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New Fluorescent Symmetrically Substituted Perylene-3,4,9,10-Dianhydride-Azohybrid Dyes: Synthesis and Spectroscopic Studies

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Abstract

Five phenolic azo-dyes (**3a-e**) were synthesized by diazo coupling of the suitably substituted anilines (**1a-e**) with phenol at low temperature in alkaline medium. The resulting dyes have low solubility in aqueous medium due to lack of carboxylic or sulfonic solubilizing functionalities. The hybridization of perylene dianhydride with phenolic azo-dyes was achieved by the nucleophilic aromatic substitution (SNAr) reaction of perylene-3,4,9,10-dianhydride **4** with phenolic azo-dyes **3a-e** in basic medium. The hybrid dyes exhibit absorption maxima λ_{max} in the range 440-460 nm in aqueous medium due to presence of azo linkage and highly conjugated system of π bonds. Fluorescence spectra of these dyes in water show sharp emission peaks with small band widths. The structures of perylene-azo dyes were confirmed by FTIR and NMR spectroscopy.

Key words: Phenolic dyes, perylene-3,4,9,10-dianhydride, azo linkage, fluorescence.

Introduction

Perylene-based chromophores have found unique eminence as dyes and pigments due to boasting brilliant colors, large extinction coefficients, near-unity fluorescence quantum yields, and remarkable photostability [1]. Particularly, perylene-3,4,9,10-dianhydride derivatives are suitable for the demanding applications, such as photovoltaic devices, [2] dye lasers, [3] organic light-emitting diodes, [4] and molecular switches [5]. The excellent charge transporting character of aligned perylenes is suitable for organic thin films transistor (OTFT) applications and as the n-type semiconductor for the fullerene derivatives [6].

1,6,7,12-Tetrachloroperylene tetracarboxylic acid dianhydride (TPA) is a bright red crystalline compound insoluble in water and organic solvents, displaying strong luminescent properties, and stability against heat and light [7,8]. Perylene dianhydride undergo various types of reactions such as addition reactions, nucleophilic substitution, electrophilic substitution and condensation reactions. Important derivatives of TPA include diimides, halogenated, alkylated as well as arylated compounds. The related perylene-3,4-dicarboximides can be monofunctionalized more readily and find certain applications, such as fluorescence labeling and controlled conjugation to other fluorophores and are widely used as dyes and pigments duet to their exceptional chemical, thermal and photochemical stability [9,10]. In perylene tetracarboxdiimide pigments, the color tuning is achieved by variation of the substituent of the imide functions, resulting in modification of the crystal structure. Perylene pigments cover the whole range of the visible spectrum and find applications in paints and lacquers, specifically in the car industry. Perylenes are key chromophores for high-tech applications such as reprographic processes, [11] fluorescent solar collectors, [12] photovoltaic cells, [13] optical switches, [14] and lasers [15]. In this context, perylene teracarboxdiimides are generally referred to as functional dyes. Nevertheless, further developments in the field of perylene tetracarboxdiimide based functional dyes have been limited by their insolubility in common organic solvents, hindering a fine-tuning and shift of their absorption to longer absorption wavelengths.

The fabrication of colored and luminescent materials of organic and hybrid organic–inorganic structures requires the use of soluble dyes [16]. This problem is frequently solved by the introduction of organic substituents in the aromatic framework of the anhydride. Good results were obtained on introduction of long-chain aliphatic amines with branched organic radicals [17]. Symmetric bisimidazole and asymmetric imide-imidazole perylene derivatives with long, hyperbranched alkyl groups, attached to the benzimidazole moeity, enhanced the solubility of the imidazole derivatives. Soluble asymmetric imide-imidazoles were prepared using 1,2-

diaminophenyls which contained methoxy, nitro and ester groups. The effects of both electron-withdrawing and donating groups has been examined optically and electronically using both absorption and emission spectroscopy. Discotic liquid crystalline materials based on TPA are shown in Figure 1 [18].

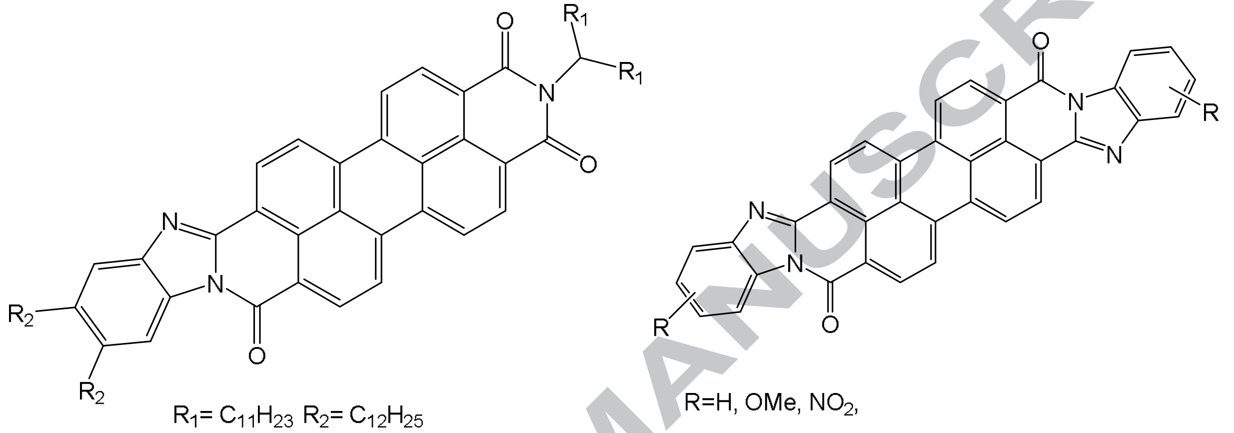


Figure1. Some symmetric and asymmetric perylene imide-benzimidazole derivatives

The individual importance of azo-dyes on one hand and that of tetrachloroperylene dianhydride, on the other, prompted us to synthesize some new fluorescent perylene-azo dyes leading to compounds with enhanced absorptions and emissions properties. Herein, we wish to describe synthesis of some symmetrically substituted (in bay area) perylene dianhydride-azo dyes. Furthermore, their solubility, absorption and fluorescence properties have also been studied. These are found to exhibit fairly high emission, good solubility in aqueous and organic media, as well as high thermal stability.

2. Experimental

2.1 Materials: Tetrachloro perylene dianhydride was obtained from Honest Joy Holdings limited China. Sodium nitrite was obtained from BDH. Hydrochloric acid and phenol were purchased from Merck. Potassium carbonate was purchased from Daejing Korea. Solvents such as ethanol, ethyl acetate, DMF, and methanol were common laboratory grade chemicals.

2.2 Methods: All raw materials and reagents used for analysis were of 99% purity. Proton NMR spectra for all the compounds were recorded on a 300 MHz Bruker NMR spectrometer in D_2O solvent. Splitting patterns were as follows: s (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. 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 CPA hybrid azo dyes.

2.3 Synthesis of Phenolic Azo Dyes (**3a-e**).

Suitably substituted anilines (**1a-e**) (0.01mol) were dissolved in 20 ml water and 3.5 ml concentrated HCl, with stirring maintaining the temperature at 0-5 ^{o}C. A solution of $NaNO_2$ (0.01 mol) in 10 ml water was added promptly to solution of aniline with continuous and vigorous stirring. Stirring was further continued for 1h maintaining the temperature in the same range. After 1h the reaction mixture was checked for the completeness of reaction on a paper chromatogram using water as mobile base. The dried chromatogram was sprayed with solution of p-N,N-dimethyl aminobenzaldehyde in ethanol as spraying agent. On completion of reaction the diazonium salts (**2a-e**) were kept in a freezer.

Phenol (0.01mol) was dissolved in water (15ml) and K_2CO_3 (2g), kept in the ice bath at temperature 0-5 ^{o}C with stirring. The diazo solution was added drop wise to the well stirred solution of phenol during 30 minutes, maintaining the pH above 8. The progress of reaction was monitored by paper chromatography using H-acid solution in alkaline media. On completion the solids were filtered, dried in oven at 70^{o}C, for 3hs to afford the 4-hydroxyazobenzene derivatives (**3a-e**) in 87-90% yields (scheme-1). In case where regioisomeric products were obtained; column chromatography was used for separation.

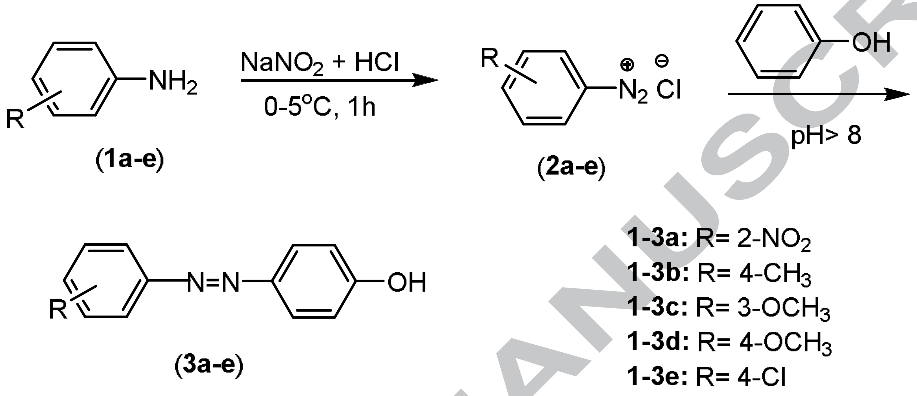
2.4 Synthesis of Tetrachloro Perylene Hybrid Azo Dyes:

Tetrachloroperylene dianhydride (**4**) 0.001 mol (0.53g) was charged in 250ml round bottomed flask containing 20ml DMF positioned on hot plate having oil bath. Started stirring and heating, and added 4-hydroxyazobenzene derivatives (**3a-e,** 0.004 mol), then added 2.0 g of K_2CO_3. the reaction mixture was Kept at 110^{o}C for 3 hours. The reaction progress was monitored by taking the TLC of reaction mixture in 4:1 ethyl acetate: pet ether. On completion the reaction mixture was filtered and residue was dissolved in 30ml of water. On acidification with conc. HCl, (1ml), the precipitation occurred immediately, filtered and dried to afford the products (**5a-e)** in 90-95%. Dyes **5a-e** were named as CPA-1, CPA-2, CPA-3, CPA-4 and CPA-5 respectively (scheme-2).

3. Results and discussions

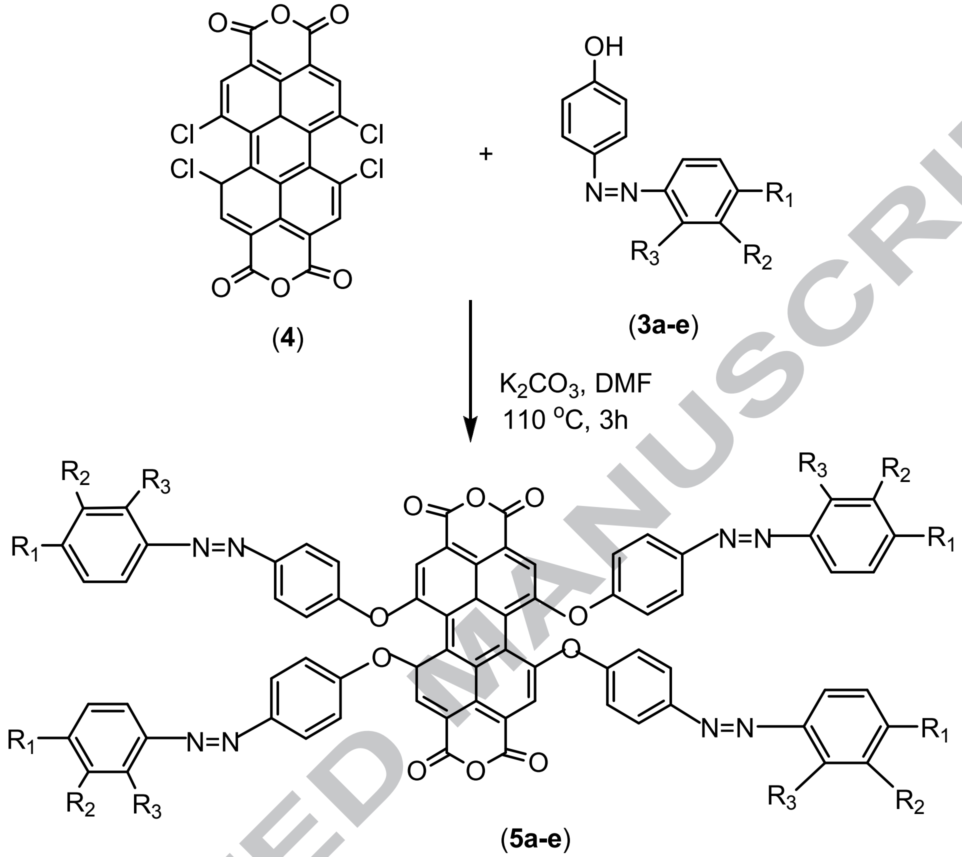
3.1 Synthesis

For the synthesis of pereylene-azo hybrid dyes, the phenolic azo coupling partners were synthesized according to scheme 1. Thus potassium phenolate was treated with diazonium salts **2a-e** of the suitably substituted anilines in aqueous medium to produce phenolic azo dyes **3a-e** in excellent yields. Diazotization of nitro, methyl, methoxy and chloro substituted anilines was carried out at low temperature 0-5^{o}C to avoid the decomposition of thermally labile diazonium salt. The completion of diazotization was checked by absence of yellow coloration which is developed on reaction with N,N'-dimethylamino benzaldehyde with unreacted aniline. The diazonium salts were treated with phenol at low temperature maintaining the pH above 8 using K_2CO_3. High pH increases the nucleophilicity of phenol, makes aromatic ring more nucleophilic and more of the *p*-substituted product is obtained due to stability and high electron density at *p*-position (scheme 1).



Scheme 1 Synthetic route to phenolic azo dyes

After having prepared the phenolic azo dyes **3a-e** the next step ahead was the coupling with dianhydride to produce title hybrid compounds (**5a-e**; CPA-1 to CPA-5) according scheme-2. Tetrachloroperylene dianhydride (**4**) was treated with separately synthesized phenolic azo dyes **3a-e** in dry distilled DMF 110°C for three hours to afford the CPA azo dyes in good yields [19, 20]. Temperature was maintained at 110°C to avoid the decomposition of DMF, which may result in substitution of ring oxygen by the nitrogen. A molar ratio of 1:4 for tetrachlorperylene dianhydride and phenolic azo dyes was employed for the substitution of all the four chloro groups by an addition elimination mechanism. The use of potassium carbonate in excess increases the nucleophilic character of 4-hydroxyazobenzenes to complete the reaction rapidly and to neutralize the acid generated during the reaction to avoid the hydrolysis of the dianhydride. The solids were filtered, dissolved in a minimum amount of water and acidified to afford the products devoid of the base. (scheme 2).



5a: CPA-1, R_1R_2,=H, R_3= NO_2,
5b: CPA-2, R_1= CH_3, R_2, R_3=H,
5c: CPA-3, R_1, R_2=H, R_3= OCH_3,
5d: CPA-4, R_1=OCH_3, R_2, R_3= H,
5e: CPA-5, R_1, R_2=H, R_3= Cl,

Scheme 2 Synthetic route to tetrachloroperylene based azo dyes (**5a-e**)

3.2 UV, IR, NMR Studies of CPA-Azo Dyes (CPA-1 to CPA-5)

The structures of newly synthesized dyes were elucidated by UV, IR and NMR studies. The strong solvatochromic behavior was observed for dye molecules with large dipole moment changes during transitions between two electronic states. The solvatochromic behavior of a dye is the shift of absorption wavelength due to the presence of solvent with different polarity, which is due to the interaction between the solute and solvent molecules. The U.V. visible absorption spectra of the CPA hybrid azo dyes (1×10^{-4} M) were obtained at room temperature in various organic solvents with different polarity (Fig 2) and the selected spectral data is summarized in Table 1.

Table 1 Wavelength of maximum absorption λ_{max} of CPA hybrid Azo Dye in Different solvents.

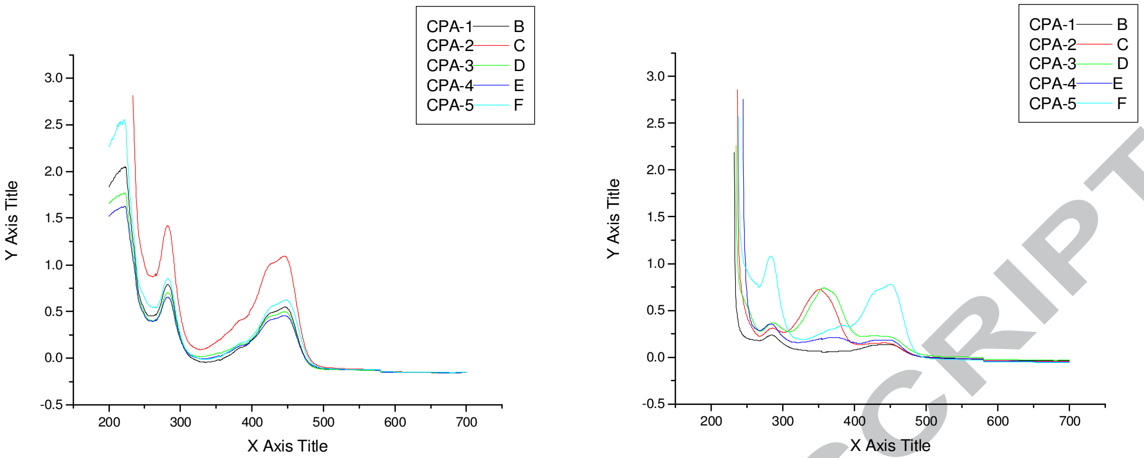
Dye	**Solvent**	**λ_{max} (nm)**
CPA-1	Water	278, 439
	Ethanol	269, 426
	Methanol	273, 432
CPA-2	Water	279, 423
	Ethanol	262, 340, 423
	Methanol	266,328, 432
CPA-3	Water	279, 430
	Ethanol	271, 349, 416
	Methanol	273, 351, 428
CPA-4	Water	279, 428
	Ethanol	268, 347, 422
	Methanol	277, 348, 425
CPA-5	Water	280, 442
	Ethanol	266, 426
	Methanol	270, 428

UV-visible spectra of dyes were taken in water, ethanol and methanol. The electronic transition of UV-visible spectra in water gave rise to two absorption maxima (λ_{max}), first at 260-280 nm and other at 420-440 nm and three λ_{max} when ethanol or methanol were used as solvents. The λ_{max} for all the compounds is a result of π-π* transition of the compounds indicating the presence of C=C characteristic of 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 [21]. The λ_{max} in range 420-440 nm is due to π-π* transitions of azo linkages N=N. Difference in λ_{max} of the synthesized dyes is not too much high for different substituents. All CPA hybrid azo dyes have λ_{max} highest in water and lowest in ethanol which is in accordance with polarity of solvents. More will be solvent polarity greater will be shift in λ_{max}. Water is more polar than methanol and ethanol so it shifts π-π* transitions to higher wavelength. CPA-1 shows the lowest λ_{max} in all solvents because of the fact that it has NO_2 group at the *o*-position of azobenzene which decreases the possibility of π-π* transitions and produces hypsochromic shift. CPA-3 and CPA-4 shows highest λ_{max} because they have OCH_3groups at *o* and *p*-positions of azobenzene ring and these are electron donating groups, and cause bathochromic shift. CPA-5 has chloro group at *p*-position of phenolic azo dyes which is electron donating group by resonance causes red shift as it is obvious from figure 5 and it has λ_{max} 442 nm. CPA-2, 3 and 4 show the absorption maximum in the range 335-350 nm in ethanol and methanol, is due to n-π* of N=N transitions, which confirm the presence of azo linkage in the structure of dyes. These results show that the solvent effect on UV/vis absorption spectra of investigated CPA hybrid azo dyes is multifaceted and strongly depend on the nature of the substituent on the aromatic rings. This phenomenon is due to the difference in the conjugational or migrating ability of the electron lone pairs on nitrogen atoms and the azo-hydrazo tautomerism of azo dyes in accordance with their structure (Table 1).

This also indicates that the electronic behavior of the nitrogen atoms of azo group is to some extent different in different derivatives and in solvents of different polarity.

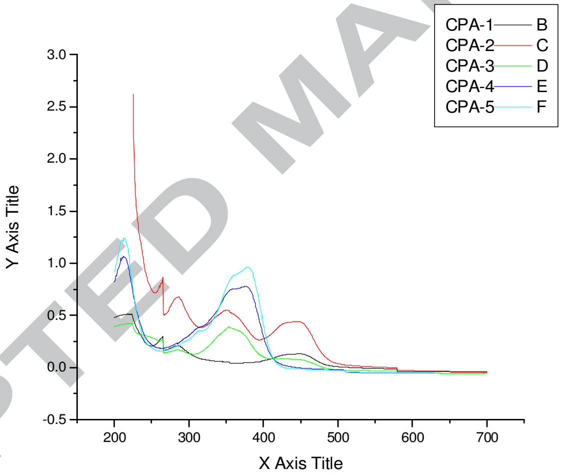
The FTIR spectra of hybrid dyes showed absorption bands due to Ar-H, C=O of dianhydride, C=C and N=N, stretching and bending vibrations at 3050- 3190, 1730-1780, 1589 - 1637, 1230-1250 and 723-750 cm^{-1} respectively. In particular the peak observed at 1150-1100 cm^{-1} was as a result of C-O-C functionality. The absorption bands at 1618 cm^{-1} and 750 cm^{-1} depicted the present of C=C stretching and bending vibrations respectively. Azo linkage was confirmed by absorptions at 1445-1490 cm^{-1}.

The ^{1}HNMR spectrum of CPA-1 showed a multiplet downfield in the aromatic region at 7.72-8.39 ppm and a double doublet at 6.93-7.76 ppm due to diazo component of phenolic azo dyes. Perylene dianhydride ring system gave a singlet at 8.22(s) ppm due to four symmetrical protons. The position of perylene ring system of these dyes is not affected much in different azo dyes. CPA-2 showed 3H singlet at 2.35 ppm because of CH_3 and 7.26 -7.81 ppm double doublets due to 16H in the diazo component of phenolic azo dyes and 8H doublet at 7.76 and 6.93 ppm due coupling component of phenolic azo dyes. CPA-3 and CPA-4 showed 3H singlet peaks at 3.9 ppm due to OCH_3 attached at o and p-positions of diazo component and all other signals in range 7.76-6.93 and 7.45 ppm are same like other CPA dyes. Difference between CPA-3 and CPA-4 is to 16H multiplet for CPA-3 diazo component and for CPA-4 16H double doublet. CPA-5 showed 32H double doublet for diazo 16H at 7.47 and 7.86 ppm, and coupling component 16H at 7.65 and 7.63 ppm. The ^{13}C-NMR spectrum of products showed sixteen aromatic carbon atoms in the range 130.7-117.4 ppm.



U.V Spectra in water

U.V Spectra in ethanol



U.V Spectra in methanol

Fig 2. U.V Visible spectra of CPA-1 to CPA-5 in water, ethanol and methanol.

3.3 Fluorescence Studies of CPA hybrid Azo Dyes

When a fluorophore absorbs a photon of light, an energetically excited state is formed. The fate of this species is diverse, 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 [22].

Fluorescence data of all the synthesized CPA-azo dyes is shown in Table 2. Fluorescence spectra of the dyes 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 (Figure 3). 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 dyes show single distinct emission peak at 500-513 nm at a concentration of 10^{-4} to 10^{-5} M. Among these dyes CPA-3 having OCH_3 at *o*-position of phenolic azo dye, shows highest fluorescence. This high emission may be attributed to non aggregation of dyes molecules, due to presence of OCH_3 at *o*-position which intricate the parallel alignment of dye molecules, making dye highly fluorescent. Emission peak of high intensity at 500-513 nm for different CPA dyes corresponds to absorption peaks at 442.8, 446 nm, 445 nm 448 nm and 443.6 nm for CPA-1 to CPA-5 respectively. This observed phenomenon of absorption and emission verify the mirror image rule [19].

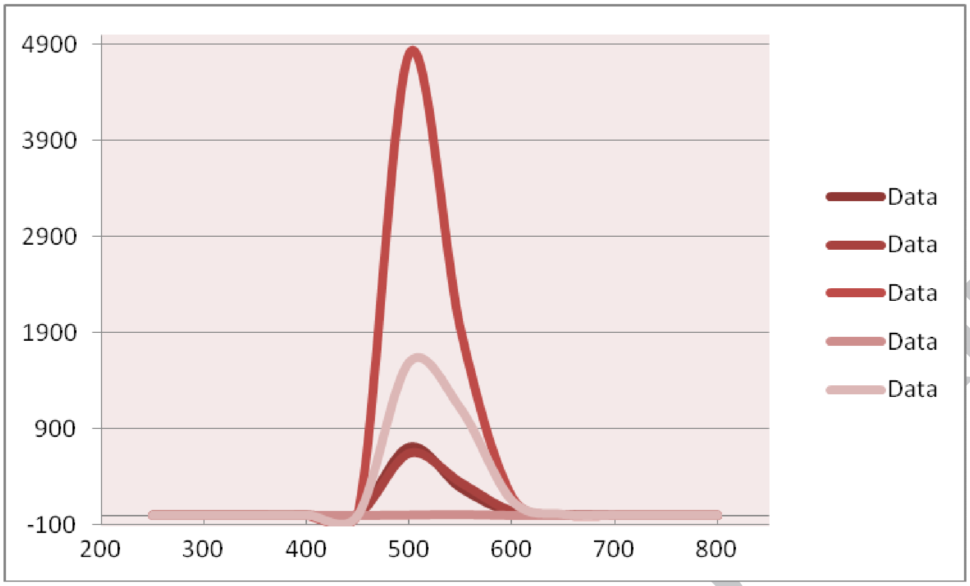


Fig 3. Fluorescence Spectra of Dyes, CPA 1-5

Fluorescence of all CPAs dyes is high in water and low in other solvents. In water high fluorescence is due to non aggregation of dye molecules because of high polarity and small size of water molecules. 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 solvent like ethanol, methanol and so fluorescence decreases [22].

Stoke shift of CPA-1 and CPA-3 is high as it depends on rapid decay of excited electrons to the lowest vibrational energy level of the excited state and on the molecular structure as it is depicted in the sharpness of emission peak in fluorescent spectra. In both cases *o*-positions of azo dyes have substituents, which reduce the chances of self association and increase the stoke shift value.

Table 2 Fluorescence values of CPA hybrid Azo Dyes in water

Dye	Solvent	Excitation wavelength	Emission wavelength	Emission Height	Stoke Shift
CPA-1	Water	424nm	502nm	720	78
CPA-2	Water	451nm	510nm	698	59
CPA-3	Water	422nm	503nm	4859	81
CPA-4	Water	550nm	555nm	12.58	5
CPA-5	Water	464nm	513nm	1894	49

4. Conclusion

Some new water as well as polar solvent soluble perylene-azo hybrid dyes have been synthesized in high yields via a short synthetic route. The newly synthesized dyes show absorptions in the range 415- 450 nm which impart them an orange yellow color. The absorption wavelength (λ_{max}) and emission height of all the dyes were found to be maximum in water. Moreover the dyes show excellent thermal stability (upto 350^{o}C) for potential high-tech applications requiring dyes with tailor-made absorption and emission in a specific region of the visible spectrum can be envisaged.

5-Acknowledgments

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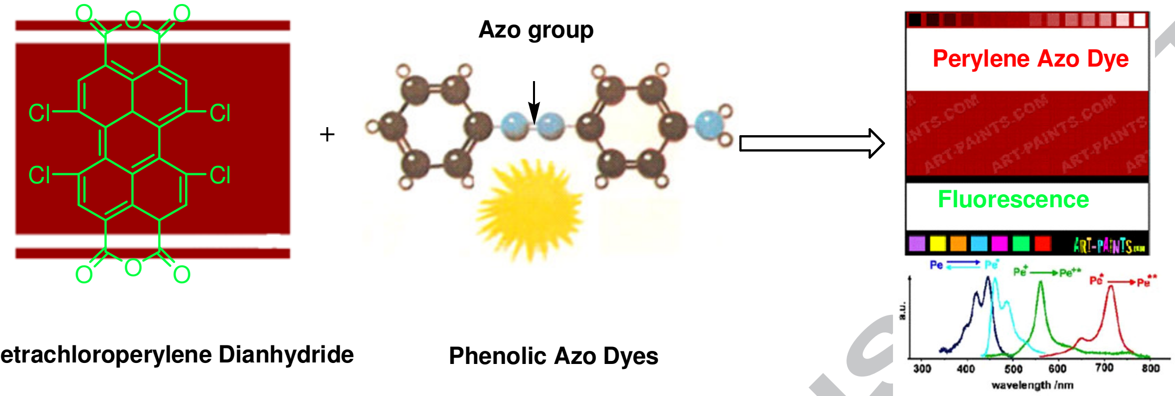

Research Highlights

- ✓ Five phenolic azo dyes were coupled with perylene dianhydride to afford hybrid azo-perylene dyes.
- ✓ These exhibit greenish yellow fluorescence due to extensive conjugation and prevention of parallel alignment of perylene.
- ✓ Fluorescence and absorption of hybrid azo-perylene dyes is related directly to the solvent polarity.