

Synthesis and Photophysical Properties of the New Dyes Contained Benzenesulfonamide and 1,8-Naphthalimide

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ABSTRACT: In this study preparation and thermal, electrochemical, photophysical properties of the compounds are reported. New series of compounds consisting of 4-Allylamino-N-4-aminobenzenesulfonamide-1,8-naphthalimide, 4-Amino-N-4-amino-N-(2-pyrimidinyl) benzenesulfonamide-1,8-naphthalimide and 4-Allylamino-N-4-amino-N-(2-pyrimidinyl) benzenesulfonamide-1,8-naphthalimide were synthesized via sonic method from intermediate 4-nitro-1,8-naphthalimide by imidation, reduction and allylation reactions. These compounds were characterized by thin layer chromatography (TLC), differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FT-IR), ¹H-nuclear magnetic resonance (¹HNMR), ¹³C-NMR, liquid chromatography, UV-Vis spectroscopy and fluorimetry. New acceptor-donor compounds were obtained with the photoluminescence quantum yields (PLQY) of 33.68-79.70% in solution and 0.85-3.39% in non-doped solid film. The synthesized dyes absorb electromagnetic radiation in the range of 434-440 nm and emit solid films exhibited fluorescence in the range of 561-614 nm. The ionization potentials of the synthesized dyes were found to range from 6.00 eV to 6.09 eV.

KEYWORDS: Ultrasound method, Naphthalimide dyes, Sulfonamides, Electrochemical properties, Photophysical properties

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1. INTRODUCTION

Synthetic fluorescent labels are indispensable tools for quantitative detection in various fields of modern sciences [1]. Conjugated compounds containing both donor and acceptor moieties have been extensively synthesized and studied because of their potential applications in electronics and optoelectronics [1, 2]. Several fluorescent dyes reported in the literature suffer from serious drawbacks such as their cumbersome synthesis, limited availability and biological interference [4].

Furthermore, many organic fluorescent dyes were prepared and their properties were investigated. One group of fluorescent dyes are 1,8-naphthalimide derivatives, which make a well-known class of dyes with a large range of applications [1,2,3].

Derivatives of 1, 8-naphthalimide are widely used for various applications [1]. They were utilized in such fields as coloration and brightening of polymers [1], as laser active media [2,3], fluorescent markers in biology [4], anticancer agents [1], analgesics in medicine [2], fluorescence switchers and sensors [1,2], as electron-transporting and emitting materials in light emitting diodes [4,5]. They were also used in liquid crystal displays [1] and as ion probes [2,3]. Derivatives of 1,8-naphthalimide generally have high electron affinity due to the existence of an electron-deficient center [4] and

display good electron-transporting or hole-blocking capabilities. 1,8-Naphthalimide moiety can be easily functionalized [4]. By introducing different electron-donating substituents at C-4 position of 1,8-naphthalimide moiety the emission color of the compounds can be readily tuned from near infrared to pure blue [2,3,4].

Substitution of electron donating groups usually raises the fluorescence emission, particularly when amino and allylamino groups are situated at the C-4 position [2,3]. Ultrasound is a kind of sound wave with the high frequency. When the ultrasound propagates in the medium, a series of physical and chemical changes occur in the media. The changes are accompanied with ultrasonic effect, mainly including the mechanical effect, acoustic cavitation effect, heating and chemical effects. Ultrasonic cavitation effect refers to the dynamic process of cavitation bubble with micro-gas-nuclear in the liquid [2]. When the ultrasonic treatment is applied in solid-liquid reaction, it can greatly enhance the rate of solid-liquid heterogeneous reaction, realizes uniform mixing of reactants, accelerates the spread of reactants and products, promotes the formation of the new product phase and controls their particle size and distribution [29]. Recently, ultrasound method has been employed for synthesis of organic components due to offering a versatile and facile pathway [2,3]. Based on our

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knowledge there are no report on sonic synthesis of benzenesulfonamide substituent in 1,8-naphthalimide dyes.

2. EXPERIMENTAL METHODS

2.1 Materials and Instrumentation

4-Nitro-1, 8-naphthalicanhydride, 4 Amino benzenesulfonamide (sulfanilamide), 4-amino-N-(2-pyrimidinyl) benzenesulfonamide (sulfadiazine) (Sigma-Aldrich), 4-amino-N-2-hiazoylbenzenesulfonamide (sulfathiazole) (Sigma Aldrich) and hydrochloric acid and zinc chloride (Merck Co.) were used without further purification. The FTIR spectra were recorded on a PerkinElmer Spectrum GX II FT-IROne spectrophotometer on a KBr disc. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX AVANCE spectrometer operating at 500 MHz. The elemental analysis CHNS was determined on a Costech instruments (Elemental Combustion System 4010). Differential scanning calorimetry (DSC) measurements were carried out using a DSC (DSC 214 Polyma NETZ5CH) under nitrogen environment. Cyclic voltammetry measurements were performed on a PGSTAT 302, electrochemical experiments were carried out at room temperature using a three-electrode cell consisting of a platinum coil as counter electrode, a glassy carbon working electrode, and a silver wire as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) was used as supporting electrolyte at a scan rate of 100 mVs^{-1} . For the measurements, silver reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc^+) redox couple as an internal standard [2].

Theoretical calculations and molecular simulations had been carried with Gaussian 09 and Gauss view software and carried out with B3LYP hybrid functional mixed with basis set of 6-311G. For evaluated compounds ground state geometries were optimized with no symmetry limitations to a local minimum, which was followed by frequency calculations also all simulations were conducted with polarizable continuum model using dichloromethane as solvent as implemented [2,3].

The UV-Vis absorption spectra were recorded on a Cecil 9200 double beam spectrophotometer and the fluorescence spectra were taken on a Perkin and Elmer LS50B spectrofluorimeter with both excitation and emission slits set at 10 nm and controlled by a personal computer data processing unit. To record photoluminescence decay curves dependencies on laser flux, with Pico Quant LDH-D-C-375 laser with wavelength equals 374 nm as the excitation source were used and the ionization potential (IP) of the vacuum deposited films was obtained using photoelectron emission spectrometry in air [2,3].

3. SYNTHESIS OF INTERMEDIATES AND DYES

3.1 General Procedure for the Preparation of Intermediate

A mixture of 0.02 mol 4-nitro-1,8-naphthalimide (1) and 0.02 mol amine in 10 ml water was sonicated at 35

KHz in a sonic bath maintained at 25 °C. Thin-layer chromatography (TLC) was performed at the end of the reaction, and then the contents were filtered and the synthesis route is presented in Scheme 1.

4-Nitro-N-4-aminobenzenesulfonamide-1,8-naphthalimide (2)

Y=78%; MP=315.5 °C; FT-IR (KBr)(cm^{-1}): 3355: NH str., 1711, 1658: C=O str., 1521, 1325: NO_2 str., 1236: SO_2 str.; $^1\text{HNMR}$ (500MHz, CDCl_3 , δ/ppm): 7.60 (s, 2H, NH_2), 7.65-7.68 (d, 2H, $J=7.5\text{Hz}$), 7.82-7.86 (d, 2H, $J=7.1\text{Hz}$), 7.92 (t, 1H), 8.21-8.26 (d, 4H, $J=7.8\text{Hz}$); Elem. Anal. Calcd. (%) for $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_6\text{S}$: C, 54.40; N, 10.57; H, 2.77. Found: C, 54.49; N, 10.39; H, 2.82.

4-Nitro-N-4-amino-N-(2-pyrimidinyl) benzenesulfonamide-1,8-naphthalimide (3)

Y=71%; MP=319 °C; FT-IR (KBr) (cm^{-1}): 3256: NH str., 1708, 1650: C=O str., 1517, 1339: NO_2 str., 1241: SO_2 str.; $^1\text{HNMR}$ (500MHz, CDCl_3 , δ/ppm): 6.98-7.03 (t, 1H), 7.55-7.62 (d, 2H, $J=7.3\text{Hz}$), 7.78-7.84 (d, 3H, $J=7.5\text{Hz}$), 8.11-8.19 (d, 2H), 8.34-8.39 (d, 4H, $J=7.7\text{Hz}$), 11.22 (s, 1H, NH); Elem. Anal. Calcd. (%) for $\text{C}_{22}\text{H}_{13}\text{N}_5\text{O}_6\text{S}$: C, 55.57; N, 14.73; H, 2.73. Found: C, 54.89; N, 14.11; H, 2.19.

4-Nitro-N-4-amino-N-2-thiazoyl benzenesulfonamide-1,8-naphthalimide (4)

Y=74%; MP=281 °C; FTIR (KBr) (Cm^{-1}): 3225: NH str., 1700, 1658: C=O str., 1521, 1345: NO_2 str., 1239: SO_2 str.; $^1\text{HNMR}$ (500MHz, CDCl_3 , δ/ppm): 6.78-6.81 (d, 1H, $J=4.8\text{Hz}$), 7.21-7.28 (d, 1H, $J=6.5\text{Hz}$), 7.42-7.49 (d, 2H, $J=7.2\text{Hz}$), 7.63-7.72 (d, 2H, $J=7.1\text{Hz}$), 7.98-8.05 (d, 2H), 8.12 (t, 1H), 8.44-8.49 (d, 4H, $J=7.5\text{Hz}$), 11.34 (s, 1H, NH); Elem. Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}_6\text{S}_2$: C, 52.5; N, 11.66; H, 2.50. Found: C, 53.17; N, 12.28; H, 2.34.

3.2 General Procedure for the Preparation of Organic Dyes

A mixture of 0.03 mol intermediate (2, 3 or 4) and was dissolved in 8 mL of acetic acid and 0.015 mol of Fe powder was added in the mixture. The reaction solution was sonicated at 35 KHz in a sonic bath maintained at 25 °C for 30 min. Thin-layer chromatography (TLC) was performed at the end of the reaction, and then the contents were filtered.

4-Allylamino-N-4-aminobenzenesulfonamide-1, 8-naphthalimide (Dye 1)

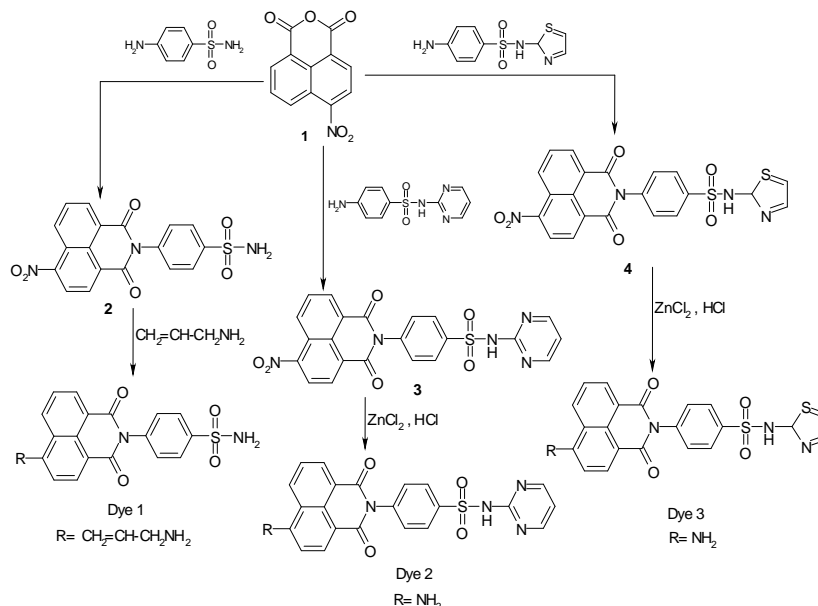
Y=82%; MP=229.6 °C; FT-IR (KBr) (cm^{-1}): 3368: NH str., 1695, 1642: C=O str., 1244, 1159: SO_2 str.; $^1\text{HNMR}$ (500MHz, CDCl_3 , δ/ppm): 3.23 (s, 1H, NH allyl), 4.19 (s, 2H, allyl NCH_2), 4.85 (1H, $=\text{CH}_2$ allyl), 5.28 (s, 1H, $\text{CH}=\text{allyl}$), 6.82-6.89 (d, 1H, $J=7.6\text{Hz}$), 7.17-7.25 (d, 2H, $J=7.5\text{Hz}$), 7.52 (s, 2H, NH_2), 7.68 (t, 1H), 7.74-7.59 (d, 3H, $J=7.1\text{Hz}$), 8.17-8.23 (d, 3H, $J=7.7\text{Hz}$); Elem. Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$: C, 61.91; N, 10.32; H, 4.17. Found: C, 62.15; N, 10.69; H, 4.95.

4-Amino-N-4-amino-N-(2-pyrimidinyl) benzenesulfonamide-1,8-naphthalimide (Dye 2)

Y=71%; MP=259.5 °C; FTIR (KBr) (Cm⁻¹): 3389: NH str., 1690, 1640: C=O str., 1239, 1144: SO₂ str.; ¹HNMR (500MHz, CDC1₃, δ/ppm): 6.78-6.86 (d, 1H, J=7.2 Hz), 7.12 (t, 1H), 7.26-7.34 (d, 2H, J=7.3 Hz), 7.41 (s, 2H, NH₂), 7.54-7.58 (d, 3H, J=7.5 Hz), 7.82 (t, 1H), 7.89-7.93 (d, 3H, J=7.6 Hz), 8.07-8.16 (d, 1H, J=7.7 Hz), 10.98 (s, 1H, NH); Elem. Anal. Calcd. (%) for C₂₂H₁₅N₅O₄S: C, 59.32; N, 15.73; H, 3.37. Found: C, 58.63; N, 14.70; H, 3.72.

4-Allylamino-N-4-amino-N-(2-pyrimidinyl) benzenesulfonamide-1,8-naphthalimide (Dye 3)

Y=75%; MP=267.8 °C; FTIR (KBr) (Cm⁻¹): 3379: NH str., 1695, 1653: C=O str., 1236, 1158: SO₂ str.; ¹HNMR (500MHz, CDC1₃, δ/ppm): 6.82-6.88 (d, 1H), 6.92-6.97 (d, 1H), 7.16-7.21 (d, 1H, J=7.3Hz), 7.32-7.38 (d, 2H, J=7.3 Hz), 7.56 (s, 2H, NH₂), 7.62-7.69 (d, 2H, J=7.3 Hz), 7.95 (t, 1H), 7.91-7.98 (d, 3H, J=7.5 Hz), 11.17 (s, 1H, NH); Elem. Anal. Calcd. (%) for C₂₁H₁₄N₄O₄S₂: C, 56.0; N, 12.44; H, 3.11. Found: C, 56.68; N, 12.86; H, 3.61.



Scheme 1 Synthesis route of Dyes 1-3

4. RESULTS AND DISCUSSION

4.1 Geometries and frontier orbitals

The molecular configuration and the frontier molecular orbital distribution of Dye 1-3 were analyzed by density functional theory (DFT) calculations using Gaussian 09 software at the B3LYP/6-311G (d,p) level. The theoretical geometries and the distribution of HOMO and LUMO of synthesized dyes are presented in Figure 1.

4.2 UV and Fluorescence properties

Absorption and photoluminescence (PL) spectra of the dilute solutions of compounds (10⁻⁵ M) and solid films are shown in Figure 2 and 3 respectively and wavelength ranges of the main absorption bands and fluorescence were shown in Table 1.

According to the Figure 2, the region of strong absorption bands (~ 413-440 nm) can be attributed to the localized aromatic π - π^* transitions of donor units in compounds. The shift to longer wavelengths observed for compounds especially for dye 2, which is suggested an increase in the conjugation level of the π orbitals [2]. The effect of different solvents on the emission spectra of compounds were studied and bathochromic shift of PL maxima of solutions increases with increasing dielectric

constant of solvents in the order Isopropanol ($\epsilon=17.9$), Methanol ($\epsilon=32.7$) and Acetonitrile ($\epsilon=37.5$), with an overall different relocation. The wavelengths of maximum intensities exhibited bathochromic shifts leads to strong red shift from the lowest polarity (Isopropanol) to highest polarity (Acetonitrile) ambient, compared to the individual D and A emission spectra and PL spectra move to longer wavelengths with increasing polarity of solvent, showing a strong positive solvatochromism and as displayed previously in other D-Atype of molecules [2,3]. Furthermore, increases of solvents polarity observed CT energy red shifted and investigated in less LES (Local Excited State) parameter and higher energy difference between CT_{axial} and CT_{equatorial} [2,3,4] and indicates that existed certain degree of CT character with a large dipole moment which is derived from low lying singlet excited state [2,3]. Moreover solvent sensitivity to polarity can be analyzed in terms of difference dipole moments in the ground and excited states [2,3]. The spectra of synthesized dyes in solid film state (Figure 3) shows orange color for dye 1, green color for dye 2 and dye 3 near to yellow color respectively and they are characterized by chromaticity coordinates and criteria of CIE coordinates and submitted in Figure S6.

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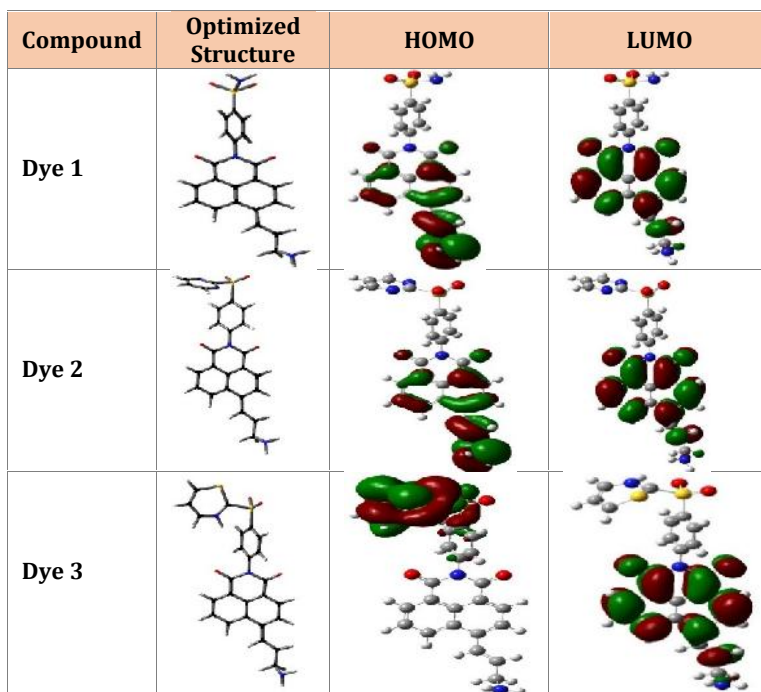


Figure 1 HOMO and LUMO of dyes 1-3 calculated at B3LYP/6-311G (d,p) level

The value of PLQY for dye 1 was 79.70% in acetonitrile and versus of solid film was failed with value 0.85% and PLQY of dye 2 and 3 also in Acetonitrile and solid film were 66.94 and 1.78% (for dye 2) and 33.68% and 3.39% (for dye 3) respectively. Low value of PLQY of the solid film of dyes can apparently be explained by large dipole moment of the compounds. However, many luminophores are highly luminescent in dilute solutions and light emissions are often quenched in the solid state due to aggregation of their chromophoric units in the condensed phase [2]. ACQ affect the solutions and dispersions of dyes 1-3, in water/THF mixtures at room temperature, were studied in Figures 4 and Figures S2.

The π - π supramolecular interactions also play an important role in the ACQ. This data (Figure 4-b) shows that the properly disturbing the close molecular packing and diminishing the intermolecular quenching effects are

advantageous for increasing the PLQY value of solutions phases.

In contrast, although π - π interactions, it shows loose packing with weak molecular interactions, thus resulting in non-radiative of pathways through rotation or vibration [2]. Fluorescence decay profiles of solutions and solid films were recorded using single photon counting spectrofluorimeter. PL decays were monitored at the corresponding emission maximum of the dyes and software experimental fluorescence allowed the fitting of value the decay spectra 1 until 1.3 and considered excitation of instrument response 374 nm. According to the Figure 5 and Table S1, appearing of the slower decay dyes for dye 2 in solid film, occurred 4.64 ns that probably reasons are associated with the weak intermolecular interactions or crystalline aggregate formations in the neat films [3]. Moreover, the spectra of life time for dyes in solutions presented in Figure S3.

Table 1 Spectroscopic properties and PLQY of the dyes specified in mode of non-polar and polar solutions and solid film

Dye	Isopropanol		Methanol		Acetonitrile			Solid Film		
	λ_{abs}^{max} , nm	λ_F^{max} , nm	λ_{abs}^{max} , nm	λ_F^{max} , nm	λ_{abs}^{max} , nm	λ_F^{max} , nm	PLQY %	λ_{abs}^{max} , nm	λ_F^{max} , nm	PLQY%
1	428	503	436	520	426	525	79.70	434	614	0.85
2	429	507	413	522	423	528	66.94	440	561	1.78
3	425	505	422	525	424	527	33.68	438	586	3.39

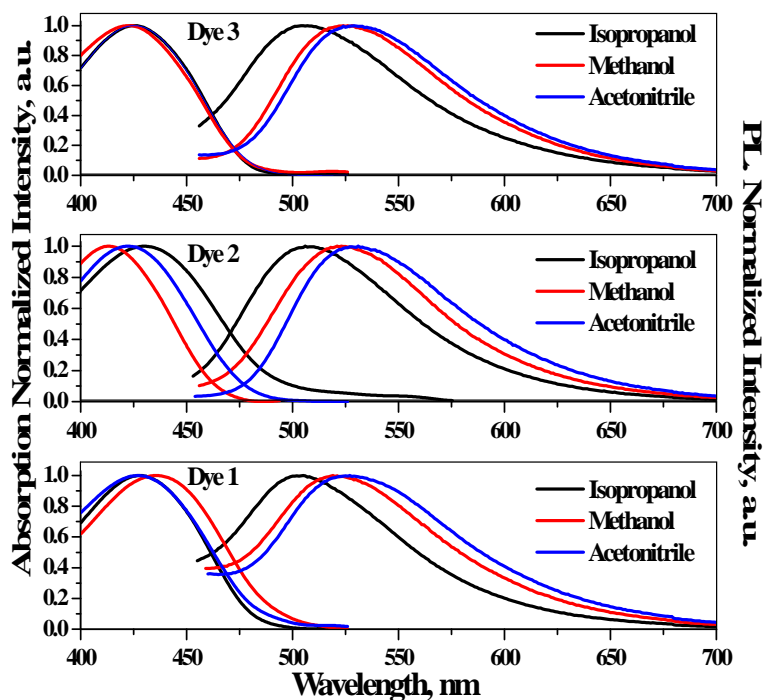


Figure 2 Absorption spectra and photoluminescence (PL) spectra of dilute solutions in different solvents (10^{-5} M) of dyes 1-3 (Excitation=330nm)

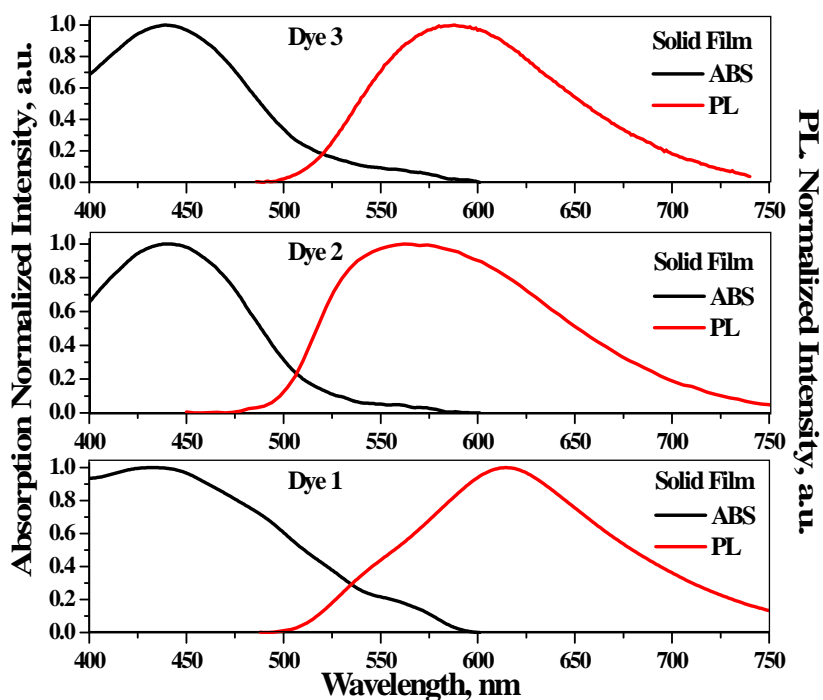


Figure 3 Absorption spectra and photoluminescence (PL) spectra of solid film of dyes 1-3 (Excitation=330nm)

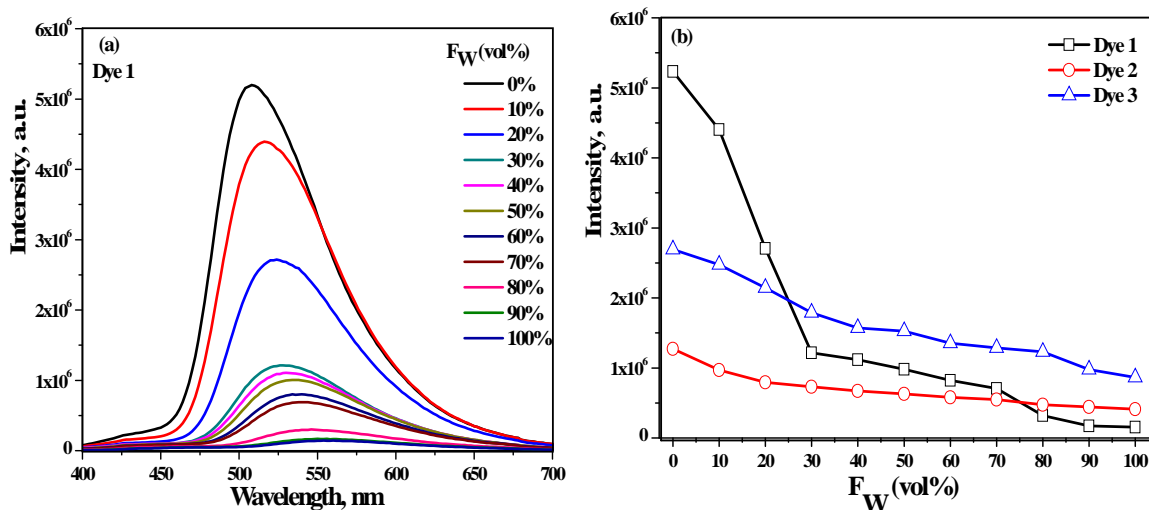


Figure 4 (a) PL spectra of Dye 1 in the THF/Water mixtures and (b) The inset plot of Dyes indicated the relationship between PL maximum intensities and water volume fraction in THF/Water mixtures

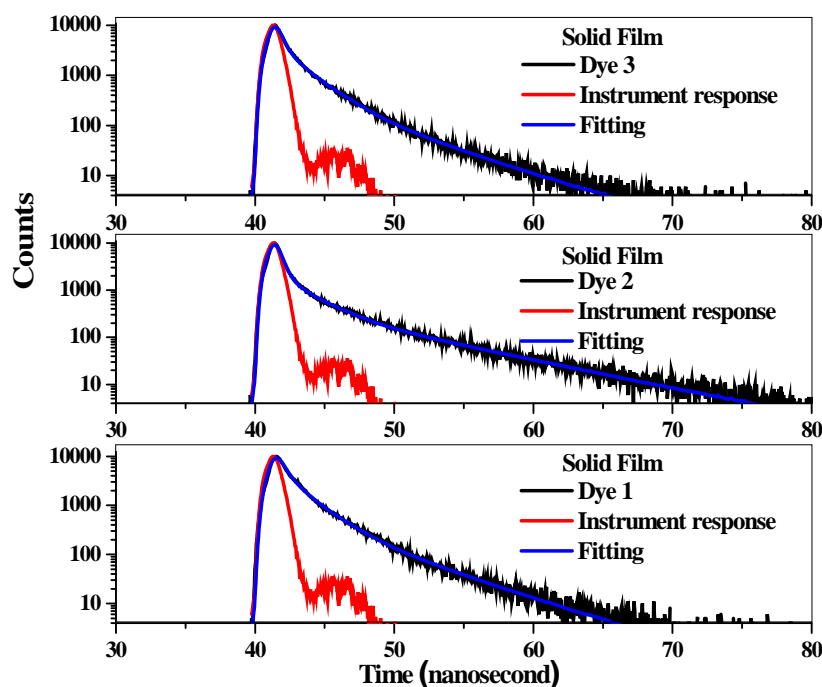


Figure 5 PL decay of Dyes equilibrated solid film at room temperature

4.3 Electrochemical and Photoelectrical Properties

The electrochemical characteristics of dyes are summarized in Table 2. As well as Cyclic Voltammetry (CV) of dyes are shown in Figure S1. The ionization potential (I_P^{CV}) values of dyes were estimated from the onset potentials of the first oxidation event after

calibration of the measurements against ferrocene. I_P^{CV} for compounds were found to be range of 5.67-5.70V.

Furthermore, Ionization potentials (I_P^{PE}) for vacuum deposited layers of compounds were taken from photoelectron emission spectra and presented in Figure 6. Electron affinities (E_A^{CV}) of dyes 1, 2 and 3 were estimated to be 3.12, 3.13 and 3.19 eV, respectively.

Table 2. Investigation of Electrochemical properties and HOMO/LUMO energies of dyes 1-3

Compound	E _{ox} (V)	E _{red} (V)	E _{Acv} (eV)	IP _{CV} (eV)	LUMO (eV)	HOMO (eV)	E _g ^{opt} (eV)	IP _{PE} (eV)
1	0.79	-1.19	3.12	5.70	3.09	5.43	2.58	6.00
2	0.77	-1.21	3.13	5.68	3.05	6.55	2.55	6.09
3	0.76	-1.20	3.19	5.67	2.98	6.50	2.48	6.03

Explanations about parameters of Table:E_{ox}: Potential of onset of oxidation and estimated from CVE_{red}: Potential of onset of reduction and estimated from CVE_{Acv}: Calculated with the relation $E_{Acv} = -(|IP_{CV}| - E_g^{opt})$ IP_{CV} = Ionization potentials calculated with the relation $|-(1.4 \times 10^{-1} \times E_{ox} \text{ vs } Fc/V) - 4.6| \text{ eV}$

LUMO: Energy level Estimated by DFT, HOMO: Energy level Estimated by DFT

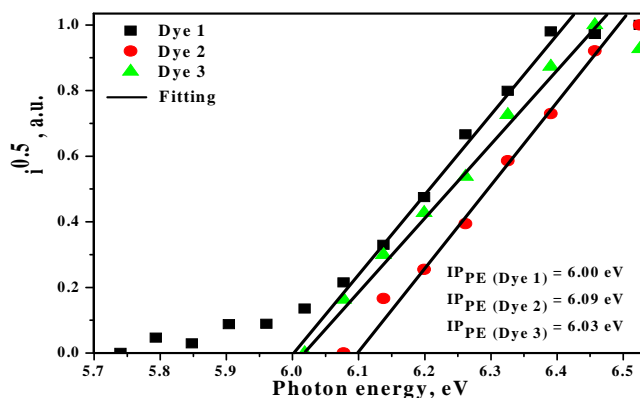
E_g^{opt}: Calculated with the relation $1239.75/\lambda$ of UV spectra (diluted Acetonitrile)

Figure 6 Photoelectron emission spectra of compounds

5. CONCLUSIONS

In this study, a series of novel 1,8-naphthalimide dyes incorporated with benzenesulfonamide heterocycles with ultrasound method was prepared. The synthesized dyes and their intermediates were characterized. According to the photophysical properties of prepared dyes the absorption spectra were in the range of 434-440 nm in solid film, while photoluminescence spectra were in the range of 561-614 nm. Furthermore, the result of ionization potential of dyes demonstrated values between 6-6.09 eV. The PLQY of dyes in acetonitrile were high values and aggregation caused quenching (ACQ) for dyes reported. Moreover the τ of PL Decay spectra of dye 3 was higher than dye 1 and 2 in solid film (7.07 (19.83%)). Based on our knowledge there are no report on sonic synthesis of benzenesulfonamide substituent in 1,8-naphthalimide dyes.

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