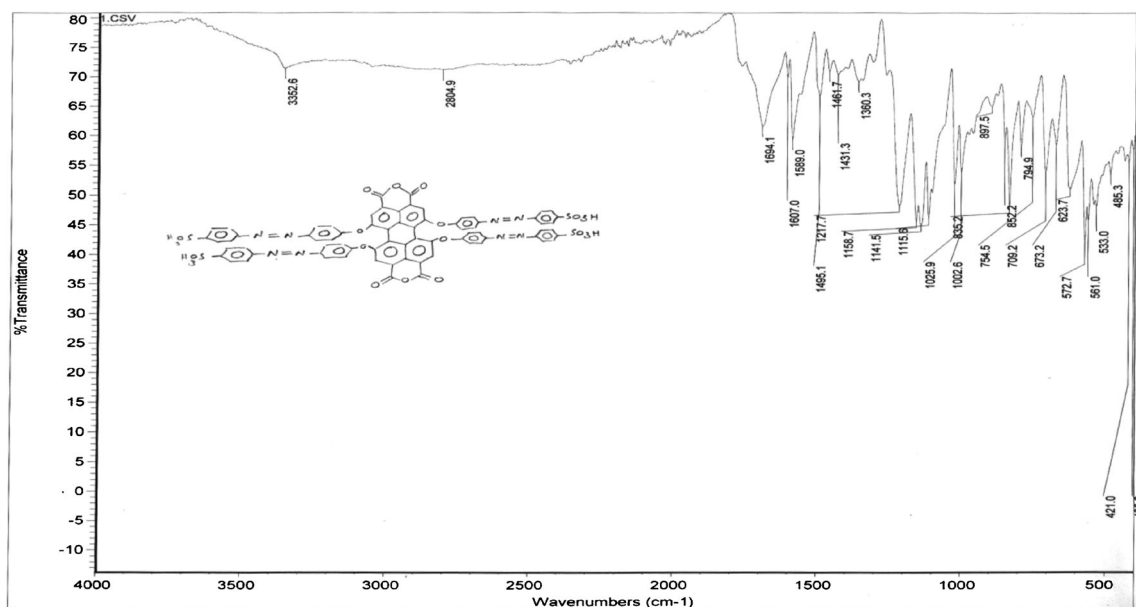
Fig. 4 FTIR Spectrum of TPA-1

7.27 respectively. The ^{13}C-NMR spectrum of TPA-1 showed 16 aromatic carbon atoms in the range 130.7–117.4 ppm.

Fluorescence Studies of TPA Dyes

When a fluorophore absorbs a photon of light, an energetically excited state is formed. The fate of this species is varied, depending upon the exact nature of the fluorophore and its surroundings, but the end result is deactivation (loss of energy) and return to the ground state. The main deactivation processes which occur are fluorescence (loss of energy by emission of a photon), internal conversion and vibrational relaxation (non-radiative loss of energy as heat to the surroundings), and intersystem crossing to the triplet manifold and subsequent non-radiative deactivation [19].

Fluorescence data of all synthesized TPA azo dyes is shown in Table 2. Fluorescence spectra of the dyes which are synthesized were recorded by selecting different excitation wavelengths of the source because excitation spectrum is the dependence of emission intensity at single wavelength, upon different excitation wavelengths. In other words it gives the intensity contribution to the observed emission at a given wavelength by different excitation wavelengths for the sample is exposed. The fluorescence spectra of all TPA hybrid azo dyes show only one fluorescence peak clearly in range 503–511 nm when excited by different wavelengths at
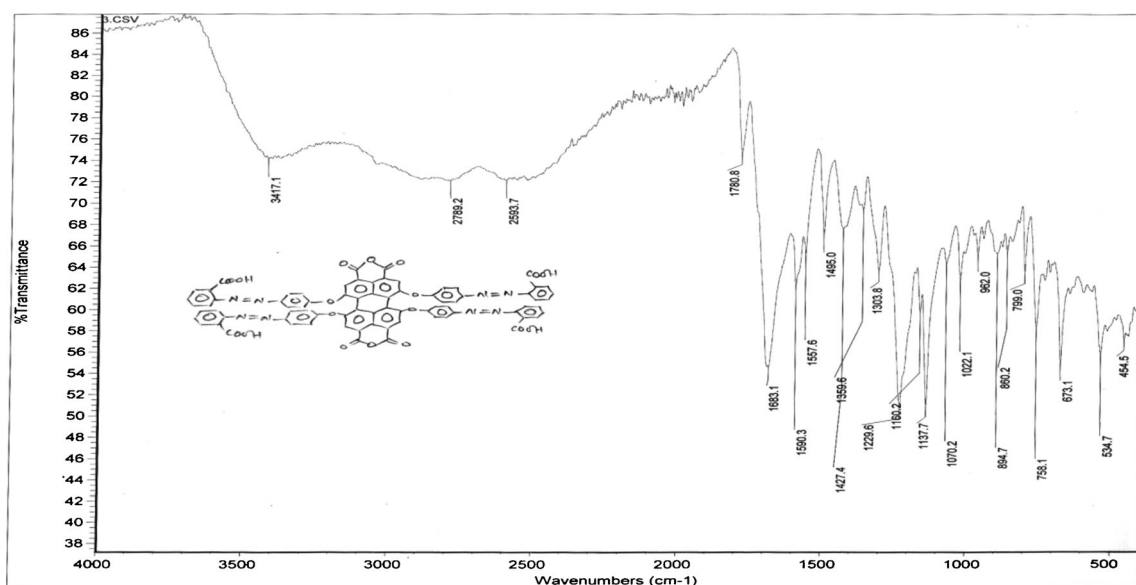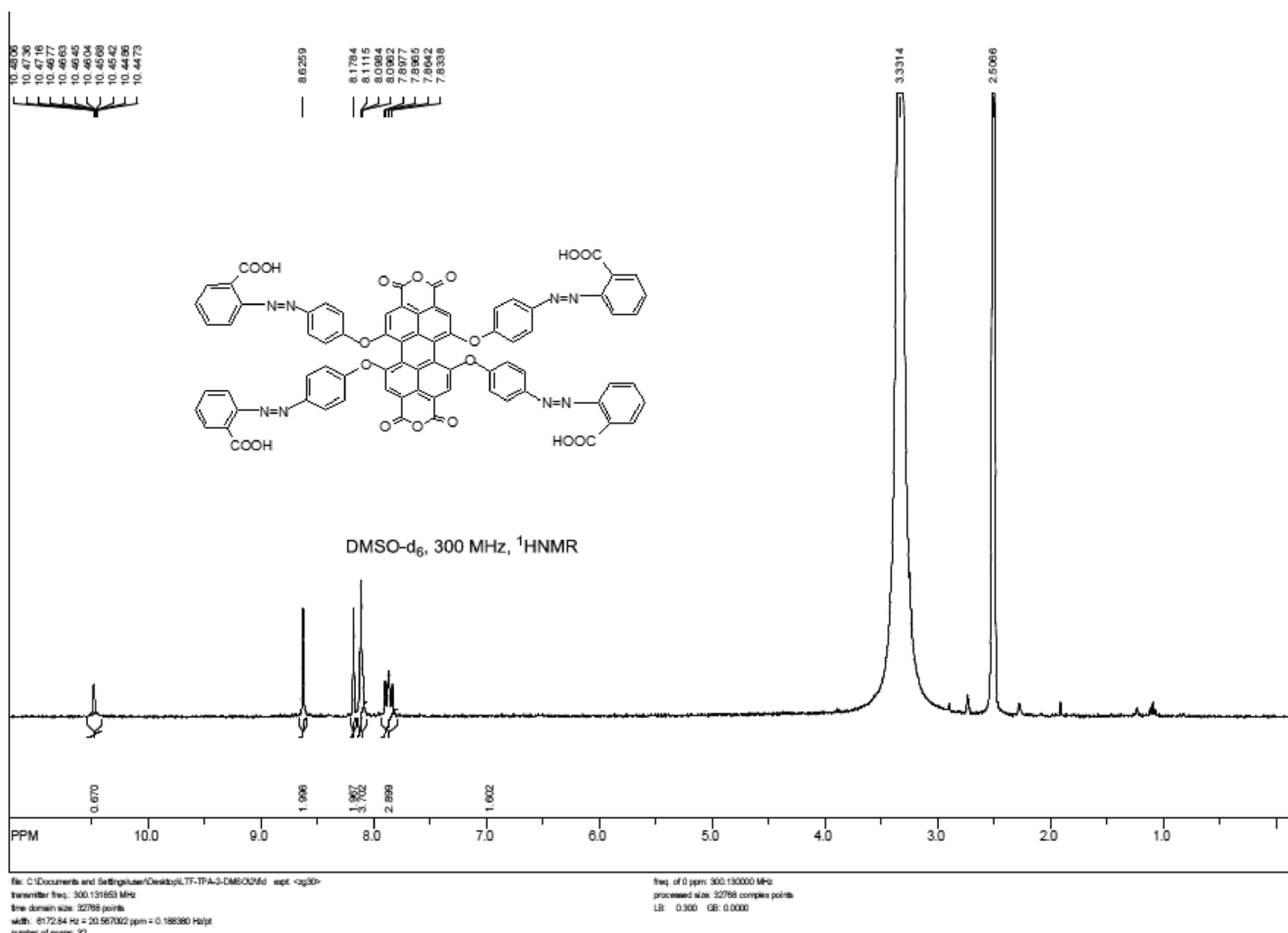

Fig. 5 FTIR Spectrum of TPA-3

Fig. 6 ^{1}HNMR Spectrum of TPA-3

concentration range of 10^{-4} to 10^{-5} M. With so much high degree of fluorescence intensity of all TPA synthesized dyes, it is observed that dyes are highly fluorescent as represented in Fig. 7. Among these dyes TPA-2 is found to highly fluorescent which has carboxyl group at p-position of phenol azo dye used for the nucleophilic replacement of halogen atom from TPA. Emission peak of high intensity in range 503–511 nm for different TPA dyes corresponds to absorption peaks at 442.8, 446 nm, 445 nm 448 nm and 443.6 nm for TPA-1 to TPA-5 respectively. This observed phenomenon of absorption and emission verify the mirror image rule [19].

Fluorescence of all TPAs synthesized dyes is high in water and low in other solvent used for visualizing the fluorescence. In water high fluorescence is observed due to non aggregation of dye molecules because of high polarity and small size. While other solvents have larger size, they cannot penetrate and solvate completely the individual molecules of dyes having bulky structure. Self association of dye molecules occur in polar solvent like ethanol, methanol and DMF, so fluorescence decreases [20].

Stoke shift of TPA-1 is high as it depends upon rapid decay of excited electrons to the lowest vibrational energy level of

Table 2 Fluorescence data of TPA Dyes in water

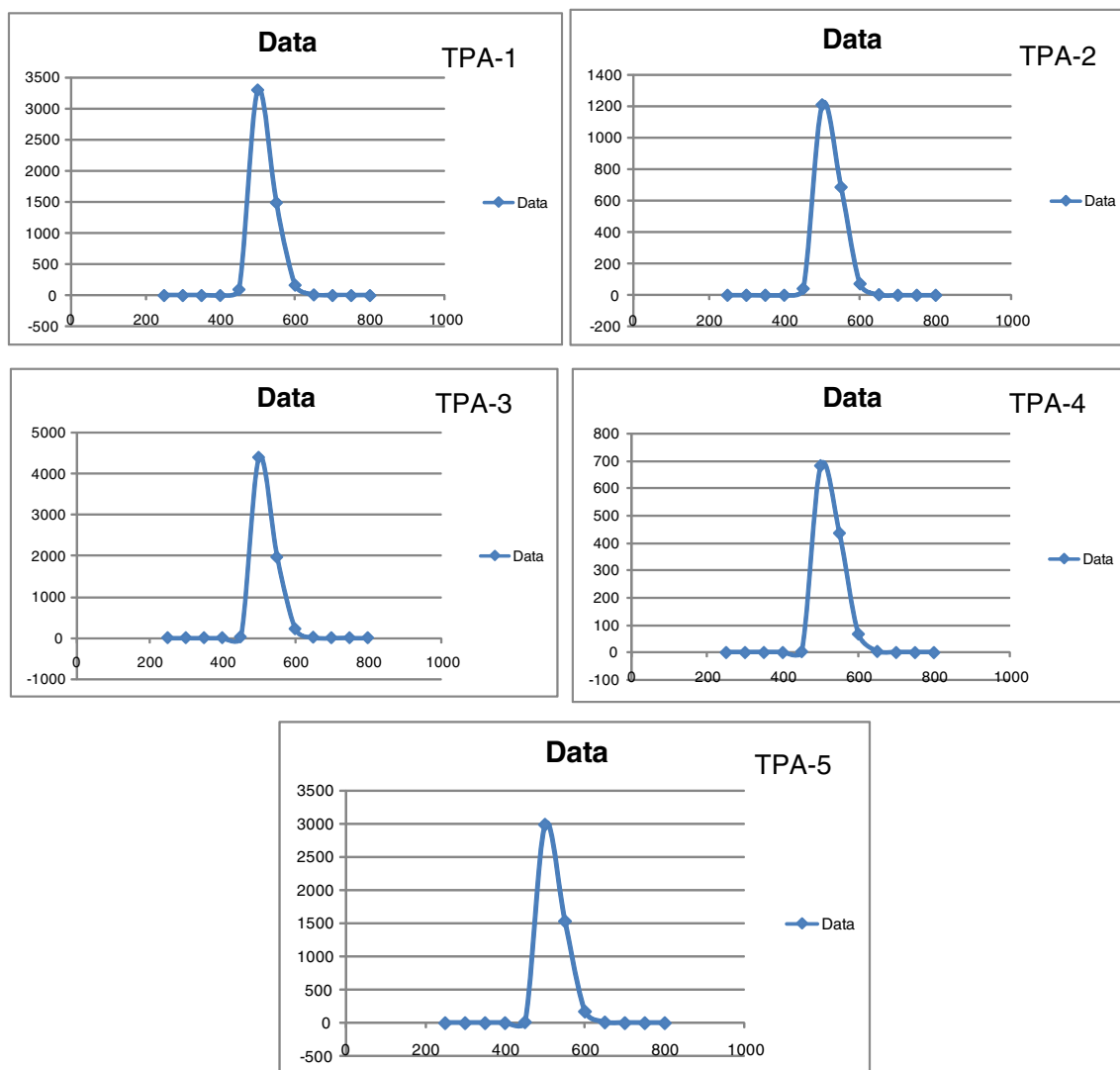| Dye	Solvent	Excitation wavelength	Emission wavelength	Emission Height	Stoke Shift
TPA-1	Water	446 nm	511 nm	3,304	54
TPA-2	Water	448 nm	505 nm	1,207	52
TPA-3	Water	455 nm	503 nm	4,377	45
TPA-4	Water	457 nm	507 nm	679.9	43
TPA-5	Water	453 nm	509 nm	2,981	47

Fig. 7 Fluorescence Spectra of Dyes, TPA-1, TPA-2, TPA-3, TPA-4 and TPA-5

the excited state and on the molecular structure. Larger the structure of fluorescent molecule, higher is the stoke shift. TPA-1 has sulfonic group which has tetrahedral structure, more chances of association due to polarity, which is observed in case of low fluorescence in water and high stoke shift value.

Conclusion

A small series of rylene-azo dyes containing various substituents was prepared by addition elimination mechanism in alkaline medium at 110 °C and their absorption and emission properties were examined in different solvents. λ_{max} of all the dyes was found to be maximum in water, which was in accordance with the general rule that polar solvents shift π- π^* transitions to the higher wavelength. Fluorescence of all the dyes was found to be maximum in water and highest

fluorescence was observed for dyes having carboxylic group at *p*-position of azobenzene moiety of dyes. These dyes are freely soluble in water and other polar solvents, and are least so in non polar solvents. These dyes are potentially applicable in dye sensitized solar cells due to very sharp bandwidth in their emission spectra.

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